THE THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS FROM THE STANDPOINT OF FREE RADICALS. I. SATURATED HYDROCARBONS

BY F. O. RICE

When an organic compound decomposes, we may assume that it is broken up into two or more radicals depending on the number of bonds in the molecule. These radicals fly apart and the probability that they meet again and react is so small that we can neglect it. A radical produced in this way may do one of three things: first, it may react with one of the surrounding molecules; second, it may decompose into a compound and a smaller radical; or, third, it may diffuse to the wall and be absorbed there. In order to simplify our problem we will consider only a small fractional decomposition (a maximum of 5 to 10%) of the organic compound. Under these conditions the radicals produced can react only with the original substance and our problem is much less complicated. On the other hand, if we allow the organic compound to decompose to a considerable extent, the radicals react not only with the original compound but also with the products of the reaction, and the whole problem becomes hopelessly involved.

We can proceed with some confidence to examine the mechanism of the decomposition of organic compounds from this point of view because the actual existence of the simple alkyl radicals has now been demonstrated. Paneth and Hofeditz[1] heated lead tetramethyl in a rapid current of hydrogen and showed that the methyl groups were carried along the tube and could be made to react as far as 40 cm. from their point of origin. A later report by Paneth and Lautsch[2] stated that by means of similar experiments they had been successful in preparing the free ethyl radical. Less direct, although equally convincing, experiments have been made by Taylor and Jones,[3] in which they initiated the polymerization of ethylene by ethyl groups formed in the decomposition of lead or mercury alkyls.

The necessity for the use of free radicals in explaining the mechanism of organic decompositions becomes very evident even in the decompositions of fairly simple organic compounds. Propane decomposes into propylene and hydrogen, and it is conceivable that this occurs by the separation of a hydrogen molecule formed by two hydrogen atoms from adjacent carbon atoms; but it also breaks up into methane and ethylene, and for this to occur a hydrogen atom must jump from a 1 position to a 3 position, a

[1] Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

[2] Paneth and Lautsch, *Nature*, **125**, 564 (1930).

[3] Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).

behavior which to say the least would be very remarkable.[4] Even more improbable mechanisms must be used to represent the decomposition of more complicated compounds.

When a paraffin hydrocarbon decomposes, we may assume that a C–C bond or a C–H bond breaks, and that this occurs in different ways depending on the complexity of the molecule. In order to determine the nature of the different fragments it is necessary to obtain an estimate of the strength of the different bonds present. From thermochemical measurements,[5] the heat of formation of methane from gaseous carbon and gaseous hydrogen atoms is

$$C_g + 4H_g \longrightarrow CH_{4g} + 373.2 \text{ kg. cal.}$$

which gives for the strength of the C–H bond in methane the value 93.3 kg. cal. A similar calculation for ethane gives

$$2C_g + 6H_g \longrightarrow C_2H_{6g} + 630.8 \text{ kg. cal.}$$

The strength of the C–H bonds in ethane will probably be slightly less than that of the C–H bonds in methane, but for the purpose of calculating the strength of the C–C bond we may assume that the C–H bond in methane and ethane has the same strength; there are six C–H bonds in ethane so that the strength of the C–C bond in ethane is $630.8 - (6 \times 93.3) = 71.0$ kg. cal.[6] It is obvious therefore that any breaking of a C–H bond is wholly negligible compared with that of a C–C bond. Paraffin hydrocarbons therefore decompose only through rupture of a C–C bond, thus producing two free radicals which fly apart and whose fate we will now consider.

A methyl group formed in this way probably undergoes only one reaction, namely, it takes a hydrogen atom from a molecule of the surrounding hydrocarbon to form methane and leave a free radical containing the same number of carbon atoms as the original hydrocarbon. It is true that this reaction will require some energy of activation, but even if it requires as much as 50,000 cal. it will go a great deal faster than the decomposition of the original hydrocarbon which requires a minimum activation energy of 71,000 cal. Furthermore, this process can occur even if the C–H bonds in methane and in the hydrocarbon have the same strength and it is

[4] It is possible, of course, that one of the methyl groups might take one of the adjacent hydrogen atoms and the ethylidene radical then rearrange to ethylene; this mechanism, however, is not much better and could not occur in the reaction CH₃COCH₃ $\longrightarrow$ CH₄ + CH₂=CO.

[5] The necessary data were taken from the "International Critical Tables," Volume V. Similar calculations have been made by Fajans, *Ber.*, **53**, 643 (1920); **55**, 2826 (1922); see also Weinberg, *ibid.*, **53**, 1347, 1353, 1519 (1920); Hückel, *ibid.*, **55**, 2839 (1922); Thiel, *ibid.*, **55**, 2844 (1922).

[6] These figures will be used in the discussion and calculations but they are by no means certain, and will be discussed in greater detail in a separate communication. See Ellis, *Phys. Rev.*, **33**, 27 (1929); Mecke, *Nature*, **125**, 527 (1930); Iredale and Mills, *ibid.*, **126**, 604 (1930); Mecke, *Z. physik. Chem.*, [B] **7**, 108 (1930); Hogness, paper presented at Indianapolis Meeting, American Chemical Society, April, 1930.

greatly favored by the condition which we have imposed, namely, a small percentage decomposition of the original hydrocarbon and therefore a small percentage. of methane present. The methyl radical has a high chance of colliding with the hydrocarbon molecule and combining with one of its hydrogen atoms, but the hydrocarbon radical produced collides mainly with hydrocarbon molecules and only rarely with a methane molecule; furthermore, the process of methane formation from the free methyl group is also favored by the fact that the C–H bonds in methane are stronger than those in any other hydrocarbon. However, since heats of combustion are approximately additive, this difference is not great and can at most amount to 3 or 4 kg. cal. If we assume, for example, a difference of 2 kg. cal. in the C–H bonds of methane and the hydrocarbon under consideration, we can calculate the relative probability of loss of a hydrogen atom by a methane molecule or by a hydrocarbon molecule, when the two substances are present in equal concentrations. At 600° the process, CH_3 + hydrocarbon = CH_4 + hydrocarbon-radical, is $e^{2000/2 \times 873}$ = 3.2 times more probable than the reverse reaction.

It is obvious that in the decomposition of hydrocarbons, radicals higher than methyl will be produced and we shall now discuss their possible behavior. Unlike the methyl group they can undergo two kinds of reactions; first, they may take a hydrogen atom from the surrounding hydrocarbon molecules and form a saturated hydrocarbon containing the same number of carbon atoms in the molecule; or, second, they may decompose either by giving off a hydrogen atom and forming a compound containing the same number of carbon atoms as the original hydrocarbon or they may break into a compound and a smaller free radical. This behavior may be best discussed with reference to a special example.

From the preceding discussion it will be seen that propane can decompose in one way only, namely, into a free methyl group and a free ethyl group. The resulting methyl group can undergo only one reaction, forming methane, but there are two possibilities for the ethyl group; it can take a hydrogen atom from one of the surrounding propane molecules to form ethane or it can decompose into ethylene and a hydrogen atom. It is now necessary to examine whether this last reaction can occur to an appreciable extent. The heat of formation of ethylene from gaseous carbon and gaseous hydrogen atoms is

$$2C_g + 4H \longrightarrow C_2H_{4g} + 497.0 \text{ kg. cal.}$$
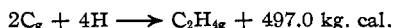
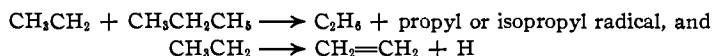The hydrogen atoms in ethylene are probably more strongly bound than those in methane, but as a first approximation we may assume that they are identical and we can thus calculate[5] the strength of the C=C bond to be 497.0 − (4×93.3) = 123.8 kg. cal. Therefore when a hydrogen atom flies off from the ethyl radical, a single bond becomes a double bond and thus 123.8 − 71.0 = 52.8 kg. cal. becomes available. The energy necessary

to break a C–H bond is 93.3 kg. cal., so that at least $93.3 - 52.8 = 40.5$ kg. cal. of activation energy must be provided. Since the propane decomposition requires a heat of activation of at least 71.0 kg. cal., a rough estimate of the ratio of its decomposition to that of the decomposition of the ethyl radical into ethylene and hydrogen atoms is given by $e^{71000 - 40500/RT}$; for 600° and equal concentrations of propane and ethyl groups this ratio is $1:10^{7.5}$.

It is possible therefore, through a process of internal compensation, for a free radical to decompose into a hydrogen atom and a compound containing a double bond; the formation of the double bond contributes to the activation energy necessary to decompose the radical and thus permits the separation of a free hydrogen atom. An ethyl radical might also decompose into a methyl radical and the methylene radical, but this reaction would require a minimum activation energy of 71 kg. cal., and is therefore much less probable than the decomposition into ethylene and a hydrogen atom, which requires only 40.5 kg. cal.

It does not seem possible to calculate the relative probabilities of the two reactions

$$CH_3CH_2 + CH_3CH_2CH_3 \longrightarrow C_2H_6 + \text{propyl or isopropyl radical, and}$$
$$CH_3CH_2 \longrightarrow CH_2{=}CH_2 + H$$

but we can predict that dilution with an inert gas will diminish the bimolecular formation of ethane and leave the unimolecular decomposition unaffected; raising the temperature should also favor the ethylene reaction, since ethylene becomes relatively more stable than ethane at high temperatures.

When a hydrogen atom is removed from propane by a methyl or an ethyl group, either a free n-propyl or free isopropyl group results. The n-propyl radical can break up in a variety of ways, such as CH_3CH_2-$CH_2 \longrightarrow CH_2{=}CH_2 + CH_3$, or $CH_3CH_2CH_2 \longrightarrow CH_3CH{=}CH_2 + H$, or $CH_3CH_2CH_2 \longrightarrow CH_3CH_2 + CH_2$. The first reaction is the most probable one since its minimum activation energy is only 18.2 kg. cal., as compared with 40.5 kg. cal. for the second and 71 kg. cal. for the third reaction. The isopropyl radical can also decompose in a variety of ways, but here again we find that the reaction

$$CH_3CHCH_3 \longrightarrow CH_2{=}CHCH_3 + H$$
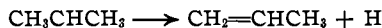
is very much more probable than any other since it requires a minimum activation energy of 40.5 kg. cal. With hydrocarbons higher than propane we obtain the corresponding higher radicals and these can decompose in a great variety of ways; in every case, however, we can make calculations similar to those made for the propyl and isopropyl radicals and we find almost without exception that one decomposition is very much more probable than any other.

We see, therefore, that if any free radical R (except methyl) is introduced

into a hydrocarbon it can decompose either into a hydrogen atom and a compound containing a double bond or into a smaller free radical and a compound containing a double bond. If a hydrogen atom is produced it will combine with one of the hydrogen atoms of the surrounding hydrocarbon to give a hydrogen molecule and the free radical R' corresponding to the hydrocarbon. This free radical, R', is also formed if the original free radical R combines with one of the hydrogen atoms of the hydrocarbon. The radical R' can only dissociate and will give a compound containing a double bond and either a smaller free radical or a hydrogen atom. Whichever is produced will then start a new cycle of reactions in which it is regenerated and this process presumably may go on for a great number of times.

Organic decompositions are therefore regarded as chain reactions in which certain atoms or radicals start a cycle of reactions at the end of which they are regenerated and start a new cycle. It follows, therefore, that the composition of the products is practically independent of the primary decomposition of the hydrocarbon and is determined almost exclusively by the chain cycle; this of course is only true if the chains are fairly long, i. e., if they consist of 100 or more cycles. The atoms or groups which are regenerated are called carriers,[7] in order to distinguish them from other radicals which do not carry on the chain; the carriers are different for different reactions and are sometimes not produced in the primary decomposition but only at the end of the first chain cycle; since in the succeeding cycle the carrier is converted into a paraffin hydrocarbon, the carriers determine the saturated part of the products of the decomposition. The carriers may be destroyed in various ways, although combination through ternary collisions is probably the most important; recombination may also occur to some extent on the walls of the vessel but this effect cannot be very great because an increase of the surface to volume ratio does not appreciably affect the rate of decomposition.

Up to the present we have assumed that the C–H bond in all hydrocarbons and radicals is the same, and this is undoubtedly true in most cases to within 1 or 2%. However, before considering in detail the decomposition of the various hydrocarbons, it seems desirable to try to make an estimate of this small correction for the different C–H bonds. If we consider, for example, a free methyl group surrounded by molecules of propane, two side reactions can occur, according as the methyl group combines with a primary hydrogen atom or with a secondary hydrogen atom; and if all the hydrogen atoms of propane were exactly alike, the relative probabilities of the two reactions would be 6:2. The experimental results[8] for small fractional decompositions of propane show that

[7] See Lewis, THIS JOURNAL, 52, 3120 (1930).

[8] Pease and Durgan. ibid., 52, 1266 (1930).

the gases contain about 30% CH₄ and 20% H₂ and if we assume that all
the hydrogen atoms are alike the calculated values are 37.5% CH_4 and
12.5% H_2; but undoubtedly the secondary hydrogen atoms are more
loosely bound and if we assume that the strength of the secondary C–H
bond is 1200 cal. less than the primary C–H bond, the calculated and the
experimental values agree.

This value of 1200 cal. was therefore fixed arbitrarily and was assumed
to be the same for all secondary C–H bonds; similarly, the strength of a
tertiary C–H bond was taken arbitrarily as 4000 cal. less than the strength
of a primary C–H bond. Table I was drawn up on the basis of these
figures; a primary C–H bond is supposed always to have the same
strength, a secondary C–H bond 1200 cal. less and a tertiary C–H bond
4000 cal. less. It is not true, of course, that all primary C–H bonds or all
secondary C–H bonds have the same strength, but we can reasonably
assume that the difference between two primary C–H bonds is small
compared with the difference between primary and secondary C–H bonds.
When measurements of the strengths of bonds can be made more precise
it will no doubt be possible to assign slightly different values within the
different classes of C–H bonds.

Column 2 gives the relative chance of loss of one particular hydrogen
atom from a hydrocarbon, leaving a free radical, at 550° and columns 3 and
4 contain the same calculations for 600 and 650°; column 5 contains a
statistical factor to take care of the number of hydrogen atoms of the
particular kind available; multiplying by this factor we obtain columns 6,
7 and 8 which give the relative probabilities of radical formation by loss
of any hydrogen atom of a particular kind from the different hydrocarbons
at 550, 600 or 650°, respectively.

<div align="center">TABLE I</div>

RELATIVE PROBABILITIES OF RADICAL FORMATION FROM DIFFERENT HYDROCARBONS

	1 ΔQ	2 $e^{-\Delta Q/1696}$ 550°	3 $e^{-\Delta Q/1746}$ 600°	4 $e^{-\Delta Q/1796}$ 650°	5 S	6 P 550°	7 P 600°	8 P 650°
CH₃CH₂CH₂–	0	1	1	1	6	6	6	6
CH₃CH₂CH₂CH₂–	0	1	1	1	6	6	6	6
CH₃CH₂CH₂CH₂CH₂–	0	1	1	1	6	6	6	6
CH₃CH(CH₃)CH₂CH₂–	0	1	1	1	3	3	3	3
CH₃CH(CH₃)CH₂–	0	1	1	1	9	9	9	9
CH₃CH₂CH(CH₃)CH₂–	0	1	1	1	6	6	6	6
CH₃CHCH₃	–1200	2.07	2	1.92	2	4.14	4	3.84
CH₃CH₂CH(CH₃)–	–1200	2.07	2	1.92	4	8.28	8	7.68
CH₃CH₂CH₂CH(CH₃)–	–1200	2.07	2	1.92	4	8.28	8	7.68
CH₃CH₂CH(CH₂CH₃)–	–1200	2.07	2	1.92	2	4.14	4	3.84
CH₃CH(CH₃)CH₂CH₃	–1200	2.07	2	1.92	2	4.14	4	3.84
(CH₃)₃C–	–4000	11.3	9.9	8.7	1	11.3	9.9	8.7
(CH₃)₂C(CH₂CH₃)–	–4000	11.3	9.9	8.7	1	11.3	9.9	8.7

The remaining part of this paper will be devoted to applying this concept to particular examples. In each case a series of equations will be given representing the course of the decomposition. The primary reactions are designated by the letter P and consist of the breaking of a C–C bond in different ways depending on the complexity of the molecule. Usually some of these radicals decompose or react with the surrounding hydrocarbon molecules in such a manner that they are not regenerated and these secondary reactions (S) are also given. However, the chain reactions designated by the letter A are the most important because they determine principally the composition of the products. An examination of these chain reactions w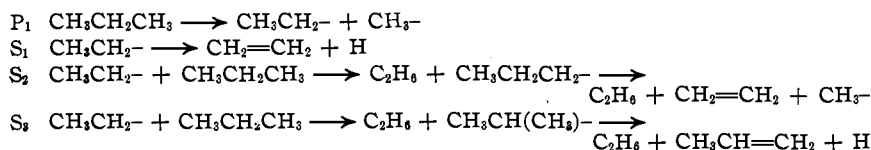ill show that many of the radicals produced in the primary or secondary changes disappear in one chain cycle and the carriers formed determine the amount of saturated hydrocarbons and hydrogen in the products. The relative probabilities of the different chain reactions are given in Table I and determine the composition of the products; this has been calculated for different hydrocarbons and compared with such experimental data as are available.

Ethane.—The thermal decomposition of ethane may be represented as

P_1 $CH_3CH_3 \longrightarrow 2CH_3-$
S_1 $CH_3CH_3 + CH_3- \longrightarrow CH_4 + CH_3CH_2-$
S_2 $CH_3CH_2- \longrightarrow CH_2=CH_2 + H$
A $CH_3CH_3 + H \longrightarrow H_2 + CH_3CH_2- \longrightarrow H_2 + CH_2=CH_2 + H$
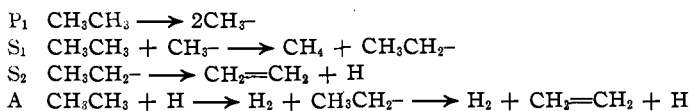
The decomposition of ethane is particularly simple because there is only one kind of chain cycle and one carrier, namely, the hydrogen atom. The decomposition should produce, therefore, ethylene and hydrogen in equal proportions providing the chains are fairly long, consisting of perhaps one hundred or more cycles. If the chain is very short and consists of only three or four cycles, there should be a considerable amount of methane present in the gases. The amount of methane present is of very great importance in connection with this proposed mechanism, because it enables us to calculate the number of chain cycles per hydrogen atom produced from a primary and secondary reaction or, in other words, the length of the chain. One molecule of methane is formed for every atom of hydrogen produced from the primary decomposition, and one molecule of hydrogen is produced in each chain cycle; consequently the ratio of H_2 to CH_4 should be the length of the chain.

Propane.—The mechanism for the decomposition of propane may be represented as

P_1 $CH_3CH_2CH_3 \longrightarrow CH_3CH_2- + CH_3-$
S_1 $CH_3CH_2- \longrightarrow CH_2=CH_2 + H$
S_2 $CH_3CH_2- + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH_2CH_2- \longrightarrow$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad C_2H_6 + CH_2=CH_2 + CH_3-$
S_3 $CH_3CH_2- + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH(CH_3)- \longrightarrow$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad C_2H_6 + CH_3CH=CH_2 + H$

A_1 $CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH_2CH_2- \longrightarrow RH + CH_2=CH_2 + CH_3-$
A_2 $CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH(CH_3)- \longrightarrow RH + CH_3CH=CH_2 + H$
$$R = CH_3-, \quad H$$
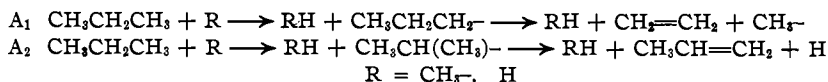
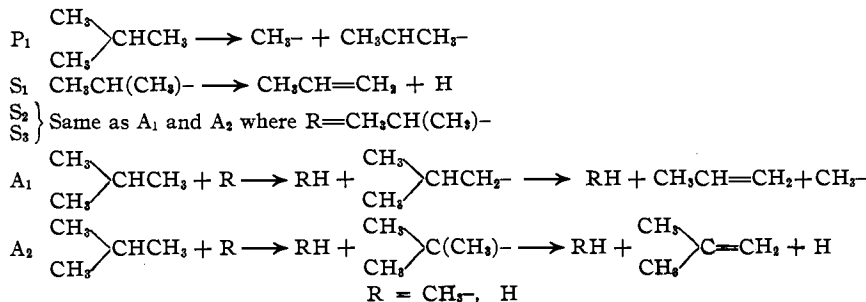The decomposition is somewhat more complicated than that of ethane since two alternative chain mechanisms A_1 and A_2 can occur depending on whether the carrier group reacts with the primary or secondary hydrogen atom of propane. Assuming the chains to be fairly long, the products must be mainly determined by Equations A_1 and A_2, and must consist of $50\%(CH_4 + H_2) + 50\%(CH_2=CH_2 + CH_3CH=CH_2)$. The ratio of methane to hydrogen and of ethylene to propylene should vary with the temperature and is given by the relative probabilities of reactions A_1 and A_2. Using the relative probabilities given in Table I, the analysis of the products has been calculated, and is given in Table II together with some experimental results taken from a paper by Pease and Durgan.[8] Since reactions S_2 and S_3 produce ethane, we should find a small percentage of this substance in the products, the amount depending upon the length of the chain; this will be given by the ratio $(CH_4 + H_2) : C_2H_6$.

TABLE II

DECOMPOSITION OF PROPANE

Upper Part: Pease and Durgan's results
Lower Part: Values calculated from Table I

Temp., °C.	Decomp., %	H₂, %	CH₄, %	C₂H₄, %	C₂H₆, %
625	17	21	31	48	
625	26	18.5	34.5	47	
650	15	22	28	50	
650	21	21.5	31	47.5	
550	5–10	21.4	29.6	29.6	20.4
600	5–10	20.0	30.0	30.0	20.0
650	5–10	19.5	30.5	30.5	19.5

Some C_2H_6 will be present, since it is formed in reactions S_2 and S_3.

Isobutane.—The decomposition of isobutane may be represented as

P_1 $\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} CHCH_3 \longrightarrow CH_3- + CH_3CHCH_3-$

S_1 $CH_3CH(CH_3)- \longrightarrow CH_3CH=CH_2 + H$

$\left.\begin{array}{c} S_2 \\ S_3 \end{array}\right\}$ Same as A_1 and A_2 where $R=CH_3CH(CH_3)-$

A_1 $\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} CHCH_3 + R \longrightarrow RH + \begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} CHCH_2- \longrightarrow RH + CH_3CH=CH_2 + CH_3-$

A_2 $\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} CHCH_3 + R \longrightarrow RH + \begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} C(CH_3)- \longrightarrow RH + \begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} C=CH_2 + H$

$$R = CH_3-, \quad H$$

The chain mechanism is given by Equations A_1 and A_2, from which it will be seen that the only carriers are CH_3- and H. The decomposi-

tion products should consist therefore of 50% (H_2 + CH_4) + 50% (CH_2=$CHCH_3$ + $(CH_3)_2C$=CH_2) and the ratio of methane to hydrogen should be the same as the ratio of propylene to isobutylene. Table III contains some experimental results taken from a paper by Pease and Durgan and also the calculated results. Pease and Durgan find small quantities of ethane in the products but there does not seem to be any way of accounting for this on the basis of the proposed mechanism; methane together with a small quantity of propane produced by reactions S_2 and S_3 should be the only paraffin hydrocarbons present.

TABLE III

DECOMPOSITION OF ISOBUTANE

Upper Part: Pease and Durgan's results
Lower Part: Calculated using Table I

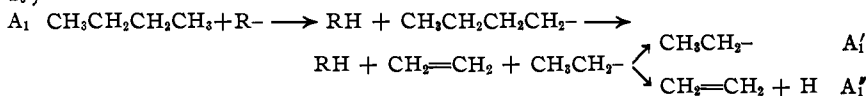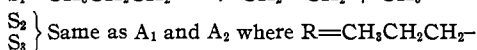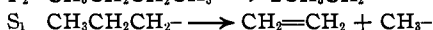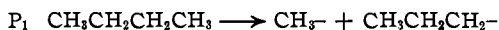| Temp., °C.	Decomp., %	H_2, %	CH_4, %	C_2H_6, %	C_2H_4, %	C_3H_6, %	C_4H_{10}, %
600	18	25	22	3		50	
625	15	25	24	1		50	
650	18.5	24.5	24.5	1.5		49.5	
550	5–10	27.8	22.2	0	0	27.8	22.2
600	5–10	26.2	23.8	0	0	26.2	23.8
650	5–10	24.5	25.5	0	0	24.5	25.5

n-**Butane.**—The decomposition may be represented as

P_1 $CH_3CH_2CH_2CH_3$ ⟶ CH_3– + $CH_3CH_2CH_2$–

P_2 $CH_3CH_2CH_2CH_3$ ⟶ 2CH_3CH_2–

S_1 $CH_3CH_2CH_2$– ⟶ CH_2=CH_2 + CH_3–

S_2
S_3 } Same as A_1 and A_2 where R=$CH_3CH_2CH_2$–

A_1 $CH_3CH_2CH_2CH_3$+R– ⟶ RH + $CH_3CH_2CH_2CH_2$– ⟶

RH + CH_2=CH_2 + CH_3CH_2– ⟨ CH_3CH_2– A_1'
                 CH_2=CH_2 + H A_1''

A_2 $CH_3CH_2CH_2CH_3$ + R ⟶ RH + $CH_3CH(CH_2CH_3)$– ⟶
                       RH + CH_3CH=CH_2 + CH_3–

R = CH_3–, CH_3CH_2–,   H
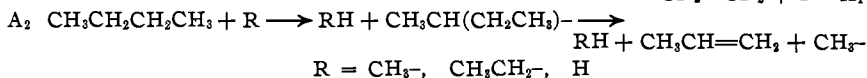
Equations A_1 and A_2 give the chain mechanism in which the carrier groups are methyl and ethyl groups and hydrogen atoms. A complication is introduced into reaction A_1 because the carrier group may react with the surrounding butane molecules or may decompose into ethylene and hydrogen atoms. If none of the ethyl groups produced in the chain mechanism decomposes, the products would consist of 50% (CH_4 + C_2H_6) + 50% (CH_2=CH_2 + CH_3CH=CH_2). On the other hand, if all of the ethyl groups produced in the chain mechanism decomposed, the products would consist of 40% (H_2 + CH_4) + 60% (CH_2=CH_2 + CH_3CH=CH_2). Table IV contains some experimental results obtained by Pease and Durgan on the decomposition of *n*-butane and also the calculated results using Table I. Since we do not know the relative probabilities of reactions
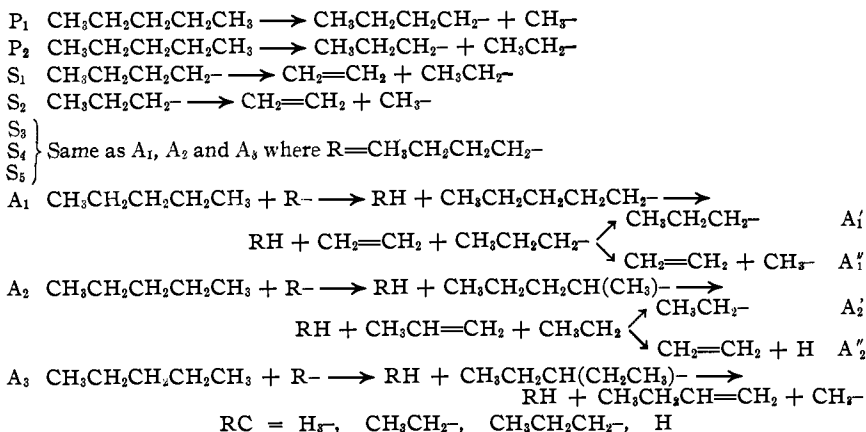
A_1' and A_1'', we cannot calculate the relative amounts of ethane and hydrogen; however, it is clear that raising the temperature should favor the production of hydrogen because ethylene becomes relatively more stable than ethane at higher temperatures; dilution with an inert gas would have the same effect because the bimolecular formation of ethane would be retarded and the unimolecular formation of hydrogen atoms would not be affected. The products should contain a small amount of propane produced by reactions S_2 and S_3 and this amount will be determined by the length of the chain.

TABLE IV

DECOMPOSITION OF n-BUTANE

Upper Part: Pease and Durgan's results
Lower Part: Calculated using Table I

Temp., °C.	Decomp., %	CH₄, %	H₂, %	C₂H₄, %	C₂H₄, %	C₂H₆, %
600	18.5	33.5	4.5	11	51	
625	22.0	31.0	5.0	13	51	
650	26.0	30.0	6.0	12	52	
550	5–10	29.0	21.0		21.0	29.0
600	5–10	28.5	21.5		21.5	28.5
650	5–10	28.0	22.0		22.0	28.0

The relative amounts of H_2 and C_2H_6 cannot be predicted, but increase in temperature or dilution with an inert gas would increase the ratio of H_2 to C_2H_6. The figures for C_2H_4 and C_3H_6 have been calculated assuming that reaction A_1 is negligible. The products will contain a small amount of propane produced by S_2 and S_3.

n-**Pentane.**—The decomposition may be represented as

P_1 $CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2- + CH_3-$
P_2 $CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2- + CH_3CH_2-$
S_1 $CH_3CH_2CH_2CH_2- \longrightarrow CH_2=CH_2 + CH_3CH_2-$
S_2 $CH_3CH_2CH_2- \longrightarrow CH_2=CH_2 + CH_3-$
$\left.\begin{array}{l}S_3 \\ S_4 \\ S_5\end{array}\right\}$ Same as A_1, A_2 and A_3 where $R = CH_3CH_2CH_2CH_2-$

A_1 $CH_3CH_2CH_2CH_2CH_3 + R- \longrightarrow RH + CH_3CH_2CH_2CH_2CH_2- \longrightarrow$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \nearrow CH_3CH_2CH_2-$ A_1'

$\qquad\qquad RH + CH_2=CH_2 + CH_3CH_2CH_2- \Bigg\langle$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \searrow CH_2=CH_2 + CH_3-$ A_1''

A_2 $CH_3CH_2CH_2CH_2CH_3 + R- \longrightarrow RH + CH_3CH_2CH_2CH(CH_3)- \longrightarrow$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \nearrow CH_3CH_2-$ A_2'

$\qquad\qquad RH + CH_3CH=CH_2 + CH_3CH_2 \Bigg\langle$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \searrow CH_2=CH_2 + H$ A_2''

A_3 $CH_3CH_2CH_2CH_2CH_3 + R- \longrightarrow RH + CH_3CH_2CH(CH_2CH_3)- \longrightarrow$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad RH + CH_3CH_2CH=CH_2 + CH_3-$

$\qquad\qquad RC = H-, \quad CH_3CH_2-, \quad CH_3CH_2CH_2-, \quad H$

We have now a considerably more complicated reaction and it seems desirable to discuss in some detail the reactions that the different radicals can undergo. The methyl group probably does not decompose, and therefore reacts only with the surrounding pentane molecules according to

reactions A_1, A_2 and A_3. The ethyl group can either decompose into an ethylene molecule and a hydrogen atom or it can take a hydrogen from the surrounding pentane molecules. We do not know the relative probability of these two reactions and in the calculations I have neglected the decomposition into ethylene and hydrogen atoms. The normal propyl group can react with the surrounding pentane molecules to form propane or it can decompose into propylene and hydrogen atoms; probably both of these reactions occur but here also I have neglected the decomposition into propylene and hydrogen atoms. High temperatures will favor reactions A_1 and A_2 since ethylene becomes relatively more stable at higher temperatures; furthermore, dilution with an inert gas will have the same effect, since it does not affect the unimolecular formation of ethylene but retards the reaction between the radicals and the surrounding hydrocarbon. If we wish to avoid the production of methane and hydrogen the best conditions, so far as reactions A_1 and A_2 are concerned, would be low temperatures and high pressures.

All three amyl radicals produced can decompose through scission of a C—C bond and it is probable that they decompose practically completely in this way. Thus the n-amyl radical would decompose into ethylene and the n-propyl radical, and only to a very small percentage into 1-pentene and a hydrogen atom; the first reaction requires a minimum activation energy of $71.0 - (123.8 - 71.0) = 18.2$ kg. cal., whereas the second reaction requires $93.3 - (123.8 - 71.0) = 45$ kg. cal.; similar considerations govern the decomposition of the other two amyl radicals, so that pentenes should be entirely absent from the reaction products in the early stages of the decomposition.

The chain mechanism gives the following composition for the products: 50% ($CH_4 + C_2H_6 + C_3H_8 + H_2$) $+ 50\%$ ($CH_2{=}CH_2 + CH_3CH{=}CH_2 + CH_3CH_2CH{=}CH_2$). We have neglected reactions A_1'' and A_2'' which produce ethylene, methane and hydrogen instead of ethane and propane. Table V contains some experimental results obtained by Caling-
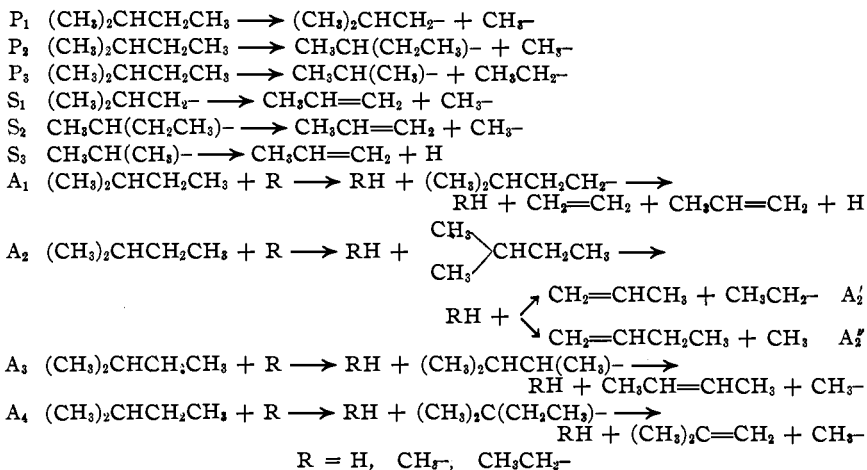
TABLE V

DECOMPOSITION OF n-PENTANE

Upper Part: Calingaert's results
Lower Part: Calculated from Table I

Temp., °C.,	Decomp., %	H_2	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_4H_8	C_4H_4
	30	5	12	26	10	10	24	3	6
550	5–10	0^a	11.2	22.5^a	16.3^b	16.3^c	22.5	11.2	0
600	5–10	0^a	11.1	22.2^a	16.7^b	16.7^c	22.2	11.1	0
650	5–10	0^a	11.0	21.9^a	17.1^b	17.1^c	21.9	11.0	0

^{a} The calculated $\% H_2$ should be higher and the calculated $\% C_2H_6$ should be lower, because reaction A_2 has been neglected. ^{b} The $\% C_3H_8$ is too high and the $\% CH_4$ too low because reaction A_1 has been neglected. ^{c} C_2H_4 is produced in reactions A_1 and A_2 which have been neglected; this would make the calculated $\%$ still higher.

aert,[9] who has made a careful study of the decomposition of n-pentane; for comparison the calculated results are also given using the probability values in Table I.

Isopentane.—The decomposition may be represented as

P_1 $(CH_3)_2CHCH_2CH_3 \longrightarrow (CH_3)_2CHCH_2- + CH_3-$

P_2 $(CH_3)_2CHCH_2CH_3 \longrightarrow CH_3CH(CH_2CH_3)- + CH_3-$

P_3 $(CH_3)_2CHCH_2CH_3 \longrightarrow CH_3CH(CH_3)- + CH_3CH_2-$

S_1 $(CH_3)_2CHCH_2- \longrightarrow CH_3CH=CH_2 + CH_3-$

S_2 $CH_3CH(CH_2CH_3)- \longrightarrow CH_3CH=CH_2 + CH_3-$

S_3 $CH_3CH(CH_3)- \longrightarrow CH_3CH=CH_2 + H$

A_1 $(CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + (CH_3)_2CHCH_2CH_2- \longrightarrow$
$RH + CH_2=CH_2 + CH_3CH=CH_2 + H$

A_2 $(CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!CHCH_2CH_3 \longrightarrow$

$RH + \begin{cases} CH_2=CHCH_3 + CH_3CH_2- & A_2' \\ CH_2=CHCH_2CH_3 + CH_3 & A_2'' \end{cases}$

A_3 $(CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + (CH_3)_2CHCH(CH_3)- \longrightarrow$
$RH + CH_3CH=CHCH_3 + CH_3-$

A_4 $(CH_3)_2CHCH_2CH_3 + R \longrightarrow RH + (CH_3)_2C(CH_2CH_3)- \longrightarrow$
$RH + (CH_3)_2C=CH_2 + CH_3-$

$R = H,\ CH_3-,\ CH_3CH_2-$

The chain mechanism is given by Equations A_1, A_2, A_3 and A_4, from which it will be seen that the carrier groups are H, CH_3 and CH_3CH_2. There is no difficulty in deciding how the amyl groups in Equations A_1, A_3 and A_4 will decompose because they can dissociate in only one way if a C–C bond is broken and a compound and a radical formed; on the other hand, the radical $-CH_2(CH_3)CHCH_2CH_3$ can dissociate according to Equations A_2' and A_2'' and in each case a C–C bond is broken and a compound and a free radical formed. As we do not know the relative probability of these two dissociations, reaction A_2'' has been neglected in the calculations. Table VI shows Calingaert's experimental results and the calculated results using the relative probabilities given in Table I.
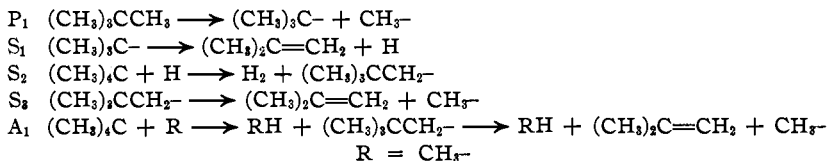
TABLE VI

DECOMPOSITION OF ISOPENTANE

Upper Part: Calingaert's results
Lower Part: Calculated using Table I

Temp., °C.	Decomp., %	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	$C_4H_8{}^a$	$C_4H_8{}^b$	C_5H_{10}
600	30	6	30	24	..	15	20		4
550	5–10	6.1	31.6	12.3^c	6.1	18.4	8.4	24.2	0
600	5–10	6.5	30.4	13.1^c	6.5	19.6	8.7	21.7	0
650	5–10	7.0	29.1	13.9^c	7.0	20.9	8.9	20.2	0

^{a} $CH_3CH=CHCH_3$. ^{b} $(CH_3)_2C=CH_2$. ^{c} Since reaction A_2'' has been neglected, the % C_2H_6 is too high and the % CH_4 too low; this reaction also produces butene-1.

⁹ Calingaert, This JOURNAL, **45**, 130 (1923).

Neo-pentane.—The decomposition may be represented as

P_1 $(CH_3)_3CCH_3 \longrightarrow (CH_3)_3C- + CH_3-$

S_1 $(CH_3)_3C- \longrightarrow (CH_3)_2C{=}CH_2 + H$

S_2 $(CH_3)_4C + H \longrightarrow H_2 + (CH_3)_3CCH_2-$

S_3 $(CH_3)_3CCH_2- \longrightarrow (CH_3)_2C{=}CH_2 + CH_3-$

A_1 $(CH_3)_4C + R \longrightarrow RH + (CH_3)_3CCH_2- \longrightarrow RH + (CH_3)_2C{=}CH_2 + CH_3-$

$$R = CH_3-$$

Neo-pentane is of special interest because of the simplicity of the reaction, and it seems surprising that it has not been studied experimentally. There is only one primary reaction, namely, scission into a methyl and a *tert.*-butyl group; this can decompose in only one way, forming isobutylene and a hydrogen atom, which in turn forms a CH_3^- group according to Reactions S_2 and S_3.

Equation A_1 represents the chain mechanism, from which it will be seen that the methyl group is the only carrier and that the products of the reaction should be 50% methane and 50% isobutylene. The amount of hydrogen present is determined by the length of the chain.

Discussion

The application of the concept of chain reactions to the thermal decomposition of organic compounds gives a very satisfactory mechanism for these reactions and it becomes important therefore to consider whether organic compounds really decompose in this manner, especially in view of the fact that the experimental evidence supports the view that paraffin hydrocarbons undergo a simple unimolecular decomposition.[10] In this connection it may be pointed out that whenever two radicals collide, the reaction $2C_nH_{2n+1} = C_nH_{2n+2} + C_nH_{2n}$ can occur by transfer of a hydrogen atom and this reaction liberates a great deal of energy. Consequently we may assume that every collision[11] between two radicals is effective in forming hydrocarbons and, in this way, the chains are broken rather than by collision with the wall. The ordinary way to test for chain reactions is to increase the surface area per unit volume of the containing vessel and this method would fail if the chains are terminated chiefly by collisions between the alkyl radicals. The most promising method of verifying experimentally these proposed mechanisms would appear to be an attempt to prove the existence of the carriers and other fragments by conducting experiments similar to those of Paneth and his co-workers but using hydrocarbons instead of lead alkyls.

Summary

1. When a hydrocarbon decomposes, we may assume that it dissociates into two free radicals which fly apart. Comparison of the strength of a

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[10] Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., 1929, pp. 64–68.

[11] Probably a small correction would be necessary to take care of the steric factor.

C–H bond (93.3 kg. cal.) with that of a C–C bond (71.0 kg. cal.) shows that the dissociation occurs only through rupture of a C–C bond; any breaking of a C–H bond is wholly negligible compared with that of a C–C bond.[12]

2.   The probability that the two radicals collide again is negligibly small and therefore free radicals produced in this way can only decompose or react with the surrounding hydrocarbon molecules.   For example, a free methyl group can take a hydrogen atom from the surrounding hydrocarbon and form methane and a hydrocarbon radical.   An ethyl group produced in this way can undergo two reactions; the first is similar to the methyl group and produces ethane and a hydrocarbon radical; the second is a dissociation into ethylene and hydrogen atoms.   Radicals higher than ethyl can decompose in a similar manner into an ethylene hydrocarbon and either a hydrogen atom or a free radical.

3.   This dissociation of free radicals is possible because, in the process, a single bond becomes a double bond; this process of internal compensation releases 52,800 cal. which can contribute to the minimum activation energy (93,000 cal.) necessary to break a C–H bond, or to the minimum activation energy (71,000 cal.) necessary to break a C–C bond.[12]

4.   The decomposition of paraffin hydrocarbons is represented as a chain type of reaction in which free hydrogen atoms or free radicals combine with one of the hydrogen atoms of the surrounding hydrocarbon molecule. The hydrocarbon radical then decomposes into a compound and either a smaller free radical or a hydrogen atom.   Thus we have a cycle of changes in which certain groups called carriers are regenerated and start a new cycle and this process presumably may go on for a great number of times.

5.   The composition of the products is determined therefore almost exclusively by the chain cycle and is practically independent of the primary decomposition of the hydrocarbon.   It is possible to calculate the composition of the products when a hydrocarbon is allowed to decompose to a small extent.   In these calculations all primary C–H bonds are considered to have the same strength, all secondary C–H bonds 1200 cal. less and all tertiary C–H bonds 4000 cal. less than a primary C–H bond. The only arbitrary assumption made in the calculations is the assignment of the relative strengths to the different classes of C–H bonds.

BALTIMORE, MARYLAND

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[12] The actual values given need not be accepted since it is only the relative strengths of the bonds which are important; it is only necessary that the C–H bond and the C=C bond are each at least 10,000 to 15,000 cal. stronger than the C–C bond.