The Role of Free Radicals in Elementary Organic Reactions

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The primary reactions between radicals and organic molecules are discussed from the point of view of a principle which states that there shall be least change in atomic position and least change in electronic configuration during an elementary reaction. We have concluded that alkyl radicals will attack most easily exposed positive atoms, i.e., in organic molecules, the hydrogen atoms. The attack on exposed negative atoms such as N, O or Cl is less probable whereas a completely shielded carbon atom should certainly not be attacked in the primary step. A doubly or triply bonded carbon atom can, however, react with a radical. These statements are discussed from the experimental point of view, together with the question as to when it is necessary to assume that organic reactions proceed through radical chains.

1. Introduction

ONE of the questions in connection with the thermal decomposition of organic compounds is whether the product molecules are formed in a single elementary act or through some sort of radical chain mechanism or whether both processes occur simultaneously to an appreciable extent. If we assume a radical mechanism, there are a great many more possibilities than with a non-radical mechanism and this leads to one evident objection: we know so little about radicals that we might postulate any sort of reaction and thereby could attribute any effect to them. However, our experience is not altogether so small and we can learn something about them from chemical physics and compare the results with the chemical behavior.

In this paper we shall try to consider how our chemical experience with organic molecules and free radicals can be summed up in terms of shielding effects and effects connected with the electronic structures of the reacting particles. The views expressed, however, are not intended to be definite statements of how molecules and radicals react; it is our intention to consider how strongly we can restrict the properties of radicals and to discuss some of the various possible reaction schemes, emphasizing those that are not in disagreement with organic experience and with chemical physics.[1]

[1] We have not attempted a quantitative treatment of these problems such as that of Eyring and Polanyi, Zeits. f.

2. Principle of Least Motion [2]

It is most desirable that the activation energy necessary to bring the atoms from the old to the new positions be as small as possible and, in general, this is fulfilled if there be as little motion as possible in passing from the old to the new configuration. The principle of least motion is a statement of certain conditions that favor a low activation energy and this principle will be discussed from the standpoint of least motion of (a) the atoms and (b) the electronic configuration of the reacting system. From both these standpoints it is plausible to assume that in general the activation energy of an elementary reaction will be smaller if not many bonds have to be broken.

(a) From the first standpoint, in order for maximum gain of resonance energy to occur, it is necessary for the atoms of the system to move through a considerable fraction (approximately half) of the distance towards the configuration which they will have after the new bond forms.

physik. Chemie **B12**, 279 (1931). The practical application of such calculations seems to us to be valuable only insofar as they suggest qualitative ideas. To draw quantitative conclusions from them is extremely difficult because the approximations which must be made in order to make the calculations feasible are of the same order of magnitude as the quantities calculated.

[2] Statements very similar to that which we call the principle of least motion have been proposed by Franck and Rabinowitch, Zeits. f. Elektrochem. **36**, 794 (1930). Calculations of Eyring and collaborators, J. Am. Chem. Soc. **54**, 2661, 3876 (1932) on the reaction complexes also contain this principle in an implicit form.

The energy necessary to do this can be estimated from the known vibrations of the original molecules together with the contribution of the van der Waals energy. In this connection we note that it takes about four or five times more energy to make a displacement along the direction of a bond, stretching the bond thereby, then to make the same displacement perpendicular to the direction of the bond, merely changing the valence angle; and that as the nuclei move further from their equilibrium positions the energy required becomes greater with displacements according to a quadratic law. Thus it is most desirable that there should be little change of the position of atoms and in particular little change in the valence distance while passing from the old to the new configuration.

(b) From the second standpoint, if the atoms have assumed a configuration similar to the one where the new bonds can be written, i.e., to a point about halfway between the initial and final configuration, the electronic configuration becomes important; if the electron orbits do not have to change much in order to get from the old to the new valence picture we will have a strong resonance and a lowered activation energy.

The principle of least motion is illustrated in Fig. 1. The abscissae correspond to atomic configurations, point A being the configuration before and point B the configuration after the reaction. The ordinates show the potential energies corresponding to each atomic configuration. Curve I represents the potential energies to be expected if the bonds (electron orbits) remain as they have been in the original configuration A. Curve II shows the potential for the bonds arranged as they are in the final state B.

At the crossing point C the same energy will correspond to two different electronic configurations. This resonance will lower the energy as is shown in Fig. 1 by the dotted curve. Thus we may expect a low activation energy if (a) the distance AC is small (principle of least motion of the atoms), if (b) the lowering of the energy by resonance is great; one necessary condition for the latter is that the spacial distribution of the electrons for the two resonating valence systems should not be very different (principle of least motion of the electronic configuration).

3. REACTIONS OF RADICALS WITH POSITIVE ATOMS

A reaction of this type in which a univalent radical R reacts with a hydrocarbon such as ethane is,

$$R + C_2H_6 \rightarrow RH + CH_3CH_2. \tag{1}$$

The radicals which most commonly come into question according to chemical experience are methyl and ethyl groups or hydrogen atoms; larger radicals are very unstable and in any case would behave in the same way.

(a) From the standpoint of least motion of the atoms everything is in favor of reaction (1). Inasmuch as the positive atoms of an organic molecule are on the periphery, a minimum of atomic motion is required. If R is a methyl radical,[3] the three hydrogen atoms are probably in a plane with the carbon atom and therefore must approach the tetrahedral position before the new bond forms. This is discussed in the following paragraph.

(b) Reaction (1) is also favored from the standpoint of least motion of electronic configuration. The unshared electron of the methyl radical "moves" perpendicularly and is outside the plane of the three hydrogen atoms. We would expect that as the methyl group approaches an organic molecule it becomes polarized, the free electron is drawn to one of the protons and the three C−H bonds of the methyl are repelled by the orbit of the unshared electron and bend away. The form

$$R \cdots H \cdots CH_2CH_3 \tag{2}$$
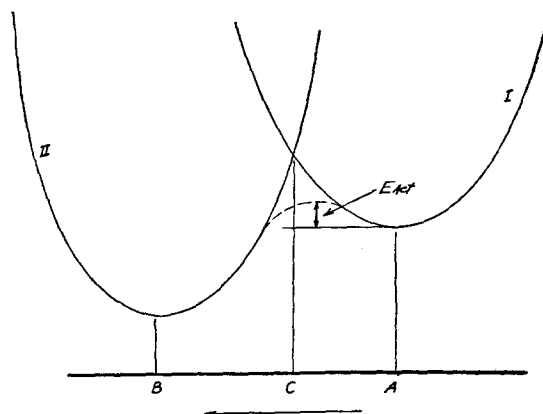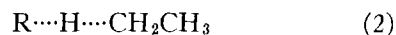
[3] Penney, Trans. Far. Soc. 31, 734 (1935); see, however, Nordheim-Pöschl, Ann. der Physik 26, 258 (1936).

intermediate between the two forms in reaction (1) can therefore probably be formed with a relatively low activation energy.

Another type of reaction of a radical with a positive atom is illustrated by the equation

$$
\begin{array}{cc}
\quad\quad\quad\quad\text{H} & \quad\text{H} \\
-CH_2CH_3 + C_2H_6 \rightarrow CH_2\text{:}\text{:}C\cdots H\cdots H\cdots CCH_3 \\
\quad\quad\quad\quad\text{H} & \quad\text{H}
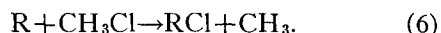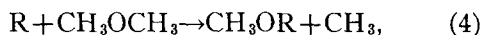\end{array}
$$

$$
\rightarrow CH_2 = CH_2 + H_2 + -CH_2CH_3. \quad (3)
$$
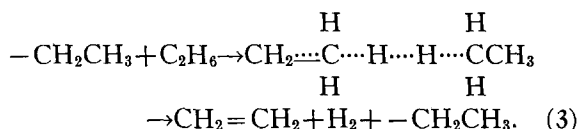
In this case not only are two bonds broken but also saturated parts of the compounds get into contact with each other preceding the reaction; it seems probable from both the (a) and (b) standpoints that the simpler reaction (1) will have a lower activation energy.

4. REACTIONS OF RADICALS WITH EXPOSED NEGATIVE GROUPS

Examples of this type of reaction are given by ethers, amines and halogen compounds.

$$
R + CH_3OCH_3 \rightarrow CH_3OR + CH_3, \quad (4)
$$

$$
R + CH_3NH_2 \rightarrow RNH_2 + CH_3, \quad (5)
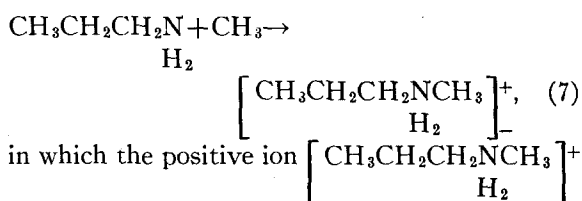$$

$$
R + CH_3Cl \rightarrow RCl + CH_3. \quad (6)
$$

(a) Since there is very little shielding effect in any such reactions we can say, from the standpoint of least motion of the atoms, that there may always be attack on exposed negative atoms.

(b) We should expect that the resonance factor would be less favored in reactions (4), (5), and (6) than in reaction (1) because of the following reason: The negative atom (O, N or Cl) repels the unshared radical electron; on the other hand because of the partially polar nature of the bond to be formed, the radical electron will be shifted in the reaction product towards the negative group. Thus the radical electron has widely differing positions at the beginning and the end of the reaction. Although, according to this consideration, the principle of least motion of the electrons does not favor the attack of radicals on negative groups we do not think that on the basis of this reasoning alone we can definitely exclude such reactions. Also from the experimental point of view this type of reaction has not been excluded definitely since even if the exposed negative groups would be attacked by methyl radicals, this

could not be noticed unless the reaction complex splits off a radical different from the original one.

The attack of a radical on, for example, n-propylamine may be represented as first forming an intermediate complex,

$$
CH_3CH_2CH_2N + CH_3 \rightarrow
$$
$$
\begin{array}{c}
H_2 \\
\left[\begin{array}{c} CH_3CH_2CH_2NCH_3 \\ H_2 \end{array} \right]^+_-, \quad (7)
\end{array}
$$

in which the positive ion $\left[\begin{array}{c} CH_3CH_2CH_2NCH_3 \\ H_2 \end{array} \right]^+$

is combined with an electron moving in an outer orbit instead of with a negative ion. The tendency of the negative atom to push away the radical electron will in this case produce an electron configuration approaching that of the final product. The reaction product in (7) has an ionic nature but there is probably no actual dissociation so that it would not be possible to prove its existence experimentally by testing for free electrons; the ionic form in (7) may, however, decompose into a free radical and a molecule differing from those out of which it was built up so that an experimental test could be made by adding methyl radicals to higher amines. Another experimental test would be to look for absorption in the visible or near ultraviolet during the reaction since the loosely bound electron would probably give rise to absorption of relatively long wave-length; however, such experiments do not permit one to distinguish between the different possible kinds of attack on the negative group. A reaction of type (7) could also occur with organic oxygen compounds with formation of oxonium compounds but this is presumably much less likely than with nitrogen.

The somewhat inadequate experimental evidence available indicates that free radicals do not react to an appreciable extent with exposed negative groups. The decomposition of n-propylamine appears to proceed through a chain reaction [4] but a careful examination of the products of the partially decomposed material indicated the absence of lower amines.[5] Also methyl ethyl ether was decomposed by the introduction of methyl radicals and dimethyl ether was found to be

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[4] Sickman and O. K. Rice, J. Am. Chem. Soc. 57, 22 (1935).

[5] Unpublished work by F. O. Rice and P. M. Ruoff.

absent [6] from the products proving that the reaction,

$$CH_3+CH_3OCH_2CH_3 \rightarrow CH_3OCH_3+CH_3CH_2 \quad (8)$$
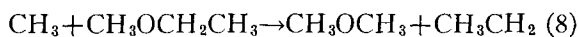
did not occur to an appreciable extent. The experimental results with n-propylamine and methyl ethyl ether indicate that if there is any formation of ammonium or oxonium ions, it is followed by redissociation into the original parts.

5. REACTIONS OF RADICALS WITH SHIELDED NEGATIVE GROUPS

An example of this type of reaction is,

$$R+CH_3CH_3 \rightarrow R-CH_3+CH_3. \quad (9)$$
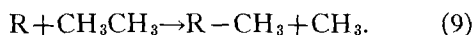
(a) From the standpoint of least motion of the atoms, there seems to be an insuperable objection to any reaction similar to Eq. (9), even in the case where R is a hydrogen atom. The shielding effect of the hydrogen atoms or other groups surrounding the carbon atom that is being attacked is so powerful that it seems extremely improbable that a radical can combine with a carbon atom in a paraffin hydrocarbon.

In order to obtain an estimate of this shielding effect, we will consider the exchange reaction between a hydrogen atom and methane. We will calculate the energy required to push three of the $C-H$ bonds of methane into a plane since we may assume that at least this amount of motion of the three hydrogen atoms must occur before the new bond can form. This we will do in two steps which we do not consider as taking place in succession but actually simultaneously. Our reason for separating the process into these two steps is that in this way we can deal in the first step with those effects for which a fair estimate is possible. This first step will consist in pushing the three $C-H$ bonds of methane into the same plane with the carbon in order to make room for the new substituent which we shall add in the second step.

Methane has four proper vibrations but only in one, namely in that of 1304 wave numbers do the atoms move strongly towards the configuration where three hydrogen atoms lie in the same plane with the carbon. In this vibration, the $C-H$

[6] Unpublished work by F. O. Rice and W. D. Walters.

distances remain approximately constant but the valence angles change considerably. We shall make two approximations, (1) that the mass of the carbon is infinite and (2) that the three hydrogen atoms move in a direction parallel to the line joining the fourth hydrogen to the carbon; this involves errors of about ± 10 percent. The anharmonicity of the forces during this fairly large displacement has also been neglected.

Combining the equation for the relation between the frequency and mass of the hydrogen atom,

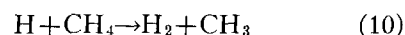$$\nu = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{\frac{1}{2}}$$

with the equation for its potential energy as a function of distance,
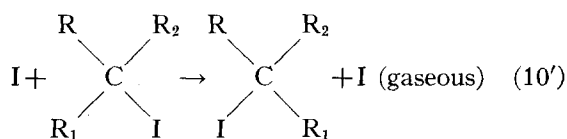
$$E = \frac{1}{2}kx^2$$

and remembering that there are three hydrogen atoms, we obtain

$$3E = 6\pi^2 m\nu^2 x^2.$$

The value of x is $1.09 \times \frac{1}{3} = 0.36A$ and after making the other substitution we obtain $3E = 40$ Cal. per mole which is the energy required to push the three hydrogen atoms into a plane. After the methane molecule has been distorted, a hydrogen atom is brought into position at the antipole of the fourth hydrogen atom of the original molecule and the fourth hydrogen atom itself is then expelled; this is analogous to the well-known hydrogen exchange reaction, $H+H_2 \rightarrow H_2+H$. We should not expect therefore any very strong attraction between the distorted CH_4 and the oncoming hydrogen atom; indeed even a slight repulsion is more probable. Thus the whole reaction will probably not have a much lower activation energy than 40 kcal., whereas the measured activation energy for

$$H+CH_4 \rightarrow H_2+CH_3 \quad (10)$$

is less than 20 kcal. It should however be mentioned in this connection that the similar reactions

$$I+ \begin{matrix} R & & R_2 \\ & \diagdown\diagup & \\ & C & \\ & \diagup\diagdown & \\ R_1 & & I \end{matrix} \rightarrow \begin{matrix} R & & R_2 \\ & \diagdown\diagup & \\ & C & \\ & \diagup\diagdown & \\ I & & R_1 \end{matrix} +I \text{ (gaseous)} \quad (10')$$

and

$$I^- + \begin{array}{c} R \\ \diagdown \\ \diagup \\ R_1 \end{array} C \begin{array}{c} R_2 \\ \diagup \\ \diagdown \\ I \end{array} \rightarrow \begin{array}{c} R \\ \diagdown \\ \diagup \\ I \end{array} C \begin{array}{c} R_2 \\ \diagup \\ \diagdown \\ R_1 \end{array} + I^- \text{ (solution)} \qquad (10'')$$

seem to proceed[7] with activation energies in the range 14–18 kcal. However it is not impossible that the first of these reactions is really more complicated, taking place actually on the walls whereas in the second case, the attraction between the iodine ion and the substrate molecule may appreciably lower the actual activation energy that is needed.

(b) From the standpoint of least motion of the electrons, the arguments that might be used are similar to those given in Section 4 (b) for the attack of a free radical on *exposed* negative groups. However such arguments are less valid here because carbon is only slightly negative; moreover the principle of least motion of the atoms excludes the reaction so definitely that it seems unnecessary to discuss the question from the standpoint of electronic structure.

6. REACTIONS OF RADICALS WITH UNSATURATED COMPOUNDS

Examples of this type of reaction are found in the great variety of polymerization reactions that occur. For example, when methyl radicals are produced in the presence of ethylene,[8] a reaction occurs as follows,

$$CH_3 + CH_2 = CH_2 \rightarrow CH_3CH_2CH_2 \qquad (11)$$
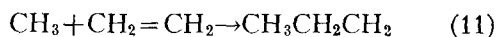
and this building up process continues until the large radicals combine or disproportionate. The effect is shown by many unsaturated hydrocarbons but not by paraffin hydrocarbons; it also occurs with formaldehyde but not with acetaldehyde or acetone.[9]

(a) From the standpoint of least motion of the atoms, it is clear that the shielding effect of the

[7] Bergmann, Polanyi and Szabo, Zeits. f. physik Chemie **20B**, 161 (1933); Ogg and Polanyi, Trans. Far. Soc. **31**, 482 (1935).

[8] Taylor, Proc. Am. Phil. Soc. **65**, 90 (1926); Taylor and Jones, J. Am. Chem. Soc. **52**, 1111 (1930).

[9] Sickman and Allen, J. Am. Chem. Soc. **56**, 1251 (1934); see, however, Blacet and Volman, J. Am. Chem. Soc. **60**, 1243 (1938). Leermakers, J. Am. Chem. Soc. **56**, 1899 (1934).

hydrogen atoms is not present to the same degree as in paraffin hydrocarbons and the situation so far as atomic motion is concerned is somewhat analogous to the reactions with exposed negative groups discussed in Section 4. However substitution of the hydrogen atoms in ethylene, by radicals, should increase the difficulty of reaction and it has been found experimentally[10] that the rate of polymerization of propylene $CH_3CH = CH_2$ by methyl radicals is only about one-tenth the rate of ethylene. Similarly the substitution of one or two hydrogen atoms in formaldehyde by methyl groups to give acetaldehyde and acetone, respectively, greatly diminishes the tendency to polymerize.

(b) From the standpoint of formation of a homopolar bond, the first action is in a slightly unfavorable sense because the approach of the methyl or other radical to the dense electron cloud surrounding the doubly bound carbon atoms, induces a dipole in the radical and its free electron is repelled; this effect, however, is not as unfavorable as the similar one in the case of exposed negative groups. The induced dipole is smaller and the final product is homopolar so that the difference in electron position at the beginning and end of the reaction will be here appreciably less than for the negative groups. This same contrast between the behavior of a double bond and a negative group may also be brought out in the following way. A bond such as $N-R$, $O-R$ or $Cl-R$ can be formed only by the radical donating an electron, that is reducing the negative atom; this as we have seen meets with difficulties. In case of attack on a double bond, the alternative possibility exists, namely that the methyl group can draw out an electron from the double bond. This will depend on the electron affinity of the methyl group; it is certainly less oxidizing than chlorine and could not therefore draw an electron from chlorine; however, the fact that double and triple bonds are readily oxidized suggests that the methyl radical may be in this case regarded as analogous to an oxidizing agent and can accept an electron from the double bond. The widely spread electronic structure of the double bond and its high polarizability would aid this possibility. Of course this process

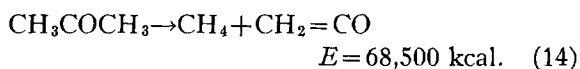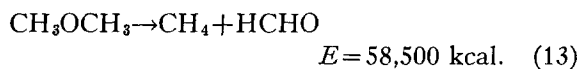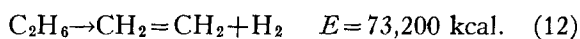[10] Private communication from Dr. D. V. Sickman.

of oxidizing the double bond should not be taken too literally since the bond to be formed is homopolar; the electron to be drawn out from the double bond will get only to about half the distance between the two groups so that one cannot say whether the radical or the double bond is really oxidized.

Another difference between the attack on negative groups and the addition reactions is that in the latter energy is liberated during the addition, whereas in the former the energy change during the reaction is negligible. It will be seen from Fig. 1 that if in the reaction, energy is gained (i.e., if point B is lower than point A) then the activation energy for the reaction (starting from A) will be lowered.

These factors will tend to make the activation energy for the addition reactions smaller than the activation energy for the attack on negative groups.

7. DECOMPOSITION OF SMALL ORGANIC MOLECULES

It is convenient to consider first the decomposition of smaller molecules of not more than four or five atoms in a chain. The following equations represent the chemical course of the reactions for some typical smaller organic molecules; the measured activation energies for the over-all reactions are also included.
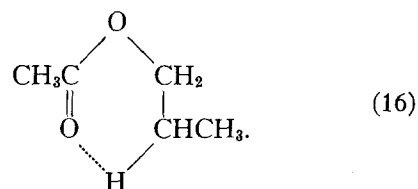
$$C_2H_6 \rightarrow CH_2 = CH_2 + H_2 \quad E = 73,200 \text{ kcal.} \quad (12)$$

$$CH_3OCH_3 \rightarrow CH_4 + HCHO$$
$$E = 58,500 \text{ kcal.} \quad (13)$$

$$CH_3COCH_3 \rightarrow CH_4 + CH_2 = CO$$
$$E = 68,500 \text{ kcal.} \quad (14)$$

$$CH_3CHO \rightarrow CH_4 + CO \quad E = 45,500 \text{ kcal.} \quad (15)$$

Considering first reactions (13), (14) and (15), the direct molecular decomposition may proceed in one of two ways: either a $C-H$ bond is broken first, the hydrogen atom migrates through a rather long distance to another part of the molecule and reacts there with a shielded carbon atom (according to our previous considerations it is highly unlikely that this could happen with the activation energies found experimentally which in the first place would have to exceed the energy of the $C-H$ bond); or one may assume

that a $C-O-$bond in (13) or a $C-C$ bond in (14) and (15) is broken first and that the radicals formed in that way rotate and recombine. In this case the expected activation energies would not be much greater than those found; however once the radicals are formed, the chain mechanism seems to be the more likely one.

The decomposition of ethane according to Eq. (12) is by no means so unlikely as the reactions represented in (13), (14) and (15). Although two $C-H$ bonds have to be broken, the energy of an $H-H$ bond and the energy difference between a double and a single bond may be gained without moving the atoms through very large distances. Even so we believe that the radical mechanism is the more probable alternative.

8. DECOMPOSITION OF CHELATE COMPOUNDS

In those cases of large organic molecules with exposed negative groups or with double or triple bonds, the principle of least motion of the atoms suggests the possibility of a direct intramolecular decomposition into product molecules. The pyrogenic decomposition of esters and acetals has been studied experimentally [11] and the possibility has been considered of the ester decomposition proceeding through an intracyclic compound. This may be illustrated for n-propyl acetate by the equation,
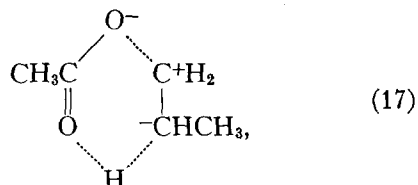
$$
\begin{array}{c}
O \\
CH_3C \diagup \quad \diagdown CH_2 \\
\| \qquad\qquad | \\
O \qquad\quad CHCH_3. \\
\diagdown \qquad \diagup \\
H
\end{array}
\qquad (16)
$$

For this type of decomposition to occur, the radical R' in an ester R COOR', must have at least two carbon atoms and also a chemical structure such that a substituted ethylene or other molecule can split off.

Equation (16) seems however to meet an objection from the point of view of least motion of electrons, since in this case also the electron of the hydrogen atom will be repelled while approaching the oxygen atom of the carbonyl

[11] Sielisch & Grund, *Uber den Mechanismus intra-und intermoleculare Reaction,* (Verlag Walters Blank, Berlin, 1932); Bilger and Hibbert, J. Am. Chem. Soc. **58**, 823 (1936). See in this connection, Kassel, J. Chem. Phys. **1**, 749 (1933); O. K. Rice and Gershinowitz, ibid., **3**, 486 (1935).

group and thus the formation of a homopolar bond will be made more difficult. On the other hand the reaction is helped on by the fact that the initial state is in resonance with the electron configuration

$$
\begin{array}{c}
\text{O}^- \\
\text{CH}_3\text{C} \quad\quad \text{C}^+\text{H}_2 \\
\text{O} \quad\quad {}^-\text{CHCH}_3, \\
\text{H}
\end{array}
\tag{17}
$$

which provides an intermediate step to the electron configuration of the final product. The broken valence bonds may be regarded as purely electrostatic. The same sort of reasoning may be applied to other similar reactions (Eqs. (18) to (22)). We may expect therefore that the direct decomposition of esters into product molecules will occur to a greater or less extent even to the almost complete exclusion of the radical chain process.[12] Indeed this appears to be the case for the thermal decomposition of esters of the general formula $(R'\,COO)_2CHR$ which decompose homogeneously in the gaseous state giving an aldehyde and an acid anhydride.[13] These esters decompose at a measurable rate in the temperature range 200–300°C and have an activation energy of approximately 33,000 Cal. The decomposition may be represented as follows:
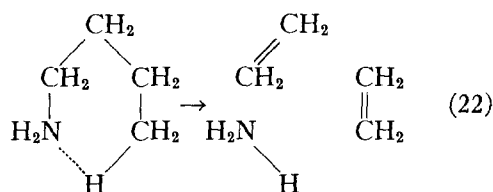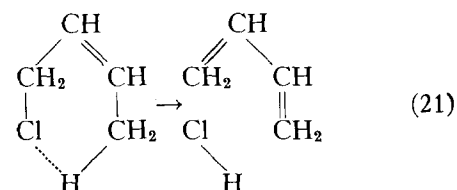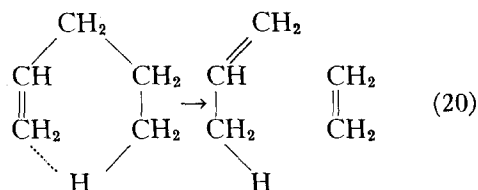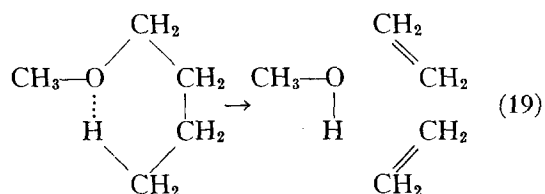
$$
\begin{array}{c}
\text{O} \quad\quad \text{O}^- \\
\text{CH}_3\text{CH} \quad \text{CR}' \quad \text{CH}_3\text{C}^+\text{H} \quad \text{C}^+\text{R}' \\
\text{O} \quad\quad \text{O} \quad\rightarrow\quad \text{O}^- \quad\quad \text{O}^- \quad\rightarrow \\
\text{C} \quad\quad\quad\quad \text{C} \\
\text{O} \quad \text{R}' \quad\quad \text{O} \quad \text{R}'
\end{array}
$$

$$
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{CH} \quad\quad \text{CR}' \\
\text{O} \quad\quad\quad \text{O} \\
\text{C} \\
\text{O} \quad \text{R}'
\end{array}
\tag{18}
$$

Indeed this reaction proceeds more easily than any other mentioned in this group. In this case, from the point of view of electronic structure, the first action is in a favorable sense; the positive carbon atom attracts the electron of the neighboring negative oxygen. Also in the intermediate structure all the negative ions are oxygen ions which will form more easily than the negative carbon ions used in (17).

Many other decompositions of this type may be given and a few examples are shown in the following equations:

$$
\begin{array}{c}
\text{CH}_2 \quad\quad\quad\quad \text{CH}_2 \\
\text{CH}_3\text{—O} \quad \text{CH}_2 \quad \text{CH}_3\text{—O} \quad \text{CH}_2 \\
\text{H} \quad\quad \text{CH}_2 \quad\rightarrow\quad \text{H} \quad\quad \text{CH}_2 \\
\text{CH}_2 \quad\quad\quad\quad \text{CH}_2
\end{array}
\tag{19}
$$

$$
\begin{array}{c}
\text{CH}_2 \quad\quad\quad\quad \text{CH}_2 \\
\text{CH} \quad \text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \\
\text{CH}_2 \quad \text{CH}_2 \quad\rightarrow\quad \text{CH}_2 \quad \text{CH}_2 \\
\text{H} \quad\quad\quad\quad \text{H}
\end{array}
\tag{20}
$$

$$
\begin{array}{c}
\text{CH} \quad\quad\quad\quad \text{CH} \\
\text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} \\
\text{Cl} \quad \text{CH}_2 \quad\rightarrow\quad \text{Cl} \quad \text{CH}_2 \\
\text{H} \quad\quad\quad\quad \text{H}
\end{array}
\tag{21}
$$

$$
\begin{array}{c}
\text{CH}_2 \quad\quad\quad\quad \text{CH}_2 \\
\text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{H}_2\text{N} \quad \text{CH}_2 \quad \text{H}_2\text{N} \quad \text{CH}_2 \\
\text{H} \quad\quad\quad\quad \text{H}
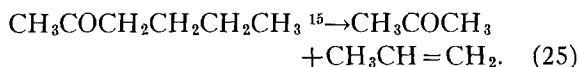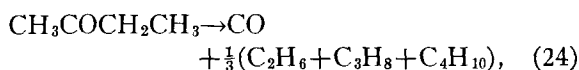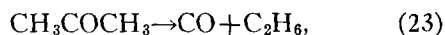\end{array}
\tag{22}
$$

Such thermal decompositions have not been studied very extensively, and not very much is known concerning them.

However, there is more evidence on the photochemical decomposition of higher ketones and aldehydes. Since light acts primarily on the electrons, the principle of least motion of the atoms must be upheld for the primary photochemical process; indeed it becomes in this case identical with the Franck-Condon principle stating that during light absorption, the position of the heavy

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[12] See in this connection Hurd and Blunck, Abstract read at Chapel Hill meeting Am. Chem. Soc., April, 1937; Hurd, Seventh Organic Symposium, 1937.

[13] Coffin, Can. J. Research 5, 636 (1931); idem., Trans. Roy. Soc. Can., Section III, 27, 161 (1933); Dacey and Coffin, Can. J. Research, 15, 260 (1937).

particles should not change. This rule holds for the primary photochemical process much more strictly than the principle of least motion of atoms in thermal decompositions. On the other hand, light absorption may change the electronic configuration essentially, and thus invalidate the principle of least motion of electrons.

The over-all equations for the photochemical decomposition of the following three ketones may be represented as follows:[14]

$$CH_3COCH_3 \rightarrow CO + C_2H_6, \quad (23)$$

$$CH_3COCH_2CH_3 \rightarrow CO + \tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}), \quad (24)$$

$$CH_3COCH_2CH_2CH_2CH_3 \; [15] \rightarrow CH_3COCH_3 + CH_3CH=CH_2. \quad (25)$$

These results indicate that the lower ketones undergo a primary decomposition into radicals which combine to give hydrocarbons whereas higher ketones decompose in the primary step according to the equation:

$$(26)$$
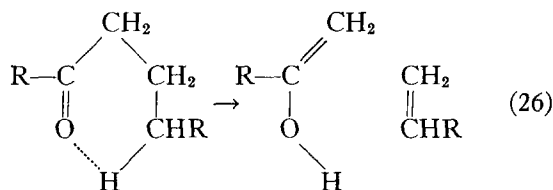
followed by isomerization on the wall or in the condensate, of the enolic form of the ketone to the ordinary form, CH_3COR. With more complicated higher ketones and aldehydes both processes occur[16] but this might be expected since there would be some shielding effect of the negative oxygen atom. We may note that the conclusion that aldehydes decompose mainly in one act according to the equation [17] $RCHO \rightarrow RH + CO$ is in disagreement with the conclusions of Section 7.

9. EXPERIMENTAL OBJECTIONS

There are a number of experimental results,[18] such as the enlargement of rings by the use of diazomethane, that appear to contradict the views expressed in the preceding sections. Since this reaction and many others occur in solution and require a consideration of the effect of solvent, acid or basic catalysts, etc., we will omit from consideration all reactions that occur in condensed systems. However, there are two gaseous reactions that require some discussion because they appear to lead to the conclusion that shielded carbon atoms are subject to attack by radicals.

The effect of deuterium atoms on ethane has been recently studied [19] and the authors concluded that the main reaction could be represented by the equation,

$$D + C_2H_6 \rightarrow CH_3 + CH_3D.$$
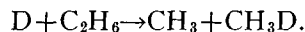
This is an example of reaction (9) which we have rejected mainly on the ground of the shielding effect of the hydrogen atoms surrounding the carbon atoms. However, we have discussed this question with Professor Taylor and an interpretation of his experiments consistent with the scheme presented in our paper has proved to be possible; Professor Taylor will discuss this question in a future paper.

The second reaction occurs in the decomposition of the n-heptyl radical which appears to decompose in part to give a ring hydrocarbon, possibly cyclohexane.[20] Presumably the radical polymerization of olefins yields naphthenic hydrocarbons by a similar mechanism. A unimolecular decomposition of the heptyl radical into cyclohexane and a methyl radical would mean an attack by the open end of the radical on a shielded carbon atom. However, it is possible that an attack by another radical might remove a second hydrogen atom from an appropriate position and thus lead to ring closure. Also in this case both the reaction mechanism and the final products are not very well known and so definite conclusions cannot be reached at present.

[14] Norrish, Crone and Saltmarsh, J. Chem. Soc. 145 (1934); Spence and Wild, ibid., 352 (1937) have shown that below 60°C, diacetyl is formed, so that presumably the primary step is formation of methyl and acetyl radicals.

[15] Norrish and Appleyard, J. Chem. Soc. 874 (1934).

[16] Bamford and Norrish, J. Chem. Soc. 1504 (1935).

[17] Norrish and Bamford, Nature 140, 195 (1937); Norrish and Kirkbride, J. Chem. Soc. 1518 (1932); Norrish, Trans. Far. Soc. 30, 107 (1934); idem., Acta Physica Chemica URSS, 3, 171 (1935).

[18] Mosettig and Burger, J. Am. Chem. Soc. 53, 2295 (1931); Robinson and Smith, J. Chem. Soc. 371 (1937).

[19] Trenner, Morikawa and Taylor, J. Chem. Phys. 5, 203 (1937). See also Chadwell and Titani, J. Am. Chem. Soc., 55, 1363 (1933); Steacie, J. Chem. Phys., 6, 37 (1938).

[20] Rice and Polly, Ind. Eng. Chem. 27, 915 (1935).