REACTIONS OF ORGANIC MOLECULES IN THE GASEOUS STATE

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The study of organic reactions from the physicochemical standpoint has been carried out intensively only during the past few years. The work done prior to this time resulted in the accumulation of a great many data concerning the products obtained in the pyrogenic decomposition of organic compounds, so that we now have a detailed knowledge of the products of organic decompositions (1), although the fundamental laws governing these processes are very incompletely known and the mechanisms of the reactions are still quite uncertain. A number of empirical rules have been evolved as a result of experience, and these, although of limited applicability, are useful in codifying our knowledge, and in many cases enable us to predict the method of decomposition. More general attempts, such as Peytral's rule (2) of least molecular deformation, which states that when a compound decomposes the products are those which have bonds most nearly identical with the original substance, are not satisfactory.

Perhaps the most fundamental information that we require in studying the decomposition of organic molecules, is the strength of the different carbon-carbon and carbon-hydrogen bonds. The earlier work of Fajans (3) and others appeared to show that the carbon-hydrogen bond has a strength of approximately 93,000 cal. and the carbon-carbon bond a strength of approximately 65,000 cal. These figures were obtained substantially by assuming that the energy required to remove one hydrogen atom from a methane molecule is one-quarter of that required to remove all four hydrogen atoms. This assumption, together with some uncertainty as to the heat of vaporization of carbon (4), makes these figures very problematical. Recent calculations, based partly on spectral data (5) and partly on thermochemical data, seem to show that the strengths of the carbon-carbon and carbon-hydrogen bonds are much greater than those obtained by Fajans, and indeed Mecke mentions 110–115 kg-cal. for both values. While it is true that results obtained from spectral data are far more accurate than those obtained by any other method, the interpretation of such data is not always easy. A correction must be applied to allow for the energy of excitation of fragments formed in the photochemical dissociation and this frequently introduces a large element of uncertainty into the calculated strengths of the bonds.

Differentiation has been observed in the spectra of saturated hydrocarbons (6) and this may be used as a basis for obtaining values for the binding forces and heats of dissociation. The results obtained indicate a 3.2 per cent and 2.4 per cent lowering in the binding forces of tertiary and secondary hydrogen atoms respectively as compared with that of primary hydrogen atoms; the relative heats of dissociation of the hydrogen atoms would be in about the same proportion.

It seems clear now that a great number of organic compounds decompose homogeneously and according to a unimolecular law in the gaseous state. The unimolecular decomposition may consist in breaking a bond in the molecule, with the formation of two fragments, in which case the heat of activation will give us some information regarding the strength of the bond. The measured heats of activation for the most stable organic compounds are about 65,000 cal., and if we add to this 10,000–15,000 cal. to account for the average energy of the molecules at the temperature of decomposition, we obtain 80,000 cal. as the average total energy of the activated molecules. This is the maximum strength permissible for the weakest bond if the molecule is to undergo a primary dissociation into two fragments. Of course, the results of recent spectral data, if correct, preclude such primary decomposition into free radicals. On the other hand, organic chemists have for a long time used the concept of free radicals in explaining organic reactions and there is evidence accumulating that some reactions, at any rate, occur through a chain mechanism initiated by a free radical. This question of the method of the primary decomposition is of course fundamental and will be discussed in greater detail later in the paper.

The study of certain simple reactions helps to throw light on this question as well as on others relating to the mechanism of organic decompositions. Bonhoeffer and Harteck (7) prepared atomic hydrogen by means of a discharge tube and examined its reaction, when present in large excess, with hydrocarbons at pressures of about 1 mm. Of all the hydrocarbons used, methane alone showed itself completely inactive, whereas such substances as ethane, pentane, ethylene, acetylene, and benzene all gave an immediate reaction accompanied by the emission of a luminescence similar in color and spectroscopic content to the center of a Bunsen flame. Near the point of mixing of the hydrocarbons and the atomic hydrogen, a blue band of light appeared which gradually changed into green. The spectrum of the blue band showed the Swann bands, which are supposed to be characteristic of the C_2 radical. Since the CH and C_2 spectra were always emitted we can assume that with all higher hydrocarbons some reaction is taking place in which hydrogen atoms are stripped from the hydrocarbons and the chain is broken. This cannot be a thermal effect since the temperature in the illuminated part of the tube is probably not over 300°C. and is certainly below 600°C. The authors represent the dehydrogenation reaction by the equation:

$$C_nH_m + H \longrightarrow C_nH_{m-1} + H_2$$

which seems to be followed by all hydrocarbons except methane, and therefore suggests a distinct difference in the binding forces between carbon and hydrogen in methane and in the higher hydrocarbons. In ethane, for instance, there must be at least one carbon-hydrogen bond whose strength is less than 100 kg-cal.

The splitting action of the hydrogen atoms is explained by assuming that we can have direct substitution of a hydrogen atom for a hydrocarbon residue; for example, ethane might react with a hydrogen atom according to the equation,

$$C_2H_6 + H \longrightarrow CH_3 + CH_4.$$

The authors think that this is the most probable reaction, although they consider the possibility that two hydrogen atoms may recombine on collision with a hydrocarbon molecule and that their heat of combination could then be used to break the chain; however, this second reaction would probably not proceed fast enough to account for the observed results.

In the decomposition of the hydrocarbons, methane was always present in very considerable quantities, and was accompanied by ethane, ethylene, and acetylene. The atomic hydrogen must therefore have a hydrogenating action in addition to its other effects.

v. Hartel and Polanyi (8) have investigated some simple examples of bimolecular reactions between sodium vapor and organic halogen compounds, in which a sodium atom combines with a halogen atom and leaves a free radical. In previously published papers of Polanyi and coworkers (9) a large number of decompositions have been reported in which free atoms react at each collision with a molecule, provided only the reaction is exothermic. If methyl iodide is brought into contact with sodium vapor in a highly dilute flame there is an immediate reaction; therefore the heat of activation of this reaction must be very small. On the other hand, when various organic halogen compounds were substituted for methyl iodide, it was found that more than one collision was necessary in order to bring about reaction at 300°C. A quantitative determination was made of the velocity constants in the series CH_3I, CH_3Br, CH_3Cl and CH_3F at 240°C. It was found that whereas sodium and methyl iodide react at every collision, sodium and methyl bromide require on the average 25 collisions, and sodium and methyl chloride require 5,000 collisions for reaction to occur; this gives 0, 3200, and 8800 cal., respectively, for the heats of activation of these reactions. The reaction of sodium and methyl fluoride is slowest, requiring on the average more than 10^7 collisions and thus having a heat of activation greater than 25,000 calories.

The reaction mechanism suggested by the authors is represented by the equation,

$$Na + CH_3X \rightarrow NaX + CH_3$$

where X is a halogen atom. The activation energy is discussed from the point of view of the London theory (10) of a reaction between a free atom and a molecule, according to which the free atom does not attack the molecule from the side but rather the three members arrange themselves in a straight row and the middle halogen atom separates from the methyl group and becomes attached to the sodium atom. The experimental results can be very satisfactorily interpreted from the standpoint that the energy content of the transition stage Na—X—CH_3 determines the activation energy of the reaction.

PREPARATION AND REACTIONS OF FREE RADICALS

The isolation of free methyl groups was first accomplished by Paneth and Hofeditz (11) by passing lead tetramethyl in a current of hydrogen through a furnace heated to 500° or 600°C. The essential part of the apparatus was a quartz tube, into which very pure hydrogen containing a trace of lead tetramethyl was admitted; the pressure at the inlet end was 2–4 mm. and at the outlet end was kept as low as possible by a high capacity mercury-vapor pump; thus a stream of hydrogen containing a small quantity of lead tetramethyl passed down the tube at the rate of 10–15 meters per second. When a small piece of metallic lead was placed near the outlet end and heated to form a lead mirror, and when the tube was again heated to about 600°C. at a point nearer the inlet, the lead mirror was gradually removed, the time required depending on the distance of the point of heating from the mirror. Their experiments proved conclusively that free methyl groups were liberated to combine subsequently with the lead mirror to give lead tetramethyl.

Similar results were obtained using lead tetraethyl (12), indicating that this may be a general method for the preparation of free radicals from organometallic compounds. It was further shown that the hydrogen may be replaced by nitrogen without causing any substantial difference in the results, and that in a quartz tube of 5 mm. diameter the methyl radical disappears according to a first order reaction, the half-life being approximately 6×10^{-3} sec. The free radicals are exceedingly reactive and combine readily with such metals as lead, antimony, zinc, and bismuth and such non-metals as sulfur and iodine. A more recent publication by Paneth and Herzfeld (13) discusses these reactions in greater detail. In various experiments hydrogen was replaced by several other transport gases, such as helium, nitrogen, or a mixture of three parts of neon and one part of helium; the half-life of the various radicals was not significantly changed in these experiments and the radicals seemed to disappear in the same manner whether carried in the inert nitrogen, in the completely reactionless noble gases, or in hydrogen. The diameter of the tube, however, had a very considerable influence on the half-life period: for example, the half-life in a tube of 1.5 cm. diameter was almost four times that in a tube of 0.5 cm. diameter. Some very interesting experiments were carried out to investigate this effect of collision with the walls; for example, a standard test mirror was formed at a certain distance from the furnace, its time of removal giving a measure of the concentration of free methyl groups. In another experiment a second mirror, varying in width, was formed between the test mirror and the furnace; when this second, or guard, mirror was 10 mm. wide it prevented all free radicals from passing to the test mirror, but when its width was only 5 mm. the test mirror was fairly rapidly removed. It is possible to calculate how wide a guard mirror must be in order that each methyl group will make just one collision with the mirror; and it was found that a mirror of this width stopped the methyl groups almost entirely. This observation is sufficient basis for the assumption that each radical reaching the metallic surface is bound by its first collision, and that when four methyl groups meet on the same lead atom the volatile lead tetramethyl is formed. A similar study of the rate of disappearance of the ethyl groups showed that their recombination occurred mainly on the walls.

More recently it has been reported that the preparation of free alkyl radicals from organometallic compounds (14) can be simplified by the use of some easily condensable material as the transport gas; for example, water vapor, or a hydrocarbon such as heptane, or acetone may be used and, as these are completely frozen out by a liquid air trap, an ordinary oil pump may replace the much more elaborate pumping system required when hydrogen is used. Furthermore, organic compounds (in place of the metallic compounds) may be used as the source of free radicals if the temperature of the furnace is raised to 900° or 1000°C. Under these conditions organic compounds such as hydrocarbons or ketones are broken down with the formation of free radicals which rapidly remove lead or other metallic mirrors. In such cases, however, the free radicals disappear according to a bimolecular law (14) in contrast with the unimolecular law observed in Paneth's experiments.

Bates and Spence have studied the oxidation of the free methyl groups formed in the photochemical decomposition of gaseous methyl iodide (15). When pure methyl iodide vapor is illuminated with ultra-violet light at 0°C. in a quartz vessel, it undergoes a very slow decrease in pressure with liberation of iodine. The quantum yield is very small, being in the neighborhood of one molecule decomposed per 100 quanta of light absorbed. If, however, oxygen is present, the reaction velocity increases over a hundredfold, so that it is evident that the presence of oxygen removes the methyl groups formed in the primary decomposition and largely prevents their recombination with iodine. Iodine, paraformaldehyde, methylal, and water are practically the only products of the reaction, the overall process being represented by the following equation:

$$4\,CH_3I + CO_2 \rightarrow (HCHO)_n + (CH_3O)_2CH_2 + H_2O + 2\,I_2$$

The methylal is formed by the rapid condensation of formaldehyde and methyl alcohol.

When methyl iodide is illuminated in the absence of oxygen most of the free methyl groups react to re-form methyl iodide according to the following equations:

$$CH_3 + I + \text{3rd body} \rightarrow CH_3I + \text{3rd body}$$

$$CH_3 + I_2 \rightarrow CH_3I + I$$

Since both the rate of liberation of iodine and the production of permanent gas are very slow, the following reactions must also be very slow in comparison with the two foregoing reactions,

$$CH_3 + CH_3 + \text{3rd body} \rightarrow C_2H_6 + \text{3rd body}$$
$$CH_3 + CH_3I \rightarrow C_2H_6 + I$$

When oxygen is present the only subsidiary reaction we need consider is the recombination of the methyl groups with iodine, since all other reactions will probably be so slow as to be negligible in comparison with the rate of oxidation of the methyl groups. The authors suggest the following scheme,

$$CH_3 + O_2 \rightarrow HCHO + OH$$
$$OH + CH_3I \rightarrow CH_3OH + I$$

since this agrees with the kinetics of the reaction and a scheme involving peroxide formation does not. They show that the reaction between free methyl groups and iodine molecules is 400 times more fruitful than the reaction between free methyl groups and oxygen molecules.

Taylor and Jones (16) have studied the reaction between free ethyl groups and ethylene and have shown that the former induce considerable polymerization at temperatures at which ethylene alone does not polymerize. The free ethyl groups were produced by decomposing a small quantity of mercury diethyl in the gas. They suggest a possible mechanism by which a free ethyl radical collides with an ethylene molecule (through a three body collision) to form the butyl radical; this process may then continue to give the hexyl, and higher radicals. One of these higher radicals may lose a hydrogen atom when it collides with an ethylene molecule, thus producing an unsaturated hydrocarbon and a free ethyl group which can then continue the reaction chain.

It seems, therefore, that the production and reactions of organic radicals in the gaseous state have only just begun to be investigated from the physicochemical standpoint, in spite of the fact that such investigations have been quite feasible for a long time and certainly give every promise of shedding considerable light on the field. Recently Ziegler (17) has given a review of problems and accomplishments in connection with the newer concepts of free radicals.

THE DECOMPOSITION OF PARAFFIN HYDROCARBONS

When passed through a heated quartz tube, methane produces chiefly carbon and hydrogen, accompanied by small amounts of olefinic and acetylenic hydrocarbons (18). When the decomposition is carried out in silica bulbs between 800° and 1200°C., there is a strong retardation which may possibly be caused by preferential adsorption of hydrogen, so that a false equilibrium point is reached (19). Further work has indicated that there is a primary homogeneous bimolecular reaction,

$$2\,CH_4 = C_2H_2 + 3\,H_2$$

and that the acetylene formed is rapidly decomposed to carbon and hydrogen (20).

The pyrolysis of some of the higher members of the paraffin series has been studied in detail (21, 22, 23) more especially the kinetics of the thermal dissociation of propane and the butanes (24). The experimental results indicate that all these decompositions closely approximate unimolecular homogeneous reactions and have a heat of activation of about 65,000 cal. A comprehensive review (25) has recently been prepared on the decomposition of paraffin hydrocarbons.

Until comparatively recently the work on the decomposition of paraffin hydrocarbons comprised mainly the identification of the different products formed as the result of the decomposition and a study of the laws governing the rates of decomposition. Recently, however, two attempts have been made to describe the mechanism of the decomposition of paraffin hydrocarbons from the physicochemical standpoint. Burk (26) has shown that the existing data may be represented very well by a simple equation connecting the velocity of the reaction, its heat of activation, and the average life time of the activated molecules, an estimate of this last quantity being obtained from infra-red measurements of the frequency of the carbon-carbon bond. He concludes that the primary decomposition probably consists of the formation of two molecules—a paraffin and an olefin—and that this is more likely to be correct than the primary formation of two free radicals. He also discusses the possibility that reaction chains may be propagated in the decomposing hydrocarbon by radicals, but concludes that such chains cannot play any prominent part because the main result of radical cracking should be the regeneration of the original paraffin, and furthermore that it should lead to synthesis of higher hydrocarbons; such synthesis does not seem to occur in the early stages of cracking at low pressures.

On the other hand Rice (27) has offered an explanation for the mechanism of the decomposition of paraffins based on the primary formation of free radicals. For example, a methyl group, formed in the primary decomposition, is supposed to take a hydrogen atom from one of the surrounding hydrocarbon molecules to form methane; if the hydrocarbon has several carbon atoms, the free radical thus formed will be unstable and will break down into an olefin and a smaller free radical, which then in turn will take a hydrogen atom from the surrounding hydrocarbon; in this way the chain is continued. It is possible to draw up a very satisfactory representation for the decomposition of paraffin hydrocarbons according to these ideas.

THE DECOMPOSITION AND POLYMERIZATION OF UNSATURATED HYDROCARBONS

A comprehensive review of the literature covering the pyrolysis of olefinic hydrocarbons has recently been published (28). Even in the early stages, the decomposition of these hydrocarbons is invariably accompanied by a polymerization process, which is especially marked at lower temperatures. Pease has studied the mechanism in the case of ethylene (29) and has shown that a second order polymerization reaction occurs; by increasing the pressure, in the temperature range 350–500°C., ethylene can be largely polymerized to mono-olefins, with only a slight amount of other decompositions.

Normally ethylene does not polymerize at all in the temperature range 200–250°C., but in the presence of a small quantity of mercury diethyl or lead tetraethyl (30) a considerable amount of induced polymerization occurs. This is evidently due to some sort of chain mechanism initiated by the free ethyl radical formed in the decomposition of the metallic compound; the authors discuss possible mechanisms.

When heated to temperatures above 600°C. in the homogeneous gas phase, propylene decomposes (31) unimolecularly to give, when only small fractions are decomposed, chiefly ethylene and paraffin hydrocarbons, some hydrogen and much smaller quantities of acetylene and higher olefins; it is, however, somewhat difficult to propose a satisfactory mechanism, owing to the concomitant polymerization process.

The pyrogenic decomposition of isobutylene has also been studied (32) and has given similar results; but in this case the tendency to polymerize and yield oils was found to be even more marked. For example, when only about 10 per cent of the isobutylene was decomposed, over one-half of this amount was obtained as an oil containing considerable quantities of aromatic hydrocarbons and having a high molecular weight. Among the gaseous products methane, propylene, isobutane, and hydrogen predominated, accompanied by small quantities of acetylene and ethylene; these results hold only for small percentage decompositions, since when more than 10 per cent of a hydrocarbon is decomposed, the results of the primary decomposition will undoubtedly be largely masked by the decomposition of some of the primary and secondary products. The thermal decomposition (33) of allene, $CH_2{=}C{=}CH_2$, and of methylacetylene, $CH_3C{\equiv}CH$, results mainly in polymerization; apparently the methylacetylene first changes to allene, which then polymerizes. The decompositions of methylallene and ethylacetylene have also been investigated (34), and here also polymerizations practically completely obliterated any other reactions, although this did not hold to such a marked degree in the case of ethylacetylene as for methylacetylene and allene.

Wheeler and Wood (35) have discussed the mechanism of the thermal decomposition of normal olefins and have concluded that the possible primary reactions common to all of them consist in the formation of two or four carbon atom members of the olefin series. The complex secondary reactions following such a primary decomposition are also discussed.

Pease (36) has made a study of the polymerization of acetylene and has shown that it is a homogeneous bimolecular reaction which may be partially suppressed by increasing the surface-volume ratio of the containing vessel; it is the only reaction of importance between 400° and 600°C. and yields a number of complex products, including several aromatic hydrocarbons.

It seems apparent that in order to obtain accurate information concerning the primary decomposition of unsaturated hydrocarbons, the experiments must be done under conditions such that the polymerization reaction can be almost completely suppressed; this is most nearly possible when the decomposition is conducted at low pressures in a packed vessel. Furthermore, only a small fraction of the original hydrocarbon should be decomposed, in order to prevent decomposition of the primary products as far as possible. At present it is hardly possible to say with any certainty what is the nature of the primary reaction in the decomposition of unsaturated hydrocarbons.

THE DECOMPOSITION OF ALDEHYDES, KETONES AND ETHERS

Acetaldehyde was first reported to decompose according to a homogeneous bimolecular reaction (37), but later work (38) has shown that the dependence of rate on initial pressure is that of a 5/3 order reaction. It seems doubtful therefore whether the decomposition of acetaldehyde is really a bimolecular reaction at all; possibly the decomposition into methane and carbon monoxide consists of a series of steps which only accidentally approximate a bimolecular law. If the decomposition of acetaldehyde into methane and carbon dioxide were really a bimolecular reaction, four bonds would have to be broken and four new ones completed during the time of collision; it does not seem probable that such a complicated process would occur during the time of a single collision. The decompositions of higher aldehydes probably follow a unimolecular law, since the decomposition of propionaldehyde (39) is a homogeneous unimolecular reaction at pressures above 100 mm.; at lower pressures the unimolecular velocity constants fall appreciably.

The decomposition of acetaldehyde is catalyzed by iodine (40) and the rate of this reaction is unimolecular with respect to the acetaldehyde and proportional to the total concentration of iodine. The energy of activation is 32,500 cal., which gives a calculated number of collisions between aldehyde and iodine molecules only one order smaller than the observed value.

When benzaldehyde is heated in the range 300–400°C. a condensation reaction occurs (41), forming benzyl benzoate; however, when the temperature is raised to 700°C., the characteristic decomposition of aldehydes occurs, with carbon monoxide and benzene as the main products. The kinetics of the reaction have not been investigated.

The decomposition of acetone has become a classical example (42) of this type of reaction, since it was the first of this class which was proved to be homogeneous and unimolecular when carefully investigated from the kinetic standpoint. It was first thought that acetone in silica vessels decomposed to form carbon monoxide and two methyl groups, which then reacted to give methane, ethylene and hydrogen, but later work (43) has shown that the mechanism really involves the formation of ketene and methane, followed by decomposition of the ketene. Thus the mechanism for the decomposition of acetone may be represented in two ways. According to the first, a hydrogen atom transfers from one carbon atom to another and a carbon-carbon bond breaks:

$$CH_3COCH_3 \rightarrow CH_4 + CH_2{=}CO$$

This mechanism would account for the observed unimolecularity of the process, and is not impossible from what we know of molecular transformations at the present time. It is also possible to develop a chain mechanism for the reaction, in which the acetone decomposes unimolecularly into a free methyl group and a free acetyl group. It is probable that the free acetyl group would be unstable at the temperature of the experiment and would rapidly decompose into carbon monoxide and another free methyl group. The free methyl groups formed might be expected to undergo a rapid bimolecular reaction with the surrounding acetone molecules to yield methane and the radical CH_2COCH_3; at the temperature of the experiment this radical would probably be unstable and break down into ketene and a free methyl group. If some such chain mechanism as this occurs, providing the chains are not very long, we might still obtain an approximately unimolecular reaction.

Hinshelwood and his coworkers have examined the thermal decompositions of a number of ethers (44) and have found that they are all homogeneous unimolecular reactions whose rates fall off at lower pressures, but that hydrogen seems to have a specific action in retarding this decrease; the energy of activation is between 60,000 and 65,000 cal. Diisopropyl ether has several modes of decomposition: the one most likely to occur appears to be a homogeneous reaction which is independent of the pressure down to at least 30 mm.

The decomposition of ethers is catalyzed by iodine in the same manner as is that of acetaldehyde, the rate of decomposition being proportional to the concentration of iodine and to the concentration of ether. The actual working out of the kinetics is somewhat more complicated than with acetaldehyde because the first products of the decomposition are very unstable; for example, diethyl ether under the influence of iodine first decomposes into ethane and acetaldehyde, and the latter in turn forms methane and carbon monoxide. Probably every collision between ether and iodine in which the kinetic energy exceeds 34,000 cal. leads to decomposition. Hinshelwood (45) supposes that the iodine molecule is more effective than other ether molecules in bringing energy to a part of the molecule where it is required.

THE DECOMPOSITION OF ORGANIC NITROGEN COMPOUNDS

Compounds belonging to this class have provided a fruitful field for kinetic studies of reaction rates and a very considerable number of the members of this class have been investigated.

Aliphatic amines decompose at conveniently measurable rates in the neighborhood of 550°C. The decompositions of ethylamine (46) and of propylamine (47) are both homogeneous unimolecular reactions with an energy of activation of approximately 44,000 cal. The reaction rate for ethylamine falls off below 50 mm. pressure, and for propylamine it falls off below 20 mm. pressure.

When diazomethane, $CH_2{=}N{\equiv}N$, is decomposed it yields nitrogen and ethylene. When the decomposition is brought about by heating in an atmosphere of carbon monoxide, the product is ketene, $CH_2{=}CO$ (48); this suggests that a primary dissociation into a nitrogen molecule and a methylene radical probably occurs. Steacie (49) made a preliminary study of the kinetics of the decomposition, but had to abandon the work after a number of serious explosions had occurred in handling the substance. Diazomethane explodes at a pressure above 10 cm. and a temperature above 217°C.; this explosion reaction is definitely of the chain type, since the explosion limit is lowered by the presence of an inert gas. Below 217°C. a slow decomposition occurs which the experimental results show to be a homogeneous bimolecular reaction with an energy of activation of approximately 36,000 cal.

The decomposition of aliphatic azo compounds has been extensively studied by Ramsperger and his coworkers. Azomethane (50) decomposes chiefly into nitrogen and ethane; a kinetic study of the reaction shows that it is homogeneous and unimolecular, with an energy of activation of 52,000 cal. In a similar way, azoisopropane, $C_3H_7N{=}NC_3H_7$, decomposes chiefly into nitrogen and a hexane (presumably 2,3-dimethylbutane); the reaction has an energy of activation of about 41,000 cal. The rate constants in both cases begin to fall off in the range of 5–50 mm., the falling off occurring at higher pressures when the temperature is higher. Both of these compounds decompose at a measurable rate in the neighborhood of 300°C. The mixed azo compound, methylisopropyldiimide was also investigated (51) over the temperature range 250–330°C., and was found to be homogeneous and unimolecular with a heat of activation of approximately 48,000 cal.; the rate constant falls off at pressures below several centimeters.

More recent work (52) has shown that the rate of decomposition of azomethane is maintained at low pressures if ethane is present; in fact, ethane is nearly equivalent to azomethane itself in maintaining the rate. Nitrogen, on the other hand, does not have very much effect, possibly owing to the limited internal energy of the nitrogen molecule; its frequencies may also be considerably different from those of azomethane, making an exchange of energy between the two molecules difficult. Dimethyltriazine, $CH_3N{=}NNHCH_3$, has been studied (53) at temperatures in the neighborhood of 200°C. and in the pressure range 0.02 to 8 cm. The reaction is homogeneous and unimolecular but at pressures below 1 cm. the rate begins to fall. The energy of activation is approximately 34,000 cal. Methyl azide, CH_3N_3, was also investigated and was reported to be homogeneous and unimolecular, but the measurements are somewhat uncertain because the hydrazoic acid formed as one of the products decomposes. Hydrazoic acid itself decomposes with a measurable velocity in the neighborhood of 300°C., but the reaction is catalyzed by the Pyrex walls of the reaction vessel.

THE DECOMPOSITION OF SOME OTHER ORGANIC COMPOUNDS

The decomposition of metal alkyls provides an interesting study which has already been discussed; from Paneth's work (11) and the work of Taylor and Jones (16) it seems clear that lead alkyls undergo a primary dissociation into metal and the free alkyl radical. Recently Geddes and Mack (54) have made a careful study of the decomposition of gaseous germanium tetraethyl. This substance is more stable than lead tetraethyl, which decomposes at a measurable rate at about 220°C., and is less stable than silicon tetramethyl, which decomposes at about 650°C. The investigation was carried out in the range 420–450°C. and the reaction was found to be unimolecular and practically entirely homogeneous down to pressures of 8 cm.; the energy of activation is about 51,000 cal. The work is interesting from the point of view of the decomposition of paraffin hydrocarbons, because the gaseous products of the reaction contain 60–70 per cent of ethane and ethylene, which might be expected in the pyrogenic decomposition of butane if the splitting of the butane molecule occurs predominantly in the middle. The authors found that added hydrogen and ethylene enter into hydrogenation and polymerization reactions, and that nitrogen, helium, and argon have practically no effect.

The investigation of the thermal decomposition of carbon tetrabromide (55) showed that it decomposes at a measurable rate in the temperature range 300–330°C., but that the reaction is heterogeneous.

Ethylene oxide (56) decomposes in the temperature range 380–440°C. in the homogeneous gas phase, producing mainly carbon monoxide and methane, accompanied by smaller quantities of hydrogen and ethane. There is an induction period, after which the substance decomposes according to a unimolecular law; in the later stages the products of the reaction exert a retarding effect, which may also be brought about by the addition of other inert gases. The energy of activation is approximately 52,000 cal. The authors propose a mechanism according to which the ethylene oxide first isomerizes to acetaldehyde and the activated acetaldehyde then decomposes into methane and carbon monoxide or into ethane, hydrogen and carbon monoxide. However, this mechanism cannot yet be considered as very well established.

When *d*-pinene is heated the optical activity changes. The rate was measured by Smith (57) who assumed that *dl*-pinene was formed; actually pinene isomerizes (58) to dipentene. This reaction is the only known example of a homogeneous unimolecular rearrangement (59), since all other unimolecular gas reactions are decompositions.

CHLORINATIONS AND OXIDATIONS

When methane and chlorine are heated above 200°C. at one atmosphere total pressure, a homogeneous bimolecular reaction occurs (60) readily in Pyrex tubes. Below 300°C. the reaction is strongly inhibited by oxygen, but as the temperature is raised this effect gradually disappears. This indicates a chain mechanism, and this assumption is further strengthened by the fact that the reaction is about 1000 times faster than would be expected from theory.

The chlorination of unsaturated hydrocarbons is probably a heterogeneous reaction since this has been shown to be the case for the reaction between ethylene and chlorine (61).

Bodenstein (62) has recently published a paper on the oxidation of gaseous acetaldehyde in which he suggests a mechanism applicable not only to this substance but to organic oxidations generally, particularly those of hydrocarbons. The rate of oxidation of the acetaldehyde was followed by measuring the changing pressure of mixtures of aldehyde vapor and oxygen in the temperature range of 55–90°C. and with an initial pressure of about 70 mm. Bodenstein points out that while this pressure decrease is very convenient, it is also a very insecure measure of this reaction. Several disturbing reactions were noticed which vitiated the pressure measurements toward the end of the experiment. Thus, peracetic acid is formed in the oxidation and this may decompose through an internal combustion into a large number of substances, which would cause an increase in pressure; further, the peracid and acetaldehyde may react to give acetic acid; and finally, especially at lower temperatures, some sort of condensation takes place which causes the pressure to diminish even after all the oxygen has been used up; however, none of these disturbances becomes markedly noticeable until the later stages of the reaction.

Unfortunately disturbances also occur at the beginning of the reaction; there is an irregular induction period, very occasionally long, sometimes absent, which because of its irregularity must be due to contamination and cannot have its origin in the reaction itself. It is known for example that traces of diphenylamine inhibit this reaction very markedly, and it is possible that traces of impurities from stopcock grease have a similar effect. While it is therefore not possible to carry out an exact calculation of the reaction velocity over the whole course of the oxidation, it is possible to analyze the mechanism of the process with considerable certainty. The result is interesting in that it suggests a chain reaction whose course can be followed and described very well and which can obviously be taken as representative of a large number of similar reactions.

After a short induction period, mixtures of aldehyde and oxygen in which there is a large excess of aldehyde, have a constant reaction velocity which suddenly becomes zero when the oxygen is used up; on the other hand, in the presence of an excess of oxygen, after the induction period the usual gradual decrease in reaction rate is shown.

There are two possible reaction mechanisms which can be used to represent these experimental results. According to the first, an aldehyde molecule A, becomes activated, (A′), and reacts with a molecule of oxygen to produce an activated molecule of peracid, P′, which in most cases decomposes into aldehyde (not activated) and oxygen, but is sometimes stabilized by collision with other molecules of peracid or with the wall. The following equations represent the mechanism:

$$\begin{aligned}
&(1)\ A \rightarrow A'\\
&(2)\ A' + O_2 \rightarrow P'\\
&(3)\ P' \rightarrow A + O_2\\
&(4)\ P' + P \rightarrow 2P\\
&(5)\ P' + \text{wall} \rightarrow P
\end{aligned}$$

From these equations it can easily be shown that

$$\frac{d[P]}{dt} = \frac{k_1[A](k_4[P] + k_5)}{k_3}$$

This mechanism does not lead to a chain reaction and simply states that a small fraction of the activated aldehyde molecules are converted to the peracid by three body collisions, and that the peracid already present has a favorable effect on the stabilization of the activated aldehyde molecules.

A second mechanism may, however, be used to represent the oxidation, and the equation thus obtained leads to a chain. Allowing K to represent a negative catalyst we have:

(1) $A \rightarrow A'$
(2) $A' + O_2 \rightarrow P'$
(3) $P' \rightarrow A' + O_2$
(4) $P' + A \rightarrow P + A'$
(4′) $P' + K \rightarrow P + K'$
(5) $P' + O_2 \rightarrow P + O_2$
(6) $P'\,(\text{wall}) \rightarrow P$

Assuming that reaction 4 is very much faster than reactions 5 and 6, and making certain approximations, one finally obtains,

$$\frac{d[P]}{dt} = \frac{k_1 k_4}{k_5} \cdot \frac{[A]^2}{[O_2] + k_6/k_5}$$

for the reaction when no negative catalyst is present. In this scheme all the activated aldehyde molecules are supposed to react with oxygen and the reaction $A' \rightarrow A$ is not considered.

The activation energy in these reactions must be present in some very stable form, since it is not lost either by spontaneous deactivation or in the decomposition of the activated peracid molecule. The heat of activation, calculated from the temperature coefficient of the overall reaction for the oxidation of acetaldehyde, is approximately 10,000 cal.; probably this is about the temperature coefficient for reaction 1, since it is not very likely that the other reactions are affected very greatly by changes in temperature.

Bodenstein believes that this second scheme applies to the oxidation of a wide variety of organic substances; some of these applications will be discussed in the following paragraphs.

The oxidation of paraffin hydrocarbons has been carefully investigated and a considerable number of facts are known, although the mechanism is still obscure. The oxidation of ethane has a well marked induction period during which practically no oxidation occurs (63); this interval is shortened in varying degrees by the addition of traces of moisture, ethyl alcohol, formaldehyde, iodine, or nitrogen peroxide; the addition of 1 per cent of acetaldehyde vapor causes immediate explosion; the oxidation itself has all the characteristics of a homogeneous chain reaction (64). In such oxidations of hydrocarbons, the oxygen appears to have a favorable influence, thus suggesting that the reaction determining the velocity may be

$$\text{hydrocarbon (excited)} + O_2 \rightarrow \text{oxidation products}$$

although this is not at all in agreement with the Bodenstein scheme. The oxidations of propane and of butane show similar phenomena (65). Between 300° and 350°C. it would seem that an aldehyde-producing type of reaction predominates; in the case of propane this might be represented by

$$CH_3CH_2CH_3 + 2\,O_2 \rightarrow CO + 2\,H_2O + CH_3CHO$$

This is a chain reaction, as is shown by the fact that it may be largely suppressed by using small diameter reaction tubes or by packing with broken glass. In the range 500–600°C., unsaturated compounds are formed, either by dissociation of the hydrocarbons into hydrogen and an olefin or by their oxidation to water and an olefin; these appear to be more or less normal homogeneous gas reactions.

The oxidation of *n*-octane (66) can be most simply interpreted on the hypothesis that its initial oxidation product is the octaldehyde, which in turn is further oxidized to aldehydes containing an even smaller number of carbon atoms, with the simultaneous formation of carbon monoxide and some carbon dioxide. Here also the oxidation has all the characteristics of a chain reaction, including a distinct luminescence in the tube. The oxidation of various isomeric octanes indicates that, in general, the oxygen first attacks the methyl group at the end of the longest free straight chain and then proceeds in a manner analogous to that observed for *n*-octane until a branch in the chain occurs, at which point the rate of oxidation slows down markedly (67).

Several studies have been made on the ethylene–oxygen reaction. The effect of ozone in initiating this reaction (68) at temperatures below the normal reaction temperature indicates a chain reaction; this has been confirmed by showing that one molecule of ozone can induce the reaction of seven molecules of oxygen. Thompson and Hinshelwood (69) also concluded that the reaction really proceeds through a chain mechanism in spite of the fact that it behaves as a third order reaction when the total pressure is varied. The partial pressure of the ethylene has a very pronounced effect on the rate of the reaction, which over certain ranges of pressure is approximately proportional to the third power of the ethylene concentration; the partial pressure of oxygen has some influence on the rate, but it is far less pronounced than that of the ethylene. It is probable that the reaction rate is retarded by increased surface. The same authors suggest that the first stage of the reaction may be the formation of an unstable peroxide; if this reacts with more oxygen the chain ends, but if it reacts with ethylene, various unstable hydroxylated molecules are formed which continue the chain; the chains are probably not of great length. Lenher (70) has investigated the same reaction at temperatures from 300–525°C. and concludes that there are two possible primary reactions, both resulting in the formation of ethylene oxide and formaldehyde. The other reaction products, dioxymethyl peroxide, acetaldehyde, formic acid, the oxides of carbon, hydrogen, and water, are formed in succeeding reactions. At temperatures above 500°C. the thermal polymerization of ethylene becomes an important side reaction, even in the presence of appreciable amounts of oxygen and inert gases.

The oxidation of acetylene (71) is also a chain reaction; in this case it seems most probable that the chains originate on the surface of the vessel, undergo considerable branching in the gas phase, where some deactivation by oxygen occurs, and finally are broken at the walls of the vessel. The study of the oxidation of acetylene has led to the isolation of the intermediate compounds glyoxal, formaldehyde, and formic acid (72). The rate of oxidation increases with increasing oxygen concentration until a region is reached in which the rate is practically independent of the amount of oxygen; a further increase in oxygen concentration somewhat retards the rate of reaction. At low concentrations of oxygen the rate is proportional to the first, or even lower, power of the concentration of acetylene, and at higher concentrations of oxygen the rate is very nearly proportional to the square of the acetylene concentration. Inert gases have a slight retarding effect on the rate of the reaction.

SUMMARY

We may conclude this review by a short summary of the accomplishments of the past few years toward understanding the complex pictures presented by the behavior and action of organic compounds. The isolation and study of free alkyl radicals by Paneth and his coworkers constituted a tremendous step forward since such fragments very likely play a part in chain propagation. The predominance of this type of reaction is particularly striking in polymerizations, oxidations and chlorinations. It is true that thermal decompositions appear to be simple unimolecular reactions, but it is possible that they may also be of the short chain type. The work of Polanyi constitutes an initial step in determining the nature of activation energy, so that we may hope during the next few years to be able to describe with a reasonable degree of completeness the reactions of organic compounds in the gaseous state.

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