THE REACTION OF HYDROGEN ATOMS WITH ISOBUTANE.

by

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INTRODUCTION

Although the attention of the earliest chemists was probably attracted to slowly progressing chemical changes, no definite ideas about the inherent nature of chemical action could be formed until quantitative investigations on the rate of reactions were made. Such investigations were first made by Harcourt and Esson and by Wilhelmy. Their work and that of van't Hoff, on chemical dynamics, can be said to have laid the foundation of the whole subject of modern chemical kinetics.

In as much as the reactions of the simple hydrocarbons are of great importance from both the theoretical and industrial points of view, it is not surprising that keen interest has been shown in their thermal decomposition mechanisms. Unfortunately, however, the thermal decomposition reactions of these compounds generally involve many complicated steps, difficult to untangle, with the result that to deduce a mechanism from the experimental data obtained, is, in many cases, little better than pure speculation. Consequently present day trend, in the field of gas kinetics, is to the more simple and elementary processes and for this reason investigations with the lower members of the aliphatic hydrocarbons have been favoured.

Since the available information on the reactions of the simple hydrocarbons comes from a variety of sources it is considered desirable to outline briefly, in a general way, the information that can be obtained by various independent methods. Before doing this, however, it is necessary to discuss briefly the essential features of unimolecular gas reactions generally.

The Kinetics of Unimolecular Reactions.

Chemical kinetics comprises the study of the velocity of chemical reactions and whilst it constitutes one of the oldest fields in physical chemistry, the development of the theory has been slow. However, following the discovery by Hinshelwood (1), in 1926, that a number of organic compounds decompose by a first-order mechanism, the study of gas phase reaction velocities has been a most active field. It now appears that at least the primary step in almost all organic decomposition reactions is a unimolecular change. Accordingly the stability of gaseous organic substances is therefore determined essentially by the size 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.,

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

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 mechanism of activation is obviously a problem. Perrin (2) and others (3,4) suggested that the molecule obtained the necessary activation energy by absorption of infra-red radiation. This hypothesis however floundered in difficulties almost from the start and did not last long.

The modern theory of unimolecular reactions is based on the hypothesis, originally proposed by Lindemann (5) and elaborated by Hinshelwood (6) and others (7,8,9,10), that activation occurs by collisions but that a time lag exists between activation and reaction. Consequently, most activated molecules are deactivated before they have a chance to react. Hence there exists a stationary concentration of activated molecules, which can be calculated from the Maxwell-Boltzmann distribution, and the rate of reaction is proportional to the first power of the concentration of the reacting substance. At low pressures, however, the diminished number of collisions will no longer be able to replace the activated molecules destroyed by reaction. Thus the stationary concentration will fall and the rate of reaction will diminish with decreasing pressure. Thus formally the process may be represented by

(1) $2A \longrightarrow A + A^*$ Activation by collision

(2) $A + A^* \longrightarrow 2A$ Deactivation by collision

(3) $A^* \longrightarrow$ products Reaction

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

$$-\frac{d}{dt}(A) = \frac{2k_3k_1(A)^2}{k_3 + k_2(A)}$$

At high pressures $k_2(A) \gg k_3$ and this reduces to

$$-\frac{d}{dt}(A) = \frac{2k_3k_1(A)}{k_2}$$

i.e., the reaction is of the first order. At sufficiently low pressures, however deactivation is slower on account of the decrease in the number of collisions and finally $k_3 \gg k_2(A)$. 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 gradually fall off and the order of the reaction will have a value between 1 and 2.

On the basis of the Lindemann hypothesis various theories have been proposed, especially to account for that portion of the rate-pressure curve where the velocity ceases to conform to the unimolecular law. In the development of such theories it is necessary to be more specific about the nature of the energy of activation. The older type of theory, of which Hinshelwood(11) was the chief exponent, assumes that if a molecule has an energy equal to or greater than E, it has a definite probability of reacting, independent of its excess energy over and above E. This is the simplest form of theory and it does not agree well with experimental facts. The other form of theory assumes that for reaction, energy must be concentrated in one particular degree of freedom or in one vibrational bond of the molecule. Hence the chance of getting energy 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 over E in the activated molecule.

This type of theory gives results which are in good agreement with experiments. There are a number of forms of this theory (12,13) but all are essentially the same. That of Kassel (14) is the one which is usually employed.

The essence of Kassel's theory is that the activation energy is merely the total energy of that number of quanta which must be localized in one particular bond before reaction can occur. In other words, activation energy is a measure of the bond strength. Obviously for the purpose of predicting the products of decomposition reactions, it becomes of prime importance to discover any possible relation between the activation energy of a reaction and the strength of the bonds formed and broken in it.

Free Radicals in Organic Decomposition Reactions

The mechanism involved in the decomposition of many organic compounds at high temperatures is still a matter of controversy. The various theories proposed however fall into two main classes.

The first and classical theory considers that a split into the final decomposition products occurs in a single step; applying this idea to a compound like. C_2H_6,

$$C_2H_6 = C_2H_4 + H_2$$

This involved the simultaneous rupture of two valance bonds and the formation of two new ones. It was therefore evident that the activation energy could bear no simple relation to bond strengths.

The other alternative is that the primary step consists of the rupture of a single bond to give unsaturated radicals and that these radicals undergo secondary reactions which ultimately lead to the formation of stable products. If this mechanism is the true one and if the secondary reactions are fast compared to the first, the activation energy should be a direct measure of the strength of the ruptured bond.

Paneth and Hofeditz (15), in 1929 and Paneth and Lautsch (16) in 1930, showed that methyl and ethyl radicals from the decomposition of organic products could be detected in rapidly flowing gas streams by their reaction with lead mirrors. Using this technique, F.O. Rice and co-workers (17,18) made a comprehensive study of organic decomposition reactions, and verified the existence of free radicals. These findings led Rice to formulate a general free radical theory for hydrocarbon decomposition reactions, which postulated that the primary step in unimolecular reactions is a split into free radicals, Rice points out that if two reactions have activation energies differing by 4 Kcal., then the relative rates at 600°C., are in the ratio of $e^{-4000/2 \times 873}:1$, or approximately 9 to 1. Similarly for a difference of 10 Kcal., the ratio is 500 to 1. Trusting then in the basic assumption that the activation energy is intimately connected with bond strength, we may conclude that if there are two or more ways of accomplishing a primary break in the molecule, and if one of these has an activation 10 Kcal., or more, lower, it alone will occur to any appreciable extent.

While there is some uncertainty about the various bond strengths it is however certain that the $C = C$ and $C \equiv C$ bonds are much stronger for instance than $C - C$, $C - H$, and it appears probable that the $C - H$ bond is about 15 Kcal. stronger than the $C - C$ bond. 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.

Methyl and ethyl radicals, though normally no higher radicals, can be detected by the Paneth technique (19); presumably higher radicals decompose too rapidly. It should be pointed out, however, that Pearson and Purcell (20) have detected higher radicals by photolysis at room temperature.

The primary reaction of the propane decomposition, according to the Rice scheme, would be

$$C_3H_8 = CH_3 + C_2H_5 \qquad (1)$$

and this would be followed by the series of reactions

$$CH_3CH_2CH_3 + R = RH + CH_3CH_2CH_2 \qquad (2a)$$

$$CH_3CH_2CH_2 = C_2H_4 + CH_3 \qquad (2b)$$

$$CH_3CH_2CH_3 + R = CH_3CHCH_3 + RH \qquad (3a)$$

$$CH_3CHCH_3 = CH_3CH = CH_2 + H \qquad (3b)$$

where R denotes a methyl radical or hydrogen atom. This scheme assumes, of course, that reactions (2) and (3) have activation energies much smaller than that of (1). On the basis of chance, reaction (2) would be faster than reaction (3) in the ratio 3:1, since there are six primary hydrogen atoms to two secondary. There is evidence, though, that secondary hydrogen atoms are less strongly bound. On this assumption, Rice estimates that reaction (2) is to readtion (3) as 6:4. Thus the overall reaction may be represented by

$$6\ C_3H_8 = 6\ C_2H_4 + 6\ CH_4$$

$$4\ C_3H_8 = 4\ C_3H_6 + 4\ H_2$$

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or $$10\ C_3H_8 = 6\ C_2H_4 + 6\ CH_4 + 4\ C_3H_6 + 4H_2$$

This method gives reasonably good agreement with experiment in the prediction of products, especially for the lower members of the hydrocarbons.

Thus, using Rice's mechanisms, it is possible to predict the products of reaction. To be fully successful, however, the theory must also account for the kinetics of reaction. For instance, it must explain why the overall mechanism of an organic decomposition appears to be of the first order though the mechanism is really a complex series of steps. Secondly, if most reactions occur by the rupture of a C-C bond as postulated, it must explain why the experimental activation energies for such reactions are usually far smaller than the C-C bond strength.

Rice and Herzfeld (21) answered these questions by devising mechanisms on a free radical basis which would lead to a first-order overall rate. Furthermore, by a suitable choice of activation energies of the part reactions, they were able to make the overall activation energy agree quite well with the experimental value. As an example, consider the following artifically simplified scheme for this decomposition of organic molecule (18):

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

The molecule M_1 decomposes initially into a radical R_1 and a smaller molecule M_2. The radical R_1 then reacts with the fresh molecule of reactant M_1., abstracts a hydrogen atom, and forms the stable compound R_1H and the free radical R_2. R_2 then breaks up into the radical R_1 and a molecule M_3. Thus a chain process is set up since steps (2) and (3) can repeat over and over again until the radical R_1 is destroyed to form a stable molecule M_4.

By setting up equations giving the concentrations of R_1 and R_2 in the steady state, we have assuming long chains

$$\frac{d}{dt}(R_1) = 0 = k_1(M_1) - k_2(R_1)(M_1) + k_3(R_2) - K_4(R_1)(R_2) \qquad (5)$$

$$\frac{d}{dt}(R_2) = 0 = k_2(R_1)(M_1) - k_3(R_2) - k_4(R_1)(R_2) \qquad (6)$$

The overall decomposition of M_1 may be expressed as

$$\frac{-d}{dt}(M_1) = k_1(M_1) + K_2(R_1)(M_1) \qquad (7)$$

By solving equations (5) and (6) for R_1 and substituting in

(7), we obtain:

$$-\frac{d}{dt}(M_1) = k_1(M_1)\left(1+\sqrt{k_2k_3/2k_1k_4}\right) \sim (M_1)\sqrt{\frac{k_1k_2k_3}{2k_4}}\text{approx}$$

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

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

so that substituting the assigned values of E, we obtain

$$E_{\text{Overall}} = 62.5 \text{ Kcal.}$$

which is well below the strength of the C-C bond.

The method by which the chains are terminated determines the order of the reaction. The above scheme assumes they end by the radical recombination

$$R_1 + R_2 = M_4$$

and this leads to a first-order rate. If, however, the chains were terminated by

$$2R_1 = M_5$$

the overall order would be 1,5, while

$$2R_2 = M_6$$

would give a value of 0.5. To predict successfully a first-order rate, therefore, it is necessary to make the arbitrary assumption that

$$R_1 + R_2 = M_4$$

is much faster than the other two possible recombinations.

Mechanisms of this sort are of course, to a considerable extent, based on conjecture; however, impressive support for the fundamental idea of free-radical chain reactions soon made its appearance. Frey (22) 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 (23,24), Fletcher and Rollefson (25), Echols and Pease (26) produced sensitized chain decomposition of a number of organic substances. All these observations can cause chain decomposition but they do not necessarily prove that such free radical chain decomposition occurs in the normal pyrolysis of the substances concerned.

Evidence for the presence of chains was also obtained from photochemical investigations. Leermakers (27) showed that the photolysis of acetaldehyde is a chain reaction above 80°C., and his results are in agreement with Rice and Herzfeld's predicted mechanisms. Leermakers (28) also found that chains are set up in the decomposition of dimethyl and diethyl ether induced by admixed acetone.

Further evidence for the chain character of some decompositions is furnished by Staveley and Hinshelwood (29) and others (30,31,32,33). While these investigations indicated that large amounts of added nitric oxide would catalyze the reactions, small amounts caused some inhibition. These investigators assumed that the maximum inhibition corresponds to the complete suppression of chains normally present, and thus they 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, recent work, (34,35) 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 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 theoretical values. (b) The activation energy of one of the part reactions in the Rice-Herzfeld scheme is determined in an independant way. (c) Deutero-compounds are used as indicators of the mechanism. The results of investigations using all these methods seem to indicate that the validity of the Rice-Herzfeld mechanisms leave much to be desired.

Consequently more information is necessary concerning the elementary processes involved in decomposition reactions and no great confidence can be placed in any one theory, until we have further knowledge about the individual reactions.

The methods of attack which have been directed towards this end consist of (1) thermal decomposition, (2) photochemical bond splitting, (3) photosensitized reactions, (4) reactions with atomic hydrogen. Very little information is available from the photodecomposition of the simple hydrocarbons since these compounds are transparent down to the extreme ultra-violet and the difficulties involved in working in the Schumann region are very great. Also the thermal studies have little bearing on the present work, since the temperatures used in thermal work are some 300°C - 400°C., higher. Attention will therefore be confined to reaction involving H-atoms. This will involve certain considerations of Photosensitized reactions however since H-atoms can be produced in this way.

Principles Underlying Photosensitized and Atomic Reactions.

The most straight forward means of photochemical activation of the simple hydrocarbons has been done by photosensitization with mercury vapour. In work of this kind, mercury vapour is mixed with the reactant gas and the mixture illuminated with mercury resonance radiation. Mercury possesses two resonance lines, One at 1849 A. U., and the other at 2537 A. U., but in practice, the shorter line is almost completely absorbed by the quartz reaction vessels and jackets of the light source. Thus only the one line (2537 A.U.) is appreciably absorbed by the mercury vapour in the system and the normal mercury atoms are raised to the 2^3P_1 level which lies 4.8 volts, or 112 Kcal., above the ground state. Such excited mercury atoms may then transfer their energy by collision to other molecules. If such transfers take place efficiently, a wide variety of reactions is possible since 112 Kcal., is greater than the activation energy of almost all chemical reactions.

Cadmium resonance radiation is also being employed in photochemical studies. Steacie and Potvin (36) (37), following the pioneer work of Bates and Taylor (38) have developed a powerful source of cadmium resonance radiation which they have used in their studies of the photosensitized reactions of the simple hydrocarbons. The first cadmium resonance line is at 3261 A. U., which corresponds to 87 Kcal.,

At the present time, zinc photosensitized reactions are being studied in this laboratory by Steacie and Habeeb (39). The purpose of using zinc or cadmium resonance radiation is the attainment of greater selectivity than that allowed by mercury photosensitization.

Photosensitization can also be used to study reactions involving hydrogen atoms. This was first demonstrated by the classical work or Taylor and his co-workers (40,41). In the presence of hydrogen and a reacting substance, we have;

$$\mathrm{Hg}\ (1^1S_0) + h\nu \quad = \quad \mathrm{Hg}\ (2^3P_1) \qquad (1)$$

$$\mathrm{Hg}\ (2^3P_1) + H_2 \quad = \quad \mathrm{Hg}\ (1^1S_0) + 2H \qquad (2)$$

or possibly

$$\mathrm{Hg}\ (2^3P_1) + H_2 \quad = \quad \mathrm{HgH} + H \qquad (2a)$$

$$H + X \quad = \quad \text{Products} \qquad (3)$$

$$2H + \left(\begin{matrix}\text{a third}\\ \text{body}\end{matrix}\right) \quad = \quad H_2 \qquad (4)$$

Recent wook by Olsen (42) indicates that the formation of HgH is due to secondary reactions of hydrogen atoms and excited mercury atoms so that reaction (2) is more probable than (2a).

Under these circumstances, a stationary concentration of hydrogen atoms exists and, knowing the rate of reactions (1), (2) and (4), we can calculate the velocity constant of reaction

(3). Although this method lends itself to wide application the results are not always easy to interpret.

A much more direct method for investigation of reactions with atomic hydrogen is the Wood-Bonhoeffer method. Wood (43) showed that it was possible under certain circumstances to pump hydrogen atoms out of a hydrogen discharge tube and carry them a considerable distance before recombination occurred . Bonhoeffer (44,45), adapted the idea to the investigation of hydrogen atom-hydrocarbon reactions by mixing the reactant with the atoms in a flow system. Many reactions have been investigated by this technique, but the experiments are limited to a narrow pressure range of hydrocarbons between 0.1 and 1mm., and a reaction time of the order of a second. This was the method used in the present study.

Atomic Reactions of the Simple Hydrocarbons.

METHANE.

Studies on the reaction of methane with hydrogen atoms, by Bonhoeffer and Harteck (46) using a Wood's tube, showed methane to be suprisingly stable. The results of this investigation were confirmed by von Wartenberg and Schultze (47) and later, further evidence of the inertness of methane was furnished by Chadwell and Titani (48).

Geib and Harteck (49) extended the experiments over a range of temperatures and found that no reaction occurred up to 183°C. They concluded that the reaction

$$CH_4 + H = CH_3 + H_2 \qquad (1)$$

had an activation energy of at least 17 Kcal. An alternative suggestion was that this reaction occurs readily but that the back reaction

$$CH_3 + H + M = CH_4 + M$$

proceeds more rapidly than other reactions such as

$$2CH_3 = C_2H_6$$

so that methane is regenerated as fast as it is consumed. This suggestion was ruled out by Geib and Harteck on the grounds that such a mechanism would involve the consumption of hydrogen atoms by both forward and back reactions, whereas the hydrogen atom concentration is not significantly changed by the introduction of methane. Their objection, however, could be overcome if the secondary reaction

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

occurred with a low enough activation energy. Since estimates of the activation energy of reaction (2) vary from 8 to 23 Kcal., (50,51,52,53,54) the issue is somewhat in doubt.

The reaction of methane with deuterium atoms has been studied extensively by Geib and Steacie (55,56) in an attempt to get at the problem more directly. They used the Wood-Bonhoeffer method and found no detectable reaction of methane with deuterium atoms up to 100° C., indicating that the activation energy of the exchange reaction is not less than 11 Kcal. Their investigation indicated also that the reaction was probably the analogue of the orth-opara hydrogen conversion:

$$CH_4 + D \rightleftharpoons CH_3D + H$$

rather than

$$CH_4 + D \rightleftharpoons CH_3 + HD$$

This eliminates the necessity of secondary reactions to account for the non-formation of ethane and the apparent regeneration of of atoms.

In a study of the thermal reaction between methane and deuterium at 100°C., Farkas (57) deduced that the mechanism was atomic and the same as that of Geib and Steacie.

Several estimates of the activation energy of this reaction, have been made, using mercury photosensitization as well as the Wood-Bonhoeffer method. These are tabulated below.

Investigators		Method	Result
Steacie and Phillips	(58)	Mercury photosensitization	11.7 Kcal.
Farkas and Melville	(59)	Wood-Bonhoeffer	13 Kcal.
Morikawa, Benedict and Taylor	(60)	Mercury photosensitization at 100°C	12.5 Kcal.
Steacie	(61)	Wood-Bonhoeffer up to 500°C.	12.9±2 Kcal.
Trenner, Morikawa and Taylor	(62)	Wood-Bonhoeffer 25° to 208° C.	15.6 Kcal.

According to Gorin, Kauzmann, Walter and Eyring (63) this activation energy of about 12 Kcal., must be identified with the reaction

$$CH_4 + D = CH_3 + HD$$

in view of their computations, which give a value of 9.5 Kcal., for this reaction, and 37 Kcal., for

$$CH_4 + D = CH_3D + H$$

The results of Farkas and Melville (59) indicate that hydrogen abstraction must occur at high temperature to account for a decreased atom concentration.

Methane, therefore, obviously does not react with atomic hydrogen until the temperature is over 180°C. At sufficiently high temperatures it reacts according to

$$CH_4 + H = CH_4 + H_2 \quad (12\ \text{Kcal.})$$

with subsequent reformation of methane to some extent by

$$CH_3 + H_2 = CH_4 + H \quad (10\ \text{Kcal.})$$

and by

$$CH_3 + H = CH_4$$

ETHANE.

Bonhoeffer and Harteck (64) and von Wartenberg and Schultze (65) 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, though a loss of gas up to 25% was reported by von Wartenberg and Schultze. This appears to have been methane, in the light of later work. In a preliminary investigation Chadwell and Titani (66) reported the finding of 4% methane, along with some ethylene.

Studies were made by Steacie and Phillips (58) using the Wood-Bonhoeffer technique, on the reactions of deuterium atoms with ethane. They found an activation energy of 6;3 Kcal., for the exchange. They decided that the most likely mechanism was

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

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

the primary step is in accord with the Rice-Herzfeld mechanism.

According to Trenner, Morikawa, and Taylor (62) who repeated the work by this method, 10 to 20 percent of the ethane was decomposed with formation of considerable amounts of deuterized methane. They concluded that the main reaction, at room temperature, must be

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

and that it is only at temperatures from 100°C., and up that the exchange reaction is appreciable, since below 100°C., no deuterized ethane was detected. Above 100°C., then, they postulate additional reaction by the exchange as suggested by

Steacie and Phillips, but find an activation energy of 11.4 Kcal., for this.

Recently, Steacie (67) has confirmed the production of methane, finding about 10% decomposition. This, however is not enough to bring the two activation energies into line.

The reaction of ethane with hydrogen atoms has been studied qualitatively by photosensitization with mercury, by several investigatore (68,69,70). This reaction has recently been reinvestigated by Steacie and Phillips (71). They found that methane, propane, and butane, but no higher hydrocarbons were produced and that hydrogen was consumed. In a typical experiment using a trapping temperature of -125°C., the following stoichiometric equation expresses the results

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

$$(+ \text{ traces of } C_3H_8)$$

They suggested that the mechanism is

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

$$H + C_2H_6 = CH_4 + CH_3$$

$$H + C_2H_6 = H_2 + C_2H_5$$

followed by varions radical recombination reactions.

PROPANE.

The first to investigate this reaction were Bonhoeffer and Harteck (46) using the Wood-Bonhoeffer method. They observed that the recombination of the atomic hydrogen was accelerated by the presence of propane.

Taylor and Hill (69,72), investigated the reaction of hydrogen atoms with ethane, propane and butane, using mercury photosensitization. They reported that the speed of reaction increases with higher molecular weight, a finding that is supported by the large decomposition of pentane by hydrogen atoms observed by Frankenburger and Zell.

Another investigation by Trenner, Morikawa and Taylor (62) by the Wood-Bonhoeffer method, using hydrogen and deuterium atoms, showed that the products were mainly methane, with a small amount of ethane. The methane and ethane were found to be highly deuterized, while the propane was not exchanged. Propane is thus much less reactive than ethane. They found no evidence for the catalytic recombination of hydrogen atoms observed by Bonhoeffer and Harteck.

Steacie and Parlee (73,74), investigated the reaction by the Wood-Bonhoeffer technique over a temperature range from 30° to 250°C. The products they found were methane, ethane, ethylene, but no hydrocarbons heavier than propane. The only product present at 30° was methane but as the temperature was raised, the ethane production increased rapidly and the ethylene formation more slowly. The activation energy of the primary step

$$H + C_3H_8 = C_3H_7 + H_2$$

or

$$H + C_3H_8 = C_2H_5 + CH_4$$

was found to be 10 ± 1.5 Kcal. The reaction was also studied by the same method using deuterium atoms. Methane and ethane were found to be highly deuterized but propane was less than 0.5% heavy.

BUTANE.

Little work has been done on the reactions of hydrogen atoms with either the normal or iso-form of butane.

Trenner, Morikawa and Taylor (62) made one run with n-butane and deuterium atoms produced by discharge tube method. They found about 11% decomposition at 110°C., to give methane, ethane and propane. The methane being highly exchanged while the recovered butane is not exchanged at all.

In a recent investigation Steacie and Brown (76) using the Wood-Bonhoeffer technique studied the reaction of hydrogen atoms with n-butane over a temperature of 35° -250°C. They found that the products consisted solely of methane at temperatures below 100°C; above this temperature ethane was formed in considerable amounts which increased steadily up to 250°C. It is concluded that the results indicate a mechanism in which a series of "atomic cracking" reactions play the main role. The activation energy of the primary step was found to be 9 ± 1.5. The main steps in the postulated mechanisms are;

Primary process

$$H + C_4H_{10} = C_4H_9 + H_2$$

Secondary processes at low temperatures

$$H + C_4H_9 = C_3H_7 + CH_3$$

$$= 2C_2H_5$$

$$H + C_3H_7 = C_2H_5 + CH_3$$

$$H + C_2H_5 = 2CH_3$$

$$H + CH_3 = CH_4$$

Additional secondary processes at high temperatures

$$C_4H_9 = C_2H_4 + C_2H_5$$

$$H + C_2H_4 = C_2H_5$$

$$C_3H_7 = C_2H_4 + CH_3$$

$$H_2 + C_2H_5 = C_2H_6 + H$$

$$H_2 + CH_3 = CH_4 + H$$

EXPERIMENTAL.

The experimental work in this investigation was carried out using a Wood-Bonhoeffer type of apparatus. This consisted essentially of a hydrogen and iso-butane purification and flow system (Figure 1), a discharge tube and reaction vessel (Figure 2) and a trapping and pumping system (Figure 3)

The hydrogen from cylinder Y_1 (Figure 1) was admitted to the apparatus through a purifying system which consisted of an electrically heated quartz tube Z, containing platinized asbestos and a condensing trap Q_1.

Any tendency to build up pressure, greater than atmospheric, was counteracted by means of a mercury blow-off valve, at the base of the manometer tube M_1. Small fluctuations were smoothed out by the ballast bulb V_1. The purified hydrogen, at atmospheric pressure diffused through the calibrated flow meter and passed into the discharge tube through P_2 (Figure 2).

The iso-butane gas, taken from cylinder Y_2 was expanded into volumes V_3 and V_4, through trap Q_2 and from

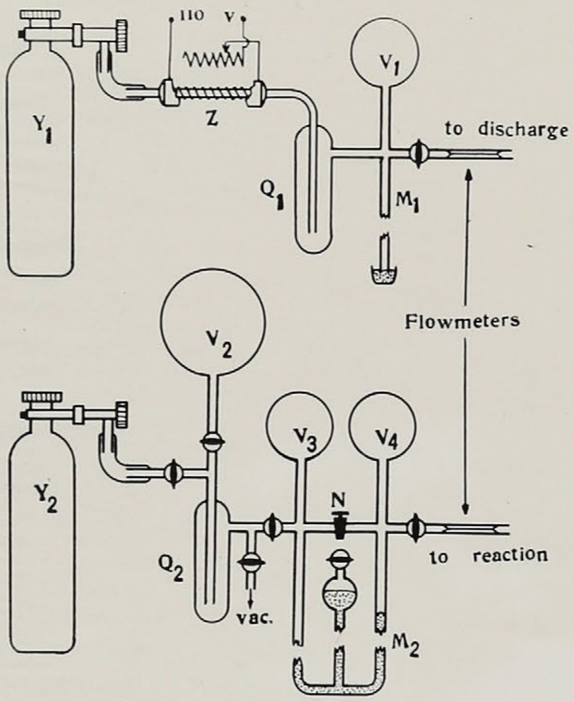


Figure 1.

Purification and Flow Regulation Systems.

there passed into the reaction vessel by diffusing through a calibrated flow meter. The iso-butane flow was maintained at a definite value by reference to the right leg of the absolute manometer M_2 and was regulated by means of a scratched stop cock N.

The hydrogen atoms were formed in the high voltage discharge tube D (Figure 2). This consisted of a pyrex tube, 2.5 cm., in diameter to which were sealed side tubes containing the aluminium electrodes E. The leads to the electrodes were heavy platinum wires which passed into the compartments through tightly sealed thickwalled capillary tubing.

In order that atomic recombination, prior to reaction with iso-butane, would be a minimum, the outlet of the discharge tube was sealed directly to the reaction chamber R (Figure 2). The pyrex reaction chamber R had a diameter of 7 cm., and a length of 70cm., it was surrounded by a close-fitting electric furnace F. Two tubes entered the reaction vessel from below, one of these T, was a thermocouple, the other P_2 served as an inlet for the iso-butane.

The products of reaction were pumped out through trap Q_3 (Figure 3), which was immersed in liquid air, This

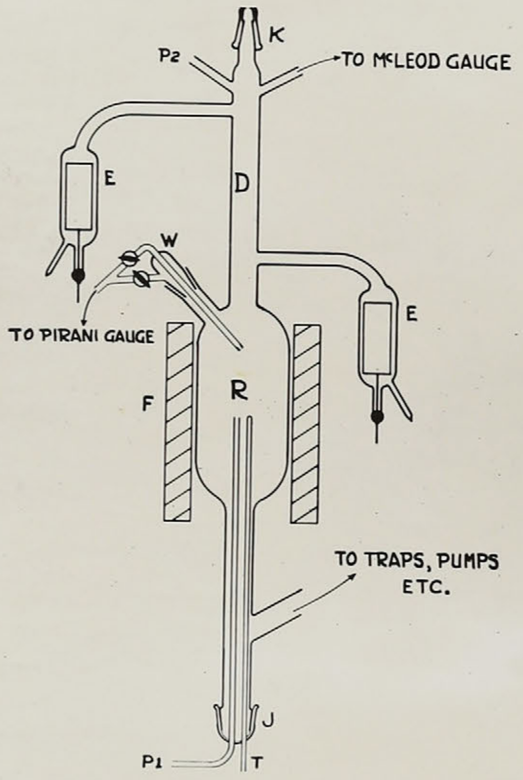


Figure 2.

Discharge Tube and Reaction Vessel.

would remove iso-butane as well as propane, ethane and ethylene, should they be present. The remainder passed through the diffusion pump U and through a silica gel trap Q_4, which was kept at liquid air temperature and which would remove methane and some hydrogen. Unadsorbed hydrogen passed out through the hyvac pump to the atmosphere.

V_5 is a volume into which the products were expanded, and the pressure measured on the absolute manometer M_3, before they were removed from the apparatus through the outlet S.

The diffusion pump, U, was a triple stage mercury pump with a potential speed of 20 litres per second. It was backed by a hyvac pump, and maintained a vacuum of 0.35 mm., under operating conditions. The diameter of all tubing in the pumping and trapping system was about 2 cm., and all stopcocks were of correspondingly large bore.

Poisoning of Reaction Vessel.

To minimize the rate of recombination of atoms on the walls of the reaction vessel, and thus obtain the greatest amount of reaction, the walls were "poisoned" with phosphoric

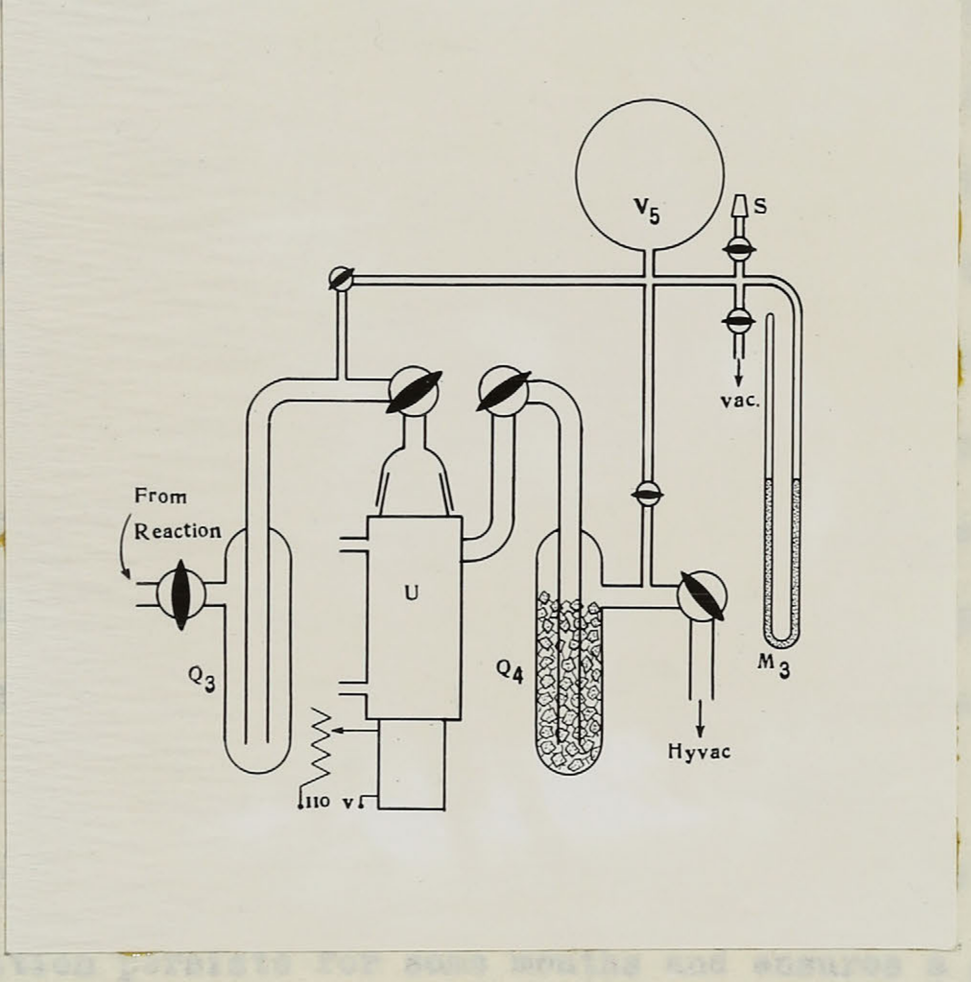


Figure 3.

Trapping and Pumping System.

acid. In order to do this it was necessary to remove cap K and the fitting J. The tips of the drainage tubes on the electrode compartments were cut off. The apparatus was flushed with large quantities of distilled water, cleaned thoroughly with fuming nitric acid, rinsed again many times with distilled water and the surface poisoned with 8% solution of phosphoric acid. This was run through several times until the whole interior surface had been thoroughly wetted, and the system was then sealed up and dried by evacuation. A coating of metaphosphoric acid was left on the walls as a result of this treatment; at higher working temperatures, the metaphosphoric acid probably dehydrated to the acid anhydride. The poisoning efficiency drops off at first until a fairly steady condition is reached, and providing operating temperatures are not above 250°C., this condition persists for some months and ensures a good working concentration of atoms. Above 250°C., the anhydride slowly distills to colder parts of the apparatus.

Gases Used.

Iso-butane, approximately 99% pure, was obtained from the Ohio Chemical and Manufacturing Company; the only impurity was n-butane and this was not removed.

Before making a run the usual procedure was to pass the gas from the iso-butane cylinder into trap Q_2 and using liquid air, freeze out a certain amount. The solidified iso-butane was allowed to warm up slowly and the first fraction of it was pumped off, to remove dissolved air. A middle fraction was expanded into volumes V_3 and V_4, which had previously been thoroughly evacuated; the residual fraction of gas was discarded.

Hydrogen was taken from the industrial cylinder Y_1, by means of a needle valve and purified by passing over platinized asbestos in the quartz tube Z, heated electrically to 500°C. This converted any oxygen present to water vapour, which was subsequently condensed out, along with other impurities, by means of a liquid air trap Q_1.

Procedure of a Typical Run.

In a typical run the apparatus was first pumped down thoroughly and the reaction vessel was brought to the desired temperature by adjusting the current through the furnace F. Liquid air was put around trap Q_1 in the purification train for hydrogen, and the hydrogen tank was opened slightly.

The platinized asbestos tube was heated to 500° C., and the hydrogen was admitted to the discharge tube.

The discharge current was allowed to settle down for about five minutes, while the hydrogen was pumped through the apparatus. Traps Q_3 and Q_4 were then immersed in liquid air, and the pressure and temperature of iso-butane in the storage volumeswas observed. The iso-butane flow was then turned on and the time noted. The volume of iso-butane passing the calibrated flowmeter was kept at a constant value by maintaining a certain definite pressure head in V_4. This was accomplished by expanding gas from V_3 at a controlled rate through the scratched stopcock N so that the right arm of the absolute manometer M_2 showed a reasonably constant reading throughout a run. The flow ratio of H_2 to iso-butane was about 6.5 : 1. Knowing the volume of bulbs V_3 and V_4 and the pressure before and after each run the total flow of iso-butane during a experiment could readily be calculated. All runs were of two hours duration, as a convenient volume of products accumulated in this time. At the end of two hours, the iso-butane flow was cut off, the scratched stopcock N was closed, and the pressure and temperature of iso-butane in the storage volumes noted. The flow of hydrogen was allowed to continue for about five minutes in order to flush out all products. It was then cut off, and the apparatus pumped down to about 0,35mm.

Analysis of Products.

Two methods were used. The first consisted of combining the products from trap Q_3 and Q_4 and then separating the components by means of low temperature fractional distillation. The second consisted in removing the products from each trap separately and carrying out a combustion analysis on the methane hydrogen fraction, trap Q_4, directly, while the products from trap Q_3 were submitted to a low temperature fractional distillation. This latter method was found satisfactory in view of the fact that methane was the only product of reaction which appeared to any appreciable extent.

To remove the products from the apparatus, the liquid air was removed from the silica gel adsorber Q_4, which was then allowed to warm up to room temperature, and the methane and hydrogen were pumped off into a gas holder by means of a Toepler pump. This fraction of the products was then transferred to a combustion apparatus where its volume was measured, and the amount of methane present determined by combustion analysis. The products from trap Q_3 were expanded into volume 5, from which it was likewise pumped off into a gas holder to be put through the still.

The products were analysed in a low temperature fractional distillation apparatus of the Podbielniak type. It was found necessary to use acetone-dry ice as refrigerant at the base of the column while passing the sample into the still, since liquid air would freeze the iso-butane out solid and plug the apparatus.

As a check on unsaturates an occasional sample was analysed with a Burrell gas analysis apparatus.

Determination of Hydrogen Atom Concentration.

The hydrogen atom concentration in the reaction vessel, for each working temperature, was measured with the Wrede diffusion gauge W (Figure 2). This was of the usual type (113), and consisted of a capillary tube with a very small orifice, situated in the reaction vessel and an arrangement of stopcocks, by means of which the inside or outside of the orifice could be connected to a Pirani gauge at will.

The instrument is based on the different rates of diffusion of atoms and molecules through the small orifice, whose diameter is small relative to the mean free path of hydrogen. Atoms diffusing through the orifice recombine on the walls of the capillary tube to form molecules. Thus the pressure inside the orifice is due to molecular hydrogen alone. Hence a pressure gradient is set up between the inside and outside of the orifice. This pressure gradient could be measured on the Pirani gauge. Thus, knowing P_1, the pressure inside, and P_2 the pressure outside, the percentage H atoms is given by

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

Determinations of atom concentration could not be made during a run since the presence of iso-butane molecules would interfere with this relation. Consequently measurements were made under the same conditions as the run, but with no iso-butane present. The difference in pressure due to the absence of iso-butane was very small since the ratio of

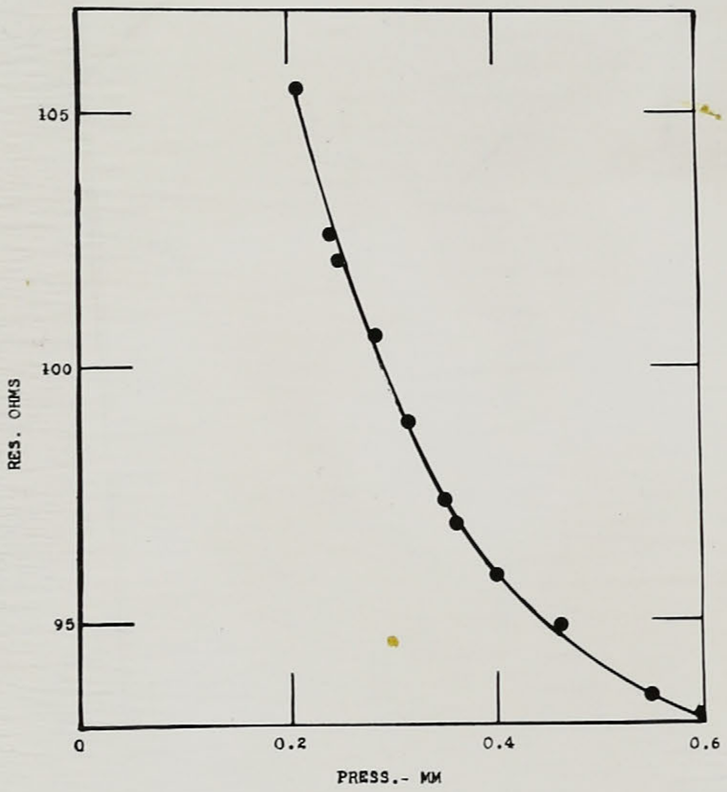


Figure 4.

Calibration of Pirani Gauge.

$H_2 : C_4H_{10}$ was high throughout all the runs.

In making the atom concentration measurements the Pirani gauge was first calibrated against the McLeod gauge, giving the curve shown in Figure 4; this being the plot of pressure in mm., of mercury against the corresponding resistance in ohms of the Pirani gauge filament.

The Pirani gauge was kept immersed in ice water. With the discharge tube operating, the inside orifice was connected to this gauge and the resistance due to the pressure was measured by means of Wheatstone Bridge arrangement. Switching over to the outside a similar series of readings were taken. This procedure was repeated several times alternating between the inside and the outside. From the measured resistance, in each case, the corresponding pressure in mm., could be obtained from the graph (Figure 4).. Substituting these values for P_1 and P_2 in the equation above, the percent atom concentration was determined.

It was observed from these measurments that the percentage atom concentration increased with rise in temperature indicating an accompanying thermal effect. Consequently it was necessary to correct for this, in arriving at the true atom concentration. This was done by making a series of (blank) measurements with the discharge off, at each operating temperature. Results of these measurements are shown graphically in (Figure 5).

Table 1.

Experimental Conditions.

Run no.	Temp. °C.	mm. Press.	Atom conc.%	Flow in mols/sec. X 10^{-5}	
				H_2	C_4H_{10}
1	32	0.36	9.1	1.54	0.245
2	31	0.36	9.1	1.54	0.250
3	32	0.36	9.1	1.54	0.246
4	101	0.35	8.2	1.54	0.239
5	101	0.36	8.2	1.54	0.247
6	100	0.35	8.2	1.54	0.245
7	101	0.35	8.2	1.54	0.245
8	101	0.35	8.2	1.54	0.239
9	171	0.37	7.1	1.54	0.251
10	171	0.37	7.1	1.54	0.245
*11	172	0.35	7.1	1.54	0.245
12	171	0.35	7.1	1.54	0.249
*13	251	0.36	5.6	1.54	0.245
14	250	0.36	5.6	1.54	0.243
15	250	0.36	5.6	1.54	0.244

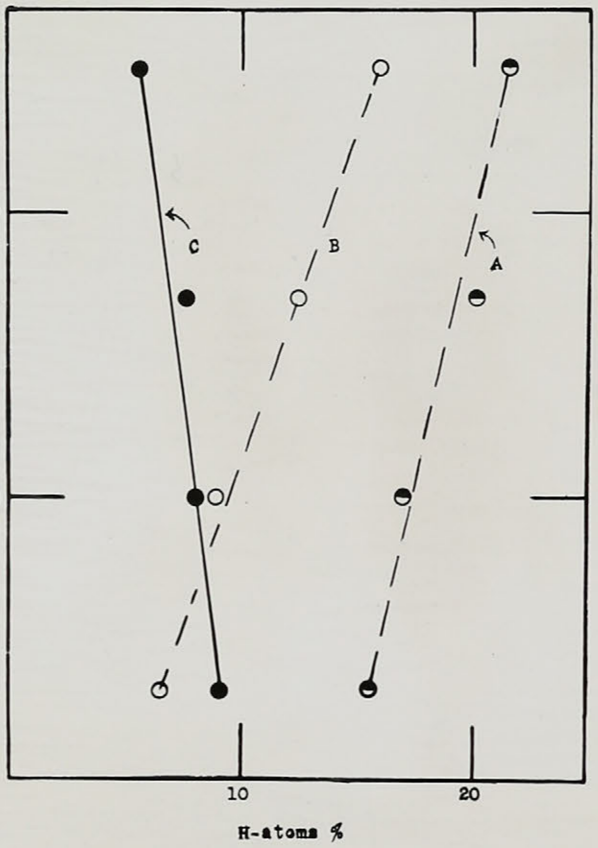
*Runs in which distillations were made on combined products from both traps.

Table 2.

Products Formed in Reaction of Iso-butane and Hydrogen Atoms.

Run No.	Products. mol percent		Total Conversion
	C_4H_{10}	CH_4	%
1	88.1	11.9	3.4
2	88.3	11.7	3.2
3	87.3	12.7	3.5
4	88.0	12.0	3.3
5	89.0	11.0	3.0
6	86.1	13.9	3.9
7	86.0	14.0	3.9
8	86.3	13.7	3.8
9	86.3	13.7	3.8
10	86.5	13.5	3.8
11	87.1	12.9	3.6
12	86.6	13.4	3.7
13	88.8	11.2	3.0
14	85.0	15.0	4.2
15	85.0	15.0	4.2

Plus definite traces of ethane, propane and possibly traces of unsaturates.



Legend

A - Apparent H atom Concentration
B - Correction Curve (due to thermal effect) in terms of H atom Concentration.
C - True H atom Concentration.

Figure 5.

Percent H atoms - Temperature Relation.

Calculation of Collision Yields and Activation Energies.

The total flow rate of gas during a run could be calculated from the flow rates of hydrogen and iso-butane, and knowing the atom concentration the total flow rate could be corrected for the hydrogen atom formation.

The reaction time (in seconds), for any run was calculated by dividing the capacity of the reaction vessel, (1370 c.c., at 0°C.,), in mols at each operating temperature, by the corrected flow rate (in mols/sec).

Then knowing the fraction of hydrogen atoms present, and the total pressure, the partial pressure (P_H) of hydrogen atoms during the run was calculated (in mm.,). Knowing Avogadro's number, and the capacity of the reaction vessel, the number of atoms of hydrogen per c.c. (N_H), could be calculated in terms of a constant times P_H/T, T being the absolute temperature of the run.

The number of collisions per second with hydrogen atoms undergone by a butane molecule is given by the relation (114,115):

$$Z_{C_4H_{10}, H} = 2\sqrt{2\pi}\left(\frac{d_H + d_{C_4H_{10}}}{2}\right)^2 \left(\frac{M_H \quad M_{C_4H_{10}}}{M_H \quad M_{C_4H_{10}}} \times RT\right)^{\frac{1}{2}} \times N_H$$

where

d_H = diameter in cm., of the hydrogen atom, (2.14×10^{-8}).

$d_{C_4H_{10}}$ = diameter in cm., of the iso-butane molecule(4.66×10^{-8}).

M_H = atomic weight of hydrogen

$M_{C_4H_{10}}$ = molecular weight of iso-butane

R = gas law constant in ergs/mol/°C.(8.313×10^7).

T = absolute temperature of the run

N_H = number of hydrogen atoms per c.c.

The value of d_H was taken from Bonhoeffer and Harteck (77) and the value of $d_{C_4H_{10}}$ from Titani (78).

Taking into account all the constant values in the above expression, which do not vary from run to run, and substituting the proper values for the constants in the expression, it reduces to the following

$$Z_{C_4H_{10}, H} = 5.16 \times 10^8 \cdot P_H/T^{1/2}$$

where P_H is the partial pressure of hydrogen atoms in mm., where T is the absolute temperature of the run.

Multiplying this value by the reaction time gave the number of collisions with hydrogen atoms undergone by an iso-butane molecule in the reaction time. Dividing the percent decomposition by this, gave the collision yield for the run,(the number of molecules of iso-butane decomposed, or of product formed per collision of an iso-butane molecule with a hydrogen atom)

From the relation

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

the activation energy E was calculated, assuming for the steric factor A, a value of 0.1 in this case.

$$E = 2.303 \times 1.987 \times T \times \log \frac{0.1}{\text{collision yield}}$$

The results of the various calculations are shown in Table 4.

Table 3.

Run no.	Temp. °C.	Total Flow Corrected for Presence of Atoms. (mols/sec X 10^{-5})	Reaction Time (sec.)	Hydrogen Atoms' Partial Pressure (mm.)
1	32	1.93	1.33	.033
2	31	1.93	1.33	.033
3	32	1.93	1.33	.033
4	101	1.91	1.09	.029
5	101	1.92	1.09	.029
6	100	1.92	1.09	.029
7	101	1.92	1.09	.029
8	101	1.91	1.09	.029
9	171	1.91	0.94	.025
10	171	1.90	0.94	.025
11	172	1.88	0.94	.025
12	171	1.91	0.94	.025
13	251	1.89	0.83	.020
14	250	1.88	0.83	.020
15	250	1.88	0.83	.020

Table 4.

Calculation of Collision Yields and Activation Energies.

Run no.	$Z_{C_4H_{10},H}$	$Z_{C_4H_{10},H}$ x Reaction time	% reaction	Collision yield	K(Kcal) A = 0.1
1	9.73 x 10^5	12.9 x 10^5	3.4	2.64 x 10^{-8}	9.2
2	9.73 "	12.9 "	3.2	2.48 "	9.2
3	9.73 "	12.9 "	3.5	2.71 "	9.2
4	7.47 "	8.15 "	3.3	4.05 "	10.9
5	7.47 "	8.15 "	3.0	3.68 "	10.9
6	7.47 "	8.15 "	3.9	4.78 "	10.8
7	7.47 "	8.15 "	3.9	4.78 "	10.8
8	7.47 "	8.15 "	3.8	4.66 "	10.8
9	5.52 "	5.18 "	3.8	7.34 "	12.4
10	5.52 "	5.18 "	3.0	5.79 "	12.4
11	5.52 "	5.18 "	3.6	6.95 "	12.5
12	5.52 "	5.18 "	3.7	7.15 "	12.5
13	4.51 "	3.74 "	3.0	8.03 "	14.6
14	4.51 "	3.74 "	4.2	11.2 "	14.2
15	4.51 "	3.74 "	4.2	11.2 "	14.2

DISCUSSION.

Over the temperature range 30° - 250°C., it has been found that methane is the sole product of reaction between H-atoms and iso-butane. The activation energy, calculated from collision yields, increases from 9;2 Kcal. at 30°C to 14.3 Kcal. at 250°C., with an average value of 11.6 Kcal.

The increase of activation energy with temperature is probably only apparent. Similar increases have been observed with other H-atom reactions, and have been explained on the basis of error in the assumed H-atom concentration at higher temperatures, where the increased amount of reaction might be expected to lower the stationary atom concentration, Steacie and Parlee (74), Steacie and Brown (76). It seems safe to take E = 11.5 ± 2 Kcal. The value reported by Steacie and Brown (76), for n-butane is 9 ± 1.5 Kcal. This value is subject to some uncertainty, since the H-atom concentration seems to have been determined with one of the connecting tubes of the Wrede gauge almost completely plugged. This was discovered only during the present study. A check run on n-butane, and a run with propane, confirmed that the H-atom concentration during the investigation by Steacie and Brown must have been about three times that reported by them. On this basis, E for the n-butane reaction with H-atoms should be about 7.5 ± 1.5 Kcal. However, a second factor must also be considered.

The values reported by Steacie and Brown, and those found for iso-butane are as follows;

Temperature.	E(n-butane)	E(iso-butane)
30	7.9	9.2
100	9.5	10.9
170	10.3	12.4
250	10.7	14.3

It is highly likely that the value 10.7 at 250°C. for n-butane is too low relative to the values at lower temperatures,again owing to error in H-atom concentration at 250°C. The value for the activation energy for n-butane should therefore probably have been chosen higher than 9 ± 1.5 Kcal. on the basis of the actual values recorded above. When the situation is reviewed as a whole it seems reasonably satisfactory to take the value of E for n-butane to be that assumed by Steacie and Brown (76), 9 ± 1.5, recognizing however, the inherent uncertainty in the value. If this is done, it is obvious that the activation energy for the iso-butane reaction may be estimated about 2 Kcal. greater than that for the n-butane reaction. This is in agreement with the relative callision yields, which show that the n-butane rate is approximately ten times that for iso-butane.

Again, propane, with an activation energy of 10 ± 2 Kcal. has been found to have a rate estimated from collision yields of about twice that for iso-butane (76). The results for isobutane therefore agree well, insofar as relative rates and activation energies ane concerned, with previous studies.

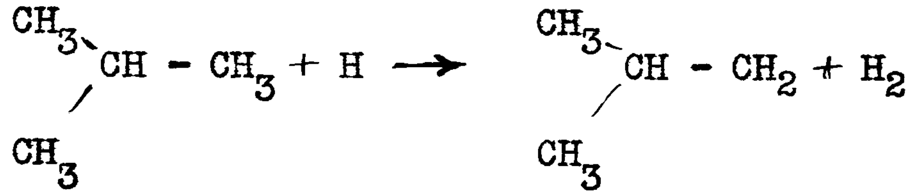
Mechanism of the Reaction.

In attempting a formulation of the mechanism of the reaction it must be remembered that methane was found to be the sole product of reaction over the entire temperature range used.

The primary step. Various possibilities for the primary step may be suggested.

A. Hydrogen abstraction

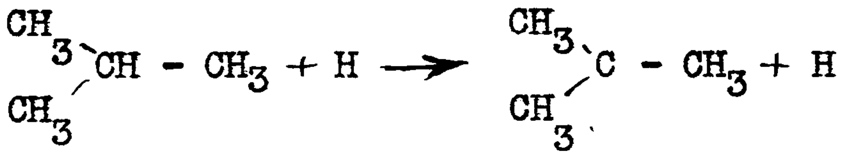
(1)



$$(CH_3)_2CH - CH_3 + H \longrightarrow (CH_3)_2CH - CH_2 + H_2$$

This type of reaction has been postulated for H-atom reactions with propane (Steacie and Parlee 74) and with n-butane (Steacie and Brown 76). It is energetically sound, leaves the nature of the products to be determined by the fate of the isobutyl radical and would seem satisfactory from a probability point of view, since there are 9 primary H-bonds accessible to attack.

(2)



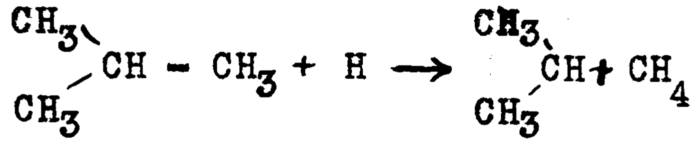
$$(CH_3)_2CH - CH_3 + H \longrightarrow (CH_3)_2C - CH_3 + H$$

This reaction involves the abstraction of a tertiary H-atom, which apparently requires some 4.4 Kcal. less energy than the removal of a primary H-atom, (Smith and Taylor 79). If the primary step in the reaction involves the rupture of a primary C - H bond, the activation energy of 11.5 2 Kcal. for the iso-butame reaction cannot correspond to the removal of a tertiary H-atom

Reaction (2) cannot then be the primary step.

B. Chain breaking

Various chain-breaking reactions may be postulated for the primary step. As an example we may consider:

(1) 

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH - CH_3 + H \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH + CH_4$$

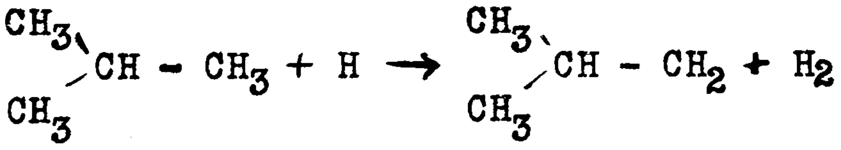
If we may consider this reaction analogous to

$$C_2H_6 + H \rightarrow CH_3 + CH_4$$

its occurrence cannot be assumed on the basis of available evidence, which fines the activation energy of reactions of this type at about 30 Kcal., (Gorin, Kauzmann, Walter and Eyring 63). The fact that the chain-breaking would occur at a tertiary carbon atom in iso-butane is not likely to modify the situation enough to allow of this type of reaction as the primary step.

Other chain-breaking reactions than the example mentioned above are entirely analogous and may be ruled out.

The primary reaction would seem then to be the removal of hydrogen according to:

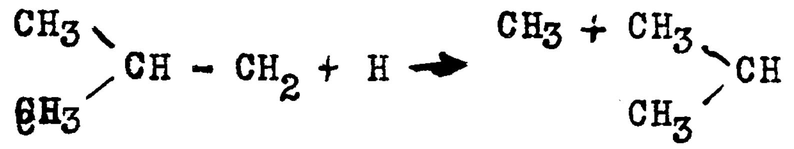


$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH - CH_3 + H \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH - CH_2 + H_2$$

Secondary Reactions.

Since the sole product at both low and high temperatures is methane, presumably the reactions subsequent to the primary abstraction of hydrogen remain unaltered as the temperature increases.

The only mechanism following the primary step that may reasonably be expected to yield methane as the sole product is a series of cracking reactions, the first of which would obviously be:



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!>CH - CH_2 + H \rightarrow CH_3 + \genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!>CH$$

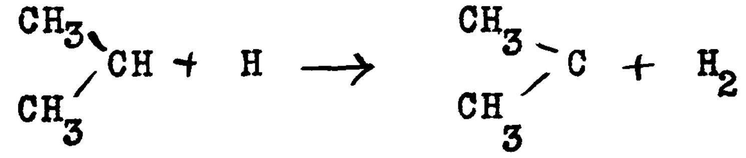
The CH_3 radicals can be hydrogenated to CH_4 only by three-body collision:

$$CH_4 + H\ (+M) \rightarrow CH_4\ (+M)$$

since the $CH_3 \cdot H$ complex has a life of about 3×10^{-12} seconds (Kimball 80). The activation energy for the process is probably small (Rice and Rice 18)

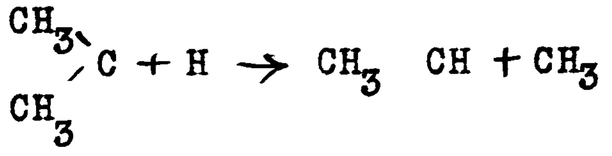
The probable fate of the isopropyl radical is of considerable interest. Keeping in mind the fact that no other product than methane is formed, even at high temperatures, there would seem to be two reasonable possibilities.

(a)



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!>CH + H \rightarrow \genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!>C + H_2$$

followed by



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!>C + H \rightarrow CH_3\ \ CH + CH_3$$

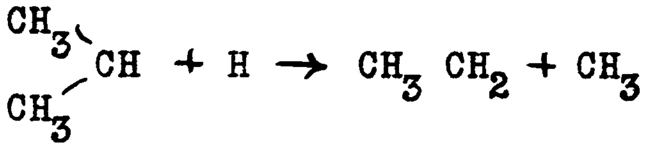
These two reactions are entirely analogous to the sequence postulated for propane (Steacie and Parlee 74) and for n-butane (Steacie and Brown 76) at low temperatures.

The subsequent behaviour of the ethyledene radical is a matter of pure speculation. Since radicals such as CH_3C or CH_2 CH would presumably give rise to products other than methane, the most logical step would seem to be

$$CH_3CH + H \rightarrow CH_3 + CH_2$$

followed by hydrogenation of CH_3 and CH_2 to give CH_4 presumably by H-atoms(Steacie, 93).

(b) The behaviour of the isopropyl radical might more logically be assumed as follows:



$$(CH_3)_2CH + H \rightarrow CH_3\,CH_2 + CH_3$$

The companion reaction with n-propyl radicals apparently has an activation energy of about 5 Kcal.(Trenner, Morikawa and Taylor 62)(Steacie and Parlee 74). The $CH_3.CH_2$ radical can then react with H-atoms according to

$$CH_3CH_2 + H \rightarrow 2CH_3$$

for which the activation energy is estimated to be about 5 Kcal.(Taylor 81) (Moore and Taylor 82)

However, it must be recognized that this mechanism is contrary to the assumption that ethyl radicals begin to undergo reaction with H_2 molecules at temperatures of about 160°C.(Steacie and Parlee 74) (Steacie and Brown 76). There is, in fact, considerable doubt as to the true activation energy for the reaction

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$

Estimates vary from 9 Kcal.(Moore and Taylor 82) up to more than 15 Kcal. (Leermakers Geddes and Mack 83),(Cramer 84) It should also be noted that the closely related reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

has been the subject of much controversy, with an activation energy variously determined as follows:

E	References
8 Kcal.	Smith and Taylor (79)
8 Kcal.	V.Hartel and Polanyi (51)
9 "	Cunningham and Taylor (87)
11.1"	Trenner Morikawa (62,94)
15 "	Paneth, Hofeditz and Wunsch (86)
20 "	Patat and Sachsse (85)
23 "	Rice,F.O. (50)

Taylor and Burton (88) have expressed the opinion that the value of about 9 Kcal. might be for the reaction

$$2CH_3 + H_2 \rightarrow 2CH_4$$

and that the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

should be assigned a value for E of about 19 Kcal.

The higher values are in qualitative accord with that calculated by Gorin, Kauzmann, Walter and Eyring (63). Moreover by assuming a value for the activation energy of 19 Kcal. for the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

and an activation energy of 13 Kcal. for the back reaction (Trenner, Morikawa and Taylor 62)(Steacie 61) the C - H bond strength is determined as 96.5 Kcal. which is in good agreement with values otherwise estimated (Rice and Herzfeld 89),(Burton 90),(Taylor and Burton 91) and (Pauling 92). The low value (9 Kcal) gives a bond strength of 106.5 Kcal. which is high compared with most estimates.

It is apparent from the above discussion that to assume an activation energy of more than 15 Kcal. for the reaction

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$

is not unreasonable. If E for thie reaction is, in fact, greater than this figure, then presumably ethyl radicals would not react with hydrogen molecules to any appreciable extent until temperatures of 250°C. or more are attained. It would then be possible to postulate the reaction between isopropyl radicals and H-atoms to form C_2H_5 radicals without there being ethane produced in a secondary reaction at high temperatures. Indeed it might be reasonably said that the present study affords additional evidence that the activation energy for the reaction of ethyl radicals with hydrogen molecules is of the order 15 - 2o Kcal.

In conclusion it might be fairly said that no real decision about the complete mechanism of the iso-butane reaction with H-atoms can be made without additional information. However, the essential point is that this reaction, like propane and n-butane, is apparently initiated by an atom-cracking process.

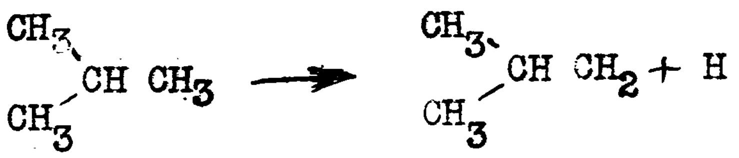
SUMMARY AND CONTRIBUTION TO KNOWLEDGE.

The reaction of atomic hydrogen with isO-butane has been studied over the temperature range of 30°C - 250°C. The wood-Bonhoeffer method was used.

Experiments were carried out at 30°C, 100°C, 170°C and 250°C. The ratio of hydrogen to iso-butane was maintained at 6.5 : 1 and the operating pressure was 0.36 mm., throughout the runs. The average concentration of atomic hydrogen was about 7·2 %. Under these conditions the only product of reaction found in measurable quantity is methane although traces of ethane and propane were indicated.

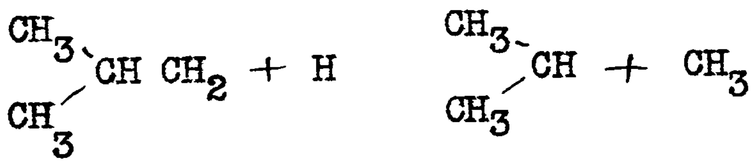
A suggested mechanism to account for the reaction involved in the present investigation is as follows:

Primary

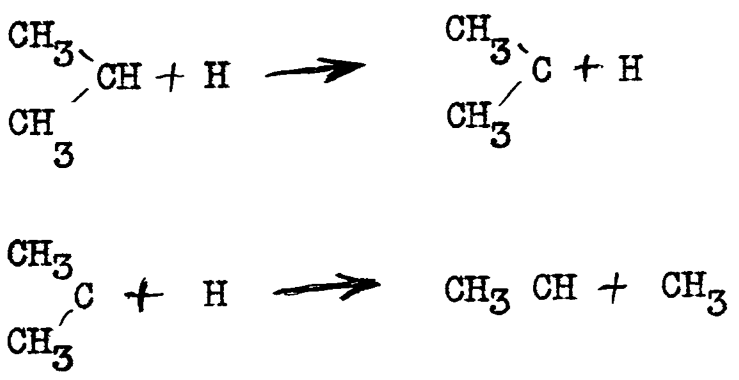


with activation energy of 11.5 ± 2 Kcal.

Secondary



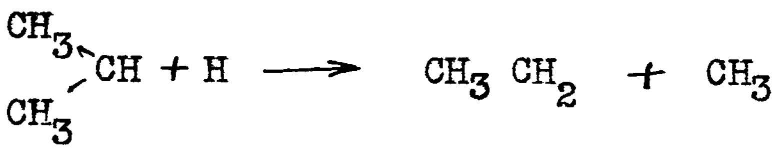
followed by



$$CH_3\quad CH + H \longrightarrow CH_3 + CH_2$$

and hydrogenation of CH_3 and CH_2 to CH_4

Alternative



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!CH + H \longrightarrow CH_3\,CH_2 + CH_3$$

followed by

$$CH_3\,CH_2 + H \longrightarrow 2CH_3$$

$$CH_3 + H(+M) \longrightarrow CH_4$$

The bearing of this last proposal on current opinion of the reaction between ethyl radicals and hydrogen molecules at high temperatures has been discussed.

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