THE DECOMPOSITION OF ORGANIC COMPOUNDS FROM THE STANDPOINT OF FREE RADICALS

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The changes which organic substances undergo when the temperature is raised have been made the subject of a great number of studies, especially during the past fifty years (10). The earlier work consisted of passing the substance to be investigated through a hot tube under conditions which brought about complete or almost complete decomposition of the original substrate. The permanent gases formed were analyzed in a gas analysis apparatus and the liquids were separated and identified by distillation. Unfortunately the immense number of data obtained in this way do not give us any appreciable understanding of the pyrolytic process. Except in the case of the very simplest substrate molecules, the products of the primary decomposition themselves decompose until finally secondary reactions predominate. This difficulty has been overcome in recent years by plotting the analysis of the products (15, 16, 34) against percentage decomposition of the original substrate; extrapolation of the curves to zero decomposition indicates the primary products of the decomposition and their relative amounts. Work of this nature has given information regarding the primary products of decomposition of certain hydrocarbons (5) and of acetone (24). However the information regarding primary products is still very meager and is not at all certain even in the case of substances such as diethyl ether, on which a large number of kinetic studies have been made (33). Further experimental work on the primary products formed in the thermal decomposition of one or two members of such series as ethers, ketones, esters, and amines is very desirable.

The existence of such a large number of empirical experimental data in this field constitutes a challenge to any chemist interested in the understanding of the mechanism of chemical reactions. In the last ten years much work has been done in investigating organic decompositions from the physical chemical standpoint. The chief pioneer in this field was Hinshelwood (6), who showed that the thermal decompositions of a number of simple organic molecules such as acetone (8) and dimethyl ether (7) are homogeneous and at sufficiently high pressures follow a unimolecular law.

The interpretation given to these experimental results (6) was that each organic molecule, depending on its energy content, has a certain probability of decomposing either directly into product molecules or at most through one or two intermediate steps. By assuming that activated molecules have a finite life and that their rate of production (except at fairly low pressures) is high compared with their rate of destruction chemically, it is possible to account for the experimental results. Indeed the development of this concept (6), especially by Hinshelwood, O. K. Rice, and Kassel, gave an apparently satisfying picture of those organic thermal decompositions which follow a unimolecular law.

There were, however, certain difficulties connected with the development of this picture. In part these were due to the inadequacy of the chemical analytical work necessary to supplement the kinetic measurements. For example, in the case of acetone we know now that the original conclusions of Hinshelwood and Hutchinson (8) regarding the chemical decomposition of acetone were incorrect (31), and in other cases, such as that of diethyl ether, the chemical data available are not yet complete in so far as the primary products of the reaction are concerned. A further difficulty arose when it was discovered (12) that acetaldehyde did not decompose according to a simple bimolecular law as originally reported, but that its decomposition could be best represented as of some fractional order (25), possibly 1.5. However it is possible that these various difficulties can be satisfactorily met; furthermore, the idea that product molecules result directly may be finally proved experimentally and the picture can then be extended to cover the calculation of the product molecules in some such way as suggested by Kassel (13).

About six years ago it occurred to the author (21) that the products of organic decompositions could be satisfactorily explained by assuming a primary decomposition into free radicals followed by a free radical chain which finally terminates by collision of the radicals. The scheme was relatively free from arbitrary assumptions and a detailed examination showed that on the basis of the available evidence it could account both qualitatively and quantitatively for the chemical products formed in organic decompositions (22). At about the time this idea was conceived, Paneth's discovery (17) of the free methyl radical was published. Experimental tests were then made with many organic compounds (27), using Paneth's technic, and it was shown that dissociation into free radicals could be experimentally demonstrated. The activation energies of these free radical dissociations were also measured (26) and shown to be not much higher than the overall decompositions. Certain free radicals were prepared (4) and their decomposition and interaction were found to be in excellent agreement with the free radical theory. Furthermore it was found that the introduction of free radicals, produced either thermally (1, 36) or photochemically (14), induced extensive decomposition in butane, acetaldehyde, and dimethyl ether. Finally it was shown that the observed kinetics of the decompositions of ethane, dimethyl ether, acetone, and acetaldehyde could be satisfactorily explained on the basis of the free radical mechanism (25).

At present the situation is that both mechanisms are in fairly satisfactory agreement with experimental studies of the kinetics of organic decompositions. Indeed it is possible that the process involving the direct formation of product molecules and that involving a chain reaction may each occur to an appreciable extent for many organic reactions. Many experiments have been made in this laboratory to find an inhibitor which would remove free radicals and thus slow up any chain reaction that might be occurring; this work is still in progress and has shown that organic nitrites probably can act as chain breakers under certain conditions (29).

It may be pointed out that the adoption of the free radical mechanism for the bulk of organic thermal decompositions, while it would complicate the kinetic picture considerably, would not affect the theoretical development (6) of Hinshelwood, O. K. Rice, and Kassel, which would apply to the primary rupture into free radicals. On the other hand the adoption of the free radical mechanism would bring a great simplification into the organic chemistry of thermal decompositions (28): a few hundred elementary reactions describing the dissociation of organic molecules into radicals and the decomposition and reactions of these radicals would suffice to describe completely many thousands of organic decompositions. Possibly the future of this branch of organic chemistry may lie in the determination of the activation energies of organic reactions.

REACTION KINETICS

The detailed treatment (25) of the kinetics of organic decompositions from the free radical standpoint has already been given and will not therefore be repeated here. Since, however, the detailed treatment is necessarily very complicated, it seems desirable to present an artificially simplified scheme which contains all the important reactions. The primary reaction may consist of a dissociation into a smaller molecule and a radical,

$$M_1 \rightarrow R + M_2$$

Examples of such primary dissociations are the dissociation of diazomethane,

$$CH_2{=}N{\equiv}N \rightarrow CH_2 + N_2$$

or of methyl nitrite (37, 38),

$$CH_3ONO \rightarrow CH_3O + NO$$

In other cases the primary dissociation may produce two radicals which may be like as in ethane or unlike as in acetone. These would be represented by the general equations $M_1 \rightarrow 2R$ or $M_1 \rightarrow R_1 + R_2$. A radical produced in the primary dissociation may decompose into a smaller radical and a molecule or may react with one of the original substrate molecules by removing a hydrogen atom to form the radical hydride and a large free radical, which in turn decomposes to give a smaller radical and a molecule. The simplest form of this radical chain decomposition may be represented by the equations:

$$M_1 \rightarrow R_1 + M_2 \tag{1}$$

$$R_1 + M_1 \rightarrow R_1H + R_2 \tag{2}$$

$$R_2 \rightarrow R_1 + M_3 \tag{3}$$

where the M's represent molecules and the R's represent radicals. The kinetics of the decomposition are not affected, except for a small factor in the chain length, if M_1 decomposes into two radicals or if the radical R_1 decomposes before reacting or if the chain radical is not the same as the radical produced in the primary dissociation.

Since the primary reaction (1) involves the dissociation of a molecule and consequent rupture of a bond, the activation energy should be high, and for those processes involving rupture of a carbon–carbon or carbon–oxygen bond may be expected to be very approximately 80 Cal. On the other hand, reactions 2 and 3, since they involve radicals, would be expected to have relatively low energies of activation. The termination of the chain may occur by collision of the radicals according to one of the three equations,

$$R_1 + R_2 \rightarrow M_4 \tag{4}$$

$$R_1 + R_1 \rightarrow M_5 \tag{5}$$

$$R_2 + R_2 \rightarrow M_6 \tag{6}$$

Equation 6 can be omitted from consideration on the basis that the large molecule M_6 is unstable and easily dissociates into R_2. Whether the chain terminates according to equation 4 or equation 5 will depend on the relative activation energies of the two chain reactions 2 and 3. Here two cases arise. In the first, we assign a low activation energy ($\sim$ 15 Cal.) to reaction 2 and a relatively high activation energy ($\sim$ 40 Cal.) to reaction 3. The effect of this, if the reaction occurs at approximately atmospheric pressure, is to keep the concentration of R_1 very low and the concentration of R_2 relatively high. The radical R_2 cannot disappear by combination with itself according to equation 6, owing to the instability of M_6, and recombination of R_1 according to reaction 5 is slow compared with reaction 4, owing to the low concentration of R_1; consequently reaction 4 breaks the chain.

In the second case we assign the same activation energy (~ 15 Cal.) to reaction 2, but a low activation energy (~ 10 Cal.) to reaction 3. This makes the radical R_2 so unstable that its concentration is very low and the chain terminates by reaction 5, in which R_1 combines with itself. It is interesting to note that at low pressures the first case passes over to the second, because the bimolecular reaction 2 is slowed up by the diminution in pressure as compared with unimolecular reaction 3; the concentration of R_1 therefore rises until finally reaction 5 predominates instead of reaction 4.

We shall discuss briefly the kinetics of the first case, in which reaction 4 is the chain-terminating reaction. In the early states of the reaction after a steady state has been reached the radicals R_1 and R_2 are produced and destroyed at equal rates and consequently their rate of change is zero. We have then:

$$\frac{dR_1}{dt} = 0 = k_1M_1 - k_2R_1M_1 + k_3R_2 - k_4R_1R_2$$

$$\frac{dR_2}{dt} = 0 = k_2R_1M_1 - k_3R_2 - k_4R_1R_2$$

By adding these two equations we obtain,

$$0 = k_1M_1 - 2k_4R_1R_2$$

We then make an approximation by assuming that the chain is fairly long, so that we can neglect k_1M_1 and $k_4R_1R_2$ in comparison with $k_2R_1M_1$ and k_3R_2 in the first equation. We then obtain,

$$0 = k_3R_2 - k_2R_1M_1$$

Solving this equation and the previous one gives:

$$R_1 = \sqrt{\frac{k_1k_3}{2k_2k_4}} \qquad R_2 = M_1\sqrt{\frac{k_1k_2}{2k_3k_4}}$$

The overall rate of decomposition of M_1 is given by

$$-\frac{dM_1}{dt} = k_1M_1 + k_2R_1M_1 = k_1M_1\left(1 + \frac{k_2}{k_1}\sqrt{\frac{k_1k_3}{2k_2k_4}}\right)$$

$$= k_1M_1\left(1 + \sqrt{\frac{k_2k_3}{2k_1k_4}}\right)$$

$$\sim M_1\sqrt{\frac{k_1k_2k_3}{2k_4}}$$

We have therefore the totally unexpected result that a highly complicated chain decomposition may yet follow a simple unimolecular law.

By following an exactly similar method for the case where the chain ends by reaction 5, we obtain

$$-\frac{dM_1}{dt} \sim M_1^{1.5} k_2 \sqrt{\frac{k_1}{k_5}}$$

The rate is therefore proportional to the 1.5 power of the concentration of the substrate molecule.

The schemes presented in this section of the paper would be expected to apply to organic molecules that contain only one kind of hydrogen atom, such as ethane, dimethyl ether, acetone, and neopentane; also it would be expected to apply to organic molecules which contain, owing to some peculiarity of structure, one kind of hydrogen atom which is much more loosely bound than any other kind. Acetaldehyde and pentene-1 are examples of such molecules.

On the other hand, when an organic molecule contains two or more kinds of hydrogen atoms, the problem becomes much more complicated A preliminary study of this case has been made by Professor Herzfeld and the author, but it has been temporarily interrupted because of the lack of reliable data for the initial rates of decomposition of large molecules. From the radical standpoint we would expect the experimental result that two organic compounds when mixed do not decompose independently of each other, since the free radicals generated by the one affect the decomposition of the other and *vice versa.* This raises a difficulty in the experimental study of large molecules, because in many cases the product molecules contain hydrogen atoms much more loosely bound than the original substrate molecule: this would be expected to bring about a catalytic effect which would make the experimental determination of the initial rate of decomposition difficult. It is also very difficult to allow for this in the calculations, since the introduction of a catalyst by the reaction itself would not permit the assumption of a steady state concentration of the chain radicals. However, the calculations made so far have indicated that the methods used in previous papers for predicting the products of chemical decompositions are justified if a regeneration reaction of the type,

$$M_1 + R_2 \rightarrow R_2 + M_1$$

occurs in these chemical decompositions. R_2 is simply a large radical formed by removal of a hydrogen atom from the original substrate molecule M_1, and the equation simply states that R_2 is in general regenerated many times before it decomposes into a molecule and a smaller radical.

FREE RADICAL CHEMISTRY

Only very few aliphatic free radicals have been isolated, namely methyl, ethyl, and methylene. In studying the radicals advantage is taken of their property, discovered by Paneth (17), of combining with certain metals. When free radicals are generated at low pressures (0.1 to 2 mm.) in a gas which is brought in contact with a cold metallic surface, the radicals diffuse to the surface and form a volatile organometallic compound. With few exceptions attempts to bring about reaction of radicals with solid surfaces other than metals and a few non-metallic elements results in recombination of the radicals with each other. Since the reaction $R_1 + R_2$ may be expected to occur after relatively few collisions to yield the molecule R_1R_2 (or two molecules) by disproportionation, it follows that the life of radicals will be very short. Actually it is found to be of the order of 10^{-3} sec.

Attempts to make radicals react with organic molecules at surfaces have not been successful up to the present, but in the gas phase radicals have been shown to react very readily with many kinds of organic molecules such as ethylene (39, 40), acetaldehyde (1, 36), dimethyl and diethyl ethers (14), and acetone (30). These reactions are probably of the type

$$R + M \rightarrow RH + R_2$$

where the free radical R removes a hydrogen atom from the molecule M to form the molecule RH and the radical R_2, which is the original substrate minus a hydrogen atom. This type of reaction, which in general generates a new free radical at each elementary reaction, is most important from the organic chemical standpoint, since a chain reaction is thus propagated which determines the chemical products.

It seems desirable to list some of the different classes of free radicals and to comment briefly on their properties:

Hydrocarbon radicals

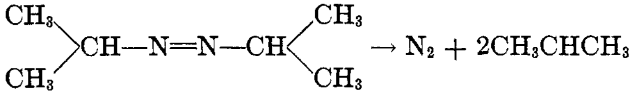
(*a*) *Univalent.* These may be considered to be derived from saturated hydrocarbons by removal of a hydrogen atom. The radicals from the paraffin series may be listed as follows: CH_3, CH_3CH_2, CH_3CHCH_3, $(CH_3)_3C$, $CH_3CH_2CH_2$, $CH_3CH_2CHCH_3$, $CH_3CH_2CH_2CH_2$, ... They have been placed in diminishing order of stability with reference to the reaction,

$$R \rightarrow M + R_1$$

where M is a molecule or atom and R_1 is a smaller radical than the original radical R. Of this series only CH_3 and CH_3CH_2 have been prepared (17, 18). Attempts to prepare $CH_3CH_2CH_2$ and $CH_3CH_2CHCH_3$ have so far been unsuccessful (18).

An attempt by the author[1] and A. T. W. Aten, Jr., to prepare the isopropyl radical by the decomposition of azoisopropane at low pressures was also unsuccessful, since only methyl groups were found.

From the following scheme



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH{-}N{=}N{-}CH\!\!<\!\!\begin{matrix} CH_3 \\ CH_3 \end{matrix} \rightarrow N_2 + 2CH_3CHCH_3$$

$$2CH_3CHCH_3 \rightarrow C_6H_{12}$$

$$CH_3CHCH_3 \rightarrow H + CH_3CH{=}CH_2$$

$$CH_3CHCH_3 \rightarrow CH_3CH_2CH_2 \rightarrow CH_3 + CH_2{=}CH_2$$

we may conclude that at low pressures the last reactions predominate, whereas at higher pressures recombination of the isopropyl radicals occurs (20). The important work of Frey on the decomposition of some mercury dialkyls (4) makes it highly probable that the *n*-butyl and *sec.*-butyl radicals do have a real existence.

(*b*) *1,1-Bivalent.* Removal of two hydrogen atoms from the same carbon atom of an aliphatic hydrocarbon gives these radicals. Examples are: CH_2, CH_3CH, CH_3CCH_3. Several claims have been made that the methylene radical has been isolated. Staudinger and Kupfer (35) indicated its transitory existence by decomposing diazomethane in carbon monoxide and obtaining ketene. This was represented by the following equations:

$$CH_2{=}N{\equiv}N \rightarrow N_2 + CH_2$$

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

Paneth has recently reported (19) that he was unable to isolate this radical by the reaction

$$CH_2Cl_2 + 2Na \rightarrow 2NaCl + CH_2$$

whereas Belchetz (2) has reported its isolation by the thermal decomposition of methane. Rice and Glasebrook (23) reported the isolation of the methylene radical by decomposing diazomethane at low temperatures and passing the products over tellurium mirrors. At high temperatures the methylene radicals disappeared and were replaced by methyl groups. More recent work in this laboratory[2] has thrown doubt on Rice and Glasebrook's earlier work, since cold diazomethane vapor appears to react with the tellurium vapor over a hot tellurium mirror to form telluroformaldehyde. When experiments were performed under conditions such that this

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[1] Unpublished work.

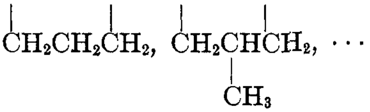
[2] Unpublished work by Rice and Bongiorni.

error was avoided, only methyl groups came out of the furnace. Thus even with pure diazomethane in pure nitrogen, methyl groups were obtained and carbon was deposited in the furnace. Similar experiments using methane or diethyl ether as carrier gas also yielded only methyl groups, so that it now appears that this radical is so exceedingly reactive that it will be very difficult to obtain it by the Paneth technic. It seems clear from attempts made to prepare the ethylidene radical that it has at best an exceedingly short life and isomerizes with great readiness to give ethylene. Probably all the 1,1-divalent radicals undergo this type of isomerization very easily.

(*c*) *1,2-Bivalent.* These are the ethylene series of hydrocarbons. They do not show the reactions of free radicals towards metals, as might be expected if they existed in an "opened up" form (11):

$$\overset{|}{\mathrm{C}}\mathrm{H_2}\text{—}\overset{|}{\mathrm{C}}\mathrm{H_2} \qquad\qquad \mathrm{CH_3}\overset{|}{\mathrm{C}}\mathrm{H}\text{—}\overset{|}{\mathrm{C}}\mathrm{H_2}$$

(*d*) *1,3-Trivalent.* These may be represented by the formulas



$$\overset{|}{\mathrm{C}}\mathrm{H_2CH_2}\overset{|}{\mathrm{C}}\mathrm{H_2},\ \overset{|}{\mathrm{C}}\mathrm{H_2}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2},\ \cdots$$

The decomposition of cyclopropane[3] does not cause removal of metallic mirrors, from which it may be inferred that if this radical is formed at all, the isomerization,

$$\overset{|}{\mathrm{C}}\mathrm{H_2CH_2}\overset{|}{\mathrm{C}}\mathrm{H_2} \quad \rightarrow \quad \mathrm{CH_3CH{=}CH_2}$$

occurs very easily; probably this is true also for its homologs.

(*e*) *1,4-Bivalent.* The simplest member of this series, $\text{—}\mathrm{CH_2CH_2CH_2CH_2}\text{—}$, might be expected to be formed in the decomposition of cyclobutane. Possibly it isomerizes very easily to butene-2, or possibly it decomposes to ethylene. The decomposition of cyclobutane does not appear to have been studied experimentally.

(*f*) *Trivalent hydrocarbon radicals.* Nothing appears to be known chemically of the behavior of 1,1,1 radicals such as CH, or 1,1,2 radicals such as the vinyl radical, $\text{—}\mathrm{CH_2}\text{—}\mathrm{CH}{=}$. The trivalent radical, $\overset{|}{\mathrm{C}}\mathrm{H_2}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{H_2}$ and its homologs have been studied theoretically (28), and it has been found possible to give a satisfactory account of the thermal decompositions of the olefin hydrocarbons by assuming the intermediate formation of these radicals.

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[3] Unpublished work by Rice and Glasebrook.

It may be of interest to list some of the various types of radicals that contain oxygen. These are formed by removal of a hydrogen atom from an alcohol, aldehyde, ether, ketone, etc.

Oxo radical	*Examples*
$R{-}O{-}$	CH_3O, CH_3CH_2O
$R\overset{\vert}{C}HOH$	CH_2OH, CH_3CHOH
$RO\overset{\vert}{C}H_2$	CH_3OCH_2, $CH_3CH_2OCH_2$
$ROCH_2\overset{\vert}{C}H_2$	$CH_3OCH_2CH_2$, $CH_3CH_2OCH_2CH_2$
$R\overset{\vert}{C}{=}O$	HCO, CH_3CO, CH_3CH_2CO
$R\overset{\vert}{C}HCHO$	CH_2CHO, CH_3CHCHO

The isolation and study of these radicals is work that lies in the future. Possibly the solution of the problems of organic reactions lies in measurements of the activation energies of radical–molecule reactions and radical decompositions and interactions.

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