

THE KINETICS OF ELEMENTARY REACTIONS OF THE SIMPLE HYDROCARBONS

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I. INTRODUCTION

The reactions of the simple hydrocarbons are of great importance from both the theoretical and the industrial points of view. From a theoretical standpoint tremendous strides have been made in the past decade. Ten years ago little was known about the mechanisms of the simple thermal reactions, in spite of the fact that an enormous mass of purely pyrolytic data had been accumulated. In the last few years the subject has advanced rapidly, owing to the application of the methods of chemical kinetics, to the investigation of atomic and photosensitized reactions, and to enquiries into the rôle played by free radicals in thermal reactions. While there is considerable doubt regarding the validity of some of his speculations, there is no question that the ideas of F. O. Rice regarding the participation of free radicals in thermal processes have given a tremendous stimulus to the investigation of hydrocarbon and other reactions.

Owing to the complexity of the subject, the many angles from which it may be approached, the rapidity of its development, and the scattering of papers through organic, physical, and industrial journals, it is very difficult to orientate oneself in this field. Numerous reviews have appeared on hydrocarbon chemistry, but they have all been concerned primarily with the products of the reactions from an industrial standpoint. The theoretical basis of the subject must, however, rest on the principles of chemical kinetics, and a review of existing kinetic data from this point of view seemed desirable to the writer. In this review an attempt has been made to include all data which seem to be pertinent to the kinetic analysis of the simple thermal and photochemical reactions of the lower paraffins, olefins, and acetylenic hydrocarbons. No attempt has been made to include references to purely pyrolytic investigations, or to catalytic processes, since a number of comprehensive reviews of this kind already exist (35, 36, 41, 42, 43, 45, 46, 48, 57, 77, 181, and especially 40). In spite of their importance, the oxidation and halogenation reactions of the hydrocarbons have not been included, since these do not seem to have advanced as yet to the stage where we can disentangle the processes into their component parts with any degree of certainty. In any case these subjects have been frequently reviewed (44, 47, 117, 132, 183).

Inasmuch as the available information regarding the reactions of the simple hydrocarbons comes from a variety of sources, it will be advantageous to give a brief discussion of a number of points in a general way before embarking on a detailed analysis of the reactions of specific substances.

A. The kinetics of decomposition reactions

Since the discovery by Hinshelwood (73) in 1926 that a number of organic compounds decomposed by a first-order mechanism, the number of known first-order reactions has increased very rapidly, and it now appears that at least the primary step in almost all organic decomposition reactions is a unimolecular change. The whole question of the stability of gaseous organic substances is therefore virtually reduced to a consideration of the magnitude of the unimolecular velocity constant. This is usually expressed over a range of temperature in terms of the integrated form of the Arrhenius equation, i.e.,

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

(A)

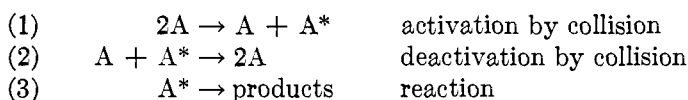
or

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

where A is a constant and E is the so-called energy 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 calculable 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.

Thus, formally, we can represent the process by:



In the steady state

$$-\frac{d}{dt}[A^*] = +\frac{d}{dt}[A^*]$$

or

$$2k_1[A]^2 - k_3[A^*] - k_2[A][A^*] = 0$$

Whence

$$[A^*] = \frac{2k_1[A]^2}{k_3 + k_2[A]}$$

Now the overall rate of reaction is the rate of reaction 3, i.e., $k_3[A^*]$, hence

$$-\frac{d}{dt}[A] = \frac{2k_3 k_1[A]^2}{k_3 + k_2[A]}$$

At high pressures $k_2[A] \gg k_3$ and this reduces to

$$-\frac{d}{dt}[A] = \frac{2k_3 k_1[A]}{k_2}$$

i.e., the reaction is of the first order. At sufficiently low pressures, however, deactivation becomes slower on account of the diminished number of collisions, and eventually we have $k_3 \gg k_2[A]$. The rate expression then becomes

$$-\frac{d}{dt}[A] = 2k_1[A]^2$$

and the reaction becomes of the second order. In the intermediate range the rate constant will fall with diminishing pressure and the reaction will have an order between 1 and 2.

The theory of unimolecular reactions is mainly concerned with the interpretation of the rate-pressure curve in the region where the velocity constants begin to fall below their high-pressure value. In the development of such a theory it is necessary to be more specific concerning the nature of the energy of activation. One type of theory assumes (72) 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 is the simplest form of theory, but it gives a rate-pressure relationship which is definitely in disagreement with the 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 (82, 83, 167, 168, 169). On this basis it is obvious that the chance of getting energy equal to or greater than E into one bond will be a function of the total energy of the molecule, and will increase rapidly with the excess of the energy of the molecule over E . This type of theory gives results which are in excellent agreement with the facts. There are a number of different forms of the theory, but all are essentially the same. That of Kassel (84) is much the simplest and is the one which is usually employed.

Kassel assumes that if a molecule has j quanta divided among s oscillators, it will react when m quanta are localized in a particular bond. He then gets directly for the rate of reaction at high pressures

$$k_{\infty} = A(1 - e^{-h\nu/kT})^s \sum_{j=m}^{\infty} \binom{j+s-1}{s-1} \frac{j!(j-m+s-1)!e^{-jh\nu/kT}}{(j-m)!(j+s-1)!}$$

which on carrying out the summation reduces to

$$k_{\infty} = Ae^{-mh\nu/kT} \quad (\text{B})$$

Here A has the general character of the reciprocal of a relaxation time, i.e., it is a measure of the frequency with which the energy of the molecule is redistributed among the various oscillators, ν is the frequency of the oscillators all of which are for simplicity assumed to be identical, and k is the Boltzmann constant. It is not necessary for us to discuss here the situation at low pressures, where the rate has "fallen off" from its high-pressure value.

A comparison of equations A and B shows that

$$mh\nu = E/N_0$$

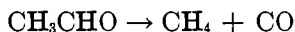
where N_0 is Avogadro's number. In other words, the activation energy is merely the total energy of that number of quanta which must be located in the pertinent bond before reaction can occur.

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. This question is discussed in the following section.

B. Free radicals in organic decomposition reactions

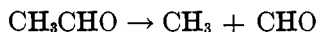
There is at present considerable uncertainty concerning the manner in which a large number of organic compounds decompose at high temperatures. Consider, for example, the decomposition of gaseous acetaldehyde to yield methane and carbon monoxide. There are two main mechanisms by which this process might occur:

(1) *The molecular mechanism:* In this case acetaldehyde splits into its final stable decomposition products in a single step,



This involves the simultaneous rupture of two valence bonds and the formation of one new one. It is obvious, therefore, that the activation energy of the process will bear no simple relation to the bond strengths.

(2) *The free-radical mechanism:* It is, however, possible that the primary step consists of the rupture of only a single bond, giving rise to two unsaturated radicals,



and that these radicals undergo secondary reactions which ultimately lead to the formation of methane and carbon monoxide. If this mechanism is the true one, and if the later reactions are fast compared with the primary step, the activation energy will be a direct measure of the strength of the only bond broken in the primary step, the C—C bond.

Rice (166) has suggested that virtually all organic compounds decompose by such a free-radical mechanism. If such a theory is to stand, it is obviously necessary to show in the first instance that free radicals are capable of existence. This had already been accomplished by Paneth and Hofeditz (134), who showed that free methyl radicals from the decomposition of organic compounds could be detected in a rapidly flowing gas stream by their reaction with a lead mirror to form volatile organometallic compounds. Following this discovery, Rice and his coworkers (156 to 166) made a comprehensive investigation of organic decomposition reactions from this point of view. They found that free radicals could be detected in the decomposition of almost all gaseous organic substances.

On account of the low pressures, fast flow, etc., which must be used in such experiments, it is necessary to work at temperatures which are from 200° to 300°C. higher than those at which the ordinary thermal decom-

position sets in. Hence, while it is certain that radicals are present at very high temperatures, such tests do not *prove* their presence during ordinary thermal decomposition at lower temperatures.

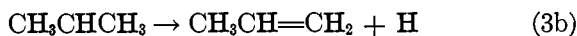
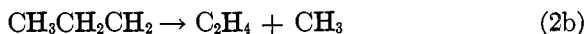
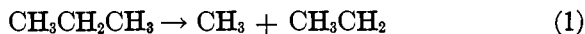
The theory has met with its greatest success in predicting the products of organic decomposition reactions (159), especially those of the hydrocarbons. The observed activation energies of the decomposition reactions of most organic substances lie between 35 and 70 kg-cal. Rice points out that if two reactions have activation energies different by 4 kg-cal., then the relative rates at 600°C. are in the ratio $e^{-4000/2 \times 873}$ to 1, or approximately 9 to 1. Similarly for a difference of 10 kg-cal. the rates will be in the ratio of 500 to 1. It follows, therefore, that if there are two or more possible modes of decomposition of a compound, then if one of these has an activation energy 10 kg-cal. or more lower than that of any of the others, it alone will occur to an appreciable extent. (This argument is usually correct. It has exceptions however, since in some cases the variation in A in equation A (page 312) is sufficient to counterbalance a difference in E . In most cases, however, the values of A are the same to within one power of 10 and equal to about 10^{18} .)

There is still some uncertainty about the values of the strengths of the C—C, C—H, C=C, and C≡C bonds. It is, however, certain that the C≡C and C=C bonds are very much stronger than the others, and it appears probable that the C—H bond is about 15 kg-cal. stronger than the C—C bond (204). We may therefore conclude that if the decomposition of a hydrocarbon occurs through free radicals it will always split at a C—C bond, and never at a C—H or a double or triple bond.

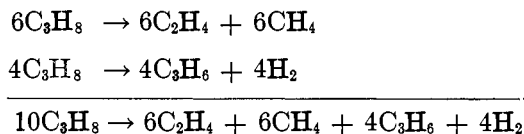
Thus in the case of propane, for example, the primary reaction can only be



Now methyl and ethyl radicals can be detected by the Paneth technique, but normally not other higher radicals, presumably because when formed they decompose very rapidly into unsaturated compounds and CH_3 , C_2H_5 , or H . Some energy of activation will, in general, be required for each step, but this will usually be much smaller than that required for the primary split. In the case of propane we thus have the following scheme, R denoting a methyl radical or a hydrogen atom,



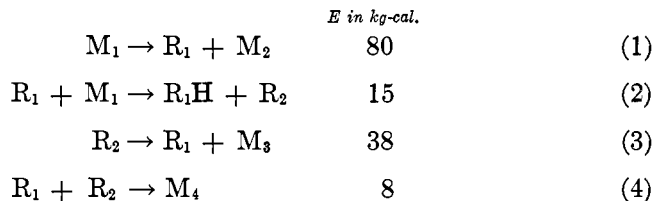
On the basis of chance we would expect reaction 2 to be faster than reaction 3 in the ratio of 3 to 1, since there are six primary hydrogen atoms to two secondary. There is, however, some evidence that secondary hydrogen atoms are somewhat less strongly bound. On this basis Rice estimates that reaction 2:reaction 3::6:4. Hence, neglecting all but the chain-carrying steps, we have for the overall decomposition



In general, this method gives rather good agreement with experiment, and the results will be discussed later for specific cases.

If the free-radical theory of organic decomposition reactions is to be accepted, however, it must account not only for the products of organic decompositions, but also for the kinetics of such processes. It is an experimental fact that almost all organic decomposition reactions are of the first order, and it is therefore necessary for the theory to answer two questions: (a) If the measured process is really the summation of a complex series of reaction steps, how is it that the overall reaction appears to be of the first order? (b) If, as is postulated, most reactions occur by the breaking of a C—C bond, how is it that experimental activation energies for decomposition reactions are usually far smaller than the strength of this bond?

Rice and Herzfeld (162) 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 a suitable choice of the activation energies of the part reactions, the apparent activation energy of the overall reaction could be made to agree perfectly with the experimental value. As an example, consider the following scheme for the decomposition of an organic molecule M_1 (166):



The molecule M_1 is assumed to decompose into a radical R_1 and a molecule M_2 . The radical R_1 reacts with a fresh molecule of the reactant, abstracts a hydrogen atom, and forms the stable substance R_1H and the radical R_2 . R_2 then decomposes into the radical R_1 and a molecule M_3 .

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.

If we set up the equations giving the concentrations of the radicals in the steady state, we have, assuming long chains,

$$\frac{d}{dt}[\text{R}_1] = 0 = k_1[\text{M}_1] - k_2[\text{R}_1][\text{M}_1] + k_3[\text{R}_2] - k_4[\text{R}_1][\text{R}_2] \quad (5)$$

$$\frac{d}{dt}[\text{R}_2] = 0 = k_2[\text{R}_1][\text{M}_1] - k_3[\text{R}_2] - k_4[\text{R}_1][\text{R}_2] \quad (6)$$

Now the overall rate of decomposition of M_1 is given by

$$-\frac{d}{dt}[\text{M}_1] = k_1[\text{M}_1] + k_2[\text{R}_1][\text{M}_1] \quad (7)$$

If we solve equations 5 and 6 for R_1 and substitute the result in equation 7, we get

$$-\frac{d}{dt}[\text{M}_1] = k_1[\text{M}_1](1 + \sqrt{k_2 k_3 / 2k_1 k_4}) \sim [\text{M}_1] \sqrt{\frac{k_2 k_3 k_1}{2k_4}}$$

i.e., the reaction is of the first order. Furthermore

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

so that, using the values of E for the part reactions given above, we get

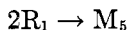
$$E_{\text{overall}} = 62.5 \text{ kg-cal.}$$

which is much below the strength of the C—C bond.

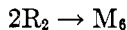
It should be emphasized at this point that the prediction of a first-order overall rate is dependent on the assumption made regarding the method of termination of the reaction chains. The above scheme assumes that they end by radical recombination



and, as we have seen, this leads to a first-order rate. If, however, we were to assume as the chain-terminating reaction



the overall order would be 3/2, while



would give 1/2. The successful prediction of a first-order rate therefore depends on the arbitrary assumption that the reaction



is much faster than the other two possible radical recombination reactions. As we shall see later, this leads to serious difficulties in the application of the scheme to specific reactions.

Mechanisms of this sort are, of course, highly speculative. Striking support for the fundamental idea of free-radical chain reactions was, however, immediately forthcoming. Frey (57) was able to start chains in butane at temperatures below its normal decomposition range by adding methyl radicals (from the decomposition of dimethyl mercury). Similarly, Allen and Sickman (1, 184) showed that chain decomposition of acetaldehyde could be caused by methyl radicals from the decomposition of azomethane. Leermakers (105) also produced sensitized chain decomposition of methyl ether at temperatures below 400°C. by photolyzing admixed acetone. All these observations prove that radicals *can* cause chain decomposition of a large number of organic substances. They do not, however, necessarily prove that such free-radical chain decomposition occurs in the normal pyrolysis of the substances concerned.

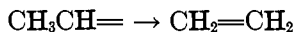
Further evidence for the chain character of a number of decomposition reactions is furnished by the work of Staveley and Hinshelwood (188b, 189, 190) and others (39, 55, 126, 194). They found that while large amounts of added nitric oxide would catalyze the reactions, small amounts caused some inhibition. They assume that the maximum inhibition corresponds to the complete suppression of chains normally present, and thus calculate chain lengths of from two to fifteen for a number of decomposition reactions. This is definite evidence for the presence of chains, but in most cases the chain lengths thus obtained are far too small to be in accord with the Rice-Herzfeld mechanisms. However, the assumption that maximum inhibition corresponds to a complete suppression of all chains is arbitrary, and makes the calculated chain lengths of somewhat doubtful significance. Recent work on some reactions (191, 191a) 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 mechanisms may hold for a small fraction of the total reaction, the remainder of the substance decomposing by a molecular mechanism.

It may therefore be concluded that, on the whole, the evidence of a general nature favors the free-radical theory. However, when the specific Rice-Herzfeld mechanisms for a number of reactions are tested the situation is quite different. Up to the present three methods have been used for this purpose: (a) The stationary hydrogen-atom concentration during a decomposition reaction is measured and compared with the value calculated from the theory (135, 136, 137, 138, 174, 175). (b) The activation energy of one of the part reactions in the Rice-Herzfeld scheme is determined in an independent way (196, 226). (c) Deutero-compounds are

used as indicators of the mechanism (193). All these methods seem to indicate that the Rice-Herzfeld mechanisms are untenable.

The status of the free-radical theory of decomposition reactions thus seems at the moment to be an open question. In a general way the theory serves to correlate an enormous number of facts, and it has pointed the way to a great deal of fruitful work. When examined closely, however, it seems to fail in almost every case. The most reasonable conclusion seems to be that the theory is in part correct, but that its present form is incomplete and too broad. We shall examine the evidence for and against its applicability in specific cases in later sections.

Numerous other suggestions have been made to explain how a molecule may split so as to give rise to several different products. Thus it has been suggested (85) that the decomposition of a paraffin might proceed by



i.e., an initial split to give an alkylidene radical which rearranges practically instantaneously to an olefin. In this case, if the second reaction were fast enough, the process would be indistinguishable from a direct split into stable molecules.

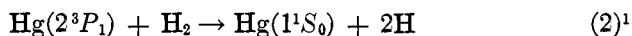
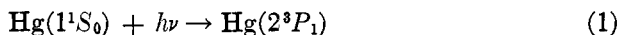
C. Photochemical and atomic reactions

From the foregoing discussion it follows that a knowledge of the "elementary" reactions of the hydrocarbons is of special importance in any attempt to unravel the kinetics of their thermal reactions. Independent methods of obtaining information concerning the reactions of radicals will thus be of the greatest importance. Information of this sort may often be obtained from photochemical investigations. Indeed the reactions of atoms and radicals really constitute the connecting link between thermal and photochemical kinetics. The activation mechanism is, of course, quite different in the two types of reaction, involving activation by collision in the one case, and absorption by the chromophoric group in the other. However, once the primary step has occurred, the subsequent stages of a photochemical process are thermal reactions, and these often involve atoms and radicals.

In the following sections, therefore, we shall discuss the photodecomposition of the hydrocarbons. 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 have deterred most investigators. Most of the photochemical

work has, on this account, been done by photosensitization with mercury vapor. In work of this sort mercury vapor is mixed with the reactant gas and the mixture is illuminated with the mercury resonance line at 2537 A.U. This is absorbed by the mercury vapor in the system, normal mercury atoms being raised to the 2^3P_1 level. This lies 4.8 volts or 112 kg-cal. 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 (28, 209, 213, 214, 216), since 112 kg-cal. is greater than the activation energy of almost all chemical reactions.

The mercury photosensitization method is especially important, since Taylor and his coworkers have shown that it allows us to investigate reactions involving hydrogen atoms. In the presence of hydrogen and a reacting substance we have

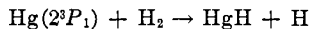


Under these circumstances a stationary concentration of hydrogen atoms exists, and, knowing the rates of reactions 1, 2, and 4, we can calculate the velocity constant of reaction 3 (2, 52, 186). The method is of wide applicability, although the results are not always easy to interpret.

The reactions of hydrogen atoms can also be investigated in a much more direct way, although not under as wide a variety of experimental conditions, by the Wood-Bonhoeffer method. It was first shown by Wood (236) that it was possible under certain circumstances to pump hydrogen atoms out of a hydrogen discharge tube in large quantities, and to carry them for considerable distances before recombination occurred. The method was adapted to the investigation of hydrogen atom reactions by Bonhoeffer (20, 21), and a large number of reactions have been investigated in this way (61).

We shall now proceed to a detailed examination of the available kinetic data for each of the simple hydrocarbons.

¹ Recent work (13, 172) makes it appear probable that reaction 2 should be



This introduces a numerical change into calculations of the hydrogen-atom concentration, but does not affect general considerations about the process.

II. THE PARAFFINS

A. *Methane*

1. The thermal decomposition

A very thorough discussion of the older work, of pyrolytic investigations, and of investigations of the equilibrium

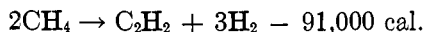


has been given by Egloff (40).

The first investigations of much kinetic importance were made by Holliday and his coworkers. Holliday and Exell (75) investigated the decomposition of methane in silica bulbs at temperatures from 800° to 1100°C. They found that the first 60 per cent of the methane present decomposed regularly, and that a "false equilibrium" was then reached which had no relation to the true equilibrium



They found that hydrogen had a pronounced retarding effect upon the reaction, so that their false equilibrium was presumably merely a pronounced slowing down of the reaction by the hydrogen formed in it. This phenomenon had been previously noted by Cantelo (27). The reaction was not sensitive to the condition of the surface, inasmuch as the same general results were obtained in clean and in carbon-coated silica bulbs and in porcelain. Holliday and Gooderham (76) made exhaustive tests of the homogeneity of the reaction. They assumed that the initial step was



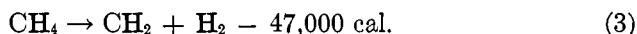
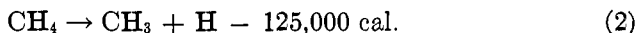
As Kassel has pointed out (86), their arguments in favor of this mechanism seem to be quite irrelevant. There is little in favor of it, and it is ruled out in any case, since it would require the activation energy of the reaction to be greater than 91,000 cal.; this is contrary to the facts.

In a thorough investigation Kassel found the reaction to be homogeneous and of the first order at from 1.3 to 29.6 cm. initial pressure, and he confirmed the strong retardation by hydrogen. According to his measurements the initial rate can be expressed by

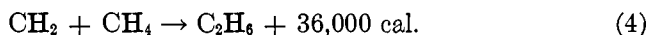
$$k = 1.0 \times 10^{12} e^{-79,385/RT} \text{ sec.}^{-1}$$

with an uncertainty in the activation energy of perhaps 6000 cal. The rate in the later stages of the reaction was found to be approximately proportional to the square of the methane concentration and inversely

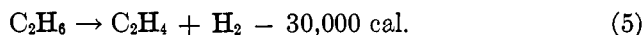
proportional to the cube of the hydrogen concentration. He suggests as possible initial steps (the numbering is his):



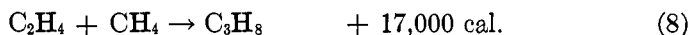
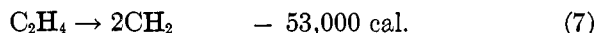
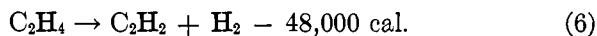
The experimental value of E strongly favors reaction 3 as the primary step. In the early stages of the reaction the only possible reaction of the methylene radical is



and at these high temperatures ethane will decompose rapidly



At the low partial pressures of ethylene which would prevail here polymerization would not be important, so that as possible reactions of ethylene we have



Reaction 6 is probably the only one of these which is important. Acetylene may also be assumed to dissociate as follows:



Using this scheme we get for the initial stages of the reaction approximately

$$-\frac{d}{dt} [\text{CH}_4] = 2k_3[\text{CH}_4]$$

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

$$-\frac{d}{dt} [\text{CH}_4] = \frac{2k_3 k_4 k_5 k_6 k_{12} [\text{CH}_4]^2}{r_3 r_4 r_5 r_6 [\text{H}_2]^3}$$

where the r 's signify the velocity constants of the reverse reactions.

The above equation is in excellent agreement with Kassel's results. In support of this mechanism Storch (199) showed that the earliest product which could be detected was ethane. This was done by decomposing methane on a carbon filament at low pressures in a bulb cooled in liquid nitrogen. Storch (200) has also discussed in detail the results of a number

of investigators who used flow methods to investigate the pyrolysis of methane. Where necessary he makes reasonable assumptions about dimensions of reaction vessels, etc., in order to calculate velocity constants from their data. He concludes that Kassel's mechanism fits the data to within a factor of 2, which is all that can be expected considering uncertainties in temperature, etc. The experiments thus considered were as follows:

AUTHORS	TEMPERATURE RANGE IN °C.
Rudder and Biedermann (173).....	900-1500
Wheeler and Wood (234).....	1050
Stanley and Nash (188).....	1100-1150
Smith, Grandone, and Rall (187).....	1200
Fischer and Pichler (53).....	1260-1600
Storch and Golden (203).....	1500

For a discussion of the sources of error in these measurements, etc., Storch's paper should be consulted.

The velocity constants referred to above are, of course, for the total conversion of methane. Storch also concludes that the conversion of methane to $(C_2H_2 + C_2H_4)$ can be formally represented as a unimolecular reaction with an activation energy of 64,000 cal., i.e.,

(per cent conversion to C_2H_x) (partial pressure of CH_4) = constant

at any temperature. Whatever the explanation of this result may be, combining Storch's equation with that of Kassel enables one to predict the rate of formation of any given product over the whole temperature range.

The decomposition of methane at very high temperatures has been investigated by Tropsch and Egloff (227).

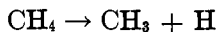
2. Free radicals and the decomposition of methane

Rice and Dooley (158, 161) investigated the primary process in the decomposition of methane by the free-radical technique. Using tellurium mirrors, they found that $CH_3Te \cdot TeCH_3$ was formed and not $(CH_2Te)_n$, and so concluded that the primary process involved methyl rather than methylene radicals. The activation energy of the split into free radicals was found to be 100 ± 6 kg-cal. Belchetz and Rideal (7, 8) passed methane rapidly over a hot filament at low pressures, and then onto a cold target about one mean free path away. Radicals were detected by their

reactions with mirrors, iodine, etc. Contrary to the findings of Rice and Dooley, they conclude that the primary step is

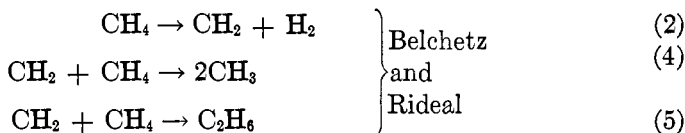
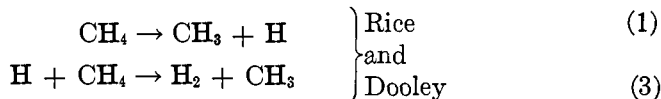


rather than



They found no evidence of the presence of methyl radicals, although this, of course, does not preclude their appearance under other experimental conditions. They point out that metallic methyl compounds may be easily formed by reduction, and hence Rice's technique might lead to false conclusions, since telluroformaldehyde is very easily reduced to dimethyl telluride. The activation energy of the split into methylene and hydrogen was found to be 95 kg-cal., in substantial agreement with the activation energy found by Rice and Dooley.

If we accept Rice and Dooley's detection of the methyl radical as valid, then, as they point out, there are two opposing mechanisms for its formation:



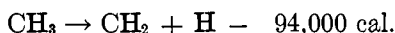
If reaction 2 is the correct primary step, rather than reaction 1, then either reaction 4 or reaction 5 must have an activation energy less than 12 kg-cal. to account for the absence of methylene radicals at the mirror in the experiments of Rice and Dooley. They consider this to be much too low, and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

Assuming a chain reaction due to methyl radicals as postulated above, Kassel (88) has shown that it would be necessary for $[\text{H}]$ to be 10^4 times greater than $[\text{CH}_3]$. It does not seem possible that such a factor could be overcome by wall recombination of hydrogen atoms to such an extent that they do not reach the mirror in appreciable quantities. Hence Kassel rules out reaction 1 as the initial step. Further, since the methylene

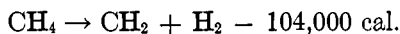
radical was not identified by the Rice technique in the diazomethane decomposition, there is no reason to expect it to be found here even if the primary step is reaction 2. He concludes that reaction 5 is probably fast enough to keep the concentration of methylene radicals down to a very low value.

In connection with the discussion of the mechanism of the primary reaction, it may be noted that Mecke (121, 122) has suggested that the second hydrogen atom in methane may be much more weakly bound than the first.

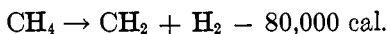
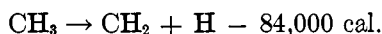
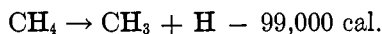
Recent calculations by Voge, however, lead to the values (229a)



whence



If we eliminate the zero-point energy correction so as to get chemical heats of reaction, and correct the results to bring them into line with a more recent and reliable estimate of the heat of sublimation of graphite (70a), Voge's values become



This would make the latter reaction just possible as the rate-determining step in the methane decomposition.

3. The photodecomposition of methane

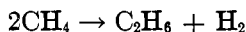
Bonhoeffer (22) has discussed the photodecomposition of methane on the basis of the spectroscopic observations of Leifson (106) and Scheibe (177, 178, 179). Methane is transparent down to the Schumann region, and hence no photodecomposition can occur above this (214). Diffuse bands appear in the neighborhood of 1600 A.U., for which he suggests that the primary process is



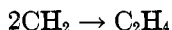
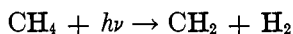
with the possible secondary reactions



We would expect reaction b to be important, and hence the quantum yield to be low for the overall reaction

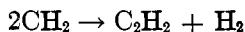
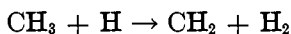
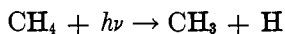


The results of two direct investigations of the photodecomposition have recently been described in brief notes. Leighton and Steiner (107) find that methane is decomposed by light from a hydrogen lamp near the limit of fluorite. Considerable hydrogen and unsaturated hydrocarbons are formed in the approximate mole ratio of 4 to 1, and the quantum yield is approximately unity. The formation of unsaturates can, of course, be easily accounted for if we assume



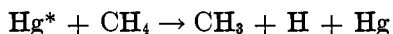
The high ratio of hydrogen to unsaturates, however, indicates that this cannot be the only process involved.

Groth and Laudenklos (66) used a Harteck xenon lamp as a source. This has strong lines at 1469 A.U. and 1295 A.U. They found that a 30-mm. layer of methane at a pressure of 1 atm. absorbed to the extent of 13 per cent at 1469 A.U. and completely at 1295 A.U. 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 quantum yield was 1.30 per mole of hydrogen formed. Their results are thus in excellent general agreement with those of Leighton and Steiner, and they suggest a somewhat similar mechanism, viz.,



In any case it appears that Bonhoeffer's suggested mechanism is not valid.

In the past all observations indicated (90, 214, 219) that methane is stable in the presence of mercury atoms excited by resonance radiation, and hence that the mercury-photosensitized decomposition of methane could not be investigated. Recently, however, Morikawa, Benedict, and Taylor (129) have shown that the reaction



has a low activation energy. This question is discussed in detail in the following section.

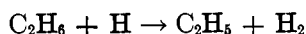
In an electrical discharge methane is decomposed into a variety of

products. Spectroscopic examination of the discharge shows (150) that at least a part of the methane undergoes all the possible dehydrogenation steps, yielding CH_3 , CH_2 , CH , and C . These then recombine in various ways to give a variety of products.

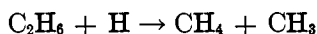
4. The reaction of hydrogen atoms with methane

The reactions of various hydrocarbons with hydrogen atoms were investigated by Bonhoeffer and Harteck (23). They pointed out that since from an energetic standpoint both $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds can be broken in a hydrogen atom reaction (except, of course, in the case of methane), we have in general three possibilities:

(a) *Dehydrogenation*, e.g.,



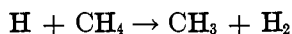
(b) *Chain breaking*, e.g.,



(c) *Hydrogenation*, e.g.,



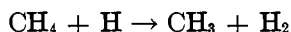
Reaction c may occur at the wall or by dreierstoss, and in the case of complex radicals it can probably occur also in two-body collisions, the multiplicity of energy levels removing the dreierstoss restriction. If reactions a and c occur simultaneously, we may have nothing more than a "catalytic" recombination of hydrogen atoms. Bonhoeffer and Harteck found that methane was surprisingly stable, and they could detect no reaction with hydrogen atoms produced by the discharge tube method, although it might have been expected that the reaction



would occur.

These results were confirmed by von Wartenberg and Schultze (231). They also found that no appreciable heat was developed on mixing hydrogen atoms and methane (apart from the normal amount due to the recombination of the atoms). Further confirmation of the inertness of methane was furnished by the work of Chadwell and Titani (29).

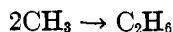
Geib and Harteck investigated the process over a range of temperatures and showed that no reaction occurred up to 183°C . (63). They therefore concluded that the reaction



has an activation energy of at least 17 kg-cal. It might be suggested that this reaction really occurs readily, but that the back reaction

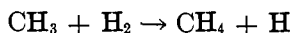


proceeds more rapidly than other possible reactions of the methyl radical such as

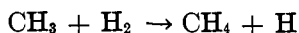
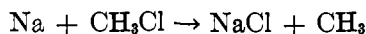


so that methane is reformed as fast as it is used up. Geib and Harteck ruled out such a suggestion on the grounds that (a) it is exceedingly unlikely that no other secondary reactions of the methyl radical should occur, and (b) the presence of methane causes no appreciable alteration in the hydrogen-atom concentration, whereas the above mechanism would involve the consumption of hydrogen atoms by both the forward and the reverse reactions.

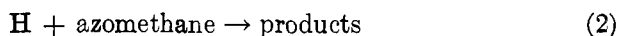
This second objection could be overcome, however, by assuming the secondary reaction to be



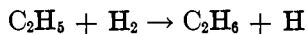
and thus regenerating the hydrogen atoms lost in the primary step. The activation energy of this reaction has been estimated to be about 8 kg-cal. by von Hartel and Polanyi (230). They investigated the reaction of sodium vapor with methyl chloride, using hydrogen as a carrier gas for the sodium. A certain amount of methane is formed under these conditions, presumably by



By using the hydrogen consumption as a measure of the latter step, they estimated its activation energy. The result is not very certain, however, since they were not really very sure of the exact mechanism of the formation of methane, and there is also a possibility of an alteration in the concentration of methyl radicals with increased temperature, owing to other secondary reactions. Further information about this reaction was obtained by Sickman and Rice (185). In an investigation of the effect of foreign gases on the azomethane decomposition they found that hydrogen is not an "inert gas," while deuterium is. They conclude that this is due to the occurrence of the processes



Either process 1 or process 2 must be slower for deuterium than for hydrogen, presumably process 1, since there would be no zero-point energy difference for process 2 other than that of the activated complex. Their results indicate, then, that reaction 1 is appreciable around 300°C. On the other hand Leermakers (104) concluded that the companion reaction



was not detectable at 275°C., indicating an activation energy greater than 15 kg-cal. There is thus considerable uncertainty about reaction 1, but it seems to be the consensus of opinion that von Hartel and Polanyi's estimate of the activation energy is much too low. Patat (135) investigated the concentration of methyl radicals and hydrogen atoms present during the photodecomposition of acetaldehyde. He found that in order to get agreement with von Hartel and Polanyi's experimental value of the activation energy of reaction 1 it was necessary to assume the very unlikely value of 10^{-4} for the steric factor. If the steric factor is taken as unity, a value of 20 kg-cal. is obtained for the activation energy of the reaction. In order to get the best agreement with free-radical mechanisms, Rice (158) arbitrarily puts E_1 equal to 23 kg-cal. He points out that if von Hartel and Polanyi's estimate of 8 kg-cal. were correct, it should be impossible to get appreciable quantities of methyl radicals in the presence of hydrogen, while in fact it is possible to do so. However, it seems almost certain that Rice's estimate is too high. Paneth, Hofeditz, and Wunsch (134a) investigated the rate of recombination of methyl radicals, using both hydrogen and helium as carrier gases. They found that the loss of methyl radicals was more rapid in hydrogen than in helium, even at room temperature. Under these conditions methane is formed, and it appears certain that this is due to the occurrence of reaction 1. Their data indicate that the activation energy of the reaction is about 15 kg-cal.

In view of these uncertainties, it follows that Geib and Harteck's arguments are not entirely conclusive. As will be seen from the following discussion, however, the investigation of the reaction of deuterium atoms with methane proves conclusively that methane is not broken up and reformed, but is really inert to atomic hydrogen.

The first investigation of the deuterium atom reaction was made by Taylor, Morikawa, and Benedict (217), the atoms being produced by photosensitization with mercury, and the resulting deuteromethanes detected by infra-red spectroscopy. They reported considerable reaction from 40°C. to 300°C., and concluded that the activation energy of the process was very low, of the order of 5 kg-cal. The paper was only a preliminary note, and their more complete results, referred to later, do not confirm their previous conclusions.

Geib and Steacie (64, 65) investigated the same reaction by the Wood-Bonhoeffer method. They found no detectable reaction of deuterium atoms with methane up to 100°C., indicating that the activation energy of the exchange reaction is not less than 11 kg-cal., in contrast to the above results. Their investigation indicates that the reaction concerned is probably the analogue of the ortho-para hydrogen conversion, viz.,

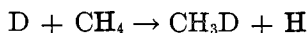
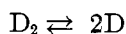


rather than



In any case a lower limit of 11 kg-cal. is set for both reactions. Subsequent work (192) furnishes further confirmation of the absence of a reaction between deuterium atoms produced by a discharge and methane at low temperatures.

A few preliminary experiments on the thermal exchange reaction between deuterium and methane at temperatures in the neighborhood of 1000°K. have been made by Farkas (50). His results show that the thermal reaction proceeds by an atomic mechanism, similar to the ortho-para hydrogen conversion, viz.,

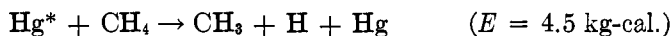


While the temperature coefficient of the reaction was not determined, an activation energy of about 11 to 12 kg-cal. was indicated.

The mercury-photosensitized reaction was reinvestigated at room temperature by Steacie and Phillips (196), who found an activation energy of 11.7 kg-cal. (assuming a steric factor of 0.1), in good agreement with the results of other methods. The reaction was also investigated by Farkas and Melville (51) over a wide range of temperature, and they found an activation energy of 13 kg-cal. In their investigation the atom concentration was determined by using ortho-deuterium-methane mixtures and measuring the rate of the ortho-para conversion as well as the exchange. They concluded, as did Steacie and Phillips, that the reaction occurring was reaction 3. They found, however, that at high temperatures the deuterium-atom concentration fell off greatly, and they suggest that the atom-consuming step is reaction 4. If this is the case, we would expect a small amount of ethane formation to accompany the exchange reaction.

In a recent paper Morikawa, Benedict, and Taylor (129) report a further investigation of the mercury-photosensitized reaction. From the collision yield at 100°C. they calculate for reaction 3 an activation energy of 12.5 to 14 kg-cal., in satisfactory agreement with the results of Steacie and

Phillips and of Farkas and Melville. The experimental value of the temperature coefficient in the range 100–200°C. is very low, however, and they conclude that the mechanism is not that postulated by these authors. They suggest that the reaction is largely

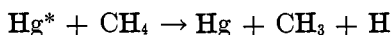
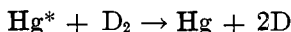
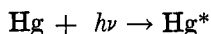


followed by a rapid exchange of the methyl radical, probably through the formation and decomposition of a quasi-molecule,

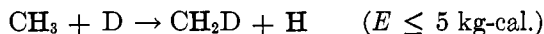


The fact that some ethane formation occurs is cited as evidence for this mechanism. They summarize the possible processes as:

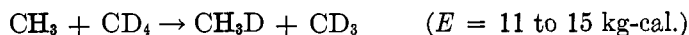
(a) *Primary processes:*



(b) *Secondary processes at low temperatures:*



(c) *Secondary processes at higher temperatures:*



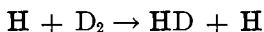
together with later condensation and decomposition reactions. They discuss in detail the justification of these steps, and conclude that one cannot obtain much information about reaction 3 by the photosensitization method.

It seems to the writer, however, that the loss of hydrogen atoms at high temperatures found by Farkas and Melville is a sufficient explanation of the low temperature coefficient of the reaction, and that it is not necessary to postulate such a complicated series of processes. If one accepts this explanation, then the results of Morikawa, Benedict, and Taylor give an activation energy for the exchange reaction in good agreement

with the values of other investigators. It should be emphasized that the disagreement is primarily one of mechanism, not of experimental fact. There is, however, a considerable discrepancy in the quantum yields of the exchange reaction obtained by Farkas and Melville and by Morikawa, Benedict, and Taylor.

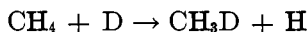
Further investigations of the reaction with deuterium atoms produced by the Wood-Bonhoeffer method have also been made by Trenner, Morikawa, and Taylor (226) and by Steacie (192). Steacie investigated the reaction up to 500°C. and obtained an activation energy of 12.9 ± 2 kg-cal., the values calculated from the temperature coefficient and from the collision yield being in good agreement.

Trenner, Morikawa, and Taylor by the same method found no reaction from 25°C. to 208°C., from which they calculate a minimum activation energy of 15.6 kg-cal. with a steric factor of 0.1. From a single run at 310°C. they calculate the activation energy to be 18 kg-cal. These values are higher than those obtained by other workers. The discrepancy is partly due to the fact that they assume that the process under investigation is reaction 4, followed by a rapid exchange of the methyl radical. Hence to get the rate of the initial step they divide the observed rate by 3. If we assume a direct exchange (i.e., reaction 3), this division by 3 should not be performed, and their activation energy would be lowered by about 1 kg-cal. They obtained the deuterium-atom concentration in their experiments by comparison with the reaction

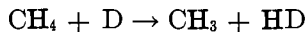


As far as one can tell from their paper, this comparison was made only at room temperature (although this is not certain). If this is the case their deuterium-atom concentration at higher temperatures would probably be somewhat lower than that assumed, and this would further lower the activation energy. It appears, therefore, that the discrepancy between their results and those of others is not large, and is mainly one of interpretation.

While there is thus some uncertainty about the exchange reaction, the main body of evidence favors an activation energy of about 12 to 13 kg-cal. for the reaction



It may also be concluded that the reactions



and

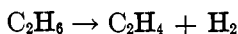


have activation energies greater than this. In an excellent recent review of atomic reactions, Geib (61) points out that further evidence of the stability of methane to attack by hydrogen atoms is furnished by the fact that methane is obtained as an end product in many reactions of hydrogen atoms.

B. Ethane

1. The thermal decomposition

The first paper on the decomposition of ethane which contained any data other than purely pyrolytic was that of Pease (140). He made a preliminary investigation of the reaction at 650°C. by the flow method and concluded that the reaction was homogeneous and probably of the first order, and that it went smoothly according to the equation



The addition of hydrogen was found to have no effect on the rate of the reaction or upon the products. A brief investigation of the reaction by the static method at 575°C. by Frey and Smith (59) gave results in excellent agreement with those of Pease. Neither of these investigations, however, was very detailed.

The first thorough investigation from a kinetic standpoint was that of Marek and McCluer (118), who used a flow method. They concluded that the reaction was homogeneous and of the first order, the rate being given by

$$\log k = 15.12 - \frac{15,970}{T} \text{ sec.}^{-1}$$

after correcting for the reverse reaction. This corresponds to an activation energy of 73,200 cal. The main source of uncertainty in their work was the temperature of the reaction vessel, which was by no means uniform. Their value of the activation energy is therefore probably uncertain to ± 5000 cal. Their results have been recalculated by Paul and Marek (139), who conclude that they are better expressed by the equation

$$\log_{10} k = 16.06 - \frac{77,700}{2.3RT} \text{ sec.}^{-1}$$

A more thorough investigation of the kinetics of the process was made by Sachsse (174), who used the static method and followed the reaction by the change in pressure. He worked at temperatures from 856° to 910°K. and at pressures from 5 to 500 mm. The velocity constants were found

to fall off with diminishing pressure in the customary way for a first-order reaction. His results for the high-pressure rates of reaction are given by

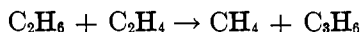
$$\log_{10} k = 14.1 - \frac{69,800}{2.3RT} \text{ sec.}^{-1}$$

He found that, in addition to ethylene and hydrogen, a certain amount of condensable products was formed, the amount increasing with the pressure.

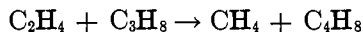
The reaction has recently been reinvestigated by Storch and Kassel (203a). They find that in addition to the dehydrogenation reaction



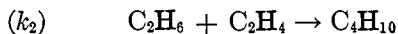
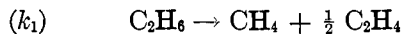
there is also methane and propylene production, which can be stoichiometrically represented by the equations



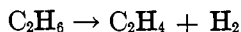
Butane may be an intermediate product for the latter reaction, but their experiments provide no direct test of this. However, Frey and Hepp (58a) showed that the analogous reactions



both occurred readily, the former being two to three times more frequent. Storch and Kassel therefore conclude that by analogy part of the methane and propylene found in their work is a product of the butane decomposition. They calculate their rate constants on this basis, using Paul and Marek's values for the rate of the butane decomposition. They thus obtain the values of the rate constants



given in table 1A. For the initial rate of the dehydrogenation reaction



at 565°C. they thus obtained the velocity constants given in table 1B. Obviously the reaction is definitely of the first order. The agreement with Marek and McCluer's calculated velocity constant at 565°C., $11.6 \times 10^{-5} \text{ sec.}^{-1}$, is not good. Paul and Marek's recalculation of Marek and McCluer's data gives $6.2 \times 10^{-5} \text{ sec.}^{-1}$, in excellent agreement with Storch and Kassel's result. Sachsse's value, $10 \times 10^{-5} \text{ sec.}^{-1}$ is not in very good agreement.

Dinzes, Zharkova, Zherko, and Frost (33c), who investigated the reaction at 635°C. and high pressures (1 to 26 atm.), also found that methane was produced. They suggested this was due to a concurrent reaction



the influence of which increased with increasing pressure, as would be expected for a second-order reaction occurring simultaneously with one of the first order.

Since the rate of the reverse reaction



has been measured by Pease (144), it is possible to calculate the equilibrium constant for the reaction and compare it with the experimental value.

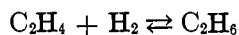
TABLE 1A
Storch and Kassel's values of k_1 and k_2

TEMPERATURE	k_1	k_2
°C.	sec. ⁻¹	sec. ⁻¹ mm. ⁻¹
541	2.62×10^{-7}	1.85×10^{-8}
565	1.00×10^{-6}	6.28×10^{-8}
600	6.14×10^{-6}	3.31×10^{-7}
650	6.44×10^{-6}	2.83×10^{-6}
	$E_1 = 75,400 \text{ cal.}$	$E_2 = 69,000 \text{ cal.}$

TABLE 1B
The dehydrogenation of ethane at 565°C. (Storch and Kassel)

INITIAL PRESSURE	k	INITIAL PRESSURE	k
mm.	sec. ⁻¹	mm.	sec. ⁻¹
99.0	9.2×10^{-5}	423.8	5.5×10^{-5}
104.0	7.9	512.6	6.0
107.7	7.7	716.3	5.5
223.8	6.0	1093.4	5.6
224.1	6.0	1432.5	6.5
420.6	6.6	1517.0	6.9

Using Marek and McCluer's rates for the ethane decomposition, we thus get for the equilibrium



$$\log_{10} K = 6.66 - \frac{30,020}{2.3RT}$$

The experimental value of Pease and Durgan (146) is

$$\log_{10} K = 6.31 - \frac{31,244}{2.3RT}$$

in excellent agreement with the calculated value. Had Sachsse's values for the ethane decomposition been used in the calculation, the result would have been much the same in the range covered by experiment, since his absolute rates are in fair agreement with those of Marek and McCluer in spite of the considerable difference in the temperature coefficient. Recent work by Storch and Kassel (203a) indicates that the situation is rather more complex. The question is discussed in detail in section III B.

The thermal decomposition has also been investigated by a static method by Dinzes and Frost (30, 31, 32). Their main object was to check accurately the unimolecular character of the reaction in the light of the Rice-Herzfeld chain theory. They followed the reaction by pressure change and by analysis at 678°C. and pressures from 1.7 to 22.3 mm. They found that the reaction did not follow the unimolecular equation well, the constants decreasing three or four times on going from 10 to 70 per cent decomposition. The course of an individual experiment could be expressed accurately by the equation

$$k = \frac{1}{t} \left(\log \frac{1}{1-x} - \beta x \right)$$

where x and t have the usual significance, and β is a constant. From the complex character of the rate equation they conclude that the reaction is probably a chain process. It seems certain, however, that at 678°C. the ethylene formed in the reaction would undergo a series of further complex changes, and one would hardly expect a first-order equation to hold up to high percentage decompositions under the circumstances. Dinzes, Kvyatkovskii, Stepukhovich, and Frost (33b) cite as further evidence for the complexity of the reaction that it is inhibited by the addition of propylene but not by ethylene or butylene.

The decomposition of ethane in sealed silica bulbs has also been investigated by Travers and his collaborators (222a, 223, 224, 225). They worked mainly with mixtures of ethane, ethylene, and hydrogen in order to eliminate the effect of the equilibrium, and thus study the formation of secondary products. Their results on the main decomposition process are very complex and are in complete disagreement with those of all other investigators. They conclude that there is a pronounced induction period, and that sharp breaks occur in curves representing the rate of formation of all the products concerned. They also find pronounced and complex surface effects, contrary to the findings of other workers. Travers (222, 222b) concludes that the whole process is governed by the "back-ground" reaction



but that the rate-controlling step is the reaction

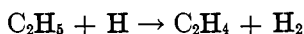
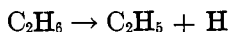


It seems to the reviewer that little confidence can be placed in this work. The induction periods which they find are almost certainly due to the experimental technique, which consists of plunging a cold reaction vessel into a heated bath, and thus yields fictitious induction periods, which are really due to a lag in reaching temperature equilibrium. Further, the most striking thing about their results is the presence in every case of sharp breaks in curves representing the rate of formation of the various products. An examination of the analytical data, however, indicates that these breaks are also fictitious and are due to placing too much confidence in unchecked analytical results.

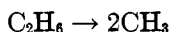
Fischer and Pichler (54) have investigated the decomposition of ethane at temperatures up to 1400°C. They find that the percentage conversion and the products are practically the same as those of ethylene at high temperatures. In other words, at high enough temperatures ethane dehydrogenates instantaneously to ethylene, which then pyrolyzes in the ordinary way.

2. The photodecomposition and the photosensitized decomposition

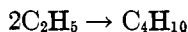
As Bonhoeffer has pointed out (22), all we can do in connection with the direct photodecomposition is to make speculations on the basis of rather meager spectroscopic information. The absorption is probably by the C—H bond, but possibly some of the energy wanders to the C—C bond. He suggests that the main process would probably be



and that the primary split



would be expected to be followed largely by recombination to ethane. It seems to the writer that, by analogy with the photosensitized decomposition, the possibility of



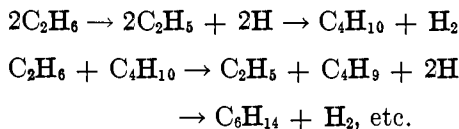
should not be overlooked. In any case this is all speculation at the moment, but the question should soon be settled, since a number of workers are now actively engaged in the photochemistry of the fluorite region.

The mercury-photosensitized decomposition of ethane was first studied by Taylor and Hill (214). They observed that in ethylene-hydrogen

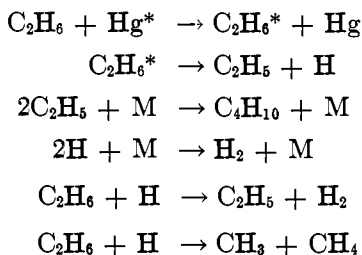
mixtures ethane and higher hydrocarbons were formed. After the pressure change accompanying this reaction was over, other changes occurred which led them to suspect that the ethane formed was being attacked both by hydrogen atoms and by excited mercury. They verified this, and suggested that radicals were undoubtedly involved in the process. Kemula (90) also showed that ethane could be decomposed by excited mercury atoms.

A more thorough investigation of the photosensitized reaction was made by Kemula, Mrazek, and Tolloczko (94), following earlier work by Tolloczko (219). In their investigation the reaction mixture was circulated through a trap at -80°C . to remove the products of higher molecular weight as fast as formed, and thus prevent secondary processes. (This is not a sufficiently low temperature to remove butane efficiently, and hence the prevention of secondary changes was only partially successful.) They found that the decrease in pressure as the reaction went on was accompanied by an exactly parallel increase in the volume of the liquid condensate. The rate was independent of the ethane pressure, but at high pressures a higher percentage of condensate was formed. The gaseous products consisted entirely of hydrogen and methane, the ratio of hydrogen to methane being considerably greater than unity and approaching infinity if the trap were kept at -20°C . instead of -80°C . The condensable products were analyzed by a rough fractional distillation, and were found to consist mainly of butane and octane, with a small amount of hexane and no propane or pentane.

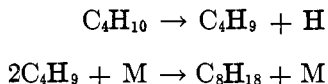
Tolloczko (219) had previously suggested that the mechanism of the process was



This assumes only a C—H rupture and leads obviously to hydrocarbons with an even number of carbon atoms only. It gives, however, no explanation of the formation of methane. Kemula, Mrazek, and Tolloczko therefore suggest



The higher hydrocarbons then result from secondary reactions of butane, etc. The fact that octane is the main higher product obviously suggests that the chief reaction of butane is



The reaction has recently been reinvestigated by Steacie and Phillips (198). They found that by operating with the trap in the circulation system at a lower temperature it was possible to remove higher products more efficiently, and thus almost completely avoid the occurrence of secondary reactions. The quantum yield and the products obtained at various trapping temperatures as analyzed by low temperature distillation are given in table 1C.

TABLE 1C

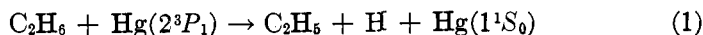
The mercury-photosensitized decomposition of ethane (Steacie and Phillips)

TRAPPING TEMPERATURE	QUANTUM YIELD	PRODUCTS IN MOLE PER CENT				
		H ₂	CH ₄	C ₃ H ₈	C ₄ H ₁₀	Higher hydrocarbons as C ₅
°C.						
-70	0.13	47	16	0.0	23	14
-70	0.14	43	23	0.0	20	14
-100	0.11				25	Present
-108	0.095	19.6	44.7	0.0	35.7	Trace
-115	0.098					None
-116	0.090	6.1	59.3	<1.0	34.6	None
-125	0.15	0.0	59.5	21.5	19.0	None
-131	0.18	0.0	58.8	23.5	17.7	None

The most striking thing about these results is that when the conditions are arranged so as to prevent secondary reactions the formation of hydrogen is entirely inhibited. It follows therefore that all the hydrogen formed in previous investigations has resulted from secondary reactions of higher hydrocarbons, and that hydrogen is not a product of the ethane decomposition itself.

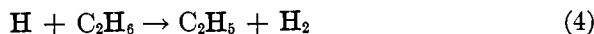
Furthermore, previous investigations reported no hydrocarbons with an odd number of carbon atoms (with the exception of methane), and previous mechanisms were formulated mainly for the purpose of explaining this. Table 1C shows, however, that propane is in reality an important product of the reaction. Previous mechanisms are therefore in need of revision.

Steacie and Phillips point out that the two most likely primary processes are:

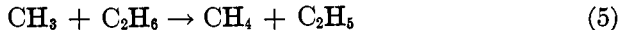


i.e., a C—H or a C—C bond split.

(a) *The C—H bond split.* If the primary reaction is reaction 1, the most likely fate of the hydrogen atoms produced would obviously be to react with ethane,



In order that this mechanism shall yield the products found experimentally it is necessary to assume that reaction 4 is slow compared to reaction 3, since the occurrence of reaction 4 to any appreciable extent would yield far too much butane relative to methane, and would also lead to the production of hydrogen contrary to the experimental findings. As pointed out in the next section, estimates of the relative rates of reactions 3 and 4 are conflicting, but it is possible that the necessary conditions may be fulfilled. We may then assume reaction 3 to be followed by



yielding the experimentally found products.

The main difficulty encountered by such a mechanism, however, is the necessity of explaining the absence of hydrogen in spite of the possibility of its formation by the reaction



In other words, it must be shown that reaction 3 is fast enough to keep the hydrogen-atom concentration so low that reaction 9 does not occur to an appreciable extent. Steacie and Phillips calculate from the known rates of reactions 3 and 9 that this condition cannot be fulfilled, and therefore rule out the C—H bond split as a possible primary process.

(b) *The C—C bond split.* It appears from the above that the primary process must be a C—C bond split. Steacie and Phillips therefore assume a mechanism in which reaction 2 is followed by reactions 5, 6, and 8,

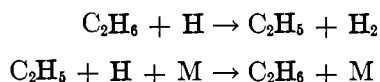
yielding methane, propane, and butane as the products of the reaction. They explain the low quantum yield of the reaction as partly due to the inefficiency of reaction 2, and partly to the occurrence of the reaction



which regenerates ethane. (Davis, Jahn, and Burton (29a) conclude from an investigation of the photolysis of azomethane that reaction 10 is slow at ordinary temperatures, but the evidence for this statement is not very conclusive.)

3. The reaction of ethane with hydrogen atoms

Bonhoeffer and Harteck (23) and von Wartenberg and Schultze (231) found that luminescence occurs on mixing hydrogen atoms and ethane, bands due to CH and CC being observed. The major part of the ethane was recovered unchanged, however. The latter authors found that there was a considerable loss of gas in their experiments (up to 25 per cent), which might have been due to methane formed in the reaction, and which with their technique would have passed through the liquid-air trap and been lost. They suggested that the main process was



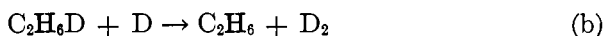
Since a complex mixture of products is not formed, it is apparent that the emission of the CC and CH bands is due to the presence of only minute amounts of C₂ and CH produced by secondary reactions. If the main process went by dehydrogenation to C₂ and CH, it is unthinkable that these could be quantitatively hydrogenated back to ethane without the formation of appreciable amounts of other products.

Chadwell and Titani (29), in the course of another investigation, also made two experiments with ethane and hydrogen atoms. They found that (1) 25 cc. of ethane gave 5 per cent methane, 1.4 per cent carbon dioxide, 1.6 per cent ethylene, and (2) 150 cc. of ethane gave 3 per cent methane, 3 per cent carbon dioxide, and 1.7 per cent ethylene. The carbon dioxide obviously comes from a reaction involving the water or phosphoric acid used to poison the walls of the apparatus. They suggest that the gas lost in the investigation of von Wartenberg and Schultze was ethane, which passed the liquid-air trap, rather than methane. It is certainly to be expected that some ethane would be lost under the experimental conditions of von Wartenberg and Schultze. On the other hand, Kemula (90) found that some methane *was* produced in the reaction of ethane with hydrogen atoms produced by mercury photosensitization.

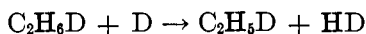
Steacie and Phillips (196) investigated the reaction of deuterium atoms

with ethane, using the Wood-Bonhoeffer method. They found an activation energy of 6.3 kg-cal. for the exchange reaction. They point out that there are three main possibilities for the mechanism of the reaction:

I. Hydrogenation:



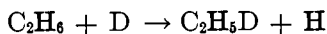
or



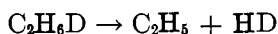
II. Dehydrogenation:



III. Exchange by metathesis:



Mechanism III is probably the correct one for the reaction of deuterium atoms with methane as discussed above, and also for the reactions with water, ammonia, etc. However, since it regenerates one hydrogen atom for each one lost, it cannot account for the "catalytic" destruction of hydrogen atoms by ethane. Furthermore the activation energy of the ethane-hydrogen atom reaction is so much lower than that of the others that it is apparent that a different mechanism exists. Mechanism I is very unlikely, since reaction Ia would have to occur at a triple collision (or else have a very low steric factor), and this would make the reaction far too slow to enable ethane to exert a strong catalytic effect on the recombination of hydrogen atoms. Also, even if reaction Ia occurred sufficiently rapidly, the very unstable molecule $\text{C}_2\text{H}_5\text{D}$ would have little chance of surviving long enough (10^{-6} sec.) to meet a deuterium atom and give Ib. Hence, in general, reaction Ia would be followed by



or



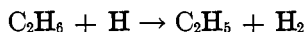
which would make the whole process indistinguishable from reaction IIa, or else by



which would give a result indistinguishable from mechanism III.

Hence they conclude that mechanism II is the correct one, and that the

measured activation energy (6.3 kg-cal.) is that of reaction IIa. They therefore conclude that the companion reaction

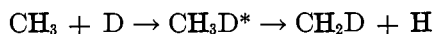
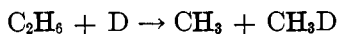


also has an activation energy of the same order of magnitude. This reaction is very important in connection with free-radical mechanisms, and the bearing of its activation energy on the mechanism of the thermal decomposition of ethane will be discussed in the next section.

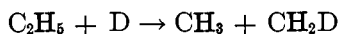
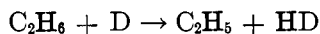
The reaction has recently been reinvestigated by the Wood-Bonhoeffer method by Trenner, Morikawa, and Taylor (226). Their results differ sharply from those of Steacie and Phillips. They conclude that at room temperature the main reaction is



and that the exchange reaction is only appreciable at temperatures from 100°C. up, with an activation energy of 11.4 kg-cal. In their experiments from 10 to 20 per cent of the ethane was found to be decomposed to methane. They made very thorough analyses of the products of the reaction, and determined the deuterium content of each product separately. The methane formed was found to be about 50 per cent deuterized, but the ethane was entirely light at temperatures below 100°C. They suggest that the methane is formed by



They rule out

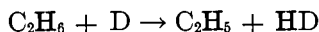


as the mechanism of methane formation, since Taylor and Hill (214) found that in the photosensitized hydrogenation of ethylene



without the formation of methane. (On the other hand, Klemenc and Patat (96) always obtained methane in the mercury-photosensitized hydrogenation of ethylene.)

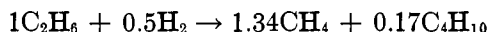
Trenner, Morikawa, and Taylor suggest that above 100°C. the reaction also occurs by



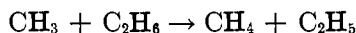
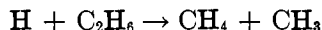
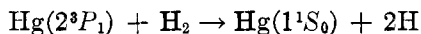
as suggested by Steacie and Phillips. There is, however, a large discrepancy in the activation energy of this process between the two investi-

gations (6.3 and 11.4 kg-cal.). In Steacie and Phillips' investigation the separate products were not isolated, it being assumed from the work of Chadwell and Titani that the formation of methane was negligible. This, however, is not a sufficient explanation of the discrepancy, since to bring the results of the two investigations into line it would be necessary to assume that about 60 per cent of the total ethane present was split into methane at room temperature in Steacie and Phillips' work. In recent work, under conditions similar to those employed by Steacie and Phillips, Steacie (192a) has confirmed the production of methane. At room temperature, however, only about 10 per cent decomposition of ethane occurred, and it appears that further investigation is necessary to determine the cause of the disagreement.

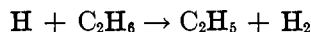
The reaction of ethane with hydrogen atoms has also been investigated qualitatively by photosensitization with mercury (90, 213, 214). It has recently been reinvestigated by Steacie and Phillips (198) by the method described in section IIB(2). It is found that methane, propane, and butane are formed, but no higher hydrocarbons. Hydrogen is consumed. Thus in a typical experiment at a trapping temperature of $-125^{\circ}\text{C}.$, the following stoichiometric equation expresses the results:



(+ traces of C_3H_8). Steacie and Phillips suggest that the mechanism is



followed by various radical recombination reactions. The possibility of the occurrence of the reaction



is not ruled out, since the quantum yield of the reaction is low, and if this were followed by

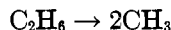


the net stoichiometric result would be zero.

4. Free radicals and the ethane decomposition

As we have seen, Rice (156, 166) has suggested that virtually all organic compounds decompose by mechanisms which involve the intermediate formation of free radicals. From a free-radical point of view, the primary step in the ethane decomposition is still a matter of controversy.

Rice and Dooley (160) found that lead mirrors were removed by decomposing ethane at 850° to 950°C. By using standard mirrors, they measured the activation energy of the split into radicals and found a value of 79.5 kg-cal. for the assumed reaction



Belchetz and Rideal (8), on the other hand, found no evidence of radical formation, and concluded that the primary reaction was

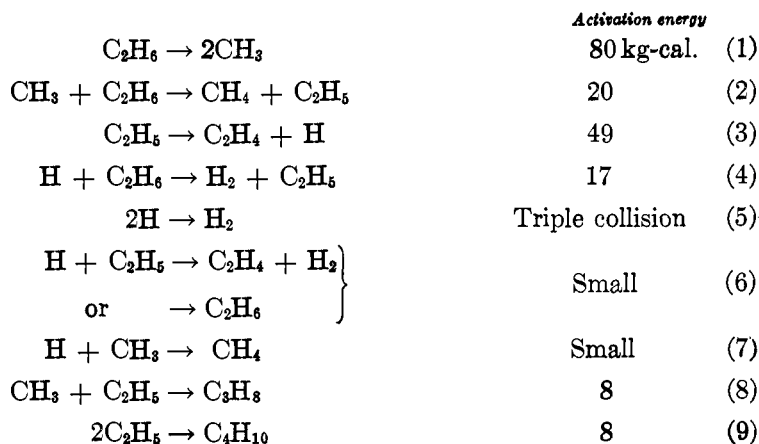


with an activation energy of 94.6 kg-cal. They suggest that it is possible that the reaction proceeds through the intermediate formation of ethylidene radicals



but if so they isomerize to ethylene so rapidly that they cannot be detected. There seems to be no doubt from Rice and Dooley's work that radicals of some sort are formed. It is, of course, possible that they arise in secondary reactions, but the evidence seems on the whole to favor the assumption that at high temperatures the main process is a split into methyl radicals.

Granting that the primary step at high temperatures is a split into methyl radicals, is not, however, a proof that the ordinary thermal decomposition of ethane at low temperatures involves free radicals. Also, as we have seen, if it is to be postulated that the decomposition proceeds by a free-radical mechanism, it is necessary to devise a mechanism which will lead to a first-order rate equation and to an activation energy in agreement with experiment. Rice and Herzfeld (162) suggested that the following mechanism would fulfil these conditions:



By virtue of reactions 3 and 4 reaction chains will occur, a large number of ethane molecules being decomposed for each primary act. The activation energies allotted to the various steps are partially based on experimental data, qualitative or quantitative, and partially frankly assigned to agree with free-radical mechanisms. Assuming reactions 5, 7, 8, and 9 to be negligible, we get from this scheme

$$E_{\text{overall}} = \frac{1}{2} (E_1 + E_3 + E_4 - E_6) = 73 \text{ kg-cal.}$$

in agreement with the measurements of Marek and McCluer. E_1 is the experimental value found by Rice and Dooley for the free-radical split, and E_6 is probably very small, so that these two are fixed. $E_3 + E_4$, however, is merely adjusted to make the mechanism agree with experiment.

For the overall rate of reaction the Rice-Herzfeld scheme leads to the expressions

$$-\frac{d}{dt} [\text{C}_2\text{H}_6] = k[\text{C}_2\text{H}_6]$$

$$\log k = \frac{1}{2} \log \frac{k_1 k_3 k_4}{2k_6}$$

i.e., the reaction is of the first order, as found experimentally. Rice and Herzfeld evaluate the velocity constants of the separate steps by adopting the reasonable approximation that all first-order reactions have rate constants given roughly by $10^{14} e^{-E/RT}$ sec.⁻¹, and all bimolecular constants are $10^9 e^{-E/RT}$ liter mol.⁻¹ sec.⁻¹. On this basis they get for the overall decomposition

$$\log_{10} k = 13.7 - \frac{73,000}{2.3RT} \text{ sec.}^{-1}$$

in satisfactory agreement with the experimental equation of Marek and McCluer

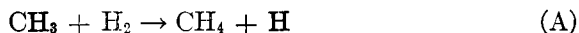
$$\log_{10} k = 15.1 - \frac{73,200}{2.3RT} \text{ sec.}^{-1}$$

The chain length calculated from the above mechanism is about 100.

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

Recently the work of Patat and Sachsse (137, 175) has thrown considerable doubt upon the idea that the reaction proceeds by a radical chain mechanism. They measured the rate of the ortho-para hydrogen con-

version in the presence of decomposing ethane, and were thus able to detect hydrogen atoms² produced by the decomposition or by the reaction



The hydrogen atoms produced in this way are being destroyed by reaction 4 above. Hence the stationary concentration of hydrogen atoms is defined by the two processes, and we get approximately

$$\frac{[\text{CH}_3]}{[\text{H}]} = \frac{k_4[\text{C}_2\text{H}_6]}{k_A[\text{H}_2]}$$

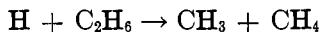
Having evaluated the hydrogen-atom concentration, we can compare it with that calculated from the Rice-Herzfeld mechanism. At 590°C. the experimentally found value is 10^{-11} moles per liter. The value predicted by the Rice-Herzfeld mechanism is about 1000 times larger, viz., $10^{-8.2}$.

As pointed out above, Steacie and Phillips determined the activation energy of reaction 4 in the above scheme. They find $E_4 = 6.3$ kg-cal. instead of the assumed value of 17 kg-cal. If we recalculate the hydrogen-atom concentration predicted by the free-radical chain theory, using this value of E_4 , we obtain a result which agrees almost exactly with experiment. Such a change in reaction 4, however, seems to introduce insurmountable difficulties into the application of the scheme of Rice and Herzfeld to the ethane decomposition. The overall order of the reaction and the theoretical value of the activation energy are largely dependent on the manner in which the chains are terminated. The change in E_4 , by altering the relative concentrations of the reacting substances, upsets the relationships between the rate constants, and it is no longer permissible to neglect reactions 8 and 9. Under these circumstances the scheme no longer predicts a first-order rate or the correct value of the overall activation energy. There has been a certain amount of disagreement between Sachsse (176) and Steacie and Phillips (197) as to the exact manner in which the Rice-Herzfeld mechanism is affected by the results of the latter authors. They are, however, in complete agreement that the main effect of the results is to make the free-radical chain mechanism for the ethane decomposition untenable, at least in its present form.

Of course, as we have seen, the recent work of Trenner, Morikawa, and Taylor (226) disagrees with that of Steacie and Phillips concerning the activation energy of reaction 4. However, even their value of 11.4 kg-cal.

² For a detailed discussion of the ortho-para hydrogen conversion and its use as a method of measuring the stationary concentration of hydrogen atoms in a system, see Farkas (49).

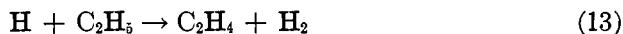
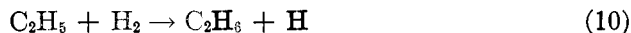
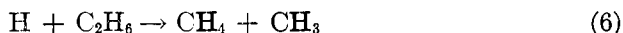
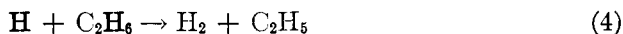
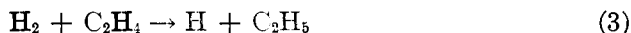
would introduce serious difficulties into the application of the free-radical chain mechanism. Also, on the basis of their work the reaction



could not be ignored. The presence of this reaction with an activation energy of 7.4 kg-cal. would fundamentally alter the nature of the chain-carrying steps in the Rice-Herzfeld scheme and would destroy its agreement with experiment.

Frost (60) concludes that the scheme is not in agreement with experimental results, and has suggested a new free-radical chain mechanism based on a retarding effect of the unsaturated products of the reaction.

Storch and Kassel (203a) in discussing the free-radical mechanism generalize the Rice-Herzfeld scheme to take into account their new results on the production of methane and propylene. They consider the following scheme:



By the customary steady-state method, assuming long chains, they conclude that for the free-radical scheme to agree with experiment the following conditions must be fulfilled:

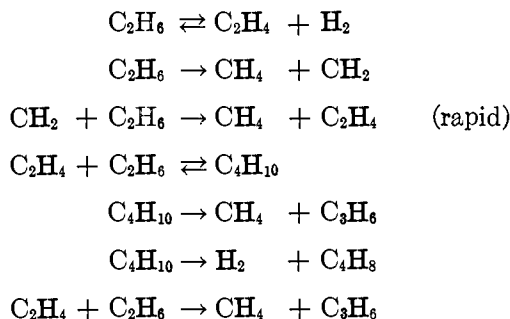
- (1) $k_9 \ll k_{10}[\text{H}_2]$ for $[\text{H}_2] \geq 300$ mm.
 (2) $k_9 \gg k_{10}[\text{H}_2]$ for $[\text{H}_2] \leq 50$ mm.
 (3) $k_4[\text{C}_2\text{H}_6] \gg k_5[\text{C}_2\text{H}_4]$ for $[\text{C}_2\text{H}_6] \sim 10[\text{C}_2\text{H}_4]$
 (4) $(k_1 + k_2)[\text{C}_2\text{H}_6] \gg k_3[\text{H}_2][\text{C}_2\text{H}_4]$ for $\frac{[\text{H}_2][\text{C}_2\text{H}_4]}{[\text{C}_2\text{H}_6]} \leq K_{\text{equil}}$.

The first two conditions are incompatible unless the reactions $\text{H}_2 + \text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$ deviate widely from second-order laws, and such a deviation is in definite disagreement with the results of Pease, Sachsse, and Storch and Kassel. Condition 3 is in poor agreement with Rice and Herzfeld's assignment of activation energies, $E_4 = 17$ kg-cal., $E_5 = 10$ kg-cal. The use of $E_4 = 6$ kg-cal., as found by Steacie and Phillips, introduces new difficulties, as discussed above. Storch and Kassel illustrate these difficulties by showing that with $E_4 = 6$ kg-cal., in order that the free-radical mechanism can hold it is necessary that

$$\frac{k_{15}}{k_{12} + k_{13}} < 2 \times 10^{-6}$$

It is extremely unlikely that the rates of two recombination reactions should differ so widely. At present there are no suitable data for testing condition 4.

Storch and Kassel therefore conclude that the free-radical mechanism is ruled out, and that the major part of the observed reaction is to be accounted for by the more or less classical mechanism



In addition, a small amount of reaction undoubtedly occurs by radical and chain processes.

Sickman and O. K. Rice (185) have found evidence that methyl radicals from decomposing azomethane will decompose ethane to some extent. On the other hand, Echols and Pease (38) found that radicals from the ethylene oxide decomposition would not cause the decomposition of

ethane at 425°C., although they would 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 no proof that the ordinary decomposition of the substance involves them.

Recently Staveley (188a) has investigated the occurrence 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. The reaction was followed by the pressure change, but it was proved that possible complications due to the polymerization of ethylene by nitric oxide were absent. The rate of the fully inhibited reaction was found to fall off with diminishing ethane pressure in the ordinary way. Its rate could be expressed by

$$\log_{10} k = 14.44 - \frac{74,500}{2.3RT} \text{ sec.}^{-1}$$

Staveley suggests that comparatively few decomposing molecules give rise to chains, but that these chains are very long, of the order of 10^6 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.

C. Propane

1. The thermal decomposition

The early papers on the propane decomposition by Pease (140), Frey and Smith (59), and others (37, 147, 182) served to establish the fact that the reaction is principally homogeneous and of the first order. The main courses of the reaction are:



a certain amount of ethane and butane being also formed.

The first reasonably accurate kinetic data were obtained by Marek and McCluer (118), using a flow method. The products found were those indicated by the above equations in approximately equal amounts. In calculating velocity constants they corrected for the back reactions, and obtained the result

$$\log_{10} k = 13.44 - \frac{62,100}{2.3RT} \text{ sec.}^{-1}$$

The main source of uncertainty in their work was the rather variable temperature of the reaction vessel. Also, as in all work with flow systems,

the effect of pressure on the rate could not be very thoroughly investigated.

Later work by Paul and Marek (139) was done by the same method, but in greater detail. They used small percentage conversions and thus cut secondary reactions down to a minimum. Nitrogen and increased surface were shown to be without effect on the rate when the reaction was carried out in either silica or copper vessels. In the range from 550° to 610°C. the rate is given by

$$\log_{10} k = 16.60 - \frac{74,850}{2.3RT} \text{ sec.}^{-1}$$

Their absolute rates are in rough agreement with those of Marek and McCluer, but, as may be seen from the equations, there is an enormous difference in the temperature coefficient.

Frey and Hepp (58) obtained rates in good agreement with those of Marek and his collaborators. They made very thorough analyses of the products by low-temperature fractional distillation. At 575°C. with a pressure of 739 mm. and a contact time of 74 sec., the products were as follows:

PRODUCTS	MOLE PER CENT	PRODUCTS	MOLE PER CENT
N ₂	0.50	C ₂ H ₆	0.49
H ₂	4.10	C ₃ H ₈	4.50
CO.....		C ₃ H ₆	81.75
CO ₂		Butadiene.....	
CH ₄	4.63	Higher hydrocarbons.....	
C ₂ H ₄	4.03		

The reaction has also been investigated by Dinzes and Frost (30, 31, 32) by the static method. They followed the reaction by the pressure change from 619° to 666°C. and 1 to 78 mm. It was found that the unimolecular constants drifted badly during an experiment, as discussed above for ethane, the rate in a given run being given by

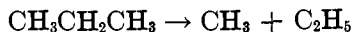
$$k = \frac{1}{t} \left(\ln \frac{1}{1-x} - 0.921x \right)$$

The addition of hydrogen, methane, or ethylene had no effect on the reaction velocity. The freshly formed products of the reaction were found to retard the decomposition of further propane, but if the products were stored for a time they lost their retarding effect. This obviously suggests that the effect is a surface phenomenon of some kind. They interpret all these complications as evidence for a chain process.

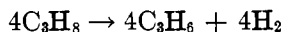
The decomposition of propane-propylene-hydrogen mixtures has been investigated by Travers (222c). The results are complex and are not in agreement with those of other workers.

2. Free radicals and the propane decomposition

Rice, Johnston, and Evering (164) showed that free radicals could be detected in the decomposition of propane, and Rice and Johnston (163) found the activation energy of the free-radical split to be 71.5 kg-cal. Rice (157, 159) suggests as a mechanism for the decomposition



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

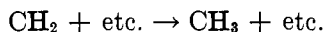
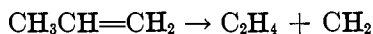


which is in satisfactory agreement with the experimentally found products of the reaction.

Belchetz and Rideal (9) 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



followed by



The activation energy of the primary process was found to be 94.2 kg-cal. There is thus a very great discrepancy between their work and that of Rice and his collaborators. Belchetz and Rideal suggest that the methyl radicals found by the latter are secondary products of the methylene radical. On the whole the evidence seems to favor the Rice mechanism for the free-radical split, although the question cannot be considered to be settled. Possibly the carbon filament is the disturbing factor in the experiments of Belchetz and Rideal, as they themselves point out.

The free-radical chain mechanism for the propane decomposition has been tested by Patat (136) by using the ortho-para hydrogen conversion as a test for hydrogen atoms, as described above for ethane. The result is

similar, viz., far too few hydrogen atoms are found as compared with the predictions of the Rice-Herzfeld mechanism. Patat concludes that the maximum possible fraction of the propane molecules which can decompose by a free-radical mechanism as opposed to a direct split into molecules is $10^{-3.2}$ if we assume that the radicals recombine (and thus end the chains) in the gas phase, and is $10^{-1.6}$ if we assume radical recombination on the walls of the reaction vessel. It must therefore be concluded that at low temperatures the Rice mechanism is not in accord with the facts, in spite of its success in predicting the products of the reaction.

There is, on the other hand, ample evidence that radicals can produce a sensitized decomposition of propane. Echols and Pease (38) showed that propane could be decomposed by radicals from the ethylene oxide decomposition at 425°C . They estimated the chain length of the sensitized decomposition by comparing the amount of olefin formed with the carbon monoxide resulting from the ethylene oxide decomposition. The result was $\text{C}_n\text{H}_{2n}/\text{CO} = 0.55$. Of course, this is an average chain length, and it is possible that there are comparatively few long chains rather than a great many short ones.

Sickman and O. K. Rice (185) also found that methyl radicals caused some decomposition of propane, the radicals in this case being produced by decomposing azomethane.

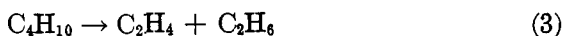
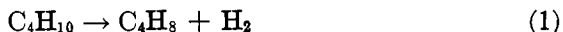
3. Atomic and photochemical reactions

Comparatively little work has been done on atomic or photochemical reactions of propane. By mercury photosensitization Taylor and Hill (213, 214) found that propane reacts faster with hydrogen atoms than does ethane, but more slowly than butane. Recently, in the course of another investigation, Trenner, Morikawa, and Taylor (226) made two runs with propane and deuterium atoms produced by the Wood-Bonhoeffer method. They found that the products of the reaction were mainly methane, together with a small amount of ethane. The amount of decomposition was quite small, being 2.4 per cent at room temperature and about 10 per cent at 109°C . The methane and ethane were found to be highly deuterized, while the propane was not exchanged. Propane is thus much less reactive than ethane, and they find no evidence of a catalytic recombination of hydrogen atoms in the presence of propane, as had been reported previously by Bonhoeffer and Harteck (23). These findings are surprising in view of all previous work in this field, and particularly in view of the fact that Frankenburger and Zell (56) found large decomposition of pentane by hydrogen atoms, indicating increased reactivity with increasing molecular weight of the hydrocarbon. Further work is promised from Taylor's laboratory.

D. The butanes

1. The thermal decomposition

As with most of the hydrocarbons, the first data of any kinetic importance were obtained by Pease (140). This investigation was merely a preliminary one, but it served to show that the decompositions of the two butanes were homogeneous and probably of the first order. Pease and Durgan (147), using a flow method, made a more thorough investigation. They concluded that the main reactions which occurred were



The reactions were found to be not more than 1 per cent heterogeneous, and the rate was slightly increased on diluting the reactants with nitrogen. The unimolecular constants fell off rapidly during the course of an experiment. They suggested that this was perhaps due to a rehydrogenation of the products, since they found that the addition of hydrogen decreased the amount of dehydrogenation. The effect of pressure on the rate indicated that the reactions were predominantly of the first order. The activation energy was found to be roughly 65,000 cal. for both butanes.

Hurd and Spence (79) investigated the reactions by a flow method at 600°C. with the object of ascertaining the products only. They concluded that *n*-butane decomposed by reactions 2 and 3, and isobutane by reactions 1 and 2, and that secondary reactions also occurred to some extent. Cambron (26) concluded that another reaction also occurred in the case of *n*-butane,



and that this was, in fact, the predominant reaction at high temperatures. Frey and Hepp (58) investigated the reactions by a flow method at 575°C. They made very thorough analyses of the products by low-temperature distillation, the results of which are given in table 1D.

The reactions were also investigated by Marek and Neuhaus (119, 120), who used various percentage conversions and extrapolated to zero to get the primary process. Their analytical results are given in table 2. In the case of *n*-butane the ratio

$$\frac{\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4}{\text{CH}_4 + \text{C}_3\text{H}_6}$$

was in excellent agreement with the predictions of the Rice theory, being 0.71 and 0.79 at 600°C. and 650°C., respectively, as compared with predicted values of 0.75 and 0.79. For isobutane the ratio

$$\frac{\text{CH}_4 + \text{C}_3\text{H}_6}{\text{C}_4\text{H}_8 + \text{H}_2}$$

TABLE 1D
The decomposition of the butanes at 575°C. (Frey and Hepp)

	ISOBUTANE		n-BUTANE	
	747	77	752	745
Pressure, mm.	747	77	752	745
Time, sec.	39.6		25.2	24.3
Per cent decomposition.	17.4	6.7	11.3	10.5
<i>k</i> , sec. ⁻¹	0.0048		0.0048	0.0046
N ₂ , mole per cent.	0.35	0.95	0.0	0.2
H ₂	6.98	3.65	0.84	0.87
CO.	0.13	0.09	0.0	0.0
CO ₂	0.43		0.0	0.0
CH ₄	6.26	2.55	6.38	5.58
C ₂ H ₄	0.33	0.0	3.14	2.84
C ₂ H ₆	0.35	0.13	2.25	2.30
C ₃ H ₆	4.64	1.94	5.85	5.41
C ₃ H ₈	1.47	0.24	0.29	0.39
Butadiene.			0.14	
(CH ₃) ₂ C=CH ₂	8.61	3.85		
C ₄ H ₁₀	70.45	86.60	79.95	82.41

TABLE 2
The initial products of the butane decompositions (Marek and Neuhaus)

PRODUCT, IN MOLES PER 100 MOLES REACTING	n-BUTANE		ISOBUTANE	
	At 600°C.	At 650°C.	At 600°C.	At 650°C.
CH ₄	48.5	48.0	35.0	36.0
C ₃ H ₆	48.5	48.0	34.0	36.0
C ₂ H ₆	34.5	36.7	2.5	1.5
C ₂ H ₄	34.5	38.7		
H ₂	16.0	12.3	63.0	63.0
C ₄ H ₈	16.0	12.3	63.0	63.0
C ₃ H ₈	0.0	1.0(?)		

was not in such good agreement. The values found were 0.55 and 0.57, as compared with predicted values of 0.91 and 1.04.

Paul and Marek (139) repeated the investigation from the point of view of the kinetics of the processes. In the temperature range 550° to 610°C. the rates are expressed as follows:

$$\text{For } n\text{-butane: } \log_{10} k = 17.05 - \frac{73,900}{2.3RT} \text{ sec.}^{-1}$$

$$\text{For isobutane: } \log_{10} k = 14.89 - \frac{66,040}{2.3RT} \text{ sec.}^{-1}$$

The large difference between the two isomers is noteworthy, if real, but is probably fictitious.

A thorough investigation of the decomposition of *n*-butane has recently been made by Steacie and Puddington (198a). They used the static

TABLE 3
The decomposition of n-butane (Witham)

TEMPERATURE	CONTACT TIME	<i>k</i>
°C.	seconds	sec. ⁻¹
600	7.3	0.0145
600	21.8	0.0106
600	58.1	0.0074
600	114.0	0.0044
600	161.2	0.0033
600	210.5	0.0021
650	11.0	0.0598
650	27.0	0.0338
650	37.4	0.0263
650	76.5	0.0098
700	3.0	0.2820
700	12.0	0.0725
700	50.3	0.0097

method and followed the reaction both by pressure change and by analysis at various stages. For the high-pressure rates they obtain

$$\log_{10} k = 12.54 - \frac{58,700}{2.3RT} \text{ sec.}^{-1}$$

There is thus good agreement between their value of the activation energy and that of Frey and Hepp. There is, however, a tremendous discrepancy between these results and those of Paul and Marek. Part of this discrepancy at least is due to Paul and Marek's not having extrapolated their rates to infinite pressure. The products of reaction in Steacie and Puddington's work are also in much better agreement with those of Frey and Hepp than with those of Paul and Marek. The products varied very little with temperature or pressure, mean values of the "initial products"

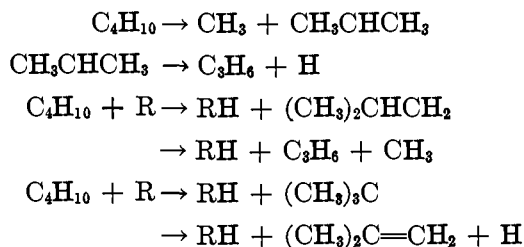
(i.e., extrapolated to zero conversion) being as follows: CH_4 , 35.5 per cent; C_3H_6 , 35.5 per cent; C_2H_4 , 15.0 per cent; C_2H_6 , 14.0 per cent; H_2 < 1.0 per cent.

Witham (235) has also measured the rate of decomposition of *n*-butane, alone and mixed with steam. His rates are, in general, lower than those of Marek and his collaborators. His velocity constants for experiments with butane alone are given in table 3. The constants vary so much with contact time that it is impossible to obtain reliable initial rates from his data, or to estimate the magnitude of the activation energy.

2. Free radicals and the butane decompositions

It was shown that free radicals could be detected in the high-temperature decomposition of the butanes by Rice, Johnston, and Evering (164), and the activation energy of the free-radical split was found to be 65.4 kg-cal. for *n*-butane by Rice and Johnston (163). The Rice mechanisms for the reactions are (166) as follows:

For isobutane:

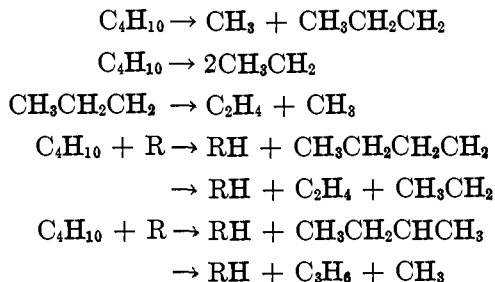


where $\text{R} = \text{CH}_3$ or H . The usual assumptions as to the relative rates of reactions involving a loss of primary or secondary hydrogen atoms lead to

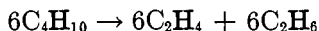


As mentioned above, the agreement with experiment in this case is not very satisfactory.

For n-butane:

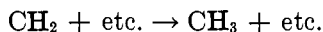
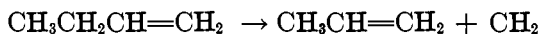


where $R = \text{CH}_3$ or CH_3CH_2 . This leads to the overall equations



in excellent agreement with experiment insofar as the relative amounts of ethylene, propylene, ethane, and methane are concerned. However, the scheme predicts no hydrogen and butene as products, whereas actually Marek and Neuhaus and Frey and Hepp found that from 8 to 16 per cent of the total reaction involved the formation of these substances.

As in the case of ethane and propane, Belchetz and Rideal (9) find a much higher activation energy for the primary split than do Rice and his coworkers, viz., 93.2 kg-cal. They assume for the mechanism



Here again the evidence seems to favor the Rice scheme for the primary split at the high temperatures used.

To what extent the decomposition of the butanes is to be regarded as occurring through free radicals is at the moment an open question. In view of the previous discussion of the ethane decomposition, the free-radical mechanism may well be regarded with suspicion. On the other hand, there is much more evidence in the case of butane to show that chains *can* be set up by radicals. Thus Heckert and Mack (69) found that *n*-butane was "cracked" by decomposing ethylene oxide. Frey (57) showed that 1 per cent of dimethyl mercury at 525°C. could set up chains twenty molecules long in *n*-butane. Echols and Pease (38) found that chains were set up in *n*-butane and isobutane by radicals from the decomposition of ethylene oxide at 425°C. They estimated that the chains were up to twelve molecules long. Sickman and Rice (185) found likewise that *n*-butane was chain decomposed by radicals (presumably methyl) from decomposing azomethane. There thus appears to be no doubt of the possibility of a free-radical chain decomposition of the butanes.

Recently Echols and Pease (39) have reported that the addition of small amounts of nitric oxide inhibits the decomposition of *n*-butane. Thus at 500°C. in a potassium chloride-coated bulb, with an initial pressure of butane of 200 mm., they obtain the following results:

P_0 (NO)	INITIAL RATE OF DECOMPOSITION OF C_4H_{10}	PER CENT DECOMPOSITION IN 120 MINUTES AS INFERRED FROM	
		Pressure change	Analysis
<i>mm.</i>			
0	1.0	26.5	31
20	0.05	7.1	13

They therefore conclude that nitric oxide is functioning as a chain breaker (188a, 189, 190), and hence that the ordinary butane decomposition involves chains. Preliminary observations by Steacie and Folkins (194) are in agreement with these results.

3. Atomic and photochemical reactions

There has been little work on the reaction of hydrogen atoms with the butanes. Taylor and Hill (213, 214) found, using mercury photosensitization, that butane reacts faster with hydrogen atoms than propane, which in turn reacts faster than ethane. Recently Trenner, Morikawa, and Taylor (226) have made one run with *n*-butane and deuterium atoms produced by the discharge tube method. They find about 11 per cent decomposition at 110°C. to give methane, ethane, and propane. The methane and ethane are highly exchanged, while the recovered butane is not exchanged at all. This is an unexpected result, for the reasons mentioned in the discussion of the propane reaction.

Steacie and Phillips (198) in the course of another investigation made one run on the mercury-photosensitized decomposition of butane. They found that hydrogen and higher hydrocarbons were produced in large amounts. The quantum yield at room temperature was 0.55.

E. The higher paraffins

These reactions are too complicated to be of much value from a kinetic standpoint, and are considered to be, in general, beyond the scope of this review. There are, however, a few investigations which are of interest by comparison with the lower paraffins, and they will be briefly mentioned. No attempt will be made to discuss the products of the decompositions of the higher paraffins.

Pease and Morton (148) investigated the decomposition of *n*-heptane. The investigation was not very thorough, but it showed that the reaction is homogeneous and of the first order. The rate was unaffected upon changing the surface of the reaction vessel, but complicating secondary processes were undoubtedly present. Their results are expressed by the equation

$$\log_{10} k = 9.85 - \frac{46,500}{2.3RT} \text{ sec.}^{-1}$$

As pointed out later, however, there is no doubt that their value of the activation energy is greatly in error. The same authors also investigated the decompositions of a number of cyclic and aromatic hydrocarbons.

Frey and Hepp (58) investigated the decomposition of a number of higher hydrocarbons by a flow method, but their data are not in general

sufficient to enable a very reliable estimate of the activation energy. They concluded that compounds with tertiary carbon atoms decompose faster than others. They give the following velocity constants at 425°C. for some of the simpler compounds: *n*-butane, 1.9×10^{-6} sec.⁻¹; *n*-pentane, 2.4×10^{-6} sec.⁻¹; isopentane, 3.7×10^{-6} sec.⁻¹; *n*-hexane, 1.1×10^{-5} sec.⁻¹

Dinzes and his collaborators (33, 34) have investigated the kinetics of the decomposition of *n*-hexane and *n*-octane. They obtained results similar to those already discussed for ethane and propane. The velocity constants are given as follows:

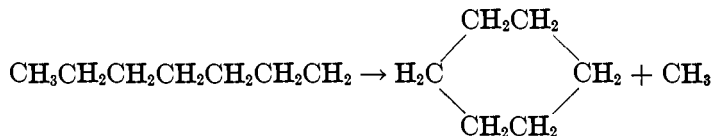
$$\text{For } n\text{-hexane: } \log_{10} k = 14.58 - \frac{64,500}{2.3RT} \text{ sec.}^{-1}$$

$$\text{For } n\text{-octane: } \log_{10} k = 14.70 - \frac{64,900}{2.3RT} \text{ sec.}^{-1}$$

They also investigated (33a) the decomposition of dodecane, 2,2,4-trimethylpentane, and 2,5-dimethylhexane, but all these reactions appear to be too complex to yield much information.

Bairstow and Hinshelwood (3) have investigated the homogeneous catalysis of the decomposition of *n*-hexane by iodine. The results are somewhat uncertain, and are not easy to interpret.

Rice and Polly (165) obtained cyclohexane from the decomposition of diheptyl mercury. They discuss the formation of alicyclic hydrocarbons from free radicals, and conclude that in this case the process is probably



Klemenc and Patat (97) investigated the mercury-photosensitized reactions of *n*-pentane. They found that decomposition and polymerization both occurred, hydrogen, methane, and other hydrocarbons being formed. Similar results were obtained by Frankenburger and Zell (56), who concluded that the primary process must involve the splitting of both C—H and C—C bonds.

A brief investigation of the mercury-photosensitized decomposition of *n*-hexane was made by Taylor and Bates (209). Much hydrogen and some methane were formed in the reaction.

F. Comparison of the paraffin decompositions

The kinetic data for the thermal decomposition of the paraffins are summarized in table 4. As is usually the case, the exponential and non-

exponential factors in the rate expression $k = Ae^{-E/RT}$ are interdependent, and their mutual fluctuations mask regularities in the data which might otherwise appear. In order to avoid this, and also to enable comparison

TABLE 4
Summarized kinetic data for the decomposition of the paraffins

SUBSTANCE	$\log_{10} A$	E cal. per mole	k_{425} sec. ⁻¹	k_{575} sec. ⁻¹	OBSERVER
CH ₄	12.00	79,385	1.3×10^{-13}	3.3×10^{-9}	Kassel (86)
C ₂ H ₆	15.12	73,200	1.5×10^{-8}	1.7×10^{-4}	Marek and McCluer (118)
	16.06	77,700	5.1×10^{-9}	1.0×10^{-4}	Recalculated (139)
	14.1	69,800	1.6×10^{-8}	1.2×10^{-4}	Sachsse (174)
				$1.0 \times 10^{-4*}$	Storch and Kassel (203a)
C ₃ H ₈		(65,000)			Pease and Durgan (147)
	13.44	62,100	9.6×10^{-7}	1.5×10^{-3}	Frey and Hepp (58)
	16.60	74,850	1.4×10^{-7}	2.6×10^{-3}	Marek and McCluer (118)
				1.9×10^{-3}	Paul and Marek (139)
<i>n</i> -C ₄ H ₁₀		(65,000)			Pease and Durgan (147)
	13.53	61,400	1.9×10^{-6}	4.8×10^{-3}	Frey and Hepp (58)
	17.05	73,900	7.8×10^{-7}	9.8×10^{-3}	Paul and Marek (139)
				2.6×10^{-3}	Stearie and Puddington (198a)
iso-C ₄ H ₁₀		(65,000)			Pease and Durgan (147)
	14.89	66,040	1.5×10^{-6}	4.8×10^{-3}	Frey and Hepp (58)
				7.1×10^{-3}	Paul and Marek (139)
<i>n</i> -C ₅ H ₁₂	13.4	61,200	2.4×10^{-6}	5.7×10^{-3}	Frey and Hepp (58)
iso-C ₅ H ₁₂	12.93	58,600	3.7×10^{-6}	6.5×10^{-3}	Frey and Hepp (58)
<i>n</i> -C ₆ H ₁₄	12.43	55,500	1.1×10^{-6}	1.3×10^{-2}	Frey and Hepp (58)
	14.58	64,500	2.3×10^{-6}	8.7×10^{-3}	Dinzes et al. (33, 34)
2,3-Di- methyl- butane				$1.9-2.4 \times 10^{-2}$	Frey and Hepp (58)
<i>n</i> -C ₇ H ₁₆	9.85	46,500	1.9×10^{-5}	7.1×10^{-3}	Pease and Morton (148)
<i>n</i> -C ₈ H ₁₈	14.70	64,900	2.3×10^{-6}	9.1×10^{-3}	Dinzes et al. (33, 34)

* Inferred by comparison with reference 139 at 565°C.

with the results of Frey and Hepp, the velocity constants have been calculated from the equations given by other observers for temperatures of 425°C. and 575°C., and activation energies have been calculated from

Frey and Hepp's results at these two temperatures. The first of these temperatures is below the usual experimental range for these reactions, while the latter is well within it. It will be seen from the table that there is fair agreement throughout at 575°C., but the calculated rates at 425°C. show large discrepancies. Thus in the case of propane, the results of Frey and Hepp and of Paul and Marek are in good agreement, and those of Marek and McCluer agree within a factor of 2 at 575°C. At 425°C., however, the results of the two latter disagree by a factor of 7. The reason, of course, is that the tremendous discrepancy of 13,000 cal. in the activation energy is balanced by a difference of a factor of over 1000 in A , so that the farther one gets from the experimental temperature range the greater is the discrepancy. It must be concluded, therefore, that in the neighborhood of 600°C. the absolute rates of the reactions are well established, but that with the exception of methane and ethane the activation energies are almost all untrustworthy.

Frey and Hepp's work constitutes the longest single set of observations and their individual results should be strictly comparable. Unfortunately, however, almost all their work was done at only two temperatures, and hence the activation energies calculated from their results are not very reliable. Their work, however, seems to indicate that the activation energies of the hydrocarbons from propane to octane are definitely lower than those for methane and ethane, but do not differ much among themselves. By comparison with other work, Paul and Marek's values of E for propane and n -butane appear to be too high, while Pease and Morton's value for n -heptane is definitely far too low. These conclusions receive support from the fact that an A factor of 10^{17} is unusually large and one of 10^9 is unusually small for a unimolecular decomposition, so that errors in the A factors in these cases apparently compensate errors in E .

In a recent review Frey (57) has plotted $\log(\text{rate})-1/T$ curves for the decomposition of various hydrocarbons, including mixtures such as "gas oil." The curves plotted correspond roughly to the paraffins from C_1 to C_{17} . It is noteworthy that the slopes of the curves (i.e., the values of E) from C_3 to C_{17} are virtually identical, although of course the points are widely scattered. Existing information, however, is much too inaccurate to permit any definite conclusions to be drawn.

As far as the absolute rates of decomposition are concerned, the very great stability of methane is noteworthy. Ethane is also considerably more stable than propane, but the higher members of the series do not differ greatly. Thus, taking Marek and McCluer's recalculated value for ethane as unity, the relative rates of decomposition at 575°C. are given in table 5.

The activation energies of the split into free radicals as determined by

Rice and his collaborators are summarized in table 6. The rapid drop in the activation energy with increasing molecular weight is noteworthy. It is evident that for the higher members of the series, say from butane on, the activation energies of the free radical and the ordinary overall thermal decomposition are not very different. It is therefore possible that, in spite of the evidence against the free-radical mechanism for ethane and

TABLE 5
Relative rates of decomposition of the paraffins at 575°C.

SUBSTANCE	k_{575} (AVERAGE OF THE VALUES OF DIFFERENT OBSERVERS)
	sec. ⁻¹
CH ₄	3.3×10^{-5}
C ₂ H ₆	1.0
C ₃ H ₈	17
<i>n</i> -C ₄ H ₁₀	73
iso-C ₄ H ₁₀	60
<i>n</i> -C ₅ H ₁₂	57
iso-C ₅ H ₁₂	65
<i>n</i> -C ₆ H ₁₄	109
<i>n</i> -C ₇ H ₁₆	71
<i>n</i> -C ₈ H ₁₈	91

TABLE 6
Activation energies of the split into free radicals (Rice et al.)

SUBSTANCE	E
	kg-cal.
CH ₄	100
C ₂ H ₆	79.5
C ₃ H ₈	71.5
<i>n</i> -C ₄ H ₁₀	65.4
<i>n</i> -C ₅ H ₁₂	64.0
<i>n</i> -C ₇ H ₁₆	63.2

propane, the higher members may actually decompose by some process involving radicals. It is unfortunate that the values of the activation energies of the ordinary thermal decompositions are so unreliable that one cannot compare them with the free-radical activation energies with any degree of certainty.

One reason for uncertainty, of course, is that we are really dealing with several different simultaneous reactions in the case of the higher hydrocarbons. Marek and Neuhaus (120) have summarized the separate velocity constants for these reactions (estimated from the results of Marek

and his coworkers) in the case of ethane, propane, and butane. The data are given in table 7.

It is illuminating to calculate the activation energies of the various splits from these data, and the results of such calculations are given in table 8. It has already been pointed out that there is considerable doubt

TABLE 7
Velocity constants of the separate reactions of the paraffins
(Summarized by Marek and Neuhaus)

SUBSTANCE	TEMPERATURE	k FOR SPLITTING OFF		
		H ₂	CH ₄	C ₂ H ₆
	°C.	sec. ⁻¹	sec. ⁻¹	sec. ⁻¹
C ₂ H ₆	575	0.00019		
	600	0.00066		
	625	0.00205		
	650	0.00650		
	675	0.01850		
C ₃ H ₈	550	0.00026	0.00019	
	575	0.00100	0.00076	
	600	0.00360	0.00274	
	625	0.01175	0.00895	
	650	0.03725	0.02830	
	675	0.11000	0.08360	
<i>n</i> -C ₄ H ₁₀	525	0.000096	0.00029	0.000207
	550	0.00040	0.00121	0.000863
	575	0.00157	0.00475	0.00338
	600	0.00552	0.01671	0.01190
	625	0.01540	0.05330	0.04050
	650	0.04610	0.18000	0.13900
iso-C ₄ H ₁₀	550	0.00132	0.000735	
	575	0.00454	0.00252	
	600	0.01368	0.00759	
	625	0.03750	0.02083	
	650	0.10400	0.05880	

whether the difference in the activation energies for *n*-butane and isobutane is real or not. (Although it should be noticed that the results of Frey and Hepp for *n*-pentane and isopentane show the same trend.) If we leave the isobutane results out of consideration, the striking thing about the remainder is that they are all probably identical within the experimental error. To split off hydrogen requires the breaking of two C—H bonds and the changing of one C—C to C=C. To split methane, on the other

hand, requires the breaking of one C—H and one C—C and the changing to one C—C to C=C. In view of the difference in the C—H and C—C bond strengths, a considerable difference in the activation energies might have been anticipated. There is no doubt that a more accurate determination of these activation energies for the whole series would be of the greatest interest.

In discussing the variation in rate as we ascend the series, Pease and Morton (148) point out that $E/\log A$ is approximately constant and equal to 4500 for all the paraffins. It is, however, very doubtful if this means more than the fact that E and A in any given case are affected by compensating errors, while the absolute rate of reaction varies very little.

There have been a number of papers which discuss the decomposition of the paraffins in a general way. Thus Burk (24) has attempted to

TABLE 8
Activation energies of the separate decomposition reactions of the paraffins calculated from the data of table 7

SUBSTANCE	E FOR SPLITTING OFF		
	H ₂	CH ₄	C ₂ H ₆
	<i>kg-cal.</i>	<i>kg-cal.</i>	<i>kg-cal.</i>
C ₂ H ₆	73.2		
C ₃ H ₈	74.2	75.4	
<i>n</i> -C ₄ H ₁₀	70.2	75.4	76.6
iso-C ₄ H ₁₀	65.7	65.7	

derive a general expression for the rate for all the members of the series. He starts from the Polanyi-Wigner expression for a first-order reaction and obtains the equation

$$k = (n - 2) \nu e^{-E/RT}$$

for the decomposition of a hydrocarbon containing n carbon atoms. ν is the frequency of the C—C valence vibrations, assumed constant for all the hydrocarbons, and E is also assumed to be constant. The relative rates calculated in this way are in rough agreement with experiment. It should be remembered, however, that any equation which makes the rate increase slowly as we ascend the series will give approximate agreement with experiment. It is probable that the main cause of the increased rate is really to be found in a slowly diminishing bond strength, and hence activation energy, as we ascend the series. (For a detailed discussion of this effect in another series of compounds see Steacie and Katz (195).)

Kassel (87) has pointed out in a note that the assumption of 1,4-de-

hydrogenation as the main mechanism of hydrocarbon decomposition, together with lesser amounts of 1,2- and 1,1-dehydrogenation, will account for all the products predicted by the free-radical theory.

There have been a number of recent reviews of the decomposition reactions of the paraffins, among which may be mentioned those of Schmidt (181), Frey (57), Egloff and Wilson (48), and especially the monograph by Egloff (40). In all of these attention is mainly focussed on the products of the reactions, rather than the kinetics of the processes. Thermodynamic and thermochemical data for the paraffins have been summarized by Rossini (172a), and by Thomas, Egloff, and Morrell (218a).

III. THE OLEFINS

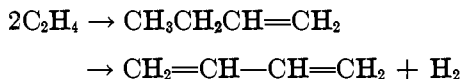
On account of the fact that the olefins both decompose and polymerize when heated, their reactions are much more complex than those of the paraffins, and from a kinetic point of view we are on much less certain ground. The literature on the qualitative aspects of the subject is enormous, and we shall touch only on those papers which have some bearing on the main kinetic details of the processes.

A. Ethylene

1. The polymerization and decomposition of ethylene

If ethylene is heated to a moderately low temperature the main reaction is polymerization. At higher temperatures it also undergoes decomposition. It is, in general, not possible to separate completely the two reactions, and hence the whole situation is complex. We shall consider the low-temperature reactions first, since they are the simpler. Insofar as the older work and theories of polymerization are concerned, reference may be made to the review of Egloff, Schaad, and Lowry (46), and to the comprehensive monograph of Egloff (40).

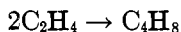
Hague and Wheeler (67, 68), on the basis of experiments complicated by a considerable amount of decomposition, concluded that butadiene was the fundamental intermediate substance in the polymerization of ethylene, the reactions being



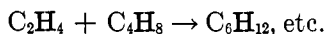
the butadiene then reacting further with ethylene to give benzene, etc. The same conclusion was reached by Wheeler and Wood (233).

Pease (142, 143, 145), in the first investigations of any value for our purpose, found that by working at pressures of about 10 atm. it was possible to suppress the decomposition almost completely, and to obtain

as products practically nothing but higher olefins. At lower pressures the reaction was complex, but at high pressures it was definitely a second-order association reaction, with an activation energy of 35,000 cal. The rate of reaction was low for a process with such an activation energy, and it was necessary to assume a steric factor of about 1/2000. This is, of course, rather to be expected on account of dreierstoss restrictions. Pease suggested for the mechanism



followed by

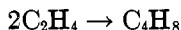


It was found by Storch (201) that the reaction is greatly accelerated by traces of oxygen. The products were analyzed by low-temperature fractional distillation, a typical analysis from a run at 377°C. being given in table 9. Storch obtained an activation energy of 42,000 cal., a value somewhat higher than that of Pease. He suggests that this is due to the

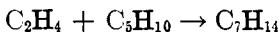
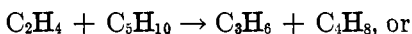
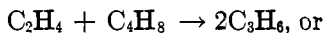
TABLE 9
Products of the ethylene polymerization at 377°C. (Storch)

SUBSTANCE	VOLUME PER CENT
Propylene.....	13.8
Butylene.....	31.7
Cyclobutane (perhaps a mixture).....	12.6
Pentenes.....	4.1
"Cyclopentane".....	8.1
Hexenes.....	12.6
Higher olefins.....	10.1
Unaccounted for (perhaps adsorbed by stopcock grease, etc.).....	7.0

presence of traces of oxygen in the ethylene used by Pease. For the mechanism he accepts Pease's suggestion that the primary step is



He then assumes secondary reactions of the following types:



Some change in the mechanism suggested by Pease is, of course, necessary, since it leads only to olefins with an even number of carbon atoms, and Storch found considerable amounts of C_3 to C_6 hydrocarbons. As Storch points out, there are not, as yet, nearly enough data to enable us to sort out all these reactions.

In a later paper (202) Storch reports an attempt to purify ethylene sufficiently to enable really reproducible results to be obtained. This was not successful, but he found that the addition of small amounts of ethyl mercaptan slowed down the average rate and made the results strictly reproducible. Further, it was found that these rates were in good agreement with the slowest rates obtained with "pure" ethylene. This suggests the presence of a catalyst of some sort under normal conditions, and he considers that the reaction is probably not a simple bimolecular change. While it is not yet certain what the initial step is, butylene probably precedes propylene as a product. The activation energy of the overall reaction is found to be 43,500 cal., in good agreement with his former estimate.

At the moment it seems difficult to assess the situation, since the results of Pease were so consistent that it does not seem to be justifiable to assume that they were largely influenced by fortuitous traces of impurities without further proof.

The reaction has also been investigated by Krauze, Nemtsov, and Soskina (98, 100), who find it to be homogeneous and of the second order. Their results can be expressed by the equation

$$\log_{10} k = 10.85 - \frac{37,700}{2.3RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

Their value of the activation energy is thus rather closer to the value of Pease than to that of Storch. They find that the second-order velocity constants fall off considerably during an experiment. They calculate a collision efficiency of 1/400, which is somewhat higher than Pease's value.

A few experiments on the polymerization of ethylene have also been made by Travers and Hockin (224).

The reaction at higher temperatures is much more complex, and consists of both decomposition and polymerization. It was shown by Frey and Smith (59) to be homogeneous in silica vessels. A typical analysis of the products of the reaction at 575°C. and 1 atm. pressure, after 4 min. reaction time, is given in table 10. These results correspond to a velocity constant of about 0.0011 sec.⁻¹ if the reaction is assumed to be a first-order decomposition. Frey and Smith found that the addition of hydrogen to the reactant decreased the amount of unsaturated products formed, which

suggests that secondary hydrogenation reactions play a part (the hydrogen being normally produced from the decomposition).

Wheeler and Wood (233) obtained the products shown in table 11 at various temperatures and with contact times of from 10 to 20 sec. Their analyses are not in very good agreement with those of Frey and Smith or of Schneider and Frolich (182).

TABLE 10
Products of the ethylene decomposition (and polymerization) at 575°C.
(Frey and Smith)

SUBSTANCE	PER CENT	SUBSTANCE	PER CENT
N ₂	0.8	C ₃ H ₈	0.0
H ₂	0.8	C ₄ H ₈	1.2
CH ₄	2.6	C ₅ to C ₈	2.2
C ₂ H ₄	84.4	Higher hydrocarbons.....	0.3
C ₂ H ₆	3.2		

TABLE 11
Products of the ethylene decomposition at various temperatures (Wheeler and Wood)

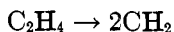
TEMPER- ATURE	VOLUME PER CENT						
	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₄ H ₈	C ₄ H ₆
°C.							
650	0.7	0.5	2.0	89.9	0.0	3.8	0.3
700	3.2	4.9	4.9	66.2	2.2	2.8	0.4
750	7.2	16.7	8.6	47.6	1.7	1.5	0.2
800	17.3	33.7	6.9	29.0	1.1	0.0	0.15
850	35.8	49.7	3.3	12.2	0.5		
900	51.0	55.2	2.2	4.6	0.0		

In a recent paper Burk, Baldwin, and Whitacre (25) report an investigation at 625°C. The products of the reaction were similar to those of Frey and Smith. The reaction was homogeneous, with an order slightly greater than one. They review the proposed mechanisms in some detail, and suggest that the results can best be interpreted by assuming that polymerization and decomposition both occur, i.e.



reaction b being followed by further reactions of acetylene to give butadiene, etc.

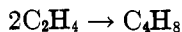
Egloff, Schaad, and Lowry (46) suggest that the primary reaction is



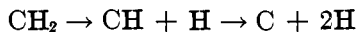
The higher hydrocarbons then result from reactions of the type



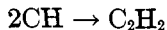
and also perhaps from the direct reaction



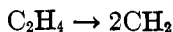
In addition they assume



acetylene being formed by



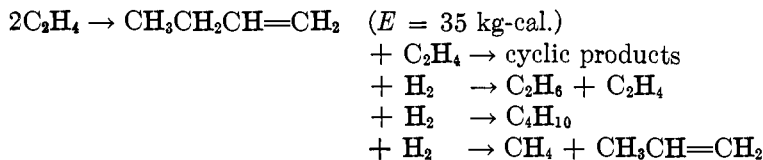
Ethane is assumed to be formed by direct hydrogenation of ethylene. It should be pointed out, however, that Rice and his collaborators have been consistently unsuccessful in attempts to prepare radicals from decomposing ethylene, and Rice assigns an activation energy of 150 kg-cal. to the reaction

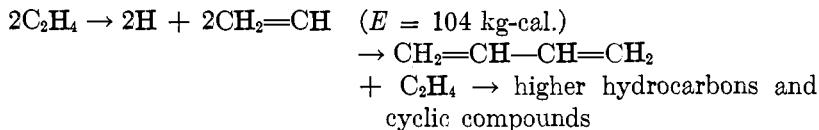
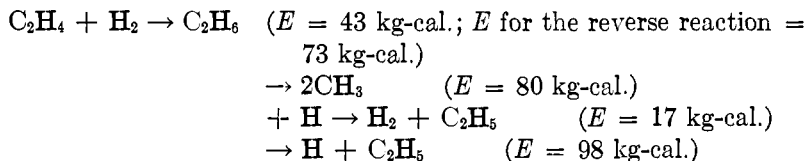
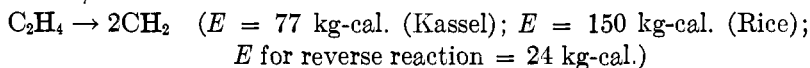
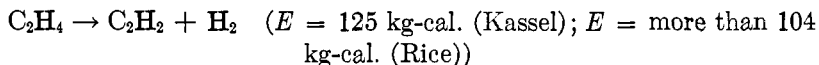


which would rule it out as the primary step. However, as previously pointed out, the Rice technique is perhaps not very successful in detecting methylene radicals, and this estimate of the activation energy may be altogether too high. Kassel assigns a value of 77 kg-cal. to the reaction, which would make it a feasible primary process.

Egloff and Wilson (48) have recently reviewed the thermal reactions of the hydrocarbons. They base practically everything on the reactions of ethylene, which they assume to be the key substance in hydrocarbon chemistry. They suggest that the following five primary reactions of ethylene are the fundamental ones, all other products being assumed to be due to secondary processes, of which there are a very large number.

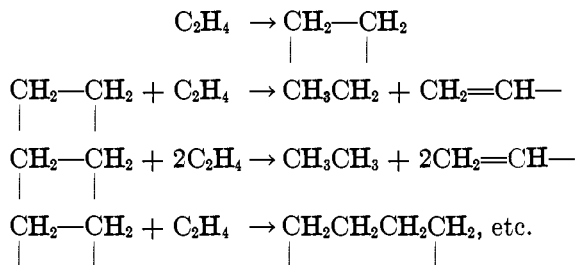
Reaction 1:



Reaction 2:*Reaction 3:**Reaction 4:**Reaction 5:*

In view of the previous discussion of some of these reactions in this review, it will be apparent that a number of these activation energies are open to question. Furthermore, the whole scheme is very speculative, and it remains to be seen whether or not free radicals really play the important rôle assumed by Egloff and Wilson. Their scheme is interesting, however, whether true or not, in that it emphasizes the tremendous variety of possible secondary reactions.

Hurd (78), in a review of the pyrolysis of unsaturated hydrocarbons, favors the "bond opening" type of mechanism, viz.,



It seems to the writer to be open to question whether mechanisms of this sort have any real physical significance, although they have been frequently suggested for various reactions (14, 15).

It will be apparent from the foregoing discussion that our knowledge of the thermal reactions of ethylene in the temperature range from 500° to 900°C. is very fragmentary, and little is known with certainty.

At still higher temperatures the reaction again becomes simpler, according to an investigation of Fischer and Pichler (54). At temperatures in the neighborhood of 1400°C. and at low pressures the reaction is almost completely a straight dehydrogenation to acetylene. The data of Fischer and Pichler have been recalculated by Storch (200).

2. The thermal hydrogenation of ethylene

The equilibrium



was investigated by Pease and Durgan (146). The formation of methane in a side reaction was a serious complication and affected the accuracy of the results. They found that the equilibrium constant (pressures in atmospheres) given by

$$K_{\text{atm.}} = \frac{[\text{C}_2\text{H}_4][\text{H}_2]}{[\text{C}_2\text{H}_6]} \cdot \frac{P}{100}$$

had the values

<i>T</i> in °C.	<i>K</i> _{atm.}
600	0.0310
650	0.082
700	0.20

or,

$$\Delta F = -RT \ln K = 31,244 - 28.88 T$$

Frey and Huppke (58b) have also investigated the equilibrium, its attainment being catalyzed by passing the gases over chromium oxide. They obtained the following values of the equilibrium constant

<i>T</i> in °C.	<i>K</i> _{atm.}
400	0.00015
450	0.00076
500	0.0032

Their results can be expressed by

$$\Delta F = 27,798 - 9.21T \log_{10} T + 2.17T$$

Their values have been recalculated by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan (95a), who give more weight to experiments at short

contact times and thus cut down the effects of secondary changes. They thus obtain

$K_{\text{atm.}}$	T in °C. ³
8.2×10^{-5}	400
5.6×10^{-4}	450
2.4×10^{-3}	500

The equilibrium has also been investigated by Vvedenskii, Vinnikova, and Frost (231a).

The equilibrium has recently been reinvestigated by Storch and Kassel (203a). They correct for the production of methane and propylene as described in section IIB, and thus obtain the values given in table 11A. These values are lower than those of Pease and Durgan, and of Frey and

TABLE 11A
The ethane-ethylene equilibrium at 565°C. (Storch and Kassel)

TIME	INITIAL PRESSURES		FINAL PRESSURES				K	
	C ₂ H ₆	C ₂ H ₄	H ₂	C ₂ H _{2n}	C ₂ H ₄	C ₂ H ₆	Uncor- rected for C ₂ H ₆	Corrected for C ₂ H ₆
<i>min.</i>	<i>mm.</i>	<i>mm.</i>	<i>mm.</i>	<i>mm.</i>	<i>mm.</i>	<i>mm.</i>	<i>atm.⁻¹</i>	<i>atm.⁻¹</i>
60	1299.9	149.9	65.0	178.2	132.4	1215.8	0.0125	0.0093
60	616.8	75.4	41.6	107.7	95.1	571.9	0.0103	0.0091
60	716.3	0.0	64.7	64.9	58.7	642.8	0.0086	0.0078
60	1432.5	0.0	108.7	108.4	85.3	1306.0	0.0119	0.0093
120	1472.3	0.0	121.2	115.1	58.4	1295.5	0.0142	0.0072
120	377.5	0.0	53.6	49.8	42.7	318.1	0.0110	0.0095
Average.....								0.0087

Huppke as recalculated by Kistiakowsky et al. However, Pease and Durgan determined ethylene by absorption with bromine water, and thus their "ethylene" was really C₂H₄ + C₃H₆. Storch and Kassel attempt to correct for this and get

$$K = 0.020 \quad \text{at } 600^{\circ}\text{C.}$$

$$K = 0.052 \quad \text{at } 650^{\circ}\text{C.}$$

These values are in good agreement with their own work. They are also in much better agreement with the calculations of Smith and Vaughan (187a) based on spectroscopic and thermochemical data.

Pease (142, 144) investigated the rate of the hydrogenation reaction.

³ In the original paper, owing to a typographical error, these temperatures are given as °K. instead of °C.

He found that, in the main, the hydrogenation went smoothly to ethane, although a small amount of polymerization of ethylene occurred as well. The reaction was almost entirely homogeneous and of the second order. A steric factor of 0.1 was found, which is surprisingly high for an association reaction between comparatively simple molecules. The rate of the reaction was given by

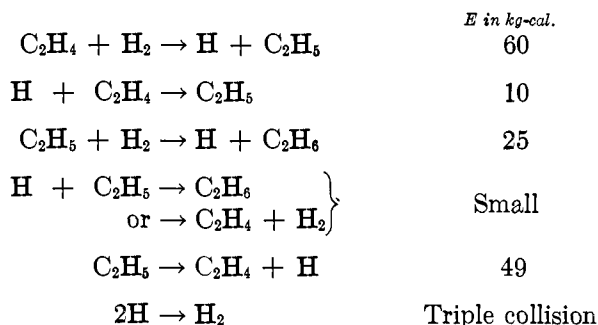
$$\log_{10} k = 5.576 - \frac{43,150}{2.3RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

As mentioned before, combination of this result with Marek and McCluer's data for the reverse reaction gives calculated equilibrium constants in excellent agreement with those found by Pease and Durgan. A few experiments on the hydrogenation of ethylene were also made by Frey and Smith (59).

Pease and Wheeler (149, 232) compared the rates of hydrogenation of ethylene with hydrogen and with deuterium. For the homogeneous reaction at 500°C. they found that the reaction with hydrogen was the faster by a factor of 2.5. This is about what one would expect on the basis of the difference in zero-point energies and collision frequencies.

3. Free radicals and the reactions of ethylene

Rice and Herzfeld (162) have suggested a free-radical mechanism for the ethylene hydrogenation, viz.,

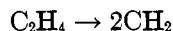


This leads to good agreement with experiment, but in view of the criticisms which have already been raised against the Rice-Herzfeld mechanism for the reverse reaction (the ethane decomposition) it seems very unlikely that the above scheme holds. In any case, the activation energies assigned to the individual steps are in need of revision.

There is abundant evidence, on the other hand, that ethylene is affected by the addition of free radicals.

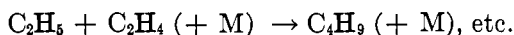
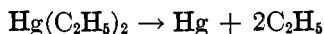
In the course of an investigation of the oxidation of ethylene, Lenher

(108) found that the substance polymerizes much faster in the presence of oxygen than it does alone. Thus from 1 to 5 per cent polymerized in 3 sec. at temperatures from 480° to 600°C. in the presence of 0.5 to 0.7 per cent oxygen. The product was propylene, together with a small amount of butylene. Lenher concluded that the only reasonable assumption was that in the presence of oxygen we have

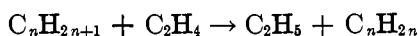
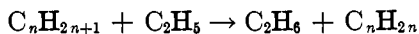


the dissociation into methylene radicals perhaps occurring through the intermediate formation and decomposition of a peroxide.

Taylor and Jones (207, 215) made the first experiments on a reaction sensitized by free radicals, following a suggestion made by Taylor (206) in 1925. They decomposed mercury and lead alkyls in a hydrogen-ethylene mixture, and found that there was some hydrogenation, but that the main result was polymerization of the ethylene. The reaction was shown to be independent of surface effects. They suggested that the mechanism was



followed by the disappearance of the radicals by reactions of the type



They pointed out the striking parallelism between these results and those of Taylor and Hill on the mercury-photosensitized reaction (q. v.).

Rice and Sickman (170, 185) found that ethylene was polymerized in the presence of decomposing azomethane at 300°C. They used a wide range of partial pressures of both substances and found that the initial rate of polymerization was proportional to

$$[\text{azomethane}]^{\frac{1}{2}} [\text{C}_2\text{H}_4]^{\frac{1}{2}}$$

Pressure-time curves of the ordinary shape were obtained, instead of the autocatalytic type usually found in thermal polymerizations. The average values of the velocity constants were

$$k_{310^\circ} = 6.5 \times 10^{-6} \text{ mm.}^{-1} \text{ sec.}^{-1}$$

$$k_{290^\circ} = 3.0 \times 10^{-6} \text{ mm.}^{-1} \text{ sec.}^{-1}$$

4. The photodecomposition of ethylene

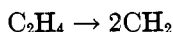
Early investigations did not distinguish very clearly between the direct photochemical reactions of ethylene and the mercury-photosensitized reaction.

The first definite information on the direct photoreaction was obtained by Mooney and Ludlam (127). They found that ethylene did not absorb light of wave length greater than 2130 A.U. to any appreciable extent, and concluded that nothing was to be expected from investigations with a mercury arc source (provided that mercury vapor is kept out of the reaction vessel, otherwise, of course, the mercury-photosensitized reaction will come into play). Mooney and Ludlam used as source an aluminum spark with a high intensity at 1860 A.U. and found that acetylene was formed. They suggested that the mechanism was perhaps

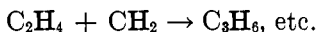


Qualitative observations by Lind and Livingston (112) are in agreement with these results. Taylor and Emeleus (211, 212), however, showed that a mercury arc did cause appreciable polymerization of ethylene, and they concluded that this was to be ascribed to absorption by ethylene of wave lengths near the limit of transmission of silica.

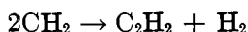
Recently McDonald and Norrish (116) have reinvestigated the reaction, using a hydrogen lamp source and a fluorite apparatus. They were thus able to work with light of shorter wave lengths. Hydrogen, a polymer, and a condensable gas were formed under these conditions. Spectroscopic observations suggest (71, 151, 152) that the primary process is



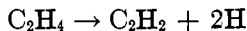
If this is so, the polymerization is easily explained as due to



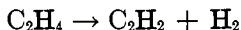
The formation of hydrogen is hard to explain, however, since on this basis it could only arise by



and this reaction would be very unlikely on account of the small concentration of methylene radicals. As an alternative explanation they suggest



together with

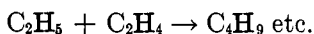
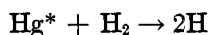
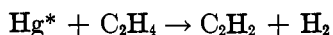


followed by secondary reactions of hydrogen atoms to yield ethane and butane. Further work is promised from Norrish's laboratory.

5. The mercury-photosensitized reactions of ethylene

The first investigation of this kind was that of Berthelot and Gaudechon (12), who found that an oily polymer was formed, with no gaseous products. Landau (103) similarly found that on long exposure to a mercury arc ethylene (in the presence of mercury vapor) could be completely polymerized to condensable products.

The first quantitative measurements were made by Taylor and Bates (4, 209), using a cooled mercury arc. They found that polymerization occurred, together with the formation of acetylene, hydrogen, and some methane. They point out that a great many different reactions are possible in such a system. Thus, for example,



It also follows that it is impossible to treat the polymerization reaction and the reaction of ethylene with hydrogen atoms entirely separately.

The polymerization was also investigated in a similar way by Olson and Meyers (133) and by Taylor and Hill (214). A brief investigation was also made by Melville (125), who found acetylene, hydrogen, and condensable products, in agreement with other investigators. He adopts the primary step suggested by Taylor and Bates, and ascribes all further changes to secondary reactions of acetylene. There is no doubt that the processes occurring are far too complicated to be disentangled at present.

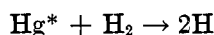
Taylor and Bates (5, 208) have also shown that ethylene can be polymerized by cadmium photosensitization, using the resonance line at 3262 A.U. as a source. This corresponds to a much smaller quantum than in the mercury-photosensitized reaction, viz., 87,000 cal. Jungers and Taylor (81) attempted to investigate the sodium-photosensitized reaction, using a commercial sodium lamp as a source (the sodium D line corresponds to 48 kg-cal.). They found that ethylene quenched the resonance, but that no polymerization occurred.

6. The reaction of ethylene with hydrogen atoms

This reaction has been investigated by the Wood-Bonhoeffer method by von Wartenberg and Schultze (231). They found that chemilumi-

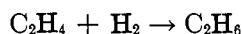
nescence occurred, the emitted light corresponding to the C—C and C—H bands, and that the reaction was rapid and yielded principally ethane, with a little acetylene. Geib and Harteck (62) found that ethane was also formed when ethylene and hydrogen atoms were brought together at liquid-air temperature.

By mercury photosensitization the reaction was first investigated in a qualitative way by Taylor and Marshall (216), using a cooled mercury arc as a source. They found that there was a steady drop in pressure, presumably owing to the formation of ethane. With a hot arc (in which the resonance line is reversed) there was no reaction, showing that the primary process was

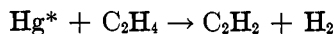
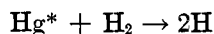


The rate was very high for the intensity of the light used, suggesting a chain reaction.

Olson and Meyers (133) also investigated the reaction by the same method. They found that the drop in pressure was not quite that corresponding to the reaction



perhaps owing to the formation of some methane. In a later paper (133a) they showed by mass-spectrographic analysis that methane, ethane, propane, and butane were formed. When hydrogen and ethylene were present in about equal quantities, considerable higher hydrocarbons were formed and very little methane. Thus with initial pressures of 39 cm. of hydrogen and 25 cm. of ethylene the relative amounts of the products were as follows: $\text{CH}_4 = 0.018$; $\text{C}_2\text{H}_6 = 1$; $\text{C}_3\text{H}_8 = 0.64$; $\text{C}_4\text{H}_{10} = 0.42$. If, however, hydrogen was in large excess the situation was reversed and very little propane and butane were formed. For example with 40 cm. of hydrogen and 2 cm. of ethylene they found the following relative amounts: $\text{CH}_4 = 0.22$; $\text{C}_2\text{H}_6 = 1$; $\text{C}_3\text{H}_8 = 0.04$; $\text{C}_4\text{H}_{10} = 0.0008$. They conclude that three primary processes occur,

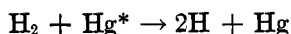
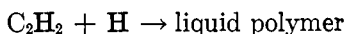
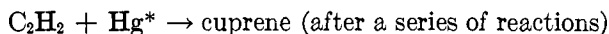
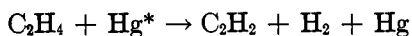


Bates and Taylor (4) also found that some polymerization accompanied the formation of ethane. The occurrence of the reaction was also noted by Hirst (74).

By far the most thorough investigation is that of Taylor and Hill (213, 214). They found that when hydrogen was in large excess the products

were practically exclusively ethane, but with relatively more ethylene higher hydrocarbons were formed (average C_4) including a liquid of molecular weight about 230. Some methane was also formed. There is thus fairly good general agreement between the work of Taylor and Hill and that of Olson and Meyers. Since the products of higher molecular weight react faster than those of lower, the process becomes extremely complicated once higher products have started to form, and the liquid product presumably results from secondary reactions of saturated hydrocarbons. (Compare with the photosensitized reactions of ethane, for example.) With a very large excess of ethylene some acetylene is formed.

Taylor and Hill conclude that the apparently simple results of von Wartenberg and Schultze were due to the low pressure and large excess of hydrogen used in their experiments. They discuss the possible reaction steps in some detail, and conclude that the main reactions are



together with various reactions of radicals, etc., leading to the formation of products of higher molecular weight.

The reaction has also been investigated by Klemenc and Patat (96). They agree with Taylor and Hill in general, but consider that the hydrogenation process is never as smooth as found by them, and is always accompanied by some polymerization. The polymerization process is complicated, but they suggest that it occurs mainly by the preliminary formation of acetylene and hydrogen, followed by polymerization of the acetylene as suggested by Taylor and Hill.

Melville (124) compared the reactions of ethylene with hydrogen and with deuterium atoms. He found no detectable difference in rate, and therefore concludes that the rate-controlling step must be hydrogen-atom or a deuterium-atom reaction, since otherwise the difference in zero-point energies would make itself felt.

Taylor and Emeleus (210) have shown that the ethylene polymerization can be photosensitized by ammonia, presumably owing to hydrogen atoms or to radicals from the ammonia decomposition. Similar results were obtained using methylamine and ethylamine (212).

In a recent paper Taylor and Jungers (215a) report an investigation of the acetone-photosensitized polymerization of ethylene over a wide range

of temperature. There is no doubt (132a) that the primary step is the photodissociation of acetone to yield free methyl radicals, which then induce polymerization of the ethylene. Taylor and Jungers find that the polymerization occurs readily at room temperature, and that the temperature coefficient of the reaction is very small. The maximum effect found was the polymerization of eleven ethylene molecules per methyl radical, assuming two methyl radicals from each decomposing acetone molecule. They conclude that the relatively high activation energy (35 to 42 kg-cal.) of the thermal polymerization process is the activation energy of the primary step, possibly involving the formation of a free radical. Once free radicals are produced, it appears that subsequent polymerization reactions proceed with a low energy of activation.

B. Propylene

Frey and Smith (59) investigated the thermal decomposition of propylene at one temperature only, but made very thorough analyses of the products of the reaction. At 575°C., an initial pressure of 1 atm., and a contact time of 4 min., they obtained the following results:

PRODUCT	PER CENT	PRODUCT	PER CENT
N ₂	0.4	C ₃ H ₆	68.9
H ₂	1.7	C ₃ H ₈	3.0
CH ₄	10.7	C ₄ H ₈	2.8
C ₂ H ₄	8.0	C ₅ to C ₈	2.6
C ₂ H ₆	1.9	Higher hydrocarbons	0.0

It will be seen that at these high temperatures the reaction is mainly decomposition rather than polymerization. Assuming the reaction to be of the first order, the above results give a velocity constant for the reaction of about 0.0012 sec.⁻¹ This is about 10 per cent faster than the decomposition of ethylene under the same conditions.

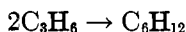
The reaction has recently been investigated by Moor, Strigaleva, and Frost (127b) by a flow method. They worked at atmospheric pressure, and at temperatures from 610° to 726°C. The products of the reaction were roughly as follows:

PRODUCTS	MOLES PER 100 MOLES OF PROPYLENE REACTING	
	At 610 to 644°C.	At 644 to 726°C.
C ₅ and higher hydrocarbons	60	50
Saturated hydrocarbons (chiefly methane)	20	30
C ₂ H ₄	40	50
H ₂	15	15

The reaction was neither of the first nor of the second order, the calculated first-order constants increasing rapidly with increasing percentage conversion. This is probably due to the fact that the primary step is of the first order, but that there are many complicating secondary processes.

A qualitative investigation of the reaction has also been made by Mitsengendler (126a).

The polymerization reaction at lower temperatures has been investigated by Krauze, Nemtsov, and Soskina (99, 101). The reaction is found to be mainly



and the rate can be expressed by the equation

$$\log_{10} k = 10.2 - \frac{37,400}{2.3RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

Frey and Smith (59) have also reported a few experiments on the "hydrogenation" of propylene at 575°C. and 1 atm. pressure. The results are given in table 12. It will be seen that the reaction is still mainly decomposition and polymerization, and that little real hydrogenation occurs at this temperature.

C. The higher olefins

Egloff and Parrish (43) point out that the activation energies of the polymerization reactions of the olefins are about 38 to 40 kg-cal. This is much less than the energy required to break bonds, and hence the polymerization reactions predominate at lower temperatures for all the olefins. For comparative purposes the "temperatures of initial decomposition" are of interest. The temperature of initial decomposition is arbitrarily defined at the temperature at which a noticeable amount of decomposition will just occur in six hours. Some typical values are given in table 13, and are compared with the values for the corresponding saturated hydrocarbons.

Most of our knowledge of the polymerization reactions of the higher olefins comes from the work of Krauze, Nemtsov, and Soskina, who have investigated the polymerization at high pressures of ethylene (98, 100), propylene (99, 101), the butylenes, and amylenes (99, 102) in the temperature range 300° to 400°C. The reactions are all of the second order, the products being mainly but not exclusively those corresponding to a straight association to give an olefin with twice the number of carbon atoms. The rate of polymerization falls off slightly with increasing molecular weight. The kinetic constants are summarized in table 14.

With the exception of the values for isobutylene, it will be seen that A

and E are almost the same for all members of the series. The difference in the case of isobutylene is of considerable interest, if real. However, the fact that both A and E alter in such a way as to compensate for one

TABLE 12

The "hydrogenation" of propylene at 575°C. and 1 atm. (Frey and Smith)

SUBSTANCE	TIME				
	0 min.	1 min.	2 min.	4 min.	6 min.
N ₂	0.7	0.5	0.6	0.7	1.0
H ₂	54.7	53.0	49.4	48.4	49.9
CH ₄	0.0	1.8	4.2	7.5	9.4
C ₂ H ₄	0.3	1.6	2.7	5.2	6.1
C ₂ H ₆		0.4	1.2	1.7	1.9
C ₃ H ₆	43.7	40.1	37.7	31.3	25.0
C ₃ H ₈	0.6	1.2	1.8	3.0	4.3
Higher hydrocarbons.....	0.0	1.4	2.4	2.4	2.4

TABLE 13

Temperatures of initial decomposition of hydrocarbons (Egloff and Parrish)

HYDROCARBON	TEMPERATURE	HYDROCARBON	TEMPERATURE
	°C.		°C.
Ethylene.....	380	Methane.....	540
Propylene.....	357	Ethane.....	450
2-Butene.....	350	Propane.....	425
1-Butene.....	325	<i>n</i> -Butane.....	400
1- or 2-Pentene.....	390 (?)	<i>n</i> -Pentane.....	391

TABLE 14

The polymerization of the olefins (Krauze et al.)

REACTION	E	$\log_{10} A$	COLLISION EFFICIENCY
	<i>cal.</i>		
2C ₂ H ₄ → C ₄ H ₈	37,700)*	10.8	4 × 10 ⁻³
2C ₃ H ₆ → C ₆ H ₁₂	37,400}	10.2	1 × 10 ⁻³
2C ₄ H ₈ → C ₈ H ₁₆	38,000	10.0	5 × 10 ⁻⁴
2 <i>iso</i> -C ₄ H ₈ → C ₈ H ₁₆	43,000†	12.3	1 × 10 ⁻¹
2C ₅ H ₁₀ → C ₁₀ H ₂₀	38,000	9.8	4 × 10 ⁻⁴

* In a later paper (102) the activation energies of these reactions are given as 38,400 and 38,000 cal., respectively.

† The equilibrium in this reaction has been investigated at high pressures by Dobronravov and Frost (34a) who found

$$\log_{10} P_{C_4H_8}^2 / P_{C_5H_{10}} = \frac{2959}{T} + 6.049$$

another makes the result somewhat open to suspicion. The difference between the values for isobutylene and the others can be shown in another way. Bawn (6) has calculated the collision efficiencies of all the above reactions (i.e., the ratio of the number of molecules reacting to the number possessing the energy of activation, as calculated from the kinetic theory). His results are given in the last column of table 14, and it seems very unlikely that there should be such a great difference between the two butylenes, although it is worthy of note that the rather uncertain results on the decomposition of *n*-butane and isobutane (q.v.) are also widely different. Of course, none of these reactions is entirely simple, and in every case some of the primary products are polymerized further. It may well be that some such secondary process is the cause of the discrepancy. In any case the results are of very definite interest, and the reactions of the two butylenes would be well worth reinvestigation.

The decomposition at higher temperatures of pentene-2 was investigated by Pease and Morton (148), but not very thoroughly. They found that the reaction was definitely homogeneous and unimolecular, the pressure increase accompanying it was almost exactly 100 per cent, and the pressure-time curve was very regular. The products of the reaction corresponded to



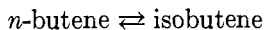
together with some formation of $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$. The rate was given by the equation

$$\log_{10} k = 13.33 - \frac{61,000}{2.3RT} \text{ sec.}^{-1}$$

The high-temperature decomposition of butene-2 has been investigated by Moor, Frost, and Shilyaeva (127a). The reaction has no simple order, presumably owing to complications due to secondary processes. A complicated set of products is obtained.

The homogeneous thermal isomerization of butene-2 was investigated by Kistiakowsky and Smith (95). The reaction is complex and the results are difficult to interpret, probably owing to chain processes.

The equilibrium in the reaction



has been investigated by Serebryakova and Frost (183a).

Frey and Huppke (58b) have investigated the equilibria in a number of olefin hydrogenation reactions. Their results are summarized in table

14A, and equilibrium constants for a few temperatures are given in table 14B. These results and others have recently been reviewed by Parks (134b). Thermodynamic data for the olefins have been summarized by Thomas, Egloff, and Morrell (218a), and thermochemical data by Rossini (172a) and Rossini and Knowlton (172b).

The only other kinetic investigations of importance are those of Vaughan (228, 229), who found that the polymerizations of isoprene and of buta-

TABLE 14A
Equilibria in a number of olefin hydrogenation reactions

REACTION	VALUES OF ΔF	VALUES OF $\Delta F_{400^\circ\text{C.}}$
		<i>calories</i>
$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	$\Delta F = 27,798 - 9.21T \log_{10} T + 2.17T$	11,730
$\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$	$\Delta F = 25,920 - 9.21T \log_{10} T - 0.21T$	8,250
$n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{C}_2\text{H}_5\text{CH}=\text{CH}_2 + \text{H}_2$	$\Delta F = 25,790 - 9.21T \log_{10} T - 0.21T$	8,120
$n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{cis-CH}_3\text{CH}=\text{CH-CH}_3 + \text{H}_2$	$\Delta F = 25,580 - 9.21T \log_{10} T - 0.21T$	7,910
$n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{trans-CH}_3\text{CH}=\text{CH-CH}_3 + \text{H}_2$	$\Delta F = 25,090 - 9.21T \log_{10} T - 0.21T$	7,420
$\text{iso-C}_4\text{H}_{10} \rightleftharpoons (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{H}_2$	$\Delta F = 23,900 - 9.21T \log_{10} T - 0.21T$	6,230

TABLE 14B
Equilibrium constants for dehydrogenation reactions of paraffins (Frey and Huppke)

REACTION	EQUILIBRIUM CONSTANT			
	350°C.	400°C.	450°C.	500°C.
$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$		0.00015	0.00076	0.0032
$\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$	0.00038	0.0022	0.0074	
$n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{C}_2\text{H}_5\text{CH}=\text{CH}_2 + \text{H}_2$	0.00045	0.0022	0.0075	
$n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{cis-CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2$	0.00083	0.0039	0.014	
$n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{trans-CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2$	0.00052	0.0025	0.0087	
$\text{iso-C}_4\text{H}_{10} \rightleftharpoons (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{H}_2$	0.0017	0.010	0.042	

diene were homogeneous second-order reactions. For 1,3-butadiene his results are given by

$$\log_{10} k = 7.673 - \frac{24,700}{2.3RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

The steric factor is small, corresponding to a collision efficiency of 1/10,300, as might be expected for an association reaction. The reaction has also

been investigated by Moor, Strigaleva, and Shilyaeva (128), results similar to those of Vaughan being obtained. For isoprene Vaughan found a rate given by

$$k = 2.19 \times 10^{10} T^{\ddagger} e^{-28,900/RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

with a steric factor of about 1/530.

Lind and Livingston (112) have investigated the photopolymerization of allene. They find the quantum yield to be about 2.5, independent of the pressure and the light intensity. The light absorption commences below 2380 A.U. and is strong below 2300 A.U. They also studied the photopolymerization of isoprene in a qualitative way.

IV. ACETYLENIC HYDROCARBONS

It will be apparent from the preceding sections that our knowledge of the reactions of the olefins is in a much less satisfactory state than is that of the paraffins. On account of the complexity of the reactions, the unsatisfactory state of our knowledge is still more pronounced in the case of the acetylenic hydrocarbons, and little is known with certainty about the elementary processes.

A. Acetylene

1. The thermal decomposition and polymerization

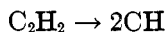
No attempt will be made to review the enormous literature on the effect of heat on acetylene, since comprehensive discussions from a pyrolytic point of view already exist (40, 42). The products of the reactions are usually so complicated as to defy analysis; consequently very little is known which is of value from the standpoint of this review. We shall therefore discuss only those papers which seem to bear on the main features of the processes.

At low temperatures (below 600°C.) polymerization is almost the only reaction of acetylene, the products being either a yellow solid, probably cuprene, or a liquid of aromatic character. From 600° to 1000°C. polymerization and decomposition both occur, the decomposition products being carbon, hydrogen, and some methane. Above 1000°C. decomposition is the only reaction of importance, and the decomposition is complete at 1200° to 1300°C. (10). At still higher temperatures some acetylene exists in equilibrium with hydrogen, carbon, and methane (18, 153, 154).

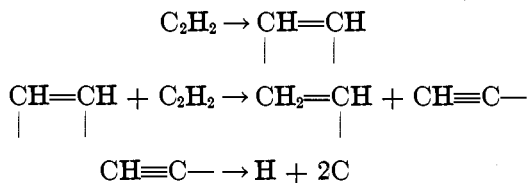
Although a very large number of papers have been published on the high-temperature decomposition of acetylene, very little is known about the kinetics of the process, and little can be added to the information derived from the early work of Bone and his collaborators. Bone and

Coward (16, 17) found that at 800°C. and higher acetylene always "flashed" on being admitted to the reaction vessel unless largely diluted with nitrogen or hydrogen. This explosive characteristic, due to the exothermic nature of the reaction, prevents any accurate determination of the rate of the reaction under isothermal conditions. The pressure and temperature limits at which explosion occurs have been determined by Schlöpfer and Brunner (180). Bone and Coward found that a certain amount of polymerization accompanied the decomposition during the "flashing." The products, apart from carbon, were mainly methane and hydrogen. At still higher temperatures polymerization decreased, and the reaction became a practically straight decomposition as shown by table 15. Bone and Jerdan (19) found that at 1150°C. decomposition was 90 per cent complete in 1 min. Methane was formed in large quantities in the early stages of the process, and was later partially decomposed.

While a great deal of further work has been done on the production of various compounds from acetylene by pyrolysis, it cannot be said that much is known about the mechanism of the process. The original mechanism proposed by Bone and Coward for the decomposition was a split into radicals



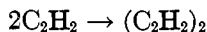
which later recombined or were hydrogenated to give methane and other products. It is now known that such a primary step would be impossibly endothermic. Hurd (78) suggests that the primary step involves the rupture of only one bond,



This type of mechanism was originally suggested by Mecke (123) and Bodenstein (14), and is, of course, purely speculative. The mechanism has also been discussed by Egloff and Wilson (48).

Rather more information is available concerning the polymerization which occurs at lower temperatures. The first data of any kinetic significance were obtained by Pease (141), using a flow method. He found that at low temperatures the reaction was almost entirely polymerization, very little permanent gases (hydrogen, methane, and olefins) being formed at temperatures below 550° to 600°C. The liquid polymerization products were a complex mixture. Pease suggests that the primary product is

(C₂H₂)₄. Zelinski (237), on the other hand, found diacetylene to be a product, and suggested that the primary step was



The reaction appears to be homogeneous, the rate being reduced to about one-half on packing the reaction vessel. Pease suggests that this is due to improved dissipation of heat in the packed vessel. (The polymerization is highly exothermic; thus for the reaction $3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$ there is an evolution of about 150 kg-cal. per mole.) Pease found that the reaction was roughly bimolecular, although he did not make a very thorough investigation of the order of the reaction. The bimolecular velocity constants for experiments at 1 atm. pressure are given in table 16.

TABLE 15
The thermal reactions of acetylene (Bone and Coward)

Temperature.....	600°C.	1000°C.	1150°C.	
Polymerization (per cent of acetylene consumed).....	19	7.5	5	
GASEOUS PRODUCTS		MOLE PER CENT		
Acetylene.....	1.35	1.55	0.0	
Ethylene.....	0.45	2.60	0.0	
Ethane.....	0.50	0.0	0.0	
Methane.....	32.40	36.00	23.45	
Hydrogen.....	63.50	59.85	76.55	

The reaction was also investigated by the static method in a rather sketchy way by Schlöpfer and Brunner (180). They found it to be homogeneous in Pyrex and quartz, a one hundred-fold increase in surface having no effect. They state that the results of analyses show that the reaction can be accurately followed by the pressure change; no analytical results are given, but presumably they followed the reaction by analyzing for unchanged acetylene. The products are complex, the average molecular weight being higher at low temperatures than at high. No data of any kind are given except for one run at 420°C., the results of which are given in table 17. It will be seen that the velocity constants fall when calculated for a first-order reaction, and rise when calculated for a second-order change. The real order is evidently about 1.5 for this experiment, but it is impossible to place much confidence in the results of a single run. For this run neither the initial pressure nor the units in which the velocity constants are expressed are given. The unimolecular constants are obviously in min.⁻¹, and the bimolecular constants are presumably expressed in liter mol.⁻¹ sec.⁻¹. If these assumptions are correct, their rates are very much faster than those of other observers.

A more thorough investigation was made by H. A. Taylor and van Hook (205), who also employed the static method. They followed the reaction by pressure change and obtained very reproducible results provided that the reaction vessel was aged for one or two runs. They found that an end point was reached when the pressure had decreased to 0.325 of its original value. No analyses of any kind were reported, but in view of Schlöpfer and Brunner's statement it is probably safe to assume that the pressure change is a reliable measure of the extent of reaction. Taylor and van

TABLE 16
The thermal polymerization of acetylene (Pease)

TEMPERATURE	BIMOLECULAR VELOCITY CONSTANTS FOR EXPERIMENTS AT 1 ATM.
°C.	<i>liter mol.⁻¹ sec.⁻¹</i>
450	0.00018-0.00022
475	0.00034-0.00050
500	0.0011 -0.0015
525	0.0030 -0.0045
550	0.0050 -0.011
575	0.0099 -0.023
600	0.024 -0.033

TABLE 17
The polymerization of acetylene at 420°C. (Schlöpfer and Brunner)

TIME	PER CENT REACTED	$k_{unimol.}$	$k_{bimol.}$
<i>min.</i>			
30	13.8		0.0054
60	27.8	0.0059	0.0065
120	47.2	0.0052	0.0074
180	56.2	0.0043	0.0071
300	71.5	0.0036	0.0084

Hook accept Pease's suggestion that the primary product is $(C_2H_2)_4$, and assume that some accompanying decomposition accounts for the final pressure being 0.325 of the initial pressure rather than 0.25. The reaction is apparently bimolecular in the early stages, but the constants deviate later. No test of the homogeneity of the reaction was made. Taylor and van Hook's velocity constants are compared with those of other workers in table 18. It will be seen that their rates are greater than those of Pease by a factor of about 2. Their results lead to an activation energy of 40,500 cal., but since no attempt was made to sort out the decomposition and the polymerization reactions this value is probably not very accurate.

On the basis of this activation energy they calculate a collision efficiency of $\frac{1}{3}$. They conclude that the simplicity of the molecule is responsible for the surprisingly high collision efficiency for an association reaction of this type (compare the polymerization reactions of the olefins). Actually one would expect a lower efficiency the simpler the molecule. It seems probable that complications due to the presence of the simultaneous decomposition reaction are responsible for the high apparent collision efficiency.

TABLE 18
The polymerization of acetylene (Taylor and van Hook)

TEMPERATURE	k	OBSERVER
°C.	<i>liter mol.⁻¹ sec.⁻¹</i>	
420	0.005-0.008	Schläpfer and Brunner
495	0.0039	Taylor and van Hook
500	0.0011-0.0015	Pease
515	0.0078	Taylor and van Hook
525	0.0030-0.0045	Pease
535	0.0145	Taylor and van Hook
550	0.0049-0.011	Pease

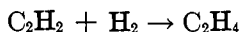
Travers (224) also gives the results of two experiments on the polymerization of acetylene. These do not contribute anything new to the situation.

2. The thermal hydrogenation of acetylene

The thermal hydrogenation of acetylene was also investigated by Taylor and van Hook. The actual hydrogenation is difficult to disentangle, since decomposition and polymerization are both occurring at a much faster rate than the hydrogenation. Taylor and van Hook attempted to separate the effect of the hydrogenation reaction from that of the others on the basis of the pressure change alone, without analyses of any kind. The results are therefore highly speculative. The velocity constants thus derived are as follows:

TEMPERATURE	$k_{\text{hydrogenation}}$
°C.	<i>liter mol.⁻¹ sec.⁻¹</i>
495	0.00019
505	0.00028
515	0.00039
525	0.00055
535	0.00076

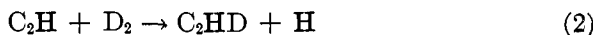
These lead to an activation energy of 42,000 cal. Taylor and van Hook calculate a collision efficiency for the reaction



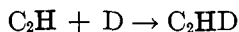
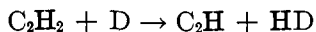
of $\frac{1}{3}$, as in the case of the polymerization. In these calculations they use the surprising value of 1×10^{-8} cm. for the diameter of the hydrogen molecule. The collision efficiency is again unexpectedly high for an association reaction involving simple molecules. It seems probable that the activation energies of both reactions are somewhat in error, the true values being lower than those given, and hence the collision efficiencies are also smaller. In any case, the existing data on both reactions are far from final.

3. The reaction of hydrogen atoms with acetylene

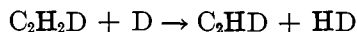
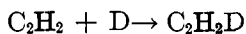
The reaction of hydrogen atoms with acetylene was investigated by Bonhoeffer and Harteck (23), and by von Wartenberg and Schultze (231). In the presence of acetylene it is found that the recombination of hydrogen atoms is strongly catalyzed, heat is given out, and there is a strong emission of light corresponding to the CH and C₂ bands. However, practically all the acetylene is recovered unchanged, so that presumably a series of reactions occur which consume hydrogen atoms and eventually regenerate acetylene. That such is the case is proved by an investigation of the reaction of acetylene with deuterium atoms by Geib and Steacie (64, 65). It was found that the acetylene recovered after the reaction was almost completely exchanged to deuterioacetylene. Apparently, then, the acetylene must be alternately hydrogenated and dehydrogenated. The reaction occurs so quickly that three-body processes are ruled out. Also, we can eliminate a mechanism of the type



both on energetic grounds, and because the atoms removed from the system by reaction 1 would be regenerated by reaction 2 and no "catalytic" recombination would occur. The mechanism, therefore, must be analogous to that previously discussed in the case of ethane, viz.,



It is also possible that the exchange occurs through the formation of a quasi-molecule, C₂H₂D, i.e.,



However, if the quasi-molecule had a long enough life to make such a mechanism possible, we would also expect the reaction

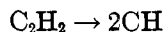


to occur, and actually no appreciable quantity of ethylene is formed. As von Wartenberg and Schultze point out, the absence of hydrogenation to ethylene is somewhat surprising, since acetylene is very easily hydrogenated to ethylene by metal catalysts. Hydrogenation of acetylene to ethylene is also absent when the hydrogen atoms are produced by photosensitization with mercury (4).

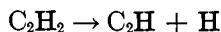
Geib and Harteck (62) have also investigated the reaction of hydrogen atoms with acetylene at liquid-air temperature. They find that no addition compounds, stable or unstable, are formed.

4. Free radicals and acetylene

The possibility that the decomposition of acetylene involves free radicals is ruled out, since the two conceivable modes of decomposition into radicals



and



are so strongly endothermic that the activation energies would be far too high to permit their occurrence to an appreciable extent. As is to be expected, therefore, Paneth and Hofeditz (134) found that the products of the acetylene decomposition had no effect on metallic mirrors.

Little work has been done on the action of free radicals on acetylene. Sickman and O. K. Rice (185) found that methyl radicals from the azomethane decomposition caused the polymerization of acetylene. Further work on this reaction is promised, but has not yet appeared. Recently Taylor and Jungers (215a) have shown that acetylene can be polymerized by the action of methyl radicals produced by the photodecomposition of acetone. At 25°C. as many as five acetylene molecules were found to disappear per methyl radical.

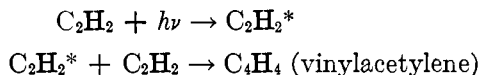
5. The photopolymerization of acetylene

The earlier papers on the photopolymerization of acetylene served to establish the fact that such polymerization occurred, the main product being a yellow solid, "cuprene." Thenard (218) reported the formation of benzene as well, but this was not confirmed by Berthelot and Gaudechon (12) or by Reinicke (155). Bates and Taylor (4) also investigated the reaction in a qualitative but much more thorough manner and found cuprene and an "oil" as products. They point out that a large number of

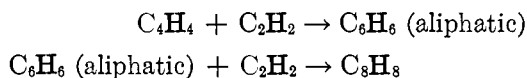
reactions are possible, particularly when the conditions are such that the photoreaction is accompanied by mercury-photosensitized reactions.

Lind and Livingston (110, 111) made the first really thorough investigation of the direct photoreaction, mercury vapor being excluded in order to avoid photosensitization. They showed that only light of wave length less than 2537 A.U. is effective (acetylene is transparent to longer wave lengths). The main cause of uncertainty in their work (and that of all other investigators) is the formation of an opaque solid deposit on the wall, which continually reduces the amount of light reaching the acetylene. They found that a solid resembling cuprene was formed, there being no gaseous products. The rate was proportional to the light intensity, and independent of the partial pressure of acetylene. The quantum yield for an average wave length of about 2150 A.U. was 9.2 ± 1.5 .

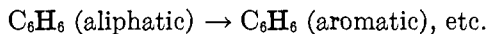
Kemula and Mrazek (93) investigated the reaction for the purpose of proving the presence or absence of benzene and gaseous products. They followed the reaction by absorption spectroscopy, so as to be able to detect transitory products. The results confirmed the work of Lind and Livingston in a general way, but showed that some benzene was formed in the reaction, together with small amounts of saturated hydrocarbons, olefins, and naphthalene derivatives. Kato (89) also found benzene to be a product. Kemula and Mrazek suggest that the primary reactions are



Various secondary changes are then postulated, such as

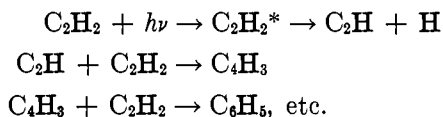


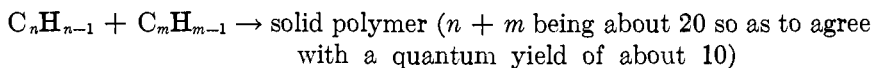
or



Criticisms of the work of Kemula and Mrazek by Toul (220, 221) seem to the writer to be entirely invalid, and have been satisfactorily answered by Kemula (91, 92).

Livingston and Schifflett (115) confirmed the results of Kemula and Mrazek, and found that benzene was formed in considerable quantities at temperatures above 270°C. Since the solid polymer found by Kemula and Mrazek had the approximate composition $(\text{C}_{10}\text{H}_8)_n$, Lind and Livingston (113) suggest the following mechanism for the photopolymerization:





They suggest that benzene may arise by



or



It must be admitted that at the moment all considerations as to mechanism are purely speculative, and nothing is known directly about any of the postulated part-reactions.

Toul (220) has also made a few rough qualitative experiments on the photodecomposition. He criticizes all previous work in a very drastic manner, owing to a lack of understanding on his part of photochemical and vacuum technique. He concludes that traces of "impurities" are largely responsible for the results obtained by others. His own technique, however, leaves much to be desired.

6. The mercury-photosensitized polymerization of acetylene

It was first shown that acetylene could be polymerized by mercury photosensitization by Bates and Taylor (4). A more thorough investigation was made by Melville (125, 171). He found that the rate was high at the start but fell off rapidly owing to the removal of mercury atoms by the polymerization process, presumably by the formation of a complex of some sort. If precautions were taken to ensure the presence of sufficient mercury vapor, the rate no longer fell off with time. All Melville's measurements were made at initial pressures below 10 mm., to prevent the formation of an opaque film on the walls of the reaction vessel. At low pressures (below 0.5 mm.) the rate was proportional to the acetylene pressure, because under these circumstances there is so little acetylene present that most excited mercury atoms radiate instead of being quenched. The quenching, therefore, does not appreciably lower the stationary concentration of excited mercury atoms, and hence the number of activated acetylene molecules produced is proportional to the acetylene pressure. At higher pressures the quenching lowers the concentration of excited mercury atoms to an appreciable extent, and the rate is proportional to $[C_2H_2]^x$, where x is less than 1 and approaches zero at high pressures.

The temperature was found to have a marked effect on the rate, viz.,

Temperature, °C.	30	99	209	267	355	436	528
Relative rate	1	8.8	12.7	9.0	7.5	6.2	5.3

It will be seen that the rate is a maximum in the neighborhood of 200–250°C. This is associated with the fact that the chain length is about 10

at room temperature, rises to about 100 at 250°C., and then decreases at higher temperatures. The chain length is independent of pressure, surface, or light intensity.

Melville gives a kinetic analysis of the polymerization process in terms of ordinary chain reaction theory, and concludes that the termination of the chains is by collision of the polymer with an acetylene molecule, the collision for some reason being not of the right type for propagation. The kinetic analysis is rather complex and will not be discussed here, since in the light of present knowledge it does not seem to be capable of either verification or disproof.

The polymerization was also investigated by Jungers and Taylor (80) for the principal purpose of comparing acetylene with deuterioacetylene. They found that at low pressures the rate for both C_2H_2 and C_2D_2 was proportional to the pressure, and that above 7 mm. it became independent of it. Over the whole pressure range the rate was 30 per cent greater for C_2H_2 than for C_2D_2 . The quantum yield was found to be about 6.5 for ordinary acetylene and 5 for deuterioacetylene. (It is noteworthy that in the polymerization of acetylene by alpha particles (114) the rates for the two acetylenes are identical.) Taylor and Jungers compare the quantum yields and ion-pair yields for ordinary acetylene under different conditions:

	<i>Quantum or ion-pair yield</i>
For beta particles (Mund and Jungers (130)).....	26
For alpha particles (Lind and Bardwell (109), Mund and Koch (131))..	18-20
For the photoreaction (Lind and Livingston (111)).....	9.2
For the mercury-photosensitized reaction (Jungers and Taylor (80))..	6.5

It will be seen that the yield produced by each primary act falls off rapidly as the energy input in the primary act is diminished. Jungers and Taylor conclude, therefore, that the polymerization process must dissipate the initiation energy fairly rapidly as it progresses.

Heinemann (70) claims in an old patent that ultra-violet light forms propylene from a mixture of methane and acetylene. The validity of the statement appears doubtful.

B. Higher acetylenic hydrocarbons

No investigations worthy of mention exist, with the exception of a few observations on the photopolymerization of methylacetylene. The reaction was first studied in a purely qualitative way by Berthelot (11). It was later investigated somewhat briefly by Lind and Livingston (112), who found that light of wave length less than 2240 A.U. was effective.

The product of the reaction was a white solid polymer. The quantum yield is about 3.5, independent of pressure and light intensity.

V. CONCLUSION

In conclusion it may well be said that tremendous advances have been made in this field in the last few years. A great deal, however, remains to be done. More work is especially needed on the rôle of free radicals, elementary processes in general, the reactions of the higher olefins and acetylenic hydrocarbons, the accurate determination of the activation energies of the various modes of decomposition of the paraffins, the photodecomposition of the simple hydrocarbons, etc. The subject is, however, an exceedingly active one, and there is no reason to doubt that its rapid advance will be continued.

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