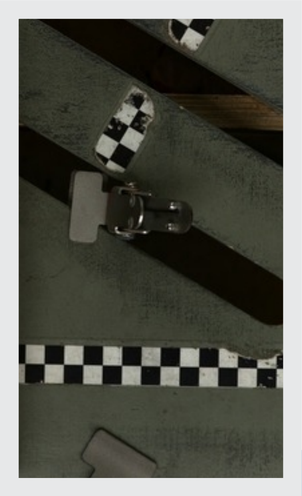

Twelfth Report of the Committee on Catalysis, National Research Council

DETAILS

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Committee on Catalysis; National Research Council

TWELFTH REPORT

OF THE

COMMITTEE ON CATALYSIS

NATIONAL RESEARCH COUNCIL

Twelfth report of
the Committee on catalysis,
National Research Council.

TWELFTH REPORT

OF THE

COMMITTEE ON CATALYSIS

NATIONAL RESEARCH COUNCIL

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PREFACE

The intention in this report is to present a somewhat critical and proportioned impression of the state of progress of catalysis, with a résumé of some of the important work published since the appearance of the eleventh National Research Council report. In the execution of this plan, certain trends have been recognized. Since the pertinent literature on catalysis is now too great to be evaluated by any one man, the various members of the committee agreed to cooperate in the writing of a single report. The committee members have been chosen with this plan in view and on the basis of their participation in major fields of the increasingly complex subject of catalysis. The committee is reorganized after each report in order that the most suitable personnel should deal with the succeeding report, the topics of which necessarily change somewhat. The report will not be encyclopedic, and some topics, such as catalysis in solution, have been reserved for future undertakings. To collect all recent instances of catalysis would involve sifting the entire chemical literature, as well as that of the medical sciences and certain others. This task exceeds the facilities of the committee.

One of the conspicuous current trends is the disappearance of any rational borderline between pure and applied research. We now know that an advance in, say, mathematical chemical physics is likely to have a rather early influence in industrial research and that the time lag between them is shortening. The many intervening stages may be regarded simply as parts of a whole development.

When industrial interest involves some field formerly the domain of academic men, this field is likely to experience a forced growth with which the academic men cannot compete experimentally. This has happened, e.g., in some phases of hydrocarbon chemistry. For such reasons, it is doubtful that academic and industrial fields can afford to remain isolated from each other. Accordingly, the committee is composed half of academic men and half of industrial men with no great effort to distinguish that knowledge which is pure from that which is applied.

Catalysis has long been important to industry, and the applications have often been ahead of our understanding of the phenomena. The continued luxuriant growth of catalysis in industry may be illustrated by the applications of polymerization, most of which are catalytic, and by the entrance of catalysis in an important way into the huge petroleum industry. Other industries involving catalysis discussed in this report have experienced further growth but are of earlier origin.

Another impressive trend is the growth of definite knowledge in the field of biochemical catalysis. This is recognized by incorporating a special section on the subject in this report.

On the theoretical side, the viewpoint of individual writers on catalysis has often been characterized by overemphasis of some particular factor. Thus some have said that catalysis is to be explained by ion formation, others by atom or radical formation, others by intermediate-compound formation, etc. Actually the phenomena of catalysis are probably too complex to fit into a single mechanism, and one advantage of a cooperative undertaking of this kind is to check tendencies to overdevelop some one aspect of the subject.

The last three years have seen no less than fifteen new books on catalysis. These are reviewed here in somewhat greater detail than in the average journal review.

This report is reasonably comprehensive on the subjects covered with respect to the literature of the years 1935, 1936, and 1937. It is a progress report. Earlier literature has been treated in former reports of the committee. It was not practical mechanically to cover the year 1938 systematically, though some excursions into that material have been made.

The committee is much indebted to Dr. G. E. Kimball, Columbia University; Dr. H. H. Storch, of the United States Bureau of Mines; and Dr. E. Teller, of George Washington University, for their contributions to this report which appear under their names in the text.

THE COMMITTEE

July, 1939

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CHAPTER I

RECENT DEVELOPMENTS IN THE THEORY OF CHEMICAL BONDS AND REACTION RATES

GEORGE E. KIMBALL

The Valence Bond

The modern theory of valence has been discussed in some detail in previous reports of this committee, and is now rather generally known. We shall therefore begin this report with only a very brief sketch of this theory.

Let us consider the simple case of two atoms, A and B, each with a single valence electron. If the two atoms are widely separated, the motion of the electron is represented as closely as quantum mechanics will allow by an eigenfunction, or atomic orbital, i.e., a function of the coordinates of the electron such that the square of the absolute value of the function at any point gives the probability of finding the electron at that point. Let us denote the orbital for the valence electron of A by a, and the orbital for the valence electron of B by b.

If we let the first electron have the coordinates x_1, y_1, z_1 and the second the coordinates x_2, y_2, z_2, then the complete eigenfunction for the state of the system in which the first electron is on A and the second on B is

$$a(x_1, y_1, z_1)b(x_2, y_2, z_2)$$

or, more briefly,

$$a(1)b(2)$$

The state of the system in which the second electron is on A and the first on B is an equally good state with the eigenfunction

$$a(2)b(1)$$

While these two states have exactly the same energy, it is often necessary to consider also states with neighboring energies. The most important of these states are those in which both electrons are on the same atom, that is, the ionic state A^-B^+, represented by

$$a(1)a(2)$$

and the state A^+B^-, represented by

$$b(1)b(2)$$

If the two atoms are brought together, all these states are modified and can no longer be represented by such simple eigenfunctions. To a first approximation the new eigenfunctions can be represented by linear combinations of the old eigenfunctions. Physically this may be interpreted as a mixing up of the states, each state taking on part of the characteristics of the other states. The amount of this mixing, or resonance, is determined by two factors. One of these is the amount of overlapping between the two eigenfunctions involved; the other is the difference in energy between the two eigenfunctions. It is greatest when the overlap is greatest and the original energy difference is least.

As the eigenfunctions mix, there is a corresponding change in the energy levels. If we consider any pair of states, the interaction between them is always such as to tend to increase the energy difference between them, the energy of the lower state being lowered still further and the energy of the higher being raised.

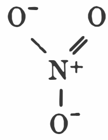
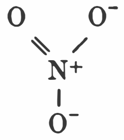
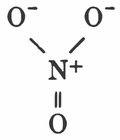
As an example let us consider that both A and B are hydrogen atoms. Since the ionization potential of hydrogen is greater than its electron affinity, the ionic states of the system will have higher energies than the non-ionic states. Since we are principally interested in the lowest state, we may therefore neglect the ionic states in the first approximation. If we consider one of the non-ionic states, say $a(1)b(2)$, its energy does not remain constant as the atoms are brought together because of the electrostatic forces between the atoms. This energy, the Coulombic energy, however, is not nearly enough to account for the observed binding energy of the hydrogen molecule. The difference is the difference in energy between the state represented by the eigenfunction $a(1)b(2)$ and the true eigenfunction, which is a mixture of all four of the eigenfunctions we have considered. Since the eigenfunction $a(1)b(2)$ has exactly the same energy as the eigenfunction $a(2)b(1)$, conditions are particularly favorable for resonance between these two, and the correct state contains the two in equal proportions (11, 37, 14). The resonance energy between these two eigenfunctions is by far the greatest contribution to the binding energy of the molecule, the remainder being composed of the Coulombic energy and resonance energy with the ionic and other states.

It is interesting to compare this quantum-mechanical picture of H_2 with the older theories of valence (18, 33, 24, 25, 34, 27, 21). H_2 is represented by these older theories of valence as being held together by a " shared pair " of electrons (H : H). This shared pair finds its quantum-mechanical counterpart in the resonance between the states $a(1)b(2)$ and $a(2)b(1)$ to form the linear combination $1/\sqrt{2}\ a(1)b(2) + 1/\sqrt{2}\ a(2)b(1)$. This particular linear combination of eigenfunctions occurs whenever two atoms with free valence electrons are brought together; it will be called henceforward the " covalent " eigenfunction. We may then restate our result for H_2 in the following way: The hydrogen molecule is held together principally by the covalent bond H : H, but there is also present a small proportion of the ionic forms H^+H^- and H^-H^+ in equal quantities.

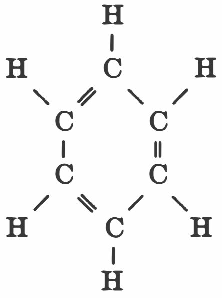
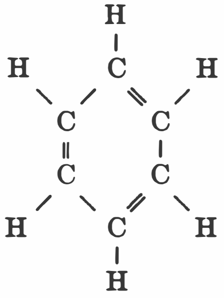
If we now consider the slightly more complicated molecule NaCl, the situation differs from that in H_2 only in two respects: First, there are a number of electrons which either are in closed shells, or (as for example the first six electrons in the outer shell of the Cl atom) are paired together; and, second, the symmetry of the H_2 molecule is now lacking. The electrons which are already paired, whether or not they are in closed shells, can play no direct part in the formation of valence bonds, but only contribute a repulsive force between the atoms. We therefore need consider only the covalent eigenfunction $\mathrm{Na : Cl} = 1/\sqrt{2}\ a(1)b(2) + 1/\sqrt{2}\ a(2)b(1)$ and the ionic eigenfunction $\mathrm{Na^+Cl^-} = b(1)b(2)$, the energy of the structure Na^-Cl^+ being too high to affect the normal state of the molecule. Although the ionization potential of the Na atom is comparatively low, and the electron affinity of the Cl atom comparatively high, the energy of the ionic state is higher than that of the covalent state when the atoms are far apart. However, as the atoms are brought together, the electrostatic energy of the ionic state makes its energy decrease much more rapidly than that of the covalent state. For close enough distances between the atoms the ionic state becomes the lower.

Because of resonance, however, the actual states of the molecule are neither purely covalent nor purely ionic. At large internuclear distances, where the covalent state is considerably below the ionic state in energy, the normal state of the molecule is mostly covalent, the ionic state being completely absent at infinite separation. As the molecule is brought together, the amount of ionic state gradually increases until the point is reached at which the energy of the ionic state is equal to that of the covalent state. At this point, the normal state is exactly one-half ionic and one-half covalent in nature. As the nuclei are brought still closer the ionic state begins to predominate, until at the separation of the atoms found in a crystal, for example, the normal state is predominantly ionic. Throughout this process the energy is lower than that which would be calculated for either a pure ionic or a pure covalent state.

As we go to more complex molecules, the possibilities of resonance increase, and there are often possibilities of resonance between different covalent structures, or structures which are partly covalent and partly ionic. Thus even as simple a molecule as carbon monoxide resonates between the structures $C^-{\equiv}O^+$, $C{=}O$, and $C^+{-}O^-$ (from now on, a covalent bond, or shared pair of electrons, will be denoted by a dash instead of a pair of dots), of which the first is predominant. The nitrate ion resonates between

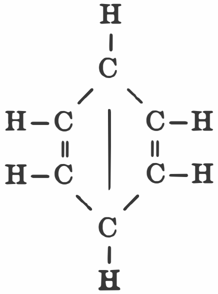
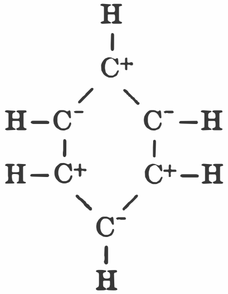
each structure being equivalent to the others, resulting in a symmetric structure. The well-known case of benzene (26, 40, 12) shows resonance between the Kekulé structures

and to a smaller extent other structures with bonds extending across the ring.

In general, any molecule (or ion) will resonate between all the structures, covalent, ionic, or mixed, which can be written for it. Of these, the one with the lowest energy will always predominate. If there are two or more structures with this lowest energy, each of these will have an equal part in the final state of the molecule. The resulting energy is always lower than the energy corresponding to the lowest valence structure, and is lowered from this value most if there are two or more states with this energy, or with energies which are nearly equal.

So, for example, in benzene we may write not only the two Kekulé structures, but also such structures as

The first of these structures, however, will have a higher energy because of the weakness of the bond bridging the ring, while the second will also have a high energy since the ionization potential of carbon is much larger than the electron affinity. We therefore conclude that in benzene the Kekulé structures predominate, but that there is a little of each of the other structures. Moreover, since there are two Kekulé structures the benzene molecule should be more firmly bound than either structure alone would indicate.

Chemical Reactions

The considerations which have been used for stable molecules may also be applied to the unstable configurations of atoms which occur during the course of a chemical reaction (4, 5, 6, 19). Suppose, for example, that we consider the reaction of sodium vapor with chlorine. During the time that a sodium atom is in the neighborhood of a chlorine molecule we may have any one of the following structures:

$$\mathrm{Na} \qquad \mathrm{Cl} - \mathrm{Cl}$$

$$\mathrm{Na} - \mathrm{Cl} \qquad \mathrm{Cl}$$

$$\mathrm{Na}^{+} \qquad \mathrm{Cl}^{-} \qquad \mathrm{Cl}$$

or a number of others with higher energies. The resonance principle then tells us that the structure with the lowest energy will predominate but that the true state is a mixture of all the possible structures. Now if the sodium atom is at a distance from the chlorine atoms, and if the chlorine atoms are at a distance from each other which is near the normal distance in the chlorine molecule, the second and third of these structures will have only weak binding, while the first is strongly bound. In such a configuration the first structure will predominate. If, on the other hand, the sodium atom is near one of the chlorine atoms and the other chlorine atom is at a distance, the third structure is the one of lowest energy and will predominate. If the distances between atoms are all large, none of these structures will have a very low energy; but the third structure will have an energy higher than the other two, and the structure of the system will therefore be intermediate between the first two structures. Finally, if all three atoms are close together, the first and third structures will have nearly the same energy and we will have resonance between these two structures.

If we confine our attention to those structures in which all three atoms are in a straight line, the energy of the system is conveniently represented by a contour map in which the x coordinate is the distance between the two chlorine atoms and the y coordinate is the distance between the sodium atom and the nearer chlorine atom. Such a map is shown schematically in Fig. 1.

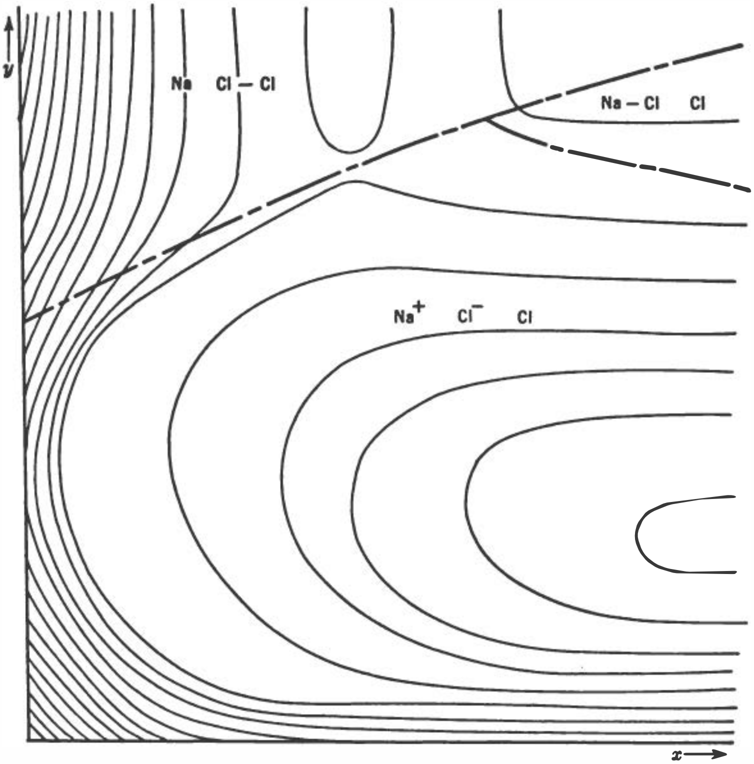


FIG. 1. Energy Contour Map of the System Na Cl + Cl.

This figure is divided into three regions, according to the structure which has the lowest energy. Within each region the energy is approximately equal to the energy which would be expected for that structure. Thus in the region along the y-axis, where the Na — Cl distance is large, the structure is predominantly Na Cl — Cl. Since there is no bond between Na and Cl in this structure, the energy is independent of y when y is large, and depends on x in exactly the same way that the energy of the Cl_2 molecule depends on the Cl — Cl distance. If y is small, however, the sodium atom is repelled by the chlorine molecule, the amount of the repulsion being roughly half the attraction which would exist if there were a bond between the Na and the Cl. The energy therefore rises as y decreases. This part of the surface is therefore like a valley whose floor rises as y decreases. Along the x-axis lies a similar valley corresponding to the structure Na^+Cl^- Cl. Near the boundary between the two valleys is a region in which both structures have nearly the same energy. Here there is strong resonance between the two structures, which results in a lowering of the energy surface in this region and a smoothing off of the sharp break which would otherwise occur at the intersection of the valleys. The third region, where the structure is predominantly Na—Cl Cl, is of little interest to the reaction. The surface as a whole is therefore seen to consist of two valleys along the coordinate axis, joined by a pass, slightly higher than either valley floor.

Now if a sodium atom is to react with a chlorine molecule it can do so only by traversing some path leading from the Na Cl—Cl valley to the Na^+Cl^- Cl valley. At some point this path must cross the boundary between the two valleys. Evidently, then, the system must have at least sufficient energy to pass through the lowest point of this boundary. The activation (or critical) energy of the reaction must therefore be at least as great as the energy difference between the lowest point on the boundary and the energy of the Na Cl—Cl valley floor. In some cases the surface may be of such a form that there is some other barrier that must be traversed and which requires a still larger energy; but such cases are rare, and the height of the boundary pass is usually the true activation energy of the reaction.

We therefore conclude that the activation energy of a chemical reaction is determined by the energy of the system in that configuration in which the energy of the initial electronic structure becomes equal to the energy of the final electronic structure. This energy is determined principally by two things: first, the amount of repulsion between non-bonded atoms; and, second, the amount of resonance energy available to overcome this repulsion.

If we examine further the case of the reaction $Na + Cl_2$, we note that the reaction is strongly exothermic, i.e., the floor of the Na^+Cl^- Cl valley is much lower than the floor of the Na Cl—Cl valley. The boundary between the two valleys is therefore not symmetrically placed between the axes, but is displaced along the y-axis. This increase in the Na—Cl distance at the activated point means low repulsion, and therefore, since the resonance here is strong, a low activation energy. If, on the other hand, we consider the reaction $H + H_2 = H_2 + H$, the boundary, because of the symmetry of the surface, must be symmetrically placed. This in turn means that the intersection of the valleys is not reached until the distance between the approaching hydrogen atom and the molecule is almost equal to the distance between the atoms in the molecule. The repulsion in this case is quite large, and in spite of a large resonance energy the activation energy is large for reactions of this type. In general the activation energies of these three atom reactions will be small if the reaction is very exothermic, moderately large if the heat of the reaction is small, and nearly equal to the heat of the reaction for endothermic reactions.

Reactions involving more than three atoms (or radicals) can be treated in very much the same way (7, 16, 32, 38), although the energy surfaces for these reactions are usually too complex to be drawn in any simple way. If we consider the reaction $H_2 + I_2 = 2HI$, for example, the activated complex consists of four atoms in a plane, with the distances H—H, I—I, and H—I all nearly at their equilibrium values, but stretched slightly because of the repulsive forces. In this position the energy of the state H—H I—I is equal to the energy of the state H—I H—I, the first requirement of an activated complex, while the placing of the atoms in a plane minimizes the repulsion between the atoms which are not bonded in either state. In this reaction, however, there are in either state repulsions between four pairs of atoms, whereas in the three-atom reactions there are only two repelling pairs. Since both types have resonance only between two structures, the amount of resonance energy in the two types is approximately the same. The high repulsion in the four-atom case therefore must lead to a higher activation energy. In most four-atom reactions this activation energy is so high that a step reaction, such as a preliminary dissociation of one of the reactant molecules followed by a series of three-atom reactions, goes faster than the simple, direct mechanism. Such is the case, for example, in the reactions of hydrogen with chlorine and bromine.

Although reaction mechanisms are possible in which more than two bonds shift places, the repulsive forces which must be overcome to bring the atoms to the activated complex are so large that very few are known. In practically every case of this kind it has been shown that the reaction proceeds by a sequence of simple steps, each step consisting usually of a shift of a single valence bond (20, 1, 23). In those cases where many bonds do shift, it is usually found that resonance is present either in the initial molecule or in some intermediate.

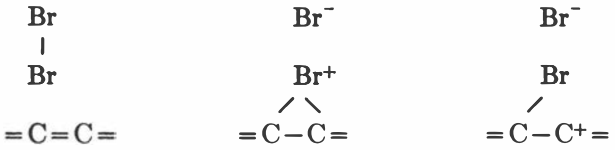
In the addition of halogens, e.g., Br_2, to double bonds, for example, the resonance between non-ionic and ionic structures plays an important role (13, 29, 39). In the original double bond, the structures

$$>C=C<$$

$$>C^+-C^-<$$

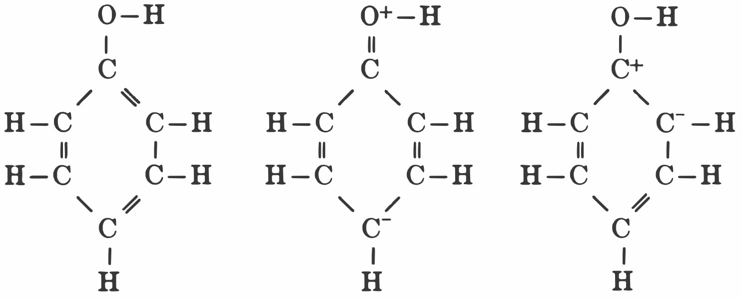
$$>C^--C^+<$$

are all present. In the isolated molecule the first of these is predominant. If the molecule is symmetric the two ionic structures are present in equal amounts, but in unsymmetrical molecules one ionic form will predominate over the other. If a Br_2 molecule is brought up to this double bond, there are two possibilities: (1) the direct addition of the Br_2, and (2) the stepwise addition of one atom at a time. The first of these mechanisms involves the shifting of two bonds, and has a high activation energy. In the second mechanism, however, we have the following possibilities for the structure of the activated complex:

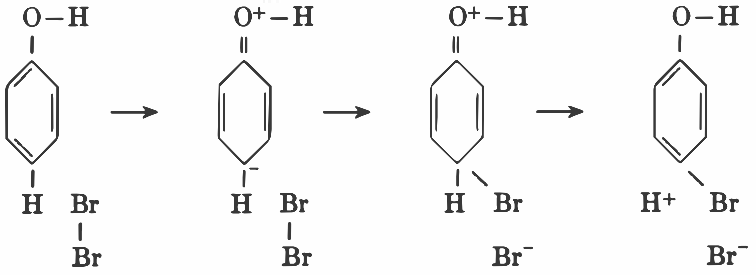


Instead of resonance between two forms we here have resonance between three, and the additional resonance energy lowers the activation energy (especially in aqueous solution where the solvation energy of the ions is an additional contribution) to such a degree that this reaction takes place rather than the simpler direct addition. Since this mechanism may be completed by the simple addition of a Br^- ion to the positive ion formed in the first step, there is no further complication.

Many of the directive effects of substituents in organic compounds have their origin in possibilities of resonance in the activated complex. If, for example, we consider phenol, the principal types of structure are:

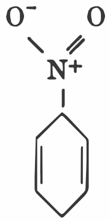
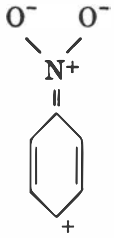
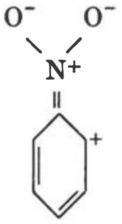


The negatively charged carbon atoms in the last two structures are particularly open to attack by halogens, e.g., bromine. If we bring up a Br_2 molecule to the para carbon, for example, we may have the structure sequence



and similarly for the ortho position. The meta position, however, has no such favorable sequence of structures, and therefore $o-p$ substitution predominates.

If, on the other hand, we start with nitrobenzene, the original structures are of the types

In these structures the positive carbon atoms are very unfavorable to replacement of their hydrogens by bromine, for, as we have already seen, this process usually proceeds by way of the formation of a Br^- ion. The replacement will therefore be slowed down at the $o-p$ positions. The least unfavorable position being the meta position, any replacement which does take place will take place here; but the reaction must be expected to be slow in comparison with the $o-p$ replacement in phenol.

It should not be concluded from these examples that directed substitution is due entirely to resonance of this type. There is also a direct influence of each substituent arising from the electric field due to the semipolar nature of many bonds. This, the inductive effect, is the controlling factor in many cases, while in some cases both effects must be taken into consideration.

It has not yet proved possible to make exact calculations of activation energies by quantum mechanics. Nevertheless approximate calculations of a semiempirical nature can be carried out, and have been for a number of simple reactions. The methods involved, however, are too complicated to treat here. For details of these calculations, and discussion of the degree of approximation which may be obtained, the reader is referred to the bibliography.

Absolute Reaction Rates

The methods we have been discussing do not give directly any information about the actual rate at which a chemical reaction can take place. To complete the method, we therefore need a means of calculating the reaction rate from the potential energy surface which is the result of these calculations. For a rough estimate it is possible to use the hypothesis first suggested by Arrhenius — the so-called collision theory of reaction rates.

According to the collision theory in its simplest form a collision between two reactant molecules leads to reaction if, and only if, the combined energies of the molecules exceed a certain activation energy, E. This leads to the expression

$$Ze^{-E/RT}$$

where Z is the number of collisions per second, for the rate of the reaction. This expression is oversimplified, for evidently there may be collisions with plenty of energy which, because of unfavorable orientation of the molecules at the moment of collisions, or other circumstances, do not react. It has therefore become customary to include a " steric factor " P in the expression for the rate to give the fraction of the collisions having sufficient energy which lead to reaction. The modified form of the collision equation for the rate of a reaction is

$$ZPe^{-E/RT}$$

a form which can be applied to any experimental data.

The principal objection to the collision theory is its lack of preciseness of definition. As long as molecules are thought of as rigid spheres, a collision between molecules is a perfectly definite event, and on this basis the collision number Z is capable of perfectly exact calculation in terms of such quantities as molecular masses and diameters. But when molecules are thought of as electronic systems, as we must now think of them, the whole concept of collision loses clarity. True, we can still take an arbitrary diameter for such a molecule, and define a collision as an approach of two molecules to within this distance. There is no reason, however, why the diameter used in one problem should have any connection with that used in another problem; and indeed, if molecular diameters are calculated from different experiments, the results are seldom in agreement.

It was also pointed out by LaMer (17), and independently by Rodebush (30, 31), that the collision theory was not thermodynamically correct (unless very improbable assumptions are made about the variation of the collision number with temperature) since the ratio of the forward and reverse rates of any chemical reaction must be equal to the equilibrium constant of the reaction. This result can be obtained only, however, if the E of the collision expression is of the nature of a free energy, such that the difference between the E's of the forward and backward reaction is equal to the free-energy change of the reaction, and if, moreover, the product PZ is the same for forward and reverse reaction — a most unlikely result if Z is really a collision number. These considerations led to the suggestion that the proper form of expression for a rate constant is

$$\nu e^{-\Delta F^{*}/RT}$$

where ΔF^* is a free energy of activation (not necessarily independent of temperature) and ν is a factor with the dimensions of a frequency which must be the same for both forward and backward reactions.

The evaluation of the factor ν was accomplished by Eyring (3, 8, 41, 15), who approached the problem by the method of quantum-statistical mechanics. If we consider the potential energy surface of the reaction we see that this surface is divided into two parts by the line (or hypersurface) drawn through those configurations in which the initial and final ways of drawing the valence bonds have equal energies. We may say that on one side of this line the molecules have not reacted and that, on the other, the reaction has taken place (cf. Fig. 1). The problem of determining the reaction rate is therefore the problem of determining, first, the number of molecules lying at any instant in a narrow strip lying along this line and, then, the mean time taken by such a molecule to cross the strip.

If we make the assumption that the molecules whose configurations lie within the strip are in equilibrium with the reactant molecules (an assumption which is probably correct if the reaction is not too fast) (9, 28, 22), the number in the strip at any instant will be determined by an equilibrium constant, which according to statistical mechanics is of the form

$$K = \frac{(2\pi mkT)^{1/2}\delta}{h} K^*$$

where m is the " reduced mass " of the system, δ is the width of the strip, k is Boltzmann's constant, h is Planck's constant, and K^* is the equilibrium constant between the reactant molecules and a hypothetical molecule which would be formed if somehow the motion of the system could be confined to the line dividing the potential energy surface, that is, allowed to move in any way except in the direction leading back to the original reactant molecules or on to the product molecules. This equilibrium constant K^* can be endowed formally with all the properties of any other equilibrium constant (2, 10). In particular it may be expressed in terms of the free-energy change in going from the reactants to the activated complex by

$$K^* = e^{-\Delta F^*/RT}$$

We may therefore write the number of activated complexes at unit concentration of the reactant molecules in the form

$$\frac{(2\pi mkT)^{1/2}\delta}{h} e^{-\Delta F^*/RT}$$

Statistical mechanics also gives the mean time for a molecule to cross the strip as

$$\left(\frac{\pi m}{2kT}\right)^{1/2}\delta$$

so that the total number of molecules crossing per second is

$$2\,\frac{kT}{h}\,e^{-\Delta F^*/RT}$$

However, since we have considered the system at equilibrium, half of these crossings take place in either direction. The number of crossings corresponding to the forward reaction is therefore half of this quantity, or

$$\frac{kT}{h}\,e^{-\Delta F^*/RT}$$

There is still, however, one factor which has not been taken into account, namely, the number of molecules which cross the dividing line, but which return again to the side from which they started. If a fraction κ of the molecules which cross return, the rate expression obtained above should be multiplied by κ, so that the expression becomes

$$\kappa\,\frac{kT}{h}\,e^{-\Delta F^*/RT}$$

The value of κ, however, will be nearly unity in most cases, and in any event there is as yet no reliable method of estimating its value. We shall therefore usually make the assumption that $\kappa = 1$.

It will be noticed that this expression is identical with that suggested by LaMer and Rodebush, but with the frequency factor ν put equal to $\kappa(kT/h)$. We thus find that, except for the relatively unimportant factor κ, the value of ν is not only the same for two opposing reactions but for all reactions.

If we wish to compare this statistical theory of reaction rates with the collision theory, it is convenient to separate the free energy of activation into a heat content of activation and an entropy of activation, using the usual thermodynamic formulas

$$\Delta S^* = -\frac{\partial \Delta F^*}{\partial T}$$

$$\Delta H^* = \Delta F^* + T\Delta S^*$$

In terms of these quantities the statistical rate expression becomes

$$\kappa\,\frac{kT}{h}\,e^{\Delta S^*/R}\,e^{-\Delta H^*/RT}$$

The ΔH^* of this expression is identical with the E of the collision expression as ordinarily calculated from the temperature coefficient of the rate constant. The remaining factors are therefore equivalent to the PZ of the collision theory.

As a matter of fact, if we make the assumption that the reacting molecules are rigid spheres the statistical theory gives exactly the same result as the collision theory. Thus in the only case in which the collision theory has a precise significance the two theories give identical results. We may therefore regard, if we please, the collision theory as a special instance of, or a first approximation to, the statistical theory.

If we now turn to the interpretation of the ΔH^* and ΔS^* of a chemical reaction, we find that each of these quantities has a definite significance in terms of the potential energy surface of the reaction. ΔH^* is determined principally by the height of the potential barrier which must be surmounted for reaction to take place. However, there are small additional terms owing to the fact that at any temperature above the absolute zero the reactant molecules will possess a mean kinetic energy, and molecules which get over the barrier will do so with a little energy to spare. These terms are also included in ΔH^* and cause it to differ from the height of the barrier by amounts of the order of a few RT.

The entropy of activation, on the other hand, is quite independent of the height of the barrier. Instead its value is determined by the general nature of the activated complex and is very sensitive to quantum effects (35). If we consider, for example, the simplest case of a bimolecular reaction, each molecule, before collision, possesses its three degrees of translational freedom and two or three degrees of rotational freedom. The activated complex, on the other hand, has only three degrees of translational freedom and three degrees of rotational freedom. There is, therefore, a conversion of three degrees of translational freedom and at least one degree of rotational freedom into vibrations. Since this change is accompanied by an increase in energy quanta for the degrees of freedom concerned, a considerable decrease in entropy is to be expected. At the same time, however, there is a decrease in the number of molecules from two to one, which has the effect of causing a compensating increase in entropy, at least if the ordinary concentration units are employed. This increase partially compensates for the decrease due to the " freezing in " of the translational degrees of freedom, but not completely, so that the net effect is a decrease of about 20 cal./deg. in the entropy.

The theory is not confined to bimolecular reactions. If the activated complex is formed from three molecules (it does not matter how), the reaction is termolecular and the same expressions hold for the rate.

The difficulties of defining a " three-body collision " are completely removed. The only difference between a bimolecular and a termolecular reaction is the order of magnitude of the heat and entropy of activation. In general the entropy of activation in the termolecular case is much smaller than that in the bimolecular case (more translational degrees of freedom are lost), so that if the rate is to be conveniently measurable the heat of activation must be fairly small.

The theory can also be applied to unimolecular reactions, at least at high pressures. At low pressures, however, where the characteristic " falling off " of the rate constant occurs, the assumption of statistical equilibrium between the activated complexes and the reactant molecules breaks down. Nevertheless it is possible to include this case as well if the reaction is considered as occurring in two steps, of which the first is the production of an energy-rich molecule by collision. These collisions may be considered in the same way as a bimolecular reaction, and the theory applied in the usual way.

Kimball (16*a*) has shown that this theory can also be applied to rates of adsorption and desorption. If an adsorbing surface is thought of as consisting of a number of " active spots," then there will be a potential energy surface for each spot over which any molecule must pass before it can be adsorbed. This surface will usually show a barrier of some sort, so that a certain amount of activation energy must be supplied before adsorption can take place.

The rate at which molecules pass over the energy barrier can then be calculated in exactly the same way as for a homogeneous reaction. The result is then the rate at which molecules are adsorbed on a single active spot. The total rate of adsorption is the sum of the rates of all the active spots. If a surface is composed of K spots, all of which are like, the specific rate of adsorption is

$$\kappa \frac{kT}{h} K e^{-\Delta F^{*}/RT}$$

where ΔF^{*} is the free energy of activation on a single spot. The same equation can also be used if the spots are not alike, provided that ΔF^{*} is interpreted as the mean free energy of activation on a spot. Since the number of active spots is not usually known, it is often convenient to absorb K into ΔF^{*}. This may be done by writing the previous equation in the form

$$\kappa \frac{kT}{h} e^{-(\Delta F^{*} - RT \ln K)/RT}$$

or, if we put $\Delta F' = \Delta F^{*} - RT \ln K$, the specific rate may be written

$$\kappa \frac{kT}{h} e^{-\Delta F'/RT}$$

If we differentiate $\Delta F'$ with respect to the temperature, we find that

$$\Delta S' = \Delta S^* + R \ln K$$

and

$$\Delta H' = \Delta H^*$$

The inclusion of the number of active spots in the free energy of activation therefore changes the entropy of activation without affecting the energy of activation. It is therefore possible to determine the energy of activation even when the number of active spots is not known.

In some cases, particularly reactions between ions in solution and smooth metallic surfaces, the whole surface may be regarded as a single active spot, and the difference between ΔF^* and $\Delta F'$ vanishes. In these cases the statistical theory reduces again to the classical collision theory.

Although the activation energies of reactions are familiar, the entropies of chemical reactions are not yet generally known. In a " normal " bimolecular reaction, i.e., one for which the collision theory gives reasonable results, the entropy of activation has a small positive value, usually in the neighborhood of 10 cal./deg. Any large departure from this value is an indication of abnormality. A very large entropy of activation (i.e., an abnormally fast reaction) indicates an activated complex in which new degrees of freedom are active. Such an example is found in the denaturation of proteins, where the entropy of activation is of the order of 100 cal./deg. This is an indication that the denaturation is essentially a dissociation process (36). On the other hand, an abnormally low entropy of activation indicates a freezing in degrees of freedom. This is illustrated by the negative entropies of activation of most termolecular reactions, and to an even greater extent by the large negative entropies of heterogeneous reactions, in which the motion of the adsorbed molecule is reduced from a three-dimensional motion to one of two or fewer degrees of freedom.

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CHAPTER II

FREE RADICALS AND SURFACE REACTIONS

F. O. RICE

Brief Review of Their Position in Homogeneous Catalysis

The question of the position of free radicals in homogeneous catalysis is intimately bound up with the question as to whether or not organic decompositions occur through a free-radical mechanism and what is the nature of free-radical reactions. It is with such questions as these that we shall mainly be concerned in this section.

As it is only ten years since the discovery by Paneth and Hofeditz (25) of the effect of free radicals on metallic mirrors provided a method of direct study of organic fragments, this whole field is necessarily in an incipient state of development, from both the theoretical and the experimental aspects. The experimental work during the first few years (1928–1933) was to a large degree directed to the preparation and study of aliphatic organic radicals by the methods developed by Paneth, namely thermal decomposition in a flowing system at low pressures and then formation of an organometallic compound by bringing the radicals produced into contact with cooled metallic mirrors. In this way Paneth succeeded in preparing the methyl and ethyl radicals (27) from the corresponding lead alkyls but was unsuccessful in attempts to prepare larger radicals by this technique. The difficulty of preparing large radicals was also shown in succeeding experiments using the Paneth technique, in which hydrocarbons, ethers, ketones, amines, etc., were decomposed (35). In the range 800 to 900°C., free radicals were formed in abundance and it was first thought that they were mainly methyl radicals accompanied by some ethyl radicals; however, as the technique of identification was improved, it was finally shown that both propane and butane gave methyl radicals only (32). It seems, therefore, that there is a sharp division between the stability of methyl and that of larger radicals (31).

This difference in stability of radicals is very probably an important factor in both homogeneous and heterogeneous reactions. In order to discuss this stability as well as the reactivity of radicals we will first present a simplified form of the Rice-Herzfeld scheme (34) for the free-radical decomposition of organic compounds (37): A molecule M decomposes thermally into two radicals R_1, which attack the substrate, removing a hydrogen atom and forming a large radical R_2; this decomposes to regenerate R_1 and to give a molecule M_2. The chain ends by the cross combination of R_1 and R_2. The following equations represent this scheme:

$$M_1 \longrightarrow 2R_1 \qquad k_1,\ E_1 \qquad (1)$$

$$R_1 + M_1 \longrightarrow R_1H + R_2 \qquad k_2,\ E_2 \qquad (2)$$

$$R_2 \longrightarrow R_1 + M_2 \qquad k_3,\ E_3 \qquad (3)$$

$$R_1 + R_2 \longrightarrow R_1 - R_2 \qquad k_4,\ E_4 \qquad (4)$$

Reactions *2* and *3* constitute the chain, and at the stationary state they have of course equal rates which are also equal (for long chains) to the rate of the overall reaction. One of the factors which control the rate of the overall reaction, therefore, is the stability of the large radical R_2; indeed, if the stability of R_2 is such that E_3 approaches in value E_1, a chain reaction becomes impossible even though the primary reaction is entirely a radical rupture as represented by equation 1. This situation probably occurs in the thermal decomposition of propylene (7) and in the sensitized decomposition of acetone (38). On the other hand, if the radical R_2 is very unstable so that E_3 has a relatively low value, the concentration of R_2 may become so low that the chain ending by reaction *4* may be negligible in comparison with the recombination of R_1 according to,

$$2R_1 \longrightarrow R_1 - R_1 \qquad (5)$$

This is the situation, according to the free-radical scheme, with acetaldehyde, in which the radical CH_3CO certainly has a low stability as shown by the experiments of Barak and Style (2).

It is clear, therefore, that quantitative measurements of the stability of radicals (i.e., of E_3 in equation 3) are required in order to determine the part played by free radicals in homogeneous catalysis. Up to the present, however, our information is extremely qualitative or is based on estimates for the individual steps in free-radical schemes; the main justification for such estimates is that they give a correct value for the overall rate. The photochemical experiments of Pearson and his co-workers (1) have shown that it is possible to prepare larger free radicals, and hence it should be possible to make a direct quantitative measurement of their stability.

Fortunately the mechanism of the decomposition of large radicals is in most cases reasonably certain. The thermal decompositions of the radicals, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$, and CH_3OCH_2 may be represented as follows:

$$CH_3CH_2CH_2 \longrightarrow CH_3 + CH_2{=}CH_2 \tag{6}$$

$$CH_3CH_2CH_2CH_2 \longrightarrow CH_3CH_2 + CH_2{=}CH_2 \tag{7}$$

$$CH_3OCH_2 \longrightarrow CH_3 + HCHO \tag{8}$$

with a fair degree of certainty since practically all considerations from the standpoint of thermodynamics and motion of the atoms (12) or electrons support these mechanisms. It should be possible to determine the activation energies of these decompositions by a chemical analysis of the products of decomposition of unstable organic compounds containing radicals; a series of analyses at different decomposition temperatures for the substrate would show the extent of disappearance of the large radical with increase of temperature. Frey (9) has made such analyses at a single temperature for mercury dibutyl and mercury di-sec-butyl and has shown that the products are in agreement with the foregoing mechanism.

The interaction of radicals with molecules (equation 2), since it is the other half of the chain-carrying process, is of equal importance with the decomposition of radicals. Radical interaction with molecules has been studied to a much greater extent than radical decompositions, and some direct measurements of activation energies are now available. However, the problem is complicated because usually a radical may react in a number of ways with an organic molecule. An attempt has recently been made to simplify the problem by formulating a principle called the principle of least motion (39), which states that, where a number of possibilities exist, an elementary reaction will be favored which involves least change of atomic position and least change of electronic configuration. From this standpoint, removal of a hydrogen atom from an organic molecule by a free radical is in general the most favored reaction. The hydrogen atoms are on the periphery of the molecule, and hence reaction with them involves least atomic motion; and incipient bond formation between a positive hydrogen atom and a negative carbon atom of the radical is also favored. According to this principle we should exclude reactions in which a free radical attacks a shielded carbon atom; as examples we may give deuterium and methane and methyl and propane:

$$D + CH_4 \longrightarrow CH_3D + H$$

$$CH_3 + CH_3CH_2CH_3 \longrightarrow CH_3CH_3 + CH_3CH_2$$

The amount of atomic motion involved in such reactions makes them exceedingly unlikely in comparison with reactions involving the removal of hydrogen atoms.

The application of this principle to the decomposition of organic molecules leads to the conclusion that dissociation into radicals (reaction *1*) is favored over schemes in which atoms or groups migrate from one part of a molecule to another. The decomposition of dimethyl ether, $CH_3-O-CH_3 \longrightarrow CH_4 + HCHO$, in a single elementary act requires a hydrogen atom to move through a rather large distance and to attack a shielded carbon atom. The decomposition of ethane is apparently a chain reaction even though the direct separation of two hydrogen atoms as molecular hydrogen does not meet the difficulties shown in the previous reaction, in which methane separates from dimethyl ether.

In the last few years there has accumulated a considerable body of evidence that a free-radical scheme consisting in outline of reactions *1*, *2*, and *3* and terminated either by *4* or *5* predominates in organic thermal decompositions. The foregoing brief outline should be read in conjunction with two comprehensive reviews of the whole subject that have recently appeared (23, 24).

A free-radical scheme of this kind leads to the conclusion that both positive and negative catalysis can occur in homogeneous reactions. The introduction of a small quantity of compound less stable than the substrate would be expected to provide radicals at temperatures lower than the ordinary decomposition temperature and in this way initiate chains. The effect of ethylene oxide on hydrocarbon decompositions (4), first noticed by Heckert and Mack (11), is most probably to be ascribed to this action; and many similar examples, such as the effect of diethyl mercury on butane (8) and the effect of azomethane on acetaldehyde (40), have been observed. The same sort of effect would be expected by a bimolecular reaction, which produces radicals, between the substrate and a small amount of added substance. Thus either chlorine or oxygen might be expected to initiate chains by reaction with organic molecules below their decomposition temperatures.

The photochemical introduction of radicals can be accomplished by direct absorption of light by the substrate, such as the photochemical decomposition of acetaldehyde studied by Leermakers (20). He also studied an example of induced photochemical decomposition in which the substrate (dimethyl ether) was transparent, but a small quantity of acetone decomposed photochemically into radicals. Mercury photosensitization is also a possible catalytic method for organic decompositions although it has been mainly investigated in connection with the production of hydrogen atoms and polymerization processes (45).

According to the free-radical theory, retardation of the rate of homogeneous reactions can be caused by the addition of a substance which diminishes the stationary state concentration of the free radicals. Hinshelwood and his co-workers (41) found that nitric oxide inhibits the decomposition of some organic compounds but not others, and sometimes the products of a reaction have a slight but definite retarding influence. Propylene has also been found (36) to be an inhibitor for hydrocarbons, ethers, acetone, and acetaldehyde. Echols and Pease (5) have found the effect also in the thermal decomposition of butane.

One might also expect to find retardations of thermal decompositions by increasing the ratio of surface to volume of the reacting vessel since it is well known that oxidation chains can be profoundly affected by such treatment. However, these effects are usually small; for example, Fletcher and Hinshelwood (7) report that packing the reaction vessel reduces the rate of the acetaldehyde decomposition by about 15 per cent. In this connection it may be noted that, when free radicals were produced according to the Paneth technique, iron, nickel, copper, platinum, glass, and silica caused no perceptible difference in the lifetime of the radicals; furthermore, Paneth, Hofeditz, and Wunsch showed (26) that heating the walls of the tube greatly increased the lifetime of the radicals at first, but that the effect reached an optimum and further rise in temperature shortened the life. Because it does not seem possible to offer any satisfactory explanation of this effect at present, further investigation is necessary.

Reactions of Gaseous Radicals at Metallic Surfaces

Although the discovery that free radicals react with many metals to form volatile organometallic compounds has been a potent method for studying free radicals, it has hardly been exploited at all as a means of investigating metallic surfaces and the reactions that occur there.* Hardly anything is known about the effect of the physical state of the metal on the rate of combination with radicals. A few preliminary experiments in the author's laboratory have indicated that a lead mirror which was oxidized and then reduced would not react with radicals, nor would massive lead react very readily. On the other hand, if a piece of lead was reduced in hydrogen just before being used as a source of mirrors, the first mirror was readily removed; whereas, without such a preliminary reduction, the first mirror could not be removed.

The temperature coefficient of mirror removal should also be investigated for different metals. Some preliminary measurements made by

* Professor J. B. Tomlinson has undertaken to investigate these phenomena, and the author is indebted to him for various suggestions in connection with this section.

the author have shown that, whereas the rate of removal of lead diminishes with rise in temperature, the rate of removal of antimony over a wide range of temperature appears to be unchanged.

The actual products formed are of the greatest interest in connection with reactions at surfaces, and, in general, the primary products do not seem to be identical with the ordinary organometallic compound. This is particularly striking in the case of tellurium, which gives a deep red, bromine-like compound having the formula $CH_3TeTeCH_3$ (33), instead of the expected CH_3TeCH_3. On the other hand, mercury gives almost entirely dimethyl mercury, although there seems to be a small quantity of some unstable compound which may be the mercury analog of dimethyl ditelluride, or may be the organo-metal CH_3Hg; in any case, there is a small amount of deposition of metallic mercury from dimethyl mercury that has been prepared from free radicals (32). In this connection, it is interesting to note that benzyl radicals combine with mercury to give the compound $(C_6H_5CH_2Hg)_2$, which decomposes at room temperature to give mercury dibenzyl and metallic mercury (13). We have found that the methyl lead derivatives, formed by the action of methyl radicals on lead, also deposit some of the metal on standing.

Paneth and his co-workers (28) have investigated in considerable detail the products formed by the action of methyl and ethyl radicals at surfaces of arsenic, antimony, and bismuth. The action of methyl radicals on hot mirrors yields a bright yellow oil, having the empirical formula $(CH_3As)_n$; the data in the literature for this substance are somewhat discordant, and it does not seem to be entirely certain whether the substance has the formula $CH_3As=AsCH_3$, or is a five-membered ring, $(CH_3As)_5$. If the temperature of the arsenic mirror is lowered, apparently the bright yellow oil cannot evaporate from the surface, and the chief compound is the colorless cacodyl, $(CH_3)_2AsAs(CH_3)_2$, accompanied by some trimethyl arsine and a slight amount of the yellow oil. The action of free ethyl radicals on both hot and cold arsenic mirrors is somewhat similar.

Free methyl radicals react with metallic antimony, irrespective of the temperature, to produce trimethyl stibine and a smaller quantity of a brilliantly red substance, which was found to be the antimony analog of cacodyl, $(CH_3)_2SbSb(CH_3)_2$. Both the methyl and ethyl reactions produced small quantities of black products, but in amounts insufficient for identification.

Organometallic Complexes

It is a commonplace that certain groups of elements, none of which are metals, possess the power of forming positive ions in solution. The analogy of such groups to metals was recognized at a very early date, and various attempts were made to obtain and study the neutral group by discharging it electrically at a cathode. Palmaer (24) actually succeeded in isolating tetramethyl ammonium by electrolyzing a solution of one of its salts in liquid ammonia. Kraus (16) repeated and extended these experiments, and showed that even tetrapropyl ammonium salts yield a blue-colored solution at the cathode. However, the solutions obtained in this way are unstable, and the blue color disappears at the end of a few minutes.

There are also a number of metals which form groups with non-metallic elements, and these groups sometimes behave in an analogous manner (21). We have, for example, alkyl mercuric salts such as methyl mercuric chloride, CH_3HgCl, trialkyl tin salts such as trimethyl stannic iodide, $(CH_3)_3SnI$, and tetraalkyl stibonium salts such as tetramethyl stibonium iodide, $(CH_3)_4SbI$.

Kraus (15) performed a number of experiments in which he attempted to deposit the free organo-metal by electrolyzing a solution of the salt in liquid ammonia. He obtained positive results only with alkyl mercuric salts, and then only when the alkyl group was butyl or smaller. In these experiments, the free group was deposited on a platinum cathode in the form of a highly attenuated opaque mass, without evolution of gas or the production of appreciable heat. It was necessary to compress the deposit into a compact mass from time to time. The black deposit coheres when compressed, and sometimes, as in the case of ethyl mercury, CH_3CH_2Hg, exhibits metallic reflection, of a copper-like color. None of the alkyl mercury groups amalgamates with mercury to a marked extent. They are all unstable, and at room temperature rapidly decompose to give metallic mercury and the corresponding dialkyl derivative. Methyl mercury does not react with alcohol.

Organo-metals, such as the monoalkyl mercury complexes just described, may possibly be of importance as intermediates in heterogeneous catalysis, and may also be the primary products formed when free radicals are brought into contact with a metallic surface. Thus the mechanism of the formation of dimethyl mercury from free methyl radicals and metallic mercury might be the formation of methyl mercury, followed by its evaporation and subsequent decomposition on warming the liquid air trap. However, we have never found any evidence of this occurring, and an unpublished experiment (with Dr. B. L. Evering), in which we attempted to distil methyl mercury in a high vacuum, gave negative results.

The properties of trimethyl stannyl, $(CH_3)_3Sn$, are in sharp contrast to those of methyl mercury, and are those of a non-metal, rather than a metal. In the free state, the group is a non-metallic solid, melting at 23°C., which reacts readily with both positive and negative elements (17). The compounds with positive elements are typical salts, but the compounds with negative elements are non-conductors, so that the tendency is for trimethyl stannyl to add an electron to form a stable anion.

Diethyl tin, $(CH_3CH_2)_2Sn$, may be easily prepared by the action of sodium on the dichlor derivative, and is a slightly yellow, odorless oil (44).

Various organo lead compounds of the general formula R_3Pb and R_2Pb are known (18, 22). Thus tricyclohexyl lead is a yellow solid, soluble in benzene, and exists as the monomer in dilute solution. Diisopropyl lead has been prepared, and is a liquid, closely resembling bromine in color (44).

These curious organometallic " radicals " have not been studied to any marked extent, although this is surprising in view of their importance in connection with theories of the catalytic surface. Such compounds of catalytically active metals do not seem to have been prepared at all, although the existence of ethyl iron chloride (14), CH_3CH_2FeCl, and trimethyl platinum iodide (29) suggests that organo complexes of catalytically active metals can also be prepared.

Production of Radicals at Electrodes

Early investigations by Tafel (43), Law (19) and Renger (30) showed that organic radicals could be liberated at metallic electrodes, and their presence proved by the formation of organometallic compounds. For example, when aliphatic ketones are electrolyzed in 10 per cent aqueous sulfuric acid, using a lead cathode, a considerable yield of a red oil is obtained. This oil has been analyzed and found to consist mainly of lead tetraalkyls, with some unsaturated lead compound, believed to have the formula R_3PbPbR_3, or $R_2Pb = PbR_2$. Mercury cathodes also yielded oils, but no other cathodes were known at that time to do this.

Later investigations by Hein and co-workers (12) showed that many metals could be combined with free radicals in a similar way. Sodium ethyl dissolves in zinc diethyl to form a conducting solution containing presumably a negative ethyl ion which can be discharged at the anode. With certain anodes, such as platinum, copper, iron or tantalum, ethylene and ethane are the only products, presumably because of disproportion of the ethyl radicals formed at the surfaces. On the other hand, when a lead anode is used, no hydrocarbons are formed, but only tetraethyl lead. Similar results were obtained with a wide variety of other metals, such as zinc, antimony, aluminum, bismuth, thallium, gold, and tin. In this connection also, the work of Evans and Lee on the electrolysis of an ethereal solution of ethyl magnesium chloride should be noted (6).

Experiments in the author's laboratory have shown that when an aqueous sulfuric acid solution of an organic compound, such as acetone or acetaldehyde, is electrolyzed, there is considerable disintegration of the electrode, to give the colloidal metal, which is manyfold greater than in the absence of the organic compound; this is true whether or not there is obvious production of an organometallic compound in addition. It has been known for a long time that when either lead or mercury is electrolyzed with the metal as cathode, the electrode disintegrates, and the solution becomes diffused with metallic dust (3). Possibly this may be due to hydrogen atoms penetrating some distance into the metal and collecting there in small cavities, in which finally is built up such a high pressure that they burst, and small pieces of the metal are shot into the solution. Haber (10) supposed that the metal forms an unstable hydride which floats into the solution and decomposes to give the finely divided metal and hydrogen gas. At any rate, the enhanced formation of colloidal metal, when an organic compound is present in the solution, suggests that the formation and decomposition of a very unstable organometallic compound may be a contributing factor in this effect.

Summary

It is only to be expected that there should be a close analogy between the chemical mechanism of homogeneous organic reactions and those occurring at surfaces. The same sorts of difficulties arise as to which of many reactions we should select. More especially there is the question whether there can be attack on a shielded carbon atom. It is difficult to see how the two carbon atoms in ethane could get into contact with a surface and dissociate directly into two methyl radicals adsorbed there. Such a reaction would certainly appear to be in conflict with the principle of least motion already discussed and would be similar to the homogeneous reaction $H + C_2H_6 = CH_4 + CH_3$. The experimental production of methane from ethane at a catalyst surface must, on this basis, be explained in some other manner than by direct dissociation of ethane into adsorbed methyl radicals.

The well-known exchange reactions between saturated hydrocarbons and hydrogen or deuterium do not cause any difficulty because the hydrogen atoms are on the periphery of the hydrocarbons. Possibly the breaking of a carbon-carbon bond must be preceded by dehydrogenation and production of an ethylene or acetylene linkage, so that two carbon atoms can become attached to the catalyst surface.

Closely allied to this question is the mechanism of formation of tetra-alkyl compounds from certain metals such as lead. We know that when free radicals attack a tellurium surface dimethyl ditelluride is formed, in which one methyl group is attached to each tellurium atom. Possibly tetramethyl lead is a secondary product formed by interactions after a similar lead compound leaves the surface; it would seem well worth while to investigate the structure of the primary products of free radicals at surfaces which they attack in the hope that such reactions will lead to a better understanding of heterogeneous catalysis.

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CHAPTER III

ACTIVATED ADSORPTION

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The progress of any heterogeneous catalytic reaction can be resolved into at least five different steps: *1* the diffusion of the reactants to the catalyst, *2* the formation of the adsorption complex, reactant-surface, *3* the chemical change at the surface, *4* the decomposition of the adsorption complex, product-surface, and *5* the diffusion of the reaction products from the catalyst. Unless all these processes accidentally possess the same velocity, it is the slowest of the five which determines the overall rate of change. Originally, in contact catalysis, processes *1* and *5* were given most consideration as the slow processes. Langmuir, with the development of the concept of the unimolecular adsorbed layer, shifted the emphasis to *3*, adsorption being assumed to attain equilibrium rapidly. The possibility that *2* might be an important rate-determining process in a catalytic change arises if adsorption precedent to catalytic change may require an activation energy. The rate of decomposition, *4*, of an adsorption complex, product-surface, or of a complex, poison-surface, has long been known to exercise a controlling influence in the rate of certain reactions at surfaces.

The concept of activated adsorption was developed (30) in an effort more closely to correlate the specific activity of contact catalysts with their adsorption characteristics. The specific nature of the catalytic reactions contrasts sharply with the non-specific adsorptions of classical colloid chemistry. The adsorption theory of contact catalysis always faced the difficulty of explaining why catalytic reaction was small at low temperatures, when the non-specific adsorption was greatest, and became continuously more rapid as such adsorption steadily decreased with increasing temperature. The concept of at least two types of adsorption association of a gas with a surface and the additional assumption of an activation energy for one of them at once provided a basis upon which the adsorption theory of contact catalysis could the better be formulated. It led naturally to a search for adsorption effects in temperature ranges where molecular adsorption would be entirely negligible. These were abundantly successful. A summary of many adsorptions so located was presented in the Eleventh Report of this Committee. It is significant that the search for such adsorptions was, in almost every case.

suggested by the data of catalytic reactions. Simultaneously with such search for adsorptions, measurements were made of the velocity processes over a range of temperature in an effort to determine the magnitudes of the activation energies associated with such gas-solid interactions. In the interpretation of the significance of these slow processes the sharpest differences of opinion were revealed. Proponents of activated diffusion, activated adsorption, and of the view that the slow process measured was a cleansing of the surface have all attempted to establish their own particular thesis without, one must confess, any clear-cut decision being yet reached. In the writer's view, there are well-established cases of the first two, with positive indication that the third case of surface cleanliness is sometimes operative. It must be emphasized, however, that neither activated diffusion nor slow removal of surface impurities can have any relevance to the problem of specific catalytic action whereas an activation energy of adsorption must play a controlling role in the speed of surface catalytic processes under certain conditions.

The nature of the association between an adsorbed gas and the surface can be explored by other methods than by measurement of extent of adsorption and its velocity in a given temperature range. During the last three years a number of such researches have been conducted.

Spin Isomerization of Hydrogen and the Adsorption Process

They began with an inquiry into the influence of surfaces on the spin isomerization of hydrogen by which we designate the reversible conversion of ortho- to parahydrogen. From a series of researches (3, 4, 10, 31, 32) it is now clear that this conversion can be achieved at surfaces by two mechanisms. At paramagnetic surfaces molecularly adsorbed hydrogen undergoes a very rapid spin isomerization. This is true at surfaces of reduced iron (10), chromium oxide (32), and certain paramagnetic rare-earth oxides (32). Catalytically inactive metal salts which are paramagnetic will also induce this conversion (34). Diamagnetic rare-earth oxides, as for example, lanthanum oxide, show very feeble activity in this regard, and this is true also of other diamagnetic solids such as zinc oxide and silver. With diamagnetic substances, however, there is always some activity for spin isomerization, especially marked in the case of charcoal, and this is ascribed to the existence, on the surface, of magnetic dipoles, most probably at the atoms in the surface most detached from the normal crystalline arrangement of the solid (4). The speed of this conversion will be proportional to the quantity of adsorbed gas and the field strength. Such isomerization will bear no relation to specific catalytic activity.

The second mechanism of spin isomerization involves an actual atom exchange in the molecules and activity for this type of change parallels the catalytic activity of metal wire catalysts and the activated adsorption of hydrogen on metal and oxide surfaces (2, 35). It predominates in the higher ranges of temperature, the first mechanism being there unimportant by reason of the decrease in molecular adsorption with increased temperature, which latter favors the process of activated adsorption.

Isotope Exchange and the Adsorption Process

The extent of the atom-exchange mechanism on a given surface can be separately studied by following the interaction of hydrogen and deuterium to form hydrogen deuteride, $H_2 + D_2 = 2HD$. This must involve atom exchange and cannot be achieved by magnetic effects. A comparison, therefore, of spin isomerization and isotope exchange on various surfaces is most illuminating. At −185°C., spin isomerization is rapid and isotope exchange is immeasurably slow on charcoal (16). The mechanism of the former is therefore magnetic. At the same temperature, spin isomerization is immeasurably rapid, and isotope exchange slow but measurable, on chromium oxide gel (16). The first mechanism predominates but atom exchange is occurring even at this low temperature. Over a range of temperatures, on several surfaces, spin isomerization passes through a minimum and then increases (32). As temperature increases, there is a transition from magnetic effects to atom exchange as the predominant reaction. At room temperature and upwards, on metal wires, spin isomerization and isotope exchange are practically equal in velocity, indicating negligible contribution from magnetic influences.

Spin Isomerization on Oxygen-Covered Surfaces

Spin isomerization may be used as a criterion of two types of binding of oxygen to a surface. Oxygen adsorbed on charcoal at −185°C. is still paramagnetic and, so adsorbed, markedly accelerates the ortho-para conversion (4). The molecular state of the gas is not destroyed by the adsorption process. Above −78°C., the oxygen is adsorbed in a different manner for it is no longer paramagnetic and, in this condition of adsorption, actually retards the spin isomerization process. This change in the method of binding of a gas to a given surface as the temperature of the system is varied constitutes an excellent illustration of the phenomena which require for their understanding a concept of activation energy as applied to the adsorption process. As is well known, the higher temperature adsorption of oxygen is so strong that it is not reversible. On evacuation, at still higher temperatures, oxygen is not desorbed, the surface carbon linkages are broken, and oxides of carbon are recovered by the evacuation process. The extension of this test for two types of oxygen adsorption to various oxide surfaces would undoubtedly be illuminating. There are various oxides on which, according to other observations, activated adsorption occurs, which is reversible when the gas-adsorbent complex is evacuated at much higher temperatures.

Activated adsorption of hydrogen on charcoal at 500°C. has been shown to increase the half period of reaction of ortho-para conversion on charcoal at 20°C. (5). This is to be attributed to the saturation, by the adsorption process, of those carbon atoms in the surface which, by reason of their partial detachment from the solid lattice, behave as magnetic centers even though the bulk material is diamagnetic in the case of charcoal. It definitely indicates also that the high-temperature attachment of the hydrogen involves electrons which when not participating in the adsorption process confer, on the carbon atoms associated with them, paramagnetic properties.

Isotope Exchange and Active Centers

The isotope exchange reaction, $H_2 + D_2 = 2HD$, can be used to indicate the existence of centers on the surface at which activated adsorption and catalytic action occur with a whole series of varying activation energies. This was evident from the experiments cited above concerning chromium oxide surfaces where activity at −185°C. could not be associated with the activated adsorption of hydrogen studied in the temperature range of 100 to 300°C. In this latter range activation energies of the order of $\sim$20 kcal. and heats of adsorption as large as $\sim$25 kcal. are involved. This criterion of varied surface activity for adsorption and reaction has been most comprehensively studied in the case of zinc oxide (28) in the temperature range from −140 to 218°C., with activation energies of reaction, i.e., of desorption, ranging from 0.6 to 13 kcal. These studies also confirmed the existence of activated adsorption with different energies of activation found by measurements of velocity of adsorption in the temperature range of 100 to 184°C.

Isotope Exchange and Activation of Specific Bonds

Isotope exchange reactions may also be used to indicate the existence of activated adsorption under circumstances when no conclusive evidence may be reached from actual adsorption measurements. The exchange reaction between ammonia and deuterium is the one in which the best correlation with the data of activated adsorption has been secured. On iron synthetic ammonia catalysts (34), this exchange reaction and that between hydrogen and deuterium occur even at room temperatures. This indicates that the rate-controlling mechanism does not involve either the N—H or the H—H bond formation or rupture. By elimination, this leaves the activation of the N—N bond in nitrogen molecules as the rate-determining process, in best accord with the correlation of velocity of activated adsorption of nitrogen and velocity of ammonia synthesis on such catalysts (9).

A fruitful field for the extension of such studies has been found in the isotope-exchange reactions of the hydrocarbons. Ready exchange of deuterium with hydrogen in ethylene and in benzene, on nickel catalysts (15, 17, 18), indicated the ready rupture of C—H bonds in such molecules. This observation was later extended to the saturated paraffin hydrocarbons (22, 23). In the series methane, ethane, and propane it was found that deuterization to a given degree in unit time could be secured at progressively lower temperatures with increasing molecular weight. This points to a possible progressive, if small, decrease in energy of activation of the C—H bond as the molecule increases in complexity, though extent of hydrocarbon adsorption may also be the cause. With ethane and propane, however, containing both C—C and C—H bonds it was demonstrated that activation of the former required the higher temperature, pointing to a higher energy of activation of the C—C bond over that of the C—H bond. In this case, which involves two types of bond in one hydrocarbon molecule, any variable due to extent of hydrocarbon adsorption is automatically excluded, since the two reactions can be studied simultaneously in the one reaction mixture. The kinetics of these two processes, occurring on a given catalyst, with a given set of reaction mixtures, also demands surface areas of variable activity specific for each reaction. The two reactions have quite distinct dependences on partial pressure of hydrogen, a fact which may be cited as excellent proof of the theory of active centers specific for a particular reaction.

With a series of metal catalysts, such as nickel, cobalt (29), and copper (33), the reaction which involves the breaking of the C—C bond in ethane in the presence of hydrogen to form methane occurs at progressively increasing temperatures from 180 to 400°C. The adsorption of hydrogen is not responsible for this since, of the three metals, nickel, which is active at the lowest temperature, most strongly adsorbs hydrogen, as is well known from adsorption measurements and from the kinetic studies of the reaction on the three catalysts. One is therefore forced to the conclusion that the factor which determines the temperature of operation is the activation of the C—C bond and that this requires progressively increasing activation energy as one proceeds from nickel, through cobalt, to copper.

These conclusions, which hold for the saturated hydrocarbons, should not be generalized. In the deuterization and exchange reactions with ethylene on platinized platinum (14) foil in the range 0–150°, the evidence is definite that in the lower temperatures of this range the rate-determining step is the activation of the $H-H$ bond in the molecule. The observed activation energy for ortho-para conversion and for hydrogenation is about 10 kcal., the ethylene occupying a large area of the catalyst. The temperature coefficient of the exchange reaction is larger than that of hydrogenation and corresponds to an energy of activation of 22 kcal., the rate-determining step being $C_2H_4 = C_2H_3 + H$.

With the same catalyst, platinized platinum, the rate of exchange reaction between deuterium and water and some alcohols (12) when compared with the rate of parahydrogen conversion indicates that, at low concentration of water or alcohol, the rate-governing step is the dissociation of these at the surface into RO and H. At higher concentration of these the dissociation of the deuterium is the rate-governing step. With benzene as substrate, on the other hand, the exchange studies indicate (13) that the platinum is mainly covered with deuterium and that the benzene molecules occupy only a certain few places which adsorb them strongly. Owing to this, benzene has a negligible influence on the rate of parahydrogen conversion. The hydrogenation and exchange mechanisms proceed according to two distinct mechanisms, hydrogenation involving concurrent addition of two hydrogen atoms, the exchange consisting of a dissociation of the benzene to phenyl and a hydrogen atom, followed by reunion of the phenyl with a heavy hydrogen atom.

These researches, which indicate clearly that the rate-determining step is largely influenced in velocity by the concentration of other reactants on the surface, are in agreement with actual measurements of velocity of adsorption. Thus, the saturation of zinc oxide surfaces with water vapor has been shown markedly to retard the activated adsorption of both hydrogen and carbon monoxide (7). By overlooking such a possibility, Horiuti and Polanyi (18) were led to reject a mechanism of dissociative adsorption of the substances to be exchanged for the various exchange reactions they considered. All the researches cited in the preceding paragraphs indicate the probability of such dissociative adsorption processes, and this view is strengthened by the observation that exchange between CH_4 and CD_4 molecules occurs on nickel, and even more readily than that between CH_4 and D_2 (22). This latter fact is additional evidence that in the CH_4-D_2 system the surface is mainly occupied by deuterium. In absence of hydrogen, much more of the surface is available for the dissociative adsorption process.

Kinetics of Adsorption on Plane Surfaces

An important group of researches on the kinetics of adsorption processes is due to Roberts (24, 25, 26). He has studied the adsorption of hydrogen, oxygen, and nitrogen on a tungsten filament, the surface of which is reasonably uniform and can be made thoroughly "clean." Saturation with hydrogen occurs at a partial pressure of 10^{-4} mm., and the adsorption occurs very rapidly at these low pressures and at 79°K. The heats of adsorption range from 45 kcal. on a bare surface to 18 kcal. on a nearly covered surface. The adsorbed film contains one hydrogen atom per surface atom of tungsten. Roberts points out how this rapid process of chemi-sorption differs radically from slow processes hitherto discussed as activated adsorption. Further, van der Waals adsorption of hydrogen can be observed only after the tungsten surface is covered with the adsorbed film. With oxygen a first film is formed with one oxygen atom per surface tungsten atom with a heat of adsorption of 130 kcal. per mole of adsorbed O_2. A second oxygen film will form, with a heat of adsorption of 48 kcal. per mole O_2, which Roberts indicates would correspond to adsorption on the gaps in the first film. Diffusion of oxygen into the metal also occurs. Adsorption of oxygen occurs on a surface already covered with hydrogen with displacement of one hydrogen molecule per adsorbed oxygen molecule. Partial covering of a surface with oxygen, followed by study of the adsorption of hydrogen, showed a slow uptake of hydrogen similar to that observed by others in activated adsorption studies. This raises the query as to whether the slow processes observed on many oxide surfaces may not be connected with interaction between hydrogen and surface oxygen. In this connection it must be remembered that any such interaction would, in certain cases, have to be reversible since, in many such studies, hydrogen gas has been recovered by desorption. The slowness of the process, even though the surface is plane, suggests, definitely, an activation energy requirement considerably greater than that required by a bare tungsten surface. Also, from the standpoint of catalysis, it cannot too often be emphasized that the correlation between these slow processes and the chemical reactivity of the gas so taken up is the feature of fundamental importance even though the nature of the slow adsorption process remains at present unsolved. Roberts has also shown that nitrogen is rapidly taken up by clean tungsten at room temperatures (25), in contrast with slow adsorption of nitrogen previously observed with tungsten powder preparations.

Activated Adsorption and the Statistical Theory of Reaction Rates

The problem of activated adsorption and of surface chemical reactions, of which, indeed, activated adsorption is the simplest example, can also be approached from the standpoint of the theory of absolute reaction rates in terms of the intermediate activated complex, as developed by Eyring (11). A paper by Temkin (36) is of great interest in this connection. The fundamental equation of Eyring for the rate constant k is

$$k = \kappa \frac{F_t'}{F} \frac{kT}{h} e^{-\epsilon_0/kT} \tag{1}$$

in terms of the height of the energy barrier ϵ_0, the product of the partition functions of the initial molecules F, the partition function of the activated complex F_t' computed over all degrees of freedom except that of the "reaction path," and the transmission coefficient κ generally assumed to be unity. The other symbols have their usual significance.

Temkin shows that this equation leads directly and with a very brief proof to the classical kinetic-theory expression for the number of impacts, M, per second on a uniform plane surface 1 sq. cm. in area at a pressure p, namely $M = p/(2\pi mkT)^{1/2}$. The assumptions underlying the classical treatment are well brought out by this approach. The statistical mechanical treatment shows that, in the classical kinetic-theory treatment, the gas molecules are assumed to be elastic spheres, the rotational states remain unchanged on impact, the surface is an ideal plane, and any forces between the surface and molecules are absent. The activated complex obtains at the moment when the distance between surface and molecule is very small. Repulsive forces normal to the surface between plane and molecule would create an energy barrier ϵ_0 and so the velocity of adsorption would become

$$k = p(2\pi mkT)^{-1/2}e^{-\epsilon_0/kT} \tag{2}$$

A gas so adsorbed would exist in the adsorbed layer as a two-dimensional gas. In the Langmuir theory the adsorbed molecules do not so move but vibrate about definite equilibrium positions, only rarely passing to other positions. For such cases the equation 2, just developed, is invalid. The statistical-mechanical, activated-complex treatment of the Langmuir case, when applied to diatomic molecules dissociatively adsorbed to occupy two elementary spaces, gives in the denominator of equation 1 translational, rotational, and vibrational terms, and five vibrational terms in the expression for F_t'. The effect of these is to introduce an additional factor α into equation 2. This factor, as Temkin shows, has values which may be considerably less than unity. For hydrogen and oxygen on metals at room temperatures he finds values of 2×10^{-2} and

1.8×10^{-5}, respectively. It has been known, for some time, that activated adsorption occurs much less readily than is calculated by the molecular-impact equation 2 with the observed values of ϵ_0. Data of Leypunsky (21) for the rate of adsorption of hydrogen on plane surfaces of nickel indicate an α value of the order just cited. For porous catalysts the experimental values of such a factor as α are very much smaller, and this may be taken as indicating that other factors such as diffusion to inaccessible areas are important.

A chemical reaction occurring upon collision of a gas molecule with an adsorbed molecule on a surface will be governed by the same rate equations as the equation for activated adsorption. Temkin finds evidence for such α values in his studies with Pyzhow (37) of the reaction of oxygen and nitric oxide on glass at 80°K., where the nitric oxide is absorbed, and, with zero activation energy, only one collision in 10^{-4} of the oxygen molecules with the adsorbed nitric oxide leads to reaction. Temkin similarly interprets an efficiency of 10^{-4}, found by Schwab (27) in a study of the reaction $H_2 + CO_2 = CO + H_2O$ on platinum. The reaction is assumed to be between adsorbed hydrogen and colliding carbon dioxide molecules. Schwab concluded that only the 10^{-4}th part of the surface was catalytically active.

Slow Adsorption on Plane Surfaces

Temkin and, also, Roberts call attention to a phenomenon which may cause a slow adsorption even on a plane surface. If a dissociative adsorption of a diatomic molecule to yield atoms bound to the surface is involved, a random distribution of adsorbed atoms may be achieved either if the atoms have surface mobility or, alternatively, in absence of mobility, by the reverse process of desorption. This latter is most readily understood by consideration of adsorption along a line. Initially the atoms will be adsorbed rapidly in pairs. Four adjacently adsorbed atoms may, however, lead to evaporation of atoms 2 and 3 as the desorbed molecule, leaving, as isolated atoms, incapable of evaporation, atoms 1 and 4. By such processes, a random distribution of atoms will ultimately result, but with incomplete covering of the surface, areas on which the diatomic molecule cannot find two adjacent elementary spaces being bare. Temkin estimates the area thus bare as 18 per cent when two spaces are adjacent to a given one. The calculation is more difficult when 4 and 6 such spaces are neighbors to a given space. For the case of 4 adjacent spaces Roberts, by the laws of chance, found that about 8 per cent of the total surface atoms remain bare. It was on these areas that Roberts assumed his second oxygen film was adsorbed.

Adsorption on such areas will be slow. Also, desorption from such surfaces even though plane and uniform will show a time phenomenon. The first evaporation into a vacuum will be rapid as adjacent pairs come off as molecules. Later, the isolated atoms will be much less readily removed, if at all, without surface mobility. Their desorption, however, could be facilitated by the presence, in the gas phase, of some of the molecules, at pressures below the equilibrium pressure. These will aid the removal of isolated atoms by the reverse of the slow process of production of isolated atoms mentioned above.

Slow Adsorption on Heterogeneous Surfaces

In actual catalytic surfaces all the resource of the experimenter has normally been exercised to produce as varied a surface as possible, as unlike the plane surfaces of Roberts' experiments as can be attained. With such heterogeneity, it is obvious that the complexities of the problem are considerably multiplied. There will be areas of different binding energies, there will be varying degrees of mobility on the several surfaces, varying accessibility of the areas of surface to impinging gas molecules. For these reasons, it seems probable that the observed slow processes will, in such cases, be composite of many possible factors, and that a simplified formulation of the total process cannot be attained. It is for this reason that the alternative methods of approach to the problem of the activation of specific bonds and the activation energies of the same, outlined in previous paragraphs, appear to the writer of greater import at the present time.

The difficulty of reaching a compelling conclusion with regard to the nature of the rate-determining step in the activated adsorption of gases with porous substances is well illustrated by the interpretations placed on experimental data for the adsorption of hydrogen on chromic oxide gel at various temperatures (383 to 457°K.) and pressures of 0.125 to 1 atm. Clarke, Kassel, and Storch (8) interpret the data on the basis of activated adsorption on primary centers followed by diffusion, requiring an activation energy, to secondary centers on which no direct sorption occurs. Kimball (19), who has given a treatment of adsorption from the statistical-mechanical activated complex theory of reaction rates, similar to that of Temkin already discussed, reaches a conclusion similar to that of Clarke, Kassel, and Storch. Kimball shows that, for a surface with centers of varying activity, the rate equation is similar to that developed by Temkin for a uniform surface, but, for the activated state, a " super-partition function," formed by adding together the partition functions for all the active spots, is required. In analyzing the data for hydrogen on chromium oxide he concludes that they may best be interpreted in terms of a " gateway " with activation energy less than 21.7

kcal. followed by migration from these areas over potential passes all with nearly the same height 21.7 kcal. The passes are different in shape so that the entropies of activation are different, thus leading to different absolute rates of adsorption.

Burwell and Taylor (6), on the other hand, interpreted their experimental results on the assumption that the surface is composite, that areas exist on which activated adsorption may occur with activation energies ranging from low values to a value of ~21.7 kcal. per mole. This latter obtains on an area relatively uniform and large in extent. The pressure dependence led them to the conclusion that the slow process was a reaction between surface atoms which receive the necessary activation energy and hydrogen molecules adsorbed by van der Waals forces. This is in accord with the observation that hydrogen and deuterium are adsorbed under such experimental conditions on chromic oxide gel at the same rates (20). On the other hand, it is obvious that, at sufficiently low hydrogen pressures, the velocity of the hydrogen and deuterium gas molecules must begin to play a preponderant role, and hydrogen will be more rapidly adsorbed. Some unpublished data indicate the correctness of this conclusion, when the gas pressure is a fraction of a millimeter.

Measurements by Beebe and Orfield (1) of the heats of adsorption of hydrogen on chromic oxide gel at −183°C. indicate the existence of adsorption with heats of relatively low value and yet higher than the heats commonly ascribed to van der Waals adsorption of hydrogen at this low temperature. With increasing coverage, values between 5 and 3 kcal. per mole were measured. Of this adsorption some is not readily recoverable by pumping but the areas laid bare by evacuation readsorbed gas with heat evolutions of the order of 4–3 kcal. Extension of these studies to other diatomic gases such as O_2, CO, and N_2 indicate that, under conditions where practically all the gas is rapidly adsorbed, the initial heat liberated is succeeded by a further heat liberation (without change in the amount adsorbed) amounting to 7–8 kcal. with CO, 15 kcal. with O_2, and 3.5 kcal. with N_2. No such dual effect was found with argon as the adsorbate. These measurements provide evidence of a transformation from one type of association of the gas with the surface to a second in which the heat of binding is stronger than that initially obtaining. This appears to be definite evidence of interaction between van der Waals adsorbed gases and a surface, requiring an activation energy.

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CHAPTER IV

ACTIVE CENTERS

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In the formulation of the concept of non-uniform catalytic surfaces, the concept of " active centers," the evidence from the quantitative data of poisoning in catalytic reactions was especially stressed. The data of Pease and Stewart (24) on the extraordinary effect of traces of carbon monoxide on the velocity of hydrogenation of ethylene on copper catalysts were cited as especially convincing evidence. The subsequent researches of Almquist and Black (1) on the poisoning of ammonia synthesis catalysts by water vapor indicated that, in the most active preparations, only one atom in a total of 200 had catalytic activity. Many of the atoms may have been inaccessible in the interior of the crystallites but, from the equilibria involved in the poisoning process, of those that participated in the synthesis process, it was shown that they had free energies differing by as much as 11 kcal. from the free energies of bulk iron in such equilibria. Inequalities in the catalytic efficiencies of surface atoms were also indicated by a series of researches on the possibility of progressive poisoning in which the suppression of one catalytic process could be secured by suitable poisoning without a simultaneous suppression of another catalyzed reaction on the same poisoned catalyst.

A whole series of recent researches extending over several years, directed principally by Maxted (18–21), has led to a point of view which appears to be in direct conflict with the evidence just summarized, without offering any alternative solution for the problem of quantitative poisoning efficiency, for which the concept of active centers provides at least one of directness and simplicity. It appears wise, therefore, to review some of the more recent studies in the domain of poisoning to ascertain how far these are compatible with the concept of a surface of non-uniform activity. We shall first report some newer data on the affirmative side and then examine what it is necessary to assume in order that the supposedly adverse data may be reconciled with the concept of active centers.

Outstanding in the recent literature is a research by Burstein (6) on the effect of poisons on the interaction of hydrogen and deuterium on charcoal surfaces. Farkas and Farkas (10) reported no formation of hydrogen deuteride on charcoal surfaces at the temperature of liquid air. This result was confirmed by measurements of Gould, Bleakney, and Taylor (11) on charcoal surfaces which had been exhausted for 15 hours at 400°C. Burstein now shows that, on the purest sugar charcoal surfaces, cleaned by evacuation at 900°C., the interaction of hydrogen and deuterium to form the deuteride readily occurs at liquid-air temperatures with a half period of reaction measured in seconds. The research shows that the reaction occurs only on areas of the surface which are uncovered by the high-temperature evacuation and that the earlier work yielded negative results because the evacuation procedure was inadequate to uncover the active areas. It is evident that, on areas of charcoal capable of adsorbing large quantities of hydrogen, no catalytic activity towards its isotopic molecule is manifest, but more thorough evacuation opens up active areas. The quantitative extent of the active areas so produced is made evident by the work of Burstein, who found that active areas so uncovered by evacuation could be poisoned by minimal quantities of hydrogen (0.14 cc. per gram) adsorbed on the areas, not at the working temperature of −185°C., but at the temperature of 500°C. (!) Thus, 0.14 cc. so adsorbed per gram of charcoal could decrease the activity to negligible proportions.

This case of poisoning is unique in many respects. In addition to revealing that, of a surface which, according to various independent estimates, should reach 20–60 sq. meters per gram, an area of 500 sq.cm., which is approximately that covered by 0.14 cc. per gram, is alone active in the particular process, the reaction at liquid-air temperatures between isotopic varieties of hydrogen is poisoned by hydrogen but only by hydrogen made to cover the active areas nearly 700°C. above the reaction temperature. The active areas in question must be such that adsorption, exchange, and desorption must be readily occurring at liquid-air temperatures. The activation energy of adsorption on these areas must be negligibly small and, similarly, the heat of adsorption. This is confirmed by Burstein's estimate, from the temperature effect, of an overall activation energy of ∼200 calories. And yet, this surface is poisoned by the reactant, adsorbed at a temperature of 500°C. It seems obvious that this poisoning hydrogen is not held to the surface at such temperatures by a heat of a few hundred calories. It is, however, significant that the poisoning temperature is in the range in which Barrer (2) found activated adsorption of hydrogen by charcoal with an activation energy of adsorption of 10–30 kcal. and a heat of adsorption of 50 kcal.

Burstein interprets the low activation energy as due to a collision process of a molecule from the gas phase with a molecule adsorbed by van der Waals forces on the special area, the reality of which she concedes. This view, however, raises the very difficult question as to why similar collisions are not effective between molecules from the gas phase and molecules adsorbed by van der Waals forces on the very much larger areas of the surface already uncovered by evacuation at 400°C. The writer prefers another explanation, frankly *ad hoc*, but conforming to observed behaviors on surfaces other than charcoal. According to this view, the high-temperature evacuation uncovers areas, limited in number, on which, with negligible activation energy by reason of their geometric configuration [see Sherman and Eyring (26)], at least two molecules, H_2 and D_2, can be adsorbed and with negligible heat of reaction. Four elementary spaces in a suitable, possibly square, configuration would suffice. All four such spaces cannot be poisoned at 500°C. by hydrogen because of the negligible heat of desorption. But, activated adsorption at high temperatures, requiring a fairly large energy of activation and heat of adsorption, on two of the diagonally opposite spaces would destroy entirely the catalytic area in question. The two diagonal spaces in question might be filled at 500°C. by molecules adsorbed atomically on one of the spaces in question and one other space from the surrounding area. Such an interpretation requires both the concept of active centers and that of activated adsorption. It represents one possible solution of the problem — but the question must remain open as to whether it is a unique solution.

The solution proposed gains in strength from the observations of Gould, Bleakney, and Taylor (11) on the slow rate of exchange between hydrogen and deuterium on chromic oxide gel at −185°C., which obviously cannot be produced by areas of the surface investigated as to activated adsorption at temperatures of +184°C. and upwards, where energies of activation of adsorption of $\sim$20 kcal. obtain. The work of Burwell (7) indicates that, on this catalyst, even in the upper temperature range, there are areas which are composite or non-uniform, with characteristic activation energies ranging from low values to a value of $\sim$21 kcal. per mole adsorbed and with heats of adsorption similarly varying from low to higher values. The same conclusion is explicitly reached in the work of E. Smith (27) on zinc oxide surfaces, where the kinetics of interaction of hydrogen and deuterium led to the interpretation of continuously varying areas of activity with increase in temperature from areas operative at −140°C. with an activation energy not exceeding 600 calories to areas above +110°C., where the activation energy of the reaction reaches more than 12 kcal. The work of Burstein suggests that poisoning, by hydrogen, of such surfaces might be illuminating in their results with this isotopic exchange reaction and other similar exchanges.

Evidence of this type in support of active centers is available in the researches of Morikawa (22) on the interaction of the saturated hydrocarbons with hydrogen and with deuterium on nickel catalysts. In these cases the reactant hydrogen is revealed kinetically as a poison for the reactions. Its poisoning activity varies with the nature of the reaction. Two reactions are possible in such systems, and they may be followed with the aid of deuterium. The one involves a breaking of a C—H bond and the formation of a C—D bond, $C_2H_6 + D_2 = C_2H_5D + HD$. The other involves a breaking of the C—C bond, $C_2H_6 + D_2 = 2CH_3D$. In the latter reaction the inhibitory power of the hydrogen is much greater than in the former, the rate being inversely proportional to the 2.6 power of the hydrogen as compared with the inverse 0.75 power in the former. These differing inhibitory effects of hydrogen point definitely to different active centers specific for a particular reaction, even though the reactions are occurring between the same two reactant gases present in the same concentrations. It is evident that advantage could be taken of such differences in inhibitory effect to suppress one type of reaction in favor of the other by large increase in working concentration of the inhibitory substance. Such a procedure is known as " beneficial poisoning " and has been utilized technically. A very recent illustration of this, of technical significance, is reported by Myddleton (23), who states that cobalt-thoria catalysts, in the Fischer synthesis, may be conditioned by sulfur-containing gases to yield synthetic gasolines rich in olefins rather than paraffins, by reason of the poisoning of areas on which hydrogenation of olefins occurs without markedly destroying the activity of those areas on which the reduction of carbon monoxide and polymerization of the resulting methylene occurs. Such selective poisoning, of which there are now many well-established examples, is difficult to interpret on the basis of a uniform surface.

The high value, 2.6, of the retardation exponent, observed with hydrogen as poison in the fission of the C—C bond, is worthy of note since, with a uniform surface on the Langmuir theory an exponent greater than unity in the denominator would not be expected for a given elementary space. Kubokawa (16) has shown that retardation exponents greater than unity can be interpreted when the heterogeneity of a surface is taken into consideration, and has cited three such cases: the decompositions of methane on platinum, carbon monoxide on nickel, and ammonia on platinum, with carbon as the retardant in the first two and hydrogen the retardant in the last.

The evidence of Maxted and his co-workers, which tends to indicate uniform surfaces, is varied in character. Maxted and Lewis (18), studying the decomposition of hydrogen peroxide on platinum black, found a linear decrease in activity when the catalyst was poisoned with small quantities of mercury salts, when measured at three temperatures. Maxted and Stone (19) studied similarly the hydrogenation of three unsaturated acids. They found a linear effect of poisons representable in each case by the expression

$$k_e = k_0 (1 - \alpha c)$$

where c is the poison concentration and α has the same value for each of the three acids, although the activation energies of hydrogenation are markedly different in the three cases. A further research by the same authors covered catalytic reduction of the oxygenated compounds, nitrobenzene and acetophenone, as well as hydrogenation of benzene and oleic acid. With mercury salts and carbon disulfide as poisons, they found a linear variation with poison concentration and the same α value in the different processes, characteristic, however, for a given poison. Maxted and Moon (20) strengthened the argument by examining the effect of heat treatment on a given catalyst. They showed that "sintering" did not change the ratio of reaction rates at 10°C. and 30°C., although it affected the absolute rates in the ratio of 5.4 to 1. There was no indication of preferential destruction of active centers. Against such a result must be set the well-known data of Pease, where the kinetics of the hydrogenation of ethylene was completely changed when a given copper catalyst was subjected to progressive sintering. In the most recent researches of Maxted with Evans (21) the linear poisoning was observed on a given reaction with two catalysts, platinum and nickel, with α values characteristic for the given poisons, H_2S, S, CS_2, C_4H_4S, cysteine, but having the same values on the two catalysts. This cumulative evidence in support of uniformity of catalyst surface needs to be faced if the concept of active centers is to be retained for the advantages which its adoption has produced.

It should be observed that this linear variation with poisoning found by Maxted is not confirmed by the recent work of Kubokawa (17), who, in the catalytic decomposition of hydrogen peroxide by finely divided platinum and by platinized platinum plates, found that the effect of mercuric chloride poisoning did not yield a linear poisoning effect but, on the contrary, a linear relation between log k and the logarithm of the poison concentration c. Kubokawa formulated a general treatment of successive poisoning on a non-uniform surface on which the velocity k is determined by an equation of the form

$$k = \sum_{i=1}^{i=m} n_i x_i$$

where n_i is the number of surface atoms composing centers of a given kind and x_i is the velocity constant for each such atom. From an analysis of this equation as to the effect of poisoning, following closely earlier treatments of the problem of centers of varying activity due to Constable (8) and to Cremer and Schwab (9), Kubokawa derived an equation yielding the observed linear relation between log k and log c. Kubokawa further showed that the data of Pease and Stewart (24), already mentioned, on carbon monoxide poisoning also obeyed excellently the log k-log c linear relation. He therefore concluded that the active surface is by no means homogeneous and that the adsorption of the poison proceeds from the most active centers to the less active ones.

It must be emphasized that it is this latter condition which must be satisfied if poisoning experiments are to reveal decisively the uniformity or non-uniformity of the surface. From such a viewpoint, the linear variation with poisoning observed in Maxted's experiments may not be so much a proof of homogeneity of surface as a proof that the poisoning process was entirely non-selective, covering equally efficiently both active and inactive areas. That non-selective poisoning on a heterogeneous surface can simulate the results to be expected if the surface were uniform is quite evident from the research of Russell and Ghering (25) on the poisoning of copper catalysts by oxygen in the hydrogenation of ethylene. These authors found a linear poisoning effect, as in the examples of Maxted, when oxygen was introduced directly into the reaction vessel. They, however, attributed the effect to a non-selective poisoning, the oxygen being taken up by successive layers of catalyst. At each addition a certain aliquot fraction of the available surface is rendered inactive, the layer first reached by the poison being completely inactivated, the remainder unaffected, and similarly for successive additions. Measurements of the heat of poisoning confirmed this view.

When Russell and Ghering studied decrease of poisoning by progressive reduction of the surface by means of hydrogen, however, the linear relation between poison and activity no longer held. An exponential poisoning curve indicative of non-uniform surface was obtained. To obtain a more selective poisoning of a copper surface, Russell and Ghering then used nitrous oxide as the poison. Here they found a most interesting result. The first few tenths of a cubic centimeter of oxygen thus brought as nitrous oxide to the copper surface produced no poisoning effect. The activity for ethane formation was unaffected. After a certain quantity of oxygen was adsorbed, characteristic for each catalyst preparation, subsequent additions gave the poisoning effect to be expected on the assumption of a non-uniform surface. Russell and Ghering give as the plausible explanation of this behavior that the centers which are active in ethane formation are not those which are most active for the decomposition of nitrous oxide; it is only after the poisoning of these latter that the poisoning of the centers active in ethane formation begins.

Beebe in his calorimetric work on the heat of adsorption of gases on catalysts has, on frequent occasions (3, 4), made definite reference to the existence of non-selective adsorption of gases and the consequent misconceptions which might arise. Also, in his recent work on the heat of adsorption of hydrogen on chromic oxide at −183°C. he has emphasized that, on the most active parts of the surface, the heats of adsorption are apparently too high to permit rapid desorption of the products in the reaction $H_2 + D_2 = 2HD$, and that the observed reaction occurs on a part of the surface which possesses medium activity in the adsorption of hydrogen. Such data, as well as the numerical values of heats of adsorption, supply additional evidence indicative of non-uniform surfaces, although the forces operative between adsorbed molecules may give rise to heats of adsorption varying with surface covered in the manner to be expected of heats of adsorption on non-uniform surfaces. Other reasons can be assigned also for such a variation, so that such evidence is not alone conclusive.

Mixed Catalysts and Lattice Structure

Detailed investigation of the properties of mixed catalysts has developed very rapidly in recent years, and the results of such studies contribute to the support of the concept of active centers. The literature of the subject is so large that it would not be possible here to summarize even the principal conclusions. A study of the interaction of two solid phases with one another, one of which solids has catalytic properties, and of the properties of the products obtained from such interaction at successively increasing temperatures is the method employed by Hüttig and his students (14). The breadth of their survey is indicated by the observation that there are now upwards of 113 communications from this school concerning this topic. Similar investigations, less voluminous in amount, have been reported by Hedvall (13) and, together with those of Hüttig, Jander (15), and others are summarized in his recent book " Reaktionsfähigkeit Fester Stoffe."

As typical of the individual communications we may cite a recent summarizing report of one system, $ZnO-Fe_2O_3$, contributed by Hüttig to the German Bunsengesellschaft, 1938. Among the properties of the mixed catalysts studied are: (1) surface area by dye adsorption, (2) catalytic activity in carbon monoxide oxidation, methanol and nitrous oxide decomposition, (3) adsorption of vapors to measure pore volumes,

(4) density, (5) magnetic susceptibility, (6) X-ray analysis for line intensities characteristic of reactants or products. Preparations obtained at 100° intervals from 300 to 800°C. are studied and compared with the unheated intimate mixtures of the two constituents. Quite generally, it is found that, even at temperatures not exceeding 300°C., interaction between two oxides sets in, giving rise to the " Abdeckungsperiode " in which already dispersion of one solid phase, probably *on* the other, is occurring. In a second region between 300 and 400°C. the interaction augments, with rise in catalytic activity, and the formation of quasi molecules of surface complexes, with marked unsaturated surface valence fields, with high adsorption activity. From 400 to 500°C. there is a strong fall in sorption activity, called by Hüttig the region of deactivation of the molecular surface covering. From 500 to 620°C. is the region in which exchange of places in the lattices of the oxides is beginning. This diffusion does not immediately result in definite compound formation but yields, on the other hand, a disordered and unevenly distributed, incompletely developed, and loosely bound state with which is associated a pronounced chemical activity. In this region marked changes in magnetic susceptibility occur. As yet, the X-ray lines characteristic of the new compound are diffuse and weak. Finally, above 620°C., the development of product structure, in the case of $ZnO-Fe_2O_3$, a spinel, becomes more and more prominent. The greater lattice stability is naturally associated with a decrease in sorption and catalytic activity. There is naturally no sharp division between the several stages, which merge into one another and are dependent on many factors such as particle size and form, degree of intermixing, molar ratio, and other properties of the components. The affinity between the two oxides also plays a controlling role, the basicity and acidity of the two oxides. Further, even among oxides which do not interact to form definite compounds as products, the above behavior is found. The observations made lead to the quite general conclusion that, in any such mixture so treated, there must be present a whole spectrum of areas of differing properties and differing chemical and catalytic activities. Kinetically, they reveal themselves in reaction velocities with continuously varying apparent activation energies and large variations of number of active centers as measured by the quantity C in the expression $k = Ce^{-E/RT}$.

The preceding paragraph describes the behavior normally observed in such systems. There are, however, in the many systems studied, considerable variations and deviations from such a norm. The behavior observed is not confined to two-phase solid systems so produced. Similar phenomena obtain when a solid phase decomposes to form a gaseous and a solid phase. Similar considerations as to the catalytic characteristics of the intermediary stages in such processes will apply. As this is a general method of catalyst preparation, e.g., ZnO from zinc oxalate, $ZnO \cdot Cr_2O_3$ from zinc ammonium chromate, similar conclusions with regard to non-uniformity of surface areas should hold. In the preparation of mixed catalysts by precipitation methods, X-ray examination, coupled with simultaneous catalytic studies, indicate that the production of solid solutions of unordered lattice characteristics can be attained and that the physical characteristics, as well as the chemical and catalytic activity, can be controlled. The aging of precipitates of single substances or mixtures is a further example of labile behavior in solid systems of fundamental significance in the technique of preparation of non-uniform surfaces.

Quite recently A. Taylor and J. Weiss (29) have examined by means of X-rays the nickel catalyst produced by dissolving out aluminum from nickel-aluminum alloys, one of which has the formula $NiAl_3$. In this case, the alloy structure and the nickel-nickel spacing are maintained until approximately 95 per cent of the aluminum has been dissolved away; when the aluminum content falls below 5 per cent, the alloy structure collapses and the ordinary nickel lattice is obtained. The collapse of structure is accompanied by a marked decrease in catalytic activity. This evidence emphasizes how directly the activity is related to surface architecture and hence how, in any randomly oriented crystalline preparation or in any disordered lattice structure, there will be large variations in surface activity. This variation in surface activity with surface atom spacing emerges clearly from the theoretical considerations of Sherman and Eyring (26) on the relation between activation energy and atom spacing in the simplest of all heterogeneous surface actions, the adsorption of a gas by valence forces at a surface.

Convincing evidence of the enhanced activity of particular crystal faces in catalytic metals has recently emerged in the work of Beeck, Wheeler, and Smith (5). Metal films of high and reproducible catalytic activity were prepared by condensation of their vapors in an atmosphere of an inert gas (N_2, A, etc.) at low pressures and room temperature. Complete orientation of nickel was secured with an inert gas pressure of 1 mm., and the crystals formed had their (110) plane, the least dense of the planes, oriented parallel to the background, the two remaining axes showing random distribution., Iron films were oriented with their (111) plane parallel to the backing, again the least dense plane thus oriented. In the hydrogenation of ethylene the oriented nickel had ten times the activity per gram of randomly oriented crystals and twice the available surface as revealed by adsorption of hydrogen at liquid-air temperatures and carbon monoxide at room temperature, both measurements at low pressures of adsorbed gas. The oriented films have therefore fivefold the activity of the unoriented films. The activity per unit weight of the oriented films was constant, indicating accessibility to the interior of the film by the reacting gases. The enhanced activity appears therefore to be associated with the larger distances between the nickel atoms in the (110) plane, the maximum distance in this plane being 3.6 Å, as compared with a unit distance of 2.5 Å as a maximum in the other planes. The data were similar with iron and palladium. These experiments constitute a fundamental experimental approach to a definition of active centers in terms of lattice spacing as developed theoretically by Sherman and Eyring (26). It is indicative of much possible development in the technique of catalyst preparation to produce preferred orientations. It suggests that the high activity of the active centers may be a function of normal lattice spacings on certain planes and that, in many cases, lattice distortion of the catalytically active agent as, for example, that produced by alloying nickel with aluminum, may not be necessary.

The recent discussion of chemical reactions involving solids, conducted by the Faraday Society, supplies additional evidence of the heterogeneity of surfaces and the diversities of surface-gas interactions. The observations of Strickland-Constable (28) on the interaction of oxygen and of nitrous oxide with charcoal surfaces indicate the occurrence, on such surfaces, of a number of distinct, covalent, carbon-oxygen compounds with decomposition temperatures varying over a wide range and with types of interaction between carbon and oxygen varying from a high degree of reactivity to a nearly complete inertness. Experiments by van der Ley and Wibaut (30) indicate the possibility of building nitrogen similarly into the carbon structure, perhaps even more readily than oxygen. The kinetic evidence given in the opening sections indicates similar behavior with hydrogen amply confirmed by the work of Barrer (2) with both graphite and diamond. Griffith (12) emphasizes the similarity between such observations on carbon and his own work on the behavior of the metallic sulfides.

With non-uniform catalyst surfaces there is always the possibility that several modes of covalent attachment, other than van der Waals adsorption, may be obtained. Because of the small number of electrons in the molecule it is possible that, in the case of hydrogen, there will be few, if any, intermediate stages between the van der Waals adsorbed molecule and the covalent bond between hydrogen atom and surface atom. Quite obviously, however, in the case of oxygen, there is the possibility of a mole-oxide type of adsorption, $\underset{|}{O}-\underset{|}{O}$, essentially different from the linkage between single oxygen atoms and the catalyst atoms. Langmuir's early work on tungsten filament reactions abundantly illustrates differences in strength of attachment of oxygen to tungsten surfaces. With a non-uniform surface, the distribution as between such differing modes of attachment will vary distinctly. The more penetrating analysis of this phase of the problem is one of the tasks of the future.

Summarizing the present position, as it now appears, it is to be remarked that surfaces of predominantly uniform activity undoubtedly exist. Methods of experimental investigation may, however, give rise to misleading results indicative of uniformity where none exists. In all branches of the science, from the simplest reactions on elementary catalysts to the most complex biochemical catalysts, with their very specialized functions, a broad range of phenomena has resulted from experimental investigations, in the interpretation of which the concept of active centers has proved illuminating, fertile, and, in the view of many, indispensable.

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CHAPTER V

PHYSICAL ADSORPTION IN THE STUDY OF THE CATALYST SURFACE

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Since the discovery of the phenomenon of catalysis it has been recognized that in selecting a catalyst the two principal factors to be considered are its chemical composition and the extent of its surface. The first of these has gradually come to include not only the chemical nature of the major component of the catalyst but also the nature of various added promoters or activators. Such guiding principles as have been deduced for choosing the proper catalyst material and promoter for a given reaction are treated fully in the chapters dealing with the application of catalysis to various types of reactions. It is the second factor, the physical state of subdivision, that will be discussed in the present chapter.

It has long been the practice of those seeking to develop catalysts to increase the " surface area " of the catalytic material as much as possible, either by using more finely divided catalyst particles or by increasing the porosity of the catalyst, or by both. No common understanding has existed, however, as to quantitative relations between particle size, porosity, catalyst surface area, and catalyst activity. Within the last few years experimental and theoretical investigations have thrown new light on the interrelation among these four factors. It will be the purpose of the present chapter to summarize briefly the progress that has been made in this approach to a study of catalysis.

The subject matter will be considered under the three subdivisions into which it conveniently falls:

1. The measurement of the surface areas of catalysts and catalytic materials.
2. The relative contributions of the " inner " and " outer " surface areas to the activity of catalysts.
3. Methods for determining the distribution of promoters on catalyst surfaces.

MEASUREMENT OF THE SURFACE AREAS OF CATALYSTS

Porous materials are usually considered to have " inner " as well as " outer " surfaces. The " inner " surface comprises the surface of the cracks, crevices, and capillaries that extend into the individual particles; the " outer " surface is, roughly speaking, the portion of a porous material subjected to direct and free bombardment by the molecules of the enveloping gas. Sometimes the term " outer " surface is used synonymously with the term " geometric surface," the extent of the latter being estimated from a measurement of the diameter of particles, together with an assumption as to the shape of each separate particle. The " total " surface area refers to the sum of the areas of the " inner " and " outer " surfaces.

It is at once evident that different values for the area of the total surface of a porous material are likely to be obtained depending upon the particular method used for making the measurements. A general discussion of the various methods (45) for measuring surface areas cannot be included here both because most methods have been known for a number of years and, hence, would not come within the scope of the present survey of recent literature on the subject, and because a majority of the standard methods for measuring surface areas could not be applied to all kinds and classes of finely divided or porous catalysts. The present discussion will, therefore, be restricted to those methods of measuring surface areas that depend upon measuring the volume of gas adsorbed by the solid catalysts. Such methods in general have the advantage of being applicable to all types of porous or finely divided catalysts, including those whose nature and surface might be altered by suspension in any of the liquid media that are common to a number of methods for measuring surface areas. They also have the advantage of yielding a value for the surface area of a catalyst that includes all the surface to which gases have ready access.

Both physical and chemical types (50) of adsorption have been used in obtaining estimates of the surface areas of catalysts. Among the earliest attempts to use activated adsorption for this purpose was the work of Benton (2) on Pt catalysts. More recently de Boer and Dippel (9) estimated the surface of vacuum sublimed CaF_2 to be 240 sq. meters/gram from the chemisorption of water on the surface of the tiny CaF_2 crystals. Similarly, Emmett and Brunauer (16) have made use of the chemisorption of CO at $-185°C.$ to measure the surface areas of iron synthetic ammonia catalysts. These examples serve merely to illustrate instances in which surface areas can be estimated by chemisorption or activated adsorption. In general, the use of chemical adsorption for this purpose is not widely applicable in catalytic work because of certain limitations inherent in the method. In the first place, one must find a gas that will be chemically adsorbed by the surface of the catalyst and must find a means of ascertaining the volume of gas corresponding to a complete monolayer. Furthermore, if the catalyst contains a promoter or activator it is very probable that the surface area obtained will be that of only one of the two or more constituents of which the catalyst is composed. However, chemisorption or activated adsorption is very useful in studying promoter concentrations on catalyst surfaces if used in conjunction with surface area determinations by means of physical isotherms as outlined below (17).

Within the last few years a new method has been developed that (16, 18, 19, 20, 21) appears to give great promise for measuring surface areas of catalysts and other finely divided or porous materials. A critical discussion of the method will now be presented.

The principle of the method is simple. If the volume of some gas such as nitrogen or argon required to form a monolayer of physical adsorption over the entire " inner " and " outer " surface of a catalyst can be determined, the total area can be calculated by multiplying the cross-sectional area of each adsorbed molecule by the number of molecules in the monolayer. The area covered by each molecule in the monolayer is calculated from the density of the solidified or liquefied gas.

The method can be illustrated by the isotherm shown in Fig. 1 for the adsorption of nitrogen on a singly promoted, iron synthetic ammonia catalyst (16) at 77°K. The S-shaped isotherm is typical of those so far obtained for a variety of gases on about thirty-five porous materials, including oxide and metal catalysts, finely ground salts, powdered bacteria, soil colloids, paint pigments, decolorizing carbons, gels, and catalyst supports. On charcoal only have the isotherms been found to be the conventional Langmuir type, shown in curve 2, rather than the sigmoid variety.

It is evident that the reliability of the method will depend largely upon the accuracy with which one can choose the point on the isotherm corresponding to a monolayer. The following evidence has indicated that point *B*, the beginning of the linear portion of the isotherm, marks closely the completion of the monolayer and the beginning of a second layer of adsorbed gas:

1. Isotherms of a number of different gases, including O_2, CO, CO_2, A, N_2, SO_2, and C_4H_{10}, determined at temperatures close to their respective boiling points yield values for the surface area of a given catalyst that are in excellent agreement (16) with each other. Usually the areas so calculated do not differ from a mean by more than 10 per cent.

2. Calculation of the heat of adsorption corresponding to the volume of gas at point *B* yields a value (16) that is about midway between that which corresponds clearly to adsorption in the first layer and that which is nearly equal to the heat of liquefaction of the gas and apparently corresponds to adsorption in the second layer.

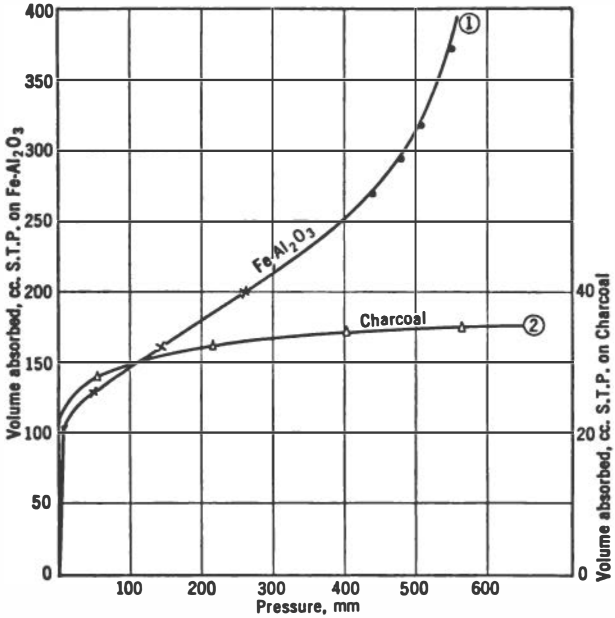

FIG. 1. Adsorption of N_2 at − 195.8° on Charcoal and on Fe − Al_2O_3 catalyst

3. The pure iron synthetic ammonia catalysts were found to chemisorb rapidly at −183°C. an amount of CO agreeing approximately with the volume of physically adsorbed CO at point *B*. This chemisorption is irreversible at −183°C. and has a heat of adsorption (1) considerably above that of physical adsorption. The manner in which this chemisorption occurs makes it probable that a complete layer of chemisorbed CO forms quickly over the entire surface of the iron catalyst at −183°C. and helps confirm point *B* on the physical isotherms as corresponding to a monolayer.

4. Brunauer, Emmett, and Teller (5) have developed an equation for S-shaped isotherms of the type shown in curve 1, Fig. 1. The theory upon which the equation rests postulates that the S-shaped nature of the isotherms is to be attributed to the formation of multimolecular layers. The equation that has been derived has in it a term V_m, the volume of gas corresponding to a monomolecular adsorption layer. Table I illustrates the agreement between the volumes for point *B* and those for

V_m obtained by plotting the experimental, low-temperature adsorption data according to the developed equation. As is evident, point B and V_m agree within a small percentage on all of the solids listed. For the adsorption of butane on some finely divided materials point B yields too low a value, whereas V_m from the derived equation yields a value for the surface area that is in good agreement with those obtained from other gases.

TABLE I

VALUES OF CONSTANTS FOR ADSORPTION OF NITROGEN AT 90.1°F. ON VARIOUS ADSORBENTS

Substance	V_m in cc. per gram	Point B in cc. per gram
Unpromoted Fe catalyst 973I	0.13	0.12
Unpromoted Fe catalyst 973II	0.29	0.27
Fe—Al_2O_3 catalyst 954	2.86	2.78
Fe—Al_2O_3 catalyst 424	2.23	2.09
Fe—Al_2O_3—K_2O catalyst 931	0.81	0.76
Fe—Al_2O_3 catalyst 958	0.56	0.55
Fe—K_2O catalyst 930	0.14	0.12
Fused Cu catalyst	0.05	0.05
Commercial Cu catalyst	0.09	0.10
Cr_2O_3 gel	53.3	50.5
Cr_2O_3 glowed	6.09	6.14
Silica gel	116.2	127.0

Space does not permit a detailed discussion of all the work that has been published relative to the application of this method for measuring surface areas. The four arguments listed above summarize the bulk of the evidence that has led the author to be confident that the proposed method will yield a reliable value for the surface areas of catalysts. It must, of course, be emphasized that the application of the method to other substances than iron synthetic ammonia catalysts entails the assumption that isotherms similar in shape to the one shown for iron in Fig. 1 can be interpreted in the same manner.

A survey of the recent literature reveals a considerable amount of experimental work that is consistent with the proposed method for measuring surface areas and affords confirmation of the general principle involved. Perhaps the most striking confirmation of the method is to be found in the experiments of Palmer (38) and Palmer and Clark (39). They have measured the adsorption of acetone, benzene, and methyl alcohol on silica glass, whose surface area was known. Their method of measuring surface areas consisted in the comparison of the rate of solution in hydrofluoric acid of crushed quartz glass and of a known area of a smooth plane surface of quartz glass. The isotherms obtained by them afford mutual confirmation of their surface area measurements and our proposed method since they yield adsorption values for point *B* that are within about 10 per cent of those to be expected from the measured area of the adsorbents and the known size of the adsorbed molecules.

Other examples of physical adsorption isotherms that appear to be susceptible to the same interpretation as employed by Emmett and Brunauer for iron synthetic ammonia catalysts are to be found in the recent literature. Frankenburger (24) obtained S-shaped isotherms for ammonia on tungsten at 20°C. which yield surface areas by the proposed interpretation that are in good agreement with areas estimated microscopically. Similar isotherms were obtained by Durau and Muller (13) for the adsorption of propane at −45°C. on lead chloride pellets. Whipp (54) concluded that the adsorption of iodine and potassium iodide at 0°C. extended to a layer two molecules deep at saturation. The isotherms obtained by him resemble curve 1, Fig. 1, in appearance except that the linear portion extends all the way to P_s. Maass (14, 15, 37) and his co-workers measured the adsorption of dimethyl ether and of propane on aluminum oxide at temperatures and pressures in the neighborhood of the critical phenomena. He interpreted his results as indicating the formation of multimolecular layers on the aluminum oxide adsorbent. The isotherms of dimethyl ether were the usual S-shaped variety; those for propane were somewhat unusual at and above 75°C. in that they show little adsorption below 5 atm.

One objection that may be raised to the proposed method for measuring surface areas is that such isotherms are likely to be complicated by the occurrence of capillary condensation. For iron catalysts the evidence afforded by the chemisorption of carbon monoxide suffices to show that capillary condensation does not occur at a sufficiently low pressure to interfere with the selection of the point on the isotherm corresponding to a monolayer. For materials other than iron catalysts capillary condensation is usually interpreted as occurring for the most part only at relative pressures of 0.5 or greater. The work of Foster (23) for alcohols on SiO_2 and of Higuchi (26, 27) for SO_2 on TiO_2 and for ammonia on TiO_2 is illustrative of results that have led to this conclusion. On these materials the region throughout which capillary condensation is supposed to occur is characterized by marked hysteresis. This hysteresis, in fact, appears to be the principal criterion for judging the occurrence of capillary condensation in an adsorption isotherm. Recent papers discussing the theory of capillary condensation have been published by Kubelka

(32), Lindau (36), Lemcke and Hofmann (34), Shuchkovitzku (48), and Polanyi (42). No definite means of differentiating with certainty between capillary condensation and multimolecular adsorption, however, is indicated.

The latest confirmation of the reasonableness of surface-area values obtained by determining point *B* on the low-temperature (−195°C.) adsorption isotherms is to be found in some as yet unpublished results on finely crystalline compounds whose surface areas had already been obtained by one or two other methods. Briefly, the results show that the surface areas of samples of $ZrSiO_4$, TiO_2, $BaSO_4$, and graphite are 2.25, 1.35, 2.56, and 5.9 times as great when measured by the low-temperature nitrogen isotherms as when determined by the adsorption of stearic acid from solutions. Furthermore, the value for the surface area of the $BaSO_4$ sample was twice as great as the area determined by the radioactive indicator method.* Since both the stearic acid and radioactive indicator methods entail adsorption from solution, it appears reasonable to expect the values for surface areas obtained by those methods to be a little smaller, as found, than the area measured by the nitrogen isotherms.

Several of the papers in the recent literature that appear to disagree with the proposed interpretation of S-shaped isotherms can be shown to be in error. This is true of the papers by Bradley (3, 4) relative to the adsorption of argon at liquid-air temperature upon particles of dehydrated copper sulfate and aluminum sulfate. He interpreted his isotherm as corresponding to a layer of adsorbed gas about twenty molecules thick at the point interpreted by Emmett and Brunauer as corresponding to a monolayer. Bradley's estimate of the thickness of the layer has been shown to be manyfold too great, as a result of his obtaining the surface area by microscopic examination of the individual particles and overlooking the fact that the latter were highly porous and therefore possessed of a large " inner " surface.

Certain of the experimental isotherms obtained by Reyerson (43, 44) and his associates for the adsorption of halogens on silica gel appear, at first, to be in radical disagreement with the multimolecular adsorption equations developed to account for S-shaped isotherms proposed for measuring surface areas. The chlorine and bromine isotherms were

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* The samples of $ZrSiO_4$, TiO_2, $BaSO_4$, and graphite were very kindly sent to us by Dr. George Boyd of the University of Chicago, together with his surface-area measurements by the stearic acid method and a value for surface area of $BaSO_4$ determined by Dr. Kolthoff, of the University of Minnesota, by the radioactive indicator method. Dr. Boyd suggested that we measure the surface areas of these materials by the adsorption isotherm method.

considerably smaller than one would have expected on the basis of surface-area measurements using the low-temperature, S-shaped isotherms for nitrogen, oxygen, CO, CO_2, SO_2, and other gases (19) on the same silica gel used by Reyerson. The iodine isotherms are especially puzzling, both because they correspond to very small iodine adsorption and because they are not S-shaped, being convex to the pressure axis throughout. At 198.5°C., fourteen degrees above the boiling point, the iodine covers less than 1 per cent of the surface up to 400 mm. pressure, though adsorption increases rapidly with pressure above this point. The difficulty with the interpretation of the halogen isotherms appears to have been entirely cleared up by recent as yet unpublished calculations* which show that reasonable assumptions as to the heats of adsorption of the halogens on silica gel will reconcile the iodine as well as the chlorine and bromine isotherms with the multimolecular adsorption equations already referred to.

The remaining isotherms presented in recent literature that do not conform to the proposed interpretation indicate clearly that all the factors that determine the shape of an adsorption isotherm are not yet understood. For example, Durau and Tschoepe (12) obtained isotherms for benzene on pellets of compressed lead chloride crystals, but they claim that extended drying of the benzene by sodium greatly altered both the size and shape of the isotherms. Schluter (46) found S-shaped isotherms for carbon disulfide on powdered glass and on finely divided silver, but Langmuir-type isotherms for pentane on the same materials. Furthermore, whereas the adsorption of carbon disulfide on powdered glass is slightly greater than on silver, the adsorption of pentane is about one-third greater on silver than on glass. Recent work by Keesom and Schmidt (31) on glass yields adsorption isotherms that, for neon at liquid-hydrogen temperature and for helium at the temperature of liquid helium, are not S-shaped. Pidgeon (41) reports Langmuir-type isotherms for benzene on silica gel and S-shaped isotherms for water vapor on the same adsorbent.

Within the last few years a number of excellent papers have appeared on the theory of physical adsorption and on experimental work at pressures that are ordinarily far removed from the saturation pressure P_s. These papers do not relate directly to multimolecular physical adsorption but are included because they illustrate many of the complexities encountered in dealing with even the first layer of gas held to the surface by physical adsorption. Wilkins (55) and Wang (30) have each derived generalized adsorption equations that take into consideration interac-

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* These calculations have been made by S. Brunauer of the Fertilizer Research Division of the Bureau of Chemistry and Soils, U. S. Dept. of Agriculture.

tions among the adsorbed molecules. Wilkins (56) has measured the adsorption of A, N_2, and O_2 on plane platinum foil at low temperature and at pressures below 0.2 mm. and compared the experimental curves with his theory.

Shereshefsky and Weir (47) have noted a very odd phenomenon in the adsorption of O_2 or N_2 on glass spheres. The adsorption isotherm is linear, according to these authors, up to some pressure of the order of 3×10^{-5} cm.; when more gas is added, the pressure decreases, the adsorption increases, and after an hour or so follows an entirely new isotherm. Itterbeek and Dingenen (28), on the other hand, noticed no such peculiarity in their measurements for O_2 and N_2 on glass.

One of the most puzzling aspects of the low-temperature adsorption work is the question of the mechanism by which gas molecules are able to reach the " inner " surface in tiny capillaries of solid catalysts at a rate sufficiently fast to account for the observed rate of adsorption. Clausing (7) has calculated that the rate of diffusion in the gas phase through capillaries smaller than 10^{-6} cm. is very low. This would lead one to suspect that surface diffusion might be the mechanism by which gas molecules quickly penetrate small capillaries. Against this view is the belief expressed by Tompkins (52) that migration of gases such as N_2 and O_2 on the surface of NaCl does not occur below 150°K. Furthermore, Lambert and Heaven (33) find that the ratio of O_2 : A, adsorbed on SiO_2 at 0°C., may be 3 : 1, 1 : 2, or 1 : 1, depending on whether O_2 is added first, last, or simultaneously. The explanation offered appears to be very improbable, for it postulates a double layer of these adsorbed gases at 0°C., whereas there is probably only a small portion of a single layer formed under those conditions. It seems more likely that the effect is the result of interference of one gas with the diffusion (probably in the gas phase) of the other constituent. This interpretation is strengthened by Patrick's (40) observation that partial pressures of inert gas in excess of 1 mm. greatly reduce the rate of adsorption of water vapor by silica gel.

De Boer and Custers (8, 10) conclude from work on the adsorption spectra of adsorbed iodine that plane surfaces of crystals of SiO_2, Al_2O_3, CaF_2, and the like exert only "active center" adsorption of iodine. They contend that porous solids are required for van der Waals' adsorption.

The present status of the proposed method for measuring surface areas, in view of the above results, can be summed up by saying that a majority of the pertinent experimental results described in the literature conform to the isotherms obtained for various gases on iron synthetic ammonia catalysts. The extension of the method to other materials appears to afford great promise for surface-area measurements; on the other hand, the various examples that appear not to conform to the proposed theory and the lack of any clear understanding of the mechanism by which gases are able to reach the surface of tiny capillaries suggest that the whole story is not yet known and that one should proceed with caution in applying the method to miscellaneous materials.

The Part Played by the "Inner" Surface in Catalysis

One contribution which a determination of total surface area of catalysts may be able to make is the partial elucidation of the part played by the "inner" surface in effecting the catalytic reaction between gases. Workers have proceeded to devise ways and means of increasing the porosity and hence the surface area of catalysts without, perhaps, appreciating fully that there is little or no information available as to the depth within a catalyst particle to which reacting gases penetrate with sufficient rapidity to play a part in the catalytic reaction as a whole. There is little doubt that it is desirable to increase the total surface area of catalysts; nevertheless, there is a great need for experimental data that will tell more as to the part played by the "inner" surface of a catalyst in catalytic reactions.

An excellent attack on this problem is contained in a recent paper by E. W. Thiele (51). A quantitative approach has been worked out by which the value for f, the ratio of the actual activity of the catalyst to the activity that would exist if all the "inner" surface were as active as the "outer" surface, is related to a modulus which, for a first-order reaction, is of the form $x_s\sqrt{c/kr}$, where x_s is some linear function fixing the grain size, c is the activity of unit area of the catalyst surface, k is the coefficient of diffusion of gases into pores, and r is the average area of pore cross-section per unit length of perimeter of the pore cross-section (the hydraulic radius of the pores, in other words). The results obtained by Thiele can be illustrated by Fig. 2. Cases I and II are for a first-order reaction occurring on a catalyst composed of plates and spheres, respectively; case III is for a second-order reaction, the catalyst being in the form of plates. The conclusions that can be drawn from the curves in Fig. 2 are ably summarized by Thiele:

> It will be noted that all the curves have substantially the same trend. For values of the modulus much smaller than unity, the relative reaction rate is nearly unaffected by changes in the modulus (which would arise, other things being equal, from a change in the catalyst grain size x_s). For values of the modulus much greater than unity, the relative reaction rate falls off inversely as the modulus, and is, therefore, proportional to the external surface.

While numerous other cases might arise, most of which would not be amenable to mathematic treatment, it seems probable that in all cases the results would be substantially similar to those shown. Unfortunately, the quantities c and r are not directly determinable, so that it will not be possible to compute in advance the effect of grain size in any given case. However, it may be said that for any given reaction under given conditions of temperature and pressure with a given catalyst, there will be a certain grain size below which the catalyst volume will tend to control the rate of reaction, and above which the catalyst external surface will tend to control. A knowledge of this size, which should be determinable experimentally, will help in determining the optimum size of catalyst for any given process, and furnish additional insight into the character of the catalyst.

One important consequence of the discussion relates to the effect of temperature. A rise in temperature will greatly increase c. Suppose the modulus is large and let c increase fourfold; then the modulus will double, and the relative rate of reaction will be halved, so that the increase in observed reaction rate will be only twofold instead of fourfold. If, therefore, the catalyst grain size be such that the reaction rate is proportional to the external surface, then the activation energy of the reaction will appear to be abnormally low. However, the same thing might happen when the modulus is small, if there exists a small (second order) pore system in which most of the reaction takes place.

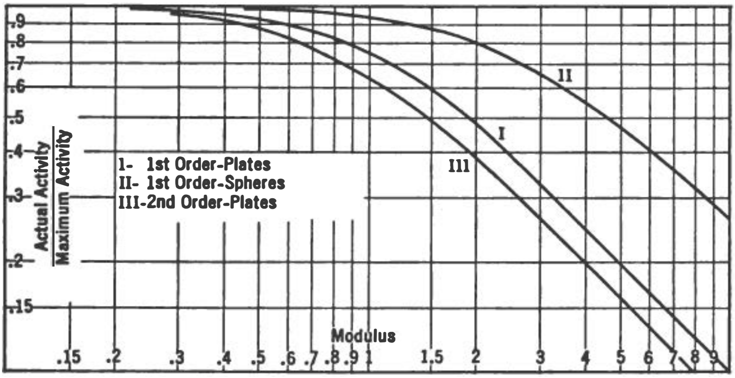

FIG. 2. Activity of Catalysts of Various Structures as a Function of Pore Size.

It is also obvious that where successive reactions occur, large values of the modulus will tend to give a different product composition than small values for a given amount of the primary reaction, but a quantitative treatment of this case is quite difficult.

Only a few experimental data relative to particle size and catalytic activity have been published. Juliard (29) noted that a fourteenfold change in the size of cobalt catalyst particles from .05 to .70 mm. produced no change in the activity of the catalyst for the dehydrogenation of cyclohexane. Cawley and King (6) drew similar conclusions in regard to the molybdenum oxide catalyst used in hydrogenating tar. A change in mesh size from $\frac{1}{4}''-\frac{1}{8}''$ to $\frac{1}{8}''-\frac{1}{16}''$ produced no change in catalytic activity.

Another experimental contribution to this subject has been made in some preliminary experiments by Miss Katherine Love and the author (20) in the Fertilizer Division of the Bureau of Chemistry and Soils. Two one-gram samples of a promoted iron synthetic ammonia catalyst, one 8 to 14 mesh and the other 40 to 60 mesh, were reduced according to identical reduction schedules and compared as to activity in decomposing NH_3 at 400°C. from a 25 per cent NH_3, 75 per cent H_2 mixture. The rates were found to be equal as were also their total " inner " plus " outer " surface areas as measured by means of low-temperature adsorption isotherms. The equality of activities of these two catalysts, which differ severalfold in particle size, indicates that subdivision of this catalyst below 8 to 14 mesh size will not enhance the overall activity per unit weight of catalyst for the decomposition of ammonia. It was concluded, therefore, that either the entire inner surface of the iron catalyst or a given fraction of it is active in ammonia synthesis or decomposition. In terms of Thiele's work one would say that the activity of the ammonia catalyst becomes substantially independent of the value of the modulus for particle sizes that are 8 mesh or smaller. Probably a system of large capillaries permeates each catalyst particle, the walls of these capillaries being as active as the outer surface and readily accessible (by diffusion) to the gaseous atmosphere surrounding the particle.

In Thiele's calculations gaseous diffusion of reactants into capillaries was assumed. The question may well be raised as to whether or not a surface diffusion of reactants into the cracks and capillaries may also contribute to the ingress of reactants and egress of products. The known high-temperature coefficients for the diffusion of certain gases such as O_2, N_2, and H_2 through metals, combined with the total inability of inert gases such as A and He to diffuse through these metals (49), make it evident that some type of activated surface diffusion may easily constitute a major means by which gases reach the " inner " surface of metallic catalysts. Lennard-Jones (35) has, in fact, calculated the rate of surface diffusion of H_2 along copper at 350°C. from the experiments of Ward (53) and found it to be about 10^{-5} cm. per second. Final conclusions as to the part played by surface diffusion in catalytic reactions must await additional experimental results.

PROMOTER CONCENTRATION ON CATALYST SURFACES

For years it has been known that a small percentage of a foreign substance (promoter) in a catalyst frequently has the effect of greatly increasing the activity of the catalyst. Little has been known, however, about the distribution of the promoter in the solid, or about the fraction of the total promoter that may be accumulated or concentrated on the surface of the catalyst in the course of preparation. Recently several experimental attacks seem to throw considerable light on this subject.

While measuring low-temperature adsorption isotherms for gases on iron synthetic ammonia catalysts, Emmett and Brunauer (17) noted that carbon dioxide was chemisorbed at −78°C. only by those catalysts containing an alkali as a promoter. On such catalysts the amount of chemisorbed CO occurring instantaneously at −183°C. was noticeably smaller than on catalysts without the promoter. The sum of the chemisorbed carbon dioxide and chemisorbed CO on promoted catalyst containing K_2O seemed about equal to the amount that one would need to form a monolayer over the entire catalyst. It seemed reasonable, therefore, to interpret the results as indicating that the carbon dioxide was adsorbed by the alkali on the surface of the catalyst and the carbon monoxide by the surface iron atoms. On the basis of this interpretation one can calculate the fraction of the surface that is iron and the fraction that is covered with promoter molecules. The results indicate that a doubly promoted catalyst containing 1.39 per cent Al_2O_3 and 1.59 per cent K_2O actually has between 60 and 75 per cent of the surface covered with promoter. Similar experiments on catalysts promoted with Al_2O_3 alone indicate that this substance also tends to accumulate in the catalyst surface. One catalyst containing 10.2 per cent Al_2O_3 was found to have 50 per cent of its surface covered by promoter. The combination of such chemisorptions with the measurement of the total surface area of the catalyst by low-temperature isotherms appears to be a very promising means of elucidating promoter action and of distinguishing between promoters that merely increase the total surface area of the catalysts and those that enhance the activity per unit catalyst area.

Experiments similar to the above have been reported (11) by Dubrovskaya and Kobozev in Russia. Their work was conducted with Fe_2O_3 containing Al_2O_3 as a promoter. By measuring the quantity and energy of activation of the oxygen chemisorption, together with the low-temperature adsorption of oxygen on the samples, they were able to deduce that small concentrations of Al_2O_3 in the sample as a whole resulted in large fractional coverage of the iron oxide surface.

The chemisorption experiments on the alkali containing iron synthetic ammonia catalysts yielded results that are qualitatively similar to, but perhaps more susceptible of, quantitative interpretation than those of Erofeev and Mochalov (22), who concluded from some high-frequency coherer experiments that "at the surface of a promoted iron catalyst there is a film of adsorbed aluminum oxide."

In conclusion it may be well to emphasize that no direct correlation is to be expected necessarily between surface area of a catalyst and its catalytic activity. The influence of various factors such as promoter addition, temperature of preparation, and miscellaneous other conditions may alter the activity per unit area manyfold and may more than compensate for a smaller catalyst area. The advantages that will arise from being able to measure the total surface area of a catalyst will probably become manifest in enabling one to obtain a better and more quantitative understanding of the relation existing between promoter distribution, porosity of catalyst, particle size, and catalytic activity.

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CHAPTER VI

THE ROLE OF IONS IN SURFACE CATALYSIS

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It has been attempted repeatedly (5, 18, 19, 21) in a more or less wholesale manner to explain catalytic action of surfaces by the hypothesis that atoms or molecules of reactants are converted on the surface to ions which then react with each other. The purpose of this review is to re-examine the question briefly from three angles: First, under what conditions is it possible to speak of the presence of ions in an unambiguous way? Second, what can be said about the rates of reactions involving ions? Third, does it seem probable that ionization of reactants on catalytic surfaces precedes reaction?

THE IONIC STATE

Definition of an Ion

An ion is a stable assembly of atomic nuclei and electrons carrying a total charge. If only one nucleus is present we have an atomic ion. If more nuclei belong to the ion we call it a molecular ion. The concept of an ion also implies that not too many nuclei should be present in the assembly — just as the idea of a molecule excludes the association of too many atoms. Of course, there is no sharp limit which would decide when we have to speak about an ion and when about a charged colloidal particle.

Only in the gaseous state has the concept of an ion a strictly defined meaning. In the gaseous state the presence of ions can be detected and their properties can be investigated in various ways. Because of their charge they will be acted upon by electric fields and, if they have a velocity, also by magnetic fields. Making use of these facts, one can show their presence and, moreover, measure their mass and their charge. It is also possible to identify them with the help of their characteristic spectra.

Ionic and Non-ionic Binding in Diatomic Molecules

The answer to the question as to whether the constituent parts of molecules are atoms or ions is very difficult to formulate and even more difficult to arrive at experimentally. One has only to remember the continuous transition between what is called a homopolar bond and a heteropolar bond to realize the kind of difficulties which one meets.

It is of course possible in principle to consider the question of the presence of ions from the point of view of quantum mechanics since the latter allows us to ascribe to any system — atom, ion, molecule, or crystal — a proper function. And it may be asked whether a molecular proper function is approximated more closely by ionic or by atomic proper functions. However, such a discussion can never yield anything but an arbitrary answer to our questions. Furthermore, even such an answer as this cannot be obtained, for it is practically hopeless to obtain rigorous expressions for the proper function of any molecule in which the total number of electrons is more than two.

Experimentally there are two general criteria, with the help of which it has been attempted to decide whether a molecule consists of ions or of atoms. These are the magnitude of the dipolemoment and the nature of the dissociation products of the molecule.

The mere presence of a dipolemoment is, of course, not sufficient to establish the ionic character of the binding. In fact, one will have to expect a small dipolemoment whenever a diatomic molecule is built of two different atoms. Even the van der Waals molecule, built of two different rare-gas atoms, will have a very small moment, since as soon as the electronic structures of the two atoms start to overlap a distortion of the electronic distribution will result.

A pure ionic binding, on the other hand, would give rise to a dipolemoment equal to the product of the electronic charge and the ionic distance. But owing to the polarizability of the ions, such strong dipolemoments never can be expected; not even for alkali halide molecules are they completely realized. Thus, the dipolemoment will give no decisive answer to the question of ionic binding of diatomic molecules. All one can say is that with increasing dipolemoment the ionic character of the binding of diatomic molecules increases.

The investigation of the dissociation products seems to offer a more definite criterion. We might, for example, investigate what happens to the molecule if the atoms are separated slowly from each other and assume that if we obtain atoms we have atomic binding, whereas if we obtain ions the molecule is ionic. However, it can be shown that in most cases, during the dissociation, simply those products are formed which have the lowest total energy. Thus this criterion does not show us any essential property of the molecule but only of the dissociation products. The electronic structure and chemical properties of the latter will differ from those of the molecule.

There are, however, reasons for the dissociation products being different from the products of lowest possible energy. A detailed discussion of this aspect of the problem will be presented in connection with the escape of particles from a surface upon which they have been adsorbed, since space does not permit the treatment of the more general problem of the diatomic molecule.

IONIC REACTIONS

As a general rule, ionic reactions in solutions proceed at an immeasurably fast rate. The reason for this is that the formation of the molecule need not be preceded by the breaking of a shell or even by a pronounced rearrangement of the electronic structure. The ions are separated only by the dipoles of the solvent. Though these cling strongly to the ions, the attraction between the ions is in general strong enough to dislocate them. Effects to the contrary, however, are known. Thus some cobalt, iron, and nickel complexes cannot easily be destroyed but rather enter into the molecular combinations as greater units. Of course, reactions in which two ions of the same charge participate will be slow.

It will be expected that formation of molecules by the combination of a positive and a negative ion can proceed also in the gas phase with no activation energy. However, the reaction velocity may be slower than one would expect, owing to the necessity of a three-body collision or of wall reaction (20).

Another type of ionic reaction is one in which an ion collides with a neutral atom or molecule and an electron is exchanged. This type of reaction occurs also in solutions. Thus if an ion can exist in several states of ionization, such as the Fe^{++} and Fe^{+++} ion, electron exchange may give rise to reactions which are not of the simple ionic recombination type but which, nevertheless, proceed at a great speed (12). Only if the ion of changing charge is strongly shielded by other groups [$(Fe(CN)_6)^{+++}$ and $(Fe(CN)_6)^{++++}$, for example] so that the exchanged electron has to overcome a considerable barrier will we have a slower reaction (11).

Similar reactions may be also expected in the gaseous state. It has been pointed out (14), however, that such an electronic jump can occur only if there is resonance between the two positions between which the jump takes place; otherwise the slowly moving atoms will not be able to take up the energy liberated by the electron jump. Nevertheless, if we consider that the electronic energies change continually with the atomic positions it may be expected that for some nuclear configuration resonance will be established and electron exchange may, therefore, be a frequently occurring phenomenon. In fact, measurements on mobilities of positive ions have yielded the mobility of the ion (24) with the smallest ionization energy, showing that electron transfer will actually occur quickly if allowed from the point of view of energy.

This electron transfer has been used (6) to interpret the rule that a reaction will proceed if the positive ion of the reactant most difficult to ionize is produced. It is assumed that this ion will then draw an electron from the other reactant and the difference in ionization energies will become available for the reaction. This theory may describe many cases of ionic reactions. It is not sure, however, that the difference of ionization energies is actually utilized to furnish the activation energy for the reaction. Furthermore, the difference in ionization energies may be altered if the reactants form a reaction complex.

In the reaction of an ion and a molecule it is the positive rather than the negative ion which — as a general rule — can be expected to react faster. Though a positive ion may possess a complete shell, this shell need not be destroyed in order that reaction shall occur. Again, a lack of outer electrons will allow the partner to approach with less difficulty.

Negative ions may also enter gaseous reactions with comparative ease. But there are also cases where the negative ion will probably react slower than the corresponding atom or molecule. Such will be the case if the negative ion has a closed shell, e.g., Cl^- or CH_3^-, which has to be broken before the reaction can proceed.

Although the statements in this section must be regarded as qualitative guiding principles rather than established laws in kinetics, we see nevertheless that ions can enter into reactions in a multiplicity of ways and that one can expect to find many ionic reactions which will proceed with a small activation energy or with no activation energy.

Does Ionization of Reactants on Catalysts Precede Reaction?

In light of the preceding discussion of the definition, nature, and general properties of ions, we can now turn to the two questions with which this chapter is primarily concerned:

1. Under what conditions can we speak of adsorbed ions on the surface of catalysts?
2. Does such surface ionization of reactants on the catalyst surface probably precede reaction?

Adsorbed Ions on the Surface of Catalysts

Catalysts may in general be divided into two classes, metals and non-conductors. The catalysts that are termed non-conductors or insulators include oxides and salts of both metals and non-metals. It will be convenient in discussing the existence of ions on surfaces to treat the metallic and non-metallic catalysts separately.

The question of the possible existence of ions on the surfaces of metallic catalysts is intimately related to the modern theory of the ionic structure of metals. Among both physicists and chemists an ionic model of the metals is widely accepted. The atoms of a metal are said to have lost a certain number of electrons, and they are present, therefore, as positive ions; the electrons, on the other hand, are shared by the whole lattice and have many properties of free electrons. This picture accounts qualitatively and, as Sommerfeld (23), Bloch (2), and others have shown, to a considerable extent quantitatively for the conductivity of metals and will doubtless be retained by the physicists. From the point of view of chemical systematics, however, it must be admitted that this concept contains some of the same indefiniteness that surrounds the statement that a hydrogen molecule is composed of two positive hydrogen ions, the two electrons being shared by the molecule as a whole. Though this statement is quite true, chemists will be reluctant to say that H_2 is an ionic molecule.

It becomes evident at once from the theory of the structure of metals and from the discussion of the nature and definition of ions that the question as to whether atoms or molecules are adsorbed on a surface in an ionic rather than a neutral form cannot be answered in an unambiguous way. The same two criteria that were helpful but inconclusive in our treatment of ionic and non-ionic diatomic molecules can also be applied to surfaces. We may in judging the ionic or non-ionic nature of adsorption ask two questions. First, does the adsorption produce a dipole on the surface, and what is its magnitude? Second, if the adsorbed atom or molecule is removed from the surface, do we obtain an ion?

The first question can be answered experimentally for adsorption on metallic surface by investigating the dependence of the threshold for photoelectrons as a function of the adsorption. This threshold measures the work which is necessary to remove an electron from the metal. If ν is the frequency corresponding to the threshold, $\phi = h\nu$ (h = Planck's constant) gives the energy necessary to remove the electron. This energy is also called the work function. It can be interpreted as the drop in electric potential which accompanies the attaching of the electron to the metal.

If now N atoms or molecules are adsorbed on a unit area of the surface and each of these produces a dipolemoment M, there will be an additional potential $4\pi MN$ through which the electron must move in order to leave the surface. If the positive ends of the dipoles point away from the metal, the work function will be decreased by $4\pi MN$ and the photoelectric threshold will move toward the red by the amount $4\pi MN/h$. If the positive ends of the dipoles point toward the metal, the work function will increase correspondingly and the photoelectric threshold moves toward the violet. Thus it becomes possible to determine the magnitude and direction of the dipoles produced on the surface.

The application of the method above meets two experimental difficulties. First, it is not easy to produce quite clean surfaces and the photoelectric threshold for the clean metal is known accurately only in a few cases. Second, the dipoles produced on the surface may interact with each other and produce, by this reason, rather complicated phenomena. It is observed, for instance, that adsorption of a small quantity of potassium on iron shifts the threshold value toward the red whereas increased potassium adsorption causes a shift back toward the violet (9). Thus, in using great dipolemoments as a qualitative indication of ionic adsorption one must bear in mind that the ionic character will depend on the quantity already adsorbed.

Just as for the diatomic molecules, the investigation of the dipolemoment can give only a qualitative indication and not a sharp criterion for the presence of ions on surfaces. Thus it is wrong to conclude (3) that wherever adsorption affects the photoelectric threshold at all some ions must be present on the surface. In principle any adsorption will affect the photoelectric threshold just as any diatomic molecule consisting of two atoms of different kinds will have a finite, though sometimes very small, dipolemoment.

The other criterion of ionic adsorption is whether the particles when removed from the surface appear in the ionic form. If the adsorbed particles are separated from the surface infinitely slowly, one will obtain a positive ion wherever the ionization potential of the ion is smaller than the work function of the surface from which it is escaping, and one will obtain a negative ion if the electron affinity of the atom leaving the surface is greater than the work function. This corresponds exactly to our statement about diatomic molecules to the effect that dissociation will yield the products of lowest total energy.

Though, according to experimental evidence, the above simple rule is generally valid, it is of interest in this connection to discuss in detail the way atoms or ions escape from the surface, particularly since this mechanism may also have some significance in catalytic processes taking place near the surface. If an ion (for the sake of definiteness we shall consider a positive ion) approaches a metallic surface, it will cause polarization on it and as a consequence will be attracted. The attraction is the same as would be produced by a charge of the opposite sign located symmetrically at the other side of surface of the metal, i.e., inside the metal. Since this charge can be considered as the image of the charge of the ion, the resulting force is called the image force. If, as shown in Fig. 1, the charge of the ion is e and its distance from the surface is r, the image force will be $e^2/4r^2$. Let us separate an adsorbed particle from a metallic surface and let us suppose that at infinite distance the atomic state would be energetically more favorable. We can now draw Fig. 2. The ion will be attracted to the metal by the image force whereas the force acting on the neutral particle is at great distance negligible. At some distance the ionic state may become more favorable. In Fig. 2 this is shown to happen at the distance r_1 from the surface. If at r_1 the electronic structures of the metal and the particle which is being removed are sufficiently separated, one might expect the particle to appear in an ionic form even though the work function ϕ is smaller than the ionization potential I, and the emission of an atom will, therefore, be energetically more favorable. The question would be whether the particle leaving the surface crosses the region around r_1 sufficiently slowly to allow an electron to jump over between the metal and the particle. Fewer ions would be expected in the region beyond r_1 if the particle moves slowly through r_1 and if the electronic

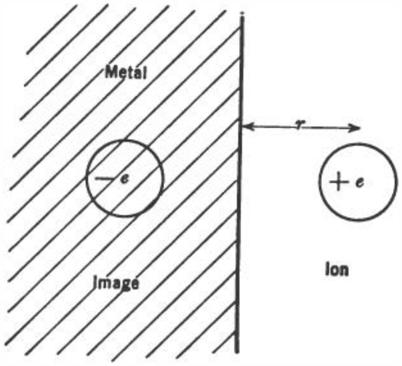

FIG. 1. The Image Force of an Ion in the Neighborhood of a Surface.

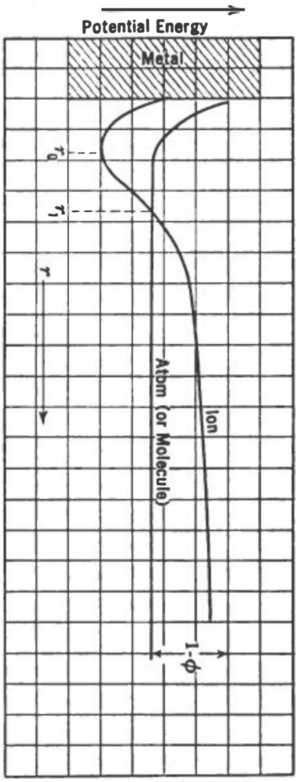

FIG. 2. Potential Energy of Atoms and Ions in the Neighborhood of a Surface.

structures of metal and particle are not sufficiently separated. Fewer atoms would be expected in that region if the particle moves with a great velocity around r_1 and if the electronic structures at r_1 are far apart. Actually the ratio of the number of ions to the number of atoms leaving the surface is given by the Boltzmann factor $e^{-(I-\phi)/RT}$ (I = ionization potential of the atom to form a positive ion), indicating that one obtains thermal equilibrium between atoms and ions in a region close to the surface and that the obtained result does not depend on the details as to how an atom or an ion leaves the surface.

An important factor which helps to explain why thermionic emission becomes negligible for $I > \phi$, even if at r_1 the electronic structures are separated, is the following: Of the number of particles which get as far as r_1 from the surface, a small fraction (namely, $e^{-(I-\phi)/RT}$) will have sufficient kinetic energy to leave the surface in the ionic form. Even if it happens only a few times that an electron can jump over between the particle and the metal while the particle is near r_1, whenever such a jump occurs the particle, not being retarded any more by the image force, can get away from the metal.

The connection between the thermionic emission and the work function indicates that the former will vary with the amount adsorbed on the surface, just as the latter does. In fact it has been found that thermionic emission of alkali ions, for example, stops as soon as a certain amount of alkali is adsorbed on the surface. It will not be necessary for us to discuss in detail the interaction mechanism of the alkali atoms on the surface by which this result is caused.

It becomes clear, therefore, that the only thermionic emission of ions that one would expect from a surface would be of particles whose ionization potentials are not materially greater than the work function of the surface. Furthermore, the only particles that could by this type of evidence be definitely classed as ions on the surface are those which yield positive ions by thermal emission. On the other hand, the failure to obtain positive ions during desorption of adsorbed material does not either prove or disprove the existence of ions on the surface. Experimentally (9) the only positive ion emission that has been analyzed by a mass spectrograph has been found to consist of ions of alkalis, alkaline earths, or similar atoms with ionization potentials not appreciably greater than the work functions of the surfaces from which they were emitted. Brewer (4) has found that the presence of small partial pressures of hydrogen, nitrogen, or ammonia materially enhances the emission of positive ions, though the nature of the ions is not established.

A number of articles have been published by Nyrop (4, 16, 17, 18) in recent years in an endeavor to correlate the catalytic activity of a material with its ability to effect surface ionization of the adsorbed reactants. At this point it is pertinent to discuss the aspects of his theory dealing with his explanation of chemisorption as a process of ionization of molecules that come in contact with the surface. His most fundamental mistake appears to be his attempt to utilize the kinetic energy of the free electrons of the metal to ionize the oncoming atom or molecule. This is in principle like using the kinetic energy of the K-electron in lead to ionize atoms which are reacting with lead. In fact, energy gain which one can obtain by adding an electron to the lattice is $\phi + kT$, where ϕ is the work function and where the energy kT does not exceed a small fraction of a volt. This can be seen with the help of Fig. 3. Here ϕ represents the energy level of free electrons outside the metal. $P = E + \phi$, and is the potential energy of the electrons in the metal. This whole energy will not be liberated, however, if an electron is added to the crystal. At absolute zero, all levels up to the Sommerfeld energy E will be filled, and the maximum energy gain that accompanies the addition of an electron to the metal is ϕ. At high temperatures some electrons of the metal will be raised to energies $\sim kT$ above the ϕ level, and some of the states $\sim kT$ below the ϕ level will be free. This band of $\pm kT$ around the original upper limit of the metal electrons may, of course, exchange energies $\sim kT$ with any adsorbed particles (13). Thus, the greater part of the Sommerfeld energy E postulated by Nyrop to be usable for effecting ionization of atoms or molecules approaching the surface can in reality not be so used. Therefore, the main quantitative argument of Nyrop in favor of the ionic explanation of catalysis must be rejected.

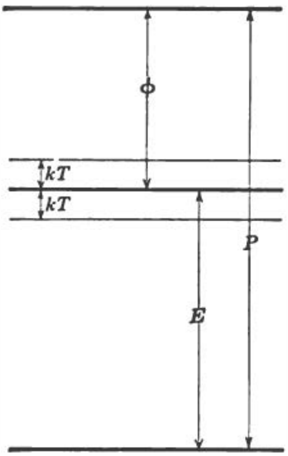

FIG. 3. Energy Levels in the Vicinity of a Metal Surface.

Nyrop's theoretical treatment of " free " electrons in metallic catalysts has additional shortcomings that it may be well to point out. His quantitative relations between kinetic energy of the free electrons in the metal and ionization potentials of the adsorbed atoms and molecules which he has proposed must be rejected definitely. Such attempts do not take into consideration that " free " electrons moving in a metal have apparent masses (2) different from really free electrons. Nyrop does not distinguish properly between the kinetic energy of electrons in their motion through the crystal and the kinetic energy of an electron around a metal ion. This latter energy does not vanish even if the electron is at rest with regard to its propagation in the lattice.

It is of course possible to describe some surface compounds or chemisorbed molecules as having an ionic linkage in the same sense that HCl may be described as having it. However, as we have seen, such a description is arbitrary and does not have any very definite meaning. It may be considered more in the light of shared electron phenomena, which topic will now be treated.

In the same sense in which the atoms of a metal share their electrons, it is possible that the electrons of adsorbed particles should participate in the sharing. An alkali atom having a lower ionization potential than the work function of iron may give at greater distance its electron to the iron. If, however, the ion approaches the metal, the electron density in the parts of the metal adjacent to the ion will increase and electrons will be drawn to some extent towards the ion. It thus becomes doubtful whether the electronic structure is described better by the ionic picture or by the alkali atom sharing its electron with the metal.

If, according to the absence of thermionic emission, the adsorption is non-ionic, the picture using shared electrons may prove to be good. A patent objection to this picture, however, is that it cannot be distinguished easily from the picture of a homopolar bond or — if the above argument about the alkali adsorption is admitted — from a heteropolar bond.

At least for one case, namely, for the adsorption of hydrogen in palladium, a more definite statement can be made about the electron sharing. Hydrogen diffuses readily in palladium (21) and, if a current flows through the palladium, the hydrogen will travel along with the positive current (8). Comparison of the diffusion coefficient with the rate of transportation of hydrogen in the current shows that a force equal to $eE/50$ acts on the hydrogen (E = electric field, e = electronic charge). The simplest explanation is that the hydrogen atoms present share their electrons with the metal (10). The charge of the proton, however, is not neutralized completely by the shared electrons. The motion of the proton, on the average, will be accompanied by a motion of a " shared " electron that is but 2 per cent less than that of the proton so that the proton acts as though it would carry only one-fiftieth of its charge.

The behavior of hydrogen in palladium has been considered as analogous to the behavior of ions in solution. The influence of the metallic electrons would parallel the influence of the dielectric constant; but there is a very definite difference between the two cases. Whenever an ion in solution is transported through a certain distance the electronic charge (or its multiple) will be transported too. In the hydrogen-palladium system only a fraction of an electronic charge is transported with the hydrogen. There is thus a continuous transition between the " ionic " solution and the atomic solution with shared electrons.

Nyrop's attempt to describe all activated adsorptions as ionic may be classed best with this picture of electron sharing. The indefiniteness of this picture allows us to describe with its help almost any electronic configuration where close contact between the electronic shells of adsorbate and adsorbent is established.

Turning now to the consideration of non-metallic catalysts such as oxides, salts, etc., one has to discuss the structure of insulators. It is usually accepted that no free electrons are present in insulators. The electrons are localized near atoms or ions, or they are shared between two neighbors and belong to a definite bond.

It has been shown, however (22), that most of the properties of alkali halide crystals can be obtained if one assumes that the electrons are shared by the crystal as a whole. These " free " electrons must be pictured as completing a closed shell within the crystal. This closed shell accounts also for the absence of conductivity, the current of any free electron being always compensated by the current of another electron of the shell.

There is, of course, an actual theoretical difference between insulators and conductors; but it does not depend on the idea of " shared " or of " free " electrons. It is much more similar to the difference which exists between closed electronic shells and electron structures with valency electrons. Thus, the electronic configuration of an incomplete shell can be changed much more easily than that of a closed shell. The consequence for atoms and molecules with incomplete shells and also for metals will be that they absorb light of relatively long wave length. In the metals it also accounts for the conductivity. A similar distinction which may be of importance for the questions of adsorption and catalysis is the following: In a closed shell it makes a very great difference in energy whether one wants to add an electron to the shell, which is already closed, or whether one wants to take away an electron, thereby breaking the shell. The former process liberates only a negligibly small amount of energy, whereas the latter usually requires an amount considerably in excess of 10 e.v. The same situation holds for insulators. This, of course, remains true irrespective of whether or not the electrons are treated as " shared." For incomplete shells the electron affinity, i.e., the energy gained if an electron is attached to the atom giving a negative ion, and the ionization potential, i.e., the energy necessary to draw out an electron from the atom and to form a positive ion, are of the same order of magnitude. Owing to the great number of electrons present in a metal and, particularly, to the conductivity, these two quantities actually become identical for a metal. The electron work function ϕ may be defined either as the energy necessary to draw out an electron from the metal or as the energy gained if an electron is absorbed by the metal.

In principle the same criteria as have been used for metals may be applied to decide whether adsorption on an insulator is ionic or not. Actually, however, it is practically impossible to carry out either the photoelectronic or the thermionic experiment. Perhaps the most decisive difficulty is that, because of the charge accumulating on the insulator, no steady current can be obtained.

Surface Ionization and Catalysis

On surfaces many or all the factors which promote catalysis may frequently be expected to act. A surface furnishes — as adsorption shows — an attracting center for the reactants. It distorts their electronic structures by physical or chemical forces and its presence makes a "third body" in the reaction unnecessary. In some instances it seems certain that the geometry of the catalyst surface has an all-important influence on its activity. Long, Frazer, and Ott (13*a*) found that only alloys of Fe—Co—Ni—Cu that were face-centered cubic in structure were active for the hydrogenation of benzene to cyclohexane. This conforms to the theory advanced by Balandin (1).

The general hypothesis of Nyrop, to the effect that surface catalysis occurs primarily through a mechanism of ionization, appears difficult to substantiate. As pointed out above, the mechanism by which he proposes to insure all chemisorption as being ionized adsorption appears to be erroneous. His attempts to correlate catalytic activity and ionization capacity of the surface are equally unimpressive. In Table 2, Chapter 5, of his most recent publication a list of chemisorptions and catalytic reactions is presented and the various metallic and oxide adsorbents and catalysts arranged on the basis of their abilities to bring about activated adsorption and catalytic reaction. The table does not merit detailed consideration, for it is very qualitative at best, being filled with many questionable conclusions. However, if properly revised, it might constitute an interesting summary of the relative catalytic activities of different metals and oxides as catalysts and adsorbents. The rejection of the part of his paper giving the theoretical reasons for expecting ionization on surfaces destroys the effectiveness of the paper as an attempted correlation between the fundamental physical properties of metals and their activities as catalysts.

Search of the literature reveals that the ideas incorporated into Nyrop's work have also been advanced by Pisarzhevskii (19). Recently Cady and White (7) attempted to obtain experimental evidence as to the part played by ions in catalysis. They subjected a Ni strip to a current of 50 ma. at a frequency of 50 kilocycles and measured the activity of the wire for the synthesis of water from hydrogen and oxygen with and without the current. There was no difference in the activities, indicating that if surface ions do exist and play a part the superposition of a current of this magnitude and character does not influence the ionic behavior of the adsorbed gases.

Schmidt (21) in a series of articles has also suggested that the hydrogenation of organic compounds on solid catalyst proceeds through the interaction of surface ions of hydrogen and of the organic molecules. He concludes that protons exist in cracks and crevices that are so narrow as to allow the hydrogen ions to be surrounded by metal atoms or ions in much the same manner in which they would be surrounded if actually dissolved in the metal. This picture is not attractive in view of the obvious difficulty of ingress and egress of large organic molecules into and out of such capillaries.

In non-metallic catalysts many kinds of unsaturated atoms on the surface may act as centers for attraction and distortion. Metals, on the other hand, have the properties of unsaturated atoms or compounds, being in particular able both to donate and to accept electrons, and, therefore, to enter into various intermediate compounds.

As has been pointed out, such intermediate compounds on metallic surfaces may be called " ionic " without getting into direct contradiction with our physical or chemical knowledge about metals. The arbitrariness of such a terminology has been discussed in detail.

It has been proposed that ions are responsible for the catalytic action of surfaces in a more specific sense (5). If thermionic emission can take place, ions may escape so far from the metal surface that their electronic structure separates from that of the metal. This may happen even if I is greater than ϕ and if, therefore, thermionic emission does not occur because the image forces may make the atoms energetically more stable before they get entirely away from the surface.

If, now, the ions react near the surface, but while being separated from it, one may call the reaction properly " ionic." Both the reactivity of ions as described in the previous section and the mobility of these ions on the surface make the picture plausible. Also, positive and negative ions may be produced in this way. In fact this picture is not unlike that of ionic reactions in solutions. The only difference is that in the solution the dielectric constant (i.e., the dipoles) of the solvent stabilizes the ions, whereas near the metallic surface the stabilization is brought about by the image forces (i.e., by the conduction electrons). We may accept this picture as one which might often — though certainly not in all cases — be useful.

It is not permissible, however, to assume positive ions in this sense near the surface if the ionization energy is much greater than the work function ϕ, or negative ions if the electron affinity is much smaller than the work function. Indeed, if these differences are greater than 2 or 3 e.v., the crossing point r_1, if it occurs at all, will lie so close to the surface that the electron structures come into contact, and there is no proper way in which to distinguish adsorbed atoms and adsorbed ions.

Thus surface catalysis may be explained in some cases by action of ions. But it is not justified to postulate that all surface reactions have an ionic nature. In very many cases the question whether or not we are dealing with ionic reaction reduces to a question of definition. For surface phenomena this is much more true than for the gaseous state or for solutions where the presence of ions can be decided by less ambiguous methods.

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CHAPTER VII

CONTACT CATALYSIS IN THE HYDROGENATION OF COAL, COAL TAR, AND OIL*

H. H. STORCH†

INTRODUCTION

F. Bergius in 1913 discovered that it was possible to add hydrogen to coal at pressures of 100 to 200 atm. of hydrogen and at temperatures between 300 and 500°C. The World War diverted Bergius' attention from coal to oil hydrogenation, and it was not until 1921 that the principal difficulties in developing high-pressure apparatus were overcome. Further experimentation by Bergius showed that about 200 atm. pressure of hydrogen and 450°C., with about two hours' contact time, were the optimum conditions for most of the coals examined by him (2).

Subsequently the I. G. Farbenindustrie A. G. found contact catalysts which increased the rate of hydrogenation; and this company developed the processes which are now in operation on a large scale in Germany and England. The role of contact catalysis in the hydrogenation of coal and heavy oils is of fundamental importance, for without such catalysis the development of these processes on a large scale would not have been possible.

The catalysts developed for coal and oil hydrogenation were direct descendants of those designed for the synthesis of alcohols and higher hydrocarbons from water gas. In the latter processes catalysts of only mildly hydrogenating character were necessary to avoid methane production. In coal and oil hydrogenation mild hydrogenation was also essential, but additional prerequisites were also necessary, viz., resistance to sulfur poisoning and stability at temperatures between 400 and 500°C. Thus, while some of the catalysts used for the syntheses of alcohols or hydrocarbons from water gas are more active at about 300°C. than coal and oil hydrogenation catalysts, often the reverse is true at tempera-

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tures above 400°C. This is due, sometimes, to an irreversible sintering of the catalysts for syntheses from water gas, and at other times to a reversible but large decrease in the amount of activated adsorption of the reactants (1) by these catalysts.

Liquid-Phase Hydrogenation

In the first step of the hydrogenation of highly carbonaceous materials such as coal or coal tar, it is necessary, because of the low vapor pressure and thermal instability of these materials, to operate in the liquid phase. Another reason for such operation is the relatively rapid deterioration of the stationary (or " fixed ") catalysts which are necessary for vapor-phase operation. In the hydrogenation of coal, for example, a mixture of powdered coal and a heavy oil plus a small amount (about 0.1 per cent) of a solid catalyst, such as tin oxalate or sulfide, is forced, along with hydrogen at 200 atm. pressure, through a preheater, where the temperature is raised to about 450°C., and subsequently through three converters in series. The time of contact is about two hours.

In the hydrogenation of coal, one appears to be dealing with a reaction involving three solids (coal, converter walls, catalyst), one liquid phase, and one gas phase. It is probable, however, that most bituminous and sub-bituminous coals are dissolved very rapidly by the heavy oil (obtained from previous coal hydrogenation). All the experiments (28) on solvent extraction of coal under conditions comparable with those used in coal-hydrogenation practice indicate that solution of the coal constituents, except ash, fusinite, and some opaque attrital matter, is rapid and complete. Hence, during the very early stages of the primary liquefaction of coal, the number of solid phases increases, so that one has, in addition to solid catalyst particles and the converter walls, the particles of the coal ash, the fusinite, and some resistant attrital material. The ash may contain traces of active catalysts such as germanium or tin, but the amounts are so small that their catalytic effect may be neglected. The patent literature, however, indicates that it is desirable for some coals to neutralize the alkaline constituents of the ash by pretreatment of the coal with acids (17, 19, 20). Some recent patents state that it is desirable to recirculate the carbonaceous solid residue (22, 23) so that there is, perhaps, some positive catalytic action or some ability to remove catalyst poisons possessed by this residue.

The catalytic behavior of the converter walls was investigated recently by the British Fuel Research Laboratory (5) and found to have considerable importance. These experiments were conducted by using a glass " liner " made of Pyrex; the results are given in Table I. Experiment 5 shows that Pyrex glass has very little catalytic effect and, hence, conclusions concerning the catalytic effects of the converter walls and of the stannous hydroxide are sound.

TABLE I

EXPERIMENTS ON WALL CATALYSIS WITH TWO-LITER CONVERTER

Beamshaw coal, low-temperature tar vehicle. Contact time, 2 hours; temperature, 450°C. Initial pressure, 100 atm. of H_2

Experiment	Liner fitted	Catalyst	Insoluble residue (percentage of dry, ash-free coal)
1	No	None	12.0
2	Yes	None	45.0
3	No	0.1 per cent $Sn(OH)_2$	9.8
4	Yes	0.1 per cent $Sn(OH)_2$	14.5
5	No	50 per cent Pyrex glass	15.3

In present industrial coal-hydrogenation practice the converters are about one meter in diameter, and hence catalysis by the converter walls may be of less importance than indicated in Table I. It should be remembered, however, that in engineering development work, such as was done by Valette (32) in France and recently by Morgan and Veryard (27) in Great Britain, where very much narrower tubes were used than those in the experiments of Table I, the catalytic effect of the converter walls is of considerable importance. One might suppose that the activity of converter walls would be rapidly decreased by poisoning. Such is not the case, as shown in experiments done in the British Fuel Research Laboratory (6). The only way in which converter-wall activity could be avoided was by a glass liner.

Some data on the kinetics of the primary liquefaction of coal by hydrogenation have recently been obtained by C. H. Fisher and his co-workers at the Central Experiment Station of the Bureau of Mines in Pittsburgh, Pa. (8). This work was done in a rotating 1200 cc. bomb, using equal weights (100 grams of each) of tetralin and coal plus 1 per cent of tin sulfide, and an initial (cold) pressure of 1000 pounds per square inch of hydrogen. The results of this work indicate the following mechanism for the primary liquefaction of coal by destructive hydrogenation:

1. The curves of hydrogen consumption versus time in the temperature range of 370 to 430°C. are practically straight lines whose slope indicates a temperature coefficient of 1.20 per 10°C. and hence a diffusion process. The rates of all the reactions mentioned in paragraphs 3, 4, and 5 below are independent of the rate of hydrogen consumption.
2. Below 370°C. the extent of coal liquefaction (as measured by solubility in acetone and benzol) is dependent upon depolymerization by the solvent. The activation energy of this reaction is about 7 kilogram calories.
3. Above 370°C. another reaction with an activation energy of about 65 kilogram calories occurs. The rate of this reaction is rapid above 400°C. and is independent of the rate of hydrogen consumption. The reaction is probably a thermal decomposition of the coal substance. It is accompanied by a rapid elimination of about 60 per cent of the oxygen of the coal, and by the absorption of only a negligible quantity of hydrogen.
4. In the range 370 to 400°C. a reaction of about 40 kilogram calories activation energy occurs, involving the elimination of the remaining 40 per cent of the oxygen of the coal. This is a much slower reaction than paragraph 3 and is probably catalytic in nature. A large consumption of hydrogen occurs concomitant with this reaction, although its rate is independent of the rate of hydrogen consumption.
5. At all temperatures above 370°C. there is a condensation of free radicals or unsaturated compounds (generated by thermal decomposition of the coal substance) into materials more stable than the original coal substance. This new polymer dehydrogenates at temperatures above about 450°C. at a sufficiently rapid rate so that, despite the presence of hydrogen under pressure and of hydrogenation catalysts, some coke is formed. This condensation reaction obscures the kinetics of the reactions mentioned in paragraphs 3 and 4 and results in apparent negative temperature coefficients for the liquefaction and oxygen removal reactions at temperatures above 400°C.

The above outline of the probable mechanism of coal hydrogenation indicates that the chief function of catalytic hydrogenation is to saturate the free radicals or unsaturated compounds provided by the thermal decomposition of the coal, and to hydrogenate carbon to oxygen and double bonds in the later stages of the liquefaction. The kinetics of these hydrogenation reactions is largely obscured by the variety of other reactions proceeding at the same time. Additional work similar to that of C. H. Fisher (8) should be done with a glass liner and in the absence of catalysts. The results of such work may make it possible to disentangle the kinetics of the thermal and the catalytic reactions.

The rather high activity of halogens (31), especially small amounts of iodine in the liquid-phase hydrogenation of coal and coal tar, provides an additional clue to the nature of the slow step in this reaction, for iodine has been shown by Hinshelwood and his co-workers (15) to be an effective catalytic agent for the decomposition of oxygenated organic compounds.

VAPOR-PHASE HYDROGENATION

The destructive hydrogenation of low-temperature coal tar proceeds mainly in the vapor phase. A considerable amount of experimental work has been published in England (24, 29) and Japan (7) on the hydrogenation of low-temperature tar; but there is very little published information on catalysts for the hydrogenation-cracking of high-temperature tar (25) and of petroleum fractions (30).

A survey of catalysts for the destructive hydrogenation of low-temperature tar (7, 24, 29) shows the outstanding efficiency of small amounts of halogens and halogen compounds, and of a few amphoteric sulfides, namely, molybdenum, tungsten, and tin sulfides. The latter are, in general, more active than the oxides; in fact, it appears desirable to maintain a minimum partial pressure of about one atmosphere of hydrogen sulfide to avoid conversion of metal sulfides to oxides or metals (18, 21). The work of Varga and Makray (33) shows that hydrogen sulfide used along with a molybdenum catalyst promotes the hydrogenation of naphthalene, metacresol, and tar oils in general. Hydrogen selenide has a selective effect when used with a molybdenum catalyst, in that it promotes the hydrogenation of naphthalene more energetically than does hydrogen sulfide, and retards the hydrogenation of metacresol and tar acids in general.

Molybdenum oxide supported on alumina gel is a satisfactory catalyst at about 480°C. for the hydrogenation of crude low-temperature tar (24, 29). It deteriorates at a relatively slow rate and can be reactivated by oxidation with air. However, for partly hydrogenated middle oils that are free from asphaltic and bitumen-like materials, much more active catalysts, such as pelleted molybdenum and tungsten disulfides, may be used. These catalysts may be prepared by precipitation of the sulfide by acidification of an ammonium thiomolybdate (or thiotungstate) solution, followed by washing, drying, and pelleting of the powdered trisulfide and subsequent reduction to the disulfide. They are extraordinarily active for vapor-phase hydrogenation, some hydrogenation being effected by them at as low a temperature as 250°C., although 380 to 400°C. is the practical operating temperature zone (24, 29). In addition to being much more active than molybdenum oxide supported on alumina gel, the composition of the gasoline products obtained by the hydrogenation of middle oils (from coal hydrogenation) with the pelleted molybdenum disulfide is characteristically different (3, 14), as shown in the following table:

	Alumina-gel-supported catalyst	Pelleted catalyst
Aromatic hydrocarbons, percentage by weight	27	2
Naphthenic hydrocarbons, percentage by weight	66	50
Paraffinic hydrocarbons, percentage by weight	7	48

The enormous differences in the results obtained with these catalysts cannot be due entirely to the fact that one is initially molybdic oxide and the other the disulfide; for it is probable that the oxide catalyst is at least partly converted to sulfide during operation. An X-ray study of these two catalysts would probably be profitable.

The experiments of Hollings, Bruce, and Griffith (16) on the influence of silica as a promoter for molybdic acid in the hydrogenation of tars showed that, when the yield under a given set of conditions was plotted against the atom percentage of silicon, a curve was obtained containing two maxima at 3.0 and 5.5 per cent and a minimum at 4.5 per cent. These authors also studied the adsorption, at temperatures up to 450°C., of hydrogen, benzene, hexane, and cyclohexane by molybdic acid containing varying amounts of silica. An inspection of the data given for the rate of activated adsorption of hydrogen shows that large decreases in the energy of activation occur between 0.0 and 3.0 atom per cent silicon and between 4.4 and 5.5 per cent, whereas this energy is virtually constant between 3.0 and 4.4 per cent. If one assumes a steadily increasing retardation by coal tar or its hydrogenation products with increasing atom-percentage of silicon, it is reasonable to predict on the basis of the changes in energy of activated adsorption of hydrogen precisely the form of curve actually obtained; that is, two maxima, one somewhere between 0.0 and 3.0 per cent silicon and the other between 4.4 and 5.5 per cent.

The efficiency of various promoters in increasing the catalytic activity of molybdenum oxide in the catalytic hydrogenation of phenol to benzene was studied by Kingman and Rideal (4, 26). It was found that a very effective method of introducing the promoter was to prepare the catalyst from the appropriate heteropoly acid, with the promoter as the central atom in the complex. The ammonium salts of the acids were used, and the catalysts were treated with hydrogen for 6 hours at 480°C. before testing. Of the four catalysts prepared from $(NH_4)_n[X(Mo_2O_7)_6]$, where X = P, Si, Sn, Th, those containing phosphorus and silicon were much more active than molybdenum oxide, whereas those containing tin and thorium were appreciably less active than molybdenum oxide. The three catalysts prepared from $(NH_4)_n[M(MoO_4)_6]$ containing nickel, chromium, and copper were much more active than molybdenum oxide. X-ray analysis of the first group of catalysts showed an extremely small particle size for the phosphorus- and silicon-promoted catalysts, the phosphorus catalysts' structure being entirely different from that of pure molybdenum dioxide. The thorium-promoted catalyst is more crystalline than that promoted with phosphorus, and both the thorium- and the tin-promoted catalysts have structures similar to that of pure molybdenum dioxide. The efficiency of a promoter in the first group of catalysts may therefore be dependent on the prevention of the sintering of nearly amorphous catalysts. X-ray analysis of the second group shows a fairly well-developed crystalline structure similar to that of pure molybdenum dioxide, and hence the high activity of these catalysts may be due to an effect different from that for the phosphorus- and silicon-promoted catalysts of the first group. This effect may be the distortion of the space lattice caused by the introduction of the promoter. The relative surface areas of some of the catalysts were measured and it was found that, while the more active catalysts presented larger areas, the variations in surface areas were not directly proportional to the measured differences in catalytic activity. Since, however, it is known that in heat sintering the activity of some catalysts decreases manyfold faster than the surface area, this lack of proportionality is not necessarily indicative of a new or qualitatively different phenomenon.

A detailed study of promoters for the dehydrogenation of hexane and the hydrogenation of phenol was recently published by Griffith (11, 12). The optimum promoter concentration for hexane decomposition at 500°C., using a molybdenum oxide catalyst, is found to be 4.3 atom per cent for sodium, chromium, cerium, aluminum, barium, boron, and thorium, and 2.2 atom per cent for iron, copper, and lead. The metal oxides of the first group are not reducible under the operating conditions, whereas iron, copper, and lead oxides are reduced to the respective metals. For the hydrogenation of phenol at 400°C., the optimum promoter concentrations for a molybdenum oxide catalyst were 16 atom per cent for cerium, 16.5 for aluminum, and 15.0 for silicon. No adsorption measurements for phenol or hydrogen are reported, and until further data are available it will be difficult to determine the significance of these optimum promoter concentrations.

The same author also presents a series of dehydrogenation rate determinations for decahydronaphthalene, decane, hexane, and cyclohexane, using chromic oxide gel plus various amounts of magnesia (10, 13).

For decahydronaphthalene, the activity is constant from 0.0 to 90.0 per cent magnesia, and then it drops off linearly with increasing magnesia content. For decane the constant activity range is 0.0 to 50.0 per cent, for hexane 0.0 to 20.0 per cent, and for cyclohexane the activity drops continuously with increasing magnesia content. Griffith explains these data by assuming that the larger hydrocarbon molecules cover many active centers upon adsorption, and hence the dilution effect due to the inert carrier magnesia is not apparent until the active centers are farther apart than the necessary distance for activation and reaction. Similar experiments with a chromic oxide-silica catalyst and addition of various amounts of magnesia show an immediate dilution effect with all hydrocarbons. Griffith concludes from this that chromic oxide promoted with silica presents a surface that is qualitatively different from unpromoted chromic oxide and not merely one with a larger number of active centers.

This research will unquestionably be of importance in developing the chemistry of vapor-phase hydrogenation. It would, however, be desirable to have catalytic rate studies on the destructive hydrogenation of larger molecules. There is also a dearth of rate measurements on destructive hydrogenation in liquid phase of pure compounds of high molecular weight.

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Chapter VIII

CATALYTIC DEHYDROGENATION OF OXYORGANO COMPOUNDS

E. C. Williams and M. de Simo

Although a large number of papers and patents dealing with the catalytic dehydrogenation of oxyorgano compounds have been published during the past two years, little new work of fundamental importance on the theoretical or physical aspects of the subject has been reported. Nevertheless, the reactions themselves continue to hold the attention of many workers and are becoming of increasing industrial importance.

New types or arrangements of catalysts have been investigated and the dehydrogenation of many different organic compounds has been accomplished. Particularly, attention has been paid to less straightforward reactions where some other product than the usual primary product of dehydrogenation is sought; for example, ketones of higher molecular weight have been produced from lower ketones, or alcohols and esters directly from alcohols by the use of mixed catalysts and appropriate reaction conditions.

The commercial production of various organic chemicals, particularly a range of different ketones, by catalytic dehydrogenation processes, has vastly increased during the period under review.

The most widely used dehydrogenation catalyst is still metallic copper, either alone or in combination with other elements, or the chromite-type catalyst in one or other of its modifications. Palladium, selenium, cerium, charcoal, and others have been used or suggested in only a few specific cases.

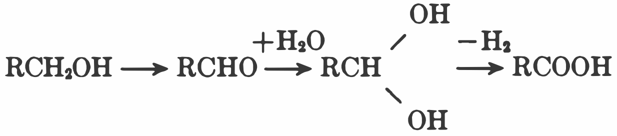
Improvements or modifications of the well-known copper or brass catalysts continue. Lorang (32) in a recent patent suggests the addition of zinc, thorium, cerium, or zirconium oxides with sodium carbonate to a precipitated copper catalyst, such additions being claimed to extend the active life of the catalyst when used for the dehydrogenation of lower alcohols at reaction temperatures below 350°C. In two other patents (7, 4) tin and magnesium are claimed to be beneficial additions to a copper-zinc catalyst.

Ivannikov *et al.* (26), by promoting the action of a copper catalyst by additions of uranium, obtained high conversion of secondary butyl alcohol to methyl ethyl ketone at temperatures of only 250 to 290°C.

The mechanism by which such mixtures, or promoters of catalytic activity or catalytic life, achieve their effects is still largely unexplained, but work is in progress which may eventually shed light on this matter. Bork and Balandin (9, 10, 11, 12, 13) have studied the time of residence of ethyl and propyl alcohols and their primary dehydrogenation products (aldehydes) on the surface of a copper catalyst and consider that their results will serve for study of deactivation or poisoning of the catalyst.

A group of Russian investigators (27, 17, 16, 15, 28, 18, 1) reports that lower primary alcohols may, on dehydrogenation, yield esters; the catalyst was copper or copper promoted by cerium, uranium, and zirconium. Ethyl alcohol, for example, at 250 to 275°C. was converted to ethyl acetate in yields up to 50 per cent over an electrolytic copper catalyst, and 51 to 65 per cent over a copper +0.9 per cent zirconium catalyst. It is of interest that such ester formation occurred only when aldehyde and hydrogen or aldehyde and alcohol were present together in the reaction zone; aldehyde alone gave no ester.

Hale (23, 24) claims that by a double dehydrogenation of alcohols (in the presence of water) over a copper catalyst, modified by the addition of small amounts of manganese and chromium, acids can be produced directly. This result is explained by the formation of aldehydrol by the union of the aldehyde first formed and water; the aldehydrol is then further dehydrogenated to the corresponding acid.



$$\mathrm{RCH_2OH} \longrightarrow \mathrm{RCHO} \xrightarrow{+\mathrm{H_2O}} \mathrm{RCH}\begin{matrix}\diagup \mathrm{OH}\\ \diagdown \mathrm{OH}\end{matrix} \xrightarrow{-\mathrm{H_2}} \mathrm{RCOOH}$$

The above type of transformation to acid without the agency of oxygen is claimed to occur also in aldehydes and to take place over a catalyst consisting of copper and oxides of amphoteric elements, such as aluminum, chromium and manganese.

Masina (33) investigated mixed dehydration and dehydrogenation catalysts containing, on the one hand, aluminum oxide, on the other, copper chromite or nickel. With small amounts of Al_2O_3 in the catalyst the dehydrogenation predominated, and cyclohexanol and methyl cyclohexanol yielded the corresponding ketones. As the proportion of Al_2O_3 was increased, the reaction yielded benzene and toluene. It is noted that except at low temperatures, 260 to 300°C., no phenol forms; hence dehydration is a faster reaction than dehydrogenation.

Krauze and Slobodin (29) investigated the reaction of lower alcohols with similar catalysts at around 450°C. They found that the extent of dehydrogenation relative to dehydration is determined by the relative amounts of the two types of catalyst present. With some catalyst combinations, the combined dehydration and dehydrogenation proceeded to some extent all the way to diene hydrocarbons.

Over a copper-zinc (brass) catalyst, lower alcohols appear to dehydrogenate at around 500°C. even under pressure (50). Dehydrogenation under pressure facilitates the recovery of low-boiling reaction products from the formed hydrogen.

Chromite type of copper catalyst has been used extensively in the past, both for dehydrogenation and hydrogenation of a large number of organic compounds. More recently, it has been claimed for the dehydrogenation of hydrogenated polycyclic phenols at a temperature of 50 to 400°C. (31). Several proposals have been made to improve such catalysts. Salzberg (45) proposed to extract an ignited copper chromite catalyst with ammonia to obtain a highly efficient dehydrogenation catalyst especially adapted to liquid-phase processes. Lazier (30) and Lazier and Arnold (5) claim an improved catalyst consisting of cadmium-promoted nickel and zinc chromite. Dunbar *et al.* (22) precipitated a copper chromite catalyst on pumice and found it to be active even after 15 to 20 hours' use.

A chromite type of catalyst containing copper, zinc, and cadmium has been claimed to be efficacious even for removing hydrogen from the alkyl radical of an oxyorganic compound (53). According to this patent, isobutyraldehyde, for example, can be dehydrogenated at 400 to 465°C. to α-methacrolein.

A copper chromite catalyst or copper alone appears to cause a simultaneous dehydrogenation, dehydration, and hydrogenation when glycerol is passed over it at 240 to 260°C. The principal product of such a reaction is said to be acetol (25).

A similar reaction is claimed to take place when secondary aliphatic and cyclic alcohols are contacted with a catalyst consisting of 82.5 per cent zinc, 10 per cent copper, and 7.5 per cent cadmium (6). With such catalyst, at long contact times and under 100 pounds pressure, 69 per cent of isopropyl alcohol was converted to higher-boiling products, principally methyl isobutyl and diisobutyl ketones.

Simultaneously occurring hydrogenation and dehydrogenation have been conducted in the presence of nickel as catalyst; thus Belopol'skii and Maksimov (8) dehydrogenated a number of primary and secondary alcohols in presence of methyl oleate and linoleate as hydrogen acceptors. With primary alcohols the dehydrogenation was found to be the faster reaction, but with secondary alcohols the velocity of the two reactions appeared to be equal. Taylor (51), also with nickel as catalyst, carried out the simultaneous dehydrogenation and hydrogenation under pressure of a mixture of primary (or secondary) alcohols and olefins to the corresponding aldehydes (or ketones) and paraffins.

Palladium has been used for the dehydrogenation of several complicated organic compounds. Hydrogenated isoquinoline was dehydrogenated to isoquinoline over palladium on asbestos (40). Dihydrocumarins were found to lose two atoms of hydrogen easily with regeneration of cumarin (47) over palladium sponge. Späth and Galinovsky (49) dehydrogenated cytisene over palladium asbestos at 270°C. to hydroxymethylquinoline, and α-piperidones (48) to the corresponding α-pyridones. Doree and Petrow (19) used palladium on charcoal at 330 to 360°C. to dehydrogenate lanosterol.

Selenium has been used for the dehydrogenation of a number of oxyorganic compounds; Ruzicka (44) dehydrogenated hydroaromatic ketones and found that the formation of phenols over this catalyst is a general phenomenon. Ruzicka *et al.* (42, 43), Drake, Haskins, and Duvall (20, 21), and Pfau and Plattner (35) used selenium in dehydrogenation of various triterpenic compounds in their work on the constitution of these types of compounds, while Diels and Stephan used it for the dehydrogenation of cholesterol and ergosterol (14).

Copper, nickel, and cobalt have proved satisfactory as catalysts for the dehydrogenation of borneol and isoborneol at 205°C. to camphor, (52, 54).

Several articles have been published on rhenium as a dehydrogenation catalyst. Ethyl, propyl, and butyl alcohols were dehydrogenated (3, 36, 37, 38, 39) over this catalyst, and its activity was found to be comparable to that of copper, although it appears that rhenium reaches its maximum activity at higher temperature than copper.

Cerium oxide was proved to be also an active catalyst for the dehydrogenation of ethyl alcohol (2).

Charcoal (34) is claimed to be a dehydrogenation catalyst and has been proposed for the dehydrogenation of isopropyl alcohol to acetone.

Rivkin *et al.* (41, 46) investigated the activity of a zinc oxide catalyst alone and with 5 per cent MgO or Al_2O_3. Over such a catalyst, butyl alcohol gave, at 450°C., 50 per cent aldehyde.

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CHAPTER IX

DEHYDROGENATION OF HYDROCARBONS

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GENERAL

The large number of publications and patents on dehydrogenation of saturated and unsaturated aliphatic and cyclic hydrocarbons which have appeared during the last two years indicate that the rapidly growing commercial importance of dehydrogenation processes is by no means restricted to oxyorgano compounds which were dealt with in the preceding section.

General articles (17, 30) on catalytic reactions give only meager information on progress in this field, but van Alphen's (2) review of the new synthetic methods of organic chemistry contains a short section on this subject, with pertinent references to some recent work. Diels (13) points out the possibilities of dehydrogenation, specifically with a selenium catalyst, as a tool in the development of organic chemistry. Taylor (48) in giving a brief summary on progress made in industrial contact catalysis states that it had been possible to demonstrate the catalytic activation of specific molecular bonds with the aid of the isotope deuterium, a statement which seems of particular interest in connection with the mechanism of dehydrogenation.

With respect to the theoretical aspects of the problem of dehydrogenation, two of Balandin's articles are of interest. In one (4) Balandin's multiplet theory is discussed in the light of new experimental evidence and with reference to the results of other workers which tend to support this theory as applied both to the chemical and physical aspects of catalysis. In the other paper (5) on molecular orientation and catalysis, Balandin and Brussov propose the division of dehydrogenation catalysts into two classes, according to the orientation of the reacting molecules on the catalyst surface. On the basis of this classification, it is contended that Pt, Pd, Ni, and other metals which crystallize in the hexagonal or cubic system catalyze the dehydrogenation specifically of six-membered rings into aromatics at about 300°C. The flat sextet-type orientation is assumed in this case. The catalysts of the other group, which includes the oxides of Cr, Mo, Zn, and Ti, effect dehydrogenation at about 450°C. and are active also for the dehydrogenation of cyclic hydrocarbons other than those with six-membered rings. The edgewise adsorption of the rings in doublet orientation is assumed in this second case. This strained attempt to defend the multiplet theory against serious objections originally raised by Lazier and Vaughen (31), who first found that cyclohexane could be dehydrogenated over chromium oxide, undoubtedly weakens the multiplet theory* unless chromium oxide gel catalysts have favorable atomic arrangements different from that of Cr_2O_3.

Beeck (7) has found that, while a larger amount of water inhibits dehydrogenation of paraffins, enough water to maintain a monomolecular adsorption layer seems necessary on a Pt-carbon catalyst surface to obtain any reaction at all. This result was obtained by a molecular beam method which made possible the complete elimination of homogeneous reactions.

Kassel (27) calculated on purely theoretical basis the equilibrium constants of the dehydrogenation reaction of several hydrocarbons of lower molecular weight; no great accuracy was claimed and only a fair agreement with available experimental data was obtained.

DEHYDROGENATION OF SPECIFIC CLASSES OF HYDROCARBONS

Dehydrogenation of Paraffins

Information on progress in the field of the dehydrogenation of paraffinic hydrocarbons to the corresponding olefins is mainly contained in the patent literature. In two patents, a porous activated Al_2O_3 catalyst has been proposed (40, 41) for the dehydrogenation of lower paraffins to olefins in the vapor phase at 500 to 800°C., using contact times sufficiently short that cracking is substantially avoided. Several modifications of this catalyst have since been suggested: alumina catalysts, for example, have been modified by the addition of Cr_2O_3 (42, 53). Improved activity and longer life are said to result if this catalyst is prepared by precipitating the hydroxides of chromium and aluminum together so as to obtain a mixed vitreous gel catalyst (18, 19). It is claimed that this catalyst may be improved further by the addition of small amounts of thallium oxide.

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* Added after completion of manuscript: H. S. Taylor [*J. Am. Chem. Soc.*, **60**, 627 (1938)] examined the dehydrogenation reactions in question from the standpoint of equilibrium, using the newest heat data. He concluded that dehydrogenation of cyclopentanes and cycloheptanes at 300°C. is thermodynamically unfavorable as compared to the dehydrogenation of cyclohexane, and that Balandin's theory is not necessary to explain why cyclopentanes and cycloheptanes are not dehydrogenated.

The activity of the Al_2O_3 catalyst can be maintained by introducing, with the feed, controlled amounts of water, not more than 3 per cent (volume) hydrogen sulfide, etc. (8).

Granulated activated charcoal also may act as a dehydrogenation catalyst for paraffinic hydrocarbons such as isobutane in the vapor phase at about 500 to 600°C. An ultimate yield of 75 per cent isobutylene is claimed (45) which is considerably higher than could be obtained by direct pyrolysis.

Dreyfus (14) suggested dehydrogenation of paraffinic hydrocarbons of lower molecular weight by passage at 350 to 900°C., under pressure, through a liquid or semiliquid composition containing more than 80 per cent carbon in a finely divided form.

For the dehydrogenation of paraffinic hydrocarbons of higher molecular weight, such as paraffin wax, molybdenum oxide on carbon was recommended along with other elements of the fifth and eighth groups of the periodic system (43). The dehydrogenation is carried out at 200 to 450°C. and under 10 to 50 atm. pressure in such a manner that the olefins formed condense to a lubricating oil. It may be mentioned that from the same raw material, dehydrogenation is accomplished and olefins are obtained by chlorinating paraffin wax at 130 to 210°F. and decomposing the resulting higher alkyl chlorides at 300 to 550°F. (20).

Using chromic oxide alone as catalyst in connection with paraffinic hydrocarbons, Moldavskii and Kamusher (36) observed cyclization as a reaction secondary to dehydrogenation. Thus octane gave at 460°C. *o*-xylene, and heptane at 470°C., toluene. Nickel chromate, molybdenum sulfide, oxides of Zn, Al, Th, U, were tried as catalyst for this dehydrogenation-cyclization reaction, but only MoS_2 gave results comparable to those obtained with Cr_2O_3. Another group of catalysts was investigated by Yur'ev and Pavlov (58). They tested the isomerizing action of Pt on charcoal, Ni on zinc oxide, and Ni on aluminum oxide at 310°C. on octane. Since the smallest degree of isomerization occurred with Ni on aluminum oxide, it was concluded that this catalyst is preferable for dehydrogenation.

With nickel catalysts, at least at higher reaction temperatures, carbon formation is likely to accompany the dehydrogenation. To avoid this it was suggested (55) that the dehydrogenation be carried out in presence of steam at 600 to 900°C., in a chromium-steel reaction tube which contains less than 2 per cent Ni. Such steel tubes may be shrunk into a heat-resisting, nickel-chromium iron tube.

To effect dehydrogenation in the paraffinic side chain of an aromatic compound, cerium oxide was suggested (21) as catalyst and above 600°C. good yields of styrene were obtained from ethylbenzene. For the same purpose, a mixture of 10 per cent ZnO and 90 per cent Al_2O_3 was found to be satisfactory at 660 to 670°C. (59).

Dehydrogenation of Olefins

The dehydrogenation of olefins to diolefins has been investigated by Yakubchik (57) in the presence of several materials which could be regarded as catalyst for this reaction. Experiments were carried out with β-butylene over magnesium oxide, copper, copper wool, glossy carbon precipitated on unglazed porcelain, Lebedew catalyst, Glukhov clay, Glukhov clay and 1 per cent sodium nitrate, reduced Cu powder, and pumice stone. Over such catalysts and in the temperature range 500 to 760°C., the maximum yield of butadiene-1, 3 was 22 per cent, without recycling, and 78 per cent, with recycling. Batalin *et al.* (6) found that the formation of butadiene from isobutylene is a pyrogenic process and the dehydrogenation depends only to a small extent upon the action of. the glossy carbon. In a copper tube at 700°C. without any catalyst, an 18 per cent yield of butadiene was obtained. Chromic oxide was used as a catalyst in a flow system to determine the equilibrium dehydrogenation of butylene to butadiene (11).

A recent patent suggests the use of Florida earth, fuller's earth, and similar materials after a treatment with water, dilute caustic, organic compounds, ammonia, etc., as carriers for the usual catalyst to be used in the dehydrogenation of unsaturated hydrocarbons (23). Colloidal or quasi-colloïdal sodium has been proposed for the dehydrogenation of unsaturated constituents of lubricating oil (54). The highly unsaturated compounds obtained after the dehydrogenation form a solid sludge, leaving behind an improved lubricating oil.

Dehydrogenation of Cyclic Compounds

Much work has been done on the catalytic dehydrogenation of cyclic compounds with and without side chains. MoS_2, WS_2, CoS, CoS + MoS_2, as such or precipitated on activated carbon or silica, have been tested for the dehydrogenation of cyclohexane at 410 to 440°C. (38). Of these only MoS_2 was found to be stable enough and gave 9–11 per cent conversion to benzene. The dehydrogenation of cyclohexane was investigated also with ZnO, TiO_2, MoO_2, MoS_2 as catalysts (37); further, with iron coated with carbon from the pyrolysis of hydrocarbons and with wood carbon (35).

Taylor and Joris (49) found that a catalyst prepared by co-precipitating 1 part $Cu(OH)_2$ and 4 parts $Mg(OH)_2$ is active for both hydrogenation and dehydrogenation; cyclohexane could be converted into benzene at 330 to 460°C. without side reaction. This copper-magnesium oxide catalyst was found to be less active than nickel for breaking carbon-carbon bonds. An active dehydrogenation catalyst suitable for converting hydroaromatic compounds to aromatics was obtained also by precipitating copper and zinc from an ammoniacal solution (3).

The Adkins-Connor type of copper-chromium oxide catalyst was found to be satisfactory for dehydrogenating cyclohexane to benzene (26). Al_2O_3, $Al_2O_3 + ZnCl_2$, and $Al_2O_3 + H_3PO_4$ were less effective, and furthermore formed gaseous reaction products and produced isomerization.

The catalytic dehydrogenation of hydronaphthalenes with and without angular methyl groups was studied by Linstead *et al.* (34) over Pt and Pd catalysts, in both liquid and vapor phase. Karzhev *et al.* (25) investigated $Cr_2O_3 + CuO$ activated with BaO, $Cr + H_3PO_4$, $Cr + Mo_2O_3$, and $Cu + Cr + H_3PO_4$ as dehydrogenation catalysts for tetraline and decaline. Chromium-molybdenum oxide and copper-chromium-phosphoric acid combinations were found to be the most effective.

According to Haberland (22), sulfur itself may be regarded as dehydrogenation catalyst; tetralin derivatives were dehydrogenated to naphthalene almost quantitatively on fusion with sulfur at 200 to 230°C.

Ipatieff and Komarewsky (24) observed that over a $Ni-Al_2O_3$ catalyst at 350°C., not only are cyclohexane and ethylcyclohexane dehydrogenated but toluene also is obtained by respective alkylation and dealkylation of the dehydrogenation products. The alkylation reaction is explained by the formation of an AlO(OR) type of esters as intermediates. No alkylation was observed when Pt on carbon or Pd on asbestos was used as catalyst.

The dehydrogenation of the pentamethylene ring does not take place as easily as that of the hexamethylene ring. Tarasova (47) found that alkylcyclopentanes do not dehydrogenate in a stream of H_2 or CO_2 at 300°C. over Pt-charcoal. Denissenko (12) found that cyclohexylcyclopentylethane dehydrogenates over platinum on charcoal at 290°C. to phenylcyclopentylethane, i.e., complete dehydrogenation of the C_6 ring, and no dehydrogenation of the C_5 ring. A similar observation was made with unsubstituted cyclohexylcyclopentane by Khromov (29); with Pt-charcoal as catalyst, at 310°C., however, the pentamethylene ring undergoes a cleavage and, if 2 atoms of hydrogen are added, forms an alkyl benzene as final reaction product.

With the same catalyst in presence of hydrogen the lower alkyl-substituted homologs of cyclopentane gave paraffins (61) while the higher ones such as butyl, secondary butyl, and isoamyl gave paraffins and about 10 per cent aromatics (28). Kasansky and Plate (28) explain aromatic formation with the higher alkyl derivatives by cyclization of the alkyl chains onto the original ring to form the aromatic nucleus.

The resistance of the C_5 ring to dehydrogenation was also reported by Nenitzescu and Cioranescu (39). Methylcyclopentane remained unchanged even at 310 to 350°C. when passed over 18 per cent Pt-charcoal. Dehydrogenation of C_7 and C_8 rings in presence of Se as catalyst at around 390 to 440°C. proceeds with a ring contraction. Ruzicka and Seidel (46) have found that cycloheptane gave toluene and cyclooctane gave *p*-xylene.

The specific behavior of the C_5 ring is the basis of a patent (56) for the production of chrysene from indene by dehydrogenation at 500 to 850°C. in presence of carbon on MgO or ZnO as catalyst.

The dehydrogenation of cyclohexylallene, allylcyclohexene and cyclohexylallylene over a Pt-carbon catalyst at 200 to 205°C. yields a mixture of aromatic and hydroaromatic compounds with saturated side chains formed possibly according to the general equation (33)

$$3C_nH_{2n-4} \longrightarrow C_nH_{2n} + 2C_nH_{2n-6}$$

Similar reactions take place when trans Δ^2 octalin is passed over Pt-charcoal at 200 to 205°C., yielding naphthalene and trans-decalin (52), or when carane is passed at 160 to 180°C. over Pt-asbestos, giving menthane and cymene (32).

Dehydrogenation of Hydrocarbon Mixtures

Dehydrogenation as a means of obtaining improved motor fuel directly or indirectly from petroleum gases is gaining in importance. Dunstan and Howes (15) deal with the catalytic and non-catalytic dehydrogenation of individual hydrocarbons and mixtures at some length. Zelinskii and Shuikin (60) found that Pt on charcoal would dehydrogenate narrow fractions of Surakhanskii and Balakhanskii gasoline at 300°C., forming a product which contained 65 to 58 per cent aromatics. Nickel on Al_2O_3 gave above 300°C. a product containing 84 per cent aromatics, possibly as a result of secondary reactions (aromatization). Tropsch (51) suggests the use of an alumina containing 5 to 10 per cent water in the temperature range 450 to 600°C. as a catalyst for increasing the antidetonating character of gasoline by dehydrogenation. Towne (50) prefers natural bauxite free of iron, impregnated with Ni for dehydrogenating motor fuel of low antiknock value at 500 to 700°C., at contact times sufficiently short that no appreciable amount of low boiling product forms.

An improved antiknock fuel resulted also on dehydrogenating a gasoline fraction at 550°C. in presence of a MoS_2 catalyst at 180 to 220 atm.

pressure (9). Karzhev *et al.* (26) obtained a product containing 80 per cent aromatics after passing an aviation gasoline (boiling range 70 to 110°C.) over a Cr—Cu catalyst. Pier *et al.* (44) suggest for the dehydrogenation of a cracked product of middle oil a catalyst consisting of 80 per cent tungstic acid and 20 per cent magnesium oxide or other oxides and sulfides of the elements in the fourth and eighth groups of the periodic system.

Preparation of Dehydrogenation Catalysts

Methods of preparing dehydrogenation catalysts have also been investigated. Faucounau (16) found that a very active hydrogenation and dehydrogenation catalyst may be prepared from a copper-aluminum alloy by reacting it with 30 per cent NaOH. A similar catalyst can be prepared also from a cobalt-aluminum alloy, and the finely divided cobalt is more active, and active at a lower temperature, than copper. Cooper *et al.* (10) prepared a copper-chromic oxide catalyst precipitated on Italian acid-washed pumice.

The thermal stability of a chromium-tin dehydrogenation catalyst was raised by the addition of 3 per cent $SbCl_3$ (1), and the product was more satisfactory than one obtained when BaO or Al_2O_3 was substituted for the $SbCl_3$.

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CHAPTER X

HYDROGENATION OF HYDROCARBONS

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GENERAL AND THEORETICAL

The hydrogenation of hydrocarbons, especially of the simpler olefins, has long been an attractive field for study of catalysis in a broader sense. General discussions on this subject may be found in several new books reviewed elsewhere in this report. Apart from these and from such review articles as deal more specifically with the hydrogenation of oil and coal (Chapter VII) no review articles on hydrogenation of hydrocarbons were published during the last two years.

Original contributions of a theoretical nature are numerous, however, and though the important ones are dealt with in the theoretical section of this report, a short mention of these papers seems warranted not only for a completeness of reference but also because of their definite stimulating effect on applied research. The kinetics of the catalytic hydrogenation of ethylene have continued to attract wide attention. Schwab and Zorn (30) work with Ni-skeleton contacts between 0 and 180°C. and with pressure from 50 to 250 mm. Hg. Through extremely careful kinetic considerations, based on reaction velocity measurements which strictly follow the Langmuir-Hinshelwood theory, they arrive at the *true* activation energy of the hydrogenation and find 18.7 kcal. ± 1 kcal. Toyama (36) investigates the kinetics of this reaction on an ordinary Ni catalyst between 0 and −78°C. and finds that the activation energy remains substantially constant at 6 kcal. over this range, which allows the conclusion that the same hydrogenation mechanism must hold from 0 to −78°C. Tucholski and Rideal (38), Wheeler and Pease (39), and Klar (24) compare rates of catalytic hydrogenation of ethylene with heavy and light hydrogen with the result generally that at lower temperatures (about 0 to 100°C.) the reaction with light hydrogen is faster while at higher temperatures the reverse is true. This is in agreement with theoretical expectations involving the zero-point energies of the two hydrogen molecules, and also with direct measurements of the activated adsorption of these two molecules. Russell and Ghering (29) study the poisoning of Cu catalysts by oxygen and N_2O

together with the heat of adsorption of O_2. In support of the active-center theory they conclude that only a small portion of the catalytic surface is active. Dobuichin and Frost (5) and Gel'bart and Dobuichin (16) study the hydrogenation of ethylene and butylene over palladium. They find that pre-adsorbed hydrogen at −78°C. hydrogenates faster than gaseous hydrogen merely in the presence of Pd. The hydrogenation is also more rapid than the rate of desorption observed. Oxygen is found to have no effect on the reaction, while a mixture of O_2 and CH_4 promotes the reaction, possibly through creation of new active centers which also could be produced by alternative oxidation and reduction of the Pd surface. Fischer and Knorr (14) study the relative hydrogenation of acetylene and ethylene by Pd-sorbed hydrogen. In the case of acetylene, the reaction rate is independent of the C_2H_2 pressure, while with C_2H_4 the rate is approximately proportional to the pressure. This shows that acetylene is more strongly absorbed than ethylene. Hedvall and Hedin (18) find a discontinuity of the rate of hydrogenation of ethylene on nickel at the Curie Point. It seems impossible at present to explain this phenomenon satisfactorily.

Two papers seem to deserve particular attention because they present a considerable advance in our picture of the hydrogenation process. From a study of the reaction of deuterium with ethylene, A. Farkas and L. Farkas (13) show that on a catalytic surface a hydrogen molecule can react with an olefin molecule in two ways: (*a*) the hydrogen may add to the double bond of the olefin, yielding a saturated compound; and (*b*) an exchange reaction may take place between the hydrogen atoms of the ethylene molecule and the atoms of the heavy hydrogen molecule. The first reaction has the lower activation energy and, therefore, predominates at low temperatures. Further, by showing that the rate of hydrogenation of ethylene is greater than the rate of the orthohydrogen-parahydrogen conversion (both reactions proceeding simultaneously on the same catalytic surface), they conclude that the complete dissociation of hydrogen into atoms is unnecessary for catalytic hydrogenation. This subject has been discussed in previous reports of this committee.

A theoretical treatment of the catalytic hydrogenation has been indicated by Sherman, Sun, and Eyring (31) and, using their methods as a basis, Okamoto, Horiuti, and Hirota (27) have calculated activation energies of the hydrogen adsorption for pairs of adjacent metal atoms on the three crystal planes in the unit cell of nickel (cubic face centered). In finding that the activation energy is lowest for adjacent nickel atoms with the distance 3.32 Å, reactions involving hydrogen adsorption should take place most easily on the 110 plane. (The denser arrangement of the metal atoms in the 100 plane, which also contains this distance, will increase the activation energy to such a degree that this plane becomes relatively unimportant.)

Experimental work in progress at the Emeryville Laboratories of the Shell Development Company* has shown that nickel and various other metal films are increasingly more catalytically active the more completely they are oriented with certain crystal planes parallel to the backing.

HYDROGENATION OF PARTICULAR HYDROCARBONS

Olefins

Of special interest here is the synthesis of especially desirable hydrocarbon structures for use as non-detonating fuels in internal-combustion engines. The synthesis has been developed during the last few years into an important technical process involving hydrogenation. One of the octane isomers (2,2,4-trimethylpentane), which up to only a few years ago served merely as a standard for comparing all gasoline motor fuels, because of its high antiknock properties was used in increasing quantities for blending commercial fuels and in the highest grades of aviation fuel. The early process involved primarily polymerization of isobutylene to diisobutylene by a cold sulfuric acid catalyst, with subsequent hydrogenation yielding almost exclusively 2,2,4-trimethylpentane. With increasing demands for " high octane " fuels, however, processes have been developed for the interpolymerization of isobutylene with one or the other straight-chain butylenes in the presence of hot sulfuric acid or phosphoric acid catalysts. Upon hydrogenation of their polymerization products, these processes yield a mixture of isooctanes of an antiknock value very close to the standard 2,2,4-trimethylpentane.

A basic patent for the combined stages of the process for the polymerization of isobutylene and the manufacture of saturated higher octane fuels by the above methods from petroleum was granted to Deanesly, Williams, and Steck (2).

For the hydrogenation process itself a number of patents have been

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* Note added after completion of manuscript: In the meantime this work has been presented at the Annual Meeting of the American Physical Society, December, 1938, in Washington, D. C. See Bulletin of the American Physical Society, Vol. 13, No. 7, paper 57, "Catalytic Activity and Crystal Orientation of Metal Film," by Otto Beeck, A. Wheeler, and A. E. Smith, and paper 58, " Preparation and Structure of Oriented Metal Films," by A. E. Smith and Otto Beeck. These papers are discussed in more detail by H. S. Taylor in his contribution on active centers. (See Chapter IV.)

granted in the last two years, all of them either to the Shell Group or to International Hydrogenation Patent Co., Ltd. (34, 19, 35, 20). The catalyst most often referred to is nickel, sometimes promoted by a metal of the titanium subgroup. Hydrogenation is carried out at 100 to 300°C. It is perhaps surprising to find nickel, known to be particularly sensitive to poisoning by sulfur compounds, in such prominence. Its use was possible only after elimination of catalytic poisons from the raw material. M. D. Taylor (34) showed that a preliminary chamber containing catalyst introduced before the catalytic chamber proper will serve as a "guard tube" for absorption of catalytic poison even after complete loss of its own catalytic activity. He showed furthermore that poisoned catalysts in the liquid-phase process could be regenerated by flushing with pure reactants. M. D. Taylor (35) also developed a process for the hydrogenation of diisobutylene by reaction with a secondary alcohol, ketone and isooctane being formed by hydrogen exchange between the olefin and the alcohol.

Ipatieff and Komarewsky (21) have tried the simultaneous polymerization and hydrogenation of isobutylene in the presence of solid phosphoric acid-nickel oxide-iron catalyst at high pressure. Yields of only about 50 per cent are reported.

Two other papers need be mentioned in this group, mainly for completeness of reference. Dupont (6) in a paper on selective properties of Raney nickel found this material superior to platinum oxide for the selective hydrogenation of substituted ethylenes, of which the mono substitute is most easily reacted. Similar steric hindrance effects are reported by Lagerev and Babcock (26), who investigated the relative rates of hydrogenation of various hexenes.

Acetylenic Compounds and Dienes

Apparently some interest still exists in the partial hydrogenation of acetylene to ethylene. Dupont (6) investigated the selective influence of Raney nickel on acetylenic compounds and was able to establish that the hydrogenation takes place in two definite steps, yielding ethylenic compounds first, which could be isolated. But under his particular experimental conditions, his final products were saturated. Ackermann (1) reports a 71 per cent conversion to ethylene, with 1 : 10 mixtures of acetylene to hydrogen over a 1 : 1 Ni-Kieselguhr catalyst at 100°C. E. I. du Pont de Nemours and Company were granted a patent (9) on partial hydrogenation of straight-chain acetylene polymers up to C_8H_8 or their mixtures over a nickel catalyst to give in the case of C_4H_4, for instance, an oil product with a boiling range between 5 and 10°C., consisting of a mixture of butane, butylene, butadiene, and ethylacetylene.

Interesting from the standpoint of selectivity of the catalyst is a paper by Zal'kind and Smagina (40), who report that 2,5-dimethyl-1,5-hexadiene-2-ine is hydrogenated to a saturated hydrocarbon on platinum but that only three hydrogen molecules are added when palladium is used.

Kwal (25) reports the simultaneous polymerization and hydrogenation of acetylene to a gasoline-like product on a mixture of active charcoal and cuprous oxide.

Benzene

Little now is to be reported on the hydrogenation of benzene and other aromatics. Foresti (15) investigated the catalytic hydrogenation of benzene in liquid phase over platinum with respect to the influence of the pH of the solution. An acid solution was found to promote this reaction while alkaline solution caused complete inactivity. The effects are reversible. The authors attribute the effect to the electrical double layer as affecting the potential of the metal and covering preferentially the active zones by the cations.

Tsutsumi (37) reports the promotion of nickel by various oxides for the hydrogenation of benzene. A mixture of nickel with 10 per cent Al_2O_3 was found most effective.

Other Aromatics

Russian investigators (12, 11, 3, 23, 32, 28, 22) (see also German and U. S. patents (33, 17)), have shown considerable interest in the destructive hydrogenation of aromatics like naphthalene, anthracene, phenanthrene, xylene, and others. Catalysts employed in these experiments show a wide variety of metals and metal oxides and their combinations. Of some particular interest perhaps is the hydrogenation of naphthalene reported in a German patent (4) in which rupture of the carbon skeleton is avoided by working at a temperature not above 460°C. and under pressures of about 1000 atm. Mo and Mo—W, with an addition of 1 to 5 per cent of H_2S or an agent yielding H_2S, are used as catalyst. Noteworthy also is the hydrogenation of phenanthrene over Cu—Cr oxide reported by Durland and Adkins (10). This catalyst was formerly thought inactive for the hydrogenation of aromatics.

Dupont and Desreux (7, 8) show chemically and by Raman spectra that products and mechanism of the hydrogenation of myrcene (a terpene of the formula $C_{10}H_{16}$ = 2-methyl-6-methylene-2,7-octadiene) depend largely on the type of catalyst used.

Catalysts for Hydrogenation

The literature, especially the patent literature, describing hydrogenation catalysts and their use and preparation is very extensive, and it has seemed to us better to condense it in tabular form. The table contains a list of the most important catalysts, but references to original work have been selected primarily from publications during the period under review; however, many older references are also included. For further convenience, the references to the table have been separated from the references to the preceding text. The table references follow the table.

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TABLE OF HYDROGENATION CATALYSTS

(THEIR PREPARATION AND PROPERTIES)

Group in Periodic Table	Catalytic Substance	Preparation	Activity	Uses and Remarks
VIII (Transition Group)	Ni	(*a*) Reduction of oxide, nitrate, etc., usually impregnated on a supporting material. (*b*) Action of caustic on Ni—Al alloy (Raney nickel). (*c*) Decomposition of Ni-carbonyl or Ni-Formate (29). (*d*) Electrolytically deposited, followed by anodic oxidation, and finally reduction by H_2. (*e*) Activation of Ni and related metals by HF and F_2 (3).	Great activity, even below 0°C. Destructive at high temperatures but excellent for low temperature hydrogenations (16).	Many uses; see reference (16). Recent use in hydrogenation of octylenes to octanes for aviation fuels. Quite sensitive to poisons, especially sulfur compounds (16).
	Fe	Similar to nickel.	Great.	Considerable commercial use, especially in Fischer-Tropsch process and ammonia synthesis.
	Co	Similar to nickel.	Great.	Small use in commercial hydrogenations. Sometimes used in mixtures with Ni, Cu, etc., for high-pressure, destructive hydrogenations (30).
	Pt, Pd	(*a*) Reduction of $PtCl_4$ by formaldehyde. (*b*) Preparation as colloids (22*a*). (*c*) Preparation by igniting chloroplatinates.	Great.	Technical use for hydrogenation is limited by their great cost. Pt and Pd have selective properties (22*b*). Pd is stable toward poisoning by O_2 (17).

	NiO, FeO, O, PtO	(20)	Great for high pressure hydrogenations at moderate temperatures.	General hydrogenation catalysts for high-pressure work, (20).	It is by no means certain that the active agent in these catalysts is not metallic Ni or Co, formed by the reduction of these compounds.
		Usually mixed with other metals or their oxides.	High-pressure hydrogenation catalysts.	Hydrogenation of oils and petroleum derivatives (9).	
	O_2, $O_2)_2$, des of	(27)		Nickel carbonate used in hydrogenation of vegetable oils, etc. (27).	
		(37)	Active at high H_2 pressure, 300°C.	Hydrogenation of aromatics, unsaturated petroleum derivatives, etc.	
Cu, Ag	Salts of Na, K	Used in small quantities as promoters.		Ammonia and methanol synthesis.	
	Alkali metal hydrocarbides	(34)	(34)	(34)	
	Cu	(*a*) Reduction of oxide. (*b*) Action of 30 per cent NaOH solution on Cu–Al alloy (cf. Raney nickel). (*c*) Precipitation from solution by other metals.	Action is milder than nickel, but very active Cu catalysts can be prepared by reduction of the oxide at low temperature.	Used in methanol synthesis and water-gas reaction (16*b*). Often mixed with other metals and oxides, especially Ni and Cr_2O_3 (2).	
	Cu	(16*b*)	Small.	Mixed with other oxides in the hydrogenation of mineral oils and methanol synthesis (16*b*, 20*b*).	
	$Cu-Cr_2O_3$	(See chromium.)			
	Ag	Reduction of the oxide or nitrate.	Small (26).	Very small commercial use (8).	
II Ca, Mg, Zn, Cd	Ca	(25)	Small.	No commercial use.	
	Mg, Zn, Cd		Small.	Some use in destructive hydrogenation of coal and oil (8). Cd is used as a promoter in methanol synthesis (13).	

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CHAPTER XI

HYDROGENATION OF THE OXIDES OF CARBON*

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Aside from the important economic and commercial considerations involved (50), hydrogenation of the oxides of carbon is a subject peculiarly close to the interests of the catalytic chemist because of the multiplicity of products obtainable from a single set of reactant gases, and the importance of the catalyst in determining the outcome of the process. In certain cases it is possible by means of a judicious selection of the catalyst to exercise a considerable degree of control over the course of the reaction without necessarily varying the conditions of temperature, pressure, space velocity, or other physical factors. In other instances equilibrium considerations may require adjustment to a more favorable pressure. Finally, the activity characteristics of a specific catalyst may dictate the selection of a more appropriate temperature. Nevertheless, it is probably safe to say that catalyst specificity is the most important directive influence. For example, it had long been known as a result of the pioneering work of Sabatier (75) that finely divided nickel will catalyze the hydrogenation of carbon monoxide to methane, but it was not until after the discovery and development of specific non-methanating catalysts that the synthesis of methanol and other oxygenated compounds from water gas could be considered a practical reality. The degree to which success has been achieved in this direction by the use of copper and zinc oxide catalysts has been reviewed by Frolich (31).

The catalytic hydrogenation of carbon dioxide is a subject of secondary importance in this discussion for the reason that the first step in the reduction is conversion to carbon monoxide and water vapor, a reaction readily identified as the reversal of the familiar and important water-gas reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

This reaction proceeds rapidly in the presence of a wide variety of contact agents and under many of the conditions suitable for a further

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hydrogenation of carbon monoxide. If we limit the discussion, therefore, to the hydrogenation of carbon monoxide, the more important reactions taking place may be listed as follows:

$$CO + H_2 \rightleftharpoons HCHO$$

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

$$(n)CO + (2n)H_2 \rightleftharpoons C_nH_{2n+1}OH + (n-1)H_2O$$

$$(n)CO + (2n+1)H_2 \rightleftharpoons C_nH_{2n+2} + (n)H_2O$$

The intriguing possibility of synthesizing formaldehyde directly from carbon monoxide and hydrogen has attracted the attention of investigators for a much longer time than the more successful direct synthesis of methanol. The idea appears to have arisen from the classical investigations of Jahn in 1889 (44). More recent efforts reported in the literature have been summarized by Mayer (58). Although Jaeger (43) has patented the use of certain catalysts, it seems evident that the process has not achieved commercial success. After carefully considering the possible causes for failure, Newton and Dodge (67) made a direct attack on the problem by employing a copper-zinc catalyst for determining experimentally the equilibria involved in the system: carbon monoxide-hydrogen-formaldehyde-methanol. These authors concluded that, even if it were possible to find a specific catalyst that would bring about the synthesis of formaldehyde to the exclusion of its hydrogenation to methanol at 200°C. and 300 atm. pressure, the equilibrium conversion to formaldehyde would be only 0.35 per cent. If equilibrium were simultaneously established for both the formaldehyde and the methanol synthesis reactions at 350°C. and 300 atm., the limiting conversion to formaldehyde would be about 0.10 per cent. These results are in general agreement with conversions of 0.5 to 1.2 per cent reported by Bocharova and Dolgov (9), with water gas over a magnesia-manganese oxide catalyst at 400°C. and 150 atm. pressure.

In contrast to the formaldehyde situation, the equilibrium in methanol synthesis is sufficiently favorable to permit attractive yields under conditions that can be realized in the high-pressure plant. For example, Larson (52) states that at 200°C. and 10 atm. the equilibrium conversion is 28 per cent. Since no practical catalyst is active at this low temperature, higher operating temperatures and pressures are used in commercial practice, i.e., 350 to 400°C. and 200 to 700 atm. Newton and Dodge (66) have redetermined the value of the equilibrium constant for several temperatures in the synthesis range, and Natta and Pastonesi (65) have discussed the kinetics of the reaction. Fracasso (29) has compared the values for K cited in the literature and has constructed a nomograph of the equilibrium conditions.

The experience in high-pressure technique gained in connection with ammonia synthesis has been of material assistance in the early development of carbon monoxide hydrogenations. Accordingly, the technology of methanol synthesis has matured rapidly since the small beginnings made only fifteen years ago. Economy in gas production and purification has been largely responsible for a pronounced tendency to associate the manufacture of synthetic methanol with that of synthetic ammonia and to concentrate the operation in large manufacturing units. General accounts of the present status of methanol synthesis have appeared in three recently published texts (18, 38, 39), and the fundamental principles have been set forth in a review paper by Pier (71). The process steps as conducted in two of the world's largest plants have been outlined by Bosch (10) and Wardenburg (83). The development and present status of the synthetic methanol industry in Japan have been discussed recently by Oshima (68). From the catalytic point of view the major problems of the industry are concerned with (*a*) reducing the extent of side reactions responsible for raw material losses and (*b*) protecting the catalyst against adverse factors affecting its useful life (52).

Larson (52) points out that, although partially reduced copper oxide is an active catalyst at first, it rapidly becomes inactive, the loss in activity increasing with increase in temperature. The addition of copper to zinc oxide produces a definite improvement in its methanol-forming properties, but again this combination has one characteristic which limits its commercial usefulness. As the temperature is raised the catalyst begins to form methane, and in large synthesis units the almost inevitable result is a run-away temperature. Larson reports further that several oxides are active in promoting zinc oxide, but unfortunately many of these also encourage secondary reactions. $ZnO-Al_2O_3$, for example, is very active but gives a product containing a considerable amount of dimethyl ether. Chromic oxide is one of the most effective agents in improving the methanol-forming property of zinc oxide, and the combination is one of the few that confine the reaction to methanol over a wide range of temperatures. An added advantage of the $ZnO-Cr_2O_3$ type catalyst is that it is not poisoned for methanol synthesis by small amounts of sulfur compounds, and consequently gas purification is not required to the degree necessary for ammonia synthesis. Chromium oxide-promoted catalysts are conveniently prepared by precipitating the double ammonium salts of the hydrogenating metals and igniting to reduce the valence of the chromium (54). Molstad and Dodge (62), in a comprehensive study of $ZnO-Cr_2O_3$ compositions, found that a catalyst thus prepared, having a Zn/Cr atomic ratio of 1, increased in activity during extended testing, the improvement being accelerated by operation at temperatures up to 100°C. above the usual temperature of maximum activity. This catalyst also produced very pure methanol, appeared to be uninjured by long use at high temperatures, and exhibited good mechanical qualities. This work is interesting in view of earlier patent claims (61). In fact, patents have been taken out on the claim that a molecular preponderance of the acidic oxide is beneficial from the standpoint of heat resistance and activity (55, 57).

Larson (52) has pointed out the lack of correlation between Sabatier's characterization of individual oxides and their performance in methanol synthesis. Frolich (31), on the other hand, in reporting on a more restricted field of catalyst testing has demonstrated good correlation between the methanol synthesis and decomposition activities of copper-zinc oxide catalysts of various compositions.

Some of the more important patents issued in the last few years deal with catalyst improvements resulting from fusing and reducing mixtures of copper oxide with other oxides (53), activating oxidic catalysts with hydrogen (5), and promoting zinc-copper catalysts with chromium oxide (13). A synthesis for methanol has been patented by Scott (78) wherein simultaneous absorption of hydrogen and carbon monoxide is obtained under pressure in an alcohol solution of a plurality of metal alcoholates. Methyl formate is formed as well as methanol under these conditions.

The addition of a small amount of an alkali metal compound to the usual methanol synthesis catalyst is still the preferred device for inducing higher alcohol formation, although somewhat higher temperatures may also be advantageous (31, 52). Besides alcohols, certain amounts of esters, acids, and other oxygenated compounds are formed. Taylor (80) found that with a $Cu-MnO-CoS$ catalyst the production of ethyl alcohol is greatly increased over the amount formed in the presence of the usual alkali type of higher alcohol catalyst. The further observation was made that the higher alcohols formed by the new catalyst were for the most part of the straight-chain type rather than the branched-chain type ordinarily obtained. For higher alcohol synthesis, Natta (64) prefers to use a zinc oxide-potash catalyst prepared by impregnating calcined smithsonite with potassium acetate. If the gas contains an excess of carbon monoxide, he reports, the alcohols contain a high percentage of ketones, aldehydes, and acids. It is, however, difficult to understand how ketones and aldehydes in more than negligible amounts can survive hydrogenation under the conditions of synthesis. Sartori (76) has reported the results of adsorption measurements on Natta's zinc oxide (ex-smithsonite) catalyst.

The hydrogenation of carbon monoxide to methane, although historically the oldest reduction of all (75), has not yet achieved technical importance comparable with several of the other reduction processes. There are, however, three potential uses for the process, namely: (*a*) the detoxification of manufactured gas for domestic use; (*b*) enhancement of the calorific value of water gas for fuel purposes; and (*c*) the purification of hydrogen for use in certain hydrogenation processes employing catalysts susceptible to carbon monoxide poisoning. Sabatier is reported (40) to have devoted a great deal of attention to the detoxification problem. Aside from the expense involved (60), technical difficulties have been experienced with sulfur poisoning and choking of the catalyst pores with carbon resulting from the parasitic reaction:

$$2CO \longrightarrow C + CO_2$$

Nickel and iron catalysts are active in the formation of methane at atmospheric pressure, but carbon dioxide and carbon are also formed in varying amounts, depending on the temperature and other conditions, and both catalysts are susceptible to sulfur poisoning. Conditions tending to favor the formation of methane rather than hydrocarbons of higher molecular weight are (*a*) high temperatures and (*b*) a high ratio of hydrogen to carbon monoxide in the reacting gases. Temperatures in the range of 450 to 600°C., however, tend to promote carbon deposition and carbon dioxide formation. Water gas as usually prepared is, of course, too deficient in hydrogen content to allow for complete conversion of the carbon monoxide to methane. Kemmer (46) has therefore favored a two-step process involving a preliminary conversion of a part of the carbon monoxide to dioxide by the water-gas reaction. The relative merits of the one-stage and two-stage processes have been the subject of considerable discussion. The single-stage process has been operated on a large scale in Europe in connection with detoxifying gas for the town of Hameln (34). Mezger (60), however, is of the opinion that for Swiss conditions, at least, the cost is excessive and out of proportion to the hazard removed by the treatment.

Recent work on the methanation reaction has been directed towards attempting to solve the catalyst deterioration problem (69). Brückner and Jacobus (12) have investigated the effect of various oxide promoters for nickel at 300°C. Alumina and thoria in concentrations of

10 per cent were found best and these masses were further promoted by the addition of alkaline earths. Cobalt decreased the effectiveness of nickel, and copper extinguished it altogether. Other investigators have used alumina-nickel (45) and alumina-manganese oxide-nickel catalysts (73). Manganese oxide appears to favor carbon dioxide formation. Perhaps the most significant approach to a solution of the problem has been stimulated by the catalytic developments in coal and oil hydrogenation wherein catalysts completely tolerant to sulfur are used. Molybdenum catalysts, for example, have been reported to produce methane in the temperature range 350 to 400°C. (73), although Meyer and Horn (59) claim that temperatures of about 400°C. are required even at 100 atm. pressure. Sebastian (79) reports that good conversions of carbon monoxide to methane were obtained at atmospheric pressure over a catalyst comprising molybdenum sulfide on a silica gel support. In spite of the progress apparently being made on this problem, there is undoubtedly much room for improvement in perfecting catalysts suitable for the methanation process.

Carbon dioxide may be hydrogenated to methane (51) in one step at about 300°C. over a pure iron catalyst. If carbon monoxide is also present in the gas mixture, no reaction of the dioxide takes place until the monoxide is completely converted to methane (77). By using ruthenium powder or a mixture of ruthenium and thoria supported on asbestos, Fischer and co-workers (25) were able to reduce the temperature of methanation of carbon dioxide to 100°C. The inclusion of alkali in the catalyst induces the formation of higher hydrocarbons, as in the case of carbon monoxide over iron catalysts. An indirect method for the hydrogenation of carbon dioxide to formic acid has been disclosed by Farlow and Adkins (16). In the presence of a variety of amines and Raney nickel catalyst, reduction of carbon dioxide takes place at 80 to 100°C. and several hundred atmospheres pressure with the formation of the amine formate. At higher temperatures the amine salts are subsequently dehydrated to amides.

With proper selection of the catalyst the methane reaction of carbon monoxide and hydrogen may be modified so drastically that the principal product is a complex mixture of higher paraffin hydrocarbons originally known as “ Synthin ” but more recently given the appropriate name “ Kogasin.” Like the Bergius process, the Kogasin process provides a new method for the chemical conversion of coal to liquid products and is looked upon as a further solution to the petroleum deficiencies of certain European countries, notably Germany. It is not surprising, therefore, to find that technological progress has been very rapid, and that synthesis of paraffin hydrocarbons by this method is already an important factor in supplying the motor fuel requirements of Germany (15). Recent technical developments in this field have formed the subjects of several reviews (2, 4, 6, 7, 17, 20, 21, 22, 23, 24, 30, 37, 42, 48, 70, 74, 82), which have been ably summarized by Ellis (14). The status of this process has been outlined in somewhat lesser detail by Hilditch and Hall (41) and by Fenske (18).

Although the specificity of the catalyst plays an important part in the success of the process, there are other factors as well. These have been summed up by Friedwald (30) as follows:

1. Increase of pressure ⟶ " Synthol "(methanol, higher alcohols, and other oxygenated compounds).
2. Increase in hydrogen content ⟶ methane.
3. Decrease in hydrogen content ⟶ olefinic hydrocarbons.
4. Increase of temperature ⟶ methane and finally carbon.
5. Catalysts increase the degree of saturation of the product in the order iron, cobalt, and nickel.
6. Presence of carbon dioxide is without influence.
7. Increase of life of catalyst gives an increase of light fraction and a decrease in oil content.

For the purposes of this report we are primarily concerned with the influence of the catalyst, and the reader is referred to Ellis (14) for further details on the influence of operating conditions.* After years of investigation Fischer (21) prefers to use a thoria-promoted cobalt catalyst supported on kieselguhr that is operative in the temperature range of 180–200°C. This cobalt catalyst is less prone to form methane than is nickel, but even so the reaction temperature must be controlled within narrow limits. Kogasin catalysts are sulfur sensitive and satisfactory purification of water gas has proved to be one of the chief obstacles to commercialization on a large scale.

Despite the apparent success of the Fischer catalyst, there has been considerable activity in the search for improved catalysts, which has led in some cases to sharp differences of opinion between various investigators. Table I shows some of the recommendations for preferred catalysts that have been published in recent years.

From this table a general idea of the range of materials suggested as catalysts may be obtained. As pointed out by Fujimura (32), the mode of preparation and the physical condition of the finished catalyst are probably quite as important as the last details regarding composition. It would appear that the process calls for a combination of a poly-

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* The points enumerated above are taken from Ellis, Ref. 14, p. 1227.

merizing agent and a not-too-active catalyst of such a character that it will allow sufficient time for the methylene groups to polymerize before they can be hydrogenated completely to methane.

Although precipitation methods have been used most for compounding hydrocarbon synthesis catalysts, attention has more recently been centered on some of the novel methods developed in connection with other catalytic processes. Aicher, Myddleton, and Walker (1) have devised a clever method for granulating powdered catalysts which involves moistening with a silicate ester, shaping, and setting by hydrolyzing the ester to silicic acid with moist air. Fischer and Meyer (27) and Tsuneoka and Murata (81) have investigated the applicability of alloy skeleton catalysts to the Kogasin synthesis and believe that the higher density, and hence the greater heat conductivity, thus obtained are definitely advantageous. Nickel-aluminum and cobalt-aluminum alloys are prepared and activated by extraction of the aluminum with caustic alkali according to the method described and patented by Raney (72). Silicon has been used in place of aluminum as an alloying medium but apparently offers no outstanding advantages (81).

TABLE I

CATALYSTS RECOMMENDED FOR KOGASIN SYNTHESIS

Investigator	Reference	Catalyst
Antheaume	3	Fe—CaO, Fe—Cu
Fischer and Tropsch	28	Eighth group, preferably Co. Same plus promoting oxides.
Fujimura and Tsuneoka	33	Ni, Ni—ThO_2 Ni—Al_2O_3 Ni—Fuller's earth
Muszkat	63	Ni—ThO_2, Ni—Al_2O_3 Ni—BaO
Klyukvin and Volnov	47	Ni—ThO_2, Ni—ThO_2—Hg, Ni—MgO
Tsutsumi	82	Ni—MnO—U_2O_3—ThO_2, Ag—Co
Fischer and Koch	26	Co—ThO_2—MnO—Kieselguhr
Fujimura	32	Co—Cu—ThO_2—U_2O_3—Kieselguhr
Gillet	36	Fe with Ni, MnO, Al_2O_3, ThO_2 or Co
Ghosh and Sen	35	Fe—Cu—Ni and trace of Th or Cr
Braune	11	Fe and $CaCl_2$
Kodama and Fujimura	49	Fe—Cu—Na_2CO_3
Lefebvre and LeClerc	56	Magnetite plus KOH

Kogasin consists almost wholly of paraffin hydrocarbons. Although it is unsuitable for motor fuel unless re-formed by cracking or blended with antiknock agents, the higher fractions are eminently suited to use as Diesel fuels and lubricants. Thus Berthelot (8) points out that the Bergius coal hydrogenation process and the Fischer-Tropsch Kogasin process are really complementary rather than competitive, and it remains to be shown whether a proper balance between the two processes can provide a completely satisfactory economy in the manufacture of products otherwise derived from crude petroleum.

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CHAPTER XII

PROGRESS IN THE CATALYTIC HYDROGENATION OF FATS AND OILS*

WILBUR A. LAZIER

It is perhaps presumptuous to imply that anything like an authoritative review of catalytic developments in oil hydrogenation can be based on the technical literature alone. The industry, founded over thirty years ago and nurtured throughout its early years in a melee of patent litigation, perhaps finds ample justification for eschewing publication of the details of its latest catalytic achievements. In the United States in particular, where five or six large concerns are thought to conduct 80 to 85 per cent of the nation's oil-hardening business, there is currently a dearth of pertinent journal literature.

Notwithstanding this unique situation, it would be unwise to conclude that no technical progress is being made. In perspective, two rather definite trends are discernible. More attention is undoubtedly being given to the various aspects of selective hydrogenation as it affects the quality of hydrogenated products; and rapid technological progress is being made on the newer art of converting fats and fatty acids into long-chain alcohols. Both processes have been outlined by Fenske (19) as unit processes in organic synthesis, and more comprehensive treatises have recently appeared in the German language (31, 35). The progress of the German, American, and Russian vegetable shortening industries have been reviewed by Norman (54), by Weber and Alsberg (74), and by Heublyum (25), respectively. Modern plant practice abroad has been described by Schneider (62), Taussky (67), and Hugel (36). Soviet Russia's determination to gain self-sufficiency in edible oils and soap stocks has stimulated an amazing scientific interest and publication activity (78) in many details of the hydrogenation art which are probably already well known to those working in the field (16).

No important innovations in the commercial practice of oil hardening have been announced recently. On the basis of statements made in the most authoritative reviews (36, 62, 67), it is the writer's belief that the usual practices are similar to the batch liquid-phase methods already

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* Contribution No. 184 from the Experimental Station of E. I. du Pont de Nemours and Company, Wilmington, Delaware.

described by Ellis (16), and that processes for the continuous hydrogenation of fats and oils, such as the Bolton-Lush process (27, 46), have not yet replaced the batch method of operation to any appreciable extent in the United States or Germany (54, 63). These methods, however, are receiving a great deal of technical attention in Russia, where at least one plant is reported to have been in operation for over three years (55). The advent of the Raney nickel-aluminum alloy (2, 57), which may be crushed to grains and surface-activated with sodium hydroxide, provides a new form of activated granular mass (6, 23, 38) that is being examined critically for its applicability to continuous hydrogenation (24, 25).

For use in the conventional liquid-phase batch method of hydrogenation, nickel in various forms apparently remains unchallenged as the preferred catalyst for all commercial operations involving saturation of olefin bonds. The methods of activation principally used (37) are (*a*) decomposition of nickel formate in oil and (*b*) reduction of nickel carbonate-on-kieselguhr, either by the dry process or immersed in oil. In either case the reduction step may be facilitated by the presence in the unreduced catalyst of a small amount of copper (50). Waterman appears to have obtained exceptional activity from nickel prepared from nickel carbonyl (72). Other catalysts recently investigated for use in oil hydrogenation are reduced nickel chromite (11, 20, 40), reduced nickel borate (7), nickel from nickel amalgam (10), and nickel supported on silica black (75). It is gratifying to note that much progress has been made on clearing up the vagaries of preparation of good nickel-on-kieselguhr catalyst (1). For a trouble-free procedure, assured ease of reduction, and a high activity, it has been recommended that the nickel be precipitated as the bicarbonate (53) under conditions that will preserve in the unreduced product a relatively high carbon dioxide content (18).

The complexities of the progressive hydrogenation of multiple-unsaturated glycerides give rise to the important practical applications of " selective hydrogenation " and provide a fruitful field for painstaking academic research (32). Unfortunately, the term " selective " has been used loosely in the interpretation of various divergent experimental results as will be explained below.

From a large number of scattered reports on the selective hydrogenation (13, 52, 66, 69, 71, 72, 73, 76) of oils and fatty acids, some of which are apparently contradictory, the following picture emerges. Naturally occurring fats consist of mixed glycerides of saturated and unsaturated acids in which the number of double bonds in individual acid radicals varies from none to as many as three or four. The most desirable condition in partially hydrogenating a fat is to add hydrogen atoms in such an order that the more unsaturated acids are progressively reduced to those of a lower degree of unsaturation before any appreciable amounts of the completely saturated members are formed. Moreover, between individual glyceride molecules, each of which may contain three unsaturated acid radicals of the same or different kind, the distribution of the added hydrogen should at all stages of the process coincide as nearly as possible with the average composition of the composite oil. Aside from these considerations, the isomerization of unsaturated acids to higher melting isomers through a shifting of double bonds is to be avoided as far as possible.

A hydrogenation operation that will approach this ideal is said to be "selective" and will produce an oil with a relatively high degree of saturation at a relatively low melting point, a condition that is favorable to good homogeneity and excellent keeping qualities. Low pressures and a rapid reaction appear to favor selectivity. Whether or not a high degree of selectivity in the catalyst is better achieved through the use of a highly active catalyst capable of rapid performance at low temperature (77) or by one that has been partially and selectively deactivated (15) appears to be a matter requiring further study (52). Furthermore, the results achieved with any particular oil sample are by no means generally applicable to others.

In connection with efforts directed towards the use of more active catalysts, the efficacy of the highly active Raney nickel (2, 26, 57) is believed to have been demonstrated on a commercial scale in one or more plants. The use of high hydrogen pressures, while important in connection with the conversion of fats to the corresponding long-chain alcohols and hydrocarbons, appears to have conferred no advantages on oil-hardening practice (56). Whereas the saturation of highly unsaturated glycerides under the usual conditions of temperature and pressure normally proceeds stepwise, completely saturated compounds, according to Waterman (70), are formed in appreciable quantities from the start when high hydrogen pressures are used.

The high degree of selectivity attainable in the laboratory has permitted Hilditch to make further valuable contributions to the structure of the glycerides from fats of authentic natural origin (9, 28, 29, 30, 33).

It is becoming only too evident that hastily formed generalizations of the past regarding poisons for nickel hydrogenation catalysts (8, 17) will require revision as the number and diversification of the observed cases continue to increase. For example, it is generally stated that nickel is sulfur-sensitive, at least under the conditions usually employed for liquid-phase hydrogenation. Yet it is quite possible to prepare an active, reduced nickel catalyst from nickel sulfate (1); and Frazer, Bennett, and Jackson (11, 20) have demonstrated that, in the case of nickel chromite, the presence of sulfur in the catalyst during reduction with hydrogen actually enhances the activity of the catalyst for the hydrogenation of oils. Ueno (68) found the poisoning of nickel by dyestuffs to vary widely according to the chemical constitution of the dyestuff molecule. It has been reported also (15) that the presence of carbon monoxide in hydrogen permits hydrogenation of an unsaturated oil only to the oleic acid stage; but Lyubarskii (49) makes the extraordinary statement that, while other types of nickel catalyst are readily poisoned by hydrogen sulfide, carbon monoxide, phosphine, etc., nickel formate is activated by these so-called poisons. When all variables involved in the phenomena of enhancement and poisoning are finally brought under control, selective poisoning is likely to become a most useful tool of the catalytic chemist.

The application of special catalysts and high pressures and temperatures in the reduction of glycerides and fatty acids to the corresponding alcohols (3, 51, 59, 64) is undoubtedly a development of outstanding interest to the oil-hydrogenation industry, particularly in view of the fact that the sulfated higher alcohols are competitive with soap in the detergent field. Several large industrial research organizations have apparently been active in exploring the technical aspects and commercial possibilities of the process. In the United States, basic patents covering the process for hydrogenating acids (41), esters (42), and glycerides (43) have recently been issued, as well as a number of patents on alternative catalysts (4, 21, 22, 60) and starting materials (34, 58).

The carboxyl-reduction process differs from the usual oil-hardening process mainly in the use of higher temperatures and pressures. With copper catalyst the product consists of the corresponding alcohols which are free from hydrocarbons. At temperatures above 250°C., the ordinary nickel catalyst also reduces the carboxyl group, but hydrocarbons are formed as the principal products (65). In either case the glycerol residue is degraded to lower alcohols and glycols. By the use of difficultly reducible oxides (61) such as zinc oxide, preferably in the form of a compound catalyst such as zinc chromite (5, 41), the process may be controlled reasonably well to produce unsaturated alcohols. Incomplete reduction of the fatty acid leads to the formation of waxy esters resulting from reaction of the alcohol product with the unconverted acid or glyceride.

The long-chain alcohols are valuable intermediates for detergents (39) and insecticides (14), and are probably destined to find many new applications in chemical industry (45). The carboxylic hydrogenation has recently been extended to the production of new long-chain dihydric alcohols from castor (44) and oiticica oils (12) and to the production of high-molecular-weight alcohols corresponding in structure to the fatty acids produced by the oxidation of paraffin wax (47, 48).

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CHAPTER XIII

THE SYNTHESIS OF AMMONIA

P. H. EMMETT

For twenty-five years the commercial catalytic synthesis of ammonia has been an accomplished fact. This field of catalysis is, therefore, somewhat unique in that the catalysts used have become fairly well standardized. Publication concerning development work on ammonia catalysts has in most countries greatly slackened. The present chapter will summarize all work published during the four-year period terminating in July, 1938, including (*a*) the portion dealing with the mechanism of ammonia synthesis and (*b*) the part concerned with directly improving the commercial synthesis.

STUDIES ON THE MECHANISM OF AMMONIA SYNTHESIS

The experimental work published prior to 1934 was ably covered by Frankenburger (25, 26, 27, 28) in four review articles. The present summary of the work published since that date will be considered from the standpoint of adsorption, kinetics, and poisoning and promoter action.

Iron catalysts adsorb nitrogen at an appreciable rate above about 200°C. (8, 9). The heat of adsorption is about 35,000 calories, the energy of activation of the process being about 15,000 calories. The quantities and rates of adsorption at a given temperature and one atmosphere pressure are in the same relative order on pure Fe, $Fe-Al_2O_3$, and $Fe-K_2O-Al_2O_3$ catalysts as their activities for synthesizing ammonia at one atmosphere pressure. On $Fe-Mo$ and $Fe-MoO-Al_2O_3$ catalysts, on the other hand, no activated adsorption of nitrogen could be detected according to Roiter, Gaukhman, and Leperson (55), even though the catalyst was active for ammonia synthesis. On the other hand, experimental work* by S. Brunauer and the author showed a large activated adsorption of nitrogen on an iron-molybdenum catalyst containing about 50 per cent molybdenum.

Activated hydrogen adsorption on iron catalysts is of two types

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* Unpublished work from the Fertilizer Research Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

(15, 35). Type A occurs at and above −78°C. Above 0°C., a second kind of activated adsorption of hydrogen (type B) sets in. The lower-temperature activated adsorption is effective in rapidly hydrogenating ethylene (34) and in effecting the high-temperature (non-paramagnetic) orthohydrogen to parahydrogen (36) conversion. Furthermore, the various nitrides of iron reduce readily (17) in hydrogen at about 200°C. It therefore seems probable that hydrogen can combine rapidly at this temperature with chemically adsorbed nitrogen to form ammonia. The slow step in the synthesis of ammonia is apparently not the reduction of chemically adsorbed nitrogen but the rate of activated adsorption of nitrogen by the iron catalyst. This agrees with the results of Taylor and Jungers (59), who found that an $Fe-K_2O-Al_2O_3$ catalyst would in less than twenty-four hours at room temperature effect appreciable exchange between deuterium and ammonia to form the deuteroammonias.

Kagan, Morozov, and Podurovskaya (37) found that NH_3 is strongly adsorbed by Al_2O_3 at 600 to 700°C., the heat of adsorption being 30,000 calories per mole of ammonia. Addition of K_2O to the Al_2O_3 lessens the adsorption of ammonia and decreases the heat of adsorption by about one-third. It is suggested that K_2O promoter in doubly promoted catalysts may function by accelerating the desorption of ammonia (12).

The kinetics of ammonia synthesis and decomposition have received considerable attention. Jungers and Taylor (59) found that ammonia decomposes on tungsten at a rate that is about 1.6 times as great as that for ND_3. The difference in the rates corresponds to a zero-point energy effect of about 900 calories. Barrer (1) obtained similar results and concluded that the breaking of the $N-H$ bond, rather than the desorption of nitrogen, is the slow step in the reaction over tungsten. The absolute rate of reaction is about 1/1000 that which one would expect from the equation of Topley (60). Christiansen and Knuth (6) have measured the decomposition of ammonia on quartz at 1062°K. The kinetic treatment given to the stepwise reaction assumed to take place is similar to that given chain reactions and appears to be very successful in interpreting their experimental results. Khrizman (41) reports the decomposition of ammonia over an $Fe-K_2O-Al_2O_3$ catalyst between 360 and 575°C. to be proportional to $(NH_3)^{2.2}/(H_2)^{0.2}$. These kinetics are in disagreement with previous work (62) on iron catalysts, the rate of decomposition usually being proportional to approximately the first power of ammonia and inversely proportional to about the first power of hydrogen present. Kurin (45) reports the decomposition of ammonia over the Kazal catalyst at atmospheric pressure to be unimolecular with an energy of activation of 37,200 calories. A catalyst prepared by fusing Bakal siderite is reported to be satisfactorily active (19).

Finkel'shtein earlier (21) reported kinetics for ammonia decomposition identical to those mentioned above as having been published by Khrizman (41).

The synthesis of ammonia was erroneously reported by Finkel'shtein and Rubanik (22, 23) to be second order. On the basis of this conclusion they criticized the conclusion of Emmett and Brunauer (15) that the slow step in the synthesis of ammonia was the activated adsorption of nitrogen by the iron catalyst. They claimed that imide formation rather than nitride formation was indicated as the first step in the synthesis. Later Finkel'shtein and Rubanik (24) corrected their statement and admitted that the reaction was apparently of the first order, i.e., the rate depends upon the first power of the total pressure. Presumably their reason for suspecting imide formation as the rate-determining intermediate step in synthesis was thereby removed. Komarov (61) has done additional work on the well-known poisoning effect of CO_2, CO, O_2, and SO_2 on iron ammonia catalysts. Morozov and Kagan (52) have obtained evidence that the abrupt momentary increase in ammonia that occurs when a poison such as H_2O strikes a catalyst is due to hydrogenation of chemically bound nitrogen on the catalyst surface rather than to a mere displacement of adsorbed NH_3 from an $Fe-Al_2O_3$ or $Fe-Al_2O_3-K_2O$ catalyst. The nitrogen is removed faster from an $Fe-K_2O-Al_2O_3$ catalyst than from $Fe-Al_2O_3$. The poisoning experiments of Kamzolkin and Livshits (39) conform to generally prevalent views in indicating that water vapor poisons iron catalysts by reacting with active centers, the action being greater at high pressure and low temperature. Kamzolkin and Avdeeva (38) report that H_2S and PH_3 are detectable as poisons at concentrations as low as .001 per cent.

Considerable progress has been made in elucidating some of the important factors of promoter action in ammonia synthesis. By use of surface-area measurements by low-temperature adsorption isotherms (11, 12, 13, 14, 5), and with the help of values for the volumes of chemisorbed carbon monoxide and carbon dioxide on promoted-iron catalysts, it has been possible to show (11) that the small percentage of K_2O and Al_2O_3 added as promoters may cover 50 to 75 per cent of the catalyst surface. Similar conclusions were reached by Dubrovskaya and Kobozev (7) in regard to the accumulation of Al_2O_3 on the surface of Fe_2O_3 catalysts by comparing the energy of activation of the desorption of chemisorbed oxygen from the surface of Fe_2O_3 and $Fe_2O_3-Al_2O_3$ catalysts whose relative surface areas were known. Kamzolkin and Livshits (40) have called attention to the necessity of Al_2O_3 being in solid solution in Fe_3O_4 before it becomes effective as a promoter. This is in agreement with the work of Brill (4) and of Mittasch and Keunecke (51).

Kobozev (43, 44) points out that $Fe_3O_4-Al_2O_3$ spreads when heated to melting point on a plate, whereas Fe_3O_4 does not. This means that Al_2O_3 promoter is " surface active " and indicates an accumulation of the promoter in the surface of the oxide and probably in the surface of the reduced catalyst. This conclusion is consistent, Kobozev points out, with the well-known inhibitive effects of the promoters on the reduction of Fe_3O_4 catalysts. Papers by Lachinov and Telegin (48, 49) on the promoter action of K_2O, Al_2O_3, MgO, SiO_2, and their various mixtures conform to the conclusions already well known in the literature; $K_2O + Al_2O_3$ or $MgO + SiO_2$ produce the most active and stable catalysts.

Khrizman and Korniichuk (42) have concluded that iron and not iron nitride is the active catalyst in ammonia synthesis. Above 410°C., ammonia decomposed into $3 : 1$ $H_2 : N_2$ gas over a nitride made from an $Fe-Al_2O_3-K_2O$ catalyst; below 350°C., nitrogen with only a trace of hydrogen was obtained as a product of reaction.

APPLIED CATALYTIC WORK ON AMMONIA SYNTHESIS

The published articles that are here classified as " applied " deal either with new catalysts, with improved reduction schedule of standard catalysts, with the influence of the ratio of reactants or the partial pressure of inert gases on the rate of synthesis, or with the potential synthesis of ammonia at superpressures.

The proposed new catalysts vary from those that resemble the usual standard iron synthetic ammonia catalysts to new combinations whose activities have not been published in other than patent literature. Geid proposes the addition of potassium aluminate to fused iron turnings, followed by burning the catalyst mass in air (30). A French patent (29) suggests the addition of alkali or alkaline-earth metals to the gas stream immediately ahead of the ammonia synthesis catalyst. It is also claimed that active ammonia catalysts can be prepared by precipitation from a chromi- or chromo-cyanide solution with a manganese salt (31) and that $H_3Co(CN)_6$ (32) and iron carbide (33), stabilized by adding sulfur compounds, are active as ammonia catalysts. Plotnikov and Kikets (54) compare a Fauser catalyst with one made from $(NH_4)_6Mo_7O_{24}$ and $Al(NO_3)_3$ in a ratio of $2 : 1$ (I), $Fe(NO_3)_2$, $Mn(NO_3)_2$, and $MgCl_2$ in the ratio $98 : 1 : 1$ (II), and a combination (III) of 84 parts of catalyst I and sixteen parts of catalyst II. III has the greatest activity. Epshtein and Upolovnikov (18) recommend $KAlFe(CN)_6$ and also a titanomagnetite ore. Finally, Zenghelis and Stathis (63) report a slow synthesis of ammonia over rhenium catalysts at 85°C.

Stefanovskii, Tatarskii, and Zelyakov (58) have shown that the reduction of an iron catalyst at 600°C. yields a catalyst only about one-thirtieth as active for ammonia synthesis as though it were reduced at 500°C. The decrease in activity is probably correctly attributed to a decrease in the quality of the surface (loss of active points) rather than to a surface-area decrease. Lachinov and Telegin (50) and Selyakov and Telegin (57) have re-examined the dependence of the activity of an $Fe-Al_2O_3-K_2O$ catalyst on the temperature, pressure, and space velocity during reduction. The decrease of activity with decrease in space velocity, increase in temperature, and increase in pressure of reduction conforms to prevailing ideas relative to these factors. Lachinov (47) has obtained a kinetic equation relating the rate of reduction to temperature, pressure, and the rate of flow. Rubanik, Zabolotskii, and Rusov (56) report $Fe-Mo-Al_2O_3$ catalysts less active than $Fe-Al_2O_3$. Feldman, Kozlov, and Ivanov (20) claim that increasing the nitrogen to values greater than 25 per cent in a hydrogen-nitrogen mixture will give better yields of ammonia if the conversion is considerably smaller than equilibrium. Thirty per cent nitrogen is, for example, superior to 25 per cent nitrogen at 450°C., 15,000 space velocity, and 250 atm. pressure. Pastonesi (53) reports that inert gas causes a decrease in the rate of ammonia synthesis, the decrease being proportional to $(P_{\text{Inert}})^2$ at low pressures and to (P_{Inert}) at higher pressures.

Within the last few years Basset (2, 3) has published some very puzzling results indicating an enormous influence of superpressures on the yield of synthetic ammonia. The optimum temperature at 2000 kilograms/sq. cm. is 700°C., and at 5000 kilograms/sq. cm., 850°C. Under the latter conditions 10 grams/hr. of ammonia were obtained per cc. catalyst space, the conversion being about 98 per cent complete. The rate of ammonia production at these high pressures is said to be independent of the material of which the catalyst chamber is made, and is not decreased by poisons such as CO and H_2S. Kurin (46) concludes that Basset's experiments are best interpreted as indicative of a heterogeneous catalytic reaction occurring over the entire walls of the catalyst chamber. The yield versus temperature plots obtained by Basset do not appear to correspond with the equilibria expected for the synthesis reaction on the basis of the known behavior up to 1500 atm. It seems probable to the author that the temperatures corresponding to the observed yields are considerably lower than those given by Basset, owing to the possible equilibration of the exit gases with the cooler portions of the furnace through which they leave the reaction chamber. The work is, nevertheless, very surprising and merits further experimental study.

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CHAPTER XIV

CATALYTIC OXIDATION

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The following publications deal, entirely or partly, with the oxidation processes taken up in the sections of this chapter.

LEWIS, BERNARD, and VON ELBE, GUENTHER, " Combustion, Flames, and Explosions of Gases," The Macmillan Co., New York, 1938, 415 pp.

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NASH, A. W., and HOWES, D. A., " The Principles of Motor Fuel Preparation and Application," Vol. 1, 2nd Edition, Chapman and Hall, Ltd., London, 1938.

OXIDATION OF HYDROCARBONS

Hydrocarbons, ranging from methane to the most complex, furnish the greatest source for experiments on oxidation, which may have for their purpose anything from the formation of intermediate oxidation products to elucidation of combustion mechanism in internal-combustion engines. The reason for this has been often remarked, and apparently the work is justified. However marked may have been the advances in aromatic hydrocarbon oxidation to form useful products

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and in combustion phenomena interpretation, progress in the economic utilization of the aliphatic hydrocarbons as a class for the formation of partial oxidation products has been slow.

However, progress is also being made with respect to aliphatic hydrocarbons (166). Commercial quantities of methanol and formaldehyde have been obtained in Oklahoma by the partial oxidation of natural gas (75, 76) in the presence of catalysts such as platinum, palladium, copper, chromium, manganese, iron, nickel, or their oxides, at temperatures of 800 to 900°F. and at pressures of 100 to 300 lb. per sq. in. (33). Synthesis of fatty acids from petroleum waxes has been established on a large-scale manufacturing basis in the U. S. S. R. A factory at Kasan is reported to have produced 2000 tons of acids in 1935, and a factory at Gorki is reported to be starting production (19). German production of fatty acids from paraffin oxidation is also reported (75).

Catalysts and catalytic activity from the standpoint of kinetics have no place in the present discussion. Mention may be made, however, of some general discussions dealing with the effects obtained in practice and of some of the patented catalytic materials. A review of the literature arranged in tabular form containing 116 inorganic and organic substances and a variety of catalysts showing test conditions, reaction products, methods, and author references has been prepared by Kutzelnigg (127). The most effective oxidation catalysts were reported to be the elements with atomic numbers 23 to 29, e.g., V, Cr, Mn, Fe, Co, Ni, and Cu (128). That platinum oxide also falls into the category of effective oxidation catalysts has been frequently noticed. Heating ordinary platinum in an oxygen atmosphere under pressure has been suggested as a method of preparation (130). A number of catalytic materials have been arranged as follows in decreasing order of effectiveness for the oxidation of various substances in concentrated sulfuric acid at 237°C.: hydrogen — Pd, Hg, Pt, Se, Cu, Ce, Sb, Ag, Au; carbon monoxide — Pd, Se, Pt, Cu, Te, Hg, Sb, As, Ag; carbon oxysulfide — Pd, Pt, Se, Ag, Cu, V, Hg, Te, Sb; ferrous sulfate — Se, Ag, Pd, Pt, Te, Se, Pd, Hg, Pt, Te, V, Ag, Cu, Sb (149). Numerous catalysts have been patented both as to general form and composition as well as for specific purposes.

Aliphatic Hydrocarbons

Whereas, perforce, the lower aliphatic hydrocarbons must be oxidized in vapor phase, materials of the kerosene range of petroleum fractions may be oxidized either in vapor or liquid phase, and the wax fractions or paraffins of petroleum must be oxidized in liquid phase. However, the application of high pressure to oxidation of the lower aliphatic hydrocarbons tends to give results approaching in nature those obtained from liquid-phase oxidations presumably because of the effect of pressure in lowering the reaction temperatures (184) and in stabilizing the products intermediately formed. Thus, the effect of pressure on reaction rate is indicated by the following results (155) from work with hydrocarbon-oxygen mixtures, low in oxygen content.

TEMPERATURE AT WHICH OXIDATION IS FIRST DETECTABLE (FROM COMPOSITION OF PRODUCTS) WHEN PRESSURE IS:

Hydrocarbon	1 Atm.	50 Atm.	100 Atm.	150 Atm.
Methane......	420°C.	350°C.	330°C.	320°C.
Ethane.......	285	276	260	......
Propane......	270	255	245	232
Butane.......	......	248	220	210
Benzene......	......	270	260	......
Toluene......	......	210	195	......

Furthermore, pressure changes the point of oxygen attack on the molecule of the higher aliphatic hydrocarbons, there being an increasing tendency for direct oxidation to occur at some mid-point in the chain at higher pressures (155) as is observed also in the liquid-phase oxidation of paraffin waxes.

Experiments on propane oxidation at propane/air mole ratios of 1 to 3.6, pressures of 5 to 65 atm., and a temperature of 275°C. show that the oxidation of propane under high pressures follows two routes. One route leads to formation of normal propanol and propaldehyde and the other to isopropanol and acetone. The oxidation also results in the formation of ethanol and methanol, but higher pressures favor the higher alcohols (157).

Although Newitt adheres to the hydroxylation theory for explanation of the effects of pressure oxidation, von Elbe and Lewis believe a better explanation of the experimental results may be obtained on the basis of peroxidation (190, 214). The experimental results of Boomer, which showed no detectable peroxide, seem to lend support to the hydroxylation mechanism (30).

Boomer studied the effects of various catalysts on the high-pressure oxidation of methane (natural gas) by air and oxygen. At temperatures in the range of 300 to 350°C. with oxygen and 350 to 500°C. with air, and pressures in the range of 100 to 230 atm., methanol was the major oxidation product, low yields of formaldehyde and formic acid being obtained. Yields up to 74 per cent of the carbon oxidized were obtained, but, because of the deficiency of oxygen required, conversions of only 5 per cent can be obtained — too low for commercialization (29). Copper and silver catalysts were found best for methanol formation.

The oxidation of natural gas with 0.8 to 10 per cent by volume of available oxygen at pressures of 100 lb. per sq. in., or over, by heating to temperatures favoring partial oxidation to alcohols and aldehydes has been recently patented (219).

Oxidation of methane over a catalyst mass, prepared from iron borate and tin phosphate, at 600 to 610°C. yielded 19.3 milligrams formaldehyde per liter of gas. Addition of 0.3 per cent hydrogen chloride to the gas was found to increase the yield of formaldehyde in presence of iron and aluminum phosphate catalysts (146). The addition of methyl nitrite to mixtures of methane or ethane and air or oxygen was found to increase the oxidation reaction and eliminate any induction period. Up to about 50 per cent oxidized, the velocity of reaction is roughly proportional to the methyl nitrite concentration (90).

Oxidation of paraffin hydrocarbons above methane to form formaldehyde, acetaldehyde, and formic acid is effected at 500 to 800°C. with the addition of about 1 per cent of NO in the presence of catalysts comprising elements of the second and fourth periodic groups, plus chromium, vanadium, molybdenum, aluminum, tungsten, manganese, or cobalt (96, 151).

Catalysts or special conditions mentioned in patents for the oxidation of lower aliphatic hydrocarbons include: bleaching earths activated or mixed with silica gel or activated carbon (100), ozone (36), large excess of steam (68), mixing preheated hydrocarbon with cold oxygen-containing gas (111), etc.

Mechanism studies of methane oxidation in the presence of heated platinum wire catalysts show the reaction to be a heterogeneous-homogeneous catalytic reaction, materially influenced by the nature and extent of the platinum surface (178, 179, 180) and resulting in the formation of peroxidic substances as intermediate products of reaction. In mixtures of acetylene with air, oxygen, hydrogen and air, and methane and air, combustion over heated platinum shows pronounced effects of surface combustion at temperatures of 500 to 600°C., with acetylene interfering with the hydrogen but not the methane reactions; gold, silver, copper, and iron were found not to promote surface combustion, whereas nickel was found to be a catalyst (57). Steacie and McDonald investigated the kinetics of acetylene oxidation by the static method and found marked irregularities due to surface variation (201).

The slow oxidation of propane at about 300°C. with mixtures containing from 10 to 30 per cent oxygen indicates MeO and C_3H_7 to be chain carriers giving an indicated stoichiometric equation (169) for the reaction of:

$$C_3H_8 + 2O_2 = CH_3OH + H_2CO + CO + H_2O$$

The treatment of the glass walls with KCl in these experiments gives results that indicate that peroxides play an important role in the oxidation of hydrocarbons higher in molecular weight than ethane (170). Peroxides are found in the products only when the walls do not destroy them too rapidly to prevent their detection (99).

Lower alkyl ethers, such as methyl ether, are claimed to facilitate the oxidation of propane to produce intermediate oxidation products (42).

Oxidation of olefins by hydrogen peroxide in the presence of such catalysts as osmium tetroxide, vanadium pentoxide, and chromium trioxide results in the formation of dihydroxy alcohols, respectively, as follows (147):

Olefin	Glycol	Yields, Per Cent		
ethylene	ethylene glycol	88	93	97
propene	propene glycol	68		
cetene	cetene glycol	77	82	
styrene	phenyl glycol	50		
pentene-2	pentanediol-2, 3	26	29	30
isobutene	isobutene glycol	38		
2-methyl butene-1	2-methyl butanediol-1, 2	45	51	
trimethylethylene	trimethylethane glycol	40		
hexene-3	hexanediol-3, 4	36		
cyclohexene	cis-cyclohexanediol-1, 2	58		
diallyl	hexanetetrol-1, 2, 5, 6	45		
alpha-limonene	*p*-methanetetrol-1, 2, 8, 9	35		

Further oxidation results in formation of aldehydes, ketones, and acids. Benzene yields 23 per cent of phenol.

Oxidation of olefins with selenium oxide in acetic acid always occurs alpha to the double bond. Thus, cyclohexene gives a 20 per cent yield of cyclohexenylacetate (91) by oxidation, followed by esterification with the solvent.

When alkyl groups are adjacent to a double bond, oxidation occurs more rapidly than otherwise, on the basis that peracetic acid oxidizes Δ^{α}-heptene more slowly than γ-heptene or β-methyl-α-hexene (27).

Catalytic vapor-phase oxidation of olefins leads to the formation of olefin oxides, aldehydes, and acids as intermediate oxidation products. Thus, oxidation of the ethane-ethylene fraction of cracked gas at 400°C. gives a maximum yield by volume of ethylene oxide 3, aldehydes 4 to 5, and carbon monoxide 11 parts per 100 parts of ethylene (173), and oxidation of relatively pure propylene gives propylene oxide 15 and aldehydes 35 parts per 100 parts of propylene reacted.

A number of catalysts have been patented for the useful oxidation of the lower aliphatic unsaturated hydrocarbons, thus: silver catalysts formed by the thermal decomposition of silver oxalate (212), silver catalyst deposited on reactor tubes which are immersed in a liquid bath (133), molybdenum oxide deposited on silica gel (101), vanadium oxides (47), finely divided silver or gold separately or mixed or alloyed with other metals (134), nitrogen oxides (175), copper oxide or naphthenate or naphthenate of aluminum or manganese (112), silver activated by small amounts of gold, copper, or iron (135), etc.

Oxidation of the gasoline, kerosene, and gas-oil fractions of petroleum gives rise to such a mixture of products that recovery of useful material is difficult. Nevertheless, experimental work goes on. Oxidation of petroleum fractions of specific gravity 0.770 to 0.850 and boiling range 170 to 250°C. by heating to 150°C., atomizing into a stream of air heated to 300°C., and passing the mixture through a catalytic reaction chamber leads to the formation of products containing olefins, dienes, aromatics, saturated and unsaturated aldehydes, saturated and unsaturated ketones, alcohols, acids, phenols, and resinous matter (218). The products have been used for odorizing fuel gases and for denaturing alcohol.

Russian kerosene of naphthene base oxidized in vapor phase over a vanadium pentoxide catalyst yields lower fatty acids, aldehydes, and ketones — formic acid, formaldehyde, acetaldehyde, acetic acid, and acetone having been identified (121).

Since oxidatively catalyzed polymerization of certain unsaturated hydrocarbons in gasoline may give rise to gum formation, information regarding individual unsaturated hydrocarbons of gasoline boiling range is of interest. Oxidation of hexadecylene ($CH_3 \cdot (CH_2)_{13} \cdot CH : CH_2$) by air at 125 to 145°C. leads to the formation of gaseous products as well as a polymerization product of acid nature that is not crystallizable. No evidence of peroxide formation was noted (15).

The vapor-phase oxidation of cyclohexane at 316°C. and at an air to hydrocarbon ratio of 0.8 gives rise to 6.5 grams of crude peroxide from 25.5 grams of hydrocarbon (114).

Blends of petroleum and terpene hydrocarbons are subject to undesirable oxidation on storage. It has been found that tricresyl phosphate, alpha-terpinol, metallic aluminum, dry lime, and dry soda ash accelerate the oxidation; borax and trisodium phosphate are without effect; and sodium hydrosulfite, ammonia, anethol, triethanolamine, methanol, ethanol, wet lime, and wet soda ash retard the oxidation (32).

Catalysts typically patented for the vapor-phase oxidation of kerosene fractions of petroleum include the blue oxide of molybdenum, chromium chromate, and uranyl vanadate (116) or manganese oxide (94).

The work of Dornte and his associates on the oxidation of lubricating fractions of petroleum has been conducted by measuring the oxygen absorbed in a circulatory system (65, 66, 67, 225). Highly refined (white) oils give rates indicating that the oxidation is an autocatalytic process involving a chain mechanism whose rate-determining step is preceded by a rapid dissociation equilibrium. With certain lubricating oils oxygen absorption is a linear function of time at constant temperature and oxygen pressure, and varies nearly linearly with oxygen pressure. No peroxides form and probably no chain process is involved. Copper causes a rapid increase in rate, increasing with larger surface exposure. Iron, tin, and lead increase the rate less markedly. Another group of lubricating oils shows a decreasing rate of oxygen absorption with time, indicating either a decreasing concentration of the reacting components or retardation by products. For this group the rate of oxygen absorption in the presence of copper is constant, indicative of a change in the type of reaction. Only copper and lead were found to have any catalytic effect. Temperatures in the range of 135 to 185°C. were used.

Grozny paraffin of 52°C. melting point, oxidized with air at 140 to 160°C., contains peroxidic compounds which liberate iodine from potassium iodide and oxidize ferrous salts. Part of these peroxides are heat stable, but all undergo decomposition in the presence of acids and alkalis and hydrolyze in presence of water, especially if calcium or sodium naphthenates are present. In the presence of active catalysts, this peroxide formation is suppressed and any present at first disappears after 4 to 5 hours (176). The use of 0.2 per cent of calcium naphthenate as a catalyst in the air oxidation of purified gas oil (d. 0.88) at 115 to 120°C. gives rise to formation of carboxylic and " oxyacid " acids (177).

Catalysts prepared by the interaction of salts with the fatty acids from paraffin oxidation at 160°C., and added in amounts of 1.5 per cent manganese, 2.5 per cent calcium, and 2.5 per cent aluminum to a paraffin hydrocarbon mixture, show the following order of decreasing activity: manganese, calcium, and aluminum. Manganese at 120°C. accelerates the oxidation fivefold in laboratory experiments and tenfold in semicommercial tests (56).

Apparatus patents for the oxidation of paraffin waxes have aimed at the intimate contact of gaseous oxidizing agent, catalyst, and the liquid hydrocarbon (43,120,140,171). Soluble catalysts are generally favored, such as those of aluminum, alkali, or alkaline-earth metal salts (palmitates) soluble in the liquid hydrocarbon being oxidized (62,113).

More rarely catalysts of the type of alkali metal compounds containing manganese in the anion, as potassium permanganate, are claimed (119). The fatty-acid products are usually recovered by saponification and separation from the unoxidized portions of the oil which may be returned to the reaction (102), or by selective extraction (213).

Aromatic Hydrocarbons

The effect of pressure in the oxidation of aromatic hydrocarbons is as pronounced as in the oxidation of the lower aliphatic hydrocarbons. Thus, mixtures containing an excess of benzene in air or oxygen oxidized under high pressures yield as high as 55.5 per cent conversions to phenol (156). Oxidation proceeds to yield hydroquinone, quinone, and then ring rupture. In toluene and ethylbenzene, oxidation of the ring and side chain occur simultaneously, after a definite induction period, to give dihydroxy compounds as well as the usual benzaldehyde and benzoic acid (159).

Vapor-phase oxidation of benzene over a vanadium catalyst was found to result in a 38 per cent yield of maleic acid at 450°C. and less than one second time of contact. Quinone to the extent of 4.23 per cent was obtained as a by-product (174).

Vapor-phase oxidation of toluene at various temperatures, vapor concentrations, and contact time has been used to evaluate 16 different catalysts (167). It was found that for the formation of benzaldehyde the best results were obtained from a catalyst composed of a mixture of uranyl molybdate and boron carbide at 575°C., primary air-space velocity of 420, secondary air-space velocity of 1010, and air to hydrocarbon ratio of 1.38 by weight. A yield of 20 per cent benzaldehyde on the basis of toluene evaporated to the reactor was obtained. Low oxygen concentrations and relatively high temperature favor the formation of benzaldehyde, whereas excess oxygen and low temperatures favor the formation of benzoic acid.

Tin vanadate has been found to be an excellent catalyst for the oxidation of toluene to benzoic acid, the reaction rate depending upon the heat treatment of catalyst, the reaction temperature, and the partial pressure of oxygen. Anthraquinone and benzaldehyde are obtained as by-products (110). Mixtures of tin oxide and vanadium oxide, tin vanadate, and manganese vanadate have also been found effective in the oxidation of polynuclear aromatic hydrocarbons (52).

Oxidation of ring compounds by hydrogen peroxide in the presence of metallic oxide catalysts has been found to be very effective. Thus, the oxidation of stilbene with hydrogen peroxide in the presence of osmium tetroxide yields 7.7 per cent benzaldehyde plus 2.3 per cent benzoic acid;

anethol gives 75 per cent of anisaldehyde; isoeugenol acetate gives 66 per cent of acetylvanillin; isosafrole gives 61 per cent of piperonal (55). When this reaction is applied to cyclohexene in ether solution, the cyclohexene is almost unaffected by hydrogen peroxide but the solvent is oxidized. In methanol, ethanol, butanol, or benzene solutions, cyclohexene is easily oxidized to cyclohexanediol. Camphene is not oxidized in ether solution but norpinene is (73). Low concentrations of tungstic, molybdic, and vanadic acids all catalyze the hydrogen peroxide oxidation of hydroquinone to quinhydrone, pyrogallol to purpurogallin, and guaiacol to tetraguaiacoquinone. At high concentrations of tungstic acid, hydroquinone is oxidized to maleic acid (117).

Liquid-phase oxidation with air at 10 atm. pressure and temperatures of 78 to 136°C. of heptylbenzene and decahydronaphthalene was found to result in the formation of mixtures of tars and acids (51).

Results on the slow combustion of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, *o*-xylene, *p*-xylene, and mesitylene have been reported (41). As a result of oxidation studies, Stephens and Roduta report that oxidation of tertiary hydrocarbons always takes place at the alpha C-atom and is not inhibited by water (202).

The oxidation of pinene, dipentene, alpha-terpinene, terpinolene with red lead in acetic acid yields four fractions boiling at 20 mm. pressure as follows: 80 to 100°C., hydrocarbons; 115 to 130°C., acetates of monohydric alcohols; 150 to 175°C., monoacetates of dihydric alcohols; above 180°C., probably polymers and higher acetates (220).

Aromatic materials of the polynuclear type in which the nuclei are joined by a single bond, as in the case of diphenyl, may be oxidized to maleic acid and anhydride by passing a mixture of the aromatic material together with an oxidizing gas, containing more than sufficient oxygen for complete combustion, over catalysts at temperatures below about 550°C. (86).

The patent literature shows the development of improved methods for obtaining mixing and proportioning of the oxidizing gas and the materials undergoing oxidation (148, 192, 203), improved catalyst chambers (181) to insure a better-grade product in phthalic anhydride manufacture, improved methods for product recovery in both phthalic anhydride and maleic acid manufacture and in the recovery of maleic acid from phthalic anhydride tail gases (115, 191, 193), and a variety of catalysts: conglomerates of materials, such as Al_2O_3 and TiO_2, coated with and bonded together with fused V_2O_5 (44), nitrogen oxides (61), oxides of V, Mo, W, U, or Sn or salt derived from such oxides as the vanadates (197), etc.

OXIDATION IN POWER GENERATION

Knock in Engines

Although the problem of knocking in the engines of automobiles seems to have been reasonably solved for the majority of automobile drivers, by the advent of tetraethyl lead and highly cracked gasolines, it has not been solved for the scientific workers. For although the attention of industrial and academic laboratories seems to have shifted from a study of substances having possible knock-inhibiting properties to a study of the phenomena occurring during combustion, and the effects thereon of knock inhibitors, there has been no noticeable diminution of activity.

One phase of this study has been concerned with the observation of the sequence of events occurring in an engine cylinder after the spark, during actual engine operation. To obtain a record of these phenomena in an operating gasoline engine, Rassweiler and Withrow (188) developed a special motion-picture camera designed to photograph the entire combustion chamber through a quartz window fastened to the top of the cylinder. This camera can photograph 30 pictures of a single explosion at rates up to 5000 per second. A recorder at the same time makes a pressure-time curve to provide a correlation between pressure and appearance of the flame. High-speed photography has been applied to a study of the velocity of the detonation or explosion wave during knocking operation of gasoline motors, and velocities of the order of 2000 meters per second have been reported (200). Flame travel in an engine by use of this photographic technique is shown by a series of 136 high-speed photographs (226).

Spectrographic studies have also been made on engines during operation (152).

Studies have likewise been applied to Diesel-engine combustion. Thus, the simultaneous variation in pressure, radiation emission, and position of the stem of the fuel injection valve have been recorded by high-speed photography through the use of photoelectric cells. An accuracy of 0.00003 second in oscillation time and a film speed of 0.0014 second per inch are obtained (194). A new method for determining the mean effective pressure in engine cylinders during high-speed operation was developed (54), the results from which permit calculation of the principal characteristics of engine performance. High-speed motion pictures have been used to study the air flow, fuel injection, and flame travel (195).

The changes in brightness of flame with changes in pressure, observed with the aid of a quartz window and photoelectric cell arrangement, have been used to study the combustion in a Junkers Diesel engine (97). Spectrographic studies were used in conjunction with brightness for interpretation of the results.

Direct measurement of the ignition point in Diesel-engine combustion has been used to study combustion processes regarding type and velocity (118).

The results arising from the use of these new tools have materially enlightened the workers regarding the effects obtained from different fuels and various addition agents. It was found that during the period from 10 to 95 per cent of combustion-time interval in a single-cylinder, L-head engine the flame speed is uniform, but increases with engine speed, decreases with increasing humidity, inlet temperature, exhaust pressure and altitude, and attains its maximum at about the air-fuel ratio and spark advance for maximum power (34).

By use of a pressure-time indicator on a modified Diesel combustion chamber various fuels have been studied (63). Heptane, isooctane, and " AMB " or B-2 reference fuels blended with benzene, toluene, diisobutylene, cyclohexane, or lead tetraethyl show that the intensity of knock is proportional to the extent and not rate of pressure rise and is inversely proportional to the time between ignition and maximum pressure. Actually, the maximum pressure during knock is not very much greater than in its absence, previous results to the contrary having been due to defective apparatus.

The most likely factors that may influence the measurement and calculation of gas temperatures in an internal-combustion engine during combustion and expansion have been pointed out by Hershey (103). Reasonable agreement between measured and calculated results is secured if, first, the temperatures are measured by the line reversal method and corrected for the effect of temperature gradients in the gas, and, second, the temperatures are calculated on the basis of thermodynamic analysis, assuming thermal and chemical equilibrium, including the effects of variable specific heat of the gases, and correcting for heat loss during the combustion.

The use of a Mollier diagram of the properties of the combustion products of octane-air mixtures makes possible the simple calculation of the effects of flame propagation and of piston movement on the temperatures attained in various parts of an Otto cycle engine charge during combustion (108). The method is applied to a consideration of the effect of spark advance on temperatures attained ahead of the flame front, and it is concluded that the results are of significance in engine studies (104).

There has been considerable discussion of the results obtained from the use of ethyl alcohol-gasoline blends in internal-combustion engines, most of the discussions being based on more or less scientifically conducted engine tests, and of the technical problems associated with preparation of such blends. Broadly, with blends of about 90 per cent nonleaded gasoline of about 65 octane number and 10 per cent ethyl alcohol, comparatively little difference is to be found in performance over that of the plain gasoline (38). On the basis of technical tests it has been claimed that there is no advantage in blending gasoline with alcohol and there may be disadvantages (167). The performance characteristics of ethyl alcohol in internal-combustion engines are such that compression ratios as high as 8 to 1 may be used with 190-proof alcohol but, even so, the specific fuel consumption is not sufficiently decreased to offset the lower heating value of alcohol compared with gasoline (109, 137). Small percentages of ethyl alcohol in a blend are more advantageous than large percentages (35).

The finding that alcohol-containing motor fuels give longer combustion periods, based on the stepwise oxidation of alcohols to aldehydes and then to peracids, is offered as an explanation of the antiknock effect obtained when such blends are used as fuel (150). Attempts to blend alcohols or benzaldehyde with gas oil for Diesel (injection) engines have led to increased pressures but also increased ignition delay (70).

Comparative effects of the addition of lead tetraethyl, ethanol, and benzene to cracked and uncracked gasolines of 68 and 65 octane numbers, respectively, by the CRF method show: addition of 0.12 per cent ethyl fluid (61 per cent lead tetraethyl) raised the knock rating to 79.6 and 83.3; 30 per cent ethanol raised it to 80.6 and 84.0; and 70 per cent motor benzol, to 82.5 and 87.0, respectively (123).

Blends of ethanol or of methanol and ethanol of 5 to 25 per cent have been used economically, and properly prepared blends containing up to 25 per cent alcohol by volume offer no technical difficulties in transportation or storage (53).

The finding that isopropyl ether is at least as good as isooctane for blending with gasoline, leaded with lead tetraethyl, to produce high octane number aviation gasoline, however, has served to place oxygen-containing fuels in a more significant position with respect to use in Otto cycle engines (40).

A number of general discussions of fuels, fuel characteristics, and operating results have appeared. Only a few will be indicated here. These include: the combustion characteristics of Diesel fuels (25), the effect of ignition quality of fuels on the useful compression ratio and delay angle (92), testing and operation of gasoline and Diesel engines (217), relative knock characteristics of fuels in service (45), a discussion of the laws governing oxidation and ignition of fuels in gasoline and Diesel engines and of factors influencing the tendency to knock and the delay period (185), octane numbers of the constituents mainly present in natural gasoline (16), effect on octane number of addition of lead tetraethyl, aniline, and mixtures in various cuts of gasoline (207).

Various reviews have been given: of compression-ignition engine combustion (138), of ignition lag in Diesel engines (204), of combustion in gaseous phase (28), and of theories regarding knocking in explosion motors (64).

The remarkable effect of ethyl nitrate in suppressing knock and diminishing ignition delay in fuel-injection engines has been noted repeatedly (21, 70, 71). For the same purpose, tetrahydronaphthalene peroxide, or a solution, has been patented (106).

Among patented materials claimed to function as knock suppressors may be mentioned: 0.5 per cent or more of ethylenediamine or hydrate of ethylenediamine (172); and 1 to 5 per cent benzene or acetone solutions of nitrocompounds of aniline and terpenes (plus urea), (210).

In the interpretation of knock phenomena in terms of combustion theory there has been a tendency to stress the importance of peroxide formation, founded on the belief that the key to an understanding of the chemistry and kinetics of hydrocarbon oxidation is to be found in the formation and decomposition of peroxide substances during combustion (136).

In the Otto cycle engine, combustion is a race between combustion by a moving flame initiated by the ignition spark and spontaneous ignition of a portion of the unburnt charge ahead of the flame. This spontaneous ignition occurs only after ignition conditions have been established for some time. In knocking operation this ignition lag is terminated by explosion before flame travel is complete. To prevent knock then, the lag must be prolonged until combustion is complete (215). Various factors influence this relationship, as, for instance, the degree of compression, the working temperature, and the speed of running (74, 189, 208, 227). The action of lead tetraethyl in suppressing the tendency of a fuel to knock under given operating conditions was early attributed to the inhibition of chain reactions occurring in hydrocarbon oxidation. Besides lead tetraethyl, finely divided metals like lead, potassium, and iron have been found effective in retarding the branching chains of combustion which involve peroxide formation.

The systematic investigation of effect of pressure on spontaneous ignition points of complex hydrocarbons has brought out new material of interest. The close relationship between both ignition points and temperature coefficients of reaction velocity of fuel-air mixtures and their propensity to knock in engines has been well appreciated. Townend's work on the inflammation of mixtures with air of a variety of hydrocarbons has been an important contribution.

Ethyl ether is a strong pro-knock in gasoline-air mixtures, and Newitt's discovery of the formation of mixed ethers in the slow combustion of olefins introduces a new field of study (178). Measurement of the formaldehyde and total aldehydes formed during operation of an engine on gasoline, hexane, cyclohexane, amylene, acetone, butanol, ethanol, isooctane, and mixtures of aldehydes and gasoline indicates that the amounts present do not account for knock and that a different source of peroxides is required for explanation (209). In engine operation, if the nitrogen of the air is replaced by argon or helium, the explosions are found to be silent under conditions that with nitrogen would cause strong knocking. Thus, nitrogen may either absorb energy or form oxides, which on disruption give rise to branched chains leading to the knocking operation. On Diesel-engine operation, nitrogen oxides appear at the beginning of combustion, rise to a maximum of about 0.06 per cent, and then decline, owing to absorption. In knocking combustion in a Delco engine, the concentration of nitrogen oxides has been found to rise to 0.5 per cent (98). Besides their effect on combustion phenomena, these nitrogen oxides become absorbed in the lubricating oil and give rise to oxidative formation of gum and sludge.

That the shape and size of the combustion space of an engine profoundly affect the tendency of a fuel to knock has long been recognized. Recent observations in an L-head engine operating under severe knocking conditions of the vibration amplitudes produced have shown the amplitude to be a function of the severity of detonation, shape and size of the combustion space, and of the point of observance. It would appear that in a consideration of detonation three typical regions are concerned: (1) where combustion of the end gas occurs, (2) where vibrating pressure effects occur, and (3) where the highest heat flow to the walls occurs (26).

Studies of the oxidation of acetylene, amylene, hexane, cyclohexane, "petroleum spirit," and ethanol by both the high- and low-pressure static method and a dynamic method with regard to the effects of rate of heating and fuel concentration on oxidation rate, products, and explosibility have shown that peroxide formation is related to the speed of heating and to preheat temperature, and affects the character of the explosion of the mixture (224). The presence of peroxides in spark-ignited explosions does not increase the useful work obtained but increases the speed of combustion and may produce or increase knocking.

Combustion of Solid Fuel

Consideration of catalytic effects in the combustion of carbonaceous fuels has been approached from the standpoint both of effects obtained in laboratory apparatus from materials added to relatively pure carbon and of effects obtained in the combustion of coals and cokes on actual grates.

Combustion of Carbon

The catalytic effect of salts on the oxidation of soot uniformly deposited from a smoky flame on glass surfaces coated with the salts was observed by noting the time required to remove the soot at predetermined temperatures (59). The results were as follows:

Composition of Layer	Time Required to Remove, Seconds		
	575°C.	550°C.	515°C.
Soot alone	20 → 180	130 → 280	630
Ba and Sr salts			300
Ca and Na salts			230
K and Li salts			170
Na and K sulfates			170

These results have been interpreted by Cassel to be due to the surface roughness rather than to catalytic effects (48). Cassel found that soot deposited on roughened glass surfaces burns much more rapidly than that deposited on smooth surfaces and observed, furthermore, that combustion of such soot layers usually started at, and progressed from, an edge rather than the surface. That the character of the soot surface very materially affects the rate of burning has been previously observed (78).

The work of Day and his associates has been considerably more extensive than the above indicates, and for more than a ten-year period this worker investigated the catalytic combustion of carbon in an effort to elucidate the effect of chemicals claimed to remove soot and to reduce the formation of smoke in the burning of soft coal (60).

Pure carbons were prepared from various sources and by different means. These were mixed with the catalyst being studied, pelleted, and burned in oxygen. The temperatures at which the effluent gases contained 4, 8, and 12 per cent CO_2 were compared to evaluate the effects. With amorphous carbon from acetylene as a basis for comparison, it was found that oxides of boron, titanium, cerium, tungsten, silicon, thorium, zirconium, zinc, tin (ous), strontium, and barium reduced the rate of combustion of carbon, boron causing the greatest reduction and barium the least. Oxides of tin (ic), ytterbium, nickel, bismuth, calcium, antimony, iron (ous), chromium, molybdenum, cadmium, lead, cobalt, copper, zinc plus chromium, manganese, and copper plus chromium increased the rate of oxidation in the order named. The more effective catalysts caused a lowering of the comparative temperature by as much as 90°C., equivalent to an increase in oxidation rate of one to two hundredfold.

The rate of oxidation of amorphous acetylene carbon by air in the temperature range of 200 to 450°C. is greatly increased by the presence of admixed copper chromite or zinc chromite (58). The quantitative increase in oxidation rate was found to be a function of the rate of activated adsorption of oxygen by the chromite. Similar adsorption effects have been observed for ferric oxide and cupric oxide (142).

With reference to the Day results, Fraser points out that nickel has been found to be an effective aid to the combustion of carbon in the form of wood, charcoal, lampblack, etc. (88).

The effect of metallic " impurities " in carbon on the oxidation mechanism has been considered and tested by Lambert (131). The kinetics of carbon oxidation were investigated by a dynamic method in the temperature range of 250 to 500°C. Two processes are considered possible: (A) direct formation of CO_2 by impact of oxygen molecules on the carbon surface, and (B) primary formation of CO and CO_2 by the decomposition of surface oxide complexes. Pure carbon (graphite or diamond) shows only process (A), process (B) occurring only when iron is present. Activated coconut charcoal showed process (A) with a trace of (B), but when activated with ferric chloride showed only process (B). Anthracite containing iron showed only process (B). To a lowering of the stability of the surface complexes by the iron is attributed the basis of the effect. High temperatures show a similar effect and may be the cause for anomalous results reported by previous workers.

Wet oxidation of carbon by solutions of potassium dichromate in syrupy phosphoric acid has been studied as a semi-quantitative measure of the extent of graphitization of carbon (22). The rate of oxidation was found to increase with increase of the temperature at which carbonization had been performed, to be higher for cokes from lower rank coals, and to be higher for highly activated carbons than for cokes or lower activated carbons. These results are felt to substantiate early work that had shown that the accessibility of the interlayer surfaces of the graphite lattice to oxygen might play an important role in the combustion of carbon.

Combustion of Coal and Coke

The belief that the combustion of coal and coke can be improved and that fuel economies can be effected by the use of chemicals has persisted for the past 100 years or more. The patents of the world show many instances of the invention of means for accomplishing these desirable results. Various products have been sold to householders, and chemical treatment of coal has been practiced by coal companies (205).

The Bureau of Mines has completed a comprehensive investigation, extending over a period of years, for the purpose of evaluating the effects of chemicals on the combustion of solid fuels in fuel beds (160, 161). These tests had for their principal purpose the investigation of the effects from treatment of coals but was extended to include cokes because of the importance of coke combustion in the burning of coal in fuel beds. Twenty-five different chemicals, not including their variations with or without water, were used. The fuels used were three high- and one low-temperature cokes and eleven coals with volatile matter ranging from 27 to 46 per cent on a moisture- and ash-free basis. Fuel beds of both overfeed and underfeed types were studied with close control in special furnaces. The proportion of treatment was varied from a light treatment of 4 lb. per ton of fuel to a heavy treatment of 40 lb. per ton in most cases and 20 in others.

The principal chemicals investigated were: sodium chloride, calcium chloride, sodium carbonate, potassium nitrate, potassium chlorate, potassium dichromate, potassium permanganate, sodium silicate, lead salts, copper salts, zinc salts, boric acid, borax, molybdenum oxide. Other chemicals such as zinc sulfide, fluorspar, and nitric and hydrochloric acids were used for special purposes, and water was used as a treatment for comparison.

The results, while showing sufficiently minor effects from the treatments to disprove largely the claims for proprietary compounds, still are of sufficient technical interest to warrant consideration. These results will be considered on the basis of effects segregated according to the factors involved in the combustion of fuels on grates.

Caking. In general, the effect of chemical treatment on the caking of coals was in the direction of improving the combustion. The effect, however, is limited. Caking of coals that have weak caking properties is reduced by this reduction, decreases rapidly as tendency to cake increases, and disappears with strongly caking coals. A thorough wetting of coal with water alone is as effective as any chemical treatment with the exception of sodium carbonate (soda ash), which is somewhat more effective than water when applied at the rate of 20 lb. per ton with 60 to 80 lb. of water per ton. Calcium chloride, boric acid, and molybdenum oxide were roughly equal in effect and rank below water. Sodium chloride was still less effective. Potassium chromate and lead nitrate, while effective, were not thoroughly evaluated to fix their relative values. Nitric acid in heavy treatment amounts was effective and in light amounts with water was somewhat better than water alone. Hydrochloric acid in a heavy treatment was not as effective as light treatments with nitric acid.

Reactivity. Some chemicals " activate " carbon in a way to decrease the temperature at which the coke ignites and to lower the temperature at which carbon dioxide reacts with the carbon to form carbon monoxide. It is thus possible with effective " activation " to increase the rate of burning with the same rate of primary air addition. Such effect, however, is not shown until the fuel-bed temperature is below that at which carbon will react readily without treatment. Thus, activating ability in overfeed tests decreases very rapidly with increase in the rate of burning.

Sodium and potassium carbonate showed the greatest activating ability of the chemicals tried, with molybdenum oxide showing about the same ability on the basis of equal weights of oxides used. Neither calcium nor sodium chloride has much effect. Boric acid and borax decrease the rate of burning, the decrease in rate being more with heavier treatments of boric acid. Other chemicals tried were potassium permanganate, basic copper carbonate, and various mixtures.

With coals, there was no evidence that the treatments influenced the release of volatile matter or rate of burning by any action of the chemicals on the hydrocarbons released; and any increase in burning rate because of activation could not be separated from that resulting from decreased caking. Strongly caking coals, however, showed little increase in burning rate.

Heavy chemical treatments decreased the rate of ignition of both high- and low-temperature coke but did not greatly affect the rate of ignition of coals, because ignition originates with the evolved volatile matter.

Tar and Soot in the Gases. No treatment was found to improve the burning of tar or soot in the fuel bed or in the combustion chamber or to reduce the amount of smoke. It was found, however, that certain volatile chemicals may leave the fuel-bed zone and deposit on soot collected on surfaces beyond the combustion chamber with resultant easier combustion of such soot when oxygen is available. Most effective of such chemicals were the salts of copper, lead, and sodium, particularly when these were used in heavy treatments of the coal.

Ash and Clinkering. In general, the oxides of the metals in the chemicals used for treatment of coal or coke combined with the ash, and, if they functioned as fluxes, increased the clinkering. All the metal oxides of the chemicals used acted as fluxes to increase clinkering except those of silicon, aluminum, and chromium. Since large quantities of silica or alumina are required to affect the fusibility of the ash, no benefits were derived from this source in these tests. Tests with chromium compounds resulted in slags with higher fusion temperatures.

Sulfur. Heavy chemical treatments with calcium compounds were found to increase slightly the amount of sulfur in the slags obtained. Even with heavy lime treatment, however, such increase was not over 3 per cent of the total sulfur in the fuel.

The effective use of water treatment of coal for combustion on grates has been considered by Kuss, with the conclusions that tempering by spraying with water (1) maintains a more uniform size of coal aggregate, (2) prevents exudation of tar, reducing caking, (3) is of value whenever fuel is fed and moved in mass, and (4) requires considerable exposure to water to insure adequate moisture penetration (126).

Practical studies have been made in an effort to decrease the amount of sodium carbonate (about 5 per cent) required for the alkali activation of coke. Experiments at Winnington, England, have shown that by using lime preferentially to neutralize the acidic constituents of the coke ash only small amounts of soda ash are required for activation (20). By using washed coal and treating with 0.5 per cent of sodium carbonate and 1 per cent of lime before coking, a finished coke may be obtained that is satisfactorily free burning.

Although the efficacy of sodium and potassium carbonates in the gasification of solid fuels has been demonstrated and the use of oxygen in continuous gasification tested experimentally, the combination of alkali activation, oxygen, and powdered fuel in the production of fuel gas has only recently been evaluated. The effects of time, temperature, and oxygen concentration were studied by Fleer and White to establish the limiting conditions (85). Powdered coke activated with 5 per cent of sodium carbonate was gasified with steam-oxygen mixtures while falling freely through a steel reaction tube heated to 900 to 1000°C. The steam decomposition rate was independent of oxygen concentration and empirically first order. At 1000°C. practically complete decomposition of steam was obtained with a contact time of approximately five seconds. Equilibrium in the water-gas reaction controlled the CO_2 concentration. Experiments were also made in a fuel bed four feet deep. They indicated that the rate of heat transfer rather than the rate of reaction limited the extent of decomposition of the reactants.

Combustion properties of solid fuels have been tested from a variety of viewpoints. Furnas (89) has proposed a new method for determining coke " reactivity " and shows a means for expressing it in terms of the reaction rate constants for the reactions:

(A) $$C + O_2 = CO_2$$

(B) $$C + CO_2 = 2CO$$

Holmes and Davis (107) have found that ignition temperature and draft requirements of coke increase with carbonizing temperature but bear no consistent and simple relationship to the rank of the originating coal. The ignition temperatures of cokes, as determined in laboratory apparatus with air and with oxygen, have been found to range from 290°C. for low-temperature vertical retort coke to 500°C. for coke oven coke (39).

OXIDATION OF ALCOHOLS

From a study of the oxidation of acetaldehyde to acetic acid, Foster and Keyes (87) direct attention to the catalytic activity of silica catalysts of the xerogel and aerogel type. They have found that silica xerogels and aerogels activated with small quantities of sodium are particularly active. An aerogel catalyst containing 0.19 per cent platinum oxide was the most active of 23 catalysts studied, giving 85 to 90 per cent acid after one passage of oxidizing mixture over the catalyst at 145 to 160°C. Of the silica xerogel catalysts, those heated to 718°C. before use were found to give the best conversions.

The effect of catalyst support on effectiveness has been shown in the use of V_2O_5 catalysts deposited on aluminum balls and on pumice in the oxidation of crotonaldehyde to maleic acid. The greater thermal conductivity of aluminum was found to favor conversion. Thus, with air/aldehyde mole ratios of 300, maximum conversion to acid was 42.2 per cent with the metal support and 31.8 per cent with the pumice support (81). At the highest air ratio tried, 520, the conversion to acid was 44.5 per cent at 450°C.

Ozonization of CH_3CHO, C_2H_5CHO, and C_3H_7CHO, each in water, carbon tetrachloride, and hexane showed a marked increase in the ratio of moles O_2 fixed to the moles O_3 consumed as the series was ascended. Formaldehyde was only slightly attacked either in gas or liquid phase. In carbon tetrachloride most of the oxygen fixed appears as acid, and in hexane as peracid (37).

The oxidation of benzaldehyde and acetaldehyde to the corresponding acids by hydrogen peroxide normally occurs slowly, but the addition of small amounts of selenium oxychloride substantially accelerates the rate (84). Oxidation of alcohols to aldehydes and acids by periodates in the presence of ferrous salts is promoted by the addition of ferric salts (132).

Electrolytic oxidation of butanol in a bath of 10 to 15 per cent sulfuric acid and with lead electrodes yields butyric acid and butyl propionate. Formation of the acid is promoted by a high sulfuric acid to butanol ratio of 11 to 1, whereas formation of ester is promoted by a low acid to alcohol ratio of 5.5 to 1. Yields of 76.8 per cent acid in the first case and 50.3 per cent ester in the latter were reported (187).

Catalysts prepared by treating a copper gauze with a 10 per cent solution of silver nitrate in excess ammonia were found not to be affected by chlorine or sulfur and to be active in promoting the oxidation of alcohols to aldehydes (17).

The results obtained from the carbon dioxide oxidation of isoamyl alcohol to form the corresponding aldehyde and acid with a variety of catalysts have been reported to give the following yields based on the alcohol reacted:

Catalyst	Temperature	Aldehyde	Acid
U_3O_8...........	450°C.	72.9 per cent	12.3 per cent
MoO_3...........	450	59.3	18.2
$Ca(VO_3)_2$........	600	58.6	3.7
$Sn(VO_3)_2$........	450	56	30.4
$MoO_3 + V_2O_5$ ...	400	40.8	37.9
V_2O_5...........	550	chiefly isoamylene	

Isobutanol over MoO_3 catalysts yields chiefly isobutylene at 350 to 500°C. and benzyl alcohol yields 54 per cent benzaldehyde and 32.5 per cent benzoic acid over MoO_3 catalyst at 400°C. (196).

The technique of adding water vapor to mixtures undergoing oxidation has been advocated for purposes of assisting in the control of the temperature of the usually highly exothermic reactions (69, 79). The use of water as a climbing film on the outside of catalyst tubes for cooling has also been suggested (165).

A catalyst specifically directed to use in the oxidation of methanol to formaldehyde comprises an inert, infusible, rigid, porous carrier, such as porous " Alundum " impregnated and coated with a mixture of vanadium oxide and the oxide of another metal of the fifth and sixth periodic group, such as molybdenum. Net yields of 90 per cent formaldehyde on the basis of methanol consumed are claimed with conversions of about 75 parts formaldehyde per 100 parts methanol charged to the converter (186).

The technique for oxidizing unsaturated aliphatic alcohols, other than tertiary carbinols, by the use of oxygen for the formation of aldehydes has been disclosed in the patent literature. Catalysts such as metallic silver, copper, nickel, vanadyl sulfate on silica gel, and activated carbon have been recommended for use in the temperature range of 300 to 500°C. (95, 162).

The oxidation of polyhydric alcohols, such as, 2, 3-butylene glycol, to polycarbonylic compounds of the same carbon and oxygen content may be accomplished by the use of not more than 1 mole of available oxygen per 2 carbinol groups in the presence of a solid catalyst, such as activated copper, at 270°C. (145). Copper is also an effective catalyst in the oxidation of the lower alkyl mono ethers of ethylene glycol to form alkoxyacetaldehyde and alkoxyacetic acid (141).

OXIDATION OF SULFUR DIOXIDE

The principal purpose for oxidizing sulfur dioxide is to manufacture sulfuric acid. Consequently, trends in the sulfuric acid industry with respect to sources of supply of the raw material, new methods of manufacture as applied to new sources of sulfur, and regional distribution of consumption have a bearing on the investigational work having to do with oxidation of sulfur dioxide (125). Recent years have seen the utilization for acid manufacture of the sulfur content of petroleum acid sludges, gypsum, ferrous sulfate, low-grade pyrites, and recovered hydrogen sulfide.

Manufacturing methods and consequently investigational work may be classified according to the catalyst type applied in the oxidation of sulfur dioxide. Broadly, there may be considered: vanadium catalysts, platinum catalysts, and nitrogen oxide catalysts.

Publications of the results of the effect of arsenic poisoning on vanadium catalysts for sulfur dioxide oxidation have been few (164). These results distinguish carefully between arsenic added to the catalyst mass at the time of its preparation and arsenic added in the gas stream. Previous workers have reported that additions of up to 10 per cent arsenic to vanadium pentoxide or copper vanadate catalysts do not affect activity adversely (154). The new results show that all types of vanadium catalysts are affected by arsenic in the gas stream, provided the exposure is for sufficiently long time. The conversion efficiency of such poisoned catalysts can be raised by increase in temperature, but the activity reverts when temperature is again lowered. The addition of barium, as a promoter, to vanadium catalysts does not increase the resistivity to poisoning.

The activity of vanadium pentoxide catalysts poisoned with arsenic trioxide from the gas phase may drop at 435°C. from an initial conversion of 98 per cent to 76 per cent, but may rise to give 90 per cent conversion at temperatures of 500°C. It has been found that the arsenic is retained by the catalyst in the quinquevalent form (199). Considerably longer life may be obtained from such catalysts by the introduction of up to 21 per cent alkali such as potassium or sodium hydroxide.

Additions of alkali metals to vanadium pentoxide catalysts, furthermore, tend to increase the activity. Sodium- and potassium-promoted vanadium pentoxide on diatomaceous earth catalysts gave a maximum activity when about 5 per cent promoter additions were made and showed maximum activity at 450°C. Such catalysts withstand heating to 600°C. without loss in activity (143). Comparison of the promoting actions of silver, barium, aluminum, lead, tin, manganese, sodium, and potassium on vanadium catalysts, determined with a gas mixture containing 7 per cent sulfur dioxide, shows that the alkali metals give the strongest action (144).

Alkali-modified vanadium catalysts containing other elements have been found to be quite effective. Thus, although the alkali vanadates are quite effective catalysts, a composition of $2Na_2O \cdot 3MoO_3 \cdot V_2O_5$ has been found to give even better results with yields of 90 per cent at 425°C. and 96.8 per cent at 500°C. when used in pellet form (46).

The more complex, so-called B.O.V. catalyst, mixture, $K_2O \cdot 2BaO \cdot 8SiO_2 \cdot 2SnO_2 \cdot V_2O_5$, has been reported as more effective yet, not only on the basis of the 95 to 97 per cent conversion to SO_3 at 450°C. but also on the basis of resistance to poisons. The replacement of tin in the above catalyst with aluminum tends to increase the activity (31). Chromium oxide catalysts deposited on porcelain and diluted with tin oxide, barium nitrate, and barium sulfate have been investigated in Russia (10). The method of preparation of the chromium catalysts has been found to be quite critical in determining the activity. Precipitation with ammonium hydroxide from 10 per cent chromium chloride solutions was found to be the most effective preparation. Precipitation by alkali metal hydroxide gave only inactive materials (183).

Mixed oxide preliminary catalysts of the copper oxide-manganese oxide type have been reported very effective as protectors for platinum catalysts against arsenic poisoning. The mechanism of this protection is by the oxidation of volatile As_2O_3 to non-volatile As_2O_5 which remains on the catalyst mass and may be washed off from time to time with caustic alkali solutions. The activity of the copper-manganese combination is increased by additions of cobalt, beryllium, or silicon, beryllium especially increasing the effective life of the catalyst (14).

Catalysis of sulfur dioxide oxidation by ferric oxide has been explained to be via the intermediate $Fe_3(SO_4)_4$ on the basis of results obtained from the thermal dissociation of this sulfate (153).

Mechanism studies of the oxidation of sulfur dioxide over vanadium catalysts show differences from that over platinum catalysts. With either of these catalysts, the conversion first increases with temperature, passes through a maximum at about 420°C., and then declines rapidly. With vanadium catalysts, however, the conversion falls decidedly below equilibrium at temperatures beyond the maximum. Changes in adsorption with temperature are used to explain the effects (49, 50).

The intensive studies that have been made in Russia during recent years have applied not only to the contact methods but also to the nitration or tower methods (198). Studies of the kinetics of sulfur dioxide oxidation by nitrosylsulfuric acid in sulfuric acid solutions show that the initial concentration of nitrous acid has no effect on the rate of oxidation of sulfur dioxide, which is very rapid. The evolution of NO is considered to be the result of secondary reactions and not to constitute the primary reaction (139). There is evolution of both N_2O and NO but not of nitrogen in the reaction. The NO content of the system apparently has no effect on the reaction (1). The mechanism of the reaction between nitric oxide and sulfur dioxide is presumed to be bimolecular, with water vapor playing a role as a homogeneous catalyst (129).

The growth in use of the Gaillard-Parrish system of sulfuric acid manufacture together with various details of the chemical engineering principles, operating methods, and construction technique has been discussed (168). Likewise the economics and operational details of the Mills-Packard, water-cooled chamber system have been explained (80, 93).

Utilization of the sulfur content of wet gases containing hydrogen sulfide for sulfuric acid manufacture by burning to form sulfur dioxide and oxidizing to sulfur trioxide has been made possible by the poisoning resistance of vanadium catalysts. Thus, gases not heretofore believed to be of economic value in this respect have been utilized (124, 223, 228).

The improvement that has been made in platinum catalysts for SO_2 oxidation is shown by the reduction that has been made in the amount of platinum required per ton per day of 100 per cent acid. Modern platinum-asbestos or platinum-magnesium sulfate catalysts require only a third to a half as much catalyst as they required 15 or 20 years ago; and the newer platinum-silica gel catalysts are reported to require only a third as much catalyst as these other improved catalysts (20*b*).

OXIDATION OF AMMONIA

For the purpose of the present discussion the work on the oxidation of ammonia may be considered from the standpoints of mechanism and catalyst nature.

By the use of a molecular beam technique, Bodenstein (23, 24) has been able to arrive at conclusions regarding the nature of the primary intermediate product of the catalytic oxidation of ammonia. The conditions of the experiments were: pressure range of 0.005 to 0.02 mm. mercury, sheet platinum catalyst, catalyst temperatures of 1140°, 1250°, and 1350°C., ammonia to oxygen molecular ratios in the range from 4 : 1 to 1 : 4, and condensing surface cooled with liquid air. Microanalytical procedures were necessary for identification of products.

Analyses showed that the products of the combustion of ammonia under these conditions were hydroxylamine, nitrous acid, and nitrogen, nitrogen being the principal product even when oxygen was present in proportions greater than that normally used in commercial practice. The presence of this amount of nitrogen may be accounted for on the basis of the low pressures used and the consequent low degree of saturation of the platinum surface with oxygen, which permitted ammonia dissociation without oxidation.

Bodenstein concludes from these results that NH_3O is the primary product of the catalytic oxidation of ammonia and that this may in turn react either with ammonia or with oxygen as follows:

$$NH_3 + O = NH_3O$$

$$NH_3O + O_2 = HNO_2 + H_2O$$

$$NH_3O + NH_3 = N_2 + H_2O + 2H_2$$

At low temperatures of about 500°C., with large excess of oxygen, and particularly with oxide types of catalysts, considerable proportions of N_2O may be obtained through the reactions:

$$NH_3O + O = HNO + H_2O$$

$$2HNO = N_2O + H_2O$$

Small amounts of HNO_3 are accounted for on the basis of oxidation reactions:

$$HNO + O_2 = HNO_3$$

$$HNO_2 + O = HNO_3$$

Of the above reactions those involving atomic oxygen must of necessity occur at the catalyst surface, whereas those involving molecular oxygen or molecular ammonia give indications of being homogeneous in nature.

Webb (221), in studying the limited capacity of a platinum catalyst for oxidizing ammonia, set out to determine experimentally whether there was a secondary reaction also catalyzed by platinum and of the same order of rate as the main reaction and also to find an explanation for the apparently anomalous results by a determination of the reaction between NO and NH_3. Webb concluded from his results that reaction between NO and NH_3 catalyzed by platinum was probably responsible for the loss of fixed nitrogen other than that lost by purely thermal decompositions not necessarily catalyzed by platinum. Increased depth of catalyst caused increased nitrogen losses, and oxygen in excess of theoretical decreased the loss of fixed nitrogen.

The parabolic region of inflammation of ammonia-nitrogen-hydrogen mixtures with air at temperatures from 20 to 700°C. has been explored (206). The limits of concentrations for explosion are 5 to 90 per cent for $(3H_2 + N_2)$ plus O_2, 6 to 87 per cent for $(3H_2 + N_2)$ plus air, and 10 to 80 per cent for NH_3 plus O_2. The temperature of self-inflammation of the first mixture is 440°C., of the second 350°C., and of the third 700°C. The temperature of self-inflammation does not vary with the percentage content of the combustible gas. A linear relationship holds between the minimum pressure and the initial temperature for explosion.

The corrosion of platinum gauze catalysts during the oxidation of ammonia by oxygen has been attributed to the formation of hydrogen which dissolves in the platinum and increases the mobility of the elements of the crystal lattice (2, 8). This causes volatilization of platinum at temperatures above 750°C. and changes the surface structure. Platinum oxide plays no part in the catalytic action but the alternating oxidation and reduction of the surface breaks up the surface to give a more active catalyst. Platinum loss is a secondary phenomenon.

Analysis of nitric acid from ammonia oxidation has shown platinum particles of colloidal size of sufficiently irregular shape to indicate that mechanical causes are involved in the deterioration of a platinum gauze catalyst (3, 82). To the presence of dust and the high velocity of gases over the surface are attributed the losses from platinum gauze.

A critical review and tests of various suggested methods have indicated that the most satisfactory means of preventing this corrosion and loss is the use of an alloy of 90 per cent platinum and 10 per cent rhodium as a catalyst (4). It had been shown previously that the use of nickel catalysts or nickel support for the platinum catalyst resulted in breakdown of the nickel structure by hydrogen penetration (12).

A study of the catalytic effects of the surfaces of molten metals on ammonia oxidation has shown the difficulties involved (9). Tin forms the solid oxide below its melting point, but the oxide functions as a catalyst for the oxidation, confirming previous work. Solid silver functions as an oxidation catalyst with slowly increasing activity as the temperature is raised to near the melting point. Just short of the melting point of silver (about 850°) the oxidation rate drops abruptly, and the catalyst temperature tends to rise sharply, indicative of a change of mechanism. This has been interpreted to be a change from the oxidation of ammonia to the decomposition of ammonia to nitrogen and the oxidation of hydrogen to water, a reaction occurring with greater net heat evolution than oxidation to NO and water.

The composition of products (NO, N_2O, N_2) from the oxidation of ammonia at 450 to 750°C. in the presence of platinum deposited on sulfates of Be, Mg, Ca, Sr, and Ba has been used as a basis for mechanism interpretation (13). By changes in the catalyst carrier the relative proportions of NO and N_2 in the product may be regulated, the amount of NO increasing linearly with temperature and in the order of increasing atomic radius. In the absence of sufficient oxygen, only decomposition to hydrogen and nitrogen occurs.

Platinum-rhodium alloys in various forms have been patented for ammonia oxidation (72, 163, 222).

Various modifications of the pure platinum catalysts have been studied by the Russian workers. A gauze of platinum alloy containing 3 per cent of tungsten is twice as active as the usual platinum gauze at 750°C. (5). Three component alloys, as 92 per cent platinum, 5 per cent rhodium, and 3 per cent tungsten, are reported to give 97 to 98 per cent oxidation of ammonia at 750°C. and to be much more stable to losses (11). The increased stability may be attributed to the non-absorption of hydrogen by rhodium and tungsten. Platinum-silver alloys also do not absorb hydrogen and are very stable as ammonia oxidation catalysts. An alloy of 90 per cent platinum and 10 per cent silver gives 87.9 per cent oxidation at 946°C. (7). Increasing ratios of silver give progressively poorer catalysts. An alloy of 80 per cent platinum, 10 per cent rhodium, and 10 per cent silver has been found to be stable and to give 95.7 per cent conversion of a 10.5 per cent ammonia-air mixture at 935°C.

Oxidation of ammonia with oxygen over a platinum-tungsten gauze showed the best reagent mixture to be: ammonia 15 parts, oxygen 30 parts, and water vapor 55 parts by volume (6, 211). At reaction temperatures below 1000°C. the yield was 34 per cent nitrogen oxides. Platinum losses were 5 to 8 times as great as in oxidation with air.

The catalytic action of rhenium toward oxidation at high temperatures is hindered by formation of highly volatile oxides (18). Cathode-deposited platinum or platinum-rhodium catalysts were found to be unsatisfactory because of cracking and flaking of the active material (122).

An 81 to 88 per cent yield of N_2O is obtained with manganese catalysts containing iron or bismuth with most of the remaining ammonia going to nitrogen (182).

Cobalt shows activity as a catalyst for ammonia oxidation (83) and may be used advantageously in conjunction with rhodium for alloying with platinum to produce catalytic material (105).

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CHAPTER XV

CATALYSIS IN POLYMERIZATION*

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In the space of a few years polymerization has grown from a reaction type receiving but brief treatment in organic textbooks to one standing very high in the interests of chemists, particularly those in industrial fields. Polymerization offers a prospective tool for synthesizing various products superior to natural ones, a result which already has been achieved in the case of rubber, gasoline, lubricating oil, and resins.

The subject as a whole has been reviewed by Burk, Thompson, Weith, and Williams (7) and special fields of application have been reviewed, sometimes in great detail, by Ellis (35), (resins), by Egloff (34), (hydrocarbons), by Morrell, Barry, Britton, and Langton (72), (resins), by Veldman (100), by Karo (56), (resins), by Kränzlein and Lepsius (59), by Brandenburger (6), (resins), by Tschirck and Stock (94), (resins), by Ulmann (98), (determination of molecular weights of high polymers).

In addition to these, several books have appeared bearing upon polymerization in the paint industry. A number of papers on the subject of polymerization appear in the Transactions of the Faraday Society for 1936.

Many books have appeared in the field of rubber, some of which should be mentioned in connection with the subject of polymerization and polymers. Among these are the works of Freundlich (38), Naunton (76), Nielsen (77), Davis and Blake (25), Memmler (68), Dawson and Porritt (26).

There is little doubt but that more cases of polymerization proceed under the influence of catalysts than has been realized by some workers. This is due in part to the widespread catalytic action of oxygen and certain oxidation products, viz., peroxides and peracids, in the polymerization of unsaturated compounds. As far as the writer is aware, nearly all technical polymerizations proceed under the influence of catalysts. Styrene polymerizes in the apparent absence of catalysts but this material is very sensitive to catalytic polymerization by peroxides, ozonides, and the like (46, 70, 75), and one is not sure at the moment if

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* Contribution from the Graduate School, Western Reserve University.

it will polymerize in their complete absence (91). The near universality of catalytic action in polymerization renders nearly the whole of the literature relevant to a discussion of catalysis in relation to polymerization.

Some 1500 examples of polymerization catalysts are summarized in Table I.

Both condensation and addition types of polymerization are included in the table. These types, of course, have little in common except that both lead to what we must call polymers, sometimes polymers of the same general structure. Condensation polymerizations are generally catalyzed by acids or bases. It is not necessary to consider in detail, at this point, the action of such catalysts, since the individual steps in condensation-type polymerizations are often instances of conventional reactions such as esterification. The effect of acid and basic catalysts in phenol-aldehyde and urea-aldehyde condensations has been summarized by Weith (103). In spite of the chemical differences between condensation- and addition-type polymerizations, acidic and basic catalysts can accelerate both types. While vinyl polymerizations are not reported to be accelerated by inorganic bases, such catalysts are effective in catalyzing the addition type of polymerization in the case of aldehydes (62).

Nitrogen bases are recognized catalysts in such reactions as phenol-aldehyde condensations. When hexamethylenetetramine is used for such a purpose, however, the methylene groups are desired as reactants as well as the catalytic effect of the ammonia. The position of nitrogen bases as catalysts for addition-type polymerizations is confusing as judged from patent literature. They are sometimes claimed as catalysts for the polymerization of some of the more sensitive compounds, but are also claimed as inhibitors for the polymerization of similar compounds. Some of the nitrogen bases certainly possess inhibiting power (17).

Certain of the catalysts are somewhat restricted in their use if not in their power. Copper appears to be effective mainly for polymerizing acetylene. The alkali and alkaline-earth metals are used largely for polymerizing diolefins and are thought to be used on a large scale in this type of polymerization. They are also effective for certain phenyl substituted olefins (8). However, isobutylene is not polymerized by sodium (60), though it will cross polymerize with butadiene-1, 3 when catalyzed by sodium, and is very sensitive to the catalytic effect of acids and halides.

Since there is evidence (1) that the alkali metals, in catalyzing the polymerization of dienes, form definite organometallic intermediate compounds, it is not surprising to see organometallic compounds them-

TABLE I

SUMMARY OF CATALYST TYPES WHICH HAVE BEEN FOUND EFFECTIVE FOR POLYMERIZATION

Type of Compound	Literature Prior to 1936	1936 Literature	1937 Literature	Total
Halides	153	66	87	306
Aluminum halides	60	17	28	105
Boron halides	25	16	13	54
Zinc halides	28	7	9	44
Tin halides	15	5	7	27
Copper halides	12	9	3	24
Iron halides	3	4	5	12
Antimony halides	5	1	1	7
Titanium halides	3	...	3	6
Halides, general	...	...	4	4
Magnesium chloride	1	1	2	4
Bismuth halides	...	...	3	3
Oxyhalides of phosphorus	...	2	1	3
Mercury halides	...	...	2	2
Organic halides	1	...	1	2
Potassium chloride	1	...	1	2
Tantalum halides	...	1	1	2
Arsenic halides	...	...	1	1
Beryllium halides	...	...	1	1
Cobalt halides	...	1	...	1
Columbium halides	...	...	1	1
Thionyl chloride	...	1	...	1
Tungsten halides	...	1	...	1
Zirconium halides	...	...	1	1
Acids	149	82	55	286
Sulfuric acid	51	20	15	86
Acids, general	39	19	6	64
Hydrochloric acid	28	13	9	50
Acids of phosphorus	12	25	9	46
Acetic acid	8	3	3	14
Hydrofluoric	4	1	...	5
Nitric acid	4	1	...	5
Boric acid	...	...	4	4
Formic acid	3	...	...	3
Oxalic acid	...	...	3	3
Sulfonic acids	...	...	3	3
Borofluoacetic acid	...	...	1	1
Chloracetic acid	...	...	1	1
Malic acid	...	...	1	1
Metals	208	25	25	258
Alkali metals	65	3	6	74
Alkaline-earth metals	24	...	...	24
Copper	19	...	3	22
Nickel	17	1	1	19
Iron	15	2	1	18
Platinum	11	...	1	12
Aluminum	8	1	2	11
Cobalt	5	2	3	10
Zinc	5	2	2	9
Tin	6	1	1	8
Magnesium	4	2	...	6

Type of Compound	Literature Prior to 1936	1936 Literature	1937 Literature	Total
Metals (continued)				
Silicon	5	1	...	6
Silver	3	1	2	6
Chromium	2	2	...	4
Manganese	2	2	...	4
Mercury (in u.v. light)	4	...	...	4
Palladium	4	...	...	4
Gold	1	1	1	3
Lead	2	1	...	3
Molybdenum	...	2	1	3
Tungsten	1	1	...	2
Bismuth	1	...	...	1
Cadmium	...	...	1	1
Iridium	1	...	...	1
Tantalum	1	...	...	1
Thallium	1	...	...	1
Titanium	1	...	...	1
Oxidizing agents	92	40	45	177
Peroxides	53	22	33	108
Oxygen	22	6	12	40
Oxidizing agents (general)	6	9	...	15
Ozone or ozonides	6	2	...	8
Ozone	3	...	...	3
Per salts	2	1	...	6
Oxides	48	15	23	86
Silica	12	2	5	19
Alumina	8	2	3	13
Other oxides	3	3	4	10
Copper oxides	6	...	1	7
Phosphorus pentoxide	1	4	1	6
Calcium oxide	...	...	5	5
Iron oxides	4	...	1	5
Zinc oxide	3	1	1	5
Alkaline-earth oxides	2	2	...	4
Manganese oxides	4	...	...	4
Molybdenum oxides	4	...	...	4
Lead oxide	2	...	...	2
Chromium oxides	...	...	1	1
Titania	...	...	1	1
Nitrogen bases	25	9	14	48
Clays	27	8	11	46
Alkalis (see also hydroxides)	17	8	15	40
Hydroxides (alkali)	24	7	9	40
Carbon	24	2	1	27
Organometallic compounds	10	1	...	11
Hydroxides (alkaline earth)	7	1	...	8
Soaps	6	1	1	8
Other classifications	70	20	47	137
(Less than five examples of each)	...	...	...	1480

For original references used in this table, see "Polymerization" (7), Chapter III, and future revisions thereof. References to seemingly unsupported statements in discussing the table will be found there.

selves claimed in nearly a dozen instances as catalysts for conjugated diene polymerization. That they are important technically in comparison with, e.g., Na, is doubtful.

While carbon, e.g., activated charcoal, has been claimed in twenty-seven instances to be a polymerization catalyst, the suggested temperatures are high and in all probability carbon has little activity. The catalytic dehydrogenating activity of carbon may assist in the formation of liquid aromatic hydrocarbons, e.g., from ethylene at elevated temperatures. It is plain from Table I that carbon is seldom proposed as a polymerization catalyst in the recent literature.

The only metals which appear to possess important catalytic power in polymerization are alkali metals and copper, whose fields are described above. Alkaline-earth metals are mentioned in some sixteen patents as the equivalent of alkali metals, but the writer has been unable to learn of any technical practice built upon this feature of the patents.

Such metals as cobalt, iron, nickel, and platinum have been mentioned rather frequently. They have, of course, an established reputation as hydrogenation-dehydrogenation catalysts which, as in the case of carbon, could aid in some polymerizations. Chromium, manganese, molybdenum, silver, silicon, tin, and zinc have each been proposed a few times as polymerization catalysts. Many of the proposed applications of these catalysts concern the polymerization of acetylene to liquid hydrocarbons, a process which appears to be in reverse, economically. There is apparently no technically important application of the metals mentioned in this paragraph as polymerization catalysts unless the definition of polymerization is stretched to include the Fischer-Tropsch synthesis of hydrocarbons.

Oxidizing agents constitute a class of polymerization catalysts of great interest. The term oxidizing agents includes free oxygen, ozone, the oxidation products of unsaturated organic compounds sometimes of unknown structure, organic and inorganic peroxides, ozonides, inorganic nitrates, etc. Their action is so widespread in the fields of diolefin and vinyl polymerizations that one must consider them guilty of activity unless proved to be innocent. In the case of the photopolymerization of vinyl acetate, oxygen is an inhibitor (89) but it has a positive catalytic effect on the thermal polymerization of this compound. The latter is representative of its usual behavior with vinyl and diolefin polymerizations in the liquid phase. Oxygen is without action on the gas-phase polymerization of some diolefins (44, 99).

The action of such commonly present catalysts is of great interest, and is no doubt related to that of consciously added oxidizing agents in technically important polymerization processes. Thus peroxides, commonly benzoyl peroxide, are mentioned as effective catalysts in much of the patent literature on the polymerization of vinyl compounds such as vinyl chloride, vinyl acetate, methyl methacrylate, and the like (2, 24, 81).

Oxygen has been suggested (9) more than once as a catalyst for the polymerization of gaseous olefins to, e.g., motor fuel. While oxygen has an undoubted action in this direction, it has not achieved technical importance for the purpose.

The reaction between sulfur dioxide and olefins forms resins with a polysulfone structure (40, 84). The reaction is catalyzed by oxidizing agents.

Clays have a wide use in the petroleum industry as polymerization catalysts. They are nearly universally used in refining lubricating oils but also have a considerable application in refining gasoline and other products (10). The complex composition of these contacts renders the chemical knowledge of their action indefinite. This uncertainty is sometimes increased by activation with acids, which catalyze various reactions on their own account (39).

Both alumina and silica have activity in polymerizing olefins at elevated temperatures. Gayer (39) found alumina deposited on silica to have marked activity for the polymerization of propylene to motor fuel at about 350°C. Phosphorus pentoxide has achieved some prominence in polymerizing olefins to motor fuel (27, 61, 93), and in alkylating with them. Here it is possible that acids of phosphorus covering the surface of the P_2O_5 particles provide the whole of the action.

Copper oxide appears to act similarly to copper in the polymerization of acetylene to cuprene (12, 41). There does not appear to be any established practice based upon the catalytic polymerizing power of any other single oxide.

Acids have wide application as polymerization catalysts, and are their most versatile class. Not only do they have an important application in condensation polymerizations such as the aldehyde-phenol and aldehyde-urea condensations (11) but are also widely applicable and extensively used in addition polymerizations.

The use of sulfuric acid as a refining agent, particularly for petroleum fractions, is an old art. The complex action here is not solely that of a polymerization catalyst (55) but this is certainly involved. This acid has been applied more recently in the petroleum industry for the polymerization of isobutylene and for the cross polymerization of isobutylene with normal butylene (65) to give octenes and 12 carbon atom olefins. These are then hydrogenated to give motor fuels of exceptional quality. Sulfuric acid may be used in indene or coumarone polymerization (86).

Attention should be drawn to an important application of phosphoric acid, the ortho acid in particular, as a catalyst for the polymerization of gaseous olefins to motor fuel (10, 31, 33, 50, 51, 52, 53, 54). The process appears to be most useful for propylene and butylenes. In this instance, the temperature used is about 200°C., and the pressure about 14.6 atm. There is some modification of these conditions when isobutylene is the olefin polymerized.

Hydrochloric acid has been proposed frequently as a catalyst for certain condensation polymerizations but appears to have no powerful action in polymerizing olefins or vinyl compounds (101).

Acetic acid, on the other hand, is reported to polymerize conjugated dienes (45, 102).

No other acid has an established reputation as a polymerization catalyst.

It will be noted from Table I that certain halides now constitute the most frequently proposed group of polymerization catalysts. Nevertheless, while zinc chloride has been proposed as a catalyst for the urea-formaldehyde condensation, the important use of halides appears to be limited to the polymerization of olefins, vinyl compounds, and conjugated diolefins.

They are powerful polymerization catalysts. Among the more interesting applications, isobutylene has been polymerized by boron fluoride to a rubbery material which, when dissolved in lubricating oil, will impart desirable viscosity-temperature characteristics (47, 73). A varnish resin has been made by polymerizing olefins and diolefins in a specially cracked gasoline using aluminum chloride as the catalyst (90). Lubricating oils of high quality have been synthesized (43, 74, 87). Commercial resins have been produced by combining olefin dihalides with aromatic rings, using aluminum chloride as a catalyst (5, 82, 92).

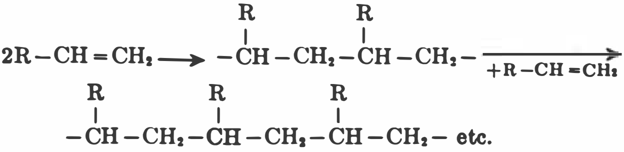
Cuprous chloride appears to be the commercial catalyst used to dimerize acetylene to vinyl acetylene (14, 19, 21, 32, 48, 57, 95, 96, 97), the first step in making 2-chlorobutadiene-1, 3, which in turn is readily polymerized to an excellent rubber. Both solid cuprous chloride and aqueous solutions of it have been proposed for the process, but the latter is thought to be better established in practice.

MECHANISMS OF CATALYTIC POLYMERIZATIONS

There is no particular reason to think that all catalytic polymerizations, even in the case of addition polymerizations, should proceed by the same mechanism.

Taylor and Jones (88) and others (23) have found that decomposing metal alkyls will polymerize olefins. This is interpreted as indicating that free radicals are formed in the decomposition of the metal alkyl which set up a material chain reaction. Hall and Nash (42) have shown that the catalytic polymerizing action of aluminum chloride in the presence of metallic aluminum differs from that of aluminum chloride in the absence of aluminum. Ethylene under pressure at temperatures above 100°C. reacts with aluminum chloride and aluminum to form aluminum ethyl dichloride and aluminum diethyl chloride. They suggest that these decompose to set up a mechanism similar to that of Taylor and Jones for the polymerization of ethylene under these conditions.

While the free-radical nature of the above cases of polymerization seems reasonable, there is a much-publicized view that addition-type polymerizations in general proceed through such mechanisms (15). These may be represented by



$$2\mathrm{R{-}CH{=}CH_2} \longrightarrow -\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{CH_2}-\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{CH_2}- \xrightarrow[+\mathrm{R{-}CH{=}CH_2}]{}$$

$$-\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{CH_2}-\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{CH_2}-\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{CH_2}-\ \text{etc.}$$

where the growing polymer is a free radical. If this were true it would be necessary to conclude that all polymerization catalysts merely initiate such chain reactions, and this is doubtful. While this is a plausible mechanism when the catalyst is a decomposing metal alkyl, the general free-radical mechanism of polymerization has not been established experimentally. Theorists who developed this mechanism differ in their assumptions relative to the component parts of the theory and with respect to the interpretation of the influence of various factors such as solvents and temperature upon polymerization (15, 28, 29, 30, 36, 63, 64, 79, 80). A more detailed discussion of these differences will be found in a paper by the writer (7*a*).

Some authors have been induced to subscribe to such a mechanism because (*a*) the probability distribution of polymer sizes which one would expect on the basis of an uncatalyzed homogeneous reaction does not exist with many liquid-phase, addition-type polymerizations (22), and (*b*) polymers of high and nearly constant molecular weight are often formed during a large change in the fraction polymerized in such cases (85). These phenomena have, however, another possible explanation.

The most charitable thing which could be said of the view that polymerization catalysts merely generate free radicals, e.g., in such cases as the polymerization of olefins by acids, is that it has yet to be demonstrated. It has been favored by Bergmann (3) for the sodium-catalyzed polymerization of butadiene, but opposed by Medvedev (66), who with

Abkin has carried out an experimental investigation of the mechanism of this reaction. According to Abkin and Medvedev, the mechanism is as follows:

$$H_2C=CH-CH=CH_2 + 2Na \longrightarrow NaCH_2-CH=CH-CH_2Na \xrightarrow[+H_2C=CH-CH=CH_2]{} NaCH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2Na, \text{ etc.}$$

The reaction could be interrupted for long periods without altering the kinetics in any marked way. Such a mechanism for this type of catalytic polymerization is confirmed by Ziegler (106) for the polymerization of 2, 3-dimethylbutadiene by lithium and is supported by a vast amount of experimental material which he has brought forward (16). In view of the catalytic nature of most polymerization reactions it is interesting to see if such a mechanism has general application. The general scheme for what may be called the catalytic-molecular, as distinct from the radical, theory may be represented as follows:

$$\text{Unsaturated compound} + \text{catalyst} \longrightarrow \underset{\text{(or complex)}}{\text{intermediate compound}} \xrightarrow[+\text{ unsaturated compound}]{} \text{dimer-catalyst compound or complex, etc.}$$

One's interest in this theory is increased by the existence of some phenomena in polymerization which seem difficult to explain by a free-radical mechanism. Thus:

1. Some of the compounds most sensitive to polymerization in the liquid phase, e.g., styrene and ketene, do not polymerize at higher temperatures in the vapor phase (at pressures in the vicinity of atmospheric). Harkness, Kistiakowsky, and Mears (44) found styrene vapor to be stable to polymerization up to its decomposition point. (420°C. at the reaction time used. Pressure was somewhat less than atmospheric.) Vinyl acetate and methyl acetylene were found by the same authors to behave similarly.

Again, Williamson (105) found ketene vapor to be stable up to about 530°C. Then decomposition products only were obtained. These substances in the vapor phase are thus scarcely more prone to polymerize than ethylene, whereas in the liquid phase, unlike ethylene they cannot be stored, unless inhibited, on account of their pronounced tendency to polymerize. No reason is apparent why free radicals should be formed in the low-temperature, liquid-phase reactions, but not at the high temperatures. Some of the strongest evidence for their existence is obtained at temperatures even higher than those mentioned above (78).

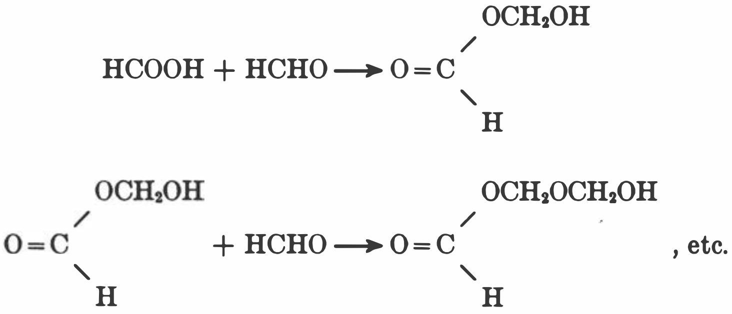
2. Some vinyl polymerizations are inhibited by the presence of other unsaturated compounds. Thus Snow and Frey (84) find that the

reaction of sulfur dioxide with butene-1 is inhibited by the presence of isobutylene. There are other instances of such inhibition. According to free-radical theories the radical polymer would react with the inhibiting olefin to form another radical. The reaction of a radical with an olefin is commonly associated with an activation energy of about 5000 calories by free-radical theorists (37). Therefore, the new radical would react in a polymerizing sense disposing of the inhibiting olefin molecule in not more than $<10^{-6}$ A second at 100°C., and one atmosphere pressure with styrene vapor. Here A is a possible steric factor. The mean life of such a radical in the liquid phase would of course be much less.

On the catalytic theory the necessary assumption to account for inhibition by an unsaturated molecule would be that the intermediate, formed with the inhibiting molecule and the catalyst complex already existing, is not capable of further rapid reaction. This too may be untrue, but since it is a new chemical compound there is no *a priori* reason for casting the assumption aside, as there is in the case of the radical theory.

Aside from these two phenomena, the free-radical and catalytic-molecular theories of polymerization appear to be parallel, and to account for the general observations in the field. Some additional cases of the catalytic-molecular theory of polymerization have been found.

Carruthers and Norrish (20) have suggested a mechanism of this type to explain their data on the catalysis of formaldehyde polymerization by formic acid, thus:

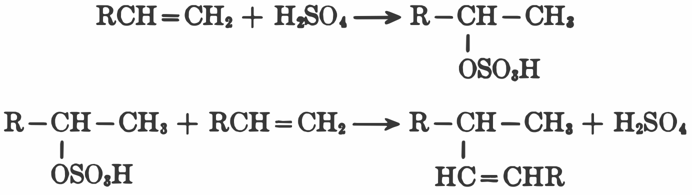


$$HCOOH + HCHO \longrightarrow O{=}C\begin{matrix} \diagup OCH_2OH \\ \diagdown H \end{matrix}$$

$$O{=}C\begin{matrix} \diagup OCH_2OH \\ \diagdown H \end{matrix} + HCHO \longrightarrow O{=}C\begin{matrix} \diagup OCH_2OCH_2OH \\ \diagdown H \end{matrix}, \text{ etc.}$$

Melville (67) concluded that the best explanation of his experiments on the polymerization of acetylene photosensitized by mercury was through the formation of a mercury-acetylene complex. This complex adds further acetylene to produce a polymer whose growth is stopped by a collision of another kind.

A catalytic-molecular mechanism was also proposed by Berthelot (4) and later by Butlerow (18) for the polymerization of olefins with acids as catalysts. Thus:



$$\mathrm{RCH{=}CH_2 + H_2SO_4 \longrightarrow R{-}\underset{\substack{|\\ OSO_3H}}{CH}{-}CH_3}$$

$$\mathrm{R{-}\underset{\substack{|\\ OSO_3H}}{CH}{-}CH_3 + RCH{=}CH_2 \longrightarrow R{-}\underset{\substack{|\\ HC{=}CHR}}{CH}{-}CH_3 + H_2SO_4}$$

This mechanism may be extended by assuming that the acid need not be split off at the dimer stage. With this revision, the mechanism is capable of explaining the peculiar character of some instances of polymer growth formerly explained by the free-radical theory (p. 187). The extent of growth of the polymer-catalyst complex would be determined in part by its mean life and this would be expected to vary from case to case and under different conditions.

Monroe and Gilliland (71) have studied the kinetics of the polymerization of propylene with aqueous phosphoric acid and have concluded that the Berthelot mechanism is supported.

But other mechanisms have been suggested for acid-catalyzed olefin polymerizations. Thus Ipatieff (49) in interpreting his work on the polymerization of olefins with phosphoric acid has introduced evidence that the monoester of phosphoric acid is first formed, but he thinks that the formation of the dimer is the result of thermal decomposition of two molecules of ester. The evidence he brought forward to support his mechanism consisted of showing (*a*) that the monoalkyl ester was formed in the reaction of an olefin (e.g., ethylene) with orthophosphoric acid and (*b*) that this ester on further heating reacted to give a polymer layer and a phosphoric-acid layer.

Whitmore (104) has suggested that in the acid catalysis of olefin polymerization the hydrogen ion of the acid adds to the double bond of the olefin. This complex then is thought to display the behavior which would be expected of a compound containing a carbon atom with only six electrons. While the theory can account for some experimental results and has a certain appeal due to its flexibility, its application in the case where anhydrous acids are used as polymerization catalysts is not so clear. Furthermore, it is odd that this free-radical theory should be advanced to explain the dimerization of isobutylene by sulfuric acid, whereas according to the free-radical theorists mentioned above free radicals proceed with great speed to high-molecular-weight polymers (or they cyclicize).

Kline and Drake (58) do not accept prior mechanisms for acid catalysis of polymerization and suggest one of their own. They propose that the olefins are activated so as to behave as two fragments, which then add to the double bond of another olefin, in accordance with the directive influence of the relative negativities of the bond and fragments.

The latest addition to this family of theories is that of Schmitz-Dumont, Hamann, and Diebold (83), who suggest an activation of the olefin by means of hydrogen ions followed by combination of two activated molecules. Thus:

$$\text{Olefin} + H^+ \longrightarrow (\text{olefin} + H^+)\ \text{complex} \longleftrightarrow H^+ + \text{olefin}^*$$

$$2\ \text{olefin}^* \longrightarrow \text{dimer}$$

The nature of the activation was left open.

Michael (69) had suggested that sulfuric acid in catalyzing the polymerization of isobutylene produced free radicals in the sense

$$(H_3C)_2\underset{\substack{|\\ OSO_3H}}{C}-CH_3 \longrightarrow H_2SO_4 + (H_3C)_2\underset{|}{C}-\underset{|}{CH_2}$$

but it would not be necessary for two such free-radical intermediates to react with each other in the sense of Schmitz-Dumont, Hamann, and Diebold, even if one were to grant the existence of such free radicals in these cases.

The light which the structure of the dimers would be expected to throw on these mechanisms is clouded by the occurrence of H shifts and also carbon skeleton rearrangements. While the former can be accounted for by the addition and splitting off of acid, the mechanism of the carbon skeleton rearrangements is not so evident. Moreover, the latter isomerization does not always occur.

The acid catalysis of olefin polymerization is of interest not only on its own account but also because of the possibility that halide catalysis of polymerization can be similarly interpreted. It has now been well established that the presence of hydrohalogen acid* is necessary for the conventional catalytic actions of aluminum halides. Since the formation of organo-aluminum halides appears to occur only with metallic aluminum present, it would seem that the catalytic action of aluminum chloride in the presence of metallic aluminum is different, or involves a factor which is different, from the usual action where there is no metallic aluminum but where hydrohalogen acid is present.

While there is little direct evidence for it, one is tempted to suppose

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* Chapter XIX of this report.

that the HA (where A = halogen) adds, e.g., to the AlA_3 to give an acid $HAlA_4$, which then acts as certain other acids do in catalyzing polymerizations. HBA_4 is, of course, a known example of such an acid. While there is a general similarity in the catalytic action of halides such as $AlCl_3$, $AlBr_3$, BF_3, etc., and acids such as H_2SO_4, H_3PO_4, i.e., both will catalyze polymerizations, alkylations, rearrangements, and to a less prominent degree, hydrogenations and dehydrogenations, the evidence that the mechanism of halide and acid catalytic action is the same is at present inferential. If the modified Berthelot mechanism of polymerization catalysis is correct, such reactions are formally similar to alkylations. The fact that the same catalysts are effective for both polymerizations and alkylations adds plausibility to the Berthelot type of mechanism. Whether the polymerizing action of such materials as clays and silica is also to be attributed to the acid reaction of these materials is an open question. This possibility also sustains interest in the true mechanism of the acid catalysis of polymerization reactions.

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CHAPTER XVI

RETARDATION OF CHEMICAL REACTIONS

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We should first consider what is meant by " retardation of a chemical reaction " since this term has never been strictly defined and different writers regard it from different viewpoints. Probably most cases of so-called retardation or inhibition of a reaction can be explained by one or the other of the following three mechanisms.

1. Removal from the reactants of a positive catalyst whose existence has previously been unrecognized. Examples are to be found in familiar reactions of oxidation and polymerization. This is strictly not a case of inhibition but is often regarded as such.
2. Addition to the reactants of a negative catalyst. It is tacitly assumed in such cases that the reactants will react except for the presence of the negative catalyst. It is unnecessary to specify the precise mechanism of such negative catalyst; no doubt there are different mechanisms.
3. The addition of a " poison " to a positive catalyst which is either unrecognized or unavoidably present. The effect of the retarder or inhibitor is then simply to neutralize the effect of the positive catalyst.

Lacking full knowledge, we may regard retardation due to one of these causes as due to another, and it can be correctly understood only after more meticulous work and the determination of more accurate data. According to this view, a large number of influences may be described tentatively and correctly as retardation pending more precise understanding of the true mechanism. As they become understood some of them become classifiable under headings 1 or 3, in which event they cease to be strictly retardation, leaving as genuine examples of retardation only cases under heading 2. In this latter classification undoubtedly many cases must yet be listed which eventually will prove to be examples of 1 or 3.

Schwab (54) has suggested a logical method of classifying catalytic reactions by considering the relation of the phase of the catalyst to that of the substrate.* Following his classification, we may consider all catalytic reactions as either homogeneous, heterogeneous, or microheterogeneous. Homogeneous catalysis includes all cases of catalysis in which the catalyst and the substrate are present in the same phase. In heterogeneous catalysis, the catalyst is present in a phase different from that of the substrate. Microheterogeneous catalysis includes those cases in which the phase difference between the catalysts and the substrate is not sharp, i.e., dispersed systems. It is of course possible that each of the above types of catalysis is subject to retardation; however, true cases of poisoning of homogeneous catalysts are rare. Retardation of the other two types of catalysis is well known; and much attention has been given in the past to the factors causing a decrease in activity of heterogeneous catalysts.

Retardation of Catalyzed Reactions

In order to comprehend fully the factors arising in the retardation of catalyzed reactions it will be helpful to consider first some of the basic concepts of what constitutes catalytic structure as such. A decrease in activity of a heterogeneous catalyst may take place either through physical and chemical changes in the structure of the catalyst or through the action of the substrate on the catalyst. Loss of activity of a catalyst due to changes in its structure is encountered often in the heterogeneous catalysis of gaseous reactions, which are usually carried out at relatively high temperatures. The more drastic conditions of such reactions cause a number of adverse effects, of which sintering is the most common. By the term sintering is meant the recrystallization of small particles of the catalyst to form coarser, less active particles at temperatures well below the fusion point of the catalyst. Other changes in the structure of the catalyst are observed when the catalyst mass consists of more than one substance, that is, catalysts supported on non-reactive substances, catalysts to which promoters have been added, and two or more component catalysts. Such catalysts may lose their activity through chemical changes taking place in the catalyst mass. Adadurov (1) recently investigated the changes which take place in vanadium-barium zeolite catalysts for the oxidation of sulfur dioxide to the trioxide and concluded that the decreased activity of the catalyst in the absence of poisons was caused not only by the adsorption of sulfur trioxide but also by the gradual decomposition of the catalyst with the separation of vanadium pentoxide, silicon dioxide, barium oxide, and alkali oxides. With two component catalysts, reactions between the components

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* The initial reactants in a catalytic reaction are called the substrate.

sometimes occur with the production of a third compound which is inactive. With alloy catalysts changes in the metallic mixed crystals influence the activity of the catalyst. Rienacker (53) investigated the factors influencing the activity of alloy catalysts and found that the internal atom arrangement influences the surface and therefore the activity of the catalyst.

The susceptibility of a catalyst toward structural changes may be reduced in certain instances by changing the composition of the catalyst mass. Kingman (33) has reported that with molybdenum catalysts the ordinary conditions of hydrogenation are such that the molybdenum trisulfide is converted to molybdenum disulfide and the catalyst becomes more crystalline and loses activity. The addition of ammonium phosphomolybdate was found to prevent this action. Furthermore, since this compound is itself a highly active catalyst, its addition would considerably improve the properties of the catalytic mass.

The beneficial effects of substances added to the catalyst are not confined to stabilizing the structure of the catalyst. It has been observed that the susceptibility of the catalyst toward poisoning may be considerably affected by the supporting material quite apart from its limited function as a supporter, and supporters are often chosen to take advantage of such effects. Recent experiments carried out by Adadurov, Tseitlin, and Orlova (5) on the poisoning effect of arsenic on platinum catalyst for the oxidation of sulfur dioxide showed that catalysts prepared by precipitating 0.015 to 0.02 per cent platinum on aluminum or chrome-nickel steel shavings are more resistant to poisoning by arsenic than platinum catalyst precipitated on any of the commonly used carriers. Moreover, the catalytic activity of a deactivated contact mass is completely restored by heating to 600°C. The same authors (6) investigated the susceptibility of platinum supported on non-metallic salts. They concluded that the ionic radius and the charge of the cation of the salt affect the sensitivity of the catalyst to arsenic poisoning. An ionic radius of 0.78 Å was found to give minimum sensitivity to poisoning, and it was found that the higher the charge of the cation in the salt the greater the activity of the catalyst. Stannic sulfate and zirconium sulfate were found to be the best supporters. The behavior of the trivalent salts of aluminum, iron, and chromium was found to be intermediate between the salts of the bivalent and quadrivalent cations.

Until the work of Bredig and Müller von Berneck (16) on the influence of foreign bodies on the catalytic decomposition of hydrogen peroxide with platinum, the knowledge concerning the poisoning of catalysts was of a general nature. The more quantitative investigations begun by these authors and carried further by many others have been a valuable aid in developing the current concepts of catalysis as well as in contributing greatly to the understanding of poisoning. Several of the later books on catalysis have treated the older literature on this subject. (See Book Review.) Berkman, Morrell, and Egloff (9) have recently published a survey of the literature on promotion and poisoning of catalysts and have attempted to classify the promoters and poisons and correlate their action with their physico-chemical properties. The booklet is a good bibliography of the subject.

The action of a specific compound on different catalysts cannot, as a rule, be predicted. Certain compounds, such as sulfides, arsenic, etc., have been shown to be harmful to almost all metallic catalysts; yet, on occasion, such action may be beneficial when the full activity of the catalyst is not desired. Platonov, Tomilov, and Tur (50) recently investigated the catalytic properties of rhenium and found that when methyl alcohol is passed over ordinary rhenium catalysts it is completely decomposed and almost no formaldehyde is obtained. However, if the catalyst is partly poisoned by hydrogen sulfide or arsenic trioxide, good yields of formaldehyde result. In general, however, small amounts of such substances often result in practically complete and permanent deactivation of the catalyst. Such poisoning is due principally to the formation between the poison and the catalyst of a compound which is itself inactive and which by coating the active surface of the catalyst prevents the substrate from coming in contact with the catalyst. Adadurov (2) found that in the oxidation of sulfur dioxide a vanadium catalyst was permanently poisoned by arsenic. The arsenic formed with the catalyst a compound which was stable and inactive. Changes in the catalyst's surface were also observed by Adadurov and Grigorovich (4) with platinum and chromic oxide catalysts for the same reaction. They reported that poisoning by arsenic resulted in an increase in the lattice constant of both catalysts. With platinum, the lattice constant increased from 3.918 to 3.935 Å. They concluded that the activity of these catalysts for the oxidation of sulfur dioxide decreased with an increase in lattice constant but that it also depended on other unknown factors. Olsen and Maisner (49) also studied the performance and poisoning of vanadium catalysts in sulfuric acid manufacture. Four catalysts containing vanadium and various support materials were subjected to poisoning by arsenic. It was observed that the activity of all four catalysts did not markedly decrease until arsenic was present in relatively large amounts. Adadurov and Gernet (3) investigated the poisoning of chromium catalysts by arsenic and other contact poisons and found that the chromium catalysts at 450 to 475° were more susceptible to poisoning than was the vanadium catalyst. At 500°C. the effect of arsenic on chromium and vanadium catalysts was identical and at 550° both catalysts were immune to poisoning by arsenic. The action of water vapor and hydrochloric acid was also studied.

Decreases in activity of a catalyst which are not the result of a permanent change in the catalyst surface take place when the substrate is displaced from the active surface by the preferential adsorption of a substance. The product sometimes acts in this manner, replacing the substrate from the surface and preventing further reaction. Bork and his co-workers (10, 11, 12, 13, 14) in a series of papers have investigated the dehydrogenation of alcohols on copper catalysts. Acetaldehyde is adsorbed on the copper catalyst to the same extent as the alcohol, and the rate of reaction diminishes, therefore, as the concentration of aldehyde increases.

Study of poisoning has, in the past, given considerable support to the theory of active centers on the surface of catalysts, and such evidence is still being reported. Burstein and Kashtanow (18) concluded from their investigation of the poisoning of wood charcoal for the conversion of parahydrogen to orthohydrogen that two types of active centers exist on this catalyst's surface.

The work of Maxted and his associates regarding the poisoning of a number of catalysts has, however, thrown some doubt on the possibility of discriminating between degrees of activity of active centers, but it does not disprove the existence of active centers, since their experiments do not exclude the possibility of the poison's being adsorbed also on inactive areas. They have shown (42) that the energy of activation for the catalyzed decomposition of hydrogen peroxide with platinum black remains constant as the catalyst is gradually poisoned with increasing amounts of mercury ions. If certain of the catalyzing points of a catalyst surface are more active than others, such points should be poisoned first and the energy of activation should increase as more and more of the highly active points are deactivated. The fact that the energy of activation remains constant indicates that, if areas of special activity exist, they all require the same increment of energy for catalytic activity. Since, however, the energy of activation is a function of the reaction as well as the catalyst, Maxted and Stone (44, 45) investigated the progressive poisoning by mercury chloride of platinum black for the hydrogenation of crotonic, oleic, and benzoic acids, and for the reduction of nitrobenzene, acetophenone, and benzene. Results again suggest the homogeneity of the catalyzing points for they show that the amount of poison necessary to reduce the activity of a standard platinum black catalyst to a given fraction of its original activity is the same for each reaction in spite of the wide differences in energy of activation between the various reactions. Maxted and Moon (43) searched for further evidence for the homogeneity of the catalyzing elements by studying the effect of sintering on the activation energy of platinum black catalysts for the decomposition of hydrogen peroxide and the hydrogenation of crotonic acid. They found that the energy of activation for each reaction did not vary with the state of deactivation of the catalyst as would be expected if peaks of varying degree of activity existed.

Maxted and Evans have recently undertaken the study of the relation of chemical structure to catalytic toxicity. The effect of hydrogen sulfide, sulfur, carbon disulfide, thiophene, and cysteine on a coarse platinum catalyst for the hydrogenation of crotonic acid, and on a finely divided nickel catalyst for the hydrogenation of olive oil, was investigated (39). The coarse platinum catalyst was found to be fifty times more sensitive to the action of these poisons than was the finely divided nickel catalyst; yet, in spite of the wide difference in sensitivity of the two catalysts, it was found that the relative toxicity of the various sulfur compounds was the same for both catalysts. It was also observed that the toxicity of the sulfur compounds increased with increasing size of the molecule, and it was suggested that the poisonous element, sulfur, acts as an anchor by being permanently adsorbed on the catalysts with the result that the entire molecule obstructs the surface. A more detailed study of the effect of chain length on catalytic toxicity (40) showed that the toxicity per sulfur atom increased with the chain length of both alkyl sulfides and alkyl thiols; however, the increase was less marked with increasing chain length. This behavior was explained by assuming that the effectiveness of the anchoring poisonous element on the adsorption of the non-poisonous chain decreased as the length of the chain increased. H_2S was found to be the least poisonous of the sulfides. Methyl sulfide was seven times as poisonous; ethyl, ten; *n*-butyl, fifteen; *n*-octyl, twenty-six; and cetyl, thirty-four times. Superposition of a scale model of the poison on a scale model of a platinum lattice showed that at most only nine Pt surface elements could be covered by the methyl sulfide model; yet methyl sulfide was found to be seven times more poisonous than hydrogen sulfide, which must cover at least one surface element. Consequently at least seven of the available nine surface elements must have been catalytically active. From this, the authors concluded that it appeared probable that all surface elements of a metal such as platinum are capable of acting catalytically and that the area of catalytic surface affected by the poison was a circle of radius equal to the chain length. The addition of a second terminal sulfur atom to a hydrocarbon chain decreases rather than increases the toxicity per gram mole. Maxted and Evans (41) consider that the addition of the second terminal atom prevents the free rotation of the residual non-poisonous chain, and thus the effective covering power of the poisonous compound is reduced by the second " anchor " at the opposite end of the chain. In support of this theory they have shown that if the two sulfur atoms are adjacent a decrease in toxicity does not occur.

NEGATIVE CATALYSIS

The work of Moureu and Dufraisse demonstrated the widespread occurrence of negative catalysis and threw considerable doubt on the general applicability of the viewpoint that negative catalysis consists only of an effective removal of a positive catalyst. It is hardly conceivable that each of the widely different systems investigated by these authors contained unrecognized traces of a very active positive catalyst. Furthermore, Moureu and Dufraisse observed that, in a number of cases, the negative catalyst reversed its action and became a positive catalyst when certain conditions were changed, a fact difficult to explain by the older theory.

Moureu and Dufraisse (47) suggested that the negative catalyst acts as a positive catalyst for the deactivation of the initial activated reaction product. Thus, if the reaction in question is the oxidation of " A " by oxygen, the first reaction:

$$A + O_2 = A(O)_2$$

produces an activated oxygenated compound $A(O)_2$, called by Moureu and Dufraisse a primary peroxide. The antioxidant " B " then reacts with $A(O)_2$, producing " AO " and " BO," which are antagonistic peroxides and mutually destroy each other, liberating oxygen and returning " A " and " B " to the system.

Backstrom's (7) demonstration of the chain character of the reactions studied by Titoff and by Moureu and Dufraisse provided a new mechanism for the explanation of the action of negative catalysts. According to the previous theories, each initial reaction, whether it consisted of the formation of a primary peroxide or an activated molecule of the autoxidant, resulted in the formation of only one or, at most, two molecules of reaction product. Therefore, one contact with an inhibitor molecule could stop the formation of only one or two molecules of oxidation product. On the other hand, the chain theory provides that the contact of an activated reactant molecule with one molecule of inhibitor may prevent the production of many molecules of oxidation product. Though Backstrom believed his work demonstrated the existence of thermal chains, his data are of equal interest whether the chains were in fact thermal or chemical.

A theory which is essentially different from any of the theories previously mentioned has been advanced by Reiff (51) and supported by Brunner (17) and Rideal (52). These writers suggested that the reaction takes place, or is initiated, at the surface of the containing vessel and that the negative catalyst is effective because it is adsorbed in high concentrations on this surface. A somewhat similar concept has been proposed by Bailey (8) who considers that the liquid-gas interface initiates the reaction and that the inhibitors are adsorbed at this interface.

Although the chain theory offers several advantages over the other theories discussed, it has not been universally accepted for reactions occurring in solutions. The recent literature on the mechanism of negative catalysis in solution is limited. Dufraisse (22), while admitting that a chain-reaction mechanism may be valid for gaseous reactions, does not consider that it can explain the action of antioxidants in solution. On the other hand, Mikhailova and Neiman (46) from their study of the autoxidation of unsaturated hydrocarbons in the liquid phase have concluded that it consists of a chain reaction initiated at the liquid-gas interface. However, in contrast to the ideas put forth by Bailey, they believe that inhibitors (such as alpha-naphthol) are not adsorbed at the interface and that their action is due to the rupture of reaction chains within the liquid.

Since the work of Moureu and Dufraisse, which pointed to the commercial possibilities of negative catalysis in protecting substances from destructive oxidation, the work along these lines has been directed mainly toward the development and testing of commercial inhibitors. Attention has been concentrated on the stabilization of gasoline and rubber, the development of antiknock compounds, and similar problems with the result that a large amount of information has been obtained on extremely complex systems which is difficult to evaluate from a scientific standpoint.

An extensive search for suitable inhibitors to prevent the deterioration of gasoline in storage has been occasioned by the adoption of the cracking process in the production of gasoline. Untreated cracked gasolines deteriorate in storage with the formation of soluble and insoluble resinous material (generally called " gum "). Many attempts have been made to demonstrate that this deterioration is intimately connected with the formation of peroxides from the unsaturated compounds in the cracked gasoline, and the addition of typical autoxidation inhibitors, such as those used by Moureu and Dufraisse, has been recommended. It has again been emphasized in the recent literature that peroxides and gum are the most characteristic deterioration products of cracked gasoline. However, there is still considerable discussion as to whether peroxides are directly responsible for the formation of gum or whether the peroxides merely accompany the gum.

The difference in susceptibility of various gasolines toward inhibition has resulted in attempts to develop methods by which the efficiency of an inhibitor may be judged without resorting to prolonged storage tests. The oxygen bomb induction period test of Hunn, Fisher, and Blackwood (30), which is a measure of the time required for the onset of rapid oxidation, is still widely used, but the results obtained have not been shown to be strictly related to the stability of gasolines. Lowry (34) has found that, when comparing the results of this test with the storage stability of samples of the same gasoline treated with different inhibitors, the induction period is a rough measure of the storage stability; but, when comparing gasolines of different sources, no exact correlation of the induction period with storage stability has been obtained. Several modifications of the induction period test have been proposed but there is still considerable disagreement as to the interpretation of the results of such methods.

Attempts have also been made to judge the effectiveness of various inhibitors by their oxidation-reduction potentials; but, again, the results are not satisfactory. Elley (28) recently, summarizing the work along these lines, stated that it has been found necessary to coordinate such measurements with a considerable amount of empirical testing in order to develop inhibitors for various systems.

For the oxidation of hydrocarbons in the vapor phase, the chain-reaction theory has been widely accepted. It provides a reasonable basis for the explanation of the combustion phenomena observed in the internal combustion engine and accounts, at least in part, for the action of antiknocks (19).

A direct demonstration that knocking is caused by the spontaneous ignition of the unburnt charge ahead of the flame front (62) has been obtained by motion pictures of the combustion in an operating engine. The instantaneous inflammation of this portion of the fuel is accompanied by a sudden vibratory rise in pressure and an audible knock.

The fuel charge ahead of the flame is subject to a slow oxidation process the velocity of which increases with temperature and pressure until a critical point is reached at which spontaneous ignition occurs. Spontaneous ignition is presumably caused by the multiplication of the oxidation reaction chains and there is some recent evidence that the multiplication is caused by the branching of the chains (26, 27). Antiknocks may thus be expected to suppress the undesirable ignition by breaking the chains at an early stage and to act therefore as negative oxidation catalysts.

The investigation of the critical conditions of temperature and pressure at which spontaneous ignition occurs has been a subject of numerous researches by Townend and his associates. These studies revealed a striking difference in the characteristics of knocking and non-knocking fuels. Townend and his collaborators have shown furthermore that the addition of lead tetraethyl raises the minimum ignition point of the fuel-air mixtures (60) whereas proknocks, such as diethyl ether, lower it (59).

A marked difference has been found between the action of organometallic and purely organic antiknocks. Spectroscopic studies showed (63) that the use of aniline as the antiknock lowers the concentration of formaldehyde which is always present in the preflame mixture under knocking conditions, whereas the use of lead tetraethyl does not. Evidence has also been found (25, 64) to indicate that the action of the metallic antiknocks is that of the free metal atom or its unstable oxide, in which case it is probable that the active atom or molecule acts repeatedly in a manner analogous to that of a positive catalyst. On the other hand, the organic antiknocks, like the organic antioxidants, are probably rendered ineffective during the chain-breaking reaction. In this respect, the observation that the antiknock effects of aniline and lead tetraethyl are additive up to the limiting effective concentrations (58) is of considerable interest.

The antiknock properties of water vapor have recently been studied by J. R. MacGregor (35), who found that the octane number of a gasoline increases appreciably with humidity, particularly for high octane fuels containing lead tetraethyl. On the other hand, Bouchard and his collaborators (15) have shown that the speed of the spark-ignited flame is decreased by the presence of water vapor, which according to Elbe (26) is conducive to knocking. It is therefore probable that water vapor also acts as an inhibitor of the chain reactions in the preflame mixture.

One of the major problems of the rubber industry is the prevention of " aging " of the finished rubber products, and a marked progress in this field was made only after it was realized that the acceleration of vulcanization and inhibition of aging should be treated as two separate problems. Until this time, the choice of an accelerator was governed to an appreciable extent by its ability to stabilize the finished article against aging. In 1924 Winkelmann and Gray (61) secured a patent on a non-accelerating compound for the specific purpose of retarding the aging of rubber. With the introduction of the independent control of aging, it became possible to choose accelerators which gave the desired rate of cure and physical properties without regard to the possible effects on the aging of the finished rubber article. This resulted almost immediately in a marked improvement in the quality of rubber goods.

The study of the role of such antiaging compounds in the stabilization of rubber has been along lines remarkably similar to those used in the study of antioxidants in gasoline. It has been shown that the aging processes are connected with the oxidation of the rubber (48), but it has been repeatedly pointed out that all types of deteriorations are not the direct result of oxidation (21, 56). A critical review and discussion of the use of antioxidants in rubber has been published by Jones (31). As with gasoline, the selection of an inhibitor for the prevention of deterioration is made difficult by variations in the properties of the crude rubber; furthermore, the wide variety of uses to which rubber goods are subjected adds an additional complication. Consequently, a number of tests have been devised for judging the effectiveness of rubber antiaging compounds. Oxygen bomb tests, similar to those employed in the gasoline industry, are widely used to accelerate aging. The effectiveness of the inhibitor is judged by the variation in physical properties (such as tensile strength) with time rather than by variations in the induction period. Ultra-violet light is also used to hasten the deterioration (32), the extent of deterioration again being determined by physical tests. Dufraisse (23) has recently described a manometric method for measuring the oxidizability of rubber. This test is similar in principle to that used by Dufraisse in his autoxidation studies and does not depend on changes in the physical properties. However, Dufraisse and Etienne (24) have not yet established a parallelism between oxidizability and aging. Attempts have also been made to judge the effectiveness of various inhibitors by their oxidation-reduction potentials (28). In addition to the chemical methods of accelerating aging, numerous mechanical methods are used, especially in estimating the probable life of rubber articles subjected in practice to continual flexing (20, 55).

The interpretation of the results obtained by several of the above methods has been studied by Tener and Holt (57). Two means are suggested for expressing the effectiveness of an antioxidant numerically, a time index and a tensile index. A comparison of the indices obtained by different accelerated tests with those obtained under more natural conditions of storage showed that the oven test at 90°C. most nearly approximated weather exposure and that the oxygen bomb test was most suited for judging dark-storage life. As is the case with gasoline, the interpretation of the results obtained with the various aging tests is still a matter of considerable discussion.

The inhibition of corrosion of metals, while being a marked case of negative catalysis, is gradually being reduced to more fundamental physico-chemical principles. The evidence that corrosion is essentially an electrochemical phenomenon is overwhelming. The complexity of corrosion is furthermore not an argument against this viewpoint and indicates rather that the simplicity of the principles governing electrochemical processes has been overestimated.

The inhibition of corrosion depends on a successful interference with the elementary electrochemical process causing corrosion. The surface of the corroding metal is considered a network of minute electrochemical cells, some areas being cathodic, others anodic. Since the velocity of an electrochemical reaction at one electrode cannot be higher than at the other, inhibition of the reaction at either electrode will slow down the rate of corrosion. Considering that the pretreatment of the metal, the presence or absence of oxygen, and a number of other factors influence the rate of dissolution, the great complexity of corrosion can be understood. Ceteris paribus, however, any step which will increase the chemical or electrical resistance at the surface will decrease the rate of corrosion. The influence of inorganic salts (phosphates, chromates, borates) has been for some time known to result in the formation of a fairly thick surface film, the existence of which has been directly demonstrated by Evans (29). The more recent observations on the influence of organic inhibitors lead essentially to the conclusion that the effectiveness of these substances is due to the adsorbed layer on the metal surface. The exact mechanism of the way this layer retards corrosion is still doubtful. It has been the subject of recent investigations by Mann and his associates (38), and by Machu, who has studied in detail the inhibition by gelatin (36). Machu has recently summarized his own researches and reviewed the older theories of inhibition by overvoltage and by adsorbed layers (37).

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CHAPTER XVII

THE HYDRATION, DEHYDRATION, AND HYDROLYSIS OF ORGANIC COMPOUNDS*

B. W. HOWK and WILBUR A. LAZIER

Chemical processes involving the addition or abstraction of a molecule of water are familiar phenomena in organic chemistry and constitute a large proportion of the known transformations of oxygenated carbon compounds. Like oxidations and hydrogenations, hydrations and dehydrations are highly susceptible to the influence of specific catalysts, and there is a tendency in industry to substitute, wherever possible, purely catalytic processes for the older chemical methods. In this paper the objective has been to summarize the more recent contributions to the literature in this important field. The task of selecting appropriate material from among the large number of more or less pertinent references has been made difficult by the high frequency of borderline cases of debatable value from the standpoint of catalysis. Accordingly, this paper has been limited to a discussion of those reactions that appeared to be of greatest commercial and catalytic significance. Reactions involving water in the role of an oxidizing agent, i.e., the conversion of carbon monoxide to carbon dioxide, have in general been reserved for appropriate treatment elsewhere.

In organic chemistry, the term " hydrolysis " is applied to any reaction that involves cleavage of a covalent bond by water with resultant attachment of the hydrogen atom to one of the products and the hydroxyl radical to the other. Lloyd (113), in his able discussion of this subject, has pointed out that in many cases the distinction between true hydrolytic reactions and others in which water is merely one of the reactants is sometimes rather poorly defined. Although Lloyd (113) has chosen to include some of the borderline cases, it seems preferable to limit the present discussion to hydrolytic reactions that come definitely within the scope of the more restricted definition. Even so, a large volume of work has been published within recent years covering investigations ranging from careful and painstaking studies relating to mechanisms, reaction velocities, and catalysts for ester hydrolysis to the more practical problems of soap manufacture.

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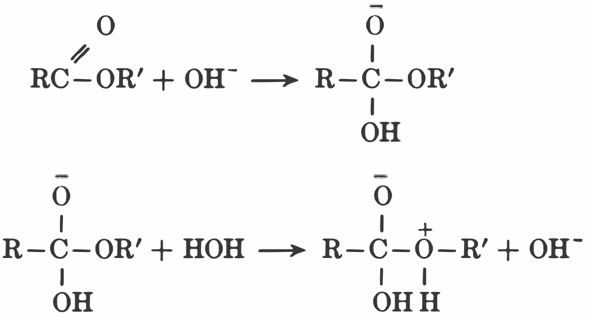
Carboxylic Ester Hydrolysis — Theoretical Studies

For many years one of the important objectives of theoretical chemistry has been to establish the true mechanism of ester hydrolysis. In 1934, the brilliantly conceived work of Polanyi and Szabo (146) seemed to provide a convincing answer to this question. These investigators carried out the hydrolysis of amyl acetate using sodium hydroxide prepared from water having an abnormal ratio of the oxygen isotopes, O^{16} and O^{18}, and metallic sodium. By recovering the amyl alcohol produced and dehydrating it catalytically they were able to obtain a sample of water showing no abnormal oxygen isotope ratio as determined by very careful density measurements. These results indicate that cleavage occurred between the oxygen of the ester linkage and the acyl radical. If the reverse were true, water derived from the amyl alcohol produced would show an abnormal density. A similar conclusion is suggested by the work of Newling and Hinshelwood (131) in connection with a study of the hydrolysis rates of substituted benzoic esters with acid and alkaline catalysts. These authors believe that the hydrolysis of esters proceeds according to the mechanism first proposed by Lowry (206), which involves the formation of an unstable complex ion in either (*a*) alkaline or (*b*) acid solutions:

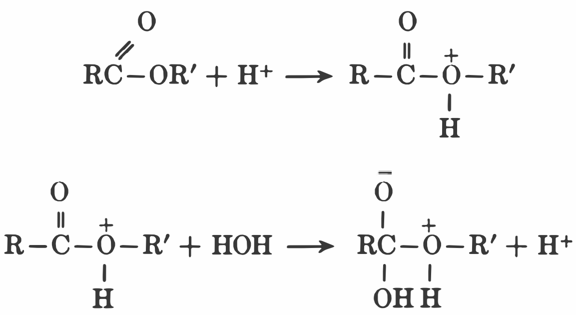
(*a*)



$$RC(=O)-OR' + OH^- \longrightarrow R-\overset{\bar{O}}{\underset{OH}{C}}-OR'$$

$$R-\overset{\bar{O}}{\underset{OH}{C}}-OR' + HOH \longrightarrow R-\overset{\bar{O}}{\underset{OH}{C}}-\overset{+}{\underset{H}{O}}-R' + OH^-$$

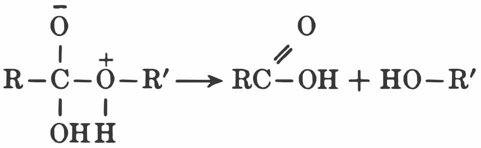
(*b*)



$$RC(=O)-OR' + H^+ \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{+}{\underset{H}{O}}-R'$$

$$R-\overset{O}{\overset{\|}{C}}-\overset{+}{\underset{H}{O}}-R' + HOH \longrightarrow R\overset{\bar{O}}{\underset{OH}{C}}-\overset{+}{\underset{H}{O}}-R' + H^+$$

It will be noted that this scheme requires the addition of both ions of water to the ester. In each case the ion lacking is furnished by a water molecule which gives up a hydrogen ion in alkaline solution and an hydroxyl ion in acid solution. The complex structure produced is thought to break down immediately into acid and alcohol by a simple electronic rearrangement (131):



$$\mathrm{R{-}\underset{\displaystyle OH}{\overset{\displaystyle \bar{O}}{C}}{-}\underset{\displaystyle H}{\overset{+}{O}}{-}R' \longrightarrow R\overset{\displaystyle O}{\overset{/\!/}{C}}{-}OH + HO{-}R'}$$

This theory is in good agreement with Polanyi's conclusion that the bond broken in the hydrolysis of esters is that between the alkoxyl and acyl radicals (146).

Newling and Hinshelwood (131) have also pointed out that the mechanism referred to above serves to explain the fundamental difference between acid and alkaline hydrolysis. They believe the formation of an oxonium ion through the addition of a proton to the alkoxyl group of the ester involves very little activation energy so that the addition of hydroxyl ion to the carbonyl carbon becomes the rate-determining process. In alkaline solution, free hydroxyl ions are available in high concentrations, and the hydrolysis may proceed at a rapid rate. In acid solution the necessary hydroxyl ions can be obtained only by further dissociation of water molecules, which probably accounts for the fact that acid hydrolysis is slower and requires a higher activation energy than alkaline hydrolysis. Typical activation energy values have been reported by Wyczalkowska (213), who observed that the heat of activation in the hydrolysis of ethyl acetate at temperatures between 25°C. and 60°C. and at various concentrations of hydrogen chloride is constant at 16,405 gram calories per mole. Hornel (75) found that deuterium ions accelerate the hydrolysis of methyl acetate in sulfuric acid solution. In view of these observations on the importance of ionic catalysts it is not surprising that Yamasaki (215) failed to obtain any appreciable hydrolysis of ethyl acetate with steam in the gas phase at 200°C. in the presence of hydrogen chloride, iodine, or X-radiation.

In the absence of added catalytic materials, ester hydrolysis is an exceedingly slow reaction. For example, Genevois (55) has found that the hydrolysis of esters, such as the tartrates, malates, etc., occurring in wine, is negligible during a period of 10 hours at *p*H 7 and 35°C. Kirrmann (96) was able to show that the reaction between pure water and pure allyl pyruvate can be expressed in terms of a unimolecular spontaneous reaction upon which is superimposed an autocatalytic effect that is due to the generation of hydrogen ions. Poethke (144) made a similar observation in the case of ethyl formate and obtained as an expression for the rate of autocatalytic hydrolysis, $R = K(A - X)X^{1/2}$, in which $X^{1/2}$ is the hydrogen-ion concentration. At room temperature the hydrolysis of methyl formate is complete in five days, although in the presence of added sodium formate a longer time is required. Ethyl acetate exhibits a similar behavior, but the reaction becomes appreciable only after several days have elapsed, and more than a year is required to establish equilibrium. In this equilibrium between water, ethyl acetate, alcohol, and acetic acid, the relative proportions of the various components at the point of equilibrium are independent of the temperature and pressure, although the rate of approach is hastened by the application of extreme pressures ranging up to 6500 atm. (129).

An interesting development in connection with the catalysis of ester hydrolysis has been the discovery by Langenbeck and co-workers (103, 104) that compounds such as benzoyl carbinol are capable of functioning as catalysts in the hydrolysis of esters. The behavior of these materials is explained by their capacity to undergo exchange reactions with simple esters to produce esters that are in turn hydrolyzed at very rapid rates. For example:

$$C_3H_7COOCH_3 + C_6H_5CO-CH_2OH \longrightarrow CH_3OH + C_3H_7COOCH_2-CO-C_6H_5$$

$$C_3H_7COOCH_2-CO-C_6H_5 + H_2O \longrightarrow C_3H_7COOH + C_6H_5-CO-CH_2OH$$

The action of these organic catalysts may be analogous to that of true enzymes such as esterase. It is interesting to note that the esterase models of Langenbeck have been criticized by Olivier (134) on the ground that they fail to promote the hydrolysis of representative esters either in strongly alkaline media or in solutions below *p*H 9.

Aside from external catalytic effects, several investigators have noted that the structure of esters may have an important bearing on their behavior during hydrolysis. Braun and Kurtz (20) observed that esters of acids having a branched chain at the alpha carbon atom are more easily hydrolyzed than normal straight-chain esters. These authors believe that in such esters the carboxyl carbon atom becomes less positive in character and accordingly has a weaker affinity for negative alkoxyl groups. Similarly, Schjanberg (165) found that the double bond has a labilizing effect on the ester linkage which becomes less pronounced the farther it is removed from the carboxyl group. Ter Horst (185) has reported that the carbethoxyl groups of diethyl malonate undergo hydrolysis at different rates, depending on their mutual proximity. Other papers dealing with the relationship of structure to the hydrolysis rates of esters have been published by Evans, Gordon, and Watson (48), Kindler (95), Morton (122), Palomaa and co-workers (138), and Senderens (170). A general review of current theory on ester hydrolysis was published by Adickes (3) early in 1937.

Catalytic Hydrolysis of Fats

Perhaps the most important industrial application of hydrolytic procedures is in connection with the manufacture of soaps. Although most of the soap produced today is manufactured by the conventional caustic alkali saponification process (114), several indirect processes involving catalytic cleavage of the fat, separation of the free fatty acids and glycerin " sweet water," and neutralization with soda ash or potash are rapidly gaining favor owing to the higher yields of glycerin obtained. In the usual saponification processes much of the glycerin remains in the soaps or is lost in subsequent processing steps. The extensive use of glycerin by the chemical industry has therefore provided an incentive to the development of catalytic fat cleavage processes that are more economical as regards glycerin recovery. Within recent years, no new methods have been announced for the catalytic hydrolysis of fats, but Heublyum (68), in a review of this subject published in 1936, has pointed to certain improvements in the four important processes already established.

The familiar process involving the use of sulfuric acid as a catalyst is perhaps the least desirable of all, owing to the inferior quality of the fatty acids produced (173). Not only are the fatty acids dark in color, but they often contain incompletely hydrolyzed products that may lead to the development of rancidity in soaps (97, 166). Wallace and Moore (205) have suggested the use of a common solvent, such as acetone, as a means of carrying out the reaction at lower temperatures. This leads to the production of lighter colored fatty acids and to a lower concentration of unhydrolyzed fats in the products. The separation of glycerin, solid acids, and liquid acids is also facilitated.

Another important process referred to by Heublyum (68) is that of Twitchell, in which aromatic sulfonic acid derivatives are employed as catalysts to promote the hydrolysis reaction. This process is said to be popular on the European continent (173), and has been improved somewhat by the development of new " Twitchell " reagents that permit the use of somewhat lower temperatures in the hydrolytic process. Nevertheless, the quality of fatty acids manufactured by the Twitchell process is believed to be inferior to that of fatty acids manufactured by other methods, excepting, of course, the sulfuric acid process. A much cleaner product is obtained by the process of Krebitz (68, 166), in which magnesium or calcium hydroxides are employed as reagents. The procedure is partly catalytic in that stoichiometrical amounts of the alkaline oxides are seldom necessary. Since the calcium and magnesium salts of fatty acids are insoluble, they are readily separated from the glycerin water by filtration and converted to sodium soaps by metathesis with sodium carbonate. The Krebitz process gives especially good results if zinc oxide is employed as a promoter (166).

The most satisfactory process for the direct cleavage of fats to glycerol and free fatty acids involves treating the fat with water in the presence of catalytic amounts of zinc oxide, magnesium oxide, and sometimes sodium carbonate in an autoclave under pressure at temperatures ranging up to 220°C. This process, which is commonly known as the "autoclave" process, yields surprisingly light-colored products and offers many advantages over those previously mentioned. Heublyum (68) and Schönfeld (166) mention several modifications of the process involving the use of different amounts of lime, zinc dust, or zinc oxide. An interesting variation developed by Rankov (152) involves the use of sulfur or phosphorus in the catalytic scission of fatty oils. One per cent by weight of sulfur or 3 per cent of phosphorus acts under a pressure of several atmospheres and temperatures up to 220°C., not only to promote hydrolysis of the glyceride, but also to cause isomerization of oleic acid to elaidic acid. The latter, which melts above 40°C., yields a much harder soap than ordinary oleic acid. Accordingly, Rankov's process can be employed to produce fairly hard soaps from fats containing otherwise objectionable quantities of olein.

Hydrolysis of Organic Halides

The commercial availability of a wide variety of haloalkanes has encouraged the development of processes for the conversion of these products to the corresponding alcohols. For the most part, processes that are favored by the chemical industry both in the United States and abroad involve hydrolysis of chlorinated hydrocarbons with inorganic bases. Recent theoretical and technological developments have been summarized by Ellis (46). Perhaps the important advances in the art have been due to the more extensive use of superatmospheric pressures and temperatures higher than 100°C. On the other hand, the investigation and commercial exploitation of gas-phase contact methods for the hydrolysis of chlorinated hydrocarbons to alcohols have seemingly been hampered to a considerable extent by low conversions, loss of materials, side reactions, and the lack of catalysts having suitable selectivity. The simultaneous formation of olefins and ethers accounts for the most serious losses.

In a study of the gas-phase hydrolysis of methyl chloride and methylene chloride, Abkin and Medvedev (1) found that stannous phosphate deposited on pumice is a fairly effective catalyst. At 460°C., using a methyl chloride and water ratio of 1 : 10, these investigators obtained a 16 per cent yield of methanol, and 18.6 per cent yield of formaldehyde. Under similar conditions methylene chloride gave a 75 per cent yield of formaldehyde. Somewhat better results were obtained by processing mixtures of methyl chloride and methylene chloride and recycling the unchanged methyl chloride. Catalysts such as titanium oxide or a mixture of iron and stannous phosphates were found to be inactive. For the conversion of alkane dihalides to glycols, Taveau (184) recommends the use of insoluble metal carbonate catalysts such as magnesium carbonate. The process is carried out at a temperature above 150°C., but below the boiling point of the glycol that is formed. The hydrolyzed product is removed from the reaction zone by introducing superheated steam. Another type of catalyst comprising activated charcoal impregnated with sodium or potassium hydroxide solutions, and calcined at 600 to 700°C., has been patented by Compagnie Française de Produits Organochimiques as a contact material active in the hydrolysis of phosgene (28). Ellis (46) has also referred to the use of alkali hydroxides, aluminum oxide, alkaline-earth oxides, and active charcoal impregnated with zinc sulfate as catalysts in the gas-phase hydrolysis of methyl and ethyl chlorides. Apparently very little work has been done on the gas-phase hydrolysis of the higher halogen compounds.

In general, liquid-phase processes for the hydrolysis of alkyl halides give higher conversions and fewer by-products than continuous vapor-phase methods (46). This may be due to the fact that (*a*) the liquid-phase process can be carried out at moderate temperatures, usually below 250°C., and (*b*) the time factor is not very critical. From a careful study of the mechanism and rates of hydrolysis of typical halides, Hughes and co-workers (15, 77, 78, 79) decided that the type and concentration of mutual solvents and the structure of the hydrocarbon chain of the halide have an important bearing on the absolute rate of hydrolysis. From the kinetic point of view it was found that the hydrolysis of isopropyl bromide, secondary butyl bromide, or tertiary amyl chloride proceeds according to a unimolecular reaction curve and is independent of the reagent ions employed. In each case, velocity constants obtained in either alkaline or acid solution were the same within the experimental error. Woodburn and Whitmore (211) have observed that tertiary alkyl chlorides are somewhat more resistant to hydrolysis than commonly supposed and may produce both olefins and alcohols in varying amounts, depending on the conditions employed. In general, the hydrolysis of terminal monochlorides or monobromides in acid, alkaline, or neutral solutions becomes more difficult with increasing chain length (135).

A substantial proportion of the phenol now consumed by the chemical processing industries is prepared by hydrolysis of chlorobenzene. The method commonly employed involves hydrolysis under pressure in the presence of caustic alkalis, which according to Lloyd (113) gives essentially quantitative yields. This development has been on a sounder basis than the hydrolysis of haloalkanes, since there are no strongly competitive processes for making phenol. A wide variety of contact materials have been suggested. Ellis (45) refers to the use of oxides of aluminum, thorium, titanium, zirconium, and tungsten, and Popov and Popova (147) have employed metallic platinum, silver, copper, cuprous chloride, copper oxide, and magnesium oxide. More recently Tishchenko and Churbakov (190) have recommended temperatures in the range from 550 to 600°C. for use with a catalyst comprising 10 per cent of copper supported on silica gel. It is stated that the yield of phenol depends mainly on the capillary activity of the silica gel support and that unreacted chlorobenzene can be recycled repeatedly. In a later paper Tishchenko and Gutner (191) claim the use of calcium, strontium, barium, magnesium, or cuprous chlorides as catalysts. These materials are employed on a silica gel support. Compositions containing about 10 per cent of active chloride catalyst are very satisfactory. These investigators report phenol conversions of 47 per cent and a recovery of about 30 per cent of chlorobenzene for recycle. Recent developments in connection with this process have been described in a review of the literature by Vorozhtsov (204). In the process developed by Prahl (148), acid-washed, iron-free fuller's earth promoted with cupric chloride is employed as a catalyst. A fuller's earth catalyst has also been employed by Rittler (157) for the gas-phase hydrolysis of chlorobenzene to phenol. The presence of aluminum hydrosilicate and promoters such as copper is said to favor the reaction. Apparatus suitable for carrying out the reaction has been described (157). Copper-containing catalysts for use at lower temperatures in the range from 150 to 250°C. have been prepared by Burroughs (24) by mixing a copper compound with 2–5 molecular equivalents of a 5 to 35 per cent aqueous solution of an alkali metal compound, such as sodium hydroxide, to which has been added 1–2 molecular equivalents of an alkaline-earth metal compound, such as strontium hydroxide. Catalysts of this type are recommended for the hydrolysis of ortho- or parachlorophenols (25).

Herdieckerhoff (64) has patented a semicatalytic process in which chlorobenzene is hydrolyzed to phenol by reaction with less than equimolecular amounts of aqueous calcium hydroxide at temperatures above 300°C. Other modifications and improvements have been described by Jenkins and Norris (133) and by Bertsch (18).

Hydrolytic Scission of the Carbon-Nitrogen Bond

Within recent years a number of papers have appeared relating to the catalytic hydrolysis of compounds containing a carbon-nitrogen bond. One of the most familiar reactions of this type is the saponification of organic cyanides or nitriles. The laboratory method of conducting this reaction involves the use of an excess of aqueous caustic alkali or aqueous alcoholic alkali, and the resulting product is the sodium salt of the corresponding carboxylic acid. The reaction is more complex than the ordinary ester hydrolysis, since apparently it involves two separate and distinct reactions. The reaction may be written in two steps, as follows:

$$(a) \qquad RCN + H_2O \longrightarrow RCONH_2$$

$$(b) \qquad RCONH_2 + H_2O \longrightarrow RCOOH + NH_3$$

In alkaline media it is seldom that the first step can be identified. It may be regarded as a hydration reaction rather than a hydrolysis reaction, since it entails addition of the elements of water without cleaving the molecule. This hydration is usually accomplished by dissolving the nitrile in concentrated sulfuric acid and pouring the resulting mixture into water (69). Good yields of the corresponding amides are obtained. Recently, a more unusual method has been applied by Ullman and Spech (195) to the hydration of *N*-phenylglycine nitrile. The corresponding amide is produced in 60 per cent yields by adding a mixture of the nitrile and 28 per cent hydrogen peroxide to 5 per cent potassium hydroxide solution at 80°C. In a similar reaction, Travagli (193) has employed mercuric oxide in solutions of sulfuric or phosphoric acids to catalyze the conversion of cyanogen to oxamide. A more important development from the commercial point of view has been the disclosure of Margolis (117) that hydrolysis of calcium cyanamide with sulfuric acid can be employed to produce pure urea in yields of 85 per cent. The hydrolysis of urea itself has been studied by Van de Velde (200). It was noted that at elevated temperatures sodium and potassium salts, as well as the phosphate ion, accelerate the rate of hydrolysis. Conversely, ammonium salts have a definite retarding action.

Closely related to the nitriles are those compounds containing a $>C=N-$ linkage. In general, this type of bond is less resistant to the action of water in acid solution. Westheimer (207) has found that hydrolysis of semicarbazones of acetone, methyl ethyl ketone, cyclohexanone, pinacoline, and citronellal proceeds bimolecularly in buffered glycol monomethyl ether solutions. In the case of oximes (194), cleavage with concentrated HCl is promoted by formaldehyde. Thus, yields of quinone exceeding 90 per cent of theory have been obtained by this process from the monoximes of anthraquinone and phenanthraquinone. Although aromatic ketimines are similar to the oximes and semicarbazones as regards stability in acid media, Culbertson, Albright, Baker, and Schweitzer (32) have pointed out that the velocity of hydrolysis of heavily substituted ketimines is markedly affected not only by the presence of catalysts but also by steric effects of the substituent groups. The larger the group, the slower is the observed rate of hydrolysis.

Hydrolysis of Ethers and Ether-like Compounds

It is common knowledge that the structure of the molecule in ethers or ether-like compounds has an important bearing on the stability of the carbon-oxygen-carbon linkage. For example, simple ethers of the type represented by methyl or ethyl ether are very stable to most reagents and can be split only under vigorous conditions by treatment with strong reagents such as halogen acids. Cyclic ethers are considerably more susceptible to hydrolysis, the carbon-oxygen bond becoming less stable as the size of the ring is diminished. Thus, pyrane resembles the open-chain ethers, whereas compounds of the type represented by ethylene oxide can be split with ease. The least stable of all ether-like compounds are those in which two oxygen atoms are attached to the same carbon atom. The acetals and ketals are the outstanding examples of this type.

Although the hydrolysis of simple ethers apparently has no very great industrial significance, a number of interesting papers on this subject have appeared within recent years. Skrabal and Zahorka (174) studied the velocity of hydrolysis of diethyl, isopropyl ethyl, and diisopropyl ethers in aqueous media between 55 and 90°C., using *p*-toluenesulfonic acid as the catalyst. It was found that the unimolecular reaction velocity constants stand in the ratio of 1 : 10 : 33. As mentioned above, ethers of this type are very slow to undergo hydrolysis, and the constant determined for ethyl ether at 25°C. was only 0.146×10^{-10}. In the gas phase, the hydrolysis of ethyl ether proceeds somewhat more readily than might be expected from its stability in the liquid phase. For example, Vansheidt and Lozovskii (203) have found that sulfuric acid and alumina will promote the hydrolysis of ether to ethanol at temperatures between 160 and 320°C. Silica gel and thorium oxide were very poor catalysts and phosphoric acid was inactive. Somewhat different results were obtained by Kagan and co-workers (93) in a study of successive reactions at the surface of a single catalyst. These investigators found that an alumina catalyst prepared by the Willstätter method and promoted with iron and magnesium oxides will effect the hydrolysis of ethyl ether with 3 parts of water at 400 to 500°C. The product obtained consisted predominantly of acetone, although small amounts of ethanol and ethylene were recovered. The appearance of carbon dioxide in the off-gases suggests that acetone is formed via conversion of ethanol to acetaldehyde and thence by the Tishchenko type of reaction to ethyl acetate, which undergoes intermolecular decarboxylation. Higher yields of alcohol were obtained by Kozlov and Golubovskaya (99) by using zinc oxide, magnesium oxide, and aluminum oxide catalysts. The most effective catalyst was a mixture of iron and aluminum oxides, which gave a 58.5 per cent conversion to ethanol. Iron oxide alone was inactive.

In the cyclic series, oxalic and sulfuric acids have been recommended as catalysts for the hydration or hydrolysis of olefin oxides to the corresponding glycols (118, 177). At 90 to 95°C. sulfuric acid not only promotes the hydrolysis of ethylene oxide to ethylene glycol, but also gives diethylene glycol, triethylene glycol, and higher polymers.

Palomaa (136) has investigated the hydrolysis of a number of different acetals, including diethyl acetal, methylal, methyl ethyl formal, methyl propyl formal, and diethyl beta-ethoxyacetal. Velocity constant values were established for each of these compounds, with HCl as the catalyst. Similarly, it has been found that alkyl-acyl acetals behave more like ethers than esters in the hydrolysis procedure (137). The hydrolysis velocities of cyclic acetals, including those prepared from 1,3-butylene glycol and formaldehyde, acetaldehyde, and acetone have been determined by Leutner (110).

Hydration of Olefins

The development of a commercially successful process for the direct vapor-phase hydration of the lower olefins to alcohols has probably been retarded by thermodynamic uncertainties and the difficulties involved in producing catalysts of sufficiently high activity. Possibly another difficulty has been the tendency for the alcohols formed to react with the olefins to form ethers, since Newitt and Semerano (130) have found this reaction to take place readily over an alumina catalyst. These problems have attracted considerable attention in the last few years, and the current status has been ably summarized by Ellis (44).

Until recently the position of the equilibrium in the system

$$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

was not well defined and the maximum theoretical conversion obtainable under any specific set of operating conditions was therefore largely a matter of doubt. Stanley, Youell, and Dymock (181) undertook to determine the equilibrium constant experimentally. This work was paralleled by similar investigations by Dodge and co-workers (19, 164), who concluded tentatively that the experimentally determined values were likely to be more reliable than those obtainable by calculation from the uncertain heat data then available. Rossini's timely and painstaking determinations of the heats of combustion of ethanol (160) and ethylene (161), and more accurate values for the heat capacity of ethylene, have made possible such accurate thermodynamic calculations for free energies and equilibrium constants (139) that the calculated values are now in good agreement with those obtained experimentally by dynamic methods over solid catalysts (19, 164, 181). The agreement is not quite so good, however, for data obtained experimentally in a static system with dilute sulfuric acid as the catalyst (56). Dodge (33) summarizes the situation in the following words: " We may conclude that the equilibrium conditions for the ethylene hydration reaction, at least at low pressures, are well established as a result both of the recent work on heats of reaction and absolute entropy and of the direct experimental measurements of the equilibrium constants."

Accepted values for the equilibrium constant for the hydration of ethylene at several temperatures are given as follows (139):

TEMPERATURE °K.	K_p
298.1	$3{,}080 \times 10^{-3}$
400	260×10^{-3}
500	15.5×10^{-3}
600	2.36×10^{-3}
700	0.63×10^{-3}

The hydration of ethylene is exothermic, and the change in the free energy with temperature indicates that the reaction would be favored by low temperatures. Increasing the steam-ethylene ratio and pressure is beneficial in raising the equilibrium conversion (53), but the first expedient results in dilution of the product with water, and the second favors polymerization of the ethylene.

In the selection of a hydration catalyst, considerable reliance has been placed upon the validity of catalyst testing carried out experimentally on the less difficult reverse reaction of dehydration of alcohols (19, 23, 164). It seems doubtful if this method is of any considerable value, for after uncovering many active dehydration catalysts, Sanders and Dodge (164) have reached the conclusion that " there is no very active catalyst yet developed for the vapor-phase hydration of ethylene." It is easy to understand how variable selectivity of the catalysts towards the competitive reactions of hydration and polymerization and unpredictable susceptibilities to poisoning by adsorption of one or both of the reactants under pressure might influence the synthesis performance while escaping detection in the dehydration process.

For the most part the experimental equilibrium studies referred to above were carried out with alumina catalysts, the preferred methods of preparation consisting of precipitation from sodium aluminate (19, 23, 164), and hydrolysis of aluminum amalgam (19, 164). Tungsten oxide was also used in a few cases (19). Other catalysts described in the earlier papers were a complex acid phosphate of manganese and boron (181), pumice impregnated with 66 per cent sulfuric acid (181), charcoal impregnated with sulfuric acid and silver sulfate (11), and cadmium phosphate (88, 202). The activity of kaolin has been reported to be improved by treatment with acids and that of alumina by the addition of zinc oxide (202).

For at least ten years the hydration of ethylene has been under intensive investigation in the laboratories of Imperial Chemical Industries, Ltd., but until recently the results of these studies were available only through the patent literature (76). In 1937, Applebey, Glass, and Horsley (5) published further details of this work and announced the development of a cadmium metaphosphate catalyst capable of functioning at temperatures as low as 175°C. Values for the equilibrium constant determined from both sides with this catalyst in the temperature range of 175 to 275°C. are in fair agreement with those of Dodge and Bliss (19). Imperial Chemical Industries, Ltd., have constructed and operated a semitechnical plant scaled to produce 6 kilograms of refined alcohol per day (5), but no indication has been given whether or not the process is considered superior to the more familiar sulfuric acid process (119, 180, 182).

Other companies have been active in investigating the catalytic hydration of olefins, and the patent literature has expanded rapidly in the last few years. No attempt will be made here to present a complete compendium of existing patents. As already noted, Imperial Chemical Industries, Ltd., were early proponents of solid phosphate catalysts, notably cadmium metaphosphate (76). Phosphate salts, particularly when used in combination with compounds of boron, are stressed in the numerous patents taken out by The (British) Distillers Company, Ltd. (92). On the other hand, the Air Reduction Company (13, 119, 208) has continued to emphasize the use of dilute sulfuric or phosphoric acids under conditions such that the hydration mixture does not substantially alter the catalyst composition in passing through it.

Several patents assigned to the Shell companies (16, 201) have disclosed detailed experimental results on the use of vanadates and tungstates as catalysts. Aside from developments in large companies, the field of hydration has attracted the independent inventor (35), but it would be surprising if more than a small fraction of the substances included under patent coverage are really efficacious catalysts. Unusual patent disclosures include the use as catalysts of organic nitrogen bases (17) and volatile halides (106).

In the hydration of olefins higher than ethylene the position of the equilibrium is generally less favorable than for ethylene (181) and only low-temperature processes (62) are likely to be considered feasible. Remiz and Frost (154, 155) have reported a process for isopropanol based on the use of silver sulfate and sulfuric acid at a temperature of 105°C. Sulfuric acid containing copper has also been recommended (199). Lucas and his students (42, 43, 115, 116) have studied the homogeneous hydration of isobutene and 2-methyl-2-butene in the presence of dilute nitric acid. The reaction is first order and is promoted by potassium and mercury nitrates. Solubility effects apparently play a part in determining the rate of reaction under the conditions of this synthesis. Similar results have been obtained with 2-methyl-1-butene (112). Alpha-pinene is susceptible to hydration technique, but is easily polymerized and rearranged to other hydrocarbons. An attempt to hydrate it in the presence of acetic acid and Japanese acid clay gave mainly bornyl acetate (102). With an alcohol-dilute sulfuric acid mixture some terpin hydrate was obtained (27).

The catalytic hydration of the olefin bond is not limited to the treatment of unsaturated hydrocarbons, for crotonaldehyde reacts with water to form aldol in the presence of dilute mineral acids (210) or in the presence of an aqueous secondary amine, such as piperidine or sarcosine (105).

Hydration of Acetylene to Acetaldehyde, Acetic Acid, and Acetone

The catalytic hydration of acetylene leads to the formation of acetaldehyde, acetic acid, or acetone, depending upon the conditions employed. The aldehyde process is so well established commercially that it needs no special introduction. Hilditch and Hall (71) and Thommen (188) have given general accounts of the conditions required, and Ellis (47) has reviewed the recent literature. Although the process is generally understood to be conducted by passing acetylene through a warm aqueous acidic bath containing mercuric salts, it is not infrequent that reference is made to the use of a heterogeneous vapor-phase process.

The mechanism of the liquid-phase reaction has been investigated by Frieman, Kennedy, and Lucas (52), who report that the reaction rate is first order with respect to the acetylene concentration and second order with respect to the mercuric sulfate concentration. An intermediate complex is probably formed between one molecule of acetylene and two molecules of mercuric bisulfate, and the reaction of this complex with water is believed to form vinyl alcohol, which rearranges to acetaldehyde.

In recent years a number of new patents have made their appearance, claiming as improvements the use of catalysts comprising an alkaline-earth metal phosphate (37), cadmium metaphosphate (60), or both (168), a solution of a heavy metal halide (159), iron sulfate and mercury sulfate (87), and a weak sulfuric acid solution containing mercury and an acid salt (121). Acetic acid may be produced directly by passing a gaseous mixture of acetylene, steam, oxygen, and mercury vapor over a porous body carrying a hydration catalyst (40).

In contrast to the usual practice in hydrating acetylene to acetaldehyde, the hydration to acetone is always conducted at high temperatures in the vapor phase over a solid catalyst such as alkalized iron (72). Kagan, Sobolev, and Lubarski (94) have obtained evidence of the intermediate formation of ethyl acetate, which is supposed to be continuously hydrolyzed to acetic acid, which in turn undergoes the familiar decarboxylation reaction. The yield appears to be good at temperatures in the range of 350 to 500°, and the process, although only recently introduced, is understood to be commercially successful (72). Zelinskii and co-workers (217) investigated the use of a catalyst consisting of seven parts of ferric oxide and three parts of manganese dioxide, obtaining at 400 to 440°C. yields of acetone of 96 per cent from acetaldehyde and 88 per cent from acetylene. Optimum conditions were found to be a temperature of 440°C. and a steam-acetylene ratio of 10. A catalyst composed of zinc oxide and manganese oxide has also been recommended (198). Recent patents cover as improvements the control of the partial pressure of oxygen between certain fixed limits (158) and the use of pressures in the range 3 to 10 atm. (145).

Intramolecular Dehydration of Hydroxy Compounds

Intramolecular dehydrations are sometimes employed in effecting important syntheses, but in some cases at least they must be suppressed as side reactions in conducting other valuable processes. The thermal decomposition of hydroxy compounds takes place either by dehydrogenation to aldehydes or ketones or by dehydration to alkenes (163). Under most conditions the reactions are competitive and a mixture of products is obtained. The catalytic dehydration of alcohols over solid surfaces has been studied extensively, but is probably less well understood than other common catalytic phenomena. In general, unsaturated hydrocarbons are less valuable than the corresponding oxygen-containing compounds. Moreover, a low chemical yield results from the abstraction of water from the more familiar organic starting materials.

A general discussion of catalytic dehydration of alcohols has been given by Hilditch and Hall (70), and a bibliography has been compiled by Motovilova (123). Balandin and Rubinstein (12) investigated the kinetics of the competitive dehydration and dehydrogenation of isoamyl alcohol and the decomposition of the resulting aldehyde over mixed nickel-alumina catalysts. The Arrhenius equation was used for calculating the activation energies which were found to depend to some extent on the method of preparation of the catalyst. The authors conclude that the seat of catalytic activity for both processes is at the contact points of the components. The heats of activation for the dehydration of ethanol, *n*-propanol, *n*-butanol, and *tert.*-butanol over tungsten and thorium oxides have also been reported (2). The catalyst requirements for the dehydration of the simple alcohols have been rather intensively investigated in connection with developing a catalyst suitable for ethylene hydration (19, 23, 164). In general, alumina and thoria continue to merit a place of prominence in the list of dehydration catalysts, although iron, zinc, beryllium, and chromium oxides have also been used (162). In recent years phosphates and borates have found considerable favor (89, 143).

The dehydration of alcohols is frequently accompanied by a rearrangement in the structure of the resultant hydrocarbon. Accordingly, considerable study has been devoted to the constitution of the products from relatively simple alcohols.

The influence of the catalyst composition and the structure of the alcohol on the nature of the products is illustrated by the results of experiments in which various butanols were vaporized at the rate of ten drops per minute and passed over 60 grams of representative supported phosphoric acid catalysts as indicated in the following table. The products were analyzed by low-temperature fractional distillation (98). The butene mixture resulting from the decomposition of 1-butanol by hot sulfuric acid is approximately 35 per cent *cis*-2-butene and 65 per cent *trans*-2-butene (209).

CATALYST	TEMP. °C.	ALCOHOL	PRODUCTS
H_3PO_4-on-Al_2O_3	250	*n*-Butanol	1-Butene 45%
			2-Butene 55%
		sec.-Butanol	1-Butene 24%
			2-Butene 76%
		Isobutanol	Isobutene 100%
H_3PO_4-on-Pumice	350–400	*n*-Butanol	1-Butene 27%
			2-Butene 73%
		sec.-Butanol	1-Butene 47%
			2-Butene 53%

Drake and Veitch (34) found that heating *sec.*-butanol under pressure with 75 per cent sulfuric acid at 80°C. for a long time gave 3,4-dimethyl-2-hexene and di (*sec.*-butyl) ether. Catalytic dehydration of 3-pentanol over alumina at 380 to 400° gives 2-pentene in 80 per cent yield (109). The dehydration of tertiary carbinols has been studied by Meyer (120) and Nazarov (127). The latter investigator used bromonaphthalenesulfonic acid as a catalyst for the cleavage of di-*tert.* carbinols. Lastly, the dehydration of tetrahydrofurfuryl alcohol over alumina leads not to a methylenetetrahydrofuran but to 1,2-dihydropyrane (140). Furfuryl alcohol, however, undergoes disproportionation to yield methylfuran and furfural (141).

One of the more interesting applications of catalytic dehydration of alcohols is found in the preparation of diolefins from glycols. A number of patents have been taken out on the preparation of butadiene from 1,3-butylene glycol (124, 156), a process which is believed to form the basis for a synthetic rubber development in Germany. Among the catalysts disclosed for this purpose are phosphoric acid-on-pumice, alkali-metal phosphates, copper sulfate, phosphorus, and aluminum silicate. Diolefins of higher molecular weight are formed by starting with abietyl alcohol (86) or oleyl alcohol (85). Castor oil loses water when heated with acidic earths (214) and octadecanediol-1,12, its reduction product, is converted to a polymeric condensation product (39) or an olefin alcohol (61), depending on the conditions employed. Urion (196) has reported on the course of the dehydration of alpha-ethylenic alpha-glycols and has found that divinyl glycol (197) dehydrates to different products over alumina and sulfuric acid. Likewise, the dehydration of *cis*- and *trans*-cyclohexanediols leads to a different distribution of products over the same catalyst (189). A mixture of potassium sulfate and the acid sulfate is reported to be superior to iron phosphate or Japanese acid clay as a catalyst for the dehydration of glycerin to acrolein (63).

Ethers from Alcohols

The catalytic dehydration of methanol and certain glycols leads to the formation of ethers in preference to olefins. The process is most frequently referred to in connection with the production of dimethyl ether from methanol, a process which may be carried out at atmospheric or higher pressures over dehydration catalysts such as aluminum phosphate (212). Kuss (101) has made a comprehensive study of the thermal decomposition of methanol and has noted that the formation of dimethyl ether is one of the primary reactions. Ether formation was most strongly catalyzed by rough aluminum with an oxidized surface. In the presence of a mixed catalyst such as $ZnO - Al_2O_3$, formaldehyde is formed besides the ether (100). Fenske (50) has patented a continuous process for etherification which employs as the catalyst an acid such as phosphoric acid in the same phase as the alcohol. According to another process (31), alcohol vapor is brought into contact first with an oxide-type catalyst followed by a second stage in which a salt-type catalyst is used. Finally, Dreyfus (36) has proposed the synthesis of cyclic ethers from glycols by heating them in the presence of hydrogen chloride.

Esterification

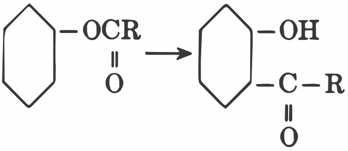
The interaction of an organic acid with an alcohol to produce an ester and water is one of the oldest and most familiar examples of intermolecular dehydration reactions. It is generally understood that such reactions involve an equilibrium

$$RCOOH + R'OH \rightleftarrows RCOOR' + H_2O$$

It has been fairly well established that the point of equilibrium is not appreciably affected by temperature changes or by the addition of conventional esterification catalysts such as strong mineral acids. The only effect of the latter is to increase the rate at which equilibrium is established when starting from one side or the other of the above equation.

E. E. Reid, in a general discussion of esterification (153), has pointed out that in order to obtain the highest possible yield of ester it is of greatest importance to establish conditions that favor displacement of the equilibrium. Various expedients have been used to accomplish this, including the use of an excess of one or the other of the reagents, or the removal of one of the products from the reaction zone. The latter procedure is usually preferable, and, during the past few years, several interesting methods for doing this have been suggested. In the preparation of ethyl oxalate from ethanol and oxalic acid, Thielpape and Fulde (187) have recommended continuous distillation of excess alcohol through a continuous extractor containing calcium carbide to remove water. Alcohol is returned to the reaction mixture. Bannister (14) has patented a process for bringing about complete esterification involving the use of a volatile solvent capable of forming a ternary mixture with the alcohol and water. Thus, in making diethyl phthalate, removal of the water by distilling the ternary mixture water-benzene-alcohol leads to nearly quantitative yields of the ester. Török (192) suggests a more complicated procedure, involving two separate working stages carried out consecutively. In the first stage an excess of alcohol is employed, and in the second an excess of acid. The excess acid in the second stage is practically completely esterified by subjection to a countercurrent stream of alcohol vapor. Conversely, the mixture of alcohol and ester vapors from the first stage are treated countercurrently with acid vapors to effect complete esterification. Holt (73) has found that propionic esters of polyhydric alcohols, such as diethyleneglycol, can be made conveniently by reacting the glycols with propionic acid in toluene solution in the presence of sulfuric acid. A recent Continental Oil Company patent (59) describes a process for esterifying monocarboxylic acids with monohydric alcohols by mixing the less volatile reactant with a strong, non-volatile catalyst and passing in superheated vapor of the more volatile reactant. Cox and Grier (30) prefer a simpler process involving heating the alcohol with the acid under pressure in the presence of a catalyst such as sulfuric acid. Butyl acetate and isopropyl acetate have been prepared in this way. An interesting improvement in the refining of such esterification mixtures (49) comprises extracting the sulfuric acid catalyst with aqueous acetic acid solution. The extracted ester layer can be refined by distillation without the undesirable effects usually encountered when sulfuric acid is present.

Although sulfuric and hydrochloric acids are conveniently used as catalysts in esterification reactions in the laboratory, they have certain disadvantages for use on an industrial scale. Hydrogen chloride is particularly unsatisfactory from the standpoint of its corrosive action on metallic equipment. Sulfuric acid is less likely to cause corrosion, but it may produce undesirable side reactions, such as olefin formation or charring. In view of this situation, several other materials, equally effective as catalysts, have been suggested. Sowa and Nieuwland (178) recommend gaseous boron fluoride or a boron fluoride-ether complex for use in the direct esterification of aromatic acids. Skraup (175) has patented the use of heteropoly acids, such as silicomolybdic, phosphotungstic, and phosphomolybdic acids as catalysts for the direct esterification of carboxylic acids and phenols. These materials will also cause rearrangement of phenyl esters to the corresponding hydroxyketones.



Recently, there has been a tendency to substitute aromatic sulfonic acids for sulfuric acid in esterification reactions. For example, in preparing methoxyalkanol esters of dicarboxylic acids, Izard (91) has found that hydroxyphenylsulfonic acid is an effective catalytic material. Similarly, " Twitchell " reagents have been recommended for the preparation of synthetic glycerides (90). Nazarov and Khain (128) have employed a mixture of petroleum sulfonic acids, called " Kontakt," as the catalyst in the synthesis of isopropyl acetate. These investigators regard " Kontakt " as a more satisfactory esterification catalyst than aromatic sulfonic acids, not only because of its greater activity, but because it is much cheaper for use on an industrial scale. Aside from true catalytic effects, Spellmeyer (179) has found that an alternating current accelerates the rate of esterification. For a more detailed discussion of earlier work on the esterification of organic acids, particularly in the vapor phase, the reader is referred to the excellent summary by Reid (153).

Another important type of esterification procedure involves the reaction of an alcohol with a halogen acid to produce an alkyl halide. Although one of the reactants is inorganic, the reaction is strictly analogous to the formation of carboxylic esters, and the same kinetic laws are applicable. For the most part, this reaction has been employed by industry for the synthesis of the lower alkyl halides, particularly ethyl chloride, and various practicable methods of operation have been suggested. Teupel (186) has obtained good results in a slow continuous liquid-phase process that involves heating ethanol with hydrogen chloride under a pressure of 16 atm. at a temperature between 110 and 180°C. The process is applicable generally to alcohols containing up to eighteen carbon atoms. Holt and Daudt (74) have developed an atmospheric-pressure ethyl chloride process that comprises passing ethanol vapor and hydrogen chloride continuously through an aqueous catalyst mixture containing 70 to 80 per cent of $ZnCl_2$ maintained at 135 to 140°C. Eberhardt (41) recommends the use of a batch process, in which a mixture of dry ethanol and dry hydrogen chloride are reacted at moderately low temperatures in the presence of dry zinc chloride. The ethyl chloride is distilled from the reaction mixture as formed.

Alkylation and Arylation of Ammonia and Amines

The reaction of alcohols or phenols with amines or ammonia to form water and nitrogen bases having a higher degree of alkylation is a type of dehydration that has recently received much technological attention. The process may be carried out as a continuous vapor-phase reaction employing alcohols or ethers as the source of the alkyl groups. The catalyst requirements have been investigated by several Russian investigators (172), who found that the performance of alumina was not enhanced by the addition of other catalyst components such as the oxides of iron, zinc, or chromium. On the other hand, with ethanol and ammonia these materials led to the formation of undesirable amounts of olefins. This problem of selectivity has been partly solved by using aluminum silicate catalysts (8) or alumina supported on activated carbon (10, 108) or silica gel (7). According to some advices (52, 89) the process is favored by the use of superatmospheric pressures. In the synthesis of methylamine there is no difficulty with dehydration side reactions, and the products may be recycled in order to obtain exclusive production of compounds of the desired degree of alkylation (6, 67). Aluminum phosphate (4) and alumina gel (6, 83) have been recommended specifically as catalysts for methylamine synthesis. Methyl ether has been used in the synthesis of dimethylamine (183), and higher ethers in the alkylation of aniline (80). Ammonia has been arylated with phenol under pressure in the presence of dehydration catalysts (51, 65). The catalytic amine synthesis has also been applied to the preparation of higher amines from higher alcohols derived from the hydrogenation of carbon oxides (66) and long-chain fatty acids and esters (9, 167, 171, 176). Yurev and Rakitin (216) have investigated the formation of pyrrole from furan and ammonia and found it to be a true dehydration reaction having a highly specific catalyst requirement.

Dehydration of Carboxylic Acids

The catalytic dehydration of formic acid to carbon monoxide has been investigated by Graebner and Cryder (57). Alumina, aluminum phosphate, and silica gel impregnated with dehydrating oxides such as thoria are effective at 300°C., and 90 to 95 per cent yields of carbon monoxide are obtainable. The contact dehydration of acetic acid has also attracted some industrial interest as a method for the production of acetic anhydride and is covered by numerous patents to Dreyfus (38). Aside from the usual dehydrating oxides and salts (38), red-hot charcoal (58) and complex acids such as silicotungstic acid (125) have been recommended as catalysts.

Synthesis of Hydrogen Cyanide and Nitriles

An interesting industrial application of catalytic dehydration is found in the synthesis of hydrogen cyanide from formic acid and its derivatives. For this purpose, Pip (142) has recommended passing a gaseous mixture of formamide with ammonia, nitrogen, hydrogen, and the like, over pumice at temperatures between 300 and 800°C. Hydrogen cyanide yields of 92 per cent are obtained. Similar yields are obtained by using fused manganese oxide as the catalyst at temperatures between 400 and 700°C. (107). Münch and Nicolai (126) have carried out the synthesis in the absence of catalysts by exposing formamide or ammonium formate vapors briefly to high temperatures in narrow tubes fabricated of iron-containing alloys. Improved heat-exchange efficiency is said to result from conducting the reaction in contact with heated metal surfaces coated with a thin layer of zinc oxide (169). Rare-earth metal oxides and alkaline-earth metal oxides promoted with copper function as catalysts in an equivalent process involving ammonia and carbon monoxide as starting materials (21, 26). The earlier literature, apparatus, and methods for preparing special alumina catalysts are discussed by Fuchs and Verbeek (54).

In general, methods employed in the catalytic synthesis of higher fatty nitriles involve less drastic conditions than have been used in the case of hydrogen cyanide. Acetonitrile can be prepared conveniently by distilling mixtures of ammonium acetate and acetic acid at 200 to 210°C. (22). A similar process applicable to fatty acids having six or more carbon atoms comprises passing gaseous ammonia through the acid heated to a temperature between 250 and 350°C. (151). Usually, however, operation in the gas phase is preferred. By passing suitable mixtures of ammonia and vaporized fatty acids over dehydrating catalysts, such as aluminum oxide, silica gel, and bleaching earths at temperatures in the neighborhood of 330 to 380°C., good yields of the corresponding nitriles can be obtained (84, 150). It has been noted by Ralston, Pool, and Harwood (149) that at temperatures above 400°C., long-chain nitriles undergo cracking reactions to produce lower nitriles. Nicodemus and Wulff (81, 132) have employed thoria, alumina, and silica gel as catalysts for converting long-chain hydroxy acids to unsaturated nitriles and resin acids to valuable resin nitriles. In the aromatic series, Linstead and Lowe have patented a process for preparing ortho- and peri-aryl dinitriles in which the corresponding amides, anhydrides, or acids are passed with an excess of ammonia over thoria, alumina, or silica gel catalysts at temperatures between 300 and 550°C. (111).

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CHAPTER XVIII

HALOGENATION AND HYDROHALOGENATION REACTIONS BY CATALYTIC PROCESSES

(Covering the period of 1936 and 1937)

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THEORETICAL CONSIDERATIONS

The theoretical aspects of halogenation and hydrohalogenation reactions received a considerable amount of attention during the years 1936 and 1937. Inasmuch as it is difficult in some instances to draw a sharp line of demarcation between catalytic and non-catalytic processes of this character, for the sake of completeness, some references to reports concerning phenomena not strictly catalytic have been included.

Recently there have appeared a number of reviews of the subject dealing chiefly with the older work. Hass (34, 35) has written several excellent articles on the chlorination reactions of olefin bonds and of methane and its homologs; Thomas (97) has discussed in some detail chemicals derived via the chlorination of pentanes. Krech (54) in a review discussed mechanism of chlorination of inorganic and organic compounds in the presence of inorganic chlorides as catalysts with and without the addition of carbon. It is widely accepted that chain mechanisms play the dominant role in reactions of homogeneous chlorination and also probably in the presence of catalysts. Semenov (80, 81) has advanced the far-reaching conception, not generally accepted, that all chemical reactions involve chains, the " classical " uni-, di-, and trimolecular reactions being special cases which conform to the mathematical formulation of his theory. He applies this theory not only to halogenation, but also to oxidation, polymerization, and decomposition reactions. Many heterogeneous reactions can be explained only as consequences of chain mechanisms developed by means of " catalytic machines."

Sun and Liu (92) have calculated by Eyring's method the activation energies involved in the addition of the hydrogen halides to a double bond; they have shown that the readiness of addition decreases in the order HI > HBr > HCl, in agreement with experiment. The scope of the paper has been extended and amplified by Sherman, Quimby, and Sutherland (82), who have statistically estimated the activation energies and heats for the possible reactions between ethylene or its derivatives and the halogens. It is shown that symmetrical addition is favored in the case of each halogen; vinyl compound formation and dichloride decomposition also are treated. In most of the reactions considered, mechanisms involving free radicals are found to be slightly more probable than the corresponding uni- or bimolecular reactions. Further attention has been given the problem of the mechanism of addition in solution, especially as regards stereo-isomer formation, by Ogg (66), Bartlett and Tarbell (7), and Roberts and Kimball (71). Ogg advances the view that the reaction is catalyzed by halide ion and the first step is the formation of a carbanion; this in turn reacts with a halogen molecule giving the saturated product and regenerating the negative halide ion. The theory is extended to explain unequal *cis* and *trans* isomer production. Bartlett and Tarbell postulate the formation of a positive ion as the intermediate, and Roberts and Kimball have shown theoretically that there can be no free rotation of component parts of the molecule about the C–C axis. However, under the influence of highly polar substitutive groups in the intermediate, rotation may occur. In this manner it becomes possible to explain qualitatively the unequal amounts of *cis* and *trans* isomers formed by such halogenation. The relation of steric orientation to the mechanism in substitution reactions involving halogen atoms also has been discussed (13).

The directed addition of hydrogen halides, especially of hydrogen bromide, has been studied extensively by Kharasch and his co-workers (48, 49, 50, 51, 52), who have been interested for some time in the " peroxide effect." The results may be summarized thus: The addition of hydrogen bromide to ethylenic compounds results in primary bromides whenever peroxides are present, while secondary bromides are formed in the presence of antioxidants. This, Kharasch claims, puts Markownikoff's rule on a firmer basis by accounting for the mechanism of exception to the rule under the influence of peroxides, applicable not only to short-chain unsaturated compounds but also to the higher alkenes. Similarly with hydrogen bromide and methylacetylene the " normal " reaction at room temperature yields 2,2-dibromopropane; the peroxide-catalyzed reaction gives the 1,2-dibromide at room temperature and the 1,1-compound at -40°C. In the presence of antioxidants, butadiene-1,3 yields 2-bromobutene-2, while peroxides cause the formation of 1-bromobutene-2; no 3-bromobutene-1 is produced. Solvents do not affect the direction of addition, but do alter rates. Peroxides greatly accelerate the side-chain halogenation of toluene. A chain mechanism involving halogen atoms is favored by Kharasch. The " effect " is now covered by patents (47).

The effect of oxygen on halogenation reactions has long been known and further observations have been made. Willard and Daniels (108) noted that the rates of photobromination of tetrachloroethylene and chloroform are increased by very small amounts of oxygen but inhibited by larger amounts. Urushibara and Takebayashi (cf. 102), who have published prolifically on the " peroxide effect," as described by Kharasch, are, in contradistinction to the latter author, inclined to attribute this phenomenon also to an action of dissolved molecular oxygen. They have found that ferromagnetic metals act like peroxides. A pictorial theory is advanced that one molecule of oxygen is capable of physically influencing in some manner a large number of molecules of the unsaturate and hydrogen bromide; this influence is associated by these authors with the magnetic susceptibility of oxygen and the active metals, but this seems to the reviewers a somewhat speculative interpretation of the data.

Brenschede and Schumacher (11) have worked on the chlorine-sensitized photoöxidation of methane and its chloro derivatives (61), and the latter has written several articles (77, 78, 79) on the catalytic activity of the halogens themselves, especially in oxidation and decomposition reactions.

Stewart (87, 88, 89, 90) has continued his extensive work on chlorination, chiefly in its photochemical aspects. Further information has been assembled concerning " induced " substitution into the addition products and into simultaneously present paraffins. Stewart proposes mechanisms involving chlorine atoms giving rise to chains which are broken by atomic recombination. In the case of 2-pentene in carbon tetrachloride, the product was largely 1-chloropentene-2, and this substitution was interpreted as a reaction " induced " by the normal addition process.

General Applications

The rapidly growing interest in chlorinated products as intermediates and as commercial products has resulted in a considerable volume of data during the past two years. The increasing use of unsaturated chlorides for synthetic rubber production, insecticides, solvents, and as intermediates is an especially important development. Aluminum chloride has been (cf. 23, 68) used extensively as a catalyst for condensation reactions giving polyhalides and is treated more fully elsewhere in this report. Further, ethyl chloride in 94 per cent yield has been prepared (73) by reacting ethylene present in cracked petroleum gases with hydrogen chloride in the presence of aluminum chloride at −78 to −12°C.; at the lower temperatures less residue is formed (5 per cent) than at the higher (11 per cent).

Saturated Hydrocarbons

The findings of Hass and his co-workers (cf. 35) have thrown much light on the chlorination of paraffins. The ratio of secondary to primary substitution at high pressures has been measured; in the vapor phase increase of pressure results in an increase of primary substitution. Various catalysts, as iodine, sulfur, and chlorides of certain heavy metals (Sb, Sn, Bi, Al, As, and Ti), have relatively little effect toward altering the ratio of substitution products. Seventy per cent yields of hexachloroethane were obtained (59) by chlorinating ethane over active carbon. The chlorinations of oils and paraffins, both in liquid and gas phase, giving rise to not too definite products were investigated extensively (12, 38, 69, 72, 95). Tarasova (96) has made the interesting observation that in the bromination of 1-methyl-2-ethyl cyclopentane over aluminum bromide the ring is enlarged, giving tetra-bromo-*p*-xylene. Grebe, Reilly, and Wiley (28) produced symmetrical tetrachloroethane by passing refinery gas mixtures of saturated hydrocarbons and chlorine through a bath of molten metal chlorides ($AlCl_3-FeCl_3-NaCl$ eutectic) maintained at 250 to 500°C. Tishchenko (15, 98, 100, 101) has worked on the chlorinations of isopentane and the chlorobutanes. Daudt, Youker, and Reynolds (14) utilized antimony fluorichloride to catalyze the reaction of hydrogen fluoride and carbon tetrachloride at 45 to 95°C. to give dichlorodifluoromethane; the latter is used as a refrigerant.

Halogenation of Unsaturated Hydrocarbons

Ruys and Edwards (75) added halogens to unsaturated hydrocarbons in the presence of calcium chloride under anhydrous conditions at 20 to 120°C. with superatmospheric pressure. Alkali and alkaline-earth ferro- and cuprocyanides mixed with chlorides were used to promote at elevated temperature the addition of halogens to olefins (63, 64). Berliner (8) chlorinated ethylenic compounds in a solution of tri- and tetrachloropropanes and butanes. A process used by I. G. Farbenindustrie (39) also employs solvents with chlorides of the fourth and seventh groups used as catalysts. Bromine is blown out of solution by means of an inert gas, mixed with olefins, and passed over a carbon catalyst to make dibromides in a process developed by Boundy and Raush (10). Tishchenko (99) used calcium carbonate and soda as catalysts for the liquid-phase chlorination of trimethylethylene. The rate of iodination of cyclohexene by iodine in the presence of salts of heavy metals (for example, $AgNO_3$, $AgClO_4 + PbCl_2$, etc.) was found (9) to depend not only on the kind but also on the amount of salt; this is taken to indicate intermediate compound formation. The effect of substituent groups on the additive reactivity of ethylene derivatives toward bromine was further studied by Ingold (3). The relative rates of addition at −70°C. in methylene dichloride are: C_2H_4, 1.0; C_3H_6, 2.0; $Me_2C{=}CH_2$, 5.0; $Me_2C{=}CHMe$, 10.4; and $Me_2C{=}CMe_2$, 14.0. Heisig and Davis (36) found that oxygen inhibits the addition of bromine to butadiene-1,3. Von Gebauer-Fuelnegg (26) succeeded in completely chlorinating butadiene polymer at room temperature.

A satisfactory process for the manufacture of some unsaturated monochlorides recently was developed by Engs and Redmond (21); allyl chloride is formed in good yield when propylene and chlorine, preheated to 200 to 500°C., are mixed with great rapidity. The control of methallyl chloride formation from isobutene and chlorine has been further investigated (16). It is also reported (62) that under certain conditions unsaturated chlorides are produced from butene-2,2-chlorobutene-2, and cyclohexene. Further reactions of unsaturated halides with halogens in the presence of water to give polyhalides or halohydrins were studied by Groll and Hearne (29, 30, 31).

Halogenation of Aromatic Hydrocarbons

Beryllium bromide was used (67, 94) as a catalyst in the bromination of benzene; both phenyl bromide and *p*-dibromobenzene are formed.

In the Soviet Union, where much research in this field is being done, Krivonos (55) studied the chlorination of benzene with the purpose of reducing the poly-substitution; Vasserman and Rafalovich (104) made highly chlorinated naphthalene, a polymer base, by reaction with chlorine in the presence of iron shavings at 100 to 130°C.

The halogenation of alkyl side chains was extensively studied. Among the investigations were the following: reaction of isopropyl and isobutylbenzenes with chlorine in the presence of powdered metals (45); production of benzyl chloride for which silica, alumina, and carbon were used (2); chlorination of ethylbenzene in the presence of organic bases such as pyridine (85); and the extensive studies of Oda (57, 65) on the halogenation of aromatic compounds.

The catalytic halogenation of halogenated benzenes was investigated by Varma and his co-workers (103), Wibaut and his associates (106, 107), van der Linden (58) and Wahl (105).

Hydrohalogenations

Jones and Ogg (44) measured the equilibrium in the addition of hydrogen iodide to isobutene at 408 to 464°C.; $\Delta H = 19{,}150 \pm 1000$ calories. ΔF of formation $(CH_3)_3CI(g) = 6260$ calories; the entropy of $(CH_3)_3CI = 60.2 \pm 3.3$ E.U. The activation energy for the addition of HF to C_2H_4 is 64.3 calories according to the calculations of Sun and Sze (93).

Considerable work has recently been done on the production of alkyl halides. The additions of hydrogen halides to olefins are promoted by a variety of materials; the newer papers include the use of alkyl halosulfonates with bismuth chloride (70); absorbent hydrous metal oxide gels (91), (gelatinous precipitates); dehydrated alumina (25); ferric chloride, zirconium chloride, or antimony chloride (17), barium chloride (6), supported zinc chloride (40), aluminum chloride (74), and oxidants such as benzoyl peroxide (1).

The addition of hydrogen bromide to styrene is influenced (86) by peroxides; with benzoyl peroxide in ethylbenzene, 92 per cent β-bromide is formed; without the catalyst, 63 per cent α and 30 per cent β result. Butadiene and its derivatives are treated (60) with liquid hydrogen chloride to give addition products. The direction of addition of hydrogen bromide to allyl chloride is profoundly influenced by temperature (83); at −19°C. 1,3-chlorobromopropane is the principal product; at 18°C. 1-chloro-2-bromo compound is dominant, while mixtures result in the intermediate zone. Acetylene with hydrogen chloride under the catalytic influence of cuprous chloride-ammonium chloride yields vinyl chloride (5). Kozlov (53) used a similar process for making vinyl bromide.

In the field of synthetic rubber du Pont (18) holds patents relating to the catalytic addition of hydrogen halides to monovinyl acetylene to produce halogenated butadienes and butene. Many catalysts are mentioned, among which are the following chlorides: mercury, magnesium, gold, calcium, copper, ammonium, pyridinium, and methyl ammonium. Khaltykyan (46) investigated the control of the acid cuprous chloride catalyst used in the production of chloroprene; he has devised an apparatus for measuring the $CuCl_2/Cu_2Cl_2$ ratio by electrode potentials. Peroxides were found (110) to direct the addition of hydrogen bromide to butylacetylene to form 1-bromo-hexene-1 and 1,2-dibromo-hexane, whereas in their absence only the 2-bromohexene-1 and 2,2-dibromohexane occur. It is worth mentioning also that Arnold and Lazier (4) have dehalogenated organic vapors, such as ethyl chloride, by reduction with hydrogen at 200 to 600°C. over sulfides such as those of chromium or molybdenum.

Reactions with Oxygen-Containing Compounds

This arbitrary classification is adopted to permit the grouping of a considerable number of catalytic processes which are not otherwise readily placed. There are several new inventions relating to the production of alkyl halides from alcohols. Haack (32) reacted alcohols with hydrogen halides at elevated temperatures (150°C.) in the presence of salts of strong acids or nitrogenous heterocyclic compounds. Bromination of alcohols by means of red or yellow phosphorus is also reported (27). Haack's invention is closely paralleled by two other patents, one by Wirth (109) relating to the use of calcium chloride in promoting the reaction of *t*-butyl alcohol with hydrogen chloride, the other by Holt and Daudt (37), who employ zinc or bismuth chlorides at 130 to 145°C. to react alcohols of less than four carbon atoms with hydrogen chloride. Finger and Reed (24) reacted hydrogen fluoride with ethyl alcohol, giving ethyl fluoride and ether; metal fluorides act as catalysts.

The catalyzed reactions of aliphatic (19, 33) and aromatic (41, 43) acids, halogens, and their hydrides also received attention. Dvornikoff (20) chlorinated molten phthalic anhydride, using ferric chloride or sulfate as a catalyst. Alkenyl esters on bromination underwent spontaneous cleavage to give bromoketones and acyl halides (84). Aluminum oxide at 280°C. promotes the reaction of ethers with alkyl polyhalides to give alkyl halides (42) and chloromethyl ethers have been made by reacting dimethyl ether with chlorine at room temperature in the liquid phase in the presence of chlorides of heavy metals (76). Dichloro derivatives (2, 3) have been quantitatively prepared by the catalytic chlorination of dioxane; iodine chloride and tin tetrachloride are used (56). Production of acetyl chloride can be easily accomplished by adding hydrogen chloride to ketene at 100°C. over carbon or silica gel (22).

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CHAPTER XIX

HALIDE CATALYSTS*

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This section is written about those halide catalysts sometimes referred to as Friedel-Crafts catalysts, which are capable of catalyzing certain classes of reactions, including but not confined to the original Friedel-Crafts reactions. Some members have been included in the discussion which are not substantially effective for the Friedel-Crafts reactions. We are particularly concerned in this review with the applications of these catalysts in isomerization, cracking, alkylation, dealkylation, polymerization, hydrogenation, and dehydrogenation reactions rather than with the original Friedel-Crafts reaction, i.e.,

$$RX + R'R'' = R'R''R + HX$$

where X is halogen, and especially chlorine, R may be, e.g., alkyl or acyl, R′, hydrogen, alkyl, aryl, etc., and R″, particularly, an aromatic ring structure. The list of reactions above is sufficient to emphasize the extraordinary versatility of these catalysts, and their corresponding importance in catalytic theory. An understanding of this chemistry not only would clarify a field itself important and rapidly growing, but also would give a better understanding and no doubt finer control of the Friedel-Crafts reactions themselves, where isomerizations, cracking, etc., detract from the value of the synthesis in some instances. It seems proper, however, to consider simultaneously theories of the Friedel-Crafts reactions since the mechanisms of the reactions being considered may be related.

A valuable review, covering 153 references, on the reactions of pure hydrocarbons in the presence of aluminum chloride has been published by Egloff, Wilson, Hulla, and van Arsdell (22). That review is more encyclopedic in character than the present one, though it is limited to aluminum halides. The work consists largely of a presentation of the

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* Contribution from the Graduate School, Western Reserve University.

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empirical results obtained by the action of aluminum halides on various *types* of hydrocarbons.

P. Kränzlein (51), extending the work of G. Kränzlein (50), has summarized recent applications of the Friedel-Crafts reaction, particularly those of technical importance. He included, however, some of the other reactions catalyzed by halides, discussed in the present report.

Calloway (15) has contributed an industrious review on the Friedel-Crafts synthesis. This review, which involves 470 references, can be recommended heartily. It is concerned primarily with syntheses of the more strictly Friedel-Crafts type, which can be accomplished by means of the catalytic effect of halides, without special consideration of their technical importance. Calloway considered the Gatterman, Gatterman-Koch, Hoesch-Houben, Fries, and Scholl reactions, as well as polymerization and cracking to be sufficiently closely related to the Friedel-Crafts reaction to be considered as subdivisions thereof. It is possible too that the Swarts reaction in which $SbCl_5$ is a catalyst and fluorine from SbF_3 is exchanged for chlorine is related to this group. Calloway's viewpoint plainly is justified at least in the case of the Gatterman-Koch reaction. Calloway's review also contains some consideration of halide catalysts other than $AlCl_3$.

The present review is supplementary to the above. It is concerned primarily with collecting and arranging evidence in the field which may improve our understanding of the mode of action of these catalysts. This is done along four lines:

1. The action of the different catalysts which have some Friedel-Crafts action is compared.
2. The simple reactions in hydrocarbon chemistry, catalyzed by halides, are enumerated and described.
3. The general features of the more complex reactions in hydrocarbon chemistry, catalyzed by halides, are described.
4. The various theories which have been proposed for the mechanism of the action of halide catalysts are compared, some effort being made to evaluate them.

The question as to what individual reactions may be catalyzed by these halides is too large for this report and in any event is reasonably well answered in the reviews of Egloff, Wilson, Hulla, and van Arsdell, and of Calloway (15), (22).

THE ACTIVE HALIDES

The halides which, from some points of view at least, may be grouped together as catalysts are listed in Table I (p. 254), together with the reaction types which they catalyze and other noteworthy remarks.

Aluminum halides, particularly the chloride, have been most used and investigated. This is partly for economic reasons, and partly because of the large background of experience with $AlCl_3$. Mole for mole, the more expensive aluminum bromide is more active than the chloride. Sometimes a less active catalyst gives a larger yield of desired products. Aluminum fluoride has been reported to have but feeble activity. This catalyst will polymerize cyclopentadiene but is inactive (103) for the reaction of acetyl chloride or fluoride with benzene or methylphenyl ether (17). Aluminum iodide will polymerize cyclopentadiene (103).

Boron fluoride has pronounced activity in some of the reactions catalyzed by $AlCl_3$, especially polymerization (see Table I). With it, cracking does not appear to be as pronounced, which is sometimes an advantage. Isomerizations accompanying polymerization may, however, go as far as carbon skeleton rearrangement, as illustrated in the polymerization of tetramethylethylene by BF_3 (12). This catalyst has received much attention in recent years (see Table I). Other reactions effected by means of BF_3 are the alkylation of aromatic compounds with olefins, e.g., benzene with propylene, and the direct esterification of acids with olefins, e.g., propylene and higher olefins. BF_3 is a catalyst for Friedel-Crafts reactions (38) but is not widely used for the purpose. It is preponderantly a polymerization catalyst. Scarcely any work has been published on the catalytic action of the other boron halides. Wiberg and Heubaum (110) did not obtain a reaction with BCl_3, ethyl chloride, and triphenylmethyl chloride.

Ferric chloride has been investigated frequently as a member of this group of catalysts (Table I).

Noller and Riddell (80) have investigated the influence of mixtures of $FeCl_3$ and $AlCl_3$ in effecting conventional Friedel-Crafts reactions. They concluded that in some instances an additive result was obtained, but in other cases an optimum result was obtained with about 50 mole per cent of $FeCl_3$.

A maximum activity at >50 per cent $FeCl_3$ with $AlCl_3$ was reported by Martin, Pizzolato, and McWaters (54) for the reaction of benzoyl chloride with toluene. Boswell and McLaughlin (11) rate $FeCl_3$ as having about one-third the activity of $AlCl_3$ for certain Friedel-Crafts reactions. But some mixtures of $AlCl_3$ and $FeCl_3$ were more active than $AlCl_3$ alone. The importance of a knowledge of the amount of HCl present must be emphasized in making such comparisons, though a variation in this factor is not the sole explanation of the effects.

Ferric chloride has been proposed as a polymerization catalyst in at least fourteen instances, and less frequently for hydrogenation, dehydrogenation, and alkylation (Table I).

TABLE I

HALIDE CATALYSTS

Catalyst	Reactions Catalyzed	Remarks	Reference No.
$AlBr_3$	Polymerization Isomerization Cracking Hydrogenation Dehydrogenation Alkylation Dealkylation Friedel-Crafts	Catalyst substantially soluble in hydrocarbon. More active than $AlCl_3$. HBr (or HCl) necessary.	See note.
$AlCl_3$	Polymerization Isomerization Cracking Hydrogenation Dehydrogenation Alkylation Friedel-Crafts	The most studied reaction. HCl (or HBr) necessary. Catalyst very slightly soluble in hydrocarbons.	Discussed in present report.
AlF_3	Polymerization	Cyclopentadiene polymerization.	98
AlI_3	Polymerization	Cyclopentadiene polymerization.	98
AsF_3	Polymerization	Cyclopentadiene polymerization.	98, 45
AsF_5	Polymerization		45
BCl_3	Polymerization	Styrene.	96
		Cyclopentadiene polymerization.	98
		Isobutene.	45
		Vinyl chloride.	86
	Friedel-Crafts	Failed with EtCl or $CH_3F + Ph_3CF$ or Ph_3CCl.	106
	Racemization	 $C_6H_5CHCH_3$ (Cl)	5

BF_3	Polymerization	Olefins, diolefins, or vinyl compounds.	2, 3, 4, 15, 36, 37, 38, 46, 48, 73, 74, 80, 83, 99, 109
	Alkylation	$C_2H_4 + C_6H_6$, isoparaffins. C_3H_6 + salicyclic acid. C_2H_6 + acetic acid ⟶ esterification. $C_3H_6 + C_6H_6$.	18, 19, 20, 50, 85, 89
	Dealkylation		
B halides	Polymerization	Vinylethinylcarbinols. Diolefins.	14 1
	Friedel-Crafts	BF_3 preferred.	
$BeCl_2$	Alkylation	$C_2H_4 + C_6H_6$. Efficiency 50 at 200°C. ($AlCl_3$ = 75 at 75°C.)	30
	Dealkylation		
$BeBr_2$	Friedel-Crafts	Efficiency < $AlCl_3$. $PhCCl_3$ as reactant.	76
$BiCl_3$	Polymerization	Cyclopentadiene.	98
Bi halides	Polymerization	Vinylethinylcarbinols.	14
$CbCl_5$	Alkylation	$C_2H_4 + C_6H_6$. Efficiency 25 at 75°C. (Al = 75 at 75°C.)	30
	Dealkylation		
Cobalt halides	Polymerization	Olefins. Linear esters depolymerized.	43, 81 90
Cr halides	Polymerization	Oil. Rubber.	71 84
Cu_2Cl_2	Polymerization		(See Cu halides.)
Cu halides	Polymerization	Olefins. Polyhydric alcohols. Acetylene.	43, 81 72 12, 16, 21, 23, 68, 69, 70, 77
	Alkylation	Acetylene + aromatic amines.	58
	Dealkylation		
$FeBr_3$	Polymerization	Cyclopentadiene polymerization.	98

TABLE I (*Continued*)

Catalyst	Reactions Catalyzed	Remarks	Reference No.
$FeCl_3$	Polymerization	*Tert.* olefins.	28
		Resins.	24
		Rubber.	84
		Cyclopentadiene.	98
		Linear esters depolymerized.	90
		Olefins.	27
		Vinyl compounds.	44, 43, 81
		Vinylethinylcarbinols.	14
		Isobutene.	45
	Friedel-Crafts	$C_6H_6 + C_2H_5Br$.	104
		Aromatic compounds + alkyl halides.	8
	Friedel-Crafts		6
		C_6H_6 + benzoyl chloride.	82
		Toluene + benzoyl chloride or benzyl chloride.	63
		C_6H_6 + allyl chloride.	67
	Dehydrogenation	Of pyridine.	65
	Alkylation		
	Dealkylation		
$FeCl_2$	Polymerization	Linear esters depolymerized.	90
	Hydrogenation	Naphthalene, anthracene.	57
Fe halides	Polymerization	Polyhydric alcohols.	72
		Tars.	17
		Dipentene.	41
		Gaseous olefins.	25
$HgBr_2$	Polymerization	Cyclohexene polymers from cyclohexyl bromide.	101
$HgCl_2$	Polymerization	Isobutene.	45, 72
	Racemization	 $\underset{Cl}{C_6H_5\overset{}{C}HCH_3}$	5
$MoCl_5$		$C_6H_6 + PhCH_2OEt$.	55

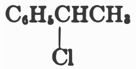
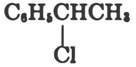
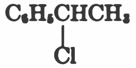
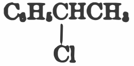
OsF_8	Polymerization	Isobutene.	45
$SbBr_3$	Polymerization	Cyclopentadiene.	98
$SbCl_3$	Polymerization	Cyclopentadiene. Linear esters depolymerized.	98 90
$SbCl_5$	Racemization	 $C_6H_5\underset{\displaystyle Cl}{\underset{\vert}{C}}HCH_3$	5
	Polymerization	Cyclopentadiene. Indene and derivs., cinnamalfluorene. Refining oils.	98 105 33
Sb chloride		Vinyl acetylene. Oil.	15 71
SbF_5	Polymerization	Cyclopentadiene. Isobutene.	98 45
Sb halides	Polymerization	Vinylethinylcarbinols.	14
$SnBr_4$	Polymerization	Cyclopentadiene.	98
$SnCl_2$	Polymerization	Linear esters depolymerized. Vinylacetylene.	90 15
$SnCl_4$	Polymerization	Isobutene. Indene, styrene, butadienes. Phenylbutadiene. Polyethylene oxide. Glycides. Unsaturated oils. Propenylbenzene. Rubber. Cyclopentadiene. Oil.	45 10, 95 94 100 29 62 99 47, 83, 107 98 71
	Friedel-Crafts	Thiophene, homologs + acetyl chloride. Fails with C_6H_6, homologs + benzyl chloride or acid chlorides.	91, 92

TABLE I (*Continued*)

Catalyst	Reactions Catalyzed	Remarks	Reference No.
$SnCl_4$	Racemization	 $C_6H_5\underset{Cl}{\underset{\vert}{C}}HCH_3$	5
Sn halides	Polymerization	Vinylethinylcarbinol.	14
		Indene and derivatives, cinnamalfluorene.	105
$TaCl_5$	Alkylation	$C_2H_4 + C_6H_6$. Efficiency 60 at 75°C. (Al = 75 at 75°C.)	30
	Dealkylation		
$TiCl_4$	Alkylation	$C_2H_4 + C_6H_6$. Efficiency 5 at 170°C. (Al = 75 at 75°C.)	30
	Dealkylation		
	Polymerization	Isobutene.	45
		Vinylacetylene.	15
		Alpha-methyl styrene.	96
	Friedel-Crafts	C_6H_6 + benzyl chloride. (Failed with benzoyl chloride.)	96
		Thiophene + benzoyl chloride. Easy reaction.	93
	Racemization	 $C_6H_5\underset{Cl}{\underset{\vert}{C}}HCH_3$	
Ti halides	Polymerization	Tars.	17
		Isoprene.	103
$TlCl_3$	Friedel-Crafts	C_6H_5 + benzyl, benzoyl, or acetyl chloride.	54
UCl_4	Friedel-Crafts	C_6H_6 + acetyl chloride.	55

UF_6	Polymerization	Isobutene.	45
WCl_6	Friedel-Crafts	C_6H_6 + benzoyl chloride.	55
$ZnCl_2$	Racemization	 $C_6H_5\underset{\substack{\mid\\ Cl}}{CH}CH_3$	5
	Polymerization	Olefins, diolefins, vinyl compounds, urea and formaldehyde, and various other reactions.	7, 9, 11, 15, 22, 24, 25, 26, 27, 31, 32, 34, 41, 42, 44, 52, 53, 56, 59, 60, 61, 66, 71, 80, 87, 88, 102
	Isomerization	Polymerization and cracking also.	78, 79
$ZnCl_2$ (with $AlCl_3$)	Polymerization	Of products of acetone cracking.	51
	Isomerization	HCl as promoter.	64
	Hydrogenation		35
	Friedel-Crafts	Allyl chloride + C_6H_6.	67
ZnF_2	Friedel-Crafts	AcCl + PhOMe and similar reactions.	13
$ZrCl_4$	Alkylation	C_2H_4 + C_6H_6. Efficiency 90 at 100°C. (Al = 75 at 75°C.)	30
	Dealkylation	N-paraffins + olefins.	49

NOTE: References to halide catalyzed polymerizations which are omitted from the table may be found in "Polymerization," Burk, R. E., Thompson, H. E., Weith, A. J., and Williams, I., Reinhold Publishing Corp., New York (1937). References earlier than 1927 have been omitted, largely, from this table. Calloway (13) gives 26 references to active halides other than Al.

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Mixed halides of an active type, e.g., $AlCl_3$, and an inactive type, e.g., NaCl, have been used (92). These halides form very stable addition compounds. Electrolysis has thrown some light upon the nature of such mixed halides as $AlBr_3-KBr$ (87, 89); $AlBr_3 + LiBr$, CuBr, and AgBr (88); $AlBr_3 + RbBr$, LiBr, CuBr, AgBr (28); but the information has not been correlated with their catalytic activity. *n*-Hexane and octane have been isomerized by mixtures of $AlCl_3$ with $ZnCl_2$, $PbSO_4$, and $CuCl_2$ (56). $HgCl_2$ has been reported to be an activator for $AlCl_3$ (3).

$ZrCl_4$ has been reported by Grosse and Ipatieff (30) to be at least as active as $AlCl_3$ for the alkylation of benzene with C_2H_4. Calloway (16), however, does not rate it so highly.

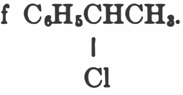
$ZnCl_2$ has been used repeatedly as a polymerization catalyst (Table I), but it has likewise been found to have catalytic powers for isomerization of hydrocarbons (86), for hydrogenation of solid fuels (37), and for the Friedel-Crafts reaction, e.g., with allyl chloride + benzene (73).

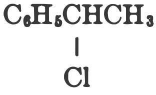
$ZnCl_2$ was used by Friedel and Crafts in 1877 (24), as well as $FeBl_3$, $FeCl_2$, and aluminum-sodium chloride for the reaction between benzyl chloride and benzene, but they observed little or no action with cobalt chloride, cupric chloride, mercuric chloride, or antimony trichloride. However, Wertyporoch, Kowalski, and Roeske (114) obtained no Friedel-Crafts reaction with benzene or benzyl chloride and chloroform in the presence of $ZnCl_2$.

Calloway (17) has found ZnF_2 to be an effective catalyst for the reaction of *t*-butyl chloride with anisole, a reaction for which AlF_3 was quite inactive. Various other reactions of the Friedel-Crafts type were either feebly catalyzed or not catalyzed at all by ZnF_2.

The catalytic polymerizing action of tin halides, especially $SnCl_4$, has been recognized for some time. The action is not, however, confined to polymerization. For example, Stadnikov (100, 101) and his associates have found that stannic chloride readily effects Friedel-Crafts reactions with thiophene or its homologs and acetyl chloride as reactants. Furan likewise enters into Friedel-Crafts reactions when $SnCl_4$ is the catalyst (26). It does not appear to be a good Friedel-Crafts catalyst with benzene or its homologs and chlorides or acid chlorides as reactants.

Copper halides, especially cuprous chloride, have a marked power of polymerizing acetylene (Table I), but Kozlov and Fedoseev (49) find that such catalysts are also able to induce acetylene to combine with aromatic amines.

Antimony halides have been used frequently for polymerization reactions. Moreover, Bodendorf and Böhme (4) have found $SbCl_5$ to be particularly effective in catalyzing the racemization of  $C_6H_5\underset{\underset{Cl}{|}}{C}HCH_3$. They can likewise catalyze some Friedel-Crafts reactions (55), e.g., the reaction of benzoyl chloride with aromatic hydrocarbons.

Titanium chloride has many of the powers of aluminum halides, though to a lesser degree. In addition to polymerization and the alkylation of benzene with ethylene, this catalyst has been found to have some action in Friedel-Crafts reactions. Thus thiophene and benzyl chloride react readily in its presence, and benzene and benzyl chloride also react (102).  $C_6H_5\underset{\underset{Cl}{|}}{C}HCH_3$ is racemized by $TiCl_4$ (4).

Kastanov (46) has found UCl_4 to have a substantial catalytic effect for the reaction of benzyl chloride or benzoyl chloride with benzene. He found WCl_6 to have somewhat less marked catalytic effect on the reaction of benzoyl chloride with benzene.

Beryllium bromide has been found by Pajeau (83) to have a feeble activity in reactions of the Friedel-Crafts type. Thus some are affected, others not. Wertyporoch, Kowalski, and Roeske (114) found that $BeCl_2$ brought about a Friedel-Crafts reaction with phenyltrichloromethane.

A similar rating for $BeCl_2$ was obtained by Grosse and Ipatieff (30) for the alkylation of C_6H_6 with C_2H_4. They also investigated BF_3, $AlCl_3$, $TiCl_4$, $ZrCl_4$, $CbCl_5$, and $TaCl_5$ for this reaction which they rated as shown in Table II.

TABLE II

Catalyst	Temperature °C.	Moles of C_2H_4 converted/ mole of catalyst
$BeCl_2$	200	50
BF_3	25	35
$AlCl_3$	75	75
$TiCl_4$	170	5
$ZrCl_4$	100	90
$CbCl_5$	75	25
$TaCl_5$	75	60

There may be some doubts of the propriety of placing all the halides of Table I in a single group. But the ability of all the members of the group to catalyze polymerization and the fact that many of them will catalyze other reactions than polymerization, including Friedel-Crafts reactions, tempt one to do so. One suspects that the halides which have catalyzed polymerization only would catalyze other reactions as well if given sufficient time. (See Calloway (15), p. 337.)

It is noteworthy that the results obtained with other halide catalysts have in some instances been reported to be nearly identical with those obtained with $AlCl_3$. Thus Calloway (15) cited a number of researches to show that $ZnCl_2$ and $AlCl_3$ give identical reactions in alkylation with alcohols under the influence of these catalysts. Also Shoesmith and McGechen (98) reported that in the reaction of butyl halides with toluene 65 to 70 parts of *m-tert.*-butyltoluenes and 30 to 35 parts of para isomer are formed, whether $AlCl_3$ or $FeCl_3$ is used as catalyst.

Calloway (17), after reviewing the activity of some halides for the Friedel-Crafts reaction, has suggested that the catalysts should be rated in the order given in Table III.

A zero rating was given by Calloway to $CuCl_2$, $CoCl_2$, $MgCl_2$, $PbCl_2$, $SiCl_4$, $CaCl_2$, $CrCl_3$. $BeCl_2$ was rated as essentially inactive. This order of activity plainly does not correspond with that found by Grosse and Ipatieff when the halides were used under relatively comparable conditions for the same reaction as shown in the same table.

TABLE III

Burk's Approximate Order of Activity from the Literature of Table I	B.P.°C. of Halide	Calloway's Order of Activity	Grosse and Ipatieff's Order of Activity (Roughly corrected for temperature.)
$AlBr_3$	268	$AlCl_3$	$AlCl_3$
$AlCl_3$	182.7	...	...
$FeCl_3$	315	$FeCl_3$	...
$ZrCl_4$	300	...	$ZrCl_4$
$TaCl_5$	242	...	$TaCl_5$
BF_3	−101	...	BF_3
UCl_4	?	...	...
$TiCl_3$	?	...	...
WCl_6	346.7	...	...
$CbCl_5$	240.5	...	$CbCl_5$
$ZnCl_2$	732	$ZnCl_2$	...
Sn	114	$SnCl_4$	...
$TiCl_4$	136.4	$TiCl_4$	$BeCl_2$
$BeCl_2$	520	$ZrCl_4$	$TiCl_4$
$SbCl_5$	92 (30 mm.)	...	...
$HgCl_2$	304	...	...
Cu_2Cl_2	1360	...	...
$BiCl_3$	447	...	...
AsF_3	63	...	...
Co Cr Mo	Some activity but difficult to evaluate on the evidence.		

From the researches cited in Table I, covering various types of reactions, the writer would rate the activity of the various halides very roughly as shown in the first column of Table III. The arrangement cannot be precise since the order of activity may vary for different reactions and for different conditions.

The question arises as to what qualities a halide must have in order for it to exhibit the property of catalyzing Friedel-Crafts reactions. Calloway (15) concluded that they had few general characteristics in common. His suggestions that the elements whose halides are active are more or less amphoteric, and are centrally located in the periodic table, while not emphasized, are vitiated by a more complete list of the halides which act as catalysts. He had already presented iron chloride as an exception. The catalysts in Table I are derived from all the groups in the periodic table. All the periods are likewise represented.

Grosse and Ipatieff (30) found that the halide catalysts effective for the alkylation of benzene with ethylene are those of metals which stand near aluminum and form a diagonal band in the periodic table. They further suggested that these halides show similar behavior towards water and in the formation of double salts or addition compounds; they form the transition between the halides of the purely heteropolar salt type and those of the typical homopolar covalent halides. While the latter point is interesting, no quantitative relation between the polarity of the halide and its efficacy as a catalyst is evident. Thus the difference in the valuation placed upon $ZrCl_4$ by Calloway and by Grosse and Ipatieff would discourage the attempt to set up such a quantitative relationship.

The boiling point of a salt is some indication of its polar character though this is complicated somewhat by symmetry considerations. Table III shows that boiling point bears no particular relation to the activity of the catalysts, though some of the better halides have boiling points in the range 150 to 300°C. Solubility properties are likewise indicative of the polar character of salts. Aluminum bromide is quite soluble in hydrocarbons indicative of low polarity, and it is probably the most powerful of the halide catalysts which have been reported. $TiCl_4$ is likewise quite soluble but has only feeble activity.

One should remember in this connection that various acids, e.g., HF, H_2SO_4, H_3PO_4, have similar catalytic action, a point which is developed later in this paper. Some of the active halide catalysts form complexes with hydrohalogen acid of the type HBF_4. A necessary quality of the halide may then be to possess the proper electronic structure to allow the formation of such complex to occur, a property which may be related to the polarity of the halide.

THE SIMPLE REACTIONS OF HYDROCARBONS CATALYZED BY HALIDES

From the practical side the petroleum industry, in particular, is interested in the control of the transformation of one type of hydrocarbon to another. While the possibilities of the halide catalysts for such purposes are evident, and while much work has been done in the field, the published understanding of the reactions is as yet too feeble to effect the desired control. Often many products are obtained.

In some cases, however, a simple (single) reaction is brought about by such catalysts. Nenitzescu and Cantuniari (65) have found that either cyclohexane or methylcyclopentane is converted by aluminum chloride to a mixture containing about 77.2 per cent cyclohexane and

22.8 per cent methylcyclopentane. The reaction occurred at 70 to 80°C. in a few hours, with 30 per cent of $AlCl_3$ present. While Zelinskii and Turova-Pollak (123) had reported the formation of 5 grams of dimethylcyclobutane when 140 grams of cyclohexane was treated with one-third of a mole of $AlBr_3$, Nenitzescu and Cantuniari found none of this secondary product.

When methylcyclohexane is used as the starting material, however, the equilibrium is thought to be so far over that very little dimethylcyclopentane forms (66).

The isomerization of cyclohexane to methylcyclopentane has likewise been found by Nenitzescu and his colleagues (64, 66, 67, 77) and by Unger (107) in the Friedel-Crafts reaction of cyclohexanes with acid chlorides. In this case the product is a methylacetylcyclopentane instead of acetylcyclohexane. If, however, cyclohexene and acetyl chloride are the reactants, methylcyclohexyl ketone is obtained under conditions otherwise the same (62). Cyclopentane structures enter into the Friedel-Crafts reaction without change in the skeleton (63).

Montgomery, McAteer, and Franke (57) have found that either liquid *n*-butane or liquid isobutane is converted by aluminum bromide into an equilibrium mixture of the two containing 78 to 82 per cent of isobutane. Five mole per cent of the catalyst was used at 27°C. and the equilibrium vapor pressure of the system. Some two months were required for the equilibrium to be approached.

Kenner, Polanyi, and Szego (47) have found that benzene in the presence of $AlCl_3$, HCl, and DCl exchanges hydrogen for deuterium. The change is very much slower in the absence of the $AlCl_3$.

Zelinskii and Turova-Pollak (123) found that $AlBr_3$ converts *cis*-decalin into the *trans* isomer.

Grignard and Stratford (29) found that either ortho- or paradimethylcyclohexane is converted to *m*-dimethylcyclohexane by aluminum chloride. This occurred in 7 hours at 115 to 120°C., using 23 per cent $AlCl_3$.

The same authors found ethylcyclohexane to yield *m*-dimethylcyclohexane, when 21 per cent of $AlCl_3$ was used at 115 to 120°C. for 8 hours. Similar results for this hydrocarbon were reported by Turova-Pollak (106).

Grignard and Stratford (29) found that *m*-diethylcyclohexane yielded tetramethylcyclohexane as the principal product when treated with 23 per cent of $AlCl_3$ at 120 to 130°C. for 4 hours. Some 1 to 5 per cent side reactions accompany the conversions of ethyl side chains to two methyl substituents. Butylcyclohexanes are transformed somewhat less smoothly to tetramethylcyclohexane.

With alkyl benzenes, the corresponding reactions do not occur as smoothly. Thus with ethylbenzene, instead of *m*-xylene, a mixture of benzene, *m*- and *p*-diethylbenzenes, and triethylbenzenes is obtained. No xylenes are formed (19, 22, 36).

Balsolın (2) found that aromatics can be alkylated with olefins in the presence of aluminum chloride. With benzene and ethylene, the product consists of ethylbenzenes when working in the temperature range 70 to 90°C.

Grosse and Ipatieff (30) have obtained similar results in the work already discussed with BF_3, $BeCl_2$, $TiCl_4$, $ZrCl_4$, $CbCl_5$, and $TaCl_5$. In each case ethylbenzenes were obtained even though temperatures of 100°C. or more were used in some of the experiments and though $ZrCl_4$ was considered to be at least as active as $AlCl_3$.

Alkylation of paraffins by $AlCl_3$ is a newer reaction studied, e.g., by Ipatieff, Grosse, Pines, and Komarewsky (42), though the reaction should not be classed with the simple reactions of the halide catalysts since cracking, isomerization, etc., also occur and complicate the products. Naphthenes are likewise alkylated with $AlCl_3$ as the catalyst (43*a*).

In the Scholl reaction (94, 95), condensation with elimination of hydrogen occurs between aromatic nuclei. Thus naphthalene at 140°C. with aluminum chloride gives 1,1′-binaphthyl and at 180°, perylene.

THE MORE COMPLEX REACTIONS OF HYDROCARBONS CATALYZED BY HALIDES

When the active halides react with various other hydrocarbons, the results are more complex, though some features of the action appear to be general. Polymerization catalyzed by halides has been discussed in another paper of this report.

Normal paraffins are decomposed and isomerized, and in this field the following generalizations appear to be valid:

1. The gaseous paraffins (except the butanes whose action is described above) react with difficulty. Temperatures of more than 300°C. appear to be necessary, and the products formed have not been very definitely described (34, 54). The effect of pressure has not been adequately described.
2. When the reaction is carried out with higher paraffin hydrocarbons, but small quantities of hydrocarbon gases below C_4 are formed even though the starting materials are nearly completely cracked (14, 27, 31, 39, 70, 97).
3. While there is some hydrogen in the gaseous products, the principal, and nearly the sole, hydrocarbon gas initially formed in some cases

is isobutane. Repeated fractionation of the gaseous products obtained (27, 39) by the action of aluminum bromide on *n*-heptane at room temperature showed isobutane to be the only butane present (97).

4. The sole demonstrated aliphatic isomers boiling higher than butane appear to be methyl isomers. This, if confirmed, is a highly significant point since one might expect branched chain paraffins to be formed by alkylation of paraffins with the olefin fragments formed in cracking the original paraffin (42).

Such a mechanism would yield ethyl, propyl, butyl, etc., side chains. While this would not change the type of C_4 and C_5 hydrocarbons formed, it would lead one to expect prominent quantities of hydrocarbon containing more C atoms than the starting material. In these products that hydrocarbon containing only one more carbon atom than the starting material should substantially be absent at small conversions, as should 2-methylpentane from hexane. In the experimental results, on the contrary, the paraffin products of higher molecular weight than the straight-chain paraffin starting material constitute minor products (27, 39, 57, 70, 97). Moreover, that hydrocarbon with one more carbon atom than the straight-chain starting material appears to be at least as prominent as any of those products of molecular weight higher than the starting material.

The reported fractionations are scarcely good enough to decide if in the C_6 and higher ranges, the 3- as well as the 2-methyl isomers are formed, but present evidence is that this is the case.

5. Gem-methyl groups have not been observed in the isomerization products (65*a*, 57*a*).

6. The present evidence is sufficient to show that cracking cannot precede isomerization as a fully segregated step, certainly not in the *n*-butane and *n*-pentane reactions. Rather the reverse is indicated, i.e., that isomerization precedes cracking. Thus, the exclusive formation of isobutane rather than normal butane and the absence of isomers with gem-methyl groups might suggest the rupture of the 2,3 bond in a 2,2-dimethyl structure. Isobutane cannot be a primary product of cracking in a normal paraffin.

7. The accelerating effect of hydrohalogen acids on the catalytic action of the relevant halides has long been appreciated, e.g., by Gustavson (34) and by Jacobson (44), and has been observed and utilized by various recent investigators (27). But the work of Ipatieff and Grosse (39) indicated that HCl is not only beneficial but also necessary to the action of $AlCl_3$ on *n*-heptane. $AlCl_3$ which had been freed of HCl by melting under pressure with powdered aluminum caused no change in *n*-heptane in 12 hours at 20 to 25°C.

This point of view is strongly supported by the work of Burk, Lankelma, and Sensel (97), who found that HBr-free $AlBr_3$ caused no appreciable reaction of *n*-heptane in several hours at the boiling point of the latter. This is an especially interesting observation since $AlBr_3$ is soluble in the hydrocarbon, and a surface explanation of the need for hydrohalogen acid is thus ruled out.

8. A lower layer of hydrocarbon chemically associated with catalyst is formed in many of the reactions of hydrocarbons catalyzed by halides, but not in all cases. Thus Montgomery *et al.* (57) reported no such layer in their work with butanes catalyzed by $AlBr_3$, and Grosse and Ipatieff (30) found no second layer with the system $C_6H_6 + C_2H_4$ catalyzed by titanium tetrachloride. The reaction had not proceeded very far in the latter instance.

The lower layer when formed is generally brown, but when produced from highly purified heptane and aluminum bromide plus dry HCl (97) is a pale yellow liquid. This liquid does not react readily with ice water, but does react at a moderate rate with water at room temperature to form a wine-red liquid. The latter liquid is a hydrocarbon n_D^{20} 1.492 to 1.495 d_4^{20} 0.899 to 0.924; C = 86 to 89 per cent, H = 12 to 13.3 per cent; molecular weight 224 to 250; bromine number by the Bacon method (1) indicated the presence of three to four double bonds. The oil absorbs oxygen so readily at room temperature as to make accurate determination of its properties a matter of some difficulty. It polymerizes and finally sets when exposure to air is sufficiently prolonged. No crystalline bromine derivatives could be obtained. The oil has a terpene-like odor.

The complex before hydrolysis contains slightly more than three atoms of bromine for each atom of aluminum. This fact may be explained by the solution of HBr or by the presence of combined HBr.

The oil obtained in hydrolyzing the complex hydrogenates to a nearly odorless, colorless liquid of kerosene consistency with n_D^{20} 1.4818, d_4^{20} 0.8685, C = about 87.3 per cent, H = about 12.7 per cent. This liquid is not readily dehydrogenated over catalysts which are active for dehydrogenating methylcyclohexane. The high density and refractive index of the hydrogenated oil point to the presence of at least one ring. The bromine numbers together with the carbon-hydrogen determinations on the original hydrolyzed product show that this ring could not have been an aromatic one. The oil is readily soluble in paraffin hydrocarbons, benzene, ether, nitrobenzene, chloroform, carbon tetrachloride, and cold concentrated sulfuric acid. It did not freeze at −30°C., pointing to a mixture or an unsymmetrical structure, or both.

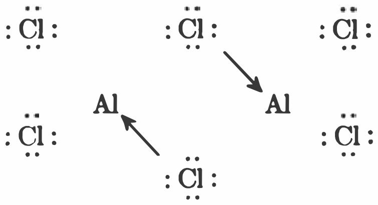
This rather detailed description of the lower layer is presented for two reasons: (*a*) because it is usually scantily described, receiving relatively less emphasis than the upper layer, (*b*) because a quite similar lower layer is obtained by the action of aluminum halides upon various other hydrocarbons. Thus, Ipatieff and Grosse found ethylene and $AlCl_3$ (41) to give a lower layer whose refractive index was 1.45 to 1.49; density, 0.81 to 0.8748; per cent C, 86.4 to 86.87; bromine number (Francis), 177 to 324; molecular weight, 201 to 324. They interpreted the material to consist of unsaturated cyclic naphthenes.

The oil from the action of $AlBr_3$ on heptane was very similar to that of $AlCl_3$ on heptane (31). Only a minor proportion of the initial hydrocarbon starting material finds its way to the lower layer.

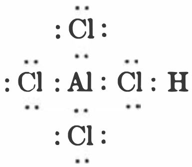
THE MECHANISM OF THE REACTION

The mechanism of the action of Friedel-Crafts halide catalysts on hydrocarbons remains uncertain. That hydrohalogen acids are necessary rather than acting merely as promoters may, however, be an opening wedge for an understanding of the reactions. Thus the real catalyst may, e.g., be $HAlCl_4$ rather than $AlCl_3$ or Al_2Cl_6.

Aluminum chloride and bromide form double molecules whose structure has been investigated by electron diffraction (84) and is thought to be, e.g.:



confirming an earlier suggestion of Fajans (23). There are two coordinate links. The expected structure of the acid $HAlCl_4$ would be:



$$\begin{array}{c} :\ddot{\mathrm{Cl}}: \\ :\underset{..}{\ddot{\mathrm{Cl}}}:\underset{..}{\ddot{\mathrm{Al}}}:\underset{..}{\ddot{\mathrm{Cl}}}:\mathrm{H} \\ :\underset{..}{\mathrm{Cl}}: \end{array}$$

Certain additional evidence would support the existence of such an acid and its participation in some of the catalytic actions of halides.

1. Aluminum chloride forms very stable complexes of the composition $MAlCl_4$, where M is a metal. Thus sodium aluminum chloride can be volatilized as such at red heat, and does not lose $AlCl_3$ at lower temperatures.

2. BF_3, whose catalytic action is closely analogous to that of aluminum halides, and which likewise will not function as a catalyst in the absence of HF or water (40), forms a well-known acid HBF_4. While this acid does not itself have a wide reputation as a catalyst, it has been claimed by Nieuwland to catalyze the reaction of acetylene with various organic compounds (78), and according to Nieuwland and Sowa (79) dihydroxy fluoboric acid can be used in place of BF_3 in reactions where BF_3 functions as a catalyst.

3. Careful analysis of the unhydrolyzed lower layer, as pointed out on page 271, shows it to contain Br and Al in a ratio greater than 3.

4. There is a rather far-reaching analogy in the action of halides of the Friedel-Crafts type and certain acids such as sulfuric and phosphoric on hydrocarbons. Both types of catalyst are effective, in particular for polymerizations and alkylations (13), but also may accelerate isomerizations and hydrogenation (largely intramolecular). This similarity in the action of aluminum chloride and acids, particularly sulfuric acid, was recognized by Boeseken (6) as early as 1910.

5. Anhydrous hydrofluoric acid itself has been found to catalyze the alkylation of aromatic hydrocarbons (98*a*, 99.)

6. Wertyporoch and co-workers (111, 113, 120) have electrolyzed solutions of aluminum halides in various organic halides. They find, for example, that on electrolyzing $AlBr_3$ dissolved in ethyl bromide, three atoms of aluminum migrate to the anode for each atom migrating to the cathode, but they attribute this to the presence of $Al(AlBr_4)_3$, a salt of the acidic complex $HAlBr_4$.

The same technique, however, did not confirm the presence of similar complexes in the case of $BeCl_2$, $ZnCl_2$, $SnCl_4$, $SiCl_4$, BF_3, BCl_3, or $TiCl_4$. These authors considered the possibility of esters of the acid $HAlCl_4$ as active intermediates but favored more complex structures. Their actual proposed intermediate is discussed at a later point.

Wertyporoch and Adamus (112) later reported that, upon introducing HCl into a solution of $ZnCl_2$ in acetonitrile, such acids as $HZnCl_3$ and H_2ZnCl_4 are formed.

Wertyporoch and Silber (116) reported that various solvates of $AlCl_3$ and $AlBr_3$ behave as true salts in formic acid solution. A wide investigation showed some solvates to be salt-like; others not.

7. The negative temperature coefficient observed by Waterman, Over, and Tulleners (109) for the polymerization of isobutylene by $AlCl_3$ receives an explanation on the basis that at low temperature relatively greater amounts of HCl are combined to form an active complex with $AlCl_3$. This explanation, if correct, should apply to other cases of $AlCl_3$

catalysis, which, however, are not generally investigated in the corresponding temperature range. The evidence of course does not point to any one structure, for example, the complex involving HCl. Sensel (97) found a negative temperature coefficient for the action of $AlBr_3$ on *n*-heptane if the concentration of HBr was properly adjusted.

8. Complexes of the type $RCOAlCl_4$ which may be formed directly from acyl chlorides and $AlCl_3$ are recognized active intermediates in the Friedel-Crafts reactions (85, 104, 118). Thus, for example, Perrier prepared the addition compound of benzoyl chloride and aluminum chloride, whose empirical formula was $(C_6H_5COCl)AlCl_3$, and found that it reacted, e.g., with diphenyl to form $C_6H_5CO \cdot C_6H_4 \cdot C_6H_5$. Some prefer a different structure for the complex (p. 280).

Nencki (61) proposed a similar action for $FeCl_3$. Steele's dynamic studies of alkylation and acylation by $AlCl_3$ and $FeCl_3$ support the mechanism.

Kohler (48) found the molecular weight of acid $Cl-AlBr_3$ complexes to agree with the formula $Al_2Br_6 \cdot 2RCOCl$.

Boeseken (5) presented similar evidence for this mechanism of action for $AlCl_3$ in the Friedel-Crafts reactions, but in 1920 (9) he appears to have discarded it on the grounds (*a*) that in some cases such $AlCl_3$ addition compounds do not form and (*b*) some addition compounds of this type are not reactive. The objections appear inadequate.

When acids derived from halides act as catalysts in alkylation and polymerization reactions (see Chapter XV of this report) it is probable that the reaction proceeds through the formation of intermediate esters of the acids. Since the cracking of hydrocarbons is in a sense the reverse of alkylation, the question of the nature of such a possible ester of the acid formed from, say, HX and AlX_3 (where X is halogen) arises. Reasons were given on p. 270 why esters containing more than two carbon atoms should not be expected to play a prominent part in the action of halides upon paraffin hydrocarbons. The participation of a methyl ester CH_3AlX_4 would explain the prominent presence of 2-methyl isomers in their products, and the presence of C_{n+1} hydrocarbons (where n = number of C atoms in the starting material). But the suggested participation of CH_3AlX_4 lands us in the field of pure speculation, which would still leave us with the question: Why do esters of certain acids alkylate?

Against such a mechanism, one may cite the observation of Nenitzescu and Dragan (70) that methyl chloride does not induce reaction with the system $AlCl_3$ + heptane, though other alkyl halides will do so. This point, however, is softened by Boeseken's observation (9) that a complex is not readily formed from CH_3Cl and $AlCl_3$.

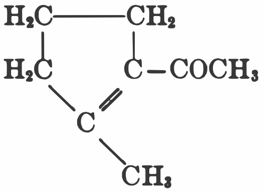
Copisarow (18) suggested a different function for HCl, which may be expressed by the equations:

1. $C_6H_5CH_3 + Al_2Cl_6 = C_6H_5Al_2Cl_5 + CH_3Cl$
2. $C_6H_5CH_3 + CH_3Cl = C_6H_4(CH_3)_2 + HCl$
3. $C_6H_5Al_2Cl_5 + HCl = C_6H_6 + Al_2Cl_6$

However, some hydrocarbons may be distilled from HCl-free $AlCl_3$ without substantial change in either the halide or the hydrocarbon (97), thus casting doubt upon equations of type 1.

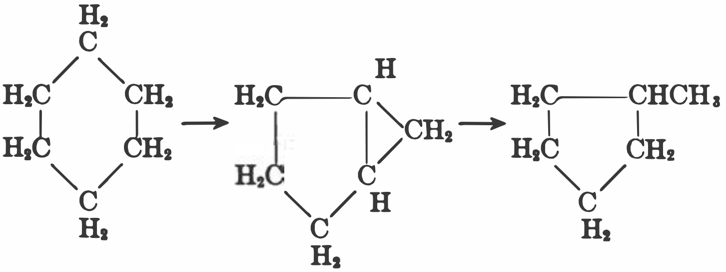
The theory involving an intermediate such as $HAlCl_4$ (or any other theory) must provide for the dehydrogenation-hydrogenation powers of halide catalysts. Some authors propose dehydrogenation as an essential step in the catalytic action of aluminum halides involving some hydrocarbons. Thus Nenitzescu and Vantu (77) suggest that dehydrogenation of methylcyclopentane precedes coupling in the formation of 1-methyl-2-acetylcyclopentane from cyclohexane and acetyl chloride, catalyzed by $AlCl_3$.

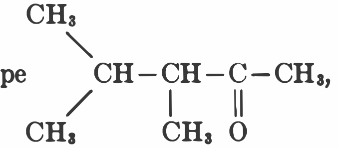
The methylcyclopentane results from isomerization of cyclohexane and this mechanism, in which we are especially interested, was left unexplained. The evidence for the dehydrogenation step was the simultaneous production of an unsaturated ketone



the amount of which could be reduced to zero by a suitable control of conditions.

Unger (107) suggested that even the rearrangement is dependent upon dehydrogenation. Thus:



Nenitzescu and Chicos (68) suggested that dehydrogenation of pentane and hexane followed their isomerization in the formation of ketones of the type  which is formed from pentane and acetyl chloride catalyzed by $AlCl_3$. In any event, the reality of the catalytic power of aluminum halides for hydrogenation-dehydrogenation reactions has been established in various researches (98*a*). H_2 is actually evolved in the Scholl reaction as previously described, where the sole reaction is a coupling with elimination of H_2.

In the action of aluminum halides on benzene, it is interesting to note that Wertyporoch and Sagel (115), working with $C_6H_6 + AlBr_3$ or $AlCl_3$ at 18°C., in 4 to 20 weeks time found only cyclic products, e.g., phenylcyclohexane and diphenyl, whereas Ipatieff and Komarewsky (43), working with $AlCl_3$ and benzene at 125°C., in 24 hours reaction time obtained ethylbenzene as well as diphenyl. The difference in temperature in the two researches is to be noted as is the fact that dehydrogenation-hydrogenation reactions predominated under the milder conditions.

Winter and Free (119) found the action of aluminum chloride on naphthalene, anthracene, and phenanthrene to result in the formation of tetrahydro derivatives, in addition to cracking and condensation products.

Nenitzescu and Isacescu (74) found $AsCl_3$, SCl_2, PCl_3, and certain other halides to be reduced by H from the reaction cyclohexane $\longrightarrow$ bicyclohexyl, catalyzed by aluminum chloride. It is noteworthy that the reaction with cyclohexane takes this course in the presence of an acceptor for the hydrogen, rather than isomerization to methylcyclopentane.

Sensel (97) found hydrogen in the off gases from the reaction of $AlBr_3$ with *n*-heptane.

Nenitzescu and Dragan (70) report the formation of cyclohexane by the action of $AlCl_3$ on *n*-hexane through a cyclicizing dehydrogenation. With *n*-heptane, they found cycloparaffins in the products boiling higher than the starting material, but not among those boiling lower. However, Sensel (97) in the action of $AlBr_3$ on *n*-heptane found no cycloparaffin in the products boiling lower than the starting material and, in those products boiling higher, the refractive indices of the various cuts would allow but minor proportions to be present.

While the mechanism of the hydrogenation-dehydrogenation action of halide catalysts is not clear, it does little damage to the theory that these halides when hydrohalogen acid is present act as acids of the type $HAlCl_4$, because other acid catalysts behave similarly. Hydrogenation powers have likewise been reported by Damiens (20) and by Boeseken and Max (10) for sulfuric acid containing small percentages of copper and mercury sulfates. Ormandy and Craven (82) showed that 98 per cent sulfuric acid produced paraffins from propylene and certain higher olefins. A similar hydrogenating action was reported by Nametkin and Abakumovskaya (58) for the action of sulfuric acid alone on cyclohexene, though the nature of the saturated dimer formed was left obscure.

The same authors (59) report saturated and unsaturated polymers in the action of concentrated sulfuric acid on isobutylene, amylenes, and octene-1. Nametkin and Rudenko (60) explain this, e.g., in the case of isobutylene by the unusual reactions:

$$HOSO_2OC_4H_9 + C_4H_8 \longrightarrow H_2SO_4 + C_8H_{16}$$

$$HOSO_2OC_4H_9 + C_8H_{16} \longrightarrow HOSO_2OC_4H_7 + C_8H_{18}$$

$$n-HOSO_2OC_4H_7 \longrightarrow n-H_2SO_4 + (C_4H_6)_n$$

They found $AlCl_3$ to have a similar action for the same reactions.

Gustavson (32) advanced the theory that the first step in the action of aluminum bromide on *n*-hexane (in which he recognized the promoting action of HBr) was an attack on the paraffin molecule by HBr to form ethyl bromide and butane. Ethyl bromide had a promoting effect similar to that of HBr, and in this case the Br appeared as HBr at the end of the reaction. Radziewanowski (91) proposed an essentially similar theory to account for the formation of anthracene from diphenylmethane under the influence of aluminum chloride.

Reasons for objecting to cracking as a first step have been presented, but there is no apparent reason for insisting that a mechanism involving halogenation as a first step should take this form. A more general variation of this theory would be simply to assume some form of halogenation as the first step.

This does not appear to be helpful in explaining the particular products one gets by the action of halides on hydrocarbons. However, both alkyl and aryl halides are reactive in the presence, e.g., of $AlCl_3$, and the reactions are helpful in explaining the products obtained in some Friedel-Crafts reactions. Thus it has been observed that the halogen in some halogenated hydrocarbons can migrate under the influence of halide catalysts. For example, according to Lohfert (53) the action of $AlCl_3$ on 1,2-dibromonaphthalene results in 1,4-, 2,6-, and 1,5-dibromonaphthalenes, although Salkind and Stetzuro (93) think his evidence for the formation of the 1,4- and 1,5-isomers is doubtful.

Nenitzescu and Curcaneanu (69) have observed that in the reaction of beta-chloro ketones or acids, or 1,2-dihalocyclohexane with benzene under the influence of aluminum chloride, the phenyl group does not always occupy the position originally occupied by the halogen. They attribute this to prior migration of the halogen, which they consider to be due to the electrostatic repulsion of the CO or COOH or the other halogen under the labilizing action of the $AlCl_3$. Nenitzescu and Gavăt (71) have observed that the COOH group in a side chain of cyclohexane has a similar directive influence upon halogen in the ring.

Whitmore, Karnatz, and Popkin (117) have observed that *n*-amyl chloride is isomerized to 2- and 3-chloropentanes by $ZnCl_2$ + hydrochloric acid.

In pursuing the analogy in the catalytic actions of aluminum halides and other halides, one is likely to recall the chlorinating action of $FeCl_3$, a halide with marked Friedel-Crafts properties. Thomas (105) noted that under conditions where $FeCl_3$ chlorinated toluene readily, its action was confined to catalyzing a Friedel-Crafts reaction when $C_6H_5CH_2Cl$ was the reactant.

The maximum activity obtained with certain optimum mixtures of $AlCl_3$ and $FeCl_3$ may conceivably be attributed to the increased chlorinating powers of the $FeCl_3$ as compared with the $AlCl_3$, combined with greater potency of the $AlCl_3$ for the succeeding steps. On the other hand, Nenitzescu and colleagues (70, 72) observed that while alkyl halides were able to activate $AlCl_3$ in the isomerization of *n*-heptane, the halides appeared to act as hydrogen acceptors, being reduced to the corresponding paraffins with the liberation of HCl. If primary halogenation is of importance in the action of halides on hydrocarbons, the fact has not been developed into a useful theory.

Since alkyl halides promote the action of aluminum chloride on paraffins, it is difficult to see why hydrohalogen acid should be necessary if the first step is chlorination in the sense that $FeCl_3$ chlorinates benzene.

The addition of hydrohalogen acid to olefins is a reaction known to be catalyzed by halides; therefore the reasonableness of assuming this rather than addition of the hydrohalogen acid to the halide catalyst, followed by addition of the acid complex to the olefin, is difficult to evaluate on the evidence when the reaction is polymerization of, or alkylation with, olefins. However, the evidence seems to be against the halogenation theory. Thus olefins in the presence of hydrocarbons will alkylate the latter, yet alkyl halides in the presence of the same hydrocarbons and $AlCl_3$ are hydrogenated to the paraffins which correspond to the original alkyl halide.

The possible participation of ions in catalysis is discussed elsewhere in this report. For the action of aluminum chloride on benzene, Prins (90) has suggested that the positive ion of aluminum chloride is the seat of the catalytic action. The action is thought to consist of a polarization or ionization of benzene with a resulting labilization of a C—H group, which then reacts as if it were an O—H group as regards the mobility of the hydrogen atom. It may be said here that solubility of the catalytically powerful $\mathrm{AlBr_3}$ in hydrocarbons, together with its relatively low boiling point, does not indicate a strongly ionic character of the compound.

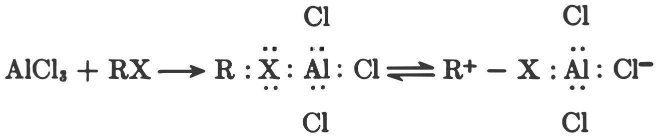
Prins imagined an ionic interchange to occur between the $\mathrm{AlCl_3}$ labilized molecules thus:

$$\mathrm{[C_6H_5AlCl_3]^-H^+ + [AlCl_4]^-CH_3^+ \rightleftharpoons [C_6H_5AlCl_3]^-CH_3^+ + [AlCl_4]^-H^+}$$

The bearing of the mobility of the hydrogen atom which is involved in a Friedel-Crafts condensation has been discussed by Wolffenstein and Hartwich (121).

Walker (108), who was one of the first to observe electrical conductivity in solution containing aluminum chloride and organic halides, concluded that ionization is the result and not the cause of the chemical activity.

Dougherty (21) has proposed an ionic theory of the action of aluminum chloride, based on the coordination theory of the polar character of the complexes which it forms. Thus:



$$\mathrm{AlCl_3 + RX \longrightarrow R:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:\underset{\underset{Cl}{\cdot\cdot}}{\overset{\overset{Cl}{\cdot\cdot}}{Al}}:Cl \rightleftharpoons R^+ - X:\underset{\underset{Cl}{\cdot\cdot}}{\overset{\overset{Cl}{\cdot\cdot}}{Al}}:Cl^-}$$

The polar complex would then react after the fashion of inorganic "ionogens," in a sense described by the above reactions of Prins. The priority in this mechanism is claimed by Dougherty. The complex $\mathrm{H^+[AlCl_4]^-}$ is involved in the mechanism but no particular importance appears to be attached to it. These theories do not bring out the required presence of HCl for the action of $\mathrm{AlCl_3}$ on hydrocarbons, since the hydrocarbon is represented as being activated without it.

There are various other theories of the action of aluminum halides involving intermediate compounds, which, however, do not reflect the indispensable function of the hydrohalogen acid. These may justify consideration in the Friedel-Crafts reaction with halides where, as far as the writer is aware, the presence of hydrohalogen acid has not been demonstrated to be necessary.

Thus the mechanism of Friedel and Crafts (25) will be recalled, and illustrated by the examples:

$$C_6H_6 + Al_2Cl_6 \longrightarrow C_6H_5Al_2Cl_5 + HCl$$

or

$$C_6H_5CH_3 + Al_2Cl_6 \longrightarrow C_6H_5Al_2Cl_5 + CH_3Cl$$

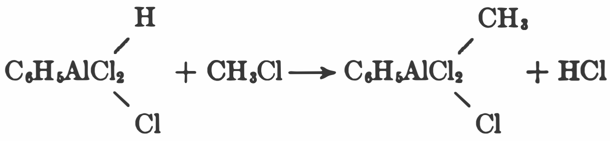
The intermediate compounds naturally were thought to be reactive. Copisarow's variation of this has been discussed.

Schroeter (96) suggested the formation and rearrangement of an addition compound of, e.g., hydrocarbon with AlCl$_3$ without splitting off HCl, thus:

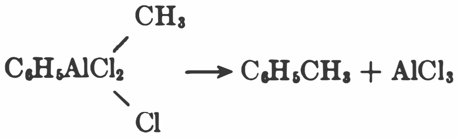
I. 

$$C_6H_6 + AlCl_3 \longrightarrow C_6H_5AlCl_2\overset{H^*}{Cl}$$

This starred hydrogen was then assumed to exchange with other groups in, e.g., alkyl halides or hydrocarbons, thus:

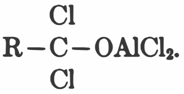
II. 

$$C_6H_5AlCl_2\begin{matrix}\diagup H\\ \diagdown Cl\end{matrix} + CH_3Cl \longrightarrow C_6H_5AlCl_2\begin{matrix}\diagup CH_3\\ \diagdown Cl\end{matrix} + HCl$$

III. 

$$C_6H_5AlCl_2\begin{matrix}\diagup CH_3\\ \diagdown Cl\end{matrix} \longrightarrow C_6H_5CH_3 + AlCl_3$$

Mechanisms involving the addition of, e.g., AlCl$_3$ to the organic halide in the Friedel-Crafts reaction rather than the AlCl$_3$-hydrocarbon complex seem preferable. Thus the former complex forms first in a mixture (6); and not only is there no evidence (16, 104) to support the idea that the Friedel-Crafts intermediates are formed under the experimental conditions, but such intermediates when separately prepared will not cause the Friedel-Crafts reaction with acyl halides.

While the intermediates formed from AlCl$_3$ and RCl may be RAlCl$_4$, Kronberg (52) suggested that in the case of acid chlorides they have the structure: 

$$R-\underset{Cl}{\overset{Cl}{C}}-OAlCl_2.$$

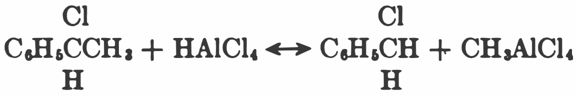
Wieland and Bettag (118), while accepting the idea that the active intermediate involves AlCl$_3$ + RCl, think that in the case of acetyl chloride it may be either AlCl$_3$ . . . $\underset{CH_3}{C}$: OCl, or CH$_3$CO . . . (AlCl$_4$).

Gustavson's suggested active intermediate (33) in Friedel-Crafts reactions, e.g., $AlCl_3 \cdot 3C_6H_6$, was opposed by Boeseken (6) on the grounds that it is not found under conditions most favorable to the Friedel-Crafts reaction, i.e., in the absence of moisture.

Various other addition compounds more complex than binary ones have been suggested as the active intermediates in Friedel-Crafts reactions. Thus Wohl and Wertyporoch (120), through conductivity and electrolysis studies of solutions containing $AlBr_3$, C_6H_6, and C_2H_5Br, concluded that the active complexes had the structure $[Al(C_2H_5Br)_n(R)_4][AlBr_4]_3$, where R represents hydrocarbon molecules bound to the Al with coordination links. This point of view was confirmed for other cases by Wertyporoch and Firla (113).

The lower layer complex which forms in at least some of the reactions of aluminum chloride has little if any effect in carrying on the reaction catalyzed by the free halide (76). It would be a mistake, therefore, to assume that all complexes formed with halide catalysts are essential intermediates in halide catalysis. Boeseken (8), going to the other extreme, suggested that none of them is essential in the sense of explaining the catalytic action. He interpreted the effect of aluminum chloride as being due to a dislocating action which sometimes involves dissociation as the first step.

Reasons have already been presented for objecting to dissociation as a first step. However, the effect of halides in catalyzing the racemization of $C_6H_5\underset{H}{\overset{Cl}{C}}CH_3$ may be interpreted to indicate a labilizing action on some of the bonds. It could also be interpreted as follows:



$$C_6H_5\underset{H}{\overset{Cl}{C}}CH_3 + HAlCl_4 \longleftrightarrow C_6H_5\underset{H}{\overset{Cl}{C}}H + CH_3AlCl_4$$

the reversal of the reaction leading to the racemic mixture, though one would expect some ring substitution in that case.

Nenitzescu, Isacescu, and Ionescu (75) favor the relatively vague theory of activation rather than an intermediate compound explanation of the action. This view was based in part upon their demonstration that some Friedel-Crafts reactions could be brought about in the absence of the inorganic halide at sufficiently elevated temperatures. This seems to the writer to be an impotent argument against the participation of intermediate compounds.

Norris (81) has expressed the thought that the function of $AlCl_3$ is essentially an activation though he recognizes the part which intermediate compounds may play.

Nenitzescu and Cantuniari (63) suggest that in such reactions as cyclohexane with acetyl chloride, catalyzed by aluminum chloride, the first act consists in the formation of a free radical, probably from the chloride. A free radical C_6H_{11} is thought to form in the chain sequence which rearranges to the methylcyclopentyl structure rather than direct isomerization of the cyclohexane.

The possibility that $AlCl_3$ in the presence of Al forms alkyl aluminum chlorides in the presence of ethylene, which at temperatures higher than about 200°C. break down to give free radicals, has been discussed in the section on catalysis in polymerization (35). The fact that quite different results are obtained under those conditions is not impressive evidence that the reactions of $AlCl_3$ itself under the normal conditions of its use proceed by free-radical mechanisms.

While a discussion of chemical mechanism could hardly be complete without including the knowledge of the effect of temperature, that topic is in a state of confusion as far as halide catalysts are concerned. Thus Burk and Sensel (97) found that pure aluminum bromide had substantially no action on normal heptane at the boiling point. Yet reaction was rapid at room temperature in the presence of HBr. The question of temperature coefficient is thus complicated by the influence of the amount of HBr present, which is generally difficult to determine.

The negative temperature coefficient in the polymerization of isobutylene by $AlCl_3$, already discussed, may be due to dissociation of the complex of hydrohalogen acid-aluminum halide, if this is the real catalyst.

It is, of course, unnecessary to insist that all the reactions catalyzed by halides should proceed by similar mechanisms. On the other hand, it seems unlikely that all the above theories should be correct. For those cases where hydrohalogen acid is necessary for the first step, some of the theories are ruled out. No mechanism will receive final approval until it is verified kinetically. The theory which appears to have most evidence in its favor, though incomplete, has been presented first. No significance is to be attached to the order in which the remaining theories appear.

Summary of Mechanisms

1. There is considerable evidence that acids of the type $HAlCl_4$ are involved in halide catalysis.

2. These probably act through intermediate compound formation, which may well be esters of such acids.

3. Such a mechanism sets up an analogy between the action of halides

and the action of acids which is real and which has been recognized before.

4. While halides form various other complexes, there is no strong evidence that they play a direct part in the catalytic action, although $RAlCl_4$ may go on to form a ternary complex before reaction is complete.

5. Theories which require merely activation by the halides seem vague and are not necessarily in conflict with the above.

6. Theories involving ions are of two kinds: (*a*) those in which ions are the cause of the activation and (*b*) those in which ionic complexes are formed but in which the driving power for the catalysis is to be found elsewhere.

7. Dehydrogenation is the sole reaction in certain reactions catalyzed by halides, and some have suggested it as the first step in other cases. It is not clear how far one can go in this respect, or how the halides dehydrogenate.

8. Halogenation has been suggested as a first step. However, little can be said for it and something against it.

9. The theory has been advanced that halide catalyzed reactions proceed by free-radical mechanisms. The published evidence for this is insecure.

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CHAPTER XX

BIOCHEMICAL CATALYSIS

DEAN BURK*

Emil Fischer, in his Faraday lecture in 1907, defined the field of biochemistry when he said that "its ultimate aim is to gain complete insight into the unending series of changes which attend plant and animal metabolism. To accomplish a task of such magnitude, complete knowledge is required of each individual chemical substance occurring in the cycle of changes and of analytical methods which will permit of its recognition under conditions such as exist in the living organism." It is probably fair to say that at the present time one-third to one-half of the newer biochemistry is catalysis, or aimed at elucidation thereof. An exceptionally high proportion of catalysis in this given field of chemistry comes about because the biochemist is so largely concerned with change. He studies processes often involving long chains or cycles of fairly definite intermediate compounds which, because of their small concentrations, indispensability, or reactivity, may well be regarded either as catalysts or as reaction components (reactants or resultants). It is very important to appreciate this particular situation in biochemical catalysis, where a given process, for instance fermentation of sugar to alcohol and carbon dioxide, is found to involve at least a score of *known* intermediates, some of these entering chains and cycles more than once. By their very complication such overall biochemical processes almost obliterate the usually easy distinction possible between catalyst and reactant in typical inorganic and organic reactions.

The present very brief chapter is intended primarily to provide the general catalytic chemist with some feeling for the vast scope of biochemical catalysis, some idea of the bewildering magnitude of the field, some orientation in regard to its myriad literature, and in particular to the numerous reviews available. For reasons which will shortly become evident, no single chapter, probably no single book, could adequately summarize this field, so diverse on the one hand and so richly descriptive

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in detail on the other, is the subject matter of biochemical catalysis. Biochemical literature is submitted to such frequent up-to-the-last-minute reviewing and restatement, not only in biochemical periodicals, but also in well-established volumes of annual reviews and textbooks, that a single encompassing chapter on biocatalysis as a whole, of critical value to either the professional expert or the casual reader in this field, has long been beyond possibility. For the general catalytic chemist, to whom the present chapter is addressed, it is feasible to present here only a review of reviews, a list of some of the most pertinent books and monographs whereby he may conveniently break into this literature.

It is perhaps no exaggeration to say that there are far more papers concerned with the study of biochemical catalysis alone than there are in all other types of catalysis described in this volume combined. As some quantitative basis for this statement it may be pointed out that in all the other chapters of this volume together there are scarcely 2000 references cited, whereas Chemical Abstracts lists some 50,000 references in biological chemistry since 1935. There are unquestionably 15,000 to 20,000 papers of direct biocatalytic interest during this period. The Annual Review of Biochemistry for 1938 (2), decidedly incomplete, lists over 2000 references in the fifteen of its twenty-three chapters that can be regarded of catalytic pertinency. In regard to the subject of the role of the minor (trace) elements in various biological processes, Riddle's recent compilation (61) lists over 8000 references, Willis' compilation (68) 4500, and whereas, if in this field there is frequent absence of knowledge of intermediate mechanism, there is compensatingly great certainty of catalytic involvement and ultimate disclosure of mechanism. It is estimated that concerning the single hormone insulin over 12,000 papers have appeared since its isolation by Banting and Best in the early twenties (92).

In order to reduce the literature to be cited in this chapter to a scale somewhat comparable to that of other chapters in this report, there is presented a bibliography of what is estimated to be approximately the hundred most pertinent books, monographs, and review volumes on biochemical catalysis. Intentionally omitted are individual articles (which bulk literally cubic yards *in toto*) and individual review articles (which bulk cubic feet); nor are article journals or abstract journals listed, since these too are adequately referred to in the appended bibliography. The hundred items of the bibliography are classified into six categories, in each of which the items are starred in accordance with *an assigned relative importance for biochemical catalysis*, due weight being given to timeliness, clarity, and speciality, as well as to general catalytic interest. Items not starred carry no implication of mere honorable mention, but have a very definite and particular interest for catalysis, which interest is only more diffuse (or less timely) in comparison with the starred items, not with items omitted from the list altogether.

The present chapter obviously cannot provide the general catalytic chemist with even the barest balanced account or outline of the major catalytic aspects of biochemistry reported in the literally many many thousands of excellent papers appearing in the last few years. Nevertheless, the general catalytic chemist need not feel unduly overwhelmed by this literature if he will make the intended use of the bibliography, and in particular commence with a brief preliminary survey of the limited number of doubly starred items, which will give him an excellent feeling for the scope of biochemical catalysis in regard to subject matter, particular catalysts, and methodology. With this excellent starred material at hand it would be idle for any chapter, such as the present one, to attempt to compete with it or repeat such readily obtainable résumés of either latest findings or general understanding.

Unfortunately, there is no one book, however large, into which are gathered and organized the distilled and purified *principles* operating throughout biochemical catalysis as a whole, but doubtless within a few years at most such a project will be attempted. The nearest approaches to anything resembling a " Principles of Biochemical Catalysis " are References 86, 78, 81, 94, 32, 49; with secondary mention for 7, 9, 11, 37, 47, 48, 55, 57, 58, 72. The monograph of Taylor written in 1907 (49), and remarkable from almost every point of view, might be said to be the most concentrated book of principles extant, but it is of course untimely.

On the other hand, if there is any one item which above all others will provide in English the spirit and lingo of modern 1939 biochemical catalysis it is Elvehjem and Wilson's " Respiratory Enzymes " (32), meriting highest recommendation both educationally and referentially. Volume VII of the Cold Spring Harbor Symposia on Quantitative Biology (7), on biological oxidation, may be anticipated somewhat similarly for its appearance later in the year. The monograph of Oppenheimer and Stern (45), also on biological oxidation, and intermediate in time of appearance in 1939 between the two works just cited, likewise takes its place with them as a means of providing a vivid picture of contemporary approach and *modus operandi* in biocatalysis; if its scope is somewhat narrower, there is an offsetting greater unity and more closely knit organization.

The most important review volume is unquestionably the *Annual Review of Biochemistry* (2) followed by the *Ergebnisse der Enzymforschung* (9), and the more recently established *Ergebnisse der Vitamin- und Hormonforschung* (11). Among the texts, for general accounts and background, there is first that of Bodansky (17), and then those of Gortner (21), Cameron and Gilmour (19), and Mathews (24).

The import of sections *d* and *e* of the bibliography, on physiological and special catalyses, is to emphasize that biochemical catalysis, in contrast to chemical catalysis generally, *must* go beyond description of phenomena in chemical (or physical) terms; it must go beyond a mere attempted description of the chemical mode of action or chemical structures involved; it must necessarily include phenomena and levels of organization involving the physiological, pharmacological, pathological, even the morphological. There is *no* escape from this point of view. There are, thus, particular series of compounds which invoke well-defined biological phenomena, with few if any of the intermediate chemical processes being worked out so far; yet in the case of each phenomenon there is a marked qualitative or quantitative correlation between chemical structure of compound applied and effect observed. Examples among many excellent ones rife are the amelioration of black tongue in dogs by a variety of derivatives of nicotinic acid; various chemical carcinogeneses; effects of the various D vitamins, sterols generally; various pharmacological series; and the actions of practically all hormones and especially the sex and plant (auxin) hormones. In each instance there is a series of a dozen to several score related compounds of known structures which elicit a given biological response that can only be described in terms *partly* physiological to morphological; the first causes and intermediate paths are chemical but the final effects are on biological levels not reducible to chemical terms only. Because we may know what the chemical compounds do, but not how they do it, makes the action none the less catalytic.

Section *f* of the bibliography, on enzymes, vitamins, hormones, provides information of the most concretely detailed biocatalytic nature. The enzymes — organic catalysts produced by living organisms, colloidal, commonly soluble, characterized by great activity, specificity, and susceptibility to physicochemical environment (temperature, *p*H, oxidation-reduction potential) — are undoubtedly the biocatalysts *par excellence*, and about which, unlike the hormones and all the vitamins except B_1, B_2, and possibly C and A, a great deal is often known concerning the intimate details of their chemical activity and even constitution. The following historically balanced statement of the present status of enzymes seems desirable.

One of the most important contributions of enzyme research during the first two decades of the present century was to show the narrowness and limitations of Ostwald's definition of catalysis (1894) as " the acceleration of a slow chemical process brought about by the presence of a foreign substance." This emphasis by Ostwald on changed reaction velocity and kinetic experimental work led indeed to a stimulation of enzyme research by the methods of physical chemistry which amounted to a major preoccupation for thirty years. But, as Haldane in his book (87) has stressed in general, and illustrated in detail, enzymes do not merely or mainly accelerate metabolic processes (alter time-scales of events) but, even more important, they select and determine their direction, especially when combinations of enzymes are acting together and not necessarily by the effect of one particular enzyme as might be thought. The nineteen-twenties provided the early serious, and nearly successful, attempts to isolate and purify enzymes. With a transition from the kinetic to the organic (isolatory) approach, the past decade has brought the efforts of the twenties to fruition and has yielded some ten pure enzymes (and more variants), all of them proteins. Now, it is important to recall that Willstätter, in his Faraday lecture of 1927, had about given up the idea — expressed by Emil Fischer in his Faraday lecture twenty years earlier — that enzymes are "derived from proteins and possess a protein-like character." Willstätter regarded them as peculiar organic compounds, with carriers to be sure, but non-specific ones, and not necessarily proteins. Some of the accompanying substances, he said, " form with the enzymes naturally occurring physiological complexes whilst others become accidentally associated with them during the isolation from the cells." And he said also: " It seems that we must consider an enzyme to be composed of a specifically active group and a colloidal carrier. To this, other substances of high molecular weight cling in various ways. The colloidal carrier seems to vary somewhat in its nature, but to be necessary for the stability of the active group." The Willstätter Faraday lecture is excellent to read to obtain the frame of mind of enzyme chemists generally in the late twenties, expressed by the greatest authority of the time, a frame of mind shortly to be eclipsed by the convincing demonstration from the Northrop school that an enzyme might at times be a pure simple protein with no demonstrable dissociable active (prosthetic) group, this to be followed by the contribution of the Warburg school showing that some pure enzymes can be reversibly dissociated into protein and low molecular-weight components of either organic or inorganic nature.

Before finally presenting the bibliography, the main feature of this chapter, a remark may be made as to the role of biochemistry in industry. The fermentation industry provides the most obvious application at present. Here, however, the isolated catalysts are still much less used than the whole living organisms themselves. The next decade will probably see a marked reversal in this situation. The lead in this direction is being taken for the moment by the hormones and vitamins isolated to date, but unquestionably the use of organism-free enzymes will likewise soon become prominently developed, probably first in medicine, and then in chemical industry generally.

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REVIEWS OF RECENT BOOKS ON CATALYSIS

BACTERIAL METABOLISM. *By* MARJORY STEPHENSON

Longmans, Green & Company, London, 1939, 2nd Edition, viii + 391 pp.
Reviewed by Dean Burk

The first edition of " Bacterial Metabolism," published in 1930 as one of the " Monographs on Biochemistry " series, may be said if not to have created this subject then at least to have established it as an independent field of investigation. The raw materials of the subject must naturally have existed before 1930 (else no book would have been written), but the coalescing of this matter into a full-fledged academic branch of knowledge — which, for example, not even a college course might exhaust — must be laid to the pen of Dr. Marjory Stephenson. One of the prominent investigators in the Biochemical Laboratory in Cambridge, Dr. Stephenson brings her subject, in the second edition of " Bacterial Metabolism," well through the stages of its adolescence to maturity. The important advances and developments that have taken place since 1930 have doubled the material to be covered, and in consequence the coordinating of the entire subject matter has been as formidable a task in the new edition as in the original. Indeed, exhaustive treatment of the whole subject by one author now being impossible, publication in monograph form has become unsuitable, and re-issue in the present enlarged, greatly revised form as an advanced textbook has been the result.

Dr. Stephenson, in the Preface, regards the most prominent recent advances in bacterial metabolism as having taken place along the lines of photosynthesis, fermentation, enzymes, and indispensable growth substances (vitamins, coenzymes), some of the advances taking directions quite unforeseen in 1930. Most of the impetus for the broad advancing front of bacterial metabolism and catalysis has, indeed, been inspired by and derived from general biochemistry, so that the catalytic chemist may accept essentially all the principles and even details of biochemical catalysis described in " Bacterial Metabolism " as being of the most general biochemical interest and application. Bacterial metabolism has largely followed, not led, general biochemical catalysis, borrowing far more than it has lent; its balance of trade has always been highly unfavorable.

The great advantage of bacteria for the study of biochemical catalysis, especially from the kinetic point of view, is, of course, the comparatively greater *physical* simplicity of the systems involved; tissues and higher organisms as a whole introduce many incidental, purely physical difficulties, such as rates of diffusion through macroscopic distances, which are avoided with the one-celled, microscopic bacteria. In addition, the actual number of naturally catalyzed reactions in bacteria very probably far exceeds those found in the animal and plant kingdoms, and " every year brings to light new and unsuspected mechanisms by which the various groups of bacteria are enabled to carry on life in the various peculiar environments which they happen to occupy." On the other hand, up to the present there have been separated in cell-free solution very few of the enzymes or enzyme systems in bacteria, and it has been necessary to work with either the active growing organism or the living but non-growing " resting-cell " form, in both of which the microscopic structures have been maintained intact. With bacteria, then, a certain physical simplicity has been traded, so to speak, for a greater chemical simplicity obtained with most other living forms, wherefrom it is ordinarily possible to extract numerous cell-free catalysts. During the past year, however, it has become much more feasible to obtain active cell-free extracts from bacteria owing to the wet-crushing mill for microorganisms developed by Booth and Green (*Biochem. J.*, **32**, 895 [1938]), the description of which, unfortunately, did not appear in time for mention in the book; much progress due to the use of this instrument, and to other techniques for the smashing of bacterial cells, may be anticipated in the near future. The strictly bacterial findings reported by Dr. Stephenson are, thus, based largely on cellular, intact material, and extensive accounts of cell-free bacterial catalysts must await a future edition of " Bacterial Metabolism."

The catalytic chemist will be interested to know that Dr. Stephenson's method of presentation is mainly to let the data speak for themselves, in the form of an unusually large number of tables, graphs, equations, and schema which permit the reader to obtain an exceptionally clear experimental understanding of the material presented and thereby a feeling of very soon being at home with the subject. Any page will provide the reader with interesting meaty material for study and digestion, seasoned with plenty of good salt but no other condiment. The only exception, however minor, that might be taken to this concentrated diet is that occasionally a cut of meat which has evidently hung for some time is passed off without apology as still fresh, the author having a penchant for here and there detailing classical experiments long since improved in surety, even if not interest, by subsequent work not indicated to the unknowing. This feature of somewhat erratically weighted references is, however, much less noticeable than in the first edition; and doubtless its disappearance *in toto* would be the more a pity since it is evidently an ineradicable characteristic of the best English books on biochemistry to present above all a broad picture in preference to a mere compendium, and to be concerned with essential content rather than too many details of form. And in a pioneering book an expressed reverence for previous pioneers, even at the expense of whittlers and refiners who follow, is unquestionably apropos.

In the writing of any book review, we must always decide how much weight to give to an impression of the book and how much to the contents. Having waxed highly approving and waned ever so slightly critical in regard to the first course, we may now say concerning what the book is about that the chapters following the introductory one are, in order of their estimated importance for the catalytic chemist: IV, " The Fermentation of Hexoses and Related Compounds "; II, " Respiration "; V, " The Decomposition of Proteins "; X, " Bacterial Photosynthesis "; VIII, " Nitrogen Fixation "; IX, " Autotrophic Bacteria "; VII, " Nutrition and Growth "; XI, " Enzyme Variation and Adaptation "; VI, " The Metabolism of Nucleic Acid and Its Derivatives "; and III, " Polysaccharides." (The general bacteriologist might well find Chapters VII and XI of prime interest.) Chapters III, VI, X, and XI are new in the second edition; IV, V, and VII have been retitled; and the order of the chapters has been somewhat rearranged. There is a very thorough and inviting subject index (15 pp.), and, following a common and excellent English system, a bibliography with titles and references to mention in the text, and also an appendix of selected bacterial growth media. Whereas all chapters, except possibly the last two, offer material of profound interest to the catalytic chemist, undoubtedly Chapters IV and II, on fermentation and respiration, will command first and most general attention; and here indeed are found a wealth of bristling principle and detail which it would be idle to list but of utmost urgency to recommend.

By way of postscript, no consideration of " Bacterial Metabolism " would be complete without reference to its younger half brother " Bacterial Nutrition," fathered by Dr. B. C. J. G. Knight (Med. Res. Council Special Report Series, No. 210, H. M. Stationery Office, 1936). The two books are closely complementary, the latter dealing with what and why bacteria " eat " what they do, and the former with what and how the bacteria do with what they eat. Both books should stand on one's bookshelf side by side. Dr. Knight's book, in addition to dealing as exhaustively as may be with bacterial nutrition, has developed a remarkable coordination of the factual material at hand into a highly original system of comparative and evolutionary physiology of bacteria based on nutritional requirements at different levels of complexity. This system, it is to be noted, commences in the evolutionary scale at the approximate point where Oparin in " The Origin of Life," reviewed elsewhere in this report, left off.

FERMENTE, HORMONE, VITAMINE

By Robert Ammon and Wilhelm Dirscherl
Georg Thieme Verlag, Leipzig, 1938, xvi + 451 pp.
Reviewed by Dean Burk

As the authors of this excellent book point out in their introduction, the actions of enzymes, hormones, and vitamins as carriers of active or prosthetic groups are all becoming more related and understood on a common basis. In a very general way, of course, enzymes are manufactured by a given organism for its own use; hormones by special organs (glands) of a higher animal organism; and vitamins must ordinarily be supplied an organism from without (nutrition), the animal vitamins in particular being largely synthesized by plants. The broad definition of an enzyme (or ferment) is a catalyst produced by a living cell; technical definitions add further qualifications and details. Hormones until a relatively short time ago were regarded as specific substances formed in special glands of higher animals and man and transported (as by the blood) to other places in the body where specific functions were performed. But there have now arisen " tissue " hormones, which are produced in several parts of the body and act at times *in situ* (thus, acetylcholine, histamine, vagotonine, vesiglandine, prostaglandine, substance P of Euler and Gaddum); also there is a large and well-established group of so-called plant hormones (phytohormones).

Evidently, then, the sharp distinctions and contrasts naturally arising during the early pioneer phases on vitamins and hormones are largely giving way before a great body of now moderately well-worked-out information. For example, the early iron-clad distinction between a vitamin and a hormone, namely, that the former was produced by plants, the latter in animals, no longer holds in that a given vitamin required by some animals may be synthesized by still others; the best well-known example is vitamin C, which is needed but not synthesized by the guinea pig and man, whereas in the rat, rabbit, and most other animals it is synthesized but not needed in nutrition. Some vitamins are formed in the animal body from precursors (provitamins) obtained nutritionally, as in the case of vitamin A from carotene or vitamin D from ergosterol or other sterols. On the other hand, a hormone itself may likewise need an exogenous building stone, as in the case of iodine for thyroxin formation; here, were it not for its being a simple inorganic substance, the iodine could scarcely escape classification as a vitamin, and one would have a vitamin as an integral part of a hormone.

Where a hormone clearly acts as a coenzyme, from the standpoint of mechanism, Euler has proposed the name hormozyme, and similarly, vitazyme (thus, vitamin B_2-active lactoflavin phosphoric acid, the coenzyme of the yellow enzyme; vitamin B_1-active pyrimidine-thiazole pyrophosphoric acid, the coenzyme of carboxylase); hormozymes and vitazymes together are called ergozymes, or, more recently, ergones, and are protein-free. In order to include the protein carrier as well as protein-free coenzyme constituents of enzymes, hormones, and vitamins, and also the proteohormones of purely protein or peptid character, Ammon and Dirscherl now propose the term ergine; by ergines are to be understood " organic compounds that are formed in living cells and that are necessary for the normal course of vital processes in the plant and animal kingdom; they act in such small quantities that their effects are not ascribable to their yielding energy by combustion."

With this correlating introduction the authors proceed to a beautifully organized and unusually scholarly presentation of the main authoritative information concerning ferments, hormones, and vitamins, in sections in turn, and conclude with an important fourth section of thirty pages with a summary of the most pertinent interrelationships between the three. The ease, naturalness, and obviousness of the organization and arrangement are matched by an exactness of statement, readability, and selection of pertinent material that cannot fail to make the reader grateful. The length of the book is adequate to avoid sketchiness on the one hand or a mechanical *Handbuch* presentation on the other. With a Continental liberality and sense of completeness, nevertheless, the authors have made a point to include mention, however brief, of the numerous minor miscellany with which this field is so replete, but the uncertainty or questionableness of any of the rarer, little-worked-out hormones or vitamins is usually accurately indicated. Doubtless some readers will take exception to the emphasis given to " tissue " hormones, and even to the legitimacy of the term. There is a good subject index but no author index, and there is comparatively little citation of references. A rounded-out, synthesized, readable account of the whole field of biocatalysis is presented, with emphasis of outlook neither unduly upon the theoretical nor the practical, but, simply, upon the actual, in the language mainly of the biochemist.

The authors, who are located at the Universities of Breslau and Frankfurt A.M., have succeeded in this book in offering one of the finer examples of what German biochemical science is still capable of providing at the present time in spite of the losses in biochemical personnel suffered by the country in recent years. In the reviewer's judgment the book is the most excellent single volume on biochemical catalysis extant.

KURZES LEHRBUCH DER ENZYMOLOGIE

By Theodor Bersin

Akademische Verlagsgesellschaft m.b.H., Leipzig, 1938, viii + 170 pp.

Reviewed by Dean Burk

This compact, aptly named book is indeed a "short textbook," valuable even if not indispensable to students and investigators of the biological disciplines (biochemistry, medicine, zoology, botany), and an excellent introduction for any reader wishing a sketchy acquaintance with the subject of enzymes from the standpoints of both theoretical principles and practical application Attractively and accurately printed, this little volume, in the words of Quastel [*Nature*, **143**, 138 (1939)], "covers a very large field in a very small space, and the author is to be congratulated on the brevity, clarity and, on the whole, the accuracy of his exposition. . . . whilst general analytical or mathematical treatment is restricted to the barest outline, prominence is given to some of the remarkable advances which have been made in the field of enzyme chemistry during the last few years." Indeed, the author himself says, "This book is no guide through a museum, but a summons to activity (*Mitarbeit*)," and goes on to point out the many unsolved problems in fermentative metabolism in both health and disease, preparative enzyme chemistry, and industrial enzyme products.

After a three-page historical introduction and orientation, the book is conveniently divided into three parts, the first of which, perhaps the least effective, treats of the general properties of enzymes: their protein-like, colloidal nature, content of some dozen chemically reactive groups, and various degrees of dissociation of prosthetic groups; kinetics, including quantum-mechanics relations, temperature sensibility, heat inactivation, cryolytic relations, optical specificity, radiation sensitivity, high-pressure effects, effects of heavy water, and inhibitors, activators, and complements; biological formation and distribution; relation to immunology; and preparative methods, including chromatography, cataphoresis, and electrodialysis.

The second section, equal in length to the other two, covers most of the various individual enzymes, which, for the readers of this report, might well be listed in some detail: esterases, which act upon organic esters (lipases, tannases, chlorophyllases), and inorganic esters (phosphatases, sulfatases); carbohydrases (glucosidases, cellulase, amylase, inulinase); amidases (urease, hippuricase, asparaginase, glutaminase, arginase); peptidases (aminopeptidase, carboxypeptidase, dipeptidase, prolinase, prolidase); proteinases (pepsin, pepsinogen, trypsin, trypsinogen, chymotrypsin, chymotrypsinogen, rennin, papain, cathepsin, thrombin); carbonic anhydrase; carboxylase; and the host of " redoxases " (*Atmungsferment*, cytochrome, peroxidase, catalase, flavo-proteins, phosphopyridine nucleotide-proteins, hydrogenlyase, aldolase, luciferase).

The third and final section is concerned with the significance of enzymes for respiration, fermentation, general metabolism, and nutrition, considering first bacteria, yeasts and fungi, then green plants, and finally animals and man, with brief reference to cancer and heredity.

Although no " guide through a museum," the treatment of this array of topics in a mere 170 pages may well be compared, in its sketchiness on the one hand and bird's-eye view on the other, to a three weeks' tour of Europe. If there are ten important points about a particular topic, the author will give two or three, if a hundred points then eight or ten; and the references provided are very casual. But if scarcely the gist of each topic is given or referred to, the reader may have the assurance that nothing is said that is superfluous. The author sticks closely to his business, which is concrete, tangible, particularized information concerning mainly recent developments, and his inductive approach presents an interesting contrast to the far more deductive treatment by J. B. S. Haldane in " Enzymes " (1930), which appeared at a time when it could not yet be said that enzymes were real, individual chemical compounds.

Dr. Bersin's primary interest in the very tangible is not to be taken as meaning that he does not offer many stimulating and creative comments and observations in passing. These are often quite individualistic, though never opinionated, and for the expert are provocative and challenging. Indeed, owing to the pervading textbookish tone and lack of qualification to almost everything that is said, there is undoubtedly much scope for a carping critic — what is often apparently so easy for the general reader to see might be very easy for a righteous critic to see through — but a consideration of such debatable or seemingly unwarranted matter need scarcely be detailed for the attention of the general catalytic chemist here beyond noting its presence. For the general catalytic chemist should turn to Dr. Bersin's book to learn, not to look up. It is not a " Handbuch," not even a baby one.

THE ORIGIN OF LIFE. *By* A. I. OPARIN

Translated, with annotations, by SERGIUS MORGULIS. The Macmillan Company, New York, 1938, viii + 270 pp.

Reviewed by Dean Burk

During past centuries there have been many books and articles entitled "The Origin of Life," but undoubtedly the latest by Professor A. I. Oparin, Associate Director of the Biochemical Institute, Academy of Sciences of the U. S. S. R., Moscow, occupies a commanding position in the field. Published in Russian in preliminary form in 1923 and in its present form in 1936, translated skilfully in both meaning and spirit by Professor Morgulis, Department of Biochemistry, University of Nebraska, and first printed in English in 1938, this book will repay a most careful study by a wide variety of readers. In spite of the agelessness of its subject, harking well back into folk legend and antiquity, and an inevitably recurrent feeling of inherent insolubility which seldom fails to overcome one upon returning from time to time to the problem, it must be said that the entirely up-to-date, authentic, concise, orderly treatment given by Professor Oparin will inspire all readers having any curiosity as to the details of how life on earth began with a fresh outlook of hopefulness and expectancy. Comparatively short, readable, and provided with excellent but brief author and subject indexes and a rough score of selected appropriate references appended to each of the eight chapters, the value of such a book for those interested in catalysis lies in a particular kind of background and enlargement of outlook it offers; attention is centered not upon a particular catalyst or catalytic reaction occurring in test tube, pilot plant, or works plant but upon a field of much vaster scope. In the reviewer's opinion, an excellent subtitle for the book would be "Biochemical Catalysis on a Planetary Scale."

The most persistent attribute of the book, which will possibly be disappointing to some, is a conservatism toward all major views, not excluding the author's, on how life on earth began and developed — or begins and develops. This conservatism, supported by a streamlined logic of argument, lends great strength to the book. In a well-balanced historical perspective provided in the first three chapters, the author spanks over a firm knee, with gentle but effective hand, each of the main previously advanced theories regarding the origin of life, such as spontaneous generation, eternity (continuity) of life, or dissemination of spores by cosmic dust (panspermia). In these introductory chapters, whose conciseness only an old student of the material will fully appreciate, Oparin sketches the essential landmarks in the history of the problem, with emphasis on lessons to be learned. He commences as far back as the Ionian school (600 B.C.), and continues with many famous names through Aristotle (300 B.C.) and Harvey (1630) who said " Omne vivum ex ovo," only to find in the twentieth century that the theory of spontaneous generation, seemingly interred forever by Pasteur, had resurrected itself in modernized form in connection with the origin of certain viruses, at the same time raising concretely embarrassing questions as to the very nature of life itself. Oparin's carefully reasoned and substantiated conservatism, itself possibly odd, coming as it does from a land of dialectics and revolution, is maintained throughout the developmental and final chapters, in which is presented a largely biochemical picture with astronomical and geological support of most of what appears to be known or soundly conjecturable concerning biogenesis.

In Chapter IV, entitled " Primary forms of carbon and nitrogen," begins the serious work of tracing in chemical detail the slow evolution of organic substances. The primary conditions for this evolution are held to be the same as those for the subsequent origin of life. Developing Pflüger's minority view advanced in the last century, that carbon dioxide represents not the primary carbon substrate of life processes but, if anything, a final resultant thereof, Oparin lays great emphasis on astrospectroscopic, meteorological, and geological evidence indicating the early appearance of carbides, cyanogen, and especially hydrocarbons, that is, reduced rather than oxidized forms. Specifically, H. N. Russell's view that the hydrocarbons of large planets resulted from the reduction of carbon dioxide by hydrogen ($CO_2 + 4H_2 = CH_4 + 2H_2O$) is rejected as based on the idea of the primary occurrence of carbon dioxide; likewise rejected, upon recent geological evidence, is Mendeleyev's view that sea water found its way through surface cracks into the glowing central core of carbon-iron in the earth's interior; the hydrocarbons were formed, Oparin holds, when carbides were erupted onto the earth's surface from the interior and then reacted with the superheated aqueous vapor of the atmosphere existing at that time (and even very occasionally now!). Not only the free oxygen but also the free nitrogen of the atmosphere is regarded as of recent biological origin, following Vernadski in his recent " Problems of Biogeochemistry " (1935); nitrogen, like carbon, first appeared on the earth's surface, in reduced form, as ammonia, derived from nitrides, cyanogen, and cyanamides.

The main problem of conjecture for Oparin, taken up in Chapter V, is what happened between the time when ammonia and methane were formed and the time when the primary ocean came into being, where " the environment in which organic substances existed resembled our own so closely that we may safely draw conclusions about the progress of chemical transformations on the basis of our knowledge of what is happening today." Saturated hydrocarbons would at sufficiently high temperatures, and even possibly without contact catalysts, yield unsaturated hydrocarbons (e.g., $2CH_4 = C_2H_2 + 3H_2$), which with superheated steam at somewhat lower temperatures would then form oxidized hydroxy derivatives (e.g., $C_2H_2 + H_2O = CH_3CHO$), including alcohols, ketones, and aldehydes, with which ammonia could readily combine, yielding, all in all, oxygen and nitrogen derivatives of hydrocarbons in great variety to be carried down, as the earth cooled off, in boiling rain into primitive ebullient oceans. Time was a matter of no consequence here, for incalculably long periods were involved, and the catalysts of the organic chemist or enzymes of the cell could be dispensed with, and likewise so it would seem, for anything Oparin says, photocatalysts and photochemistry. All this was true for many condensations, polymerizations, hydrolyses, and oxidation-reduction reactions whereby without biological agents but with similar end result were formed thermally from the simplest organic substances and water the most complicated and varied organic high-molecular weight compounds. These compounds might well comprise the material basis of living substance, including, as explained in the course of many pages, asymmetric compounds, and polypeptides of a sort, not necessarily those isolated from plant or animal material. Oparin courageously regards the primary non-biological formation of compounds of the protein type as in no way unusual or exceptional compared with the formation of the other complex non-nitrogenous organic substances, and points out that the far more fundamental issue to decide is why proteins have come to play such an exclusive role in the origin and processes of living organisms. Here he looks for no special unstable, labile atomic arrangement, but to the extensive reactivity of the ordinary dozen or so known groupings in proteins (e.g., carboxyl, amino, hydroxyl, phenyl, sulfhydryl, cyclic, imidazol, indole, guanidine) and to the many properties describable in physicochemical and colloidal terms; indeed, the colloidal state bridges the gap between organic compounds and living things. Protein itself is by no means living matter, but hidden in its chemical and physical structure is the capacity for further organic evolution, and it is in this sense that one should interpret Engels' " Life is a form of the existence of protein bodies."

It is the task of Oparin and not of the reviewer to make Chapter V convincing, and for this the reader must go to the book. The same may be said of the climaxing chapters, VI and VII, which deal respectively with the "Origin of primary colloidal systems" and the "Origin of primary organisms." The reviewer will not attempt here to anticipate Oparin nor to prejudice a reader falsely by attempting any ineffective condensation of the finale of the steady line of argument, which must be followed continuously to be appreciated or criticized. Suffice it to say, recognizing in Chapter VI that the mere property of bigness or longness of molecules (as obtained by polymerization or condensation) represents a sort of blind alley of evolution, Oparin develops at great length Willstätter's emphasis on the properties of mixtures not possessed by their components, and this leads into his acceptance of de Jong's conception of coazervates and coazervation, a developed form of the colloidal state not unsuggestive of the polyphased state of protoplasm even if certainly not the same because of somewhat differing chemical components. The formation of complex coazervates in the earth's original hydrosphere from the complex mixture of different high-molecular-weight organic compounds (lipids, carbohydrates, polypeptides, hydrophil colloids) was, in Oparin's opinion, inevitable, and a most important event in the process of *autogeneration* of life. Before that event even organic matter was indissolubly fused with its solvent medium, but with that event it became concentrated unequally at different points and at the same time sharp physical boundaries developed between organic substance and medium, which, in a sense, created an antagonism between the two of the same type occurring in living organisms. After antagonism there developed likewise assimilation, structure, and individuality.

With the coazervates, however, life was not yet attained. They obeyed the simplest laws of organic chemistry, and those of the newly superimposed colloidal chemistry; but a still higher order of (biological) law and stability was called for, involving velocity and direction of chemical reactions. Here, at last, came the catalysts, enzyme models, enzymes, the systems which determine both velocity and direction, whereby the more of these hasteners and selectors operating together the greater would be their power and influence, as concrete study of any enzyme system shows:

> The organic substances found in living cells rarely originate there as the products of a single reaction. Generally they are formed by a correlation of a number of chemical reactions following one another in a perfectly definite order. Such vital phenomena as respiration, fermentation, growth, etc., are always associated with a long succession of chemical transformations, the separate events of which are related to each other in a very definite manner . . . this orderly succession of separate reactions leads ultimately to the formation of one or another product, and every change in the succession is equivalent to a radical

> alteration of the process as a whole. A harmonious coordination of velocities of the different reactions is prerequisite for the existence of this orderly succession, and this is possible only under the condition of strict regulation of the activity of each enzyme catalyzing a particular reaction [pp. 175–176].

H. C. Urey has stated in a recent lecture that even the one-cell amoeba must have essentially the same extremely large numbers of different compounds contained within it as does man. The gaps from man to amoeba, amoeba to primary organism, and primary organism to coazervate are perhaps roughly equivalent. The transition from the still comparatively static coazervate to the primary organism is Oparin's final burden in Chapter VII, and it involved stabilization by " natural selection " and competition, analogous to such factors at Darwinian levels. With the disappearance of freely available organic matter, the more exacting did this " natural selection " of systems individually best adapted to create organic matter themselves tend to become, until finally a purely biological struggle for existence developed: the primary organism arrived and the question of the origin of life on earth was closed — says Oparin! And now here is an interesting *dénouement:*

> Natural selection [Oparin informs us] *long ago destroyed . . . all the intermediate forms* of organization of primary colloidal systems and of the simplest living things and, wherever the external conditions are favorable to the evolution of life, we find countless numbers of fully developed highly organized living things. If organic matter would appear at the present time it could not evolve for very long because it would be quickly consumed and destroyed by the innumerable microorganisms inhabiting the earth, water, and air. For this reason, the process of evolution of organic substance, the process of formation of life sketched in the preceding pages, *cannot be observed directly now*. The tremendously long intervals of time separating the single steps in this process make it impossible to reproduce the process as it occurred in nature under available laboratory conditions [p. 251] (*reviewer's italics*).

Yes, like Lewis Carroll, Oparin takes good care that the world of which he writes is closed to further visitors come for first-hand observation. But unlike Carroll, Oparin always remains on this side of the mirror, and in this real world in which he lives he is regarded as the leading sugar chemist, theoretical and applied, of his country, a Russian C. S. Hudson-C. A. Browne, and he is the mundane director or associate director of several institutes.

It has not been the scope or purpose of this review to repeat the steady stream of practical catalytic generalizations running throughout the book; the reader must underline them in his own copy. Nor has it been possible to reproduce the many fine shades of criticism, caution, and judgment exercised by the author; again the reader must appreciate these for himself, and likewise come to realize for himself how each sentence in the book is chiseled into its own logical position. Nor has this review attempted to reproduce the detailed chemistry of evolution provided by Oparin in Chapters IV–VIII, or modern enzyme chemistry in Chapter VIII. Finally, the review has been no abstract; for that the reader may turn immediately to concluding Chapter IX, where he will find in essence: "There is no absolute and fundamental difference between a living organism and lifeless matter. Life could not have existed always nor originated spontaneously in any brief span of time. The complex combination of manifestations and properties so characteristic of life must have arisen in the process of evolution of matter. There still remains the problem of the artificial synthesis of organisms, a goal very remote but not unattainable." Whether mathematician G. D. Birkhoff has been reading Oparin's book or not, he says in his Presidential Address (A.A.A.S., Richmond, 1938): "Recent advances in the chemical knowledge of large organic molecules seem to indicate an innate hospitality of matter toward the evolution of the living organism. In this way a plausible genetic account of the origin of life is suggested." Here, indeed, in these two citations, is gradualism on an aeonic scale, coming from both the most revolutionary country in the modern world and, vicariously or otherwise, the most enduring university in the United States.

STUDIES ON BIOLOGICAL OXIDATION AND SOME OF ITS CATALYSTS. *By* ALBERT V. SZENT-GYÖRGYI

Acta Med. Szeged, Tom IX, Fasc. 1
Eggenbergersche Buchhandlung, Karl Rényi, Budapest, 1937, 98 pp.
(Also J. A. Barth, Verlagsbuchhandlung, Leipzig.)

Reviewed by Dean Burk

This book is by a recent Nobel laureate, the professor of medical and organic chemistry in the University of Szeged, Hungary, and one who has carried out a considerable amount of research outside his own country, in England, the United States, and elsewhere. It is a very personal account of the work of the author and of many collaborators on the mechanism of respiration in animals and plants. As indicated in the title, however, it is not intended as a comprehensive systematic description of biological oxidation processes. Less than one hundred pages in length, it brings together in very comprehensible form many original observations buried under a mass of data scattered throughout a large number of papers from the Szent-Györgyi school, of which eighty-six are referred to in an appended bibliography. The main theme of the work springs from research devoted for the past fifteen years to the elucidation of the superficially simple reaction between biologically activated hydrogen and oxygen to form water. The experiments often led to quite heterogeneous results, such as the discovery of the catalytic nature of C_4 dicarboxylic acids, or the discovery, isolation, and identification of vitamins (C and " P "), results which have found, or promise to find, widespread application, especially in medicine. Indeed, in this latter connection an understanding of the methods and outlook presented in the book is enhanced by taking due note of the resemblance in roles between the author in Hungary, Pasteur in France, and Virtanen in Finland, where in each case there is the same curious mixture of deeply academic and widely applied accomplishment.

Following a brief introduction on " The Principles of Biological Oxidation," the book is conveniently divided, with a comfortable if not labored logic, into three parts: " The Oxidative Mechanism in Animal Tissues " (The activation of O_2 and cytochrome; The activation of H, dehydrogenases, co-dehydrogenases; The missing link; The succinate-fumarate theory; The malate-oxaloacetate theory; The united theory; Remarks on H transfer; The donator, its activator, and the yellow enzyme; Remarks on dehydrogenases; Other tissues and donators); " Problems, Objections, and Methods " (Introduction; On the Pasteur reaction; Energetics; Intermediary metabolism; C_4 acids and acetone; Objections; Methods); and " Vegetable Systems " (Introduction; The Polyphenoloxidase system; The " Peroxidase System "; On vitamin C; On vitamin P; On health, disease and vitamins); and " Post Scripta " and " Literature."

Work on biological oxidation was concerned, historically, first with overall aerobic oxidation, and then with analysis of the initial intermediate anaerobic stages. Szent-Györgyi may be said to have inaugurated a third latest phase, namely that involving the path of oxidative breakdown of the anaerobic intermediates. During the past five years he has shown that C_4-acids, such as succinic, fumaric, malic, and oxalacetic acids, catalytically promote oxygen consumption in animal tissues, and that the function of these catalysts in respiration is one of transporting bound hydrogen from compound to compound, *en route* from organic substrate or H-donator such as sugar to the Warburg-Keilin iron-pyrrole systems which provide the activated oxygen ultimately to yield water. An interesting feature is that here the C_4-acids, which operate in minute quantities and may in principle be recovered subsequently, are catalysts in a very ordinary chemical sense, whereas so much of biological catalysis is carried on by very specially elaborated materials, enzymes, coenzymes, activators, structurally complicated pigments, etc. The dehydrogenase enzymes in particular are the exact biologically elaborated counterparts of the C_4-acids in so far as they pass bound H back and forth, and of course in many overall processes both dehydrogenases and C_4-acids are inextricably intertwined, so close is the functional (even if not structural) relationship.

Szent-Györgyi gives an instructive account of the work leading up to the consideration of the C_4-acids as indispensable catalysts, in addition to their being encountered during analyses of cellular material and sometimes as substrates. The starting point was his observation that succinate dehydrogenase was unique among tested dehydrogenases in regard to ability to transfer activated H to cytochrome (or Warburg-Keilin system), and this was followed by equally interesting specific points in regard to intensive fumarase action and oxalacetic acid reduction. In final form the theory proposed H-donation by substrate (via cozymase and malicodehydrogenase) to oxalacetate to form malate, partial transformation by fumarase of malate to fumarate in an equilibrium (with elimination of water), and conversion of the malate or fumarate (via Warburg's yellow enzyme and succinodehydrogenase) to succinate which then acts upon the Warburg-Keilin (cytochrome) system. The dehydrogenases involved are, according to Szent-Györgyi, not functioning under physiological conditions as dehydrogenases at all, but as H-transportases, since they do not dehydrogenate (oxidize) the compounds for which they are named (malate and succinate) but transfer hydrogen from other compounds (substrate-donator and malate respectively) to form these namesake compounds. In further connection with this perhaps unnecessarily subtle distinction he indulges in some pretty loosely pictorial " Remarks on H Transfer " (pp. 26–27).

In the last two or three years there has been much confirmation, extension, and important modification of the Szent-Györgyi scheme, by Stare and Baumann, Greville, Boyland and Boyland, Martius and Knoop, and especially by Krebs and Johnson. Indeed the Szent-Györgyi scheme possibly appears somewhat overshadowed by a mechanism proposed by Krebs during the printing of the book, whereby the C_4-acids are but members of a more complicated cycle in which oxalacetate combines with something like pyruvate to form citrate, which in turn is oxidized step by step into succinate and fumarate and finally back to oxalacetate again (with net elimination of " pyruvate " and formation of CO_2 and H_2O); carbohydrate is thus oxidized via citrate. It is typical of the easy, gracious retraction of outlook and conclusion exercised by the author on more than one occasion throughout the book that he appends a postscript, " Undoubtedly, much can be said in favour of this theory (of Krebs), which, if found correct, would necessitate a thorough revision of this book." To this, however, it must be added that at the 16th International Physiological Congress in Zurich, August, 1938, Szent-Györgyi has meanwhile upon further study of the matter developed less inclination to accept the general applicability of the Krebs cycle or to regard it as a profoundly modifying influence. It is interesting to note in passing that both Szent-Györgyi and Krebs admit the other's mechanisms as possibilities and minor actualities, but claim quantitative predominance for their own. As one basis for this difference of opinion, there appears to be definite quantitative disagreement as to whether oxalacetic acid can be reduced by tissue-H rapidly enough to account for the whole of respiration in the Szent-Györgyi scheme. Krebs says the rate is " much too slow "; Szent-Györgyi, " strikingly fast . . . twice or thrice as much as would be necessary."

Szent-Györgyi derives on the basis of his theory a beautifully simple point of separation between the two great paths of catabolism, fermentation on the one hand, and respiration on the other — a differentiation always the aim of a biochemist! — and at the same time he obtains a qualitative explanation of the Pasteur effect (suppression of fermentation by oxygen gas), about which so much has been surmised during the past decade. In fermentation the 2H of the trioses are taken up by pyruvate to form the fermentation product lactate, whereas in oxidation they are taken up by oxalacetate to form, eventually, water. Both pyruvate and oxalacetate are activated on the same enzyme, the latter with greater affinity. In the absence of oxygen gas, oxalacetate is not formed and pyruvate is the acceptor, yielding fermentation; in the presence of oxygen gas, the oxalacetate is formed, successfully competes with pyruvate for the enzyme, and so the H of the donor-substrate (triose, or originally sugar) goes on to form water in respiration, as already outlined. The actual point of separation occurs at the dehydrogenase enzyme involved. According to this picture fermentation and respiration represent *alternate* ways of metabolism, with oxygen gas being the experimentally deciding factor along lines laid down by the foregoing theory. Szent-Györgyi then offers the following, undeniably interesting, evolutionary suggestions and reasons for C_4 catalytic activity:

> Many biochemists agree that in the course of phylogenetic development the simple process of fermentation has preceded that of oxidation, and one might wonder how Nature found its way from fermentation to oxidation. . . . nothing more was needed than to carboxylate pyruvic acid (to form oxalacetic acid). By this carboxylation the molecule was taken out from the carbohydrate cycle and stabilized as a catalyst. . . . This relation of fermentation and oxidation also answers the question why Nature has chosen the C_4 dicarboxylic acids as central catalyst of oxidation. . . . It is known that the alpha and beta position to a carboxylic group lends the C atom a special reactivity. Now there is only one group of substances which contain two unsubstituted C atoms, both alpha and beta at the same time. This unique group is that of the C_4 dicarboxylic acids. The second COOH group thus not only stabilizes the molecule but at the same time gives it a special reactivity, increasing its affinity to the enzyme. This increased affinity enables the traces of C_4-acids present in tissue to carry the whole respiration, . . . (pp. 44–46).

Szent-Györgyi's collaborator St. Huszák showed that the C_4 reactions operated in the whole animal as well as in tissues, and this recently led Korányi to test whether in diabetes there might be a deficiency of C_4 catalysts and thereby an increased acidosis and ketone body formation consequent upon a diminished oxidation, along lines suggested above in explaining the Pasteur effect. In certain cases succinic acid feeding seemed to cause acetone and acidosis to disappear (though with no effect on hyperglycaemia) but the experiments were too few to do more than draw the attention of clinicians and other experimental workers to the need for research and understanding along these lines (some later work by Lawrence and others has been negative). The experiments suggested that at least in certain cases of diabetes part of the acetone formed might be derived from pyruvic acid and thus from carbohydrate, and not from fat oxidation as is so widely held.

The second section of the book considers further details and hints concerning acetone formation, fat formation and disappearance, carbon dioxide production, carbohydrate synthesis, tumor metabolism, energy utilization, method and *modus operandi*, and makes an earnest attempt to meet objections raised by others to the C_4 theory. The most general criticism has been brought forward by F. Knoop, who points out the great number of substances, imino acids, aldehydes and ketones, and double bonds, which can be reduced in animal tissues; and he gives expression to his belief that H split off from a primary donator can be transported toward oxygen by a great number of substances; C_4 is just one of the many possible H acceptors, and along the same lines Krebs regards oxalacetic acid as just one example of CO-group reduction. Szent-Györgyi, who in general employs teleological reasoning rather freely, is at considerable pains to answer Knoop's argument by emphasizing the definite limitations of structure, kinetics, and thermodynamics imposed upon H-transference, and by refusing to allow much accidentalness to many unique facts. He is willing to make occasional minor quantitative exceptions, but in general, " the main bulk of H, however, will be combusted along fixed routes by an apparatus of which the C_4 system forms an integral part." So far as his experience goes, the main process of respiration follows strictly prescribed routes, and not arbitrary or variable substances: " According to thermodynamics, cytochrome-oxidase and cytochrome should oxidize with preference the most negative substances, like the donator. But in spite of thermodynamics cytochrome-oxidase oxidizes only cytochrome and cytochrome only succinate. They refuse to oxidize any other (known) substance, for they are made and fitted together that way. This is what we call organization . . ." (p. 60). Practically all the known stages in oxidations in the cell are by themselves theoretically reversible, yet for the most part they proceed in one direction only. Strongly specific predetermination in the chain of H-transference, indeed, is the main theme of Szent-Györgyi's " Diskussionsthemata " before the International Physiological Congress, August, 1938.

Szent-Györgyi's taste for teleological consistency leads him to the conviction that there can be no real difference in the fundamental chemical mechanisms of plants and animals, even in regard to hormones and vitamins: " Vitamin B_1, instrumental in producing thoughts in our brains, is equally indispensable for the silver membrane of rice. Insulin, the highly specific product of a highly specific organ of our body, is found also in the yeast cell . . . . So if we want to elucidate some fundamental biological principle, it does not matter whether we study a high or low animal, a plant, or a yeast cell. There is no fundamental difference between kings and cabbages" (p. 67). What Szent-Györgyi means by claiming the existence of insulin in yeast is not clear.

In the final section of the book, which concerns polyphenoloxidases, peroxides, benzpyrone dyes, vitamins C and "P", and vitamin therapy, Szent-Györgyi introduces much biochemical philosophy, humor, and incident. He tells how he "ran about for five years with crystalline ascorbic acid in his pocket without testing its vitamin activity" and how he searched the world over for a concentrated natural source of vitamin C only to find by far the best source (red pepper) in his home town, Szeged, the center of the paprika industry. Patients turned dark brown by Addison's disease could be bleached by injection of vitamin C (ascorbic acid), but there was no effect on normal pigment, and so "hopes of solving the color problem by means of ascorbic acid were disappointing."

In conclusion: Although less than one hundred pages in length, and little concerned with detailed reference to the work of others, this book is packed sentence by sentence with potent and stimulating catalytic information and suggestions.

TECHNISCHE ADSORPTIONSTOFFE IN DER KONTAKTKATALYSE. *By* Franz Krczil

Akademische Verlagsgesellschaft m.b.H., Leipzig, 1937, xxxi + 726 pp.

Reviewed by Wilbur A. Lazier and C. G. Wortz

The appearance of a volume devoted exclusively to the practice of contact catalysis as a laboratory and industrial art presents a welcome variation from the host of books recently published on various theoretical aspects of catalysis. Dr. Krczil's contribution is a book devoid of speculation but packed with factual material gleaned from patents and technical journal articles. The central idea, that adsorptive materials generally exhibit catalytic properties as well, appears to detract somewhat from the book's value as a contribution to the catalytic art, for it has apparently influenced the author in numerous cases to place improper emphasis on catalysts of lesser technical importance and in other cases to omit entirely valuable catalyst compositions which Dr. Krczil probably considers to be non-adsorptive. Nevertheless, the chosen treatment of the subject impresses the reader with the large number of important contact masses that either consist of or contain materials having well-defined adsorptive properties.

Part I appropriately deals with methods for the preparation of adsorptive (catalytic) materials. These begin with activated carbons in various forms, run through the list of natural and synthetic clays, earths, and oxides, and conclude with compound, supported, and miscellaneous contact masses. Detailed directions are the rule rather than the exception, and since these are generally quoted without change from the original sources, the author thereby assumes no responsibility for the success of these procedures. For important items such as silica gel and nickel-on-kieselguhr, the reader is dependent upon his own intuition to make a happy selection among several alternative procedures.

Part II covers the use of adsorptive materials in inorganic processes and thereby closes a conspicuous gap in the literature of contact catalysis. This part contains much suggestive material that is difficult to find elsewhere, such as the catalyzed reactions of inorganic compounds of nitrogen, phosphorus, and sulfur.

There is perhaps less justification for the final Part III devoted to the catalytic reactions of organic compounds, for an attempt to treat this huge subject adequately in the remaining space merely emphasizes the amazing scope of the subject and the futility of attempting to cover the whole field of catalysts and catalytic reactions in a single volume. This section differs from most of the earlier works on organic catalysis in containing quotations from the original sources of detailed conditions for carrying out typical experiments. It also includes hitherto uncollected material on several newly developed syntheses, such as the preparation of carboxylic acids from carbon monoxide and alcohols.

While tending to be encyclopedic, the book falls quite short of this objective. The treatment of patents is profuse but nevertheless far from complete. The German patent literature appears to be covered better than that of other countries. As regards the United States, some rather unfortunate omissions of important catalyst patents have been noted.

The most serious shortcoming of the book is its apparent lack of critical viewpoint. In deriving useful information from patent sources, considerable judicious selection is necessary. It is disappointing to find that responsibility for this must still rest on the reader. In spite of this defect, the book will be found valuable as a source of useful and stimulating information, particularly for those engaged in the formulation of contact catalysts for industrial purposes.

REACTIONS OF HYDROGEN WITH ORGANIC COMPOUNDS OVER COPPER-CHROMIUM OXIDE AND NICKEL CATALYSTS. *By* HOMER ADKINS

The University of Wisconsin Press, Madison, 1937, 178 pp.

Reviewed by E. C. Williams and O. Beeck

This book is very unusual. It is " an attempt to correlate and summarize, and to indicate the significance of experimental results from the (author's) laboratory in the development of high-pressure hydrogenation as a tool for use in synthetic organic chemistry." Thus the book deals exclusively with the author's and his pupils' work and is further " practically limited to the reaction of hydrogen at 100 to 400 atmospheres and 25° to 260° over nickel or copper-chromium oxide catalysts with quantities of 1 g. to 1 kg. of typical organic compound."

In spite of these and other limitations (for instance, no mention is made of continuous flow methods), the author has not only succeeded admirably in his objective but has created a handbook for those who wish information on a simple and safe high-pressure technique, and a textbook for the advanced student, who may safely embark on high-pressure hydrogenation experiments with Professor Adkins' book as his sole guide. In fact, details of the construction of reaction vessels and the operation of the equipment as used at the University of Wisconsin are so well worked out that one scarcely misses descriptions of other types of apparatus. Methods of preparation of catalysts are given in great detail. Theories and mechanisms of catalysis are given only a brief mention; the physical and physicochemical aspects are almost entirely omitted.

The chapter headings are: " Catalysis, Hydrogen Pressure, and Solvents "; " Apparatus and Procedure "; " Reactions with Hydrogen "; " Selective Hydrogenation and Hydrogenations." The larger part of the book is taken up by the chapter: " Reactions with Hydrogen." It is divided according to functional groups and includes

Hydrogenation of:
- (1) Carbon to carbon double bonds.
- (2) Carbonyls to carbinols.
- (3) Imines to amines.

Hydrogenation of: (*Continued*)
(4) Cyanides to amines.
(5) Benzenoid to cyclohexanoid compounds.
(6) Furanoid to tetrahydrofuranoid compounds.
(7) Pyridinoid to piperidinoid compounds.
(8) Pyrroloid to pyrrolidinoid compounds.
Hydrogenolysis of carbon to metal bonds in:
(9) Lead, zinc, and magnesium alkyl and aryls.
Hydrogenolysis of carbon to oxygen bonds in:
(10) Alcohols and glycols.
(11) Ethers.
(12) Acetals.
(13) Esters and lactones.
(14) Anhydrides.
(15) Imides.
Hydrogenolysis of carbon to carbon bonds in:
(16) Hydrocarbons.
(17) Alcohols.
(18) Glycols.
(19) 1, 3-Diketones.
Hydrogenation accompanied by hydrogenolysis of nitrogen to oxygen bonds in:
(20) Oximes.
(21) Nitroso compounds.
(22) Nitro compounds.
Hydrogenation accompanied by hydrogenolysis of nitrogen to nitrogen bonds in:
(23) Azo (or hydrazo) compounds, including pyrazolones.
Hydrogenation accompanied by hydrogenolysis of carbon to nitrogen bonds in:
(24) Diamines.
(25) Amino cyanides.
(26) Amino alcohols.
(27) Hydroamides.
(28) Amino amides.
Hydrogenation accompanied by hydrogenolysis of carbon to oxygen bonds in:
(29) Esters to alcohols or hydrocarbons.
(30) Amides and imides to amines.

In all these cases the most favorable reaction conditions are given, and yields of product, side reactions, and the like are discussed. The relatively short chapter on selective hydrogenation and hydrogenolysis not only deals with control of reactions but also includes a discussion on the relationship between structure and ease of reaction.

The material is well presented and organized. The index is unusually detailed. There are 44 references to work of the author and his coworkers and 19 references to other publications. Appearance and printing of the book are excellent; an invaluable book to have at hand in the research or industrial laboratory.

THE RETARDATION OF CHEMICAL REACTIONS

By Kenneth C. Bailey

Longmans, Green & Company, New York, 1937, 479 pp.

Reviewed by E. C. Williams and M. W. Tamele

The present knowledge concerning negative catalysis consists of a mass of observations and data, in many instances unrelated and of obscure significance. A large part of such information is difficult to trace since many observations of this nature have been incidental to other investigations and are recorded in the chemical literature under titles which do not suggest any connection with the subject. Occasional references to retardation, without pretense at completeness, are to be found in numerous books dealing with catalysis, but systematic collections are available only for a few fields of retardation (e.g., autoxidation, corrosion).

Bailey's book is the first to attempt a complete picture of the retardation of chemical reactions within the limits imposed by the size of a single volume. It deals with many subjects which have not hitherto been treated systematically but specifically omits some of the better-known examples of retardation which, because of their special interest, have been dealt with adequately elsewhere.

The author has arranged the chapters strictly according to the types of reactions involved and has included with each chapter a discussion of the theories concerned. This arrangement does not suggest that there may be a common theoretical background to a number of the subjects presented, although the author does not hesitate to make justifiable suggestions and generalizations at various points in the text. It is a pity that in a book so rich in valuable information an introductory chapter could not have been included in which, by a discussion of the fundamentals involved, a general impression of the entire field is presented to prepare the reader's mind for a broader consideration of what is to follow.

More than half the book is devoted to an excellent review of the inhibition of oxidation. The discussion is not limited to atmospheric oxidation, or " autoxidation," but includes other equally interesting cases of inhibition of oxidation, such as the oxidation of phosphorus, hydrogen, and particularly the oxidation of hydrocarbons in the gaseous phase. In the treatment of the oxidation of the hydrocarbons in the liquid phase, only the more fundamental contributions have been included and much work published recently on the inhibition of oxidation and gum formation in such complex systems as gasolines and oil has been omitted. It is surprising to see how little fundamental work has been done in spite of the great commercial interest attached to this subject.

The chapter on antiknock agents points out the deficiencies in our existing knowledge of knock suppression. Since the publication of the book, however, progress has been made in the direction indicated by the author: " Whereas in many other parts of the oxidation field the chain theory has been seized upon as an explanation of everything, and often used rather uncritically, in the study of anti-detonants less attention has been paid to it than it merits."

Other subjects of both scientific and commercial interest include fire fighting, the protection of rubber, setting of cement, stabilization of hydrogen peroxide. In all cases, a praiseworthy effort has been made to strip the subject of non-essentials and to present the subject scientifically. A number of miscellaneous reactions of organic chemistry have been included and the available information presented both from the historical viewpoint and in the light of modern ideas.

The inclusion of subjects treated elsewhere more exhaustively (e.g., prevention of corrosion) serves a useful purpose in calling attention to possible fundamental connections with other fields of retardation. In general the book provides ample evidence that no single general explanation or theory of retardation of chemical reactions can be expected. While in some instances the breaking of reaction chains is the most likely mechanism of retardation, in other cases it may be the deactivation of activated molecules, or the incapacitation of reaction nuclei. Adsorption at interfaces, the formation of protective layers, and exclusion of light or radiation may account for a number of other examples of retardation.

The book is well supplemented by an excellent bibliography of over 1600 references which is of particular value since it could not be duplicated by any normal search of the available chemical abstracts. It must represent painstaking and discriminating reading by the author of a large volume of literature. Workers in many fields will remain indebted to the author for a valuable treatise containing both an extensive assemblage of facts and an unusually readable critical discussion of the subject.

KATALYTISCHE UMSETZUNGEN IN HOMOGENEN UND ENZYMATISCHEN SYSTEMEN. *By* DR. W. FRANKENBURGER

Akademische Verlagsgesellschaft, Leipzig, 1937, 444 pp. and 22 diagrams

Reviewed by Hugh S. Taylor

Dr. Frankenburger, who is well known for his fundamental contributions in the field of heterogeneous catalysis, elected, in the present book, probably for commercial reasons, to discuss catalytic reactions in homogeneous systems and the heterogeneous reactions promoted by enzymes. The book therefore does not contain much that many readers would have welcomed from his pen on the phases of contact catalysis, with which his own work has been intimately concerned.

After an historical introduction (11 pages) is a chapter on chemical dynamics, in which the concepts of reaction inertia, order of reaction velocity, elementary and complex reactions, activation, and temperature coefficients are set forth. There follows an exposition of the current problem of calculation of reaction velocity from potential energy surfaces, and the position of catalytic processes in the light of these newer theories. This resolves itself into the resolution of a reaction path into a series of alternative paths, with lower energies of activation than that of the uncatalyzed process, exploration of the detailed steps in such alternative paths, and the mechanisms whereby the lower energies of activation are achieved. This section concludes with a systematization of catalytic processes.

The treatment of homogeneous catalytic reactions is divided into two sections: (*a*) in gaseous systems and (*b*) in liquid media. In the former the theories of intermediate compound formation, of moisture catalysis, and especially of chain reactions are developed. In respect to this last, photochemical, thermal, and moisture chain processes are discussed, with 10 pages on combustion phenomena. In a final section on true homogeneous gas catalysis some of the work on iodine catalysis described has been modified by new work appearing approximately simultaneously with the book. There is a stimulating section on alternative modes of accelerating, by foreign gases, the unimolecular decompositions of gaseous molecules.

In the section on catalysis in liquid media, acid-base catalysis naturally comes first. The historical position of H^+ and OH^- catalysis is unfolded, the gradual dethronement of these and the development of the modern Brönsted-Lowry prototropy concepts. The Polanyi-Ogg exposition of the potential energies of systems such as $I^- + CH_3Cl$ is reproduced in connection with the problem of the influence of ions on activation energy. The applicability of the intermediate compound concepts, as well as the influence of the medium and its relation to molecular properties are treated. Next there are sections on organic catalyses, involving, for example, aluminum chloride and sulfonation. Forty pages on oxidation processes in liquid media discuss chain processes and induced oxidation, as well as specific partial oxidations and autoxidation phenomena. The final section in this division deals with organic catalysts in a variety of reactions in liquid media.

The concluding 100 pages of text are devoted to a survey of microheterogeneous catalysis, more specifically the enzyme catalysts. Their general properties, their classification, detailed discussions of the separate classes, and their reactions are set forth in such a form that the reader can obtain a modern survey of a whole field which is normally covered only in the specialized textbooks in several volumes. Towards the close of the section the analogies with contact catalysis are emphasized, and the data of colloidal catalysts summarized. A 12-page name index and a 25-page subject index complete the book.

The student of these sections of the subject of catalysis can find here in one volume the most extensive single presentation of the subject in its modern aspects. The book supplements the several textbooks recently produced in the field of heterogeneous (contact) catalysis. It is much more detailed than the book by Schwab, who includes the material of the present book in less than one half the compass. It is excellently documented with literature references and serves therefore as a most useful source for orientation of student and research worker in this field.

THE MECHANISM OF CONTACT CATALYSIS.

By R. H. GRIFFITH

Oxford University Press, London, 1936, 208 pp. and 90 diagrams

Reviewed by P. H. Emmett

In the introduction the author makes it clear that his book has for its primary object the consideration of the progress that has been made in the last ten or fifteen years in elucidating the mechanism by which catalytic reactions operate. In the reviewer's opinion the author has succeeded in presenting the essential elements in the modern concepts of catalytic surface reactions in a manner that is interesting and readily understood. At the same time frequent suggestions have been incorporated as to possible directions in which new investigations might be pushed and new information obtained.

The subject matter is treated under eight headings, the various chapters dealing respectively with experimental methods, adsorption, promoters and carriers, poisoning and retardation, examination of the catalyst surface, the mechanism of catalysis, and the development of catalysts. The book is profusely illustrated with curves presenting experimental results pertinent to the discussion and diagrams showing types of experimental apparatus involved in various aspects of catalytic mechanism studies. Such illustrations and descriptions of the apparatus, technique, and procedures used in studying adsorption and reaction kinetics will be especially welcome to students of catalysis who have not yet acquired extended familiarity with experimental details of catalytic work.

The book as a whole reflects considerable care on the part of the author and a great deal of thought in correlating a large number of experiments. As is to be expected in such an undertaking, a few errors will occasionally creep in. A detailed presentation of the nature and import of these errors is hardly within the scope of this review. It will perhaps suffice to point out that errors were noted on pages 38, 111, 160, and 189 in discussions relating to iron synthetic ammonia catalysts.

Dr. Griffith's book is not and does not pretend to be an exhaustive summary of all catalytic work that has been done in recent years. It does, however, summarize the essence of the various theoretical concepts that have arisen as a result of the large amount of experimental work and includes sufficient literature references and experimental data to illustrate the various concepts discussed. The book, therefore, appears to constitute a valuable compilation of ideas relating to the theory of catalytic reactions and, as such, should be welcomed by students, teachers, and research workers interested in the fundamentals of contact catalysis.

UBER KATALYSE UND KATALYSATOREN IN CHEMIE UND BIOLOGIE. *By* ALWIN MITTASCH

Julius Springer, Berlin, 1936, 65 pp.

*Reviewed by Robert E. Burk**

In this little book an interesting picture is drawn of biology as a complicated " drama " of catalytic reactions. Mittasch, one of the most experienced catalytic chemists in the world, attaches large importance to the work of Berzelius, who was the first to recognize the part played by catalysts in biology, and on very scanty evidence.

Catalysts are important mainly in the organic world, where they may be effective in amounts less than 0.00001 mg./cc. Specificity of catalysts reaches a maximum in biological systems when enzymes may destroy one stereoisomer and not the other. Specificity, Mittasch suggests, is not related to chemical structure in an obvious way. The importance of autocatalysts in growth processes is brought out.

Industrial experience with multi-component catalysts and catalyst carriers is reviewed, and the lack of a guiding theory pointed out. Poisons are mentioned and their use in repressing objectionable reactions is explained. Activators, carriers, and poisons must have their counterpart in biocatalysts, and this is already recognized in enzymes. One gram atom of iron (as ion) converts in one second 0.00001 mole of H_2O_2, as free haemin 0.01 mole, as peroxydase 10,000 moles, as catalase 100,000 moles.

The importance of the physical structure of catalysts is emphasized, which factor must again be of special importance in biological systems. Chemical and physical factors are not sharply distinguished.

Mittasch considers the intermediate compound theory the most satisfactory for ordinary catalysis and for enzyme catalysis. However, he hedges on this sufficiently to include various forms of adsorption complexes, chain theories, active centers — in fact most of the factors which make a rigid intermediate compound theory of catalysis inadequate. On page 26 it is represented that rubber accelerators form intermediate compounds with the sulfur. He frets considerably over the precise definition of catalysis, which is not a very profitable thing to do, as the reviewer sees it.

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* Contribution from the Graduate School, Western Reserve University.

The author goes to some pains to argue that the myriad physiological chemical reactions, both normal and pathological, are catalytically controlled. Since temperature and concentration do not vary greatly, the average chemist would grant him this at the outset, though he might follow him with less assurance into catalytic explanations of inheritance, instinct, and volition. To the reviewer, the most important thought in the book was that each phenomenon in the vast experience of chemists in the field of catalysis should have its counterpart in biochemistry, and one can already go far in explaining the general lines of biocatalytic action from this point of view.

It is an admirable precedent for the director of a great industrial research organization to devote some of his later life to writing books, so that the world may benefit from the extraordinary range of experience which such persons must possess.

BERZELIUS UND DIE KATALYSE. *By* ALWIN MITTASCH.

Akademische Verlagsgesellschaft, Leipzig, 1935, 23 pp.

*Reviewed by Robert E. Burk**

Mittasch emphasizes the importance and tries to discover the origin of Berzelius' generalization that living plants and animals manifest the action of thousands of catalysts. He prefers catalytic power to the "vital force" of Liebig. Berzelius had a very definite concept of associating catalysts with secreting organs. Mittasch traces the important catalytic discoveries of the few years preceding Berzelius' generalization.

This insight of Berzelius (in general terms) in the field of biocatalysis is rather remarkable. This little book, however, is valuable mainly as a diversion. It is a rather intimate view of the thought of Berzelius' day on the general question of catalysis.

Until quite recently, the platitude was repeated that "catalysts are a mask with which to cover up ignorance." The reviewer was interested to learn that Schönbein made this statement in 1838.

* Contribution from the Graduate School, Western Reserve University.

THE CATALYTIC ACTION OF SURFACES. *By* J. E. NYROP

Levin and Munksgaard, Morregade 6, Copenhagen, 1937, 2nd Edition,
103 pp.

Reviewed by P. H. Emmett and Edward Teller

The thesis that the author attempts to develop and support by experimental and theoretical arguments is stated in these two postulates:

> Postulate A: In a chemical reaction furthered considerably by the presence of a surface, the surface is at the temperature in question able to ionize those molecules among the reactants most difficult to ionize and the surface will cause a strong adsorption as ions formed are attracted by the surface.
>
> Postulate B: A surface able to ionize molecules of a gas or liquid and hence able to yield a strong adsorption produces an increased adsorption when the molecules are substituted by others having a lower ionization potential assuming that all other conditions are the same.

The subject matter is subdivided into eight chapters as follows: I, " Catalytic Processes "; II, " Adsorption and Solution "; III, " Activated Adsorption "; IV, " Adsorption and Catalysis "; V, " The Catalytic Succession of Surfaces "; VI, " Electronic Bombardment Reactions "; VII, " The Metals "; and VIII, " The Catalytic Effect of Surfaces." Eighty-three literature referenees are cited and a considerable additional amount of catalytic work is summarized without references.

The contents of the book may be divided into two types of material. The first type includes quotations from and discussion of the literature on catalysis. This portion is marred by many ambiguous, misleading, and in some cases incorrect statements that have crept into the text apparently through a careless or uncritical presentation and interpretation of published work. In the reviewers' opinions these defects tend to make the book unattractive to readers familiar with catalysis and decidedly misleading at times to those not acquainted with the subject.

The second type of material in the book comprises the author's mathematical derivations, deductions, and formulations in support of Postulates A and B. The chapters devoted to this part of the work are in many instances so incompletely explained as to be decidedly unconvincing. Chapter II, for example, dealing with the formulation of adsorption equations in terms of the ionization concept is not sufficiently clear to enable the reviewers to appraise the derivations critically. In other instances conceptual errors appear to be involved in the attempted theoretical justification of the author's thesis. Chapter VII, for example, appears to be based upon a number of mistaken ideas. In this chapter the author takes upon himself the task of supporting by modern theoretical physics his contention that iron and nickel catalysts are able to ionize impinging molecules whose ionization potentials are as high as 17 or 18 volts and produce adsorbed ions on the surfaces of the metals. The most fundamental mistake in the chapter is, apparently, the author's attempt to make use of the kinetic energy of the free electrons of the metal in effecting the ionization of the oncoming atom or molecule. This is in principle like utilizing the K-electrons in lead to ionize atoms which are reacting with lead. There are, of course, low energy levels in a metal, and transitions into them would make a great amount of energy available. But all these levels are occupied, and thus the utilization of the Sommerfeld energy E is restricted to small energy exchanges that are of the order of kT. Accordingly, the greater part of the Sommerfeld energy E that, according to Nyrop, is usable for effecting ionization of atoms or molecules approaching the surface can in reality not be so used. Therefore, what appears to be the author's main quantitative argument in favor of the ionic explanation of catalysis must, on the basis of modern concepts of the theory of metals, be definitely rejected. It does not seem worth while to discuss the chapters in greater detail in the present review since the principal thesis is clearly not substantiated.

The reviewers recognize the desirability of new points of view in catalysis and accord the author due credit for his endeavor to shed new light on the subject. Succinctly stated, their criticism is directed primarily toward the experimental correlations and theoretical arguments by which the author attempts to establish the existence of extensive ionization of gas on the surface of catalysts and toward his attempts to demonstrate that ionization on the surface constitutes the principal mechanism through which catalytic surface reactions occur. Some of the ideas contained may well merit further study and consideration.

CATALYSIS FROM THE STANDPOINT OF CHEMICAL KINETICS. *By* GEORG-MARIA SCHWAB

Translated by HUGH S. TAYLOR and R. SPENCE
D. Van Nostrand Company, Inc., New York, 1937, 382 pp.

*Reviewed by Louis S. Kassel**

Chemical kinetics was directed by Arrhenius toward an ambitious goal. For fifty years now it has attempted to understand the basic nature of chemical change, to follow the meandering of every atom and the leaps of every electron and even to comprehend the reasons for these motions. It is in this sense that the term kinetics is used by Schwab.

The present reviewer is a scarred and disillusioned veteran of such attempts. He can see no real advance after half a century. Little parties of intrepid adventurers have pushed far into the wilderness, and established outposts beneath many various banners. These banners have proclaimed that reaction rates are related to heat changes, or to free energy changes. They have proclaimed that reactions are inhibited by drying. They have exalted the association complex, and at other times the free radical. Free radicals have had three free valences, then two, and currently have only one. Other banners have been dotted with ions, reticulated with chains, or covered with walls. But always in the end a luxuriant growth of experiments has overcome the hardiest theorists and left of their venture only a little Chichen-Itza in an endless jungle.

The basic method of chemical kinetics is very simple. It involves three steps. The first of these is the quantitative determination of the products produced from various reactants subjected to known conditions of temperature and time, and the discovery of analytical functions to express the rates of change in terms of concentrations and temperature. The second step is the construction of mechanisms and calculation of their consequences. In the ideal, this activity is carried out formally, and for all imaginable mechanisms. To give a single example:

$$\begin{aligned} A + B &= C + D \quad k_1 \\ B + D &= E + F \quad k_2 \\ B + E &= D + G \quad k_3 \\ E + E &= A + H \quad k_4 \\ C + C &= A + L \quad k_5 \end{aligned}$$

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* Contribution from the Universal Oil Products Co., Chicago, Ill.

These equations will lead to various consequences with various assumptions as to the relative values of the constants. When k_2 and k_3 are large enough, the predominant reaction becomes a chain with the final result:

$$2B = F + G$$

and with the rate:

$$-\frac{d(B)}{dt} = k_3 \sqrt{\frac{2k_1}{k_4}} (A)^{1/2}(B)^{3/2}$$

The third step in chemical kinetics is to determine correspondences between the results of the first two steps. Thus it is found experimentally that the rate of the chlorine-catalyzed decomposition of ozone is:

$$-\frac{d(O_3)}{dt} = k(Cl_2)^{1/2}(O_3)^{3/2}$$

(it may be mentioned in passing that the exponent on (O_3) is misprinted on p. 48) and it is clear that the foregoing general mechanism can be applied by putting

$A = Cl_2$ $D = ClO_2$ $G = 2O_2$
$B = O_3$ $E = ClO_3$ $H = 3O_2$
$C = ClO$ $F = O_2$ $L = O_2$

It remains only to determine that the requisite assumptions can be justified (actually they cannot, since ClO_3 is too sluggish to be considered a transitory intermediate) and that no other imaginable mechanism will give the same result. The mechanism of this reaction will then be known until further experimental work is done.

In the German edition of 1931, Dr. Schwab presented a thoroughly competent picture of the condition of catalytic kinetics at that time. Professor Taylor and Dr. Spence have made heroic efforts to bring the subject up to date (as of 1937). This might have been more easily done had they been willing to cut out parts of the original text based on such ideas as the influence of water in the hydrogen-chlorine reaction, which the present generation of experimentalists cannot find, and to rewrite portions such as that on adsorption, where the additions become an appendage that wags the chapter. In spite of these handicaps, the translation achieves a picture of the subject which this reviewer considers more satisfactory than that of the original edition.

The principal subjects treated, homogeneous catalysis in gases (50 pages), homogeneous catalysis in solution (110 pages), and gas-solid catalysis (150 pages) naturally prove to be almost unconnected fields.

It should be considered definitely commendable that no artificial attempt is made to establish relations where none are needed, but a more captious critic might ask why the three parts should be bound together. The scope and treatment have already been indicated. The industrial chemist, therefore, will find here stimulating reading for the evening hours, but must search elsewhere for help in his daily struggles with carriers, poisons, physical disintegration, declining activity, and similar problems. Superhuman intelligence could perhaps deduce truth from the available imperfect experiments, and practicing kineticists might draw correct conclusions from perfect data. Since neither combination will exist in the foreseeable future, it would seem that practical catalysis must continue to limp along with little help from limping theory.

CATALYTIC REACTIONS AT HIGH PRESSURES AND TEMPERATURES. *By* V. N. IPATIEFF

The Macmillan Company, New York, 1936, 786 pp.

Reviewed by L. F. Marek *

As the author points out in his introduction and as the reader will discover after a few moments of reading, this book is an autobiographical account of the work that Dr. Ipatieff has done in the field of high temperature-high pressure catalytic reactions. This work, much of which was accomplished in the old Russia, has already extended over a third of a century of time; it is still in progress in this country at a pace far in excess of that during the early years. The publications of this man will be encountered by anyone studying the literature in this or in related fields, but only too frequently the articles have appeared in journals that are difficult of access to many readers, and much material has not appeared in journals at all. It is indeed fortunate that it has been possible for all this material to be gathered together, correlated, and interpreted by the author of it himself.

The book fulfils its purpose, but in doing so creates for itself certain shortcomings. Thus, the reader who is not familiar with the literature of the field may be misled in some instances, since Ipatieff is inclined to refer to published work other than his own only when it serves to illustrate his point. Furthermore, in the eyes of some readers the portions of the book dealing with the early work are marred by efforts to establish priority and by repeated argument in support of a theory or point. However, these shortcomings may be looked upon as efforts to present the correct interpretation by one who believes strongly that his position is tenable.

A review of such a book must necessarily consider its author. To place the author in point of scientific history is not difficult since he has lived and worked during a period with which most of his present readers are acquainted at first hand.

It was during this period, which was to see the widespread appreciation for and adaptation of catalytic effects, that he worked in order to find out how, and where, and why catalysts did the things they did. It was before and during the industrial utilization of pressures that have

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* Arthur D. Little, Inc., Cambridge, Mass.

reached a commonplace thousand atmospheres that he explored, with many experimental difficulties, the possible advantages and novelties of high pressures in organic reactions. In many phases he pioneered in thought, method, and action, and by this pioneering spirit and unflagging activity he has contributed richly to the world's knowledge. Ipatieff has been distinctly an experimentalist in his work.

The book is narrative in style and much of it is written in the first person. It contains a few illustrations and considerable tabular material. The book is colored by Ipatieff's experimentalist attitude and is largely built around the results of laboratory investigations. There is little mathematical exposition of theories in the sense that some of the modern thermodynamicians or kineticists treat of chemical processes. As a result, the book carries a great deal of material in the form of experimental data, more in the manner of a technical paper than of a book which is best when interpretive. However, since some of this material is relatively inaccessible and since the book collects into a convenient form the material from many papers, this practice may be found to be an asset rather than a liability.

A recitation of the chapters in the book gives an impression of the range of work covered: dehydrogenation of alcohols, dehydration of alcohols, decomposition of acids, catalytic isomerization, hydrogenation, promoter action in catalysts, hydrogenation of aromatic amines, destructive hydrogenation of organic compounds, catalytic condensation, theory of catalysis, polymerization, catalytic alkylation, destructive alkylation, and gasoline by polymerization. Thus, the book begins with an account of the early study of the effect of catalysts on the thermal decomposition of aliphatic alcohols, leads up to a discussion of the author's theories on catalytic action, and ends with a touch of economic modernism by discussing the formation of high antiknock gasoline from the catalytic polymerization of gaseous olefinic hydrocarbons.

The pioneer workers in the field of high pressure-high temperature catalytic reactions had to labor under many difficulties. This should not be lost sight of in present-day interpretation of the work accomplished during the early years of this century. Workers like Ipatieff led the way in showing empirically that for many reactions, particularly the simpler ones, a catalyst is a means for speeding up the approach to equilibrium in a reaction and that, therefore, an easy way to study catalysts and their effects would be to study the decomposition of the substances it was desired to synthesize. Thus, by a choice of a catalyst which gave a high rate of decomposition of the desired substance to the chosen reactant materials a means could be provided for the subsequent high rate of synthesis by proper choice of operating conditions. Furthermore, by conducting many experiments at elevated pressures Ipatieff helped to show the feasibility of using high pressures and indicated the beneficent results to be expected.

Ipatieff's theories of catalysis, as developed from his many empirical studies and as applied to a variety of reaction types, are given a chapter of discussion. Ipatieff's theory of catalysis is based on the chemical action of catalysts and assumes the formation of intermediate compounds which decompose under certain conditions to form the reaction product and regenerate the catalyst. In the case of catalytic hydrogenation-dehydrogenation reactions, water is considered to be a significant factor by serving as a reaction intermediate between the catalyst and the main reaction. Much of his work was directed toward finding the chemical basis for a catalytic activity which not only presented a selective action but which also reduced the temperature needed for reaction to proceed. The difficulties surrounding this approach to a study of catalysts have been generally recognized. It has been possible, however, on the basis of experimental evidence to classify such catalytic reactions as dehydration, polymerization, alkylation, and isomerization as belonging definitely to the intermediate-forming type. It has not been possible so to classify many other reactions, owing largely to the paucity of experimental evidence for such chemical mechanism. Certain reactions, such as those of a photocatalytic nature, are recognized as physical in nature.

The necessity for the addition of heat energy to a reaction in order for a catalyst to exhibit activity has led Ipatieff to consider catalysts as transformers of heat energy into chemical activity. Although he reviews and takes cognizance of work done on the physical phenomena at catalyst surfaces, Ipatieff points out that an accounting for catalytic activity or a prediction of catalytic direction cannot be based on present knowledge of such physical phenomena; and in keeping with his theory that catalysis is a type of chemical phenomenon insists that catalysis should be interpreted largely through consideration of the chemical processes that occur.

In the field of hydrocarbon reactions Ipatieff has made many contributions and he is at present most actively engaged in this field of research. The chapter on polymerization gives considerable data and many results from the recent investigations on polymerization of low-molecular-weight olefins to liquid hydrocarbons of gasoline boiling range in the presence of inorganic acid-type catalysts (such as the "solid phosphoric acid" catalyst) and at mild temperatures and pressures. The use of the intermediate ester hypothesis of catalyst action is demonstrated in the choice of catalytic material and in the results obtained.

The book includes an appendix devoted to an exposition of the catalytic polymerization of refinery cracking gases to gasoline, and giving the results of the recent work of Ipatieff and his associates in this field.

The chapter on alkylation is comprised principally of the results from recent work on the alkylation of paraffinic, naphthenic, and aromatic hydrocarbons and of phenols with olefins in the presence of such catalysts as the metal halides and certain inorganic acids. The experimental conditions are generally given and the results are recorded in numerous tables with interpretive discussions regarding mechanisms and the effects of alternative catalysts.

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