THE ELEMENTARY REACTIONS OF THE HYDROCARBONS

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The trend of modern science is toward the study of the very fundamentals of things. Just as "modern physics" is the study of matter in its most elementary state, one of the more advanced fields of chemistry is the study of reactions in their most elementary form.

The reactions studied by early chemists were, kinetically speaking, of rather a complicated nature. Early experience showed that a process could or could not be made to go, but why it took place and what path it followed was beyond the ken of early investigators. From Berthollet's age until the time of Hinshelwood progress was slow, but the last decade has seen the study of reaction mechanism grow into a field by itself. When the science of kinetics had just been well opened everyone was anxious to explore the new domain. Many "would be" kineticists soon lost their zeal, because even the investigations of homogenous monomolecular decompositions yielded little more than a few tables of reaction velocities and activation energies. The best theories of Hinshelwood (37), Rice and Ramsperger (83), and Kassel (40) were found inadequate to explain more than a few classical cases.

Other investigators cast about for new methods of attack. Attempts were made to find very simple molecular reactions for study. Even these presented difficulties. The next logical step was the study of the most elementary of all processes -- reactions between atoms. With the discovery of free radicals by Paneth, and the proof of their importance in reaction by Rice, a new branch of kinetics has grown up which deals with atoms, radicals, and simple molecules.

Hydrocarbon chemistry has not lagged in the advance. The activity in this field has been enhanced by industrial stimulation. The hydrocarbon pyrolysis of yesterday has become the decomposition kinetics of today; and the study of free radical and atomic reactions has probably been carried farther in connection with this chemical type than with any other group of substances.

The importance of knowledge concerning "elementary hydrocarbon reactions" is evident. The thermal decomposition reactions of these compounds generally involve a great many steps which are extremely hard to untangle, and unless the characteristics of most of the possible steps are known, the choice of a mechanism in many cases degenerates to a case of pure speculation. A considerable amount of information about these elementary reactions can be obtained from independent methods such as photodecomposition, photosensitization, and straight atomic reaction experiments.

The experimental work described in this thesis deals with the reactions of hydrogen, deuterium and oxygen atoms with the simple hydrocarbons. The Wood-Bonhoeffer technique is employed. It was thought that investigations of this kind might also throw light on the accompanying free radical reactions. The general methods of Rice are used as a vehicle of interpretation, though admittedly there is some doubt about the part played by free radicals in some of the processes under examination.

In view of the interlocking relationship between all fields of hydrocarbon kinetic investigations, it is necessary that we review all work having any bearing on the subject for each member of the series. We must also take into consideration the rather complicated decomposition reactions. The primary bond split must be considered as an "elementary process" as well as the steps following. In fact, one of the chief ends of the study of fundamental processes is that the accumulated knowledge may lead to the formulation of satisfactory mechanisms for thermal decomposition reactions.

Therefore, the contemporary knowledge of the part reactions of the various hydrocarbons and their bearing on possible mechanisms for thermal decomposition will be discussed under the following headings:

Reactions with atomic hydrogen.
Photochemical bond splitting.
Photosensitized reactions.
Thermal decomposition.

Current Working Theory and Experimental Sources of Information [a]

Before discussing the reactions of the hydrocarbons in detail, it is probably advisable to review the current working theory and the various experimental sources of information.

Decomposition Reactions

Since the discovery by Hinshelwood (37) in 1926 that a number of organic compounds decomposed by a first order mechanism, a great deal of work has been done along this line. The results of many investigations have lead to the general conclusion that the stability of organic molecules is really determined by the size of the unimolecular velocity constant. The temperature dependence of the velocity is usually expressed in terms of the Arrhenius equation, i.e.,

$$k = Ae^{-E/RT}$$

or $$\log_{10} k = \log_{10} A - \frac{E}{2.3\ RT}$$

where A is a constant and E is the so called energy

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[a] Part of the subject matter of the following introductory section has been taken from "The Kinetics of Elementary Reactions of The Simple Hydrocarbons" by E.W.R. Steacie; Chemical Reviews, 22, 311, 1938.

of activation.

The modern theory of unimolecular reactions is based on the idea that activation is by collision but that a time lag exists between activation and reaction, most activated molecules being deactivated before they have a chance to react. As a result there exists a stationary concentration of activated molecules, which is calculated from the Maxwell-Boltzmann distribution, and the rate of reaction is proportional to the first power of the concentration of the reacting substance . At low pressures, however, the diminished number of collisions will no longer be able to replace the activated molecules as fast as they are destroyed by reaction, their stationary concentration will fall, and hence the rate of reaction will diminish with decreasing pressure.

The theory so far is wholly in accord with experiment, but incomplete. The main test of any theory of monomolecular reactions is whether it can predict where the velocity constants of a certain reaction will fall off as pressure is diminished and whether it can give the shape of the rate-pressure curve at this critical point.

Obviously some assumptions must be made about the other variable, activation energy, which appears to be intimately connected with the nature of the molecule itself. The older type of theory of which Hinshelwood was the chief exponent, assumes that if a molecule has an energy $\geq$ E, it has a definite probability of reacting, independent of its excess energy over and above E. This theory seems somewhat to oversimplify the case and appears now to be in disagreement with most experimental facts. The other type of theory assumes that for reaction, energy must be concentrated in one particular degree of freedom, or in one vibrational bond of the molecule (4,5). On this basis it is obvious that the chance of getting energy equal or greater than E into one bond will be a function of the total energy of the molecule, and will increase rapidly with excess of the energy of the molecule over E. This type of theory gives results which are in excellent agreement with facts. There are a number of different forms of the theory, but all are essentally the same. That of Kassel (4) is much the simplest and is the one which is usually employed.

The essence of Kassel's theory is that activation energy is merely the total energy of that number of quanta which must be located in the pertinent bond before reaction can occur. In other words activation energy is a measure of bond strength.

Obviously, for the purpose of predicting the products of decomposition reactions, it becomes a matter of major importance to discover any possible correlation between the activation energy of a reaction and the strengths of the bonds formed and broken in it.

Applying this idea to the decomposition of a compound like C_2H_6, difficulties are immediately encountered. Classical mechanism considered that a split into the final decomposition products occured in a single step,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

It was evident that this involved the simultaneous rupture of two valence bonds and the formation of two new ones. It was, therefore, obvious that the activation energy could bear no very simple relation to bond strengths. The other alternative was a primary break up into radicals,

$$C_2H_6 \longrightarrow 2\ CH_3$$

followed by secondary reactions which would ultimately lead to formation of the usual products. If this mechanism is the true one, and if the secondary reactions are fast compared with the first step, the activation energy should be a direct measure of the strength of the C - C bond.

Evidence for the existence of free radicals was soon forthcoming. Paneth and Hofeditz (58) showed that methyl and ethyl radicals could be detected in a rapidly flowing gas stream by their reaction with a lead mirror to form volatile organo-metallic compounds, F.O. Rice et al (72,76) seized upon this idea and made a comprehensive search of organic decomposition reactions for the presence of free radicals. They found that free radicals could be detected in the decomposition of almost all organic substances.

These findings led Rice and his co-workers to formulate a general free radical theory for hydrocarbon decomposition reactions, that has given new life to chemical kinetics in general. Postulating that the primary step is a split into free radicals, one might expect that the activation energy of the hydrocarbon decomposition reactions would be a measure of the strength of the C - C bond or the C - H bond. Though there is some uncertainity about bond strengths, there is plenty of evidence that the $C=C$ and $C\equiv C$ bonds are stronger than the other bonds in the hydrocarbon molecule. Indirect evidence from various quarters indicates that the C - H is about 10 - 15 Kcal. stronger than the C - C bond.

Rice points out that if two reactions have activation energies differing by 4 Kcal., then the relative rates at 600°C are in the ratio $e^{-4000/2 \times 873}$

to 1 or approximately 9:1. It follows that if there are two or more ways of accomplishing a primary break in a molecule, the one with the smallest activation energy will predominate. Trusting then, in the basic theory that activation energy is intimately connected with bond strength, Rice concluded that free radical decomposition of hydrocarbons would proceed by a C - C split.

For example, the primary reaction of propane decomposition could only be

$$C_3H_8 \longrightarrow CH_3 + C_2H_5$$

Methyl and ethyl radicals could be detected by the Paneth technique. Propyl radicals are unstable at high temperatures and therefore undetectable. According to the Rice method the mechanism could be

$$CH_3CH_2CH_3 \longrightarrow CH_3 + CH_3CH_2 \qquad (1)$$

$$CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH_2CH_2 \qquad (2)$$

$$CH_3CH_2CH_2 \longrightarrow C_2H_4 + CH_3 \qquad (3)$$

$$CH_3CH_2CH_2 + R \longrightarrow RH + CH_3CHCH_3 \qquad (4)$$

$$CH_3CHCH_3 \longrightarrow CH_3CH = CH_2 + H \qquad (5)$$

assuming, of course, that (2) and (3) had activation energies much smaller than the primary split (1). Making certain reasonable assumptions concerning the relative speed of reactions (2) and (3) Rice's mechanism yields the following stoichiometric equation for propane decomposition

$$10\ C_3H_8 \longrightarrow 6\ C_2H_4 + 6\ CH_4 + 4\ C_3H_6 + 4\ H_2$$

This agrees reasonably well with experimental results.

Thus, using Rice's mechanisms it is possible to predict products. To be fully successful, however, the theory must also explain the following: (a) How the overall mechanism of organic decomposition appears to be of the first order, though the mechanism is really a complex series of steps. (b) If, as postulated, most reactions occur by the breaking of a C - C bond, why it is that experimental activation energies for decomposition reactions are usually far smaller than the bond strengths.

Rice and Herzfeld (77) answered these questions by showing that mechanisms could be devised on a free-radical basis which would lead to a first-order overall rate. Further, by suitable choice of activation energies of the part reactions, the apparent activation energy of the overall reaction could be made to agree perfectly with the experimental value. For example, consider the following scheme for decomposition of an organic molecule M_1 (81) :

	E in Kcal.	
$M_1 \longrightarrow R_1 + M_2$	80	(1)
$R_1 + M_1 \longrightarrow R_1H + R_2$	15	(2)
$R_2 \longrightarrow R_1H + M_3$	38	(3)
$R_1 + R_2 \longrightarrow M_4$	8	(4)

We thus have a chain process, since steps 2 and 3 can repeat over and over again. The chain is finally broken when the radicals combine to form a stable molecule by reaction 4. By setting up equations giving the concentrations of the radicals in steady state, assuming long chains, and then calculating the overall rate of decomposition of M_1 we arrive at the expression

$$-\frac{d}{dt}\left[M_1\right] = k_1 \left[M_1\right] \left(1 + \sqrt{k_2k_3/2k_1k_4}\right)$$

$$\sim M_1 \sqrt{\frac{k_2k_3k_1}{2\ k_4}}$$

i.e. the reaction is of the first order. Also

$$E\ (\text{overall}) = \tfrac{1}{2}\ (E_1 + E_2 + E_3 - E_4)$$

so that using the rough value of E given above we get E = 62.5 Kcal. which is considerably below the C - C bond strength. It will be noticed on close examination that the prediction of a first order rate depends on the method of termination of the reaction chains.

The authors of the idea admit that mechanisms of this sort are highly spectulative but do show that the free radical theory can be fitted to experimental fact and therefore is very valuable.

Striking support for the fundamental idea of free radical chain reaction was immediately forthcoming. Frey (23) was able to start chains in butane at temperatures below its normal decomposition range by adding methyl radicals (from the decomposition of dimethyl mercury). This appears to be an important point, for the experiments of Rice and co-workers on the presence of free radicals in decomposition reactions were of necessity carried out at temperatures 200 - 300°C above the normal reaction range, which did not necessarily prove that the free radical mechanism was all-important in the usual temperature region. Similarly Allen and Sickman (1) and Leermakers (50) produced sensitized chain decomposition of a number of organic substances.

Further evidence for the chain character of this type of reaction is furnished by Staveley and Hinshelwood (92) and others (17a,26,100). From a study of the effect of different quantities of nitric oxide on reactions, they calculated chain lengths ranging from two to fifteen for a number of reactions Though this is definite evidence for the presence of chains, in most cases the chain lengths were far too small to be in accord with Rice-Herzfeld mechanisms. Recent work on some reactions indicates that in certain cases there may be a few long chains rather than a large number of short ones, i.e., that the Rice-Herzfeld mechanism may hold for a small fraction of the total reaction, the remainder of the substance decomposing by a molecular mechanism.

It may be said that in general the evidence supports the free radical theory. However, when specific Rice-Herzfeld mechanisms are tested the situation is quite different. To date three methods have been used for the purpose: (a) The stationary hydrogen atom concentration during a decomposition reaction is measured and compared with the value calculated from the theory. (b) The activation energy of one of the part reactions of the Rice-Herzfeld scheme is determined in an independent way. (c) Deutero compounds are used as indicators of the mechanism.

The above mentioned tests have been applied to the decomposition reaction of different hydrocarbons. The results are discussed in one of the sections following.

Photochemical Reactions

From the foregoing discussion it is evident that methods must be found for studying the individual reactions that make up these complex decomposition mechanisms. Until we know the rates and activation energies of the intermediate steps no great confidence can be placed in any particular theory.

Theoretically at least, photochemical means should enable us to single out the primary step for study. Thermal reaction is not selective; the products as well as the reactants are activated, which makes any reaction possible within a certain energy range. To activate a molecule photochemically it should be only necessary for it to absorb a light quantum of energy equivalent to its activation energy.

$$h\nu + A \rightarrow A^{*}$$

$$A^{*} \rightarrow \text{products}$$

$$A + A^{*} \rightarrow A + A$$

$$A^{*} \rightarrow A + h\nu_{2}$$

Thus, we can conceive of an ideal experiment where light of sufficiently high frequency would be selectively absorbed by a certain hydrocarbon, causing reaction with the production of substances not absorbing in the region of the incident light. If such an arrangement were possible, one would expect to find an activation energy equivalent to the strength of the primary bond split, for all but the very fastest secondary reactions would be cut out. Unfortunately very little information is available, since the simple hydrocarbons are transparent down to the extreme ultra-violet, and the difficulties involved in working in the Schumann region are very great.

Photosensitized Reaction

A selective effect something like the ideal case mentioned in the previous section may be attained by photosensitization. In work of this kind, mercury vapour is mixed with the reactant gas and the mixture illuminated with the mercury resonance line at 2537 A.U. This is absorbed by the mercury vapour in the system, normal mercury atoms being raised to the 2^3P_1 level. This lies 4.8 volts or 112 Kcal. above the ground state. Such excited mercury atoms may then transfer their energy by collision to other molecules. If such transfer takes place efficiently, a wide variety of reactions is possible (109,12), since 112 Kcal. is greater than the activation energy of almost all chemical reactions.

Cadmium (104) and zinc photosensitized reactions are also being studied in this laboratory, the objective being the attainment of greater selectivity.

In general the scheme of activation and reaction is like this when mercury is used:

$$Hg(1^1S_0) + h\nu \longrightarrow Hg(2^3P_1)$$

$$Hg(2^3P_1) + A \longrightarrow Hg(1^1S_0) + \overset{*}{A}$$

$$\overset{*}{A} \longrightarrow \text{products}$$

Kemula, Mrazek and Tolloczko (47) used a circulating system, passing the reactant alternately past the lamp and through a cooled trap. This technique removes products, and prevents the slower secondary reactions which require large concentration of certain products. Since the coldest trap does not remove hydrogen, hydrogen atoms may be produced in large quantities and thus introduce complications. However, as the selectivity of the method is many times greater than the thermal decomposition it is especially important.

Atomic Reactions

Photosensitization can also be used for the production of hydrogen atoms for studying their effects upon hydrocarbons. In the presence of hydrogen and a reacting substance we have

$$Hg(2^3P_1) + H_2 \longrightarrow Hg(1^1S_0) + 2H \qquad (2)$$

$$H + X \longrightarrow \text{products} \qquad (3)$$

$$2H + (\text{a third body}) \longrightarrow H_2 \qquad (4)$$

Under these circumstances a stationary concentration of hydrogen atoms exists. Knowing the rate of reactions 2 and 4, we can calculate the velocity constant of reaction 3.(2) This method is of wide applicability although the results are not always easy to interpret.

There appears to be only one direct method of investigating reactions between atoms and hydrocarbons. This is the Wood-Bonhoeffer method. Wood showed that it was possible under certain circumstances to pump hydrogen atoms out of a hydrogen discharge tube and carry them considerable distance before recombination occured. Bonhoeffer adapted the idea to the investigation of hydrogen atom-hydrocarbon reactions by mixing the reactant with the atoms in a flow system. Many reactions have been investigated by this technique, but the experiments are limited to a narrow pressure range between 0.1 and 1 mm. and a reaction time of the order of a second.

Atomic reactions in general may be classed as follows;

Recombination $(M) + A + A \longrightarrow AA + (M)$ (1)

Addition $(M) + A + BC \longrightarrow ABC + (M)$ (2)

Metathesis $A + BC \longrightarrow ABC \longrightarrow AB + C$ (3)

where A is an atom and BC a compound. Types (1) and (2) are "dreierstoss" processes and theoretically require a third body to carry off the excess energy. The three body collision restriction has been gradually losing ground and it is now admitted that even the complexity of the ethane molecule may be great enough to allow the recombination of methyl radicals without the presence of a third body. Rabinowitsch (70) has recently studied the efficiency of triple collisions in atom recombination using He,A,N_2,O_2,CH_4,CO_2 and C_6H_6 as "third bodies". The old estimate of "1 collision in a 1000 a dreierstoss at atmospheric pressure" was found to hold for helium as the third body. In the case of the iodine atom recombination when $M = H_2$ every collision in three hundred is a recombination, if $M = CO_2$ efficiency is one in sixty, and with C_6H_6 as the third body every two body collision in ten is effective. Thus, it would appear that even collisions of atoms are "stickier" than previously believed; and thus, where free radicals are concerned the Dreierstoss theory may no longer be used so freely as a "weeder" of mechanisms.

The metathesis type of atomic reaction may be written

$$A + BC \longrightarrow AB + C$$

or $$\longrightarrow \overset{*}{ABC} \longrightarrow AB + C$$

where ABC might be called a quasimolecule, in which case it will be seen that a collision between A - BC might result in addition. This would require the stabilization of the activated complex ABC.

Experiments by Geib and Harteck (28) on atomic reactions at very low temperatures have shown that reactions like

$$H + NO \longrightarrow HNO$$

are possible and that unstable compounds like HgH which have little more than a quasimolecular existence at high temperatures, could be isolated under their experimental conditions. It is to be emphasized that these findings are not without influence on the atomic reactions of the hydrocarbons.

Elementary Reactions of the Simple Hydrocarbons

In the following sections the data of previous investigations on the reactions of the simple hydrocarbons will be reviewed.

Methane

The Reaction of Hydrogen Atoms with Methane

The first serious investigations of reactions of the various hydrocarbons with hydrogen atoms were made by Bonhoeffer and Harteck (9). They found methane surprisingly stable. Similar work by von Wartenburg and Schultze (120) and Chadwell and Titani (13) confirmed the inertness of methane toward hydrogen atoms.

Geib and Harteck (29) extended experiments to 183°C and found no reaction. This suggested a primary step something like

$$CH_4 + H \longrightarrow CH_3 + H \qquad (1)$$

with an activation energy of at least 17 Kcal. followed by a faster secondary process

$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (2)$$

If reaction (2) were very fast, the absence of ethane in the products, the null stoichiometric result, and the observed regeneration of hydrogen atoms would be explained. The activation energy of this reaction had been estimated at 8 Kcal. by von Hartel and Polyani (121). However, other and later estimates of the activation energy (90, 73, 49, 62) range from 15 to 23 Kcal. The most direct source of information concerning this reaction is found in the work of Paneth, Hofeditz and Wunsch (59). They investigated the rates of recombination of the methyl radicals in inert gases and hydrogen. It appears certain that reaction (2) is the all important process for which they calculate the very reasonable value of 15 Kcal.

It follows from this discussion that little trust can be rested in Geib and Harteck's mechanism, due not only to the uncertainties about the speed of secondary reactions but also to the doubt of the existence of any reaction of methane with hydrogen atoms.

Geib and Steacie (30,31) investigated the reaction of deuterium atoms with methane and found no products up to 100°C, indicating an activation energy for the exchange reaction of not less than 11 Kcal. Their investigation indicated that the reaction was the analogue of the ortho-para hydrogen conversion

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

This explanation made it unnecessary to assume the existence of secondary reactions to account for the absence of ethane and the regeneration of atoms. Preliminary experiments on the exchange at 1000° K by Farkas served to support Geib and Steacie's suggestion.

The results obtained by various other investigators for the activation energy of this reaction are tabulated below:

Investigators		Method	Result
Steacie and Phillips	(94)	Mercury photosensitization	11.7 Kcal.
Farkas and Melville	(20)	Wood-Bonhoeffer	13 Kcal.
Morikawa, Benedict and Taylor	(56)	Mercury photosensitization at 100°C	12.5 Kcal.
Steacie	(95)	Wood-Bonhoeffer up to 500°C	12.9 2 Kcal.
Trenner, Morikawa and Taylor	(116)	Wood-Bonhoeffer 25° to 208°C	>15.6 Kcal.

In Farkas and Melville's investigations, the atom concentration was determined by using O - deuterium-methane mixtures and measuring the rate of the O - P conversion as well as the exchange. They found that at high temperatures the deuterium atom concentration fell off greatly and they suggested that the atom consuming reaction might be

$$CH_4 + D \longrightarrow CH_3 + HD \qquad (3)$$

At first sight one might expect some ethane formation. It will be noticed, however, that the relative overall CH_3 concentration would probably be too small for anything else but the recombination

$$CH_3 + H \longrightarrow CH_4$$

Morikawa, Benedict and Taylor found that the temperature coefficient was very low in the range 100 - 200°C and concluded that the mechanism was different from that postulated by Steacie and Phillips and by Farkas and Melville. They are of the opinion that the many secondary processes possible in the mercury photosensitized method make it impossible to gain any accurate information about the primary process by this means. The large value of E found by Trenner, Morikawa and Taylor for the reaction is partly due to the fact that they assume reaction (3) to be the one under investigation and partly because they were uncertain of their atom concentrations at high temperatures.

In general it may be said that the evidence favours an activation energy of about 12 to 13 Kcal.

for the reaction

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

and somewhat greater values of E for the reactions

$$CH_4 + D \longrightarrow CH_3 + HD$$

and $$CH_4 + H \longrightarrow CH_3 + H_2$$

The Photodecomposition of Methane

Methane is transparent down to the Schumann region. Spectroscopic observations by Liefson (52) and Scheibe (88) show that diffuse bands appear in the neighbourhood of 1600 A.U. Bonhoeffer (8) suggests that the primary reaction is

$$CH_4 \longrightarrow CH_3 + H$$

followed by formation of ethane and the usual atom-free radical recombinations.

Direct experimental investigation of the photodecomposition has been done by Leighton and Steiner (51) using hydrogen light near the limit of flourite. Hydrogen and unsaturates are produced. Groth and Laudenklos (32) used a Harteck Xenon lamp as a source. The 1295 A.U. line was very strongly absorbed by methane. The products of the reaction were found to be mainly hydrogen and acetylene, with some ethane and traces of ethylene and C_3 to C_5 hydrocarbons. The results of these experiments are strongly in favour of a mechanism like the following:

$$CH_4 + h\nu \longrightarrow CH_3 + H$$

$$CH_3 + H \longrightarrow CH_2 + H_2$$

$$2\ CH_2 \longrightarrow C_2H_2 + H_2$$

Comparatively recent work on the photolysis of methane by Kemula and Dyduszynski (48) led these authors to conclude that the first step is

$$CH_4 \longrightarrow CH_2 + H_2$$

Their argument, however, is not entirely conclusive.

Spectroscopic examination of the discharge (69) shows that at least a part of the methane undergoes all possible dehydrogenation steps, yielding CH_3, CH_2, CH and C. This means that a great variety of products is possible.

The Thermal Decomposition of Methane

Holliday and Exell (38) and Holliday and Gooderham (39) made the first investigations of any kinetic importance. They noticed the retarding effect of hydrogen upon the reaction and assumed that the initial step was

$$2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2 \quad -91{,}000\ \text{cal.}$$

Kassel (50) has shown that this mechanism cannot be right, since it would require an activation energy greater than 91 Kcal. which is contrary to fact.

Kassel investigated the reaction throughly and found it to be homogenous and first order from 1.3 to 29.6 cm. initial pressure and confirmed the strong retardation by hydrogen. From his measurements he calculated the initial rate

$$k = 1.0 \times 10^{12}\ e^{-79385/RT}\ \text{sec.}^{-1}$$

The rate in the later stages of the reaction was found to be approximately proportional to the square of the methane concentration and inversely proportional to the cube of the hydrogen concentration. He suggests as the initial step

$$CH_4 \longrightarrow CH_2 + H_2 \qquad -\ 47000\ \text{cal.} \quad (3)$$

followed by

$$CH_2 + CH_4 \longrightarrow C_2H_6 \qquad +36000\ \text{cal.} \quad (4)$$

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \qquad -\ 30000\ \text{cal.} \quad (5)$$

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \qquad -\ 48000\ \text{cal.} \quad (6)$$

Acetylene may be assumed to dissociate as follows

$$C_2H_2 \longrightarrow 2\ C + H_2 \qquad (12)$$

For the initial stages we have approximately

$$\frac{d}{dt}(CH_4) = 2\ k_3\ (CH_4)$$

i.e., the reaction is first order. After a certain amount of hydrogen has accumulated we get

$$-\frac{d}{dt}(CH_4) = \frac{2k_3k_4k_5k_6k_{12}\ (CH_4)^2}{v_3v_4v_5v_6\ (H_2)^3}$$

where v's signify velocity constants of reverse reactions.

Kassel's mechanism seems to fit experimental results quite accurately. Storch (105) decomposed methane on a carbon filament at low pressures in a bulb cooled in liquid nitrogen, and showed that the first product detectable was ethane. Storch (106) has reviewed the work of various investigators using flow methods and has concluded that Kassel's mechanism fits them all quite satisfactorily.

Free Radicals and Methane Decomposition

Rice and Dooley (75,76) investigated the primary process in the decomposition of methane by the free radical technique. They used tellurium mirrors and concluded that the primary process involved methyl rather than methylene radicals. Belchetz and Rideal (4,5) passed methane rapidly over a hot filament at low pressures and then onto a cold target about one mean free path away. They detected radicals by reaction with mirrors, iodine etc. and concluded that methylene radicals were involved in the primary step.

There appear to be two mechanisms possible corresponding to the results of these two investigations:

$$CH_4 \longrightarrow CH_3 + H \tag{1}$$

$$H + CH_4 \longrightarrow H_2 + CH_3 \tag{3}$$

$$CH_4 \longrightarrow CH_2 + H_2 \tag{2}$$

$$CH_2 + CH_4 \longrightarrow 2\ CH_3 \tag{4}$$

$$CH_2 + CH_4 \longrightarrow C_2H_6 \tag{5}$$

If reaction 2 is the correct primary step, rather than reaction 1, then either reaction 4 or reaction 5 must have an activation energy less than 12 Kcal. to account for the absence of methylene radicals at the mirror in the experiment of Rice and Dooley. They consider this to be much too low, and hence they favour reaction 1 as the primary step. No hydrogen telluride is formed in their experiments, as would be the case if hydrogen atoms reached the telluride mirror. They therefore conclude that hydrogen atoms must disappear from the system rapidly by wall recombination or by reaction 3.

Kassel (43) favours the mechanism of Belchetz and Rideal, for it seems to explain his results very nicely. Moreover, he calculates that if the reaction follows the Rice chain system, the relation

$$[H] > 10^4 [CH_3]$$

must ultimately hold. This result conflicts hopelessly with Rice and Dooley's experiments in which methyl groups could be detected but no atomic hydrogen. Kassel thinks that this factor is too large to be overcome by wall recombination and thus rules out (1) as the initial step. He suggests that (4) and (5) are very fast reactions, the former producing the detectable methyl radicals and the latter helping to keep the methylene concentration at a very low value. The discrepancy between Rice and Dooley and Belchetz and Rideal seems to be largely due to difference in experimental method.

Ethane

The Reaction of Ethane with Hydrogen Atoms

Bonhoeffer and Harteck (9), and von Wartenburg and Schultze (120) found that luminescence occurs on mixing hydrogen atoms and ethane, bands due to C - H and C - C being observed. They recovered the major part of the ethane unchanged, but found no methane as they had no means of trapping it out. Chadwell and Titani (13) in a preliminary investigation reported the finding of about 4 % methane along with some ethylene.

Steacie and Phillips (94) studied the reaction of deuterium atoms with ethane using the Wood-Bonhoeffer technique. **They** found that an exchange reaction was taking place which appeared to have an activation energy of 6.3 Kcal. They considered all possible mechanisms for the exchange reaction and concluded that the correct mechanism was

$$(1) \quad C_2H_6 + D \longrightarrow C_2H_5 + HD$$

$$(2) \quad C_2H_5 + D \longrightarrow C_2H_5D$$

This would account for the catalytic destruction of D atoms, found to take place.

Trenner, Morikawa and Taylor (116) reinvestigated the reaction, using the same method. They concluded that at room temperature the main reaction was

$$C_2H_6 + D \longrightarrow CH_3 + CH_3D \quad (E = 7.2 \text{ Kcal.})$$

and that the exchange reaction was only appreciable at temperatures of 100°C and upwards, with an activation energy of 11.4 Kcal. They suggested that the exchange reaction above 100°C occurred by

$$C_2H_6 + D \longrightarrow C_2H_5 + HD$$

in agreement with Steacie and Phillips. There is a large discrepancy in the activation energy of this process between the two investigations (6.3 and 11.7 Kcal.). It is mostly accounted for when it is realized that separate products were not isolated in Steacie and Phillips' investigation, it being assumed from the work of Chadwell and Titani that the formation of methane was negligible. Recently Steacie (102) has confirmed the production of methane, finding about 10 % ethane decomposition. This, however, was not enough to bring the two activation energies into line.

Several qualitative investigations of the reaction of ethane with hydrogen atoms produced by mercury photosensitization have been made (46,108,109).

Steacie and Phillips (96) have recently done some quantitative work along this line. In a typical experiment using a trapping temperature of -125°C, the following stoichiometric equation is satisfied:

$$1\ C_2H_6 + 0.5\ H_2 \longrightarrow 1.34\ CH_4 + 0.17\ C_4H_{10}$$

(+ traces of C_3H_8)

Steacie and Phillips suggested the mechanism:

$$Hg\ (2^3P_1) + H_2 \longrightarrow Hg\ (1^1S_0) + 2\ H$$

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

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5$$

followed by various radical recombination reactions.

The Photodecomposition of Ethane

So far very little work has been done on the ethane photodecomposition. Evidence gleaned from rather meagre spectroscopic sources indicates that the absorbtion is by the C - H bond.

The recent photochemical investigation of the hydrocarbons by Kemula and Dyduszynski (48) led these investigators to the general equation:

$$C_nH_{2n-2} + h\nu\ (1850\ \text{Å}) \longrightarrow C_nH_{2n} + H_2$$

as the mechanism of photolysis of ethane, propane and butane. It is very difficult, however, from this evidence to say just what the true primary step may be.

The Photosensitized Decomposition of Ethane

Taylor and Hill (108) were the first to notice that ethane could be decomposed by excited mercury atoms. Kemula, Mrazek and Tollocsko (47) carried out the first notable work on the photosensitized decomposition of ethane. They passed the reaction mixture through a trap at - 80°C to remove products of high molecular weight and thus prevent secondary processes. They found hydrogen and methane as gaseous products. Rough fractional distillation indicated that the condensable products consisted mainly of butane and octane. This pointed toward a C - H rupture as the first step, the butane and octane having for their origin, the radical recombination reactions:

$$2\ C_2H_5 \longrightarrow C_4H_{10}$$

$$C_4H_{10} \longrightarrow C_4H_9 + H$$

$$2\ C_4H_9 \longrightarrow C_8H_{18}$$

The reaction has been recently reinvestigated by Steacie and Phillips (96,97). They found that by operating with the trap in the circulation system at a lower temperature it was possible to remove higher boiling products more efficiently, and thus avoid the occurence of secondary reactions. They found as products considerable amounts of hydrogen, methane, propane, butane and some higher hydrocarbons, the relative amounts depending on the trapping temperature. The striking thing about their results with the circulating system was that at the lower trapping temperatures, the formation of hydrogen was almost entirely inhibited. This indicated that hydrogen was not a product of the ethane decomposition itself and that the initial split was in the C - C bond.

Later, Steacie and Phillips (97) tried the same reaction, this time using a flow system. By this arrangement the ethane was only subjected once to the action of the lamp. Under these conditions, the concentration of hydrogen, if formed, would be low and hence, the back reaction would be diminished; this would permit the hydrogen to accumulate in the products if it were formed in the reaction at all. Analysis of the products showed a large yield of hydrogen. These findings made it no longer necessary to rule out the C - H bond split. Steacie and Phillips, therefore, decided on the following as the best mechanism:

$$C_2H_6 + Hg(^3P_1) \longrightarrow C_2H_5 + H + Hg(^1S_0)$$

$$H_2 + Hg(^3P_1) \longrightarrow 2\,H + Hg(^1S_0)$$

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 \tag{18}$$

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \tag{17}$$

$$2\,CH_3 \longrightarrow C_2H_6$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

$$2\,C_2H_5 \longrightarrow C_4H_{10}$$

$$2\,H \longrightarrow H_2$$

The very high quenching efficiency of hydrogen necessitates the inclusion of the second step. This series of reactions explains the experimental facts very well providing reaction (18) is at least four times as fast as step (17).

The Thermal Decomposition of Ethane

As this thesis deals mainly with"elementary reactions" it is not necessary to completely review the kinetics of each hydrocarbon decomposition. The work of Pease (67), Frey and Smith (24) and others established the general first order nature of the reaction, and showed that the overall process was more or less described by the equation:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

Marek and McCluer (53), Paul and Marek (63) and Sachsse (86) have made somewhat more thorough investigations. Their rates at most temperatures agree fairly well but the activation energies vary from 70 to 78 Kcal. Pease (66) has measured the rate of the reverse reaction and has shown that the calculated equilibrium constant is in excellent agreement with the experimental value of Pease and Deugan (64).

Recent work by Storch and Kassel (107) indicates that the situation is rather more complex. They find some methane and propylene production. To account for this, they conclude from analogies with Frey and Hepp's work (25) on butane, that this hydrocarbon is an important intermediate product leading to methane and propylene production in some such manner as :

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

$$C_2H_4 + C_2H_6 \longrightarrow C_4H_{10}$$

$$C_4H_{10} \longrightarrow CH_4 + C_3H_6$$

In general Storch and Kassel lean toward a classical mechanism of this type.

Dinzes, Zharkova, Zherko and Frost (14), who investigated the reaction at high pressures, found much methane present in the products. This was attributed to the second order reaction

$$2\ C_2H_6 \longrightarrow 2\ CH_4 + C_2H_4$$

which would be favoured by high pressure. Dinzes and Frost (15) and Travers et al (117 - 119) have investigated the ethane decomposition up to high percentage reaction and have obtained rather complex results.

More exhaustive investigation of possible part reactions would probably go further toward clarifying the mechanism of ethane decomposition than continued thermal studies.

Free Radicals and Ethane Decomposition

The kinetic investigations discussed above have served to show that the important overall reaction is:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

and indicate that butane, propylene and methane may be transitory products of important intermediate steps.

The question of mechanism was considered by Rice who attempted to apply his free radical theories in order to bring about a solution. Rice and Dooley

(75) had found a value of 79.5 Kcal. for the assumed reaction

$$C_2H_6 \longrightarrow 2\ CH_3$$

by studying the rate at which standard lead mirrors were removed by decomposing ethane at 850°C to 950°C. They concluded that this should be the primary step in the ethane decomposition, followed by a system of free radical reactions leading to the ultimate products.

Granting that the primary step is a break into free radicals, one must go further to prove that the ordinary thermal decomposition of ethane at low temperatures proceeds by a free radical mechanism. As we have seen, it is necessary to devise a mechanism which will lead to a first-order rate equation and an activation energy in agreement with experiment.

Rice and Herzfeld (77) suggested that the following mechanism would fulfil these conditions:

	Activation energy Kcal.	
$C_2H_6 \longrightarrow 2\ CH_3$	80	(1)
$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$	20	(2)
$C_2H_5 \longrightarrow C_2H_4 + H$	49	(3)
$H + C_2H_6 \longrightarrow H_2 + C_2H_5$	17	(4)
$2\ H \longrightarrow H_2$	Triple collision	(5)

	Activation energy Kcal.	
$H + C_2H_5 \longrightarrow C_2H_4 + H_2$	Small	(6)
or $\longrightarrow C_2H_6$		
$H + CH_3 \longrightarrow CH_4$	Small	(7)
$CH_3 + C_2H_5 \longrightarrow C_3H_8$	8	(8)
$2\,C_2H_5 \longrightarrow C_4H_{10}$	8	(9)

By virtue of reactions 3 and 4, reaction chains will occur, a large number of ethane molecules being decomposed for each primary act. Some of these activation energies are based on experimental data and some are frankly assigned to agree with free radical mechanisms. Assuming reactions 5,7,8 and 9 to be negligible, we get from the scheme

$$E\ (\text{overall}) = \tfrac{1}{2}\,(E_1+E_3+E_4-E_6) = 73\ \text{Kcal.}$$

in good agreement with the measurements of Marek and McCluer. For the overall rate of reaction the Rice-Herzfeld scheme leads to the expressions:

$$-\frac{d}{dt}\,(C_2H_6) = k\,(C_2H_6)$$

$$\log k = \tfrac{1}{2}\log\frac{k_1k_3k_4}{2\,k_6}$$

i.e., the reaction is first order as found experimentally. Rice and Herzfeld evaluate the velocity constants roughly by assuming that first order reactions have constants given approximately by $10^{14}\ e^{-E/RT}$ sec.$^{-1}$, and all bimolecular constants are $10^{9}\ e^{-E/RT}$ litre mol.$^{-1}$ sec.$^{-1}$ On this basis they get for the overall decomposition

$$\log_{10} k = 13.7 - \frac{73000}{2.3\ RT} \quad \text{sec.}^{-1}$$

which is satisfactory agreement with Marek and McCluer's experimental equation. The chain length calculated from the above mechanism is about 100.

It follows, therefore, that it is possible to explain the ethane decomposition on the free radical basis and it is known that a free radical mechanism prevails largely at very high temperatures.

In a foregoing section the three general methods of testing the free radical theory were enumerated. The first one has been tried by Patat and Sachsse (61,62). They measured the stationary concentration of hydrogen atoms by studying the rate of ortho-para hydrogen conversion in the presence of decomposing ethane. At 590°C their experimental value is 10^{-11} mole./litre. The value predicted by the Rice-Herzfeld mechanism is about 1000 times larger, viz. $10^{-8.2}$.

Resorting to the second method Steacie, and Phillips (94), Trenner, Morikawa and Taylor (116) and Steacie (102) investigated the single reaction (4). It appears that E_4 is about 9 Kcal. instead of the assigned value of 17 Kcal. If the hydrogen atom concentration predicted by the free radical chain theory is calculated by using the lower values for E_4, we obtain a result which agrees fairly well with experiment. Such a change in reaction (4), however, by altering the relative concentrations of the reacting substances upsets the relationship between the rate constants and reactions 8 and 9 can no longer be neglected. Under these circumstances the overall activation energy is not seriously affected but the scheme no longer predicts a first order rate.

Recent work by Trenner, Morikawa and Taylor (116) indicates that the reaction

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

is not to be ignored. This step, which apparently has an activation energy of 7.4 Kcal. (faster than step 4) would fundamentally alter the chain carrying steps in the Rice-Herzfeld scheme and would destroy its agreement with experiment.

Sickman and O.K. Rice (90) have found evidence that methyl radicals from decomposing azomethane will decompose ethane to some extent. On the other hand

Echols and Pease (17) found that radicals from ethylene oxide decomposition would not cause the decomposition of ethane at 425°C, although they decompose propane and butane. In any case, however, it should be emphasized that the fact that radicals can cause the sensitized decomposition of a substance is not quite sufficient proof that the ordinary decomposition of the substance involves them.

Recently Staveley (93) has investigated the occurence of free radicals in the ethane decomposition by the inhibitory effect of nitric oxide. By this method he finds a mean chain length of 12.2 at 620°C and an ethane pressure of 150 mm. Staveley suggests that comparatively few decomposing molecules give rise to chains, but that these chains are very long, of the order of 10^5 to 10^7 units. In view of the fact that sensitized decomposition of ethane by radicals does not seem to occur easily, such a chain length appears to be very unlikely.

Frost (21) and Storch and Kassel (107) in recently published works conclude that the Rice-Herzfeld schemes are not in agreement with results. They set forth mechanisms which explain their own results.

From this discussion it would appear that the Rice-Herzfeld mechanisms are untenable in their present form. More information about single reactions, however, may lead to a revision which would be quite satisfactory.

Propane

Photochemical and Atomic Reactions

Very little work has been done on the atomic and photochemical reactions of propane. Kemula and Dyduszynski (48) have shown that the main reaction of propane photolysis is

$$C_3H_8 + h\nu \; (1850 \text{ Å}) \longrightarrow C_3H_6 + H_2$$

By mercury photosensitization, Taylor and Hill (108,109) found that propane reacted faster with hydrogen atoms than did ethane, but more slowly than butane.

Recently, in the course of another investigation Trenner, Morikawa and Taylor (116) made two runs with propane and deuterium atoms produced by the Wood-Bonhoeffer method. The products of the two runs are tabulated below.

Temperature °C	Methane	Ethane	Propane	% Decomposition
24.7	4.3	0.8	97.0	2.4
109	11.1	6.3	79.8	10.6

The ethane and methane were highly deuterized but the propane was not exchanged. Propane appears then to be much less reactive than ethane. Bonhoeffer and Harteck (9) previously reported catalytic recombination of hydrogen atoms in the presence of propane, for which Taylor and co-workers found no evidence. These findings are not in accord with the work of Frankenburger and Zell (22) which pointed toward increased reactivity with increased molecular weight of the hydrocarbon. It is quite evident that more information along this line would be desirable.

The Thermal Decomposition of Propane

The early papers on the propane decomposition by Pease (67), Frey and Smith (24) and others (16,65,89) served to establish the fact that the reaction is principally homogenous and first order. The main courses of the reaction are

$$C_3H_8 \longrightarrow C_3H_6 + H_2$$

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$

a certain amount of ethane and butane being formed.

Marek and McCluer (53) and Paul and Marek (63) have investigated the kinetics and products of the reaction in detail. Steacie and Puddington (99) have also studied the decomposition recently The various investigators are quite unanimous in their evidence concerning the products. Hydrogen, methane, ethylene, and propylene occur in approximately equimolecular amounts. Small amounts of ethane are also found. On the whole it may be said, therefore, that the two above mentioned reactions describe the overall change quite well.

Free Radicals and the Propane Decomposition

Rice, Johnston, and Evering (79) showed that free radicals could be detected in the decomposition of propane, and Rice and Johnston (78) found the activation energy of the free radical split to be 71.5 Kcal. Rice (72,74) suggests as a mechanism for the decomposition

$$CH_3CH_2CH_3 \longrightarrow CH_3 + C_2H_5$$

$$R + C_3H_8 \longrightarrow RH + CH_3CH_3CH_2 \longrightarrow RH + C_2H_4 + CH_3$$

$$R + C_3H_8 \longrightarrow RH + CH_3CH_2CH_2 \longrightarrow RH + CH_3CH = CH_2 + H$$

where R represents a hydrogen atom or any radical. From this scheme, making suitable assumptions regarding the relative reactivity of primary and secondary hydrogen atoms, he gets for the overall decomposition:

$$6\ C_3H_8 \longrightarrow 6\ C_2H_4 + 6\ CH_4$$

$$4\ C_3H_8 \longrightarrow 4\ C_3H_6 + 4\ H_2$$

which is in satisfactory agreement with the products of the reaction found experimentally.

Belchetz and Rideal (6) investigated the decomposition of propane on a carbon filament at low pressures, using the technique described above for methane. They concluded that the primary process was

$$CH_3CH_2CH_3 \longrightarrow CH_3CH = CH_2 + H_2$$

followed by $CH_3CH = CH_2 \longrightarrow C_2H_4 + CH_2$

$$CH_2 + etc \longrightarrow CH_3 + etc.$$

The activation energy of the primary process was found to be 94.2 Kcal. There is thus a very great decrepancy between their work and that of Rice and his collaborators. Rice's value for the free radical split is much closer to the experimental activation energy of the decomposition reaction. On the whole the evidence seems to favour the Rice mechanism for the free radical split although the question is still an open one.

When the free radical chain mechanism for the propane decomposition was subjected to tests similar to those used in the case of ethane, very similar results were obtained. Experiments by Patat on the stationary hydrogen atom concentration showed that there were far too few hydrogen atoms as compared to predictions of the Rice-Herzfeld mechanism.

There is, on the other hand, ample evidence that radicals can produce a sensitized chain decomposition of propane. Echols and Pease (17) showed that propane could be decomposed by radicals from ethylene oxide at 425°C. They estimated an average chain length of 0.55. As in the case of ethane it is possible that there are comparatively few long chains rather than many short ones. Sickman and O.K. Rice found that methyl radicals caused some propane decomposition.

On the whole it may be said that at low temperatures the Rice mechanism is not in accord with facts, in spite of its success in predicting products of reaction. As previously intimated, judgement cannot be passed until much more has been learned about part reactions.

THE REACTION OF HYDROGEN ATOMS WITH PROPANE

In the foregoing introduction we have had a chance to assess the great stimulus which the Rice-Herzfeld mechanisms have given to the investigation of organic decomposition reactions. The proposed scheme for the ethane decomposition, which is based on the chain steps;

$$(3) \qquad C_2H_5 \longrightarrow C_2H_4 + H$$

$$(4) \qquad H + C_2H_6 \longrightarrow H_2 + C_2H_5$$

has been discussed pro and con.

Perhaps the most serious apparent discrepancy between the Rice theory and experiment is that which arises from the investigation of the reaction of hydrogen atoms with ethane. Trenner, Morikawa and Taylor (116) found that methane was produced in this reaction, and concluded that the reaction

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 \qquad (7)$$

had an activation energy several Kcal. lower than number (4) above. The production of methane in the reaction of hydrogen atoms with ethane was confirmed by Steacie (102). Further information about the relative rates of reactions (4) and (7) comes from the investigation of the mercury photosensitized reactions of ethane (97,98). The mechanism of these reactions as proposed by Steacie and Phillips (97) accounts satisfactorily for the process and for the products of the reaction, hydrogen, methane, propane and butane, provided that it is assumed that reaction (7) is about four times as fast as (4) at room temperature. This assumption would make still more difficult the application of the Rice theory to the ethane decomposition, since it brings in reaction (7) as a major step in the process. Actually however, the occurrence of reaction (7) would have much more serious consequences than this. All the Rice mechanisms are based on the idea that reactions of the type

$$R + HX \longrightarrow RH + X$$

occur readily, i.e. a radical abstracts a hydrogen atom from a molecule, but that hydrocarbon chain breaking reactions of the type

$$R + CH_3(CH_2)_nCH_3 \longrightarrow RCH_3 + CH_3(CH_2)_n$$

never occur to an appreciable extent. Hence the occurrence of reaction (7) is contrary to general postulates of the entire Rice theory for <u>all</u> substances.

In order to account for the production of methane, but at the same time avoid the postulation of reactions like (7), Taylor has recently suggested (113) that it is possible that methane formation occurs by

$$H + C_2H_5 \longrightarrow 2\ CH_3 \qquad (13)$$

$$H + CH_3 \longrightarrow CH_4 \qquad (14)$$

Rice and Teller (82) also favour this mechanism on theoretical grounds. Steacie and Phillips have pointed out (97) that there are difficulties in applying this mechanism to the mercury photosensitized decomposition of ethane, but these are probably not insurmountable.

It is apparent from the above discussion that the decision as to the relative probabilities of the reactions

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

and $H + C_2H_5 \longrightarrow 2\ CH_3$

carries with it the fate of practically all the Rice mechanisms. Further information is therefore highly desirable, and with this in view experiments have been made on the reaction of hydrogen atoms with propane.

Experimental

The experimental work was done with an apparatus of the Wood-Bonhoeffer type (figure 2). Hydrogen atoms from the discharge A were mixed with propane in the reaction chamber C. The products were pumped off and condensed out in the trap system (figure 3).

Purification trains and flow regulation systems are shown in figure 1. Hydrogen was taken from a commercial cyclinder J, by means of a reducing valve. It was passed through a quartz tube charged with platinized asbestos heated electrically to about 500°C. The gas then passed through a blow-off trap L, through a trap M surrounded by liquid air to remove water vapour and impurities and finally gained access to the discharge by diffusing through the calibrated flowmeter F.

The propane was taken directly from a tank obtained from the Ohio Chemical and Manufacturing Company. The hydrocarbon was found to be nearly 99.8 % pure, and was used therefore without further purification. Due to a shortage in the number of tanks, the gas was generally kept stored in the ten litre volume V_1. Before making a run some propane was first expanded into V_2 and V_3, then V_1 was closed off. The volume of propane passing the calibrated flowmeter F_2 in a given

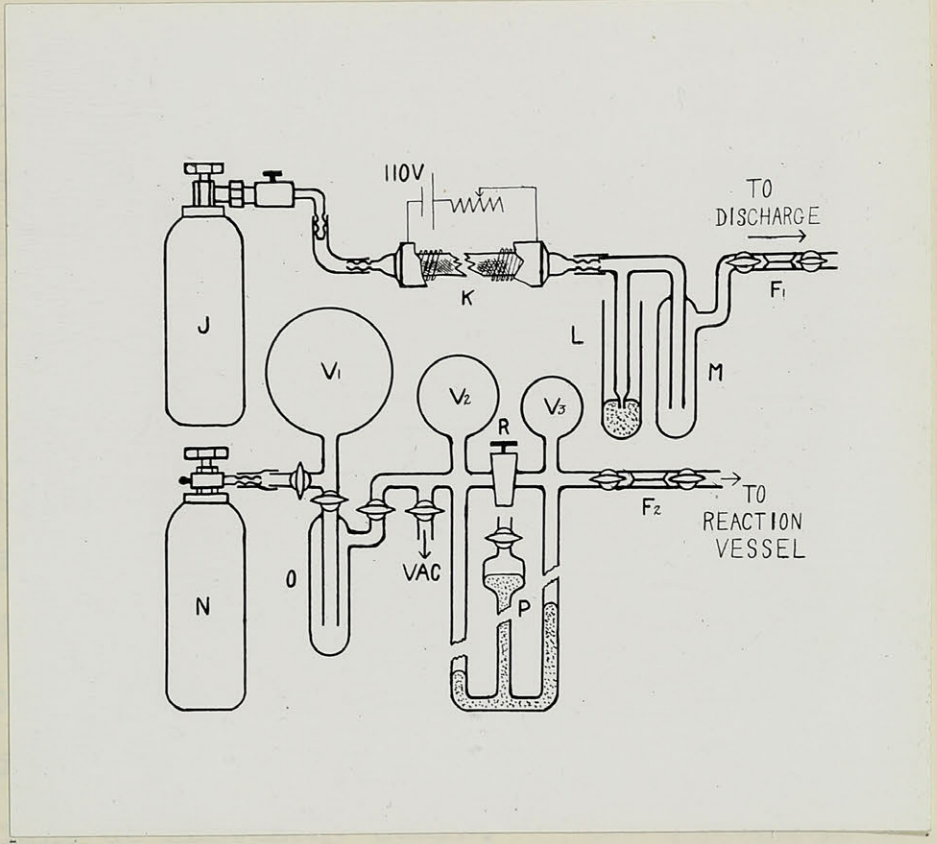

Figure I

Purification Trains and Flow Regulation Systems.

time was kept at a constant value by keeping a constant pressure head in V_3. This was accomplished by expanding gas from V_2 through the needle valve R at such a rate that the right arm of the absolute manometer P showed a reasonably constant reading throughout an experiment.

The ratio of the reactants could easily be changed at will. To vary the propane flow rate it was only necessary to change the constant head in V_3, and to change the hydrogen flow required only adjusting the depth of the blow-off tube in the trap L.

The hydrogen atoms were formed in the high voltage discharge tube A, (figure 2), which consisted of a pyrex tube of 2.5 cm. bore, to which were sealed side tubes containing the aluminium electrodes E. The cyclindrical electrodes were attached to stout platinium wires which passed out through the glass by means of tight de Khotinsky seals. The discharge was operated with an applied voltage of 3500 across the tube and a 5000 ohm resistance. The current was maintained at 200 milliamperes by means of a rhostat in the primary of the transformer.

To get maximium efficiency the discharge was as near as possible to the reaction tube C. The pyrex reaction chamber C had a diameter of 7 cm. and a length of 70 cm., and was surrounded by an electric furnace which could be slipped up and down the tube to permit observation when the efficency of the wall poisoning etc. was being tested. Two tubes entered the reaction vessel from below, one of which (not shown) contained a thermocouple; the other (F) served as an inlet for the propane.

The successful operation of this method of atomic reaction investigation requires the prevention of too fast a recombination of atoms on the walls of the apparatus. In this case the poisoning was accomplished by coating the wall with phosphoric acid. This involved cutting off the tube ends G and H and removing the tube F, by loosening the ground glass joint D. Considerable quantities of distilled water were poured through G and escaped by the drainage tubes H and the opening D. This was followed by a cleansing rinse with fuming nitric acid, then with distilled water. A 5 % phosphoric acid solution followed and when the whole surface was well wetted by this reagent, the system was sealed up and dried by evacuation. This treatment left a coating of metaphosphoric acid on the walls which under higher working temperatures probably dehydrated to phosphoric anhydride. At any rate the poisoning, insured a good working concentration of atoms for some months providing the temperatures used were

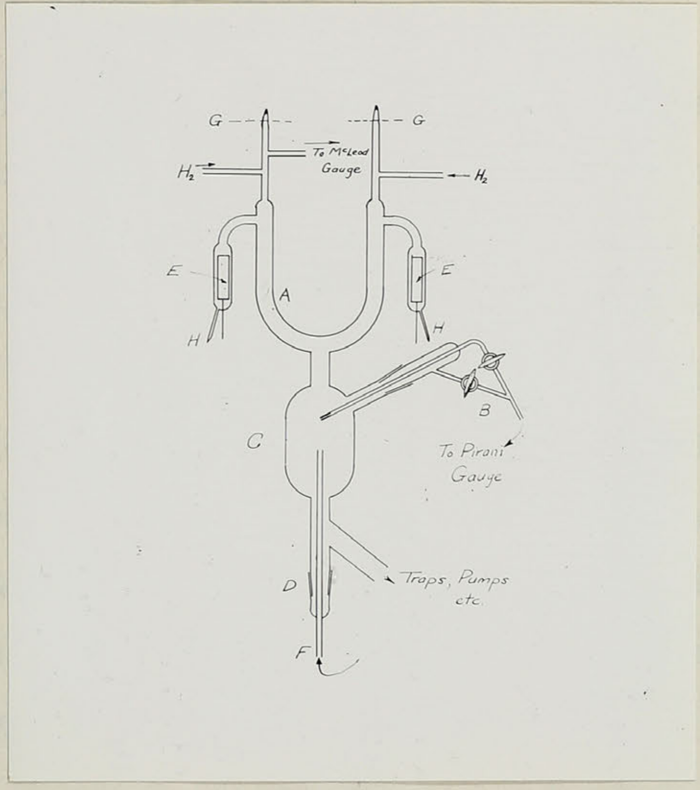

Figure II

Discharge Tube and Reaction Vessel.

not above 250°C. Above this temperature the anhydride slowly distills to cold parts of the apparatus.

The hydrogen atom concentration in the reaction vessel was measured with the Wrede guage B. This was of the usual type (123) and consisted of a tube with a very fine orifice situated in the reaction vessel, and an arrangement of stopcocks by which the inside or outside of the orifice could be connected to a Pirani guage at will.

The diameter of the orifice was small relative to the mean free path of hydrogen, thus when a mixture of hydrogen atoms and hydrogen molecules were present in C a pressure gradient was set up across the orifice due to the different diffusion rates of hydrogen atoms and hydrogen molecules. The pressure gradient could be measured on the Pirani guage which was calibrated with the McLeod guage. Thus, knowing P_1 the pressure inside and P_2 the pressure outside, the percentage atoms is given by

$$\frac{100\ (P_1 - P_2)}{P_1\ (1 - 0.5\sqrt{2})}$$

The atom concentration determinations could not be made during a run as the propane molecules present would upset the above relation. Therefore, measurements were made under nearly identical conditions of pressure, temperature, discharge current and poisoning. The absence of the propane made no great difference in pressure conditions as the ratio $H_2 : C_3H_8$ was high in most experiments.

The size of the reaction vessel and the speed of the pumping was such that the contact time was of the order of one second. After leaving the reaction vessel the products passed through a trap S (figure 3) at -183°C which removed high boiling products such as propane and most of the ethylene and ethane. The remainder passed the trap T and the three stage steel mercury diffusion pump. This had a very high speed and could maintain a pressure of 0.35 mm. in the apparatus when hydrogen was admitted at the rate of 35 c.c. at N.T.P. per minute. After leaving the diffusion pump the low boiling products were largely removed by the silica gel trap Z which was kept at -183°C. The unadsorbed gas passed out through the Hyvac pump. The trap T had no function during a run but acted as a permanent drying trap. Cooled by mixtures of acetone and dry ice, it served between runs to prevent water vapour and grease from getting into the pump and the silica gel. The diameter of all tubing in the pumping and trapping system was about 2 cm. All stopcocks were of corresponding large bore.

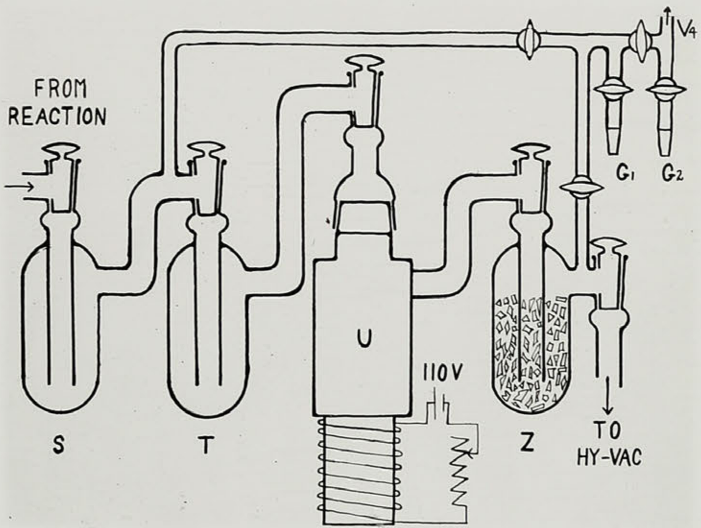

Figure III

Trapping and Pumping System.

At the end of a run, which normally lasted about two hours, the traps S and Z were allowed to warm up to room temperature. The products were pumped off into a gas holder by means of a Toepler pump attached to the joint G_1. In practice it was necessary to pump off the contents of each trap separately, otherwise the propane and ethane in S quickly distilled over to the silica gel in Z, where a great deal of hand pumping was required to remove it.

Trials showed that virtually all of the methane was trapped out in the silica gel as well as a small fraction of the hydrogen passed.

The products in the average experiment amounted to 500 - 700 c.c. A 100 c.c. sample was subjected to absorption analysis in a Burrell gas analysis outfit. This was done in order to keep a check on traces of CO, CO_2, C_2H_2 produced. Also when the volume of ethylene produced was too small to be measured with any accuracy by distillation, its quantity could be checked by ordinary absorption methods. The remainder of the products were distilled in a Podbielniak low temperature apparatus. At first the mixture gave a great deal of trouble. Due to the presence of a considerable amount of hydrogen the mixture could not all be got into the still at once and would only pass in as the hydrogen was bled off. Often "freeze-ups" occurred in this process or in the distillation proper These were traced first to a small percentage of water vapour in the products and later also to the 0.5 % CO_2 which the mixture contained. Thus, it was found necessary to remove any water vapour and carbon dioxide in the mixture by passing the gas over a tube of "dreierite" and soda lime before admitting it to the still. Once in the column the distillation proceeded in the usual manner. The first fraction which consisted of methane and hydrogen, was subjected to combustion analysis in order to determine the percentage of the former product.

Sixteen runs were made at the four temperatures 30°C, 100°C, 170°C, 250°C. The experimental conditions of the different runs are given in Table I.

Table I

Experimental Conditions

Run No.	Temperature °C	Pressure	(%) Atom Concentration	Propane flow c.c./sec at N.T.P	Hydrogen flow c.c./sec at N.T.P.
1	33	0.36	22	0.0690	0.517
2	31	0.36	22	0.0688	0.539
3	30	0.36	22	0.0674	0.521
4	32	0.36	22	0.0678	0.521
5	32	0.36	22	0.0603	0.515
6	30	0.36	22	0.0370	0.507
7	31	0.36	22	0.115	0.501
8	100	0.36	19	0.0687	0.526
9	100	0.35	19	0.0692	0.510
10	172	0.36	16	0.0705	0.526
11	171	0.36	16	0.0670	0.521
12	170	0.36	16	0.0698	0.526
13	170	0.36	16	0.0708	0.524
14	250	0.36	12	0.0693	0.505
15	250	0.36	12	0.0698	0.524
16	250	0.36	12	0.0700	0.524

Results

The analyses of the reaction products are given in Table II. A trace of acetylene was found on some occasions, but no significance can be attached to its presence in such small quantity.

When the analytical results are translated into terms of propane decomposition we obtain the values shown in Table III.

When these values are averaged we obtain Table IV. This shows the best values for reaction products and the total percentage decomposition of propane at the various temperatures.

The first results obtained revealed two striking facts. Firstly no ethane was found in the products of the runs at room temperature and secondly the reaction did not seem to yield any products heavier than propane. As these were important points they were checked with considerable care.

The still head used on the Podbielniak apparatus was redesigned. A tight fitting metal spiral was fitted into the space between the cooling jacket of the head and the column. Also, the hole through which the column passed in the lower part of the head was made so small as to be nearly flush with

Table II

The Products of the Reaction

Products, mole per cent

Run No.	CH_4	C_2H_6	C_2H_4	CO_2	C_3H_8
1	23.2	....	....	1.0	75.8
2	21.8	....	....	0.5	77.7
3	18.0	....	0.7	0.3	81.0
4	22.5	....	....	0.5	77.0
5	19.2	....	....	0.5	80.3
6	25.8	....	....	0.3	73.9
7	(b) 12.8	....	....	0.3	86.9
8	13.5	3.2	0.8	0.5	82.0
9	12.5	5.7	0.8	0.5	80.5
10	9.7	11.7	1.4	0.6	76.6
11	9.2	12.5	2.0	0.6	75.7
12	8.8	10.1	1.5	0.6	79.0
13	8.8	12.2	1.8	0.6	76.6
14	....	....	3.3	0.7	....
15	7.1	14.3	3.2	0.7	74.5
16	5.7	14.0	3.2	0.6	76.3

(b) The ratio H_2/C_3H_8 was varied in these runs, see Table I.

Table III

Per cent propane converted to :

Run No.	CH_4	C_2H_6	C_2H_4	CO_2	Total % Reaction
1	9.2	.....	.....	0.4	9.60
2	8.5	.....	.....	0.2	8.70
3	6.9	.....	0.50	0.15	7.55
4	8.9	.....	.....	0.2	9.10
5	7.4	.....	.....	0.2	7.60
6	10.4	.....	.....	0.15	10.55
7	4.7	.....	.....	0.15	4.85
8	5.03	2.52	0.60	0.20	8.35
9	4.68	4.26	0.60	0.20	9.74
10	3.64	8.78	1.05	0.22	13.69
11	3.42	9.41	1.50	0.23	14.56
12	3.28	7.50	1.10	0.22	12.10
13	3.33	8.45	1.36	0.22	13.38
14	.....	.....	.....	.....	.....
15	2.66	10.74	2.40	0.26	16.06
16	2.12	10.38	2.37	0.22	15.09

Table IV

Averaged per cent conversion to:

Run No.	Temperature °C	CH_4	C_2H_6	C_2H_4	CO_2	Total % Reaction
1,2,3,4,5,	32	8.2	.....	.....	0.2	8.5
8,9,	100	4.9	3.4	0.6	0.2	9.1
10,11,12,13,	171	3.4	8.5	1.2	0.2	13.3
14,15,16,	250	2.4	10.6	2.4	0.2	15.7

the column. This modification gave better control over the cooling, for less liquid air passed down the column and some could be made to pass up around the spiral and out the top. These changes, along with adjustment of the position of the thermocouple, decreased the time-temperature lag and generally increased the accuracy of the analysis. Several "blanks" on synthetic mixtures containing only small percentages of ethane showed that it was not possible to miss 1 % ethane in a sample of the usual size employed. Generally 0.5 % ethane could be detected. These tests along with several combustion analyses on the first part of the propane fraction proved beyond a doubt that the amount of the ethane present did not exceed 0.5 % of the total products.

The absence of hydrocarbons heavier than propane in quantities greater than 0.5 % was proved by a few combustion analyses on the heavier part of the distillate. A slight oiliness of the mercury in the Toepler pump was observed after several runs. This led to the belief that a trace of hexane was probably present.

From the conditions of experiment given in Table I and the total percentage decompositions appearing in Table III it was possible to calculate the collision yields and the activation energy of the primary reaction. This calculation, naturally, rests on the reasonable assumption that the initial reaction between hydrogen atoms and propane is the rate governing step, eventually leading to the various products by a series of much faster reactions. The results of these computations and the various preliminary steps leading up to them are shown in Table V.

Knowing the amount of propane and hydrogen at N.T.P. flowing per second, the percentage of atoms present and the experimental conditions, it is possible to calculate the total flow of gas at the temperature and pressure of the experiment. From a knowledge of the size of the reaction vessel, which was 1370 c.c., the contact time is calculated. Then from the fraction of hydrogen atoms present and the total pressure, we get the partial pressure of hydrogen atoms in the system and the number of atoms per cubic centimeter in the reaction vessel. We then calculate $Z_{C_3H_8}$, H, the number of collisions made by one propane molecule with hydrogen atoms in one second. This is obtained from the relation (36,11)

$$Z_{C_3H_8,\,H} = 2\sqrt{2}\left(\frac{d_H + d_{C_3H_8}}{2}\right)^2 \sqrt{\frac{M_H + M_{C_3H_8}}{M_H\, M_{C_3H_8}}} \cdot RT\, N_H$$

Table V (a)

Calculation of Collision Yields and Activation Energies

Run No.	Temperature °C	Total flow cc./sec. at expermental conditions (corrected for presence of atoms)	Reaction time, sec.	Partial pressure of hydrogen atoms cm.
1	33	1540	0.890	0.0071
2	31	1580	0.868	0.0071
3	30	1529	0.895	0.0071
4	32	1530	0.895	0.0071
5	32	1512	0.907	0.0072
6	30	1420	0.965	0.0074
7	31	1590	0.861	0.0066
8	100	1880	0.729	0.0061
9	100	1880	0.729	0.0059
10	172	2210	0.620	0.0051
11	171	2170	0.631	0.0051
12	170	2180	0.628	0.0051
13	170	2180	0.628	0.0051
14	250	2450	0.559	0.0038
15	250	2540	0.540	0.0038
16	250	2540	0.540	0.0038

Table V (b)

Calculation of Collision Yields and Activation Energies

Run No.	$Z_{C_3H_8,H}$ sec.	$Z_{C_3H_8,H}$ Reaction time	% Reaction	Collision Yield	E. Kcal A = 0.1
1	1.84×10^6	1.64×10^6	9.60	5.85×10^{-8}	8.7
2	1.85×10^6	1.61×10^6	8.70	5.40×10^{-8}	8.7
3	1.85×10^6	1.66×10^6	7.55	4.55×10^{-8}	8.7
4	1.85×10^6	1.66×10^6	9.10	5.50×10^{-8}	8.7
5	1.87×10^6	1.70×10^6	7.60	4.45×10^{-8}	8.8
6	1.92×10^6	1.85×10^6	10.55	5.70×10^{-8}	8.6
7	1.72×10^6	1.48×10^6	4.85	3.30×10^{-8}	9.0
8	1.44×10^6	1.05×10^6	8.35	7.95×10^{-8}	10.4
9	1.39×10^6	1.01×10^6	9.74	9.65×10^{-8}	10.2
10	1.10×10^6	6.82×10^5	13.69	2.00×10^{-7}	11.6
11	1.10×10^6	6.95×10^5	14.56	2.10×10^{-7}	11.5
12	1.10×10^6	6.90×10^5	12.10	1.75×10^{-7}	11.7
13	1.10×10^6	6.90×10^5	13.38	1.95×10^{-7}	11.6
14					
15	7.55×10^5	4.08×10^5	16.06	3.95×10^{-7}	12.9
16	7.55×10^5	4.08×10^5	15.09	3.70×10^{-7}	13.0

Where the d's are the molecular diameters and the M's are the molecular weights. Assuming the diameter of the propane molecule to be 4.2×10^{-8} cm. (114) and the collision diameter of a hydrogen atom to be 2.14×10^{-8} cm., this expression reduces to

$$Z_{C_3H_8, H} = (\text{constants})\, N_H \sqrt{T}$$

and since the number of atoms is a function of the partial pressure of the hydrogen atoms and the temperature, we have finally

$$Z_{C_3H_8, H} = 4.55 \times 10^{9} \frac{P_H}{\sqrt{T}}$$

whence we get the values given in column 2 Table V (b). We then get the number of collisions occurring during the reaction time. The next column gives the percentage reaction. The collision yield of the primary step is calculated next and the last column gives the activation energy, computed from the collision yield according to the relation

$$\text{collision yield} = Ae^{-E}/RT,$$

the value of E being calculated on the assumption that the steric factor is 0.1 in this case.

The Reaction of Deuterium Atoms with Propane

Perusal of Table V in the previous section shows that in the temperature range between 30°C and 250°C the activation energy varies from 9 to 13 Kcal. Among other explanations for this variation we cannot neglect the possibility of some propane re-forming reaction.

The work of Steacie and Phillips (94) and of Trenner, Morikawa and Taylor (116) indicate that ethane exchanges with deuterium atoms according to the reactions:

$$C_2H_6 + D \longrightarrow C_2H_5 + HD \qquad (1)$$

$$C_2H_5 + D \longrightarrow C_2H_5D \qquad (2)$$

Experiments point to a value of about 9 Kcal. for the activation energy of (1). Trenner, Morikawa and Taylor's results proved that this reaction was not appreciable below 100°C, being superseded by the chain breaking step;

$$C_2H_6 + D \longrightarrow CH_3 + CH_3D$$

at low temperatures.

Now assuming that propane behaves in an analogous manner we might expect a chain breaking reaction at low temperatures which at high temperatures would be accompanied by an exchange process. As the apparent stoichiometric result of the exchange reaction would be zero, the apparent activation energy of the overall decomposition would be expected to rise with increasing temperature. Above all it must be admitted that no value for the activation energy of any reaction can be accepted as reliable until the effect of any back reaction has been assessed.

It was thought that a study of the reaction between deuterium atoms and propane might be profitable from the following view-points:

(1) To investigate any exchange reaction taking place.

(2) To correct the values for the activation energy of the hydrogen atom-propane reaction for any reverse process.

(3) To study the deuterization of the methane and ethane products in the hope that some light might be shed upon the nature of secondary processes.

Experimental

The apparatus used in the following experiments was essentially that shown in figures I, II and III. The technique of operation was almost identical with that described in the previous section.

As before, 99.8 % propane was used and gained access to the reaction vessel C by passing through the flow regulation system shown in figure I (N,O,R,P). The deuterium used was obtained from 99.6 % Norwegian deuterium oxide by treating it with C.P. calcium metal turnings. The deuterium oxide was allowed to drop onto the calcium from a small separatory funnel. The deuterium bubbled through a mercury trap and after being dried in a liquid air trap passed to storage volumes. The height of the mercury in the bubble trap just exceeded the head of water vapour at room temperature and thus prevented mass distillation of deuterium oxide into the liquid air trap. Cold tap water circulating in a copper spiral about the calcium tube also prevented the deuterium oxide from distilling into neighbouring parts of the apparatus. This apparatus appeared to be fairly practical, as it did not require much attention and was free of the explosion hazard which the use of sodium involves.

When a run was to be made, about a litre of the dry deuterium was pumped off into a gas-holder and was fed directly into the flowmeter F_1 without further purification. It was not thought necessary to change the flowmeter F_1 which was the one used in the hydrogen atom reaction. Actually the rate of gas flow under the same pressure head was smaller in the ratio of $1/\sqrt{2}$, but the conditions in the reaction vessel were not appreciably changed for the following reasons. If the pressure is kept the same, deuterium will flow through the apparatus slower than hydrogen and will take more time to get from the discharge to the reaction vessel. During this time, however, it will undergo less collisions on account of its lower molecular velocity. These two effects nearly balance, and there will be no appreciable difference in the number of collisions undergone by hydrogen or deuterium atoms (or molecules) while travelling between the discharge tube and the reaction vessel. Also, the activation energies of the recombination reactions

$$H + H\ (+M) \longrightarrow H_2\ (+M)$$

$$\text{and}\quad D + D\ (+M) \longrightarrow D_2\ (+M)$$

will not differ appreciably since atoms have no zero-point energy. In view of these considerations any atom concentration determinations and other tests were made with hydrogen. In any case, the possible error from this source is negligible compared to the uncertainties in the atom concentration due to fluctations in the activity of the walls.

In the runs at room temperature the trapping was modified slightly. Both traps S and T were kept surrounded by liquid air. It was found that this effected a perfect separation of the propane and the methane. The propane could be frozen off easily into a tube attached to the joint G_1. The methane along with the considerable amount of deuterium adsorbed by the gel was pumped off into a gas-holder. The propane was carried to the combustion apparatus, burned in the usual manner, and the water saved for analysis.

It was found possible to separate most of the deuterium from the methane by passing the mixture through the Podbielniak apparatus and carefully drawing off the deuterium while using maximum cooling. The remaining methane, which contained a little deuterium, was combusted quantitatively and the water preserved. The methane generally contained from 1 to 5 % deuterium, thus a small correction had to be made. However, as one molecule of methane yields twice as much water as one molecule of deuterium the correction is never large. It is realized that the deuterium mixed with the methane would not be pure, but in view of the ratio 6 : 1 between the deuterium and the propane used, and the relatively small percentage reaction, the deuterium certainly would not be less than 90 % heavy.

In the higher temperature runs, the only difference was that all of the products were pumped off into the gas-holder together and then the deuterized methane, ethane and propane were separated by distillation

Table VI

Experimental Conditions

Run No.	Temperature °C	Pressure	(%) Atom Concentration	Propane flow cc./sec. at N.T.P.	Deuterium flow cc./sec. at N.T.P.
1	30	0.35	22	0.0690	0.370
2	30	0.35	22	0.0693	0.370
3	30	0.35	22	0.0698	0.370
4	30	0.35	22	0.0700	0.370
5	170	0.35	16	0.0692	0.370
6	170	0.35	16	0.0708	0.370
7	250	0.35	12	0.0700	0.370
8	250	0.35	12	0.0692	0.370

and burned separately.

The experimental conditions of the various runs are listed in Table VI.

The Deuterium Analysis

The deuterium oxide-water mixtures obtained from burning the reaction products were analysed in an apparatus of the Harteck (34) type (figure 4). The principle of this method, which was first used by Geib and Steacie, is based upon the difference in vapour pressure and heat conductivity of deuterium oxide and water. In practice standard mixtures of deuterium oxide and water, and unknowns are introduced into the apparatus by ground joint connections. The samples are distilled separately back and forth between the two traps under a vacuum of about 10^{-4} mm. of mercury. Some ten distillations generally ensures the removal of all dissolved or adsorbed gas, after which the purified water is frozen into one of the storage bulbs.

When an analysis is to be made the metal block is cooled to liquid air temperature, then quickly surrounded by a Dewar jar filled with pre-cooled saturated brine. An ice-salt eutectic quickly freezes around the block and serves for some hours as a reliable constant temperature source. The Pirani-guage tube

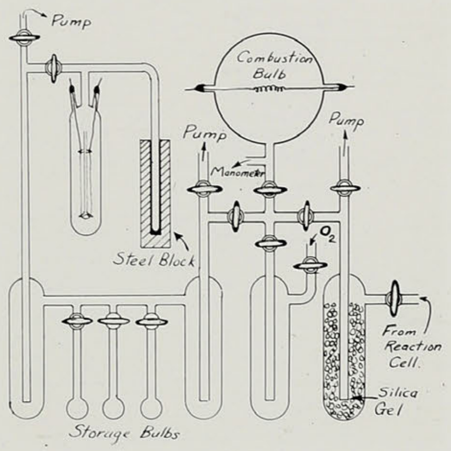

Figure IV

Harteck Apparatus for Analysis of Deuterium Oxide--Water Mixtures.

is surrounded by a well stirred ice solution. To make a determination, a small amount of vapour from a sample is allowed to enter the thermostated system. The resistance of the Pirani filament is measured. Theoretically the percentage of deuterium oxide in a certain sample is nearly a straight line function of the resistance of the filament. Thus the exchange figure for any sample is found by very simple calculations. Naturally, the method is susceptable to drift etc. and the accuracy cannot be pushed much further than 0.5 %.

Results

The results of the analyses of the various reaction products are given in Table VII.

As methane and propane were the only products of the runs at 30°C, complete separation of the hydrocarbons was easy. The experiments at higher temperatures yielded considerable ethane which was highly deuterized. In runs 5, 6 and 7 the uncertain end fractions were discarded and only the middle cuts were preserved for analysis, In the Podbielniak apparatus used, the cut between methane and ethane was always quite sharp but propane and ethane could not be separated so completely. In runs 5, 6 and 7 the first 30 or 40 c.c.

Table VII

		% deuterization			
Run No.	Temperature °C	CH_4	C_2H_6	Fraction A + B C_3H_8	Corrected C_3H_8
1	30	....	absent	....	<0.5
2	30	55.0	absent	....	<0.5
3	30	62.3	absent	....	<0.5
4	30	56.5	absent	....	<0.5
5	170	high	52.8	3.4	<0.5
6	170	high	65.8	2.5	<0.5
7	250	high	54.0	2.2	<0.5
8	250	high	....	....	<0.5

of the propane fraction was discarded. The small percentage deuterization of propane in these runs pointed to two possibilities; either the propane was exchanged about 2.5 % or it was undeuterized but contaminated with a small amount of deutero-ethane from the previous fraction.

To settle this point some highly deuterized ethane was prepared by thermally equilibriating ethylene and excess deuterium. This prepared ethane was mixed with ordinary propane and distilled. An end fraction of 35 c.c. containing ethane and propane was taken as in runs 5, 6 and 7 and then three successive 35 c.c. fractions of propane A, B and C. These samples were taken and analysed for deuterium content. When run number 8 was made, a similar set of 35 c.c. fractions were taken and analysed. The detailed results of the analyses of the fractions from the blank and from number 8 appear below.

% deuterization

Run No.	C_2H_6	$C_2H_6 + C_3H_8$	Fractions C_3H_8		
			A	B	C
Blank	49.0	25.0	7.8	<0.5	<0.5
# 8		20.1	5.9	<0.5	....

These results showed that some of the deutero-ethane was contaminating the second fraction and that a third fraction was almost entirely free of deuterium. The propane samples analysed in the case of runs 5, 6 and 7 correspond roughly to the two fractions A + B combined. Thus, by making use of the data on the exact size of the fractions taken in these runs, and the deuterization found in A and B of the blank (and # 8), it was possible to correct for contamination from the ethane fraction. The corrected value for the propane exchange appears in the extreme right hand column of Table VII.

Due to the small yield of methane at the higher temperatures, it was found very difficult to separate enough of it from the hydrogen and deuterium to give a reliable analysis. Where determinations were made high exchanges were indicated.

THE REACTION OF OXYGEN ATOMS WITH METHANE

There is considerable uncertainty regarding the theorical basis of the oxidation reactions of the hydrocarbons. According to the hydroxylation theory, which was proposed by Bone (7), and has been mainly upheld by him and his co-workers, the fundamental reactions in the oxidation of methane are

$$CH_4 + \tfrac{1}{2} O_2 \longrightarrow CH_3OH \qquad (1)$$

$$CH_3OH + \tfrac{1}{2} O_2 \longrightarrow H_2CO + H_2O \qquad (2)$$

The peroxidation theory (18) assumes, on the other hand, that the first stage in oxidation reactions is the formation of an unstable peroxide which initiates chain processes by means of which reactivity is handed on from the active products (peroxides) to the reactant molecules.

Neither of these theories is wholly satisfactory, and Norrish (57) has suggested a theory which is somewhat of a compromise between the other two. He suggests that the initial steps in the oxidation of methane are

$$O + CH_4 \longrightarrow CH_2 + H_2O \qquad (3)$$

$$CH_2 + O_2 \longrightarrow CH_2O + O \qquad (4)$$

thus setting up chain processes in which the carriers are methylene radicals and oxygen atoms.

If Norrish's assumptions are correct, then it should be possible, by the Wood-Bonhoeffer method, to cause reaction (3) to occur to a large extent by introducing atomic oxygen in high concentration into methane. If under these circumstances reaction (3) occurs largely, then in addition to reaction (4) there is also the possibility of

$$CH_2 + CH_4 \longrightarrow C_2H_6 \qquad (5)$$

No direct information is available as to rate of reaction (5), but its occurrence has been suggested by Kassel (42) as a step in the decomposition of methane. Kassel suggests a mechanism for the methane decomposition which fits the experimental data excellently. The arguments on which this mechanism is based lead to the conclusion that reaction (5) has the high activation energy of 44 Kcal. Of course, a successful mechanism is not necessarily unique, and the evidence that E_5 is 44 Kcal. is thus rather speculative.

Belchatz and Rideal (5) investigated the primary split of methane into radicals at high temperatures and concluded that the primary reaction was

$$CH_4 \longrightarrow CH_2 + H_2 \qquad (6)$$

On the other hand, Rice and Dooley (75), using the Rice technique, were unable to detect the methylene radical, and found only methyl radicals in the methane decomposition. They consider the primary split to be

$$CH_4 \longrightarrow CH_3 + H \qquad (7)$$

They also discuss the possibility of the methyl radicals having been formed by secondary processes. If this is so, then the absence of methylene radicals in their experiments must be ascribed to either reaction (5) or

$$CH_4 + CH_2 \longrightarrow 2\ CH_3 \qquad (8)$$

being fast enough to keep the concentration of methylene radicals down to a low value. They show that for this to occur either reaction (8), or more likely (5), would have to have an activation energy less than 13 Kcal., which they consider to be too low.

The concensus of opinion is thus that reaction (5) is a rapid reaction, and that the discrepancy between the work of Rice and Dooley and that of Belchetz and Rideal might be ascribed to its occurrence.

It follows that if the primary step in the oxidation is that postulated by Norrish, as appears likely, then there is the possibility of ethane formation by reaction (5). If this were found to be the case it would lend support to the Norrish mechanism, and at the same time approximately define the activation energy of reaction (5). If no ethane were found, the result would be somewhat inconclusive, since its absence could be due to nonoccurrence of either reaction (3) or (5). It appeared, however, to be worth investigating the possibility of the occurrence of ethane in the reaction of oxygen atoms with methane.

The reaction of oxygen atoms with methane has been investigated by Harteck and Kopsch (35). They used the usual Wood-Bonhoeffer type of apparatus, and froze the condensable products out of the flowing stream by means of a liquid air trap. **With this** method the only condensable products were carbon dioxide and water, since carbon monoxide and ethane would have passed through the trap and been lost. They found more water than carbon dioxide, approximately in the ratio of 2 : 1 by weight, instead of 1 : 1.22 as required if the reaction went completely by

$$4O + CH_4 \longrightarrow CO_2 + 2\,H_2O\ .$$

They therefore concluded that carbon monoxide was formed as well. From the water formed they calculated the following percentage oxidation of methane in various experiments.

Temperature, °C	30	100	189
% methane reacted	1.0,0.9,1.1	2.1,2.0	5.9,6.5

The oxygen atom concentration in these experiments was approximately 30 %. The carbon dioxide formed must have come from some intermediate product, such as formic acid, since the oxidation of carbon monoxide by oxygen atoms is quite slow. The results indicated an activation energy for the reaction of approximately 7 Kcal. (27).

Experimental

The apparatus was essentially the same as that used in the previously mentioned investigations of hydrogen and deuterium atom reactions. The current through the discharge was maintained at 320 milliamperes. In these experiments no attempt was made to measure the oxygen atom concentration, since the main purpose of the investigation was the determination of the products of reaction. Also, it is doubtful whether the Wrede guage, used in hydrogen atom determinations, would function properly with oxygen. Due to the smaller mean path of oxygen, the orifice used would have to be exceedingly small. This would introduce susceptibility to clogging, and difficulties due to the long time required for reaching equilibrium. However, from the intensity of the afterglow, as compared with previous observations of the same kind with known oxygen atom concentrations, there was approximately 20 % atoms at room temperature. The uncertainty in this value is certainly less than a factor of 2.

The walls of the apparatus were poisoned by rinsing with a 5 % solution of phosphoric acid in the usual way. Tank oxygen was used. It contained no appreciable impurity other than a small amount of nitrogen and the rare gases. The oxygen was admitted to the discharge through the blow-off tube and the calibrated capillary flowmeter F_1 (figure I). Methane was secured in cylinders from the Ohio Chemical and Manufacturing Company. It was purified by rough distillation in the trap O (figure I). The first third fraction was pumped off, the middle third was kept and stored in the volume V_1 and the heavy third fraction was discarded. The purified methane gained access to the reaction chamber by means of the same flow regulation system used for propane in the previous experiments.

The products of the reaction were trapped in the usual manner. Trap S (figure 3) was kept at -80°C in order to remove easily condensable products. The large silica gel trap Z cooled to -183°C served to remove methane and other low boiling gases.

It was soon found that no heavy products were deposited in the first trap. At the end of an experiment, therefore, trap Z was allowed to warm up and the gas desorbing was expanded into the large storage volume V_4. The remainder of the gas held by the gel was pumped off through G_1 by means of a Toepler pump and added to the calibrated volume V_4 by pumping it in through G_2. The total volume of the products then could be found from the pressure of the gas in V_4, which was registered by an open manometer.

Blank runs showed that all the methane and about 85 % of the oxygen were trapped by the gel. It was safe, therefore, to assume that all gases with boiling points higher than that of methane would be completely recovered. On account of its comparatively small amount, carbon monoxide was also completely recovered. (It should be noted that in spite of its slightly lower boiling point, carbon monoxide is more strongly adsorbed by silica gel than is oxygen (54).

Analyses of the gaseous products were made in a Burrell gas analysis apparatus for oxygen, carbon dioxide, unsaturated hydrocarbons, carbon monoxide, and saturated hydrocarbons. The hydrocarbon fraction of the reaction products was analysed in a Podbielniak

Table VIII

Experimental Conditions

Run No.	Temperature °C	Pressure mm.	Methane flow cc./sec at N.T.P	Oxygen flow cc/sec. at N.T.P	Methane used cc.	Ratio O_2/CH_4
1	37	0.32	0.0628	0.250	415	4.0
2	200	0.34	0.0628	0.254	550	4.0
3	201	0.33	0.0632	0.248	608	4.0
4	303	0.33	0.0630	0.254	697	4.0
5	330	0.35	0.0632	0.250	490	4.0
6	315	0.32	0.0630	0.248	700	4.0

Volume of reaction vessel 1370 c.c.

Atom concentration 20 %.

apparatus. As large quantities of oxygen interfered with the distillation, it was necessary to remove it before admitting the mixture to the still. As carbon dioxide is solid at liquid air temperatures and sublimes at atmospheric pressure, it is obvious that it would not only freeze in the column but also be impossible to fractionate. Thus, these gases were removed prior to the distillation by shaking the sample with a sodium-hydrosulphite--potassium hydroxide solution followed by passage through a drying tube. This procedure was very laborious and time consuming as the gas desorbed from the silica gel contained much more oxygen than hydrocarbon. Due to the low efficiency of the best oxygen absorbers and the large quantity of gas to be washed, ordinary bubble methods could not be used with success.

Results

The experimental conditions of the six experiments made are given in Table VIII. Table IX shows the products of reaction calculated as percentage methane converted, as well as the total percentage reaction.

To be doubly sure of the absence of all products heavier than methane, combustion analyses

Table IX

Products of the Reactions

		Percentage CH_4 converted to:			
Run No.	Temperature °C	CO	CO_2	C_2H_6 or Heavier	Total percentage reaction
1	37	10.5	....	None	10.5
2	200	27.1	5.7	None	32.8
3	201	28.1	7.3	None	35.4
4	303	33.4	21.9	None	55.3
5	330	30.2	19.2	None	49.4
6	315	31.3	19.7	None	51.0

were made (in runs 4, 5, and 6) on the last fraction taken off in the distillation. These tests all confirmed the absence of ethane. It is perhaps significant also that no appreciable quantity of formic acid, formaldehyde or any other intermediate oxidation product was detected.

It will be seen from Table IX that the amount of carbon dioxide formed is in good agreement with the findings of Harteck and Kopsch. These investigators could not determine carbon monoxide with their experimental arrangement and thus inferred its amount from the water formed. Our results indicate a considerably greater formation of carbon monoxide than inferred by them. This is possibly due to the absorption of water on the walls, which may have cut down the observed water formation in their work. In our case water could not be determined since the walls of the apparatus were poisoned with a solution of phosphoric acid. Part of the discrepancy is due also to the fact that we used a larger reaction vessel and hence the contact time in our work was greater than in theirs. They did not calculate collision yields from their experiments, so that the latter point cannot be directly verified.

The fact that no intermediate oxidation products were detected leads to the conclusion that the primary reactions of oxygen atoms with methane is slow compared with later steps. These probably continue until the methane has been completely oxidized to carbon monoxide, carbon dioxide and water. This slow primary step may well be that suggested by Norrish

$$O + CH_4 \longrightarrow CH_2 + H_2O .$$

Since the reaction

$O + CO \longrightarrow CO_2$ is comparatively slow (35), the carbon dioxide formed cannot have resulted from the oxidation of carbon monoxide, at least at room temperature. It seems probable, therefore, that the next steps in the oxidation may be

$$CH_2 + O \longrightarrow CH_2O$$

$$CH_2 + O_2 \longrightarrow CH_2O_2$$

and that these are followed by the oxidation of formaldehyde or formic acid. It has been shown by Geib (27) that the reaction of oxygen atoms with formaldehyde yields mainly carbon monoxide while formic acid yields mainly carbon dioxide. Both reactions are rapid at room temperature, the activation energies being below 7 Kcal. From these considerations it

Table X (a)

Calculation of Collision Yields and Activation Energies

Run No.	Total flow cc./sec at experimental conditions (corrected for presence of atoms)	Reaction time, sec.	Partial pressure of oxygen atoms cm.	No. of collisions per sec. by one CH_4 molecule with oxygen atoms
1	919	1.49	0.0052	3.58×10^5
2	1334	1.03	0.0055	3.06×10^5
3	1350	1.01	0.0054	3.00×10^5
4	1678	0.82	0.0055	2.77×10^5
5	1689	0.84	0.0057	2.83×10^5
6	1732	0.79	0.0053	2.64×10^5

Table X (b)

Calculation of Collision Yields and Activation Energies

Run No.	No. of collisions by one CH_4 molecule with oxygen atoms in reaction time	Percentage reaction	Collision yield	Activation energy, Kcal., on assumption of a steric factor of 0.1
1	5.33×10^{5}	10.5	1.98×10^{-7}	8.1
2	3.14×10^{5}	32.8	1.04×10^{-6}	10.8
3	3.03×10^{5}	35.4	1.17×10^{-6}	10.7
4	2.26×10^{5}	55.3	2.44×10^{-6}	12.1
5	2.36×10^{5}	49.4	2.09×10^{-6}	12.9
6	2.09×10^{5}	51.0	2.44×10^{-6}	12.4

would seem that fairly reliable values for the activation energy of Norrish's primary step might be obtained. Thus, by making use of the values for percentage reactions shown in Table IX, the experimental conditions shown in Table VIII, and assuming an atom concentration of 20 %, we arrive at the activation energies tabulated in Table X.

These computations were made in exactly the same manner as described before in the calculation of collision yields for the hydrogen atom-propane reaction.

It will be seen that the collision yield at room temperature leads to an activation energy of 8.1 Kcal. This value is in accord with an approximate estimate by Geib of 7 Kcal. made from the results of Harteck and Kopsch. The two investigations may be considered to be in good agreement.

The activation energies calculated from the collision yields at high temperatures are considerably higher than this value. This is undoubtedly due to the fact that the atom concentration at higher temperatures is much less than that at room temperature, since the efficiency of the wall-poisoning diminishes rapidly as the temperature is raised. If we assume that the atom concentration at 300°C had fallen to about 2 %(which in the case of hydrogen atoms is often known to occur), the activation energies calculated from experiments at higher temperatures are brought into line.

DISCUSSION

The Reaction of Hydrogen Atoms with Propane

The Products of the Reaction

Examination of Tables II and IV shows that the important facts in connection with the products are:

(1) Methane is the only product at room temperature.

(2) At 100°C, ethane is present in easily measureable quantity. Less than one per cent of ethylene is found.

(3) The percentage of ethane and ethylene increase with temperature while the production of methane falls off.

(4) The total per cent reaction increases steadily with temperature.

(5) Products heavier than propane are absent.

In figure (5) the collision yields of the various products have been plotted against temperature In this case "collision yield" is taken to mean "the number of molecules of a product formed per collision between a propane molecule and a hydrogen atom". This graph gives the truest picture of the relative yields of the products. Plotting them in this manner, presents them as corrected for fluctuations in atom concentration, and variations in reaction time.

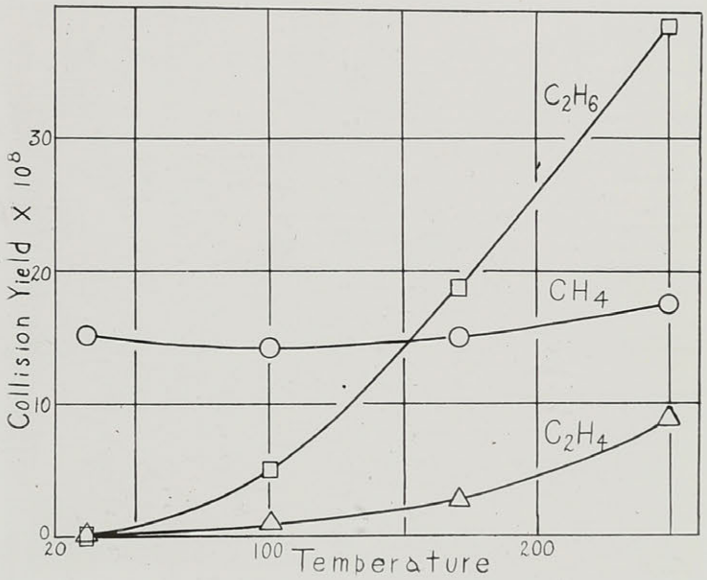

Figure V

"Collision Yields" of the Various Products.

The effect of these corrections is most striking in the case of methane. According to Tables II and IV methane production falls off with temperature, but when atom concentration and reaction times are taken into consideration, the yield is found to have a negligible temperature gradient.

Comparison of the results at room temperature and at 100°C with the two runs by Trenner, Morikawa and Taylor (116) previously mentioned, shows that the agreement is good in principle.

The Primary Reaction

There are obviously two possibilities for the primary step, the abstraction of a hydrogen atom,

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \qquad (1)$$

or a chain splitting reaction,

$$H + C_3H_8 \longrightarrow C_2H_5 + CH_4 \qquad (2a)$$

$$H + C_3H_8 \longrightarrow C_2H_6 + CH_3 \qquad (2b)$$

Preliminary results on the mercury photosensitized reaction of hydrogen and propane by Steacie and Dewar (103) shows that hydrogen and hexane are the main products, the hexane presumably being produced by the recombination reaction,

$$2\ C_3H_7 \longrightarrow C_6H_{14}\ .$$

This suggests that (1) is the primary step although the possibility of the occurence of (2) here cannot be ruled out on this evidence alone.

The non-appearance of hexane in our results is not surprising. In the mercury photosensitized reaction, pressures are high and hydrogen-atom concentration is low. These conditions favour radical recombination reactions; therefore, we would expect to find hexane if the propyl radical were present at all and had a reasonable lifetime. Under the low pressures and high hydrogen (atomic and molecular) concentrations of the Wood-Bonhoeffer method, it is to be expected that collisions between propyl radicals would be relatively scarce and that the chance of a propyl radical reacting with hydrogen would be great. From these considerations the absence of hexane is to be expected and cannot be offered as an argument against a primary step such as (1).

In general, it may be remarked that there is a very definite parallelism between the reactions of hydrogen atoms with ethane and with propane in so far as a comparison of the results of mercury photosensitization and of the Wood-Bonhoeffer method is concerned. In both cases large amounts of higher paraffins are obtained by mercury photosensitization (propane and butane from ethane, and hexane from propane) while by the discharge-tube method only lower paraffins are obtained. The difference between the results of the two methods is , of course, due to the difference in the hydrogen-atom concentration, and in the total pressure.

The possible primary step

$$H + C_3H_8 \longrightarrow 3\ CH_3$$

is ruled out on thermochemical grounds.

Secondary Reactions at Low Temperatures

As stated above, the main feature of the results at 30°C is the absence of ethane and ethylene in the products, and the large production of methane.

If the primary reaction were (2b), the results could not be explained on the assumption that the ethane formed disappeared by (3)

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 \qquad (3)$$

Trenner, Morikawa and Taylor find an activation of 7.3 Kcal. for this reaction, therefore the reaction of hydrogen atoms with ethane at this temperature is not rapid enough to enable the ethane formed to be completely destroyed. Reaction (2b) can therefore be ruled out as a primary step. In any case (2b) is intrinsically less likely than (2a), since if a C - C bond is to be broken it is much more likely that the bond nearest to the approaching hydrogen atom shall split, giving methane and an ethyl radical, i.e. (2a).

If the primary reaction is (2a), then the ethyl radicals produced must react to form methane without intermediate formation of ethane. The only possibility seems to be the reaction

$$H + C_2H_5 \longrightarrow 2\ CH_3 \qquad (4)$$

followed by $CH_3 + H \longrightarrow CH_4$ (5)

As previously mentioned Taylor (113) has recently suggested that methane formation occurs by this means. Rice and Teller (82) also have submitted theoretical evidence in favour of this mechanism. Any radical recombination reaction to form ethane is probably outstripped by (5), because of the small value of the ratio

$$\frac{\text{stationary } (CH_3)}{\text{stationary } (H)}.$$

A short time ago reaction (5), might have been forbidden by "dreierstoss restriction". The recent work of Rabinowitsch (70) discussed in a foregoing section has shown that collisions of the kind involved in reaction (5) are much "stickier" than previously supposed. At the low operating pressures the quasi-molecule has a good chance of reaching the wall and dissipating its excess energy . This chance, of course, rapidly decreases as the temperature of the wall is raised and may partly account for the fall in methane production as the temperature is raised.

If the primary reaction is (1), then the propyl radicals produced must disappear without the formation of ethane. We cannot postulate the decomposition of the propyl radical by the reaction

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 \qquad (6)$$

since all the evidence indicates that it is stable at room temperature. In any case the assumption of (6) would lead to new difficulties, since it has been shown (120) that the main product of the reaction of hydrogen atoms with ethylene is ethane, and neither ethylene nor ethane occur as products. It must therefore be concluded that if the primary reaction is (1), the propyl radicals produced disappear by a reaction analogous to (4), viz.

$$H + C_3H_7 \longrightarrow CH_3 + C_2H_5 . \qquad (7)$$

If this is the case, then the ethyl radicals formed by (7) must disappear by (4).

It follows that, irrespective of whether the primary reaction is (1) or (2), the results can only be accounted for by the assumption that reaction (4) occurs readily. The present results therefore furnish strong evidence for the occurrence of (4), and obviate the necessity of assuming reactions of the type

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

The evidence from mercury photosensitization experiments with propane also suggests that the analogous reaction to (4) also occurs with the propyl radical.

It may be noted that in considering the low temperature results the possible reaction of ethyl radicals with molecular hydrogen,

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H \qquad (8)$$

must be ruled out since it would lead to ethane formation.

Secondary Reactions at Higher Temperatures.

At higher temperatures methane production is diminished, and ethane and ethylene make their appearance. The production of ethylene is undoubtly to be ascribed to the decomposition of the propyl radical at higher temperatures by reaction (6). This is in agreement with the fact that the propyl radical can be detected in photodecompositions at ordinary temperatures by the Paneth technique (68), but cannot be detected in thermal decomposition reactions at higher temperatures (60). Bawn estimates an activation energy for reaction (6) of from 10 to 30 Kcal. (3). The appearance of ethane at higher temperatures is partly to be ascribed to the occurrence of reaction (8). Leermakers (49) estimates an activation energy of 15 Kcal. or more for this reaction. This estimate, however, is probably somewhat high, since the companion reaction

$$CH_3 + H_2 \longrightarrow CH_4 + H$$

occurs to a measurable extent at temperatures of 160°C and higher (56,112) and Taylor estimates that it has an activation energy of 9±2 Kcal. An activation energy of the same order of magnitude for (8) would account for part of the ethane production in the present instance.

The presence of ethylene in the products indicates that the process

$$C_2H_4 + H \longrightarrow C_2H_5 \qquad (10)$$

must be important as an ethane producer. The ethylene-hydrogen atom reaction is known to proceed with nearly one hundred per cent efficiency under similar conditions. Only a greatly decreased atom concentration can account for the presence of any ethylene in the products.

Examination of Figure 5 and Table II shows that at 250°C the ethane production is roughly twice that of methane. Each propane molecule broken into must yield one mono-carbon and one di-carbon molecule. Thus, if no methyl radical recombination to form ethane takes place one would expect the " collision yield" of methane to equal the sum of the "collision yields" of ethane and ethylene. As this is not the case the only other alternative is to assume ethane formation from methyl radicals at high temperatures.

This does not seem a very drastic assumption as conditions are very different at high temperatures. Reaction (5) will be favoured by a high concentration of hydrogen atoms and thus can be considered as a fast process under our low temperature conditions. The recombination reaction

$$2\ CH_3 \longrightarrow C_2H_6 \qquad (11)$$

will be favoured by low hydrogen atom concentration and high methyl radical concentration. If the Dreirstoss theory can be considered as having any influence, step (11) might be considered as faster than (5) at high temperatures due to the greater complexity of the ethane molecule. Trenner, Morikawa and Taylor (116) point out that as the recombination process (11) depends on the square of the methyl concentration, it becomes increasingly important as the stationary state concentration of methyl radicals increases with temperature.

The predominant effect, however, is that of atom concentration. The values of $[H]$ given in Table I were, of course, blanks made under conditions of no reaction. The effect of any reaction will be to lower this value greatly and at best this measured value can only be considered as relative to the actual stationary atom concentration;the effect of increased reaction at high temperatures will be to make $[H]$ even lower than the relative value. Perhaps the greatest factor in lowering $[H]$ is the presence of ethylene in the gas mixture at high temperatures. Taylor (113) states that there is plenty of evidence that the presence of ethylene serves to reduce the stationary atom concentration to small values. Under these conditions, which apparently do prevail at high temperatures, reaction (11) should be favoured and may well account for the high ethane production relative to that of methane.

The Mechanism Summarized

From the foregoing discussion it appears that the mechanism is:

At low temperatures

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \qquad (1)$$

$$H + C_3H_8 \longrightarrow C_2H_5 + CH_4 \qquad (2a)$$

$$H + C_3H_7 \longrightarrow CH_3 + C_2H_5 \qquad (7)$$

$$H + C_2H_5 \longrightarrow 2\ CH_3 \qquad (4)$$

$$CH_3 + H \longrightarrow CH_4 \qquad (5)$$

At high temperatures

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \qquad (1)$$

$$H + C_3H_8 \longrightarrow C_2H_5 + CH_4 \qquad (2a)$$

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 \qquad (6)$$

$$\begin{aligned} 2\ CH_3 &\longrightarrow C_2H_6 \qquad (11) \\ &\longrightarrow C_2H_5 + H \end{aligned}$$

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (12)$$

$$H_2 + C_2H_5 \longrightarrow C_2H_6 + H \qquad (8)$$

$$H + C_2H_5 \longrightarrow C_2H_6$$

$$H + CH_3 \longrightarrow CH_4$$

The evidence that propane does not exchange with deuterium atoms under our experimental conditions, makes it unnecessary to include any propane reforming reactions in the mechanisms.

Reactions of the type

$$CH_3 + C_3H_8 \longrightarrow C_2H_5 + C_2H_6$$

$$CH_3 + C_3H_7 \longrightarrow 2\ C_2H_5 \qquad (15)$$

have not been added though at first sight they may appear as plausible explanations for the low methane productions at high temperatures. If the first of these were important, we would expect propane consumption to rise abnormally, which is not the case. The second may be important, but the evidence for the very short life of the propyl radical at high temperatures makes it rather unlikely.

The Reaction $H + C_2H_5 \rightleftharpoons 2\ CH_3$

Since it is only recently that this reaction has been conceded any importance, it may be interesting to examine the theoretical justification for it.

It is enlightening to assume for the moment that the result of a collision of a hydrogen atom and an ethyl radical (which are sufficiently energized) is the temporary formation of an unstable ethane molecule. Evidence from atomic reactions at low temperatures by Geib and Harteck (28) indicate that quasi-moleculesmay

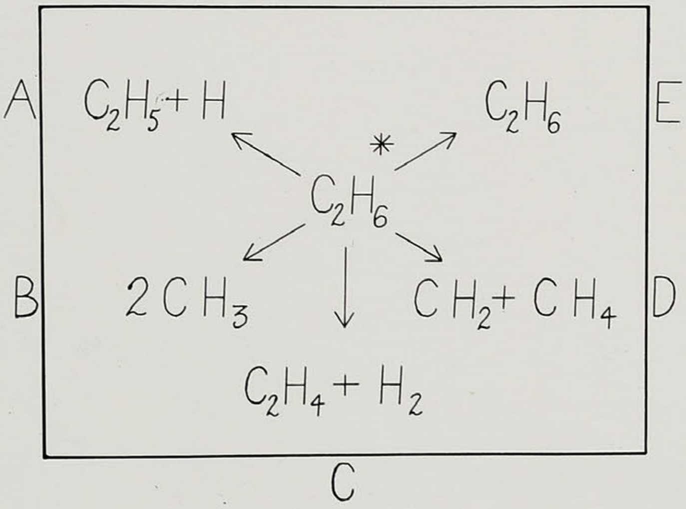

Figure VI

The "Future" of a Quasi-Ethane Molecule .

have a very real existence. The extremely high deuterizations found for methane and ethane in the hydrocarbon-hydrogen atom reactions (116,98) also support the "quasi-molecular" theory. Now granting that such a quasi-ethane molecule is formed, there are several possibilities for the future of this unstable configuration of atoms. Some of the more probable steps to be expected are shown in Figure VI. Of course, stabilization (result E) may occur, but any small effect that the "Dreierstoss restriction" may have, will work towards a greater chance of distintegration. For reaction D to result, the initial step would involve the breaking of a C - C bond and a C - H bond. For (C) to occur, two C - H bonds must be ruptured. A choice between A and B as a final step would probably depend upon the relative strengths of the bonds C - C and C - H. This would make B the most likely reaction. We might say, therefore, that the reaction

$$H + C_2H_5 \longrightarrow \overset{*}{C_2H_6} \longrightarrow 2\ CH_3 .$$

can be considered as more or less analogous to predissociation.

It must be emphasized that this argument is strictly qualitative as so very little is known about quasi-molecules. There is really no assurance that the bonds in such an unstable molecule possess their normal strengths. By making use of this method of reasoning, however, it appears that the production of two methyl radicals in such a reaction is certainly a highly probable result.

It is interesting to examine the reaction

$$C_2H_5 + H \longrightarrow 2\ CH_3$$

on the thermochemical grounds. If we take the strength of the C - C bond as 80 Kcal. and that of the C - H bond as 90 Kcal.

$$C_2H_6 \longrightarrow 2\ CH_3 \quad - \quad 80\ \text{Kcal.}$$

$$C_2H_6 \longrightarrow C_2H_5 + H \quad - \quad 90\ \text{Kcal}$$

we obtain $C_2H_5 + H \longrightarrow 2\ CH_3 + 10\ \text{Kcal.}$

It makes little difference which exact values we take for the bond strengths as the concensus of opinion (77,110,111,116) is that the strength of the C - H bond is a bout 10 Kcal. greater than that of the C - C bond. This means that the reaction (4) must be about 10 Kcal. exothermic. Allen and Bawn (1a) have recently shown that the combination of two methyl radicals requires more than ten collisions, but from the amount of methane formation at low temperatures the forward reaction must have a very small activation energy. The back reaction, forming ethyl radicals must have an activation energy of at least 10 Kcal. and thus would not come into play until the higher temperatures were reached. A reaction with this E would be fast at 250°C and could account for high ethane formation. The equilibrium constant of the reaction

$$\frac{[CH_3]^2}{[C_2H_5][H]} = K$$

cannot be large. Inspection shows the great effect of hydrogen atom concentration on this reaction. From arguments mentioned previously the value of $[H]$ must be very low at high temperatures and therefore would tend to shift the equilibrium toward high ethyl radical formation. These considerations indicate that this reaction may be highly probable as a key step in atomic free radical mechanisms.

The Activation Energy of the Primary Step

The value of E found for the primary step was about 9 Kcal. at room temperature, rising to about 13 Kcal. at 250°C. The values found at the lower temperatures are probably the most reliable. At the higher temperatures many factors may tend to yield a misleading value for the activation energy. The greatest uncertainty is in the atom concentration; first because measurements måde with the Wrede guage are susceptable to a large error, secondly because atom counts were made under blank conditions (no reaction) and therefore the tabulated values can at best only be considered as relative to the atom concentrations in the actual runs, and thirdly because the presence of ethylene in the reaction mixture has the effect of greatly lowering the stationary [H] value.

If we assume that the atom concentration at 250°C was 1 % instead of the measured blank value of 12 % we obtain an E of 10.5 Kcal. at this temperature. In view of these and other uncertainties which are inherent in the fast flow method, the best value for the activation energy of the primary step is probably 10 ± 1.5 Kcal.

There is always a possibility of a propane re-forming reaction. Any back reaction would have the effect of increasing the apparent activation energy of the primary step. This possibility was explored in a study of the propane-deuterium atom reaction, and is discussed in a following section.

The Comparative Reactivity of Propane

Frankenburger and Zell (22) found large decomposition of pentane by hydrogen atoms indicating increased reactivity with increased molecular weight of the hydrocarbon. Our work seems to show that propane is slightly less reactive to hydrogen atoms than is ethane. This is in agreement with the preliminary experiments of Trenner, Morikawa and Taylor (116). The activation energy of the initial propane reaction at room temperature appears to be about 2 Kcal. greater than the companion reaction of ethane at room temperature.

The Reaction of Deuterium Atoms with Propane

The Products of Reaction

A review of Table VII reveals the following interesting facts about the products of the deuterium atom-propane reaction:

(1) The methane formed is highly deuterized.

(2) The ethane formed is highly deuterized.

(3) The propane in the products is apparently inappreciably exchanged up to 250°C.

Methane Deuterization at Low Temperatures

If one assumes that the path of the reaction at low temperatures is given by one of the two mechanisms discussed above, let us say by (2a), (4) and (5) the greatest possible deuterization of methane would be 33 %. If the path were simply (1), (7), (4), (5) the exchange of the methane would be 42 %.

It will be noticed that none of these reactions regenerate hydrogen or deuterium atoms. At first sight it appears that there would not be enough atoms to cause this amount of deuterization by such a scheme. It is to be borne in mind that in the room temperature reaction there is only 8 % decomposition of propane. Barring any exchange reaction with propane the concentration of hydrogen or deuterium atoms would be about fifteen times that of the propane molecules which have been broken into. Thus, there are sufficient hydrogen atoms to produce a high exchange if they were made use of.

Experiment shows that the methane is exchanged about 58 %, or at least 10 % more than indicated by strict adherence to either of the mechanisms suggested. If a ten per cent error were possible the second mechanism would appear the most likely. One run at room temperature by Trenner, Morikawa and Taylor (116) indicated a much higher exchange than obtained by us. They worked with a ratio D_2/C_3H_8 of 12 to 1 and similar atom concentrations. These investigators pointed out two alternatives for this high deuterization of methane.

First there is the possibility that methyl radicals may undergo further interaction with deuterium atoms (at ordinary temperatures, reaction of methyl with hydrogen molecules is of low efficiency). The mechanism may follow a sequence of processes such as:

$$\begin{aligned}
CH_3 + D &\longrightarrow CH_3D^* \longrightarrow CH_2D + H \\
CH_2D + D &\longrightarrow CH_2D_2^* \longrightarrow CHD_2 + H \\
CHD_2 + D &\longrightarrow CHD_3^* \longrightarrow CD_3 + H
\end{aligned}$$

This represents the formation and dissociation, before stabilization by third body collisions, of quasi-methane molecules. The experimental condition of high D atom concentration would insure high conversion. Steacie, Alexander and Phillips (98) found high deuterization of methane in the photosensitized ethane-deuterium atom reaction. They accept this explanation as the best one.

An alternative mechanism would involve dehydrogenation-rehydrogenation, thus:

$$CH_3 + D \longrightarrow CH_2 + HD$$

$$CH_2 + D \longrightarrow CH_2D$$

$$CH_2 + D \longrightarrow CH_2D_2$$

There is no evidence for or against this mechanism.

The High Deuterization of Ethane

The runs at high temperatures show high exchange in the ethane. Even the assumption that the propyl decomposition reaction

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 \quad (6)$$

is very important cannot account for an exchange of more than half that found. However, if we assume that the methyl radicals produced undergo quasi-molecular deuterization (as above) and later recombine to form ethane, the high exchange is easily accounted for. This is in line with the work of Steacie, Alexander and Phillips (98) on the photosensitized decomposition of ethane. The high exchange indicates either that

$$2\ CH_3 \longrightarrow C_2H_6 \quad (11)$$

may occur readily at high temperatures or that ethyl radicals also undergo quasi-molecular deuterization.

The Propane Deuterization

The propane was found to be entirely light within the limit of error assigned to the analytical method. This is in complete agreement with Trenner, Morikawa and Taylor's preliminary results. It rules out the possibility of any back reaction and means that the value of 10 ± 1.5 Kcal. for the activation energy of the primary reaction can be accepted without further correction.

It must be admitted that the error in our analyses may be large enough to pass by a small exchange in the propane. If the action of deuterium atoms on the propane parallelled the ethane reaction we might expect high deuterization of propane. The fact, however, that methane and ethane exchanged by quasi-molecular deuterization would indicate that if propane were exchanging at all it would be found to have a high D content.

Evidence from the mercury photosensitized decomposition of propane shows that reaction (1) cannot be excluded as one of the primary steps. This means that propyl radicals are formed but never recombine or react in any way to form propane. The step

$$C_3H_7 + H \longrightarrow C_3H_8$$

would probably not be fast at high temperatures under the conditions of low atom concentration. At low temperatures, however, there is little reason to exclude it.

In general we must conclude that reactions (6), (7) and (15) consume propyl radicals very much faster than the several propane re-forming reactions mentioned. This points to a high activation energy for step

$$C_3H_7 + H_2 \longrightarrow C_3H_8 + H \qquad (16)$$

or a very low average E for the propyl decomposition and reactions (7) and (15).

The Mechanism of the Hydrogen Atom-Ethane Reaction

The strong evidence in favour of step (4) as a key reaction, makes it interesting to study the effect of substituting it for other methane producing processes, in various mechanisms.

It has been seen that the work of Trenner, Morikawa and Taylor (116) and that of Steacie (102), led these investigators to conclude that the important steps in the hydrogen atom-ethane reaction were;

$$H + C_2H_6 \longrightarrow CH_3 + CH_4 \qquad (18)$$

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \qquad (17)$$

The production of methane was thus originally ascribed to a separate primary step (18) by Taylor.

Rice and Teller (82) have recently considered reactions like number (18) in the light of their "Principle of Least Motion". They reject processes of this type chiefly on the grounds of the shielding effect of the hydrogen atoms surrounding the carbon atoms. The accumulated evidence would seem to indicate that (17) is the only important primary reaction followed by

$$H + C_2H_5 \longrightarrow 2\ CH_3 \qquad (4)$$

$$CH_3 + H \longrightarrow CH_4$$

at low temperatures and by

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H \qquad (8)$$

$$C_2H_5 + H \longrightarrow C_2H_6$$

at high temperatures.

The mechanism would account for the large methane production below 100°C, and high ethane exchange at high temperatures. The arguments for such a mechanism would be almost identical with those given for the variation of methane a nd ethane production in the propane reaction. Such a change in mechanism should help to bring values for the E of the initial step into line. The best figure is probably about 8 Kcal. for the activation energy of reaction (18). If any trust can be placed in a parallel with propane, reaction (8) must have an E greater than 9 and probably in the neighbourhood of 15 Kcal.

The Decomposition of Methane

It was hoped that the study of the methane-oxygen atom reaction would throw some light on the mechanism of the thermal decomposition of methane. Two opposing mechanisms have been suggested for the formation of the methyl radical:

$$\begin{array}{rcl}
 & CH_4 \longrightarrow CH_3 + H & \text{Rice and} \quad (1) \\
H & + \; CH_4 \longrightarrow H_2 + CH_3 & \text{Dooley} \quad (3) \\
\hline
 & CH_4 \longrightarrow CH_2 + H_2 & \text{Belchetz} \quad (2) \\
CH_2 & + \; CH_4 \longrightarrow 2\,CH_3 & \text{and} \quad (4) \\
 & & \text{Rideal} \\
CH_2 & + \; CH_4 \longrightarrow C_2H_6 & (5)
\end{array}$$

Kassel has suggested that Belchetz and Rideal's mechanism is right and that reaction (5) is fast enough to keep the concentration of the methylene radical down to a very low value. From Norrish's (57) suggestion that the primary step in the oxidation of methane is

$$CH_4 + O \longrightarrow CH_2 + H_2O$$

one might expect some ethane formation from reaction (5) providing this step is as fast as Kassel suggests.

Had ethane been found in the methane-oxygen atom reaction, it would have been strong evidence for Belchetz and Rideal's mechanism. However, no ethane was detected within the temperature range 30°C to 330°C. This finding makes it impossible to draw any definite conclusions, for there are two alternatives:

(a) The reaction

$$O + CH_4 \longrightarrow CH_2 + H_2O$$

does not occur, or

(b) The reaction

$$CH_2 + CH_4 \longrightarrow C_2H_6$$

is not a rapid reaction, its activation energy being greater than 11 to 12 Kcal. and hence the absence of methylene radicals in Rice and Dooley's work cannot be ascribed to the occurrence. However, it must be admitted that the situation is too complex to admit of very definite conclusions.

Considering the primary split on thermochemical grounds, recent calculations by Voge (122) are interesting. If we estimate the zero-point energy correction so as to get chemical heats of reaction and correct the results to bring them in line with a more recent and reliable estimation of the heat of sublimation of graphite, Voge's values become

$$CH_4 \longrightarrow CH_3 + H \quad - 99{,}000 \text{ cal.}$$

$$CH_3 \longrightarrow CH_2 + H \quad - 84{,}000 \text{ cal.}$$

$$CH_4 \longrightarrow CH_2 + H_2 \quad - 80{,}000 \text{ cal.}$$

This would make the latter reaction just possible as the rate determining step in the methane decomposition; however from the manner in which basic thermochemical values have fluctuated in the past, it hardly seems that a difference of 4000 cal. would be decisive.

Kemula, Czornodola and Kopniak (48a) have recently reported some new work on the mercury photosensitized reaction of methane. They conclude that the two initial steps

$$\overset{*}{Hg} + CH_4 \longrightarrow CH_3 + H + Hg$$

and $$\overset{*}{Hg} + CH_4 \longrightarrow CH_2 + H_2 + Hg$$

take place side by side. They point out that the necessary energy change is approximately the same in each case and offer both primary reactions as the best explanation of the product formation observed.

The Mercury-Photosensitized Reaction of Ethane

This reaction has been discussed in the introductory section. The final mechanism of Steacie and Phillips was:

$$C_2H_6 + Hg(^3P_1) \longrightarrow C_2H_5 + H + Hg(^1S_0)$$

$$H_2 + Hg(^3P_1) \longrightarrow 2\ H + Hg(^1S_0)$$

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 \qquad (18)$$

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \qquad (17)$$

$$2\ CH_3 \longrightarrow C_2H_6$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad (19)$$

$$2\ C_2H_5 \longrightarrow C_4H_{10} \qquad (20)$$

$$2\ H \longrightarrow H_2$$

The authors (96,97) pointed out that reaction (18) would have to be at least four times as fast as reaction (17) to account for the observed methane and propane formation and the fact that hydrogen is consumed in the photosensitized interaction of hydrogen-ethane mixtures.

At the time when the above mechanism was postulated there was some evidence for this satisfying condition. Trenner, Morikawa and Taylor (116) found that interaction of hydrogen atoms with ethane yielded methane below 100°C, seeming to indicate that (18) was faster than (17). This evidence, however, was not compelling. Thus, Taylor (113) suggested the possibility

$$C_2H_5 \quad + \quad H \longrightarrow 2\ CH_3 \qquad (4)$$

as the source of methyl radicals, followed, of course, by

$$CH_3 \quad + \quad C_2H_5 \longrightarrow C_3H_8$$

$$CH_3 \quad + \quad H \longrightarrow CH_4$$

Our work seems to present ample evidence, that (4) is a very fast reaction. Its activation energy is apparently very small, otherwise some ethane would have been found in the products of the hydrogen-atom propane reaction at room temperature.

This reaction is certainly many times faster than step (17)., it does lead to hydrogen consumption and would probably produce methyl radicals at the desired rate. Close examination reveals, however, that ethyl radicals are present only in small quantities due to the recombination reactions (19) and (20). Thus the requirements are more stringent than at first believed. Reaction (4) must also be fast enough to compete favourably with reactions (19) and (20) for the small number of ethyl radicals present. Though no quantitative data is available it would appear that (4) is at least as fast as (19) and (20). Conditions of concentration and the fact that it is not a Dreierstoss process may make it even more rapid. In conclusion, it may be said that in spite of these uncertainties the substitution of step (4) for (8) seems to represent an improvement in the mechanism.

The Mechanism of the Ethane Decomposition

The Rice-Herzfeld theory for the decomposition of ethane has been reviewed in the introduction. The following group of reactions make up their mechanism

(x)		Activation Energy Kcal.
(1)	$C_2H_6 \longrightarrow 2\ CH_3$	80
(2)	$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$	20
(3)	$C_2H_5 \longrightarrow C_2H_4 + H$	49
(4)	$H + C_2H_6 \longrightarrow H_2 + C_2H_5$	17
(5)	$2\ H \longrightarrow H_2$	Triple collision
(6)	(a) $H + C_2H_5 \longrightarrow C_2H_4 + H_2$	Small
	or $\longrightarrow C_2H_6$	Small
(7)	$H + CH_3 \longrightarrow CH_4$	Small
(8)	$CH_3 + C_2H_5 \longrightarrow C_3H_8$	8
(9)	$2C_2H_5 \longrightarrow C_4H_{10}$	8

It has been mentioned that if the reaction

x A change in numbering has been made here to facilitate discussion. The system is now that of Rice and Herzfeld.

(10) $$H + C_2H_6 \longrightarrow CH_4 + CH_3$$

were faster than (4) the fundamental nature of the chain carrying steps would be altered and the agreement of the scheme with experiment would be destroyed. The investigation of the interaction of hydrogen atoms with ethane by Trenner, Morikawa and Taylor seemed at first to offer conclusive proof that this reaction was faster than step (4). Taylor (113) later suggested that (4) might be the real primary step followed by a fast reaction like

$$H + C_2H_5 \longrightarrow 2\ CH_3 \qquad (11)$$

as a methane source. Our results and theoretical considerations present strong evidence that the latter is a very fast reaction. This makes it unnecessary to choose reaction (10) as a fast primary step. Thus, it would appear that the activation energy measured by Trenner, Morikawa and Taylor (116) in the hydrogen atom-ethane reaction was really that of (4). From previous considerations we have seen that the best value for the activation energy of reaction (4) is about 8 Kcal. The general effect of this evidence is to render the chain carrying steps of the Rice - Herzfeld mechanism at least qualitatively intact.

General Effect on the Free Radical Theory

The chain carrying steps in all the Rice-Herzfeld mechanisms are based on the general reaction

$$R + R_1H \longrightarrow RH + R_1$$

where R may be a hydrogen atom or a radical. The evidence gleaned from the work reported here indicates that this type of reaction may carry the chains. The activation energies of

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \qquad 10 \pm 1.5 \text{ Kcal.}$$

and $$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \qquad 8 \text{ Kcal.}$$

seem to show that Rice et al have chosen values of E which are too high for reactions of this type. In general, this change affects the mechanisms of all the hydrocarbon decompositions in about the same manner as in the case of ethane.

There is a wealth of evidence, however, that some chain system is involved in hydrocarbon decomposition and though the Rice-Herzfeld schemes cannot stand the most rigorous tests, they are useful as working princilpes and may in the future be modified to fit experimental fact more exactly.

It has been suggested (101) that some

significance may be attached to the fact that the activation energies of the free radical splits, as determined by Rice et al (71,77) approach the experimental E's of the decomposition reactions of the various parrafins as the series is ascended. Steacie (101) has mentioned the following explanation. The higher members of the series may split into radicals, followed by the setting up of short chains. Provided, then, that the temperature coefficient of the chain length is negative, the apparent activation energy would be slightly lower than the activation energy of the primary step, and in agreement with experiment. This assumption would serve to bring the free radical theory into line with kinetic data, and would at the same time be consistent with recent indications (100) that short chains actually exist in the n-butane decomposition.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1 The reaction of hydrogen atoms with propane molecules has been investigated by the Wood-Bonhoeffer technique at four temperatures, 30°C, 100°C, 170°C, 250°C.

Using an average measured atom concentration of 10 %, an internal pressure of 0.36 mm. and a ratio H_2/C_3H_8 of 8 : 1, the products were methane, ethane and ethylene. Hydrocarbons heavier than propane were not formed. At 30°C the only product was methane At 100°C some ethane and ethylene were found. From the point of view of the "collision yields" of the various products, the yield of methane is almost uninfluenced by temperature, while the ethane production increases rapidly and the ethylene formation very gradually as the temperature is raised. The activation energy of the primary step

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \qquad (1)$$

or

$$H + C_3H_8 \longrightarrow C_2H_5 + CH_4 \qquad (2)$$

was found to be 10 ± 1.5 Kcal.

Secondary reactions at low temperatures like the following account for the absence of ethane under these conditions;

$$C_3H_7 + H \longrightarrow CH_3 + C_2H_5 \qquad (7)$$

$$C_2H_5 + H \longrightarrow 2\ CH_3 \qquad (4)$$

They are strongly favoured by high atom concentration.

At high temperatures the important secondary processes seem to be:

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 \qquad (6)$$

$$\begin{aligned} 2\ CH_3 &\longrightarrow C_2H_6 \qquad (11) \\ &\longrightarrow C_2H_5 + H \end{aligned}$$

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H \qquad (8)$$

These steps are favoured by temperature and the low $[H]$ values. They explain the increased ethane and ethylene production.

Theoretical and experimental justification for reaction (4) has been discussed.

2. The interaction of deuterium atoms with propane was investigated at temperatures 30°C, 170°C, and 250°C. The experimental conditions were similar to those in the propane-hydrogen atom reaction.

The deuterization of the methane and ethane formed was too high to be accounted for by any set of straight forward equations. It was necessary to assume that quasi-molecular exchange took place;

$$CH_3 + D \longrightarrow \overset{*}{CH_3D} \longrightarrow CH_2D + H \quad \text{etc.}$$

$$C_2H_5 + D \longrightarrow \overset{*}{C_2H_5D} \longrightarrow C_2H_4D + H \quad \text{etc.}$$

The propane was found to be less than 0.5 % heavy. This points to a high activation energy for

$$C_3H_7 + H_2 \longrightarrow C_3H_8 + H$$

or a very low E for the reactions

$$C_3H_7 \longrightarrow CH_3 + C_2H_4$$

$$H + C_3H_7 \longrightarrow C_2H_5 + CH_3$$

$$CH_3 + C_3H_7 \longrightarrow 2\ C_2H_5$$

3. The reaction of oxygen atoms with methane was studied using essentially the same technique. At 30°C, 200°C and 300°C the only products were CO and CO_2.

The primary step, which may very well be

$$CH_4 + O \longrightarrow CH_2 + H_2O$$

as Norrish suggests, has an E of about 9 Kcal. The carbon monoxide and carbon dioxide are apparently formed through the intermediate production of formaldehyde and formic acid according to some such mechanism as:

$$CH_2 + O \longrightarrow CH_2O$$

$$CH_2 + O_2 \longrightarrow CH_2O_2$$

$$CH_2O + O \longrightarrow H_2O + CO$$

$$CH_2O_2 + O \longrightarrow H_2O + CO_2$$

No ethane was found in the products. This either indicates that :

(a) The reaction

$$O + CH_4 \longrightarrow CH_2 + H_2O$$

does not occur, or

(b) The reaction

$$CH_2 + CH_4 \longrightarrow C_2H_6$$

is not a rapid reaction, its activation energy being greater than 11 or 12 Kcal.

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