PRIMARY PROCESSES
IN THE REACTIONS
OF
GASEOUS HYDROCARBONS

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Norman William Frederick Phillips, M.A.

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CONTENTS

A. INTRODUCTION[a]

Studies of photochemical and atomic processes are of the greatest importance to the elucidation of the mechanism of thermal reactions. The application of these powerful modes of attack has, owing to the lack of suitable experimental techniques, until recently been limited to the more simple compounds. Lately, however, the development of improved light sources and more precise and comprehensive methods of analysis, together with the use of isotopes for the labelling of atoms in reactions, have greatly extended the scope of these methods.

The Mechanism of Thermal Decomposition Reactions

There is at present considerable uncertainty concerning the manner in which nearly all hydrocarbons decompose. For example, consider the pyrolysis of ethane to yield ethylene and hydrogen. There are two chief mechanisms by which this process might occur:

(a) The molecular mechanism.

In this case the ethane molecule would split into its final stable decomposition products in a simple step,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

This involves the simultaneous rupture of two valence bonds and the formation of two new ones. Obviously, therefore, the

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(a) Some of the material in this introduction has been used by Steacie in "The Kinetics of Reactions of the Simple Hydrocarbons" appearing in Chemical Reviews probably in April 1938.

activation energy of the process will bear no simple relation to the bond strengths.

(b) 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,

$$C_2H_6 \longrightarrow 2CH_3$$

and that these radicals undergo secondary reactions which ultimately lead to the formation of ethylene and hydrogen. If this mechanism is true, and if the later reactions are very fast compared with the primary step the activation energy will be a direct measure of the bond broken in the primary step, the C-C bond.

That all organic compounds decompose by such a mechanism has been postulated by F. O. Rice (1). To maintain this theory it is first necessary to demonstrate the existence of free radicals. Paneth and Hofeditz (2) had already accomplished this when they showed that free radicals produced by the decomposition of organic compounds at high temperatures could be detected in a rapidly flowing gas stream by their reaction with a lead mirror to form volatile organo-metallic compounds. Following on this discovery, Rice and his co-workers (3) made a comprehensive investigation of organic decomposition reactions from this point of view.

Because of the low pressures and very fast flow rates it is necessary to employ in such experiments, decompositions must be carried on at temperatures which are about 300° higher than those at which the ordinary thermal reaction can be studied. Therefore, while it is certain that radicals are present at very high temperatures, such tests do not conclusively prove their presence during ordinary thermal decomposition at lower temperatures.

The greatest successes of the theory have been in predicting the products of organic decomposition reactions (4), especially those of the hydrocarbons. The observed activation energies of most organic substances lie between 35 and 70 kcal. Rice notes that if two reactions have activation energies differing by 4 kcal., then the relative rates at 600°C are in the ratio $e^{-4000/2 \times 873}$ to 1, i.e. 9 to 1. Similarly for 10 kcal. difference the rates will be in the ratio 500 to 1. Hence it follows, that if there are two or more possible modes of decomposition of a compound, and if one of these has an activation energy 10 kcal. or more lower than that of any of the others, it alone will occur to any appreciable extent.[a]

The values of the strengths of the C-C, C=C, C-H and C≡C bonds are still somewhat uncertain. However it is certain that the C=C and C≡C bonds are by far the stronger, and it appears probable that the C-H bond is about 15 kcal. stronger than the C-C bond (5). It may therefore be concluded that if

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(a) That this argument is of general validity is because that in practically all reactions A, the non exponential factor in the reaction rate, is approximately constant and equal to within a factor of 10 to about 10^{13}.

the decomposition of a hydrocarbon occurs through free radical formation it will always split at a C-C bond, and never at a C-H or a double or triple bond.

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

$$C_3H_8 \longrightarrow CH_3 + C_2H_5$$

Now, methyl and ethyl radicals only can be detected by the Paneth technique, presumably because higher radicals when formed decompose very rapidly into unsaturated compounds and CH_3, C_2H_5 and H. In general some activation energy will be required for subsequent steps, but this is supposed to be much smaller than that required for the primary split. Continuing the scheme for propane we have the following, R denoting a methyl radical or an H atom,

(1) $CH_3CH_2CH_3 \longrightarrow CH_3 + CH_3CH_2$

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

(2b) $CH_3CH_2CH_2 \longrightarrow C_2H_4 + CH_3$

(3a) $CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CHCH_3$

(3b) $CH_3CHCH_3 \longrightarrow CH_3CH{=}CH_2 + H$

On a probability basis, considering that propane possesses 6 primary hydrogens to two secondary, one would expect (2) to be faster than (3) in the ratio of 3 to 1. However, on the basis that secondary hydrogen atoms are somewhat less strongly bound Rice estimates that (2):(3)::6:4. Hence, neglecting all but the chain carrying steps we have for the overall decomposition

$$
\begin{array}{l}
6C_3H_8 \longrightarrow 6C_2H_4 + 6CH_4 \\
\underline{4C_3H_8 \longrightarrow 4C_3H_6 + 4H_2} \\
10\ C_3H_8 \longrightarrow 6C_2H_4 + 6CH_4 + 4C_3H_6 + 4H_2
\end{array}
$$

On the whole this method has been quite successful in predicting the products of simple organic decompositions.

It would not be possible, however, to accept the free radical theory on this basis alone. The kinetics of the process must be explained, and it thus becomes necessary for the theory to answer two major questions:

(a) If the overall process is really the summation of a complex series of reaction steps, how is it that experimentally first order rates are found?

(b) Seeing that, in the majority of cases the breaking of a C-C bond is postulated as the initial step, how is it that the measured activation energies for decomposition reactions are usually much smaller than the strength of this bond?

Rice and Herzfeld (6) answered these questions by showing that mechanisms could be devised on a free radical basis which would lead to a first order overall rate. Also, by a judicious choice of the activation energies of the reactions, the apparent activation energy 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 (7):

		E kcal.
(1)	$M_1 \longrightarrow R_1 + M_2$	80

		E kcal.
(2)	$R_1 + M_1 \longrightarrow R_1H + R_2$	15
(3)	$R_2 \longrightarrow R_1 + M_3$	38
(4)	$R_1 + R_2 \longrightarrow M_4$	8

It is assumed that the molecule M_1 decomposes into a radical R_1 and a molecule M_2. The radical R_1 thus formed, reacts with a fresh molecule of the reactant, removing an hydrogen atom and forming the stable product R_1H and the new radical R_2. Subsequently R_2 decomposes yielding a molecule M_3 and reforming the radical R_1. Reactions (2) and (3) thus constitute a chain process, since they will recur over and over again until the radicals are removed by recombination by some such reaction as (4).

It will be shown that such a series of steps in which the chains are terminated by reaction (4) will give a first order expression for the overall rate. That this is somewhat arbitrary is illustrated by the fact that if the chain terminating mechanism had been assumed to be

$$2R_1 \longrightarrow M_5$$

the overall order would be 3/2 while if

$$2R_2 \longrightarrow M_6$$

completely predominated, 1/2 would result. However, since the experimentally determined rates are generally only very approximately first order, it does not seem too far fetched that a random combination of the chain terminating steps might be made to fit most cases.

Assuming that long chains are formed we may set up the equations giving the concentrations of the radicals in the steady state as follows:

$$(5)\quad \frac{d}{dt}[R_1] = 0 = K_1[M_1] - K_2[R_1][M_1] + K_3[R_2] - K_4[R_1][R_2]$$

$$(6)\quad \frac{d}{dt}[R_2] = 0 = K_2[R_1][M_1] - K_3[R_2] - K_4[R_1][R_2]$$

Now the overall rate of decomposition of M_1 is given by

$$(7)\quad -\frac{d}{dt}[M_1] = K_1[M_1] + K_2[R_1][M_1]$$

From these equations it is obvious that

$$-\frac{d}{dt}[M_1] = K_1[M_1]\left(1 + \sqrt{K_2K_3/2K_1K_4}\right) \sim [M_1]\sqrt{\frac{K_1K_2K_3}{2K_4}},$$

i.e. the reaction is first order.

Further

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

whence substituting the values of E given for the part reactions one gets

$$E \text{ overall} = 62.5 \text{ kcal.},$$

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

Until upheld by detailed experimental tests, mechanisms of this sort are, of course, highly speculative. The fundamental idea of free radical chain reactions has, however, been given striking support. Frey (8) was able to start chains in butane at temperatures below its normal decomposition range by adding methyl radicals produced by decomposing dimethyl mercury. Similarly, Allen and Sickman (9) showed that methyl radicals from the decomposition of azomethane could cause the chain decomposition of acetaldehyde. Leermakers (10) also produced sensitized chain decomposition of methyl ether at temperatures below 400°C by photolysing admixed acetone. These observations, however, merely show that chains <u>can</u> be set up by free radicals, and do not prove that free radicals are present and actually do set up chains during the normal slow decomposition of the substances concerned.

The work of Stavely and Hinshelwood (11) and others (12) furnishes additional evidence for the chain character of a number of decompositions. It was found that while large amounts of nitric oxide catalyse many reactions, small amounts caused some inhibition. Their assumption is that the maximum inhibition corresponds to the complete suppression of the chains normally present. On this basis they are able to calculate chain lengths from 2 to 15 for a number of decompositions. These chain lengths are in general too small to satisfy the mechanisms of Rice and Herzfeld. The arbitrary method of calculation however makes the quantitative application of the results somewhat doubtful although there is no question that the work constitutes a fine piece of evidence for the presence of chains.

Additional work on several reactions (13) seems to indicate that a few long chains are present rather than a large number of short ones and that the substances may decompose by both a chain and molecular mechanism.

It can thus be seen that a large body of information exists in general support of the Rice free radical theory for the decomposition of hydrocarbons. Specific confirmation of its details, e.g. the Rice-Herzfeld mechanisms, however, is lacking.

The foregoing discussion makes it evident that a knowledge of the "elementary" reactions of the hydrocarbons is necessary to unravel the kinetics of their thermal reactions. Separate methods of obtaining information on the processes of hydrogen atoms and organic radicals will therefore be of great importance. Such information is frequently forthcoming from from photochemical investigations. Indeed the reactions of atoms and radicals serve as the means of relating thermal and photochemical kinetics. Of course the two types of reaction possess quite different modes of activation; one involves a collisional process, while in the other the absorption of light by a particular molecular group takes place. But once the primary step has occurred, the subsequent stages of a photochemical reaction are thermal reactions which often involve atoms and radicals.

Since the simple hydrocarbons are transparent down to the extreme ultra-violet, and there are considerable difficulties involved in working in the Schumann region, most photochemical decompositions on these substances have been done by photosensitization with mercury vapour. In this type of work the reactant gas saturated with mercury vapour at around room temperature is illuminated with mercury resonance radiation.

Mercury possesses two resonance lines, one at 1849 Å and the other at 2537 Å. In practice the shorter line is almost completely absorbed by the quartz reaction vessels and jackets of the light sources. Thus there is only one line which is appreciably absorbed by the mercury vapour in the system, normal mercury atoms (6^1S_0) being raised to the 6^3P_1 level. These excited mercury atoms may then transfer their energy by collision with other molecules. If efficient transfer results, a wide variety of reactions may occur (14) since $Hg(6^3P_1)$ lies 4.8 volts or 112 kcal. above $Hg(6^1S_0)$ which is greater than the activation energy of almost all chemical reactions.

The mercury photosensitization method is of especial importance because it allows one to investigate reactions involving hydrogen atoms. This was first demonstrated in the classical work of Taylor and his co-workers (15). The following scheme illustrates the application of the method when we illuminate a mixture of hydrogen and the other reactant in the presence of mercury vapour:

(1) $Hg(6^1S_0) + h\nu \longrightarrow Hg(6^3P_1)$ (a)

(2) $Hg(6^3P_1) + H_2 \longrightarrow HgH + H$

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

(4) $2H + M \longrightarrow H_2 + M$

(a) Reaction (2) may be
$Hg(6^3P_1) + H_2 \longrightarrow Hg(6^1S_0) + 2H$
although the evidence (16) for it is not so probable as that involving the mercury hydride formation. In any event only a trivial change is involved in the numerical calculations but no general principles are affected.

where M is a third body. If reaction (3) is not too fast, a stationary concentration of H atoms exists, and if the intensity of illumination and rate of recombination of H atoms are known, the velocity constant of (3), (17), can be calculated. This method is of wide applicability. However since many Hg-photosensitized hydrocarbon decompositions yield hydrogen, it makes it exceedingly difficult to study such processes in absence of the H atom reaction which will generally predominate as soon as a few percent of hydrogen are formed.

It appears possible that this difficulty may be obviated by the use of cadmium resonance radiation. Recently Steacie and Potvin (18), following on the pioneer work of Bates and Taylor (19), have developed a powerful and convenient source of Cd resonance radiation. The first cadmium resonance line is at 3261 Å which corresponds to 89 kcal. This is powerful enough to break the C-C bond (80 kcal.) but has not the necessary energy to dissociate the hydrogen molecule (103 kcal.). However it should be remarked that work by Bender (20) indicates that the reaction

$$Cd(5^3P_1) + H_2 \longrightarrow CdH + H$$

may take place.

The reactions of hydrogen atoms can be investigated in a much more direct way and under a different set of experimental conditions by the Wood-Bonhoeffer method. Wood (21) was the first to demonstrate that under certain conditions

H atoms could be pumped out of a hydrogen discharge tube in high concentrations and carried for considerable distances before recombination occurred. Later Bonhoeffer (22) adapted this method to the study of H atom reactions, and subsequently a great number of reactions have been investigated by this method (23).

The following section will review the available data[a] on the atomic and photo reactions of the aliphatic hydrocarbons.

The Photochemical and Atomic Reactions of the Aliphatic Hydrocarbons

Methane

The Photo- and Photosensitized Reactions

In a preliminary communication Leighton and Steiner (24) report experiments on the decomposition of methane by the light from a hydrogen lamp near the lower limit of the fluorite region. Hydrogen and unsaturated hydrocarbons were formed in the approximate mol proportions of 4:1. No direct determination of the quantum yield was made but a "crude estimate" based on a comparison of the rate of ozone synthesis in the same cell indicated a value in the order of unity. They remarked that in consideration of the large proportion of hydrogen the processes

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(a) For the purpose of creating a logical presentation many of the papers appearing subsequent to the beginning of this work will not be referred to until the discussion in Section E.

$$CH_4 + h\nu \longrightarrow CH_2 + H_2$$

$$2\ CH_2 \longrightarrow C_2H_4$$

could not be the only ones involved.

The complete results of a thorough investigation have recently been reported by Groth (25) subsequent to a preliminary note by Groth and Laudenklos (26). They used as a source a Harteck xenon lamp (27) which produces strong lines at 1469 Å and 1295 Å. A 30 mm. layer of methane at atmospheric pressure was found to absorb completely at 1295 Å and to the extent of 13% at 1469 Å. The reaction products consisted chiefly of hydrogen and acetylene with smaller amounts of ethane, ethylene and higher hydrocarbons. The quantum yield for the production of hydrogen varied from an initial value 0.35 to 0.5 when 6.5×10^{19} quanta had been absorbed. In contrast to this increase of rate with radiation time the hydrocarbon production decreased from an initial value of 0.17 molecules per absorbed quanta to 0.10 molecules per absorbed quanta for the same total radiation. In consideration of the low quantum yield the reaction

$$CH_4 + h\nu \longrightarrow CH_2 + H_2$$

is assumed to be extremely unlikely and

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

is suggested, the following secondary reactions accounting for all the products,

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

$$CH_3 + CH_3 \ (+M) = C_2H_6 + (M) \qquad (3)$$

$$CH_3 + CH_3 = C_2H_4 + H_2 \qquad (4)$$

$$CH_3 + CH_3 = CH_4 + H_2 \qquad (5)$$

$$CH_3 + H = CH_2 + H_2 \qquad (6)$$

$$H + H + M = H_2 + M \qquad (7)$$

$$CH_2 + CH_2 + (M) = C_2H_4 + (M) \qquad (8)$$

$$CH_2 + CH_2 = C_2H_2 + H_2 \qquad (9)$$

$$CH_2 + H = CH + H_2 \qquad (10)$$

$$CH + CH = C_2H_2 \qquad (11)$$

A brief investigation of the direct reaction has been recently reported by Kemula and Dyduszynski (28) employing the shorter wave lengths of a mercury lamp ($\cong$ 1850 Å).

Previous to the initiation of this research, all investigators (29) had found methane to be stable in the presence of mercury atoms excited by resonance radiation. Further work indicating a measurable rate for the reaction

$$CH_4 + Hg(6^3P_1) \longrightarrow CH_3 + H + Hg(6^1S_0)$$

will be discussed in Section G.

<u>The Reaction of H Atoms with Methane</u>

In investigating the reaction of H atoms produced by a Wood's tube with hydrocarbons, Bonhoeffer and Harteck (30) found that methane was surprisingly stable and could detect no reaction.

These results were confirmed by v. Wartenberg and Schultze (31). In addition they found that no appreciable heat was developed on mixing hydrogen atoms and methane (apart from the normal amount due to atomic recombination). Further confirmation of the inertness of methane was furnished by the work of Chadwell and Titani (32).

Geib and Harteck (33) studied the process over a temperature range and showed that no reaction occurred up to 183°C. On the basis of this result they concluded that the reaction

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

has an activation energy of at least 17 kcal. An alternative suggestion was that this reaction takes place easily, but the reverse reaction

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

occurs with a greater velocity than all other possible reactions of the methyl radical such as

$$2CH_3 \longrightarrow C_2H_6,$$

so that methane is regenerated as rapidly as it is consumed. Such a suggestion was ruled out by Geib and Harteck on the grounds that (a) it is improbable that no other secondary reactions of the methyl radical should occur, and (b) the introduction of methane causes no significant change in the H atom concentration, whereas the above mechanism would involve consumption of hydrogen atoms by both the forward and back reactions.

This second objection could be overcome if as a secondary reaction

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

could occur with a low enough activation energy. As this has been variously estimated (34) to be from 8 to 23 kcal. the issue is somewhat in doubt.

The first investigation of the deuterium atom reaction was made by Taylor, Morikawa and Benedict (35) the atoms being produced by photosensitization with mercury, and the resulting deutero methanes determined by infra-red spectroscopy. Considerable reaction from 40° to 300°C was reported and the conclusion made that the activation energy of the process was very low, of the order of 5 kcal. The results were communicated in only a preliminary note, and their more complete investigation referred to in Section *E* does not confirm this work.

The same reaction was investigated by the Wood-Bonhoeffer method by Geib and Steacie (36). No detectable reaction of deuterium atoms with methane was found up to 100°C, indicating an activation energy for the exchange reaction of not less than 11 kcal. in sharp contrast to the above results. Their investigation shows that the reaction in question is very probably an analogue of the ortho-para hydrogen conversion, viz.

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

Whatever the mechanism, however, a lower limit of 11 kcal. is set for both reactions.

Ethane

The Photo- and Photosensitized Reactions

The only work reported on the direct photo reactions is a qualitative investigation by Kemula and Dyduszyński (37) employing radiation from a mercury arc at a wave-length of about 1850 Å. The formation of hydrogen and unsaturates was noted.

A few investigations, however, have been made on the mercury photosensitized reaction. Taylor and Hill (38) were first to make observations on the decomposition of ethane. They noted that when ethylene-hydrogen mixtures saturated with mercury vapour were illuminated with resonance radiation ethane and higher hydrocarbons were formed. After the pressure change accompanying the 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 (39) 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 (40), following on the earlier work of Tolloczko (41). In their investigation the reaction mixture was circulated through a trap at -80°C in an attempt to remove the products of higher molecular weight as fast as formed, and thus prevent secondary processes.

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 at the least 3:1 and approaching infinity if the trap were kept at -20°C instead of -80°C. The condensable products were analyzed by a very 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 (42) had previously suggested that the mechanism of the process was

$$2C_2H_6 \longrightarrow 2C_2H_5 + 2H \longrightarrow C_4H_{10} + H_2$$

$$C_2H_6 + C_4H_{10} = C_2H_5 + C_4Hg + 2H$$

$$= C_6H_{14} + H_2, \text{ etc.}$$

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

$$C_2H_6 + Hg^* \longrightarrow C_2H_6^* + Hg$$

$$C_2H_6^* \longrightarrow C_2H_5 + H$$

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

$$2H + M \longrightarrow H_2 + M$$

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

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

The higher hydrocarbons then result from secondary reactions of butane, etc. The fact that octane appears to be the chief higher product makes it plausible that the chief reaction of butane is

$$C_4H_{10} \longrightarrow C_4H_9 + H$$
$$2C_4H_9 + M \longrightarrow C_8H_{18} + M$$

The chief fallacy in this work and all other mercury photosensitized studies of the hydrocarbons has been the complication of the reaction under study by secondary processes. The difficulties introduced by secondary reactions, in attempts to unravel the mechanism of any chemical process, although by no means slight, are particularly troublesome here. Table I shows the values of the effective quenching areas for some hydrocarbons and hydrogen after Bates (43) and Zemansky (44). The last column shows the percentage of product molecules required to be present in an ethane mixture to absorb an equal amount of radiant energy. In addition qualitative investigations have shown that higher hydrocarbons decompose at a more rapid rate than ethane (45). As mentioned before, under the conditions of reaction hydrogen produces H atoms which have been shown by independent methods to react with hydrocarbons (46). It therefore follows, that in all mercury photosensitized hydrocarbon decompositions, unless the products are removed as fast as formed, no reasonably accurate estimate of the initial products of reaction or of their rate of formation can be made.

In part Kemula and his co-workers must have realized

TABLE I

The Quenching of Resonance Radiation

Compound	Mean quenching Diameter	Percentage required in ethane-gas mixture so that the gas will quench one half the $Hg(6^3P_1)$ atoms.
hydrogen	$8.60 \times 10^{-16} cm^2$	1.7%
methane	0.0852	84
ethane	0.594	--
propane	2.32	24
butane	5.88	12
deuterium (76)	12.0	1.7

this, hence the trapping at -80°C. However at this temperature the vapour pressure of butane is 11 mm. and that of propane 118 mm. No methane nor hydrogen was removed. For methane this is not serious as it is quite inactive at room temperature. Nevertheless, in view of the facts cited above, combined with the additional information that all their products contained large amounts of hydrogen in the gas phase, it must be concluded that the reaction which they studied was almost entirely the H atom reaction accompanied by the subsequent decomposition of propane and butane.

<u>The Reaction of H Atoms with Ethane</u>.

It was found by Bonhoeffer and Harteck (47) and v. Wartenberg and Schultze that luminescence occurs on mixing hydrogen atoms with ethane, bands due to CH and CC being observed. In spite of this the major part of the ethane was recovered unchanged. The latter authors found that there was a considerable loss of gas in their experiments (up to 25 percent), which might have been due to methane formed in the reaction. This, by their technique, would have been lost on passage through the liquid air trap. On the evidence that the hydrogen atoms were almost completely destroyed they suggested

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

as the main process. As a complex mixture of products is not formed, it is evident that the emission of the CC and CH bands is caused by the presence of only relatively small quantities of CC and CH produced by secondary reactions or by impurities. If dehydrogenation to CC and CH were the chief processes it is improbable that these could be quantitatively hydrogenated back to ethane without the formation of some additional products.

During the course of another investigation two experiments on the reaction of hydrogen atoms with ethane were made by Chadwell and Titani (48). They found:

(a) 25 cc. of C_2H_6 gave 5% CH_4, 1.4% CO_2, 1.6% C_2H_4

(b) 150 cc. of C_2H_6 gave 3% CH_4, 3% CO_2, 1.7% C_2H_4

The carbon dioxide must come from the action of water or phosphoric acid used as a poison for the walls of the apparatus. They suggest that the gas lost in the investigation of v. Wartenburg and Schultze was ethane rather than methane. It might be expected that some ethane would be lost under the latter authors' experimental conditions. It is difficult to understand why this was not definitely shown by the performance of a few blank runs. However, it should be noted that Kemula (49) employing the mercury photosensitized H atom method found some methane.

Higher Hydrocarbons

Comparatively little work has been done on the atomic or photochemical reactions of the higher hydrocarbons. Recently Kemula and Dyduszyński (50) decomposed propane and butane in the light of a mercury lamp at a wave length of $\cong$1850 Å. The formation of hydrogen and unsaturated compounds was noted. In their classical work on mercury photosensitized decompositions, Taylor and Hill (51) found that propane reacts more rapidly with hydrogen atoms than does ethane, but more slowly than butane. The mercury photosensitized reactions of n-pentane were investigated by Klemenc and Patat (52) and by Frankenburger and Zell (53). The products were found to consist of hydrogen, methane and higher hydrocarbons. Similar results were obtained by Taylor and Bates (54) on the mercury photosensitized decomposition of n-hexane. A few brief preliminary experiments on the reaction of D atoms with propane and n-butane have been reported by Trenner, Morikawa and Taylor (55). The results of this investigation will be referred to in Section E.

B. THE MERCURY PHOTOSENSITIZED EXCHANGE REACTION BETWEEN DEUTERIUM AND METHANE

In consideration of the large discrepancy (see page 16) between the results of Taylor, Morikawa and Benedict (35) and of Geib and Steacie (36) concerning the activation energy of the reaction

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

a preliminary investigation using the mercury photosensitization method was begun.

Experimental

The apparatus employed was of the usual static type. The reaction vessel, a cylindrical fused quartz bulb of about 140 cc. capacity, was arranged so that measured amounts of various gases could be introduced and the pressure could be continuously observed. It contained a small pool of mercury. The vessel was immersed in a thermostat filled with distilled water at 23°C.

The light source was a Hanovia quartz mercury vapour rare gas discharge tube Sc-2537. The lamp was a double -U grid type operating at 320 volts and 100 milliamperes from a 5000 volt Jefferson sign transformer. With this lamp almost all the emitted light is in the resonance line at 2537A. The light passed through a quartz tube, cemented into the side of the thermostat, filled with 25 percent acetic acid solution (56).

This serves to remove the radiation below 2300 Å to which methane may be sensitive. The tube thus acted as a window, a condensing lens, and a filter. This arrangement was not very efficient, and reflection losses from the cylindrical vessel were very high. As a result the intensity was low considering the source used, and rather long exposures were necessary.

The intensity of the absorbed radiation was inferred from measurements of the rate of the mercury photosensitized synthesis of water from hydrogen-oxygen mixtures. It was assumed that 5 molecules of (hydrogen + oxygen) disappeared per quantum of light absorbed (57). An average value of 8.77×10^{12} quanta per cc. per second was found.

In general deuterium was in considerable excess, the experimental mixture being usually about $4D_2 + 1CH_4$. The large excess of deuterium employed diminished the effect of the back reaction to a great extent and yet the quantity of methane was ample for analysis. The total pressure was in the neighbourhood of 50 cm. After illumination the reactant was separated from hydrogen, burned and the deuterium content of the water determined.

Since liquid hydrogen was not available, methane was separated from the reactant mixture by preferential absorption with silica gel at -183°C. This had previously been used in a flow system at low pressures by Geib and Steacie (36). As it was at first not realized how sensitive the method was to experimental conditions, satisfactory results were not immediately achieved. The apparatus is shown in figure 1 together with a diagramatic sketch of the analytical set-up. The technique of separation was developed as follows:

(A) The methane-hydrogen mixture was allowed to come in contact with alumina at -183°C gel for 10 minutes. After evacuation with an oil pump for 10 minutes, the gel was warmed to -80°C and the methane desorbed into the combustion bulb. Since desorption was carried out at -80°C, there was no danger of contamination from traces of residual water which might have been present on the gel. The appropriate pressure of commercial tank oxygen was then admitted through a liquid air trap. After combustion the products were pumped through trap T_1 or T_2 where water vapour was condensed at -80°C.

(B) As in (A) but using silica gel.

These procedures gave rather high blank values, i.e. accomplished only at partial separation, as is shown in Table II, so the procedure was modified as follows:

(C) The gases were pumped through silica gel at -183°C and the pumping was continued for 10 minutes. The methane was desorbed at -80°C and combusted as before.

(D) As in (C) but using higher pumping speeds.

The separations thus effected were quite satisfactory, the blanks being reduced to 1 or 2 percent.

The method employed to determine the deuterium content of the water formed was one due to Harteck(a), (58). This con-

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(a) Private communication.

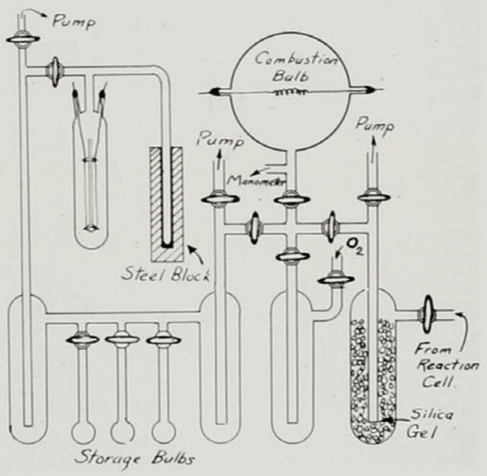

FIGURE I

Apparatus for the analysis of exchanged methane for deuterium content.

sists of measuring the heat conductivity of the saturated water vapour at the temperature of the ice-salt eutectic. The heat conductivity of deuterium oxide is thus lower than that of water on account of its lower vapour pressure, as well as on account of its higher molecular weight. The heat conductivity was measured by means of a Pirani gauge of the usual type containing a platinum wire with a thickness of 10 mu, the gauge being immersed in a well stirred ice-water bath. The resistance of the platinum filament at constant potential, and under the above conditions is a linear function of the deuterium content of the water employed. In making measurements, readings with ordinary water and with the water being analyzed were made alternately. The values reported are the mean of a number of separate determinations. In using this method precautions were taken to ensure that the water being analyzed was entirely free from gaseous impurities. The water resulting from the combustion was therefore re-distilled approximately ten times in high vacuum back and forth from traps T_1 and T_2 and was condensed each time at a temperature of approximately -60°C.

Deuterium was prepared by the electrolysis of 99.3% heavy water rendered slightly alkaline with sodium hydroxide. The electrolysis was commenced in a vacuum, and the oxygen and hydrogen were collected separately. The deuterium was passed through a furnace at 600°C containing platinized asbestos to free it from any oxygen. It was then passed through a liquid air trap to remove water, and was stored in a 5 liter glass bulb.

The gas was transferred from this vessel to the reaction vessel by means of a small Toepler pump.

Methane was procured in cylinders from the Ohio Chemical and Manufacturing Company. As it was only about 80 percent pure considerable treatment was necessary. It was therefore purified according to the directions of Moser (59) with the exception that Fieser's (59a) solution was employed in place of the usual alkaline pyrogallate. This procedure consisted of passage of the gas through ammoniacal cuprous chloride, dilute and concentrated sulphuric acid, a 50 cm. column of copper oxide at 300°C, concentrated potassium hydroxide solution, and Fieser's solution. In addition it was dried by passage through a trap at -80°C, and fractionated several times.

Results

The results are given in Table II.

In order to calculate the collision yield and hence the activation energy, it is first necessary to evaluate the stationary concentration of deuterium atoms produced by the illumination.

The initial reactions

$$\mathrm{Hg}\ (6^1S_0) + h\nu \longrightarrow \mathrm{Hg}\ (6^3P_1)$$

$$\mathrm{Hg}\ (6^3P_1) + D_2 \longrightarrow \mathrm{Hg}\ (6^1S_0) + 2D$$

can be directly evaluated, since the light intensity has been determined by the hydrogen-oxygen actinometer. The fraction of excited mercury atoms deactivated by methane can be calculated

TABLE II

The Photosensitized Reaction between Deuterium and Methane

Temperature 23°C

(1) Run No.	(2) Time Illumination (sec.)	(3) P_{D_2} (cm)	(4) P_{CH_4} (cm)	(5) Method of Analysis	(6) D Content of Methane (%)
1	0.95×10^5	39.6	9.5	A	4.5
2	0	37.5	10.5	A	6
3	4.08×10^5	45.0	10.0	B	11.5
4	1.58×10^5	52.5	12.5	B	4.5
5	3.81×10^5	39.2	14.4	B	6
6	0	39.0	13.0	B	7
7	0	40.0	14.0	C	3
8	5.68×10^5	39.6	10.8	C	6
9	0	39.8	11.2	C	2
10	0	42.2	11.3	D	1
11	2.25×10^5	38.9	12.6	D	4.5

TABLE II - (continued)

Run No.	(7) D Atom Concentration (moles cc)	(8) Fraction of Methane Converted per sec.	(9) Collision Yield	(10) Collision Yield	(11) E (Kcal)	(12) E (Kcal)
1	$\sim 6\times10^{-12}$	$< 10^{-6}$	--	--	> 11	> 10
2	--	--	--	--	--	--
3	5.8×10^{-12}	4.5×10^{-7}	2.6×10^{-10}	2.6×10^{-9}	11.6	10.3
4	$\sim 6\times10^{-12}$	$< 10^{-6}$	--	--	> 11	> 10
5	$\sim 6\times10^{-12}$	$< 10^{-6}$	--	--	> 11	> 10
6	--	--	--	--	--	--
7	--	--	--	--	--	--
8	6.5×10^{-12}	2.5×10^{-7}	1.4×10^{-10}	1.4×10^{-9}	12.0	10.7
9	--	--	--	--	--	--
10	--	--	--	--	--	--
11	6.1×10^{-12}	6.0×10^{-7}	3.2×10^{-10}	3.2×10^{-9}	11.4	10.1

to be negligible by the usual formula,

$$\left(1 + \frac{[D_2]\,\sigma^2_{HgD_2}\,\mu^{\frac{1}{2}}_{HgD_2}}{[CH_4]\,\sigma^2_{HgCH_4}\,\mu^{\frac{1}{2}}_{HgCH_4}}\right)^{-1}$$

where σ is the effective collision diameter and μ is the reduced mass of the colliding particles. The values of σ were taken from Table I. On substitution of these and also the approximate ratio of 4 for $[D_2]/[CH_4]$ we obtain a value of about 8×10^{-4} for the fraction deactivated by methane. The initial processes will be followed by

(1) $D + D + M \longrightarrow D_2 + M$

(2) $D \longrightarrow 1/2 D_2$ (wall)

(3) $D + CH_4 \longrightarrow CH_3D + H$ (or other products which use up D atoms)

The reaction

$$H + D + M \longrightarrow HD + M$$

may be neglected, since for small percentage conversions there will be an inappreciable quantity of atomic hydrogen present. Hence we may write

$$\frac{d}{dt}[D] = \frac{2I_{abs.}}{N} - K_1[D]^2[M] - K_2\frac{[D]}{[M]} - K_3[D][CH_4] = 0$$

where N is Avogadro's number, and M is a third body.

The rate of recombination of hydrogen atoms under comparable experimental conditions has been investigated by Farkas and Sachsse (60), who found that at a light intensity of

2×10^{15} quanta cm.$^{-3}$ sec.$^{-1}$ and at pressures higher than 20 cm. the term $K_2[H]/[M]$ could be neglected, and estimated K_1 (for H atoms) to be 3.4×10^{16} cm.^{6} mole^{-2} sec.$^{-1}$ at 24°C. There is some discrepancy between these results and those obtained by discharge tube methods (61). In Farkas and Sachsse's experiments the rate constant given is based on the assumption that "M" is H_2. Smallwood found 1.7×10^{16} for the case where M is a hydrogen atom, and stated that the constant for the reaction $H + H + H_2$ was at least 50 times smaller. The two values for the latter reaction differ, therefore, by a factor of 100. The conditions in the two experiments were, however, widely different, since Farkas and Sachsse worked at pressures of the order of atmospheric and used minute H atom concentrations, while the other investigations were made with high H atom concentrations and pressures of the order of a millimeter.

Since the conditions in this investigation are almost identical with those of Farkas and Sachsse, their value for the rate constant of the reaction $H + H + H_2$ will be adopted. It should be noted that Farkas and Sachsse measured the stationary hydrogen atom concentration and calculated their rate constant from it. Since their values of the rate constant are being employed to calculate the stationary hydrogen atom concentration under nearly identical conditions, we are in effect merely using their measured values of the hydrogen atom concentration. The values calculated in this way should therefore be but slightly influenced by any errors in Farkas and Sachsse's mechanism and calculations, and dependent only on the accuracy of their measurements.

The above discussion refers, of course, to hydrogen, not deuterium. It may be assumed that the only difference between the two will be in the frequency of triple collisions. Tolman (62) has calculated the number of effective triple collisions in a mixture of perfect gases for the case where molecules of kinds (1) and (3) will react if they come within a distance δ of a molecule of kind (2). The result is

$$Z = 8\sqrt{2}\,\pi^{\frac{3}{2}}\; N_1 N_2 N_3\, \sigma_{12}^{\;2}\, \sigma_{23}^{\;2}\, \delta\, (kT)^{\frac{1}{2}} \left(\mu_{23}^{-\frac{1}{2}} + \mu_{12}^{-\frac{1}{2}} \right)$$

where the N's refer to the number of molecules per cc. of each type, the σ's to the average molecular diameters, and the μ's to the reduced masses. It follows from this that the reaction $H + H + M$ should be $\sqrt{2}$ times faster than $D + D + M$(a), the result being the same for an atomic or a molecular third body. Hence for deuterium atoms we will assume for the numerical value of K_1

$$(3.4 \times 10^{16}) \;/\; 1.4 = 2.4 \times 10^{16}$$

Neglecting for the time any loss of D atoms due to wall recombination, we have the necessary data to calculate the stationary deuterium atom concentration. If α is the fraction

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(a) This relation has been confirmed experimentally by Amdur (63), using a discharge tube method. Under these conditions however, atoms, not molecules, were effective third bodies.

of CH_4 reacting per second, then

$$[D] = \left(\frac{(2I_{abs.}/N) - \alpha[CH_4]}{K_1[M]}\right)^{\frac{1}{2}}$$

In Table II, column (7) are the values calculated on this basis.

Since the mean life of the deuterium atoms is $[D] / 2I_{abs.}$ the atom lifetime under the present conditions can be calculated to be 0.2 sec. Employing the diffusion equation

$$(x^2)_{Av.} = 2\underline{D}t$$

where $(x^2)_{Av.}$ is the mean square displacement of the diffusing particle, t its mean life, and where $\underline{D}$, the diffusion coefficient, is given by

$$\frac{4}{3\pi\sqrt{\pi}} \; \frac{\sqrt{\frac{RT}{M}}}{\sigma^2 \quad N},$$

in which σ^2 is the diffusion cross section and N the number of molecules per cc. through which the particles are diffusing, the fraction of the deuterium atoms in the reaction cell which are within diffusing distance of the wall may be calculated. If $\sigma_D{}^2$ is taken as 4×10^{-16} cm^2, at 23°C and a gas pressure of 50 cm., $x_{Av.}$ may be calculated to be $\sim$ 1cm. This means that one-half the atoms in approximately three-quarters of the volume of the reaction vessel are within diffusion range of the walls during their mean lifetime. There is thus some uncertainty in the value of the D atom concentration. One would not expect however that it would be less than one order lower than that calculated on a non-diffusion basis.

Thus, in columns (9) and (10), the collision yield has been calculated assuming both D atom concentrations. This is equal to

$$\alpha / b [D]$$

where

$$b = 2\sqrt{2\pi}\left(\frac{d_D + d_{CH_4}}{2}\right)^2 \sqrt{\frac{M_{CH_4} + M_D}{M_{CH_4}\, M_D}\, RT \cdot N}$$

in which the d's are the diameters of the colliding particles and the other symbols have their usual meaning. Assuming a molecular diameter of 3.75×10^{-8} cm. for methane, and of 2.14×10^{-8} cm. for a deuterium atom (taken as being equal to the collision diameter of a hydrogen atom as found by Harteck (64))

$$b = 3.0 \times 10^{14} \text{ sec.}^{-1} \text{ at } 23°C$$

In calculating E from the collision yield a steric factor of 0.1 has been assumed in conformity with the usual practice. These values are given in columns (11) and (12).

On account of the analytical difficulties previously mentioned, the data for runs 1 to 6 are merely qualitative. Nevertheless they serve to set a lower limit for the activation energy. For, even if the blank correction were omitted entirely, values of approximately 11 kcal. would be obtained. In the last runs, where the blank corrections are smaller, a measurable exchange is established and we obtain more definite values for the activation energy.

In conclusion it is realized that the work reported here is somewhat qualitative. As previously mentioned, it was only a preliminary investigation intended to check the discrepancy between the early results of Morikawa, Benedict and Taylor (35) and those of Geib and Steacie (36). After this had been done a very thorough and complete research was reported by Melville and Farkas (65)[a] confirming the results obtained herein. The work was therefore discontinued.

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[a] For a discussion of this work together with later results by Morikawa, Benedict and Taylor (66) see Section E.

C. THE REACTION OF ATOMIC DEUTERIUM WITH ETHANE

As mentioned previously the work of Bonhoeffer and Harteck (47), v. Wartenberg and Schultze (47), and of Chadwell and Titani (48) on the reaction of hydrogen atoms with ethane demonstrated that under the conditions of their experiments there was appreciable destruction of hydrogen atoms and little decomposition of ethane. It therefore appeared possible that considerable information might be given by investigating the exchange reaction with deuterium under similar conditions.

Experimental

The deuterium was split into atoms by means of a Wood discharge tube.

The main section of the apparatus built of soft glass is illustrated diagrammatically in Fig. 2. A discharge was run through the tube A (3 cm. in diameter). The electrodes E were aluminium cylinders 3 cm. in diameter and 15 cm. long attached to platinum leads and sealed through the apparatus. The discharge was operated on an alternating current of about 3000 volts maintained across the tube with a 5000 ohm resistance in series. The voltage was varied with a step transformer and a rheostat in the primary so as to maintain a constant current of

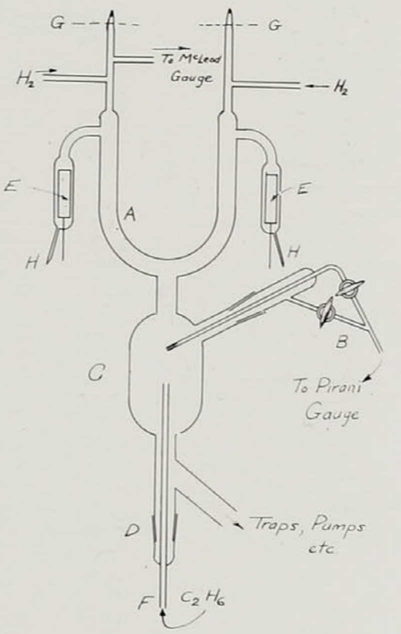

FIGURE II

Apparatus for studying the reactions of D atoms produced by a discharge tube.

325 milliamperes through the tube.

Below the discharge was a reaction vessel C, with a diameter of 7 cm. and a length of 30 cm. Ethane entered the reaction vessel through a tube F.

In work of this kind it is always necessary to poison the walls of the apparatus in order to prevent the recombination of hydrogen atoms at the surface. To facilitate this, the main section of the apparatus was made vertical as indicated. In order to wash the apparatus the tops of the tubes were cut off at G, and the inlet tubes, joint D, and the Wrede gauge B were removed. The tips were then cut off the small drainage tubes H attached to the electrodes. The apparatus was then washed with distilled water, concentrated nitric acid, water again, and finally with a 5 percent solution of phosphoric acid. The tops of the tubes G and the tips of the tubes H were sealed off, the ground joints replaced and the apparatus dried by evacuation to a pressure of 10^{-5} mm.

The hydrogen atom concentration in the reaction vessel was measured with the Wrede gauge B. This was of the usual type (67) and consisted of a tube with a very fine orifice situated in the reaction vessel, and an arrangement of stopcocks such that either the inside or outside of the tube could be connected to the Pirani gauge. This is used to measure the pressure difference set up across the orifice owing to the difference in the diffusion coefficients of hydrogen atoms and hydrogen molecules. From the pressure difference the percentage of atoms in the reaction vessel may be easily calculated, the relation being

$$\% \text{ atoms} = \frac{100(1 - P_z/P_1)}{1 - 1/\sqrt{2}}$$

where p_z = pressure inside, and p_1 = pressure outside of tube.

Deuterium was prepared as described on page 26. By means of the Toepler pump it was put into a small mercury gas-holder and delivered to the apparatus at atmospheric pressure. Ethane was secured in cylinders from the Ohio Chemical and Manufacturing Company and was stated to be 95 percent pure. It was purified by fractional distillation and stored in a large reservoir. The pressure in this vessel governed the rate of flow.

Both gases entered the reaction vessel through calibrated capillary flow-meters. After remaining there about 1 second the mixture passed out of the reaction vessel through the outlet tube L, over some gold foil which destroyed the remaining deuterium atoms, through a trap at liquid air temperature and a three stage steel mercury diffusion pump. This had a very high speed (approximately 20 liters per sec. at the mouth of the pump) and could maintain a pressure of about 0.3 mm. in the apparatus when deuterium was admitted at the rate of about 12 cc. at N.T.P. per minute.

After the gases had passed through the reaction chamber it was necessary to separate the ethane from deuterium. Experiments by Chadwell and Titani (48) have shown that ethane is only 2.5 percent decomposed by H atoms produced in a discharge so that complications of analysis due to additional products may be neglected(a). The vapour pressure of ethane at liquid air temperature was too high, however, to permit a simple freezing out. Also it was impossible to introduce an adsorbent into the main vacuum line, since the resistance thus introduced would cut down the pumping speed enormously and thus raise the pressure. This would impede the operation of the discharge. The reactants were therefore separated by adsorption on silica or alumina gel at -183°C in a trap between the diffusion pump and the oil pump.

At the end of the experiment, which normally lasted about 10 min., the silica gel trap was maintained at -183°C and pumped out for 5 min. with the Hyvac pump alone. Trials showed that it was possible to desorb virtually all adsorbed hydrogen in this way without loss of ethane. The trap was then allowed to warm up to -80°C to desorb the ethane. The ethane was then expanded into a two liter combustion pipette, dry oxygen was admitted, and the ethane was burned on a platinum filament. The resulting water was freed from oxygen and carbon dioxide by repeated distillations at -80°C in a high vacuum. The water was then analyzed for its deuterium content by the thermal conductivity method of Harteck as described on page 26.

Results

Atom Concentration

As was mentioned above, the deuterium atom concen-

(a) As will be shown later however in Section E, this conclusion was not completely justified.

tration was measured with a Wrede diffusion gauge. In order to conserve deuterium, these measurements were made in special calibration experiments using ordinary hydrogen. This introduces no appreciable error for the following reasons:

(a) At a defined pressure the hydrogen flow rate will be greater than that of deuterium and will take less time to get from the discharge tube to the reaction vessel. In this time, however, it will undergo more collisions with the wall because of its higher atomic velocity; These two effects balance.

(b) Also the activation energies of the recombination reactions

$$H + H \rightarrow H_2 \quad \text{(wall)}$$

$$D + D \rightarrow D_2 \quad \text{(wall)}$$

will not differ appreciably since atoms have no zero-point energy.

Hence we may expect the same atom concentration in the reaction vessel irrespective of whether hydrogen or deuterium is used. In any event, any possible error from this source is negligible compared to uncertainties in the atom concentration due to fluctuations in wall activity.

The average atom concentration in a number of calibration runs was 20 percent.

Results of the Reaction of Deuterium Atoms with Ethane.

The results are given in Table III. In column (5)

TABLE III

The Reaction of Deuterium Atoms with Ethane

Deuterium Flow = 0.202 cc/sec. at N.T.P.

Average Atom Content = 20%

(1) Run No.	(2) Remarks	(3) Pressure (mm)	(4) C_2H_6, cc/sec. at N.T.P.	(5) Reaction Time (sec)	(6) P_D (cm)
1	Blank, no discharge	0.27	0.049	1.11	--
2	....	0.28	0.049	1.15	0.0046
3	Blank, ethane alone, D_2 through discharge later	--	0.047	--	--
4	....	0.28	0.044	1.17	0.0047
5	....	0.28	0.044	1.17	0.0047
6	....	0.28	0.037	1.20	0.0048
7	....	0.28	0.034	1.22	0.0048
8	Blank, D_2 through discharge alone, ethane later	--	0.033	--	--

TABLE III - (continued)

Run No.	(7) $Z_{C_2H_6, D}$ ($\times 10^{-5}$)	(8) % D Content of ethane	(9) % Exchange	(10) Collision Yield ($\times 10^{6}$)	(11) E (cal.)
1	--	0.0	0.0	--	--
2	7.8	10.7	18.5	1.5	6400
3	--	0.0	0.0	--	--
4	8.3	14.4	23.7	1.7	6350
5	8.3	16.4	27.0	2.0	6250
6	8.5	19.8	30.6	2.2	6200
7	8.5	17.9	27.0	1.9	6300
8	--	1.0	1.5	--	--

mean = 6300

is given the average time during which a molecule of the reactant is in the reaction space. This is calculated from a knowledge of the amount of gas flowing, the pressure in the reaction vessel, and the volume (920 cc) and the temperature (20°C) of the reaction vessel. A correction is applied for the increase in volume due to the fact that some of the hydrogen is present as atoms. $Z_{C_2H_6,D}$ in column (7) represents the average number of collisions of 1 ethane molecule with deuterium atoms during its time in the reaction vessel. It is calculated assuming a molecular diameter of 3.75×10^{-8} cm. for ethane, and of 2.14×10^{-8} cm. for a deuterium atom (assumed equal to the collision diameter of a hydrogen atom as found by Harteck (64)). The values of the "percent exchange" in column 9 are calculated on the assumption that at equilibrium the distribution coefficient

$$\frac{D/H \text{ in ethane}}{D/H \text{ in hydrogen}} = 1$$

In calculating the collision yields in column (10) allowance has been made for the fact that 6 fruitful collisions are required to convert a molecule of C_2H_6 to C_2D_6. The activation energies in the last column are calculated assuming a steric factor of 0.1.

D. THE MERCURY PHOTOSENSITIZED REACTIONS OF ETHANE

As outlined on pages 12 to 22 no thorough study has been made of the mercury photosensitized reactions of the hydrocarbons. Since methane at room temperature had been reported inactive it was decided to investigate in as precise a manner as possible the reactions of the next member of the series.

Experimental

In the ideal experimental system for the study of photochemical reactions several conditions should be met. Some of these are mentioned below.

(a) Optical System.

The light source should be intense, monochromatic and constant in output. In addition the absorption vessel should be completely transparent to the radiation in use, and its geometrical relation to the lamp should be such that effective utilization of its light can be realized.

(b) Methods of Analysis.

Sensitive and precise methods of analysis should be available to enable a thorough estimation of small amounts of products to be made.

(c) Concentration of Products.

The concentration of the products in the reaction mixture should be kept low enough so that they will not interfere with the primary processes.

The first two conditions are not entirely independent. With a powerful enough light source efficient utilization of its radiation may not be necessary; with sensitive enough methods of analysis a weaker light source may be sufficient, etc.

To what degree these conditions were filled will be seen in the following sections.

Optical System

In dealing with mercury sensitized reactions in addition to the requirements mentioned under (a), "the form of the exciting line or lines must also be known if the kinetics are to be studied in detail in order to derive the correct sequence of reactions comprising the total process". "If the exciting line is not narrow and unreversed, then the effect of added gases and of temperature on the shape of the absorption line of the mercury vapour in the reaction vessel may become so complicated that no real use of this method of initiating reactions can be made kinetically".

"The usual type of mercury lamp having mercury-mercury or mercury-tungsten electrodes with the cathode water cooled suffers from the disadvantages that it is unsteady, generates a considerable amount of heat, radiates lines beside the resonance lines at 2537 Å, 1849 Å and emits, if the water cooling is not efficient, a partially reversed resonance line unless the additional complication of a magnet is employed to press the discharge against the walls of the lamp. Lamps with heated cathodes and tungsten anodes eliminate the majority of these disadvantages, although now it is necessary to control the temperature of the cathode accurately. This disadvantage is not, however, present in discharge lamps containing a mixture of rare gas and mercury vapour and running at some hundreds of volts A. C." (77).

Such a lamp, containing argon, is manufactured by the Hanovia Chemical and Manufacturing Company and styled the Sc-2537 rare gas discharge tube. One of these lamps, which may be referred to as source A, was procured and used in the first part of the work. When operated at 0.100 amperes and 370 volts from a 5000 volt Jefferson sign transformer it emitted 8×10^{-6} einsteins sec.$^{-1}$ at a wavelength of 2537 Å. This is an efficiency of 13 percent in the production of the 2537 line.

Having a strong lamp, utilization of an appreciable fraction of its radiation is not always easy. Interposition of filters to eliminate secondary wavelengths and heat often permit only an arc of few degrees of the total emission to be used. Luckily no filtering of any kind was found necessary in the present instance. The lamp operated at only a few degrees above room temperature and blank experiments showed that in the absence of mercury vapour in the reaction system no chemical changes were observable. The radiation was therefore used without filtering. To utilize the largest possible fraction of the light from the lamp the fused quartz reaction vessel was annular in form, being 10 cm. long, 8 cm. in diameter, with a hole 4 cm. in diameter through the middle. Its volume was 320 cc. A well in the side of the vessel was provided to accommodate a thermocouple. If a cylindrical cell had been used adjacent to the side of the lamp less than 1/50 of the light might have been absorbed. Experiments have shown that cylindrical cells placed in this way cannot utilize an amount of radiation proportional to the angle they subtend from the lamp because of the almost complete reflection losses from tangential and near tangential surfaces exposed to the light beam. For example, Melville and Farkas (78) employing a powerful resonance lamp emitting 10^{19} quanta per sec. could only utilize 5×10^{16} quanta per sec. on placing a cylindrical reaction vessel close to one limb of their lamp. Thus the advantages of an annular cell for efficient absorption of radiation cannot be overemphasized.

For the latter part of the work a very efficient light source-reaction vessel was constructed (referred to subsequently as light source B). Guided partly by the rules and principles followed in the construction of neon signs (79) and by some data published by Melville (77) a system was built in which it was possible to realize in effective resonance radiation 1.0×10^{19} quanta per sec. This is the largest number of quanta per sec. of mercury resonance radiation which has yet been reported employed in a chemical or physical process. The details of construction are shown in Fig. 3. The tube was filled with neon at a pressure of 12 mm. and a small droplet of

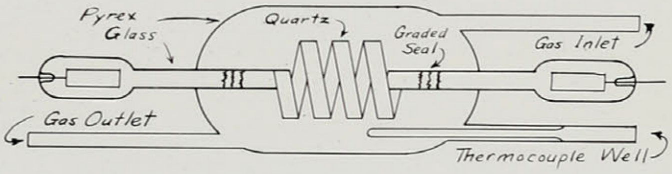

FIGURE III

Light source B.

mercury. The electrodes were coated and supplied by the Claude Neon Eastern Limited, Montreal. The filling and bombarding were done by the usual neon sign technique. The coated electrodes were found to be very cool in operation, the electrode chambers being at a temperature of not greater than 35°C during operation. This is quite an improvement over the Hanovia Sc-2537 tube whose electrode chambers attain a temperature in excess of 150°C. This results in an improved efficiency for the new lamp.

In operation source A was employed only with the reaction system at 35°C, this being the lowest temperature of efficient operation. With source B, however, it was quite convenient when the whole system exclusive of the electrodes was surrounded by a well lagged furnace to extend the range of operations from 65°C to 570°C.

Method of Analysis

A short survey of the literature will soon convince one that the only satisfactory method for the analysis of mixtures of gaseous hydrocarbons is by low temperature fractional distillation. The most convenient method for doing this has been devised by Podbielniak (79). Following his developments an apparatus slightly modified to meet the present requirements was built. The essential parts of the apparatus are illustrated in Fig. 4. With this type of apparatus the sample is condensed into the bottom of the still, the top or

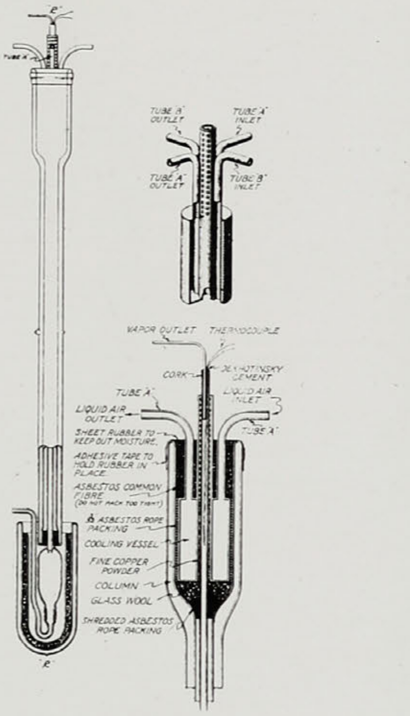

FIGURE IV

Podbielniak Distillation Apparatus.

head being cooled by liquid air. Thence by varying the distance from the bottom of the still of a wide dewar flask cooled by liquid air, and by varying the quantity of liquid air being blown in at the top, the rate of reflux and rate of distillation is controlled. In practice the still is operated at a very high reflux ratio. The temperature of the refluxing liquid is measured at the top of the column by a very fine thermocouple in conjunction with a potentiometer, and the gas is slowly drawn off through an adjustable leak (a filed stopcock) into calibrated glass bulbs, where the volume of the exit gas is estimated by means of a manometer. In distilling gases of lower molecular weight than pentane the pressure is kept at atmospheric as indicated on an auxiliary manometer connected to the still. With careful operation very sharp cuts are obtained, the separations of the different constituents being nearly 100 percent efficient.

Experimental Setups.

To lessen the complications of secondary reactions two experimental systems were used, one a circulatory system and the other a single pass flow system.

Circulatory System

One form of the apparatus employed is shown in Figure 5.

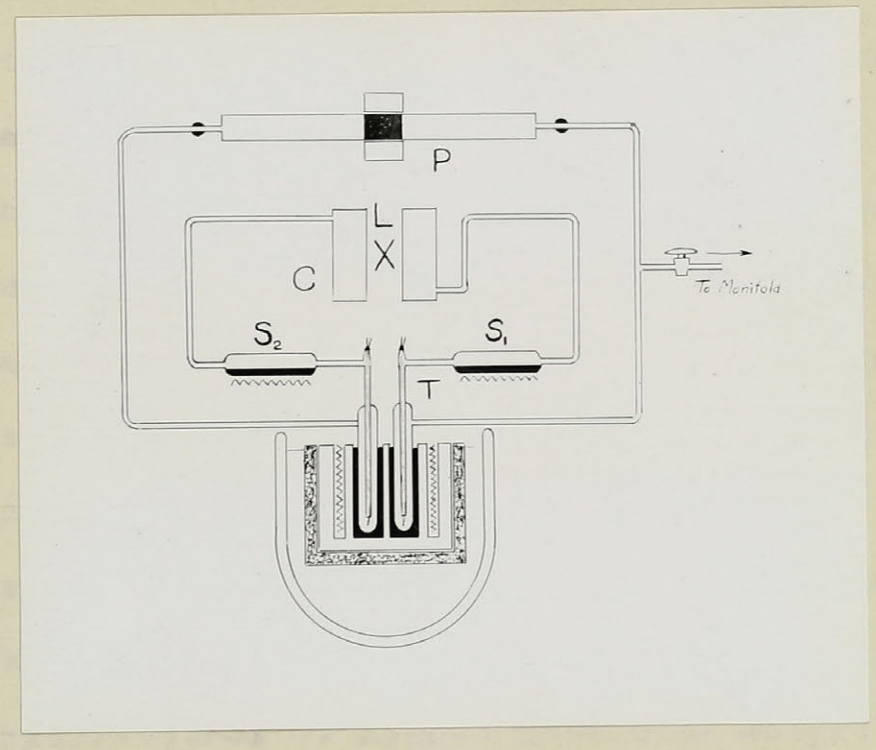

FIGURE V

The circulatory system.

The pump P consisted of a brass tube 40 cm. long and 4 cm. in diameter inside which slid a close-fitting steel cylinder lubricated with di-butyl phthalate. A solenoid of about 1000 ampere-turns was arranged to slide on the outside of the tube, and a reciprocating motion was applied to the solenoid by means of a wheel and crank. The displacement of the pump was 350 cc. so that the entire contents of reaction vessel A were displaced each half cycle.

The saturation of the gas with mercury vapor was accomplished by means of the vessels S_1 and S_2, each of which provided a mercury surface of about 30 cm.^{2} The saturators were heated electrically to about 60°C - 80°C. In addition, a small pool of mercury was kept in reaction vessel A.

As mentioned above, one of the main objects of the present work was the elimination of secondary processes by the removal of hydrocarbons of higher molecular weight from the system as fast as formed. With this end in view, the gases were circulated through the traps T. The method by which these traps were maintained at definite low temperatures for long periods of time was as follows: The traps were immersed in mercury contained in two holes drilled in a steel block. Small electric heaters were inserted in other holes in the same block. The block was surrounded by an insulating layer of cotton encased in a sheet metal container, and the container was immersed in liquid oxygen. By keeping the liquid oxygen level constant, it was possible to maintain the traps at any desired temperature in the range studied. The temperature could thus be controlled to within 1-2°. The temperature of the traps was measured by means of copper-constantan thermocouples situated inside the traps themselves. These were calibrated at the boiling points of oxygen and ethylene, at the sublimation point of carbon dioxide, and from -50° to 0°C by means of standard thermometers.

The main portion of this apparatus had a volume of about 1200 cc. It was connected to a manifold which led to the pumping system, a McLeod gauge, gas reservoirs, a Toepler pump, gas holders, etc.

In later runs some changes were made which added to the convenience of operation, without however greatly affecting the results of the experiments. Mercury valves were employed which made it possible to circulate the gas continuously in one direction. Thus it was only necessary to use one trap and one saturator, the consumption of refrigerant being very greatly reduced. Other improvements included: (1) The insertion of a trap (volume 100 cc. and packed with iron pellets 2 mm. in diameter) after the mercury vapour saturator to control accurately the mercury vapour pressure. (2) For the purpose of regulating the temperature of the trap, the arrangement previously described was replaced by a double-walled Pyrex glass container. The interior of this surrounding the trap was filled with mercury, and the space between the double walls with air. By heating the mercury bath with a small electric heater and dipping the whole arrangement in liquid oxygen as before, temperature control to ± 1/2° was achieved.

With optical system A the modified setup had a volume of about 1500 cc. and with optical system B, 2200 cc.

Flow System

Since the separate parts of this apparatus have been described above, the description here need only be brief.

The gas at constant pressure entered the system through a calibrated capillary flow-meter. It thence flowed over the mercury saturator, through the desaturating trap and into the reaction vessel B. Its pressure in the reaction vessel was regulated by means of a carefully filed stopcock controlling the rate of egress of the gases. Through this stopcock the reacted gas flowed into three traps cooled to -183°C. The last two were packed with silica gel and activated charcoal respectively. A 500 cc. expansion bulb and manometer were connected to the charcoal trap. The different parts of the system of course could be separately evacuated, and ground joints attached to the collecting traps made provision for the transfer of gases to the analytical system.

Materials

Ethane and butane were obtained in cylinders from the Ohio Chemical and Manufacturing Company. The gases were stated to be not less than 97 and 99 percent pure respectively. Analysis of the cylinder ethane showed it to contain 1.3 percent ethylene, less than 0.3 percent of $H_2 + CH_4$, and less than 0.3 percent of higher hydrocarbons. This gas was purified in several ways as follows:

(1) It was passed over 60 cm. of copper oxide at 300°C, through a 40 percent KOH solution and a trap at -80°C, and was then condensed and fractionally distilled.

(2) The gas was fractionated in a low temperature still of the Podbielniak type.

(3) For use in the flow experiments the gas was passed over 60 cm. of copper oxide at 300°C, through saturated bromine water, into a 2 liter bottle illuminated by a Point-o-lite lamp, through 40 percent KOH solution and finally a trap at -80°C.

The butane was purified merely by fractional distillation.

Hydrogen was taken from cylinders and passed over platinized asbestos at 600°C and then through a trap cooled to -183°C.

Deuterium was prepared by the interaction of 99.6 percent deuterium oxide with metallic magnesium at 485°C according to the method of Knowlton and Rossini (81) and also by the interaction of deuterium oxide with calcium at room temperature. Both preparations were performed in vacuo and the gas was dried by passage through a cold trap at -183°C.

Characteristics of the Light Sources

The intensity of the mercury resonance radiation of both optical systems A and B was determined by measuring the rate of hydrolysis of monochloracetic acid (80). Two concentrations of the acid were employed 0.5N and 0.25N. These gave identical results, showing that absorption was complete. The solution after irradiation was analyzed either by (a) neutralization with $NaHCO_3$ and titration with $AgNO_3$, using K_2CrO_4 as an indicator, or by (b) addition of an excess of $AgNO_3$ and back titrating, after the filtration of the precipitated AgCl, with KSCN using $Fe(NO_3)_3$ as an indicator.

The mean of a number of concordant measurements made at different times gave for the total resonance radiation entering reaction cell A 4.2×10^{-6} einsteins per second. This, of course, refers to the radiation emitted after the lamp's output became constant. This was attained in less than 10 minutes.

With optical system B more extensive measurements were taken. These are shown in Table IV. The efficiency in column 5 is calculated allowing for the fact that 1/2 of the tubing is of Pyrex glass and will thus not transmit resonance radiation. The data at 100 milliamperes are illustrative of the constancy of the output. The efficiency in production of mercury resonance radiation is the highest ever recorded.

The light intensity in system A was also measured by means of a Moll large surface thermopile in conjunction with a Leeds and Northup type HS galvanometer. The thermopile was placed outside the reaction vessel, and the intensity of

TABLE IV

Characteristics of Optical System B

Potential	Current	Input	Resonance Radiation in Reaction Vessel	Efficiency in Production of 2537
Volts	Milliamperes	Watts	einsteins/sec.	percent
450	120	54	1.62×10^{-5}	24
495	100	50	1.49×10^{-5}	--
---	100	--	1.48×10^{-5}	28
---	100	--	1.50×10^{-5}	--
503	80	40	1.36×10^{-5}	32
572	50	29	1.22×10^{-5}	39
655	19	--	---	--
668	11	--	---	--
706	7.7	--	---	--
708	4.2	--	---	--
713	2.5	1.8	1.54×10^{-6}	80
820	1.9	--	---	--
920	1.7	--	---	--
1000	1.5	--	---	--
	$<$ 1.5	lamp goes out.		

resonance radiation was determined by taking the difference in the thermopile readings with the cell evacuated, and with it filled with mercury vapour at 35°C in the presence of a high hydrogen pressure. This method gave a value of 3×10^{-6} einsteins per second. Considering the uncertainty in this method due to the geometry of the cell, etc., the agreement of this result with that obtained actinometrically is better than could be expected.

The Absorption of Resonance Radiation.

By means of the galvanometer-thermopile system, measurements were made of the absorption of resonance radiation in optical system A. To make the measurements more sensitive a filter to exclude visible and heat radiation was interposed between the cell and the thermopile. This consisted of an aqueous solution 1 M in $NiSO_4$ and 1 M in $CoSO_4$ as recommended by Backstrom (82). It was enclosed in a transparent vessel of fused silica 10 cm. long with plane ends. Its transmission in the region 3900-7000 Å was 2 percent. During these experiments the gases were circulated over the mercury saturators as in a normal run, the mercury vapour pressure thus being maintained at approximately 4×10^{-3} mm. With this precaution the amount of absorbed resonance radiation became constant in less than one minute after admitting the gas to the system. Measurements were made rapidly in the case of ethane in order to avoid appreciable decomposition. The results of these measurements are given in Table V.

Measurements of the efficiency of the absorption were also made by observing the rate of the mercury photosensitized hydrogen-oxygen reaction in an auxiliary quartz cell placed close to the outside of the reaction vessel. The ratio of the rates of combination of hydrogen and oxygen with the cell empty, and with it filled with ethane at 650 mm. pressure in the presence of mercury at its vapour pressure at 35°C, was 40. This is an excellent check on the absorption at high ethane pressures as determined by thermopile measurements.

General Procedure

In the original circulatory system employing the less intense light source A the procedure was as follows. Suitable amounts of the reacting gas or gases were introduced into the system, and the trap or traps were brought to the desired temperature. The pump P was started, and the saturators were heated to 60° - 80°C. The gas was then illuminated for a definite period of time. At the conclusion of this period, the traps were brought to room temperature and the products of reaction were completely pumped by the Toepler pump into a portable gas-holder. The gas was then analyzed by low-temperature distillation in the apparatus described. A 500 cc. sample could thus be analyzed for the gaseous constituents (i.e those with boiling points below room temperature) with an accuracy of about 0.5 percent. In the analysis if methane and

TABLE V

Absorption of the Resonance Line under Various Conditions

Arc current 0.100 amp.

Cell temperature 35°C

Mercury saturation at 35°C = 4×10^{-3} mm.

Foreign gas	Pressure mm.	Resonance radiation absorbed erg. cm.$^{-3}$	Fraction of resonance radiation absorbed.
H_2	180	8.0×10^{15}	1.00
	87	7.7	0.96
	72	7.6	0.95
	51	7.4	0.92
	10	5.2	0.65
C_2H_6	680	7.8×10^{15}	0.97
	420	7.8	0.97
	330	7.8	0.97
	210	7.7	0.96
	171	7.7	0.96
	151	7.6	0.95
	136	7.5	0.95
	75	7.0	0.87
	40	6.3	0.79
	10	4.3	0.54

hydrogen were both present some methane was always taken off with the hydrogen. This fraction, therefore, was analyzed by combustion in the usual manner. The distillation apparatus available was not suitable for the analysis of high-boiling products. However, as will be shown later, such products were only present when compounds of higher molecular weight than ethane were not removed from the reaction system, and were entirely absent during the more significant experiments.

This procedure introduces a slight error in the calculation of the quantum input. As mentioned before, a matter of some minutes is required before the maximum intensity is attained. With the longer periods of illumination required with optical system A, however, the error introduced by assuming the full intensity is reached at the start is well within the experimental error. It has therefore been neglected. When using the more intense optical system B, the procedure was slightly modified to eliminate this error. After the ethane had been introduced and its pressure measured it was condensed in a small auxiliary trap. If hydrogen or deuterium were to be one of the reactants also it was now admitted. The saturator and trap were then brought to temperature and the lamp switched on. After about one half hour had elapsed the pump was started and the ethane in the trap rapidly vapourized. This last operation took place in less than 5 sec. The remaining procedure followed as outlined in the last paragraph.

In the flow experiments the lamp was turned on for one half hour, the saturator heated to 60° - 80°C and the collecting traps cooled to -183°C. After adjusting the filed stopcock for the predetermined pressure of gas to be in the reaction vessel, the ethane, whose flow was controlled by the capillary, was run through for a definite period of time. Blank experiments showed that only hydrogen and methane collected in the packed traps, and that no hydrogen was condensed with the unreacted ethane in the unpacked trap. The volume of the gas condensed in the packed traps was estimated by measuring its pressure in the 500 cc. bulb and traps after the system had been brought to room temperature. The gases could then be transferred and the hydrogen determined by combustion.

Results

The results for the decomposition of ethane alone in the circulatory system are given in Table VI, and those for the decomposition in the presence of hydrogen or deuterium are shown in Table VII. The extent of deuterization of the products in the runs with deuterium ~~are~~ is shown in Table VIII. These latter results are given through the courtesy of Mr. W. A. Alexander.(a) One run was also made with butane in the circulatory system the data for which are given in Table IX..

(a) For details of the analytical method see "Free Radicals in Organic Decomposition Reactions" by W. A. Alexander, Ph.D. Thesis, McGill, May 1938.

TABLE VI

The Mercury Photosensitized Decomposition of Ethane

Volume of System	1200 cc.	in runs 1 to 6
	1500 cc.	" " 7 and 8
	2180 cc.	" " 9 to 11
Mercury Vapour Pressure	4×10^{-3} mm.	in runs 1 to 8
	1.3×10^{-3} mm.	" " 9 " 11
Arc Current	0.100 amperes	
Arc Voltage	370 volts	in runs 1 to 8
	495 "	" " 9 " 11
Resonance Radiation Absorbed		
	4.0×10^{-6} einsteins per sec.	in runs 1 to 6
	3.7×10^{-6} " " "	" run 7
	3.4×10^{-6} " " "	" " 8
	11.8×10^{-6} " " "	" " 9
	$\sim 12 \times 10^{-6}$ (a) " " "	" " 10
	15.0×10^{-6} " " "	" " 11

(a) Lamp fluctuations abnormal.

TABLE VI (continued)

(1) Run No.	(2) Time	(3) Initial Press.	(4) Final Press.	(5) Trap Temp.	(6) Circulation Rate	(7) Partial Press. of C_2H_6	(8) Cell Temp.
1	600	44.1	42.0	-70	6	40 to 15	35
2	480	43.1	41.8	-70	6	40 to 15	35
3	510	42.2	41.9	-100	1.3	40 to 20	35
4	480	75.0	75.0	-108	1.2	25	35
5	900	73.2	73.2	-115	4	15	35
6	1200	69.9	69.9	-116	6	15	35
7	525	39.0	39.0	-125	3	7	35
8	405	39.0	39.0	-131	3	4	35
9	133	26.0		-130	3	4	78
10	28	30.5		-130	3	4	450
11	30	30.9		-130	7	4	460

TABLE VI (continued)

Run No.	(9) Fraction of C_2H_6 Decomposed	(10) Decomposition rate Mols per sec. x 10^6	(11) Quantum Yield	(12) Products mol percent				
				H_2	CH_4	C_3H_8	C_4H_{10}	C_8H_x
1	0.67	0.53	0.13	47	16	not detected	23	14
2	0.60	0.58	0.14	43	23	"	20	14
3	0.50	0.44	0.11	---	---	"	25	present
4	0.23	0.38	0.095	19.6	44.7	"	35.7	trace
5	0.45	0.39	0.098	---	---	---	---	none
6	0.58	0.36	0.090	6.1	59.3	34.6		"
7	0.55	0.54	0.15	0.0	59.5	21.5	19.0	"
8	0.45	0.61	0.18	0.0	58.8	23.5	17.7	"
9	0.574	2.22	0.19	0.0	57.9	26.6	15.5	"
10	0.458	9.99	0.8	26.7	28.2	16.4	26.7	2.0
11	0.612	12.5	0.83	31.0	23.7	11.3	32.5	1.5

TABLE VII

The Mercury Photosensitized Decomposition of Ethane in the Presence of Hydrogen and Deuterium

Volume of System	1500 cc. in runs 1 to 3
	2180 cc. " " 4 to 6
Mercury Vapour Pressure	4×10^{-3} mm. in runs 1 to 3
	1.3×10^{-3} mm. " " 4 to 6
Circulation Rate	3 liters per min. in runs 1 to 4
	6 " " " " " 5 and 6
Arc Current	0.100 amperes
Arc Voltage	370 volts in runs 1 to 3
	495 " " " 4 to 6
Resonance Radiation Absorbed	
	4.0×10^{-6} einsteins per sec. in runs 1 to 3
	1.5×10^{-5} " " " " " 4 to 6
Trap temperature	-124°C in runs 1 to 3
	-130°C " " 4 to 6
Partial Pressure of Ethane	
	10 cm. in runs 1 to 3
	4 cm. " " 4 to 6

TABLE VII - (continued)

(1) No.	(2) Time	(3) Total Initial Press.	(4) Gas	(5) Percent D_2 or H_2	(6) Cell Temp.
	min.	cm.			°C
1	300	47.7	H_2	40.0	35
2	360	45.7	H_2	39.3	35
3	360	45.4	H_2	40.0	35
4	75	31.6	D_2	34.1	75
5	90	34.2	D_2	50.0	75
6	83	63.5	D_2	64.7	75

TABLE VII - (continued)

No.	(7) Fraction of C_2H_6 Decomposed	(8) Decomposition Rate of C_2H_6	(9) Quantum Yield	(10) Products Mols/Mol Ethane Decomposed			
		Mols per sec. x 10^6		H_2 (consumed)	CH_4	C_3H_8	C_4H_{10}
1	0.39	0.45	.11	0.48	1.32	0.16	(a)
2	0.44	0.46	.12	0.46	1.30	0.15	(a)
3	0.44	0.45	.11	0.50	1.34	0.17	(a)
4	0.51	2.74	.182	0.23	1.01	0.10	0.12
5	0.66	2.48	.165	0.43	1.21	0.10	0.12
6	0.40	1.95	.130	0.38	1.13	0.12	0.13

<u>Note</u> - H_2, CH_4 etc. signify the total hydrogen, methane, etc. irrespective of isotopic species.

(a) Total of butane + propane

TABLE VIII

Complete Analysis of the Products of Runs 4 and 5, Table VII

	No. 4		No. 5	
	Product Percent	Deuterization Percent	Product Percent	Deuterization Percent
Hydrogen	26.4	28.6	35.8	33.5
Methane	33.7	23.3	39.9	21.4
Ethane	32.5	4.8	17.0	11.2
Propane	3.4	17.2	3.3	15.9
Butane	4.0	16.6	4.0	16.2

The deuterium used in run No. 4 was 99 percent
and that " " " 5 " 84 "

TABLE IX

The Mercury Photosensitized Decomposition of Butane

Operating conditions	as in Table VI run No. 1
Time, hours	4.5
Initial pressure, cm.	59.5
Final pressure, cm.	40.25
Trap temperature, °C	0.0
Fraction decomposed	0.88
Hydrogen produced, cm.	30.0
Mols decomposed per second	2.2×10^{-6}
Quantum yield	0.55
Mols hydrogen formed per second	1.3×10^{-6}

TABLE X

The Production of Hydrogen in the Flow System

Rate of flow of ethane - 3.0 cc. per sec. at N. T. P.

Mercury vapour pressure - 1.3 x 10^{-3} mm.

Resonance Radiation absorbed - 1.2 x 10^{-5} einsteins per sec.

(1) Run No.	(2) Time	(3) Pressure	(4) Temperature	(5) H_2 Formed	(6) Rate of H_2 Formation	(7) Quantum Yield
	min.	cm.	°C	cm.	mols/sec. x 10^6	
1	30	4.3	90	4.4	0.96	0.080
2	30	4.3	67	4.7	1.03	0.086
3	30	4.3	67	4.3	0.94	0.078
4	61	4.8	65	8.7	0.95	0.079
5	30	4.3	--	0.0	Blank Run - arc not on	
6	60	4.3	--	0.0	Blank Run - arc not on	
7	30	4.3	450	26.8	5.5	0.48

In runs Nos. 1 and 7 tank gas was used, in all other cases purified gas.

The runs done with the flow system relative to hydrogen formation are reported in Table X.

The "initial" and "final" pressures given in columns 3 and 4 of Table VI are those with the traps at room temperature before and after a run. The values of the initial partial pressure of ethane in column 7 are lower than the values in column 3 for the later runs, since the initial ethane pressure was higher than the vapour pressure of ethane at the trapping temperature, and some ethane condensed in the traps. Column 5 gives the temperature of the traps (or trap), and thus expresses qualitatively the degree of removal of high-boiling products. In runs (4) to (11) the vapour pressures of propane and butane should be less than those inferred from the temperature of the traps, because of their solubility in the condensed ethane in the traps. The vapour pressures of propane and butane at a few temperatures are given below to show the extent to which they were removed at the various trapping temperatures employed.

Temperature °C	Vapour pressures, mm.(a) propane	butane
-70	209	19
-100	30	2
-110	13	0.7
-120	5	0.3
-130	2	0.07

(a) Values taken from International Critical Tables.

Still lower trapping temperatures were, of course, not feasible on account of the diminution in the vapour pressure of ethane.

It is apparent from the analytical data that the circulation rates employed were sufficiently high to insure complete absence of secondary decomposition products of propane and butane when sufficiently low temperatures were employed.

As pointed out previously, the analytical apparatus available was not satisfactory for the determination of higher hydrocarbons. In runs in which such products were present they are reported as C_8H_x, calculated from a carbon balance, since the boiling point of the residue corresponded with that of octane. Actually, however, the higher fraction was by no means pure octane, and its presence was not completely identified. However, in the later, and more important, runs no higher hydrocarbons were present and the analyses are therefore complete. In Tables VI and VII the quantum yields are calculated on the basis of the number of mols of ethane disappearing, in Table IX on the basis of the number of mols of butane consumed, and in Table X on the basis of the number of mols of hydrogen produced. In Table X the values given in column 5 are the pressures of hydrogen in the collecting system (volume 723 cc.) corrected for their small methane content (10 to 15 percent).

The consistency and precision of the analytical data should be emphasized. In each analysis the results were checked by a detailed carbon-hydrogen balance. A typical result is shown below:

From Table VII run No. 6

Basis - 100 mols of gas

Initial

Gas	Analysis	Mols of H	Mols of C
H_2	64.7	129.4	0
C_2H_6	35.3	211.8	70.6
		341.2	70.6

Final

Gas	Analysis	Mols of H	Mols of C
H_2	59.4	118.8	0
CH_4	15.6	62.4	15.6
C_2H_6	21.5	129.0	43.0
C_3H_8	1.7	13.6	5.1
C_4H_{10}	1.8	18.0	7.2
		341.8	70.9

Before entering on a discussion of the mechanism of the reactions in Section E, it will be convenient to summarize the main conclusions to be drawn from Tables VI to X.

(1) The decomposition of ethane in a circulatory system, Table VI.

(a) At high trapping temperatures, in agreement with the results of previous investigators, much hydrogen is produced, the H_2/CH_4 ratio being approximately 3. Considerable butane and higher hydrocarbons are formed, but no propane.

(b) When the trapping temperature is reduced to about -115° C, the formation of higher hydrocarbons is entirely inhibited, and much butane is produced. At the same time the production of hydrogen decreases greatly, the H_2/CH_4 ratio falling to about 1/3.

(c) At very low trapping temperatures where butane has a negligible vapor pressure, and that of propane is also low, hydrogen formation ceases entirely. Propane now makes its appearance in large quantities. This is a striking result, inasmuch as previous investigators have found only hydrocarbons with an even number of carbon atoms (with the exception of methane), and previous mechanisms have been designed primarily for the purpose of explaining this.

(d) It should be observed that, especially at low trapping temperatures where the partial pressure of ethane is low while the methane formed is all in the gas phase, there will be a competition for the incident energy. Under these circumstances the methane present may absorb up to 25 percent of the incident energy. It has been shown by Morikawa, Benedict, and Taylor(a) that the quantum yield in the mercury photosensitized methane

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(a) Morikawa, Benedict, and Taylor, J. Chem. Phys. 5, 212, (1937).

decomposition is very low at low temperatures. Thus they obtained values of about 0.2 at 196°C, and only 0.008 at 98°C. It appears, therefore, that the decomposition of methane is negligible at 35°C, and the methane merely quenches the resonance radiation without being chemically affected. On account of this effect the quantum yields obtained will be somewhat low, and a value of about 0.20 for the ethane decomposition at 35°C appears the most probable.

(e) At high temperatures of the reaction vessel, (i.e 450°C), hydrogen appears in large quantities; the percentage of butane also rises while that of methane and propane decreases. The quantum yield approaches unity.

(2) Experiments in the presence of added hydrogen and deuterium (Tables VII and VIII).

(a) Hydrogen (or deuterium) is consumed, not produced. The consumption decreases with a decrease in the partial pressure of deuterium.

(b) The production of methane is very large compared with that of higher hydrocarbons.

(c) No hydrocarbons higher than butane are formed at low trapping temperatures.

(d) The methane formed in the reaction in the presence of deuterium is very highly exchanged, somewhat in excess of the equilibrium value.

(e) In the reaction in the presence of deuterium, ethane, propane and butane are considerably exchanged, but below the equilibrium value. The deuterium content of the ethane is considerably increased, but that of propane and butane unaltered when the partial pressure of deuterium is increased.

(3) The decomposition of butane (Table IX).

(a) Much hydrogen is produced. The decomposition of butane is thus the source of a considerable amount of the hydrogen formed in the ethane decomposition at higher trapping temperatures. Higher hydrocarbons are also produced in large quantity. As in the case of ethane, these correspond roughly to octane.

(b) The quantum yield of the butane decomposition is definitely higher than that of the ethane decomposition.

(4) The decomposition of ethane in a flow system (Table X).

(a) In contrast with the experiments in the circulatory system hydrogen appears in large quantities when its partial pressure is kept down by rapid removal of the products of reaction.

(b) The quantum yield (in terms of hydrogen formation) is about half as great as that based on ethane disappearance in a circulatory system.

(c) The production of hydrogen goes up rapidly with temperature.

E. DISCUSSION

The reaction between deuterium atoms and methane.

The results as tabulated in Table II indicate a value of about 11 kcal. for the activation energy of the photosensitized reaction. This is in agreement with the value of $\geq$ 11 kcal. previously found by Geib and Steacie (36).

Since the publication of the earlier note by Taylor, Morikawa and Benedict (35) indicating a value of 5 kcal. for the reaction two extensive investigations have been reported. Farkas and Melville (65) studied the exchange in equimolecular mixtures of ortho-deuterium and methane at a total pressure of 100 mm. and temperatures up to 610°C. In their experiments, the isotopic content of the exchanged deuterium was measured together with the rate of the ortho-para deuterium conversion. These latter measurements of course gave the values of the D atom concentration in each of their experiments. In some separate but parallel experiments they compared the rate of the ortho-para hydrogen conversion in the absence and presence of methane. They found that above 100°C or so the half-life of the conversion was increased by factors of from 2 to 10 (i.e. the $[H]$ decreased in the inverse ratio). From the usual log $t_{1/2}$ (exchange) vs. $1/T$ plot they find an apparent activation energy of exchange of only 7 kcal. They point out that this calculation is invalid on account of the decrease in D atom concentration with increasing temperature. To correct this they calculated an additional E of 6 kcal. from their ortho-para conversion experiments thus obtaining an activation energy for the exchange of about 13 kcal.

Morikawa, Benedict and Taylor (66) studied the mercury photosensitized reactions in the systems $CH_4 + D_2$, $CD_4 + H_2$, and $CH_4 + CD_4$ from room temperature to about 500°C. The progress of the exchange was followed by measurement of the absorption spectra of the methanes in the infrared region. In addition the formation of higher hydrocarbons was measured in a semi-quantitative manner. They found that the apparent activation energies (i.e. those deduced from the temperature coefficient of the rate of exchange, assuming the D atom concentration constant) for the reaction in the system $CH_4 + D_2$ in various temperature ranges to be as follows:

Temperature Range °C	Activation Energy (kcal.) P_{Hg} at 55°C	 P_{Hg} at 0°C
98 - 196	2	3
196 - 296	7	10
296 - 392	11	12
392 - 488	14	--

By employing the value for the atom concentration calculated on the basis of Farkas and Sachsse's recombination rate for the reaction $H + H + M \rightarrow H_2 + M$ (see page 28) they calculate from the collision yield a value of 14 kcal. for the exchange reaction at 98°C. The discrepancy between this value and those tabulated above for the 98° - 196° range, together with evidence from the abnormal distribution of the different deutero-methanes at low temperatures (e.g. 7 percent CHD_3 was found compared with an equilibrium value of 2 percent) led them to conclude that the reaction is largely

$$Hg(^3P_1 \text{ or } ^3P_0) + CH_4 \longrightarrow CH_3 + H + Hg(^1S_0)$$

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

$$CH_3 + D \longrightarrow CH_3D^* \longrightarrow CH_2D + H$$

The fact that some ethane formation occurs is cited as additional evidence for this mechanism.

It is obvious in the light of the results of Farkas and Melville concerning the falling off of the D atom concentration with temperature that the temperature coefficients of Morikawa, Benedict and Taylor are too small in the low temperature region. It seems to the writer (a), however, that any reasonable assumption regarding the reduction of the D atom concentration would not completely invalidate their results, and due account should be taken of the primary decomposition of the methane. That this does take place at a measurable velocity even in the neighbourhood of 200°C has been confirmed (see Appendix). On this basis Farkas and Melville's results at higher temperatures may be too complicated to admit of any simple interpretation.

(a) For an expression of a contrary point of view see Steacie, Chem. Rev., April 1938.

The quantum yields found by the different workers were widely different, but since the two investigations were performed under different experimental conditions, (Morikawa, Benedict and Taylor used light intensities 100 times smaller and pressures 7 times greater than those of Farkas and Melville), it would appear that further work will be needed to clear up this discrepancy as well as to elucidate the nature of the processes.

However, even though the mercury photosensitized processes may be more complicated than they appeared to be on first examination, all work shows without doubt that if the reaction

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

does occur in a simple fashion its activation energy cannot be less than about 11 kcal.

It remains to mention further investigations of the reaction of D atoms produced by the Wood-Bonhoeffer method, by Trenner, Morikawa and Taylor (68) and by Steacie (69). Steacie investigated the reaction up to 500°C and obtained an activation energy of 12.9 ± 2 kcal. the values calculated from the temperature coefficient and from the collision yield being in good agreement. Trenner, Morikawa, and Taylor obtain values from 15.6 - 18 kcal. It is quite possible (69) that these latter values may be high, due to a falling off of the D atom concentration at higher temperatures. If this is so, all results for the reaction of D atoms with methane are in approximate agreement, viz:

	E
Geib and Steacie (36)	11 kcal.
Frakas (70) (Thermal. E not determined but compared with D + NH_3 reaction, and may therefore be estimated as roughly)	11
Farkas and Melville (65)	13
Morikawa, Benedict and Taylor (66)	12.5 to 14
Steacie (69)	12.9 ± 2
Trenner, Morikawa and Taylor(a)	15.6
This investigation	11

The Reaction of Atomic Deuterium with Ethane

As shown in Table III this reaction has a much lower activation energy than that of the corresponding process with methane. There are three main possibilities for the mechanism of the reaction:

I Hydrogenation

(a) $C_2H_6 + D \longrightarrow C_2H_6D$

(b) $C_2H_6D + D \longrightarrow C_2H_6 + D_2$

or $\longrightarrow C_2H_5D + HD$

II Dehydrogenation

(a) $C_2H_6 + D \longrightarrow C_2H_5 + HD$

(b) $C_2H_5 + D \longrightarrow C_2H_5D$

(a) The value of 18 kcal was determined for only 1 run.

III **Exchange by Metathesis**

$$C_2H_6 + D \longrightarrow C_2H_5D + H$$

Mechanism III is undoubtedly the correct one for a number of reactions, e.g., the reaction of D atoms with ammonia and the ortho-para hydrogen conversion. However, in view of the fact that ethane and acetylene are known to have a strong "catalytic" effect in destroying hydrogen atoms (47), some other mechanism must exist, since III regenerates one hydrogen atom for each one destroyed and hence cannot account for a catalytic recombination. Furthermore the activation energies of the reactions with ethane are so much lower than those for methane, ammonia, and water that it is obvious that the mechanisms must be distinctly different.

Mechanism I is very unlikely, since I (a) would presumably have to occur at a triple collision. This would make the reaction far too slow to enable ethane to exert a strong catalytic effect on the recombination of hydrogen atoms. Furthermore, even if I (a) occurred sufficiently rapidly, the very unstable molecule C_2H_6D would have little chance of survival long enough (10^{-6} sec.) to meet a D atom and give I (b). Hence in general we would expect I (a) to be followed by

$$C_2H_6D \longrightarrow C_2H_5 + HD$$

$$\text{or} \longrightarrow C_2H_4D + H_2$$

which would make the whole process indistinguishable from II (a), or else by

$$C_2H_6D \longrightarrow C_2H_5D + H$$

which would give a result indistinguishable from III. Hence we must conclude that II is the correct mechanism, and that the measured heat of activation (6.3 kcal.) is that of the reaction

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

and hence the companion reaction

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

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 thermal decomposition of ethane will be discussed on page 82.

Since the completion of this work the reaction has been reinvestigated by the Wood-Bonhoeffer method by Trenner, Morikawa, and Taylor (68). They obtained somewhat different results. At room temperature they found that the main reaction was

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

and that the exchange reaction was only appreciable above 100°C, with an activation energy of 11.4 kcal. In their experiments from 10 to 20 percent of the ethane was found to be decomposed to methane. They made complete analyses of the reaction products, and determined the deuterium content of each product separately. The methane was about 50 percent deuterized but below 100°C ethane was entirely light.

As mentioned before in this investigation the separate products were not isolated, it being assumed from the work of

Chadwell and Titani (48) 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 percent of the total ethane present was split into methane in the work reported here. That this is not so has been recently demonstrated by Steacie (69) working under conditions similar to those described herein. He found the mean value of the amount of decomposition of ethane at 20°C to be 8.2 percent. From this he recalculated the results of the original investigation. Tabulated values of his corrections are reproduced below:

	Original Values	Corrected Values
Mean D content of ethane, percent	15.8	11.3
Mean "percent exchange"	25.4	18.7
Mean collision yield	1.86×10^{-6}	1.37×10^{-6}
E, kcal. assuming a steric factor of 0.1	6.3	6.4

It is noted that the alteration in the results is insignificant and further investigation is necessary to determine the cause of the disagreement.

<u>Free Radicals and the Ethane Decomposition</u>.

As has been mentioned before, Rice (1) 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 great controversy (71).

Granting that the primary step at high temperatures is a split into radicals, however, is not a proof that the ordinary thermal decomposition involves free radicals. Also, as we have seen, if it is to be postulated that the decomposition proceeds by a free radical process, 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. The following mechanism has been suggested by Rice and Herzfeld (6) to fulfil these conditions:

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

Due to the occurrence of (3) and (4) reaction chains will occur, a large number of ethane molecules being decomposed for each initial split. The activation energies allotted to the various steps are based partially on experimental data, and partially assigned so as to fit the mechanism. Assuming reactions (5), (7), (8), and (9) to be negligible, they obtained

$$E_{overall} = 1/2(E_1 + E_3 + E_4 - E_6) = 73 \text{ kcal.},$$

in agreement with the measurements of Marek and McCluer (72). E_1 is the experimentally determined value of Rice and Dooley for the split into radicals, 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 the scheme leads to the expression

$$-\frac{d}{dt}[C_2H_6] = \left(\frac{K_1K_3K_4}{2K_6}\right)^{\frac{1}{2}}[C_2H_6]$$

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

$$\log_{10} K = 15.1 - \frac{73200}{2.3RT} \quad \text{sec.}^{-1}$$

The chain length calculated from the mechanism is about 100.

Thus it is possible to explain the ethane decomposition on the basis of free radicals under all conditions. In addition it is known that a free radical mechanism takes place to a considerable extent at very high temperatures.

The work of Patat and Sachsse (73) has thrown considerable doubt on the validity of the Rice-Herzfeld mechanisms for the decomposition of gaseous organic compounds. They measured the rate of the ortho-para hydrogen conversion in the presence of decomposing organic compounds and were thus able to estimate the hydrogen atom concentration. In general, using the activation energies assigned to the intermediate reactions by Rice and Herzfeld, Patat and Sachsse find the hydrogen atom concentration to be several powers of 10 lower than those calculated from the free radical chain theory.

Thus for the ethane decomposition, Sachsse (74) finds a value of $[H] = 6.3 \times 10^{-12}$ mol liter^{-1} at a temperature of 580°C. This can easily be compared with the value calculated on the basis of the Rice-Herzfeld mechanism outlined above. It is easily shown that $[H] = \sqrt{\frac{K_1 K_3}{2K_4 K_6}}$ and assuming with Rice and Herzfeld that

$$K_1 = 10^{14} \; -\frac{80000}{RT} , \quad K_3 = 10^{13} \; - \frac{49000}{RT} , \quad K_4 = 10^{9} \; - \frac{17000}{RT}$$

and $K_6 = 10^{9} \; - 0/RT$ (a), we calculate for the hydrogen atom concentration at a temperature of 580°C a value of 5×10^{-9} mol liter^{-1} a value obviously much too high to agree with experiment.

However it is noted that reaction (4) is the companion to the one studied here, viz:

(a) Rice and Herzfeld do not explicitly give E_6, but from a combination of Table A and Eq. (22) of their paper (6) it follows that they use $E_6 = 0$.

$$C_2H_5 + D \longrightarrow C_2H_5D + H$$

Hence applying the new value of 6.4 kcal. for E_4 we calculate anew for the H atom concentration a value of 1.7×10^{-12} mol liter^{-1}. At first sight this seems a complete re-justification of the Rice-Herzfeld scheme, the calculated concentration being only 4 times less than the experimental. It thus appears that if we accept the value of 6.4 kcal. as being the activation energy of the reaction

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

then the objections to the free radical scheme from the point of view of the stationary hydrogen atom concentration no longer hold. The same is true for most of the other free radical chain mechanisms if we assume that all the Rice-Herzfeld activation energies are too high for reactions of the type

$$H + RH \longrightarrow H_2 + R$$

Such a change in the activation energy of reaction (4), however, seems to introduce insurmountable difficulties into the application of the scheme to first order reactions. Thus in the case of ethane the fundamental reactions are (1), (2), (3) and (4), and these cannot be altered without virtually abandoning the entire free radical theory. As we have seen the change in E_4 brings the results into line as far as the stationary hydrogen atom concentrations are concerned. The overall order of the reaction and the theoretical value of E, however, 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 possible 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.

Storch and Kassel (75) have studied the ethane decomposition with special emphasis on the production of products other than hydrogen and ethylene. In discussing the free radical mechanism they then broaden the Rice-Herzfeld scheme to take into account their new results. For the scheme to hold they find several necessary conditions for the mechanism to be incompatible with existing data. For reactions (4), (6a) and (9) (original Rice-Herzfeld numbering, i.e.

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

(6a) $H + C_2H_5 \longrightarrow C_2H_4 + H_2$

(9) $2C_2H_5 \longrightarrow C_4H_{10}$)

they find with the new value of $E_4 = 6$ kcal, in order that the free radical mechanism can hold it, it is necessary that

$$\frac{K_9}{K_4 + K_{6a}} < 2 \times 10^{-6}$$

It is extremely unlikely that such similar reactions should have rates differing so widely. Storch and Kassel therefore conclude that for this and other reasons the free radical mechanism for ethane is ruled out and that the major part of the observed reaction is to be accounted for by more or less classical processes.

The Mercury Photosensitized Reactions of Ethane

The following are some of the reactions which may be considered in discussing the decomposition of ethane and its reaction with hydrogen or deuterium atoms:

Primary Reactions

(1) $C_2H_6 + Hg(6^3P_1) \longrightarrow C_2H_6 + Hg(6^3P_0)$

(2) $C_2H_6 + Hg(6^3P_1 \text{ or } 6^3P_0) \longrightarrow Hg(6^1S_0) + 2CH_3$

(3) or $+ C_2H_5 + H$

(4) or $+ CH_2 + CH_4$

(5) $H_2 + Hg(6^3P_1) \longrightarrow Hg(6^1S_0) + 2H$

Secondary Reactions of Atoms or Radicals with Ethane

(6) $C_2H_6 + H \longrightarrow C_2H_5 + H_2$

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

(8) $+ CH_3 \longrightarrow C_2H_5 + CH_4$

(9) $+ CH_3 \longrightarrow C_3H_8 + H$

(10) $+ CH_2 \longrightarrow C_3H_8$

(11) $+ CH_2 \longrightarrow C_2H_5 + CH_3$

(12) $+ CH_2 \longrightarrow C_2H_4 + CH_4$

(13) $+ C_2H_5 \longrightarrow CH_3 + C_3H_8$

(14) $+ C_2H_5 \longrightarrow H + C_4H_{10}$

Radical and Atom Recombination Reactions

(15) $H + H \longrightarrow H_2$

(16) $H + CH_3 \longrightarrow CH_4$

(17) $H + C_2H_5 \longrightarrow C_2H_6$

(18) $CH_3 + C_2H_5 \longrightarrow C_3H_8$

(19) $CH_3 + CH_3 \longrightarrow C_2H_6$

(20) $C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}$

(21) $CH_2 + CH_2 \longrightarrow C_2H_4$

Other Secondary Reactions of Atoms and Radicals

(22) $H + CH_4 \longrightarrow CH_3 + H_2$

(23) $H_2 + CH_3 \longrightarrow CH_4 + H$

(24) $C_2H_5 + H_2 \longrightarrow C_2H_6 + H$

(25) $C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6$

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

(27) $CH_4 + C_2H_5 \longrightarrow CH_3 + C_2H_6$

(28) $CH_2 + C_3H_8 \longrightarrow C_4H_{10}$

In the above equations H refers to either H or D.

The Reactions in the Presence of Hydrogen or Deuterium

These reactions will be considered first, since there is no doubt that the predominating primary step (after the absorption of the incident energy) is the formation of H or D atoms. Employing the relation used on page 28 together with the relative quenching areas given in Table I, we find [redacted] with the various values of $[H_2 \text{ or } D_2] / [C_2H_6]$ employed that hydrogen or deuterium molecules will quench more than 99 percent of the $Hg(6^3P_1)$ atoms. Hence (5) is the primary step. In the circulatory system as the reaction proceeds a considerable quantity of methane is produced which remains solely in the gas phase. However, this methane due to its very small quenching diameter will absorb even less energy than the ethane.

Since methane is formed and hydrogen consumed there seems to be no doubt that (7) is the predominating methane producing step. The only other ways of producing methane involve methyl radicals, and since (7) is the only reaction producing these in relatively large amounts, (7) is established with certainty. To explain the formation of butane it is necessary to have some ethyl radical producing step. For this the only possible reactions seem to be (6) or (8). To fit data for organic decomposition reactions Rice (83) assigns a value of about 17 kcal. for (8). This is much higher than theoretical estimates by London (84) for reactions of this type. The data available for (6) include the value found in Section C (6.3 kcal.) and that found by Trenner, Morikawa, and Taylor (11.4 kcal.). Recent work by Taylor[(a)] and coworkers would indicate that their previous value is somewhat high, the present estimate being roughly 9 kcal.

In absence of more positive information[(b)] it might be assumed that (8) would take place. However, the occurrence of (6) seems much more certain. The next question to be answered is: how satisfactorily will these reactions account for the results on a stoichiometric basis? Before doing this we will

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(a) Private communication.

(b) This absence no longer exists, see page 86a.

The day before the submission of this thesis some very important information was obtained concerning reaction (8) in a private communication from Professor H.S. Taylor. He says "all the evidence we have had for methane-producing processes, starting from methyl, seems to lead to the conclusion that such processes were slow. With methyl iodide and with metal alkyls it was necessary to assume activation energies of 10 kcal. or more. Morikawa found 11 to 15 kcals. for the interaction of methyl and deuteromethane. I have had some experiments made ..... on the photo-decomposition of mercury dimethyl causing this to take place in the presence of ethane and determining at 35, 90 and 160° whether any methane was formed. There are negligible amounts at the two lower temperatures and very much less at 160° than we would have got with hydrogen in place of ethane. This indicates ...... that the activation energy must be more than 10 kcals."

This establishes without doubt the untenability of Scheme II and is overwhelming evidence against the mechanism for the decomposition reaction initiated by a C-C bond split.

consider the mode of disappearance of the atoms and radicals. Present evidence seems to be in favour of assigning very fast rates to recombination reactions such as (18), (19) and (20) (see for example (85)). Reactions producing H atoms like (9) and (14) are generally considered to have high activation energies possibly in the order of 15-20 kcal. (83). The occurrence of reactions (23) and (24) presents some possibility because of the concentration factors in their favour. Leermakers (86) sets E_{24} = 15 kcal. For E_{23} we have estimates (34) from 8 - 23 kcal., though the best evidence seems to be definitely in favour of a value lower than 15 kcal. The occurrence of (23) and (24) however, would give too high a value for (hydrogen consumed)/(methane produced) as well as having chain characteristics which would not be in accord with the low quantum yield. Recombination of radicals with H or D atoms, it would seem, could hardly compete with radical recombination reactions as there are no reasons for assuming very different orders of concentration for the atoms and radicals and as the reactions involving atoms are more inefficient due to third body restrictions (see for example Morikawa, Benedict and Taylor (66)). Because of their more rapid rates of diffusion H or D atoms may be assumed to disappear at the wall as well as in the gas phase.

We then have as alternatives:

<u>Scheme I</u>

(5) $H_2 \longrightarrow 2H$

(7) $H + C_2H_6 \longrightarrow CH_3 + CH_4$
(6) $H + C_2H_6 \longrightarrow C_2H_5 + H_2$
(19) $2CH_3 \longrightarrow C_2H_6$
(18) $CH_3 + C_2H_5 \longrightarrow C_3H_8$
(20) $2C_2H_5 \longrightarrow C_4H_{10}$
(15) $2H \longrightarrow H_2$

Scheme II

(5) $H_2 \longrightarrow 2H$
(7) $H + C_2H_6 \longrightarrow CH_3 + CH_4$
(8) $CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$
(19) $2CH_3 \longrightarrow C_2H_6$
(18) $CH_3 + C_2H_5 \longrightarrow C_3H_8$
(20) $2C_2H_5 \longrightarrow C_4H_{10}$
(15) $2H \longrightarrow H_2$

In Table VII run No. 5 we obtain the stoichiometric equation

$$0.43H_2 + C_2H_6 \longrightarrow 1.21CH_4 + 0.10C_3H_8 + 0.12C_4H_{10}$$

In Scheme I if we assume for the relative rates of reactions (7), (6), (19), (18) and (20): 1.21, 0.34, 0.55, 0.10 and 0.12 the stoichiometric equation is exactly satisfied. This is also true if in Scheme II we take for the relative rates of reactions (7), (8), (19), (18) and (20): 0.87, 0.34, 0.21, 0.10 and 0.12. In both cases the rates for (19) seem reasonable.

The acceptance of Scheme I would bring definite support to the new value for the activation energy of (6) determined by Taylor and co-workers (9 kcal.) relative to Steacie's (69) value for E_8 of 8.6 kcal. To satisfy the value for E_6 of 6.3 kcal. determined in Section C, we would have to assume some reaction of comparable velocity to (6) consuming hydrogen and destroying ethyl radicals. The former is necessary to account for the overall hydrogen consumption and the latter to account for the low yield of propane and butane relative to methane. The only possible reactions seem to be

$$(17)\quad H + C_2H_5 \longrightarrow C_2H_6$$

$$(24)\quad H_2 + C_2H_5 \longrightarrow C_2H_6 + H$$

Considering the low concentrations of both colliding particles and the dreierstoss restrictions for (17) its occurrence with sufficient rapidity is impossible. In addition, even if it did occur the concentration of H or D atoms would be so lowered that the quantum yield would be reduced to a value much lower than that found experimentally. The unlikelihood of the occurrence of (24) has already been mentioned. That this reaction does not occur with an activation energy as low as 6 kcal. is demonstrated by the small exchange of ethane in runs made in the presence of deuterium.

In the runs in the presence of deuterium we first note the high exchange of the methane. Morikawa, Benedict and Taylor (66) report a quantum efficiency for exchange in methane-deuterium mixtures of 0.59 at a temperature of 98°C and a mercury saturation temperature of 55°C. To explain the high exchange of the methanes they assumed that exchange took place with radicals and atoms through the formation of a quasi-molecule

$$CH_3 + D \longrightarrow CH_3D^* \longrightarrow CH_2D + H$$

$$CH_2D + D \longrightarrow CH_2D_2^* \longrightarrow CHD_2 + H \qquad \text{etc.}$$

Farkas and Melville (65) find for the same reaction a quantum efficiency of 0.10 at 189° with a mercury vapour pressure of 0.001 mm. and state that the reaction is of the true exchange type

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

In the present experiments we notice that for Runs 4 and 5, Table VIII, the deuterium content of the methane is only 4 percent and 1 percent, respectively, above what would be expected if the deuterization of the methane took place solely by

$$(7) \quad C_2H_6 + D \longrightarrow CH_3 + CH_3D$$

As mentioned before it is not likely that reaction (16):

$D + CH_3$ (or exchanged methyl radicals) $\longrightarrow CH_xD_{4-x}$

will compete with solely radical recombination processes (18), (19) and (20). However it is quite easy to account for the slight additional exchange, in an empirical fashion at least, by assuming, consistently with other investigations, that an exchange between deuterium and methane takes place, without referring to the exact mechanism of this exchange.

With reference to the proposed schemes for the reaction it should be noted that propane and butane should be unexchanged since further reactions of these molecules are prevented by the low trapping temperatures employed. The most obvious explanation for the high exchange of about 15 percent seems to lie in the mechanism proposed by Trenner, Morikawa, and Taylor (68) and by Morikawa, Benedict and Taylor (66) of exchange of methyl radicals through the formation of quasi molecules. If we assume this for ethyl radicals also, according to the scheme

$$C_2H_5 + D \longrightarrow C_2H_5D^* \longrightarrow C_2H_4D + H$$

$$C_2H_4D + D \longrightarrow C_2H_4D_2^* \longrightarrow C_2H_3D_2 + H$$

$$\text{etc.} \quad \text{etc.}$$

the exchange is easily accounted for.

It is now necessary to consider the exchange which has taken place with the ethane molecule. To account for the products of reaction on the basis of either Schemes I or II considerable recombination of methyl radicals is necessary. If these are exchanged through quasi molecule formation as mentioned in the preceding paragraph, the exchange is adequately accounted for. If we assume that the exchange is solely due to

$$(24) \quad C_2H_{5-x}D_x + D_2 \longrightarrow C_2H_{4-x}D_{x+1} + D,$$

and assume reaction Scheme I, we may set an upper limit to the velocity of (6) relative to (7). Let us take run No. 5, Tables VII and VIII, as an example. At the beginning we have

$$D_2(84 \text{ percent}) + C_2H_5(16.2 \text{ percent } D) \longrightarrow$$
$$C_2H_6(30.2 \text{ percent } D) + D(84 \text{ percent})$$

(where the percentages refer to the hydrogen isotope content which is deuterium) and at the end

$$D_2(33.5\text{ percent}) + C_2H_5(16.2\text{ percent}) \longrightarrow C_2H_6(19\text{ percent}) + D(33.5\text{ percent})$$

This gives on the average

$$\text{hydrogen isotope molecules} + \text{ethyl radicals} \longrightarrow \text{ethane } (24.6\text{ percent}) + \text{hydrogen isotope atoms.}$$

Now in run No. 5 the residual ethane is 11.2 percent exchanged. Hence approximately 11.2/24.6 = 45 percent of the residual ethane would have reacted according to (24) if it were the only reaction causing exchange of the ethane. Then to account for the stoichiometric relationships (6) must occur to the same additional extent to compensate. In run No. 5, 66 percent of the ethane was decomposed and of this percentage according to Scheme I (omitting the recombination of methyl radicals by (19)) 121 percent proceeds by (7) and 34 percent by (6). Hence the ratio of the frequencies of (6) to (7) should be 121 to (34 + (34/66) x 0.45) = 121 to 57. Such a calculation although definitely invalid (since there must be some ethane formation by radical recombination and indeed an amount comparable to the butane or propane formation) indicates without doubt that (6) is slower than (7). With the ratio of the velocities 121 to 34, $E_6 - E_7$ would have a value of 0.8 kcal. and with the ratio 1.21 to 57, 0.5 kcal. Hence if $E_7 = 8.6$ kcal, E_6 cannot be far from 9 kcal.

The Decomposition of Ethane

There are three fundamentally different possibilities for the primary reaction, a C-C bond split (2), a C-H bond split (3) and the elimination of a methylidene radical (4). These will be discussed separately.

(a) The elimination of a methylidene radical.

This is intrinsically not a very likely mechanism. If (4) were the primary step, it would be possible to account for the products obtained by assuming secondary reactions of the methylidene radical such as (10) and (28). On this basis we would expect the amount of methane to be equal to (C_3H_8 + $2C_4H_{10}$), in exact agreement with runs 7 to 9 of Table VI. However, since in this case all the butane is formed via propane, we would expect practically no butane at the lowest trapping temperatures. As is noted this is not the case. This objection might be overcome by assuming (11) followed by (8), (18) and (20). The main objection to (4) as the primary step, however, is the absence of ethylene as a product of the reaction. It seems very unlikely that (4) could be the primary step without any combination of methylidene radicals to form ethylene by (21), especially in view of the low quantum yield of the overall reaction. The only way to avoid this difficulty would be to assume that (11) was extremely fast. To inhibit recombination of ethylene, therefore, it would be necessary for (11) to have an activation energy much lower than 7 kcal., which is very unlikely. There would also be the possibility of ethylene formation by (12). As a matter of fact Storch and Kassel (75) assume this to be very rapid. It appears therefore that (4) is not a very plausible primary step, and as the experiments with the flow system give very definite evidence as to the nature of the initial process, (4) will not be further considered.

(b) The C-C bond split.

If the primary process is (2) it is necessary, it would seem, to have some process for the generation of ethyl radicals. The only means for this to occur is by (8) forming methane and an ethyl radical. The various radical recombination reactions can then regenerate ethane by (19) or form butane (20) and (or) propane (18). Such a mechanism gives a complete explanation of the products of the reaction in a circulatory system, i.e. large formation of methane and no hydrogen production. The unlikelihood of the occurrence of reactions (9), (13), (14), (24), (26) and (27) has already been discussed (page 87). From the evidence gathered in the circulatory system there do not seem to be many objections to this mechanism. It should be noted, however, that (8) is competing with (18) and (19) for the destruction of methyl radicals. The rate of (8) involves $[C_2H_6]$ while the other processes do not. An analysis of these equations assuming a steady state of methyl and ethyl radical concentrations is somewhat complicated algebraically. However, a qualitative inspection indicates that the ratio $[C_4H_{10}] / [C_3H_8]$ should increase considerably with increase in $[C_2H_6]$. In runs Nos. 7 and 8, where the ethane pressures are 7 and 4 cm. respectively, little change in the reaction products is noted. This is very definite evidence against Scheme II for the reaction in the presence of deuterium or hydrogen. The most conclusive evidence against this mechanism, however, will be given in the next section.

The C-H bond split.

If a C-H bond split according to (3) is the primary step, we would have as secondary reactions (6) and (7) followed by recombination of atoms and radicals by (15), (18), (19) and (20). The occurrence of (8) to any extent has been ruled out in the preceding paragraph. The small probability of the occurrence of reactions (9), (13), (14), (24), (26), and (27) has already been discussed. It should be noticed that the occurrence of reaction (6) to any extent, if followed by (5), will make no alteration in the products of the reaction, the two processes

$$\begin{array}{lll} (6) & C_2H_6 + H & \longrightarrow C_2H_5 + H_2 \\ (5) & H_2 & \longrightarrow 2H \\ \hline & C_2H_6 & \longrightarrow C_2H_5 + H \end{array}$$

being equivalent to the primary step. The quantum yield of course would be diminished. Other factors which would explain the low quantum yield are the occurrence of (1) and (19). The metastable mercury atoms procuded by (1), due to their long life could be assumed to disappear at the wall.

The most important question to be answered is whether (5) will occur with sufficient rapidity to account for the absence of hydrogen in the products of reaction. A rough estimate may be made as follows: The reaction is assumed to take place through steps (1), (3), (6), (7), (18), (19) and (20). A steady state of the concentration of hydrogen can be deduced. Its formation will occur by (6) and (15) and its destruction by (5). On this basis we get

$$\frac{d[H_2]}{dt} = 0 = \frac{[H_2]\sigma_1^{\,2}\mu_1^{\,1/2}}{[C_2H_6]\sigma_2^{\,2}\mu_2^{\,1/2} + [H_2]\sigma_1^{\,2}\mu_1^{\,1/2}} \cdot I_{abs}$$

$$-f\left(\frac{[C_2H_6]\sigma_2^{\,2}\mu_2^{\,1/2}}{[C_2H_6]\sigma_2^{\,2}\mu_2^{\,1/2} + [H_2]\sigma_1^{\,2}\mu_1^{\,1/2}} \cdot \frac{eI_{abs}}{2} + \frac{[H_2]\sigma_1^{\,2}\mu_1^{\,1/2} \cdot I_{abs}}{[C_2H_6]\sigma_2^{\,2}\mu_2^{\,1/2} + [H_2]\sigma_1^{\,2}\mu_1^{\,1/2}}\right)$$

where σ_1 and σ_2 are the mean quenching diameters of excited mercury and hydrogen, and excited mercury and ethane respectively and μ_1 and μ_2 their respective reduced masses; I_{abs} is the resonance radiation absorbed in einsteins per sec; e is the efficiency of reaction (3) relative to reactions (1) + (3) and f is the fraction of H atoms which react to form H_2. The last expression will be equal to

$$\frac{K_6[H][C_2H_6] + K_{15}[H]/[C_2H_6]}{K_6[H][C_2H_6] + K_{15}[H]/[C_2H_6] + K_7[H][C_2H_6]}$$

if the H_2 is assumed to be formed mainly by diffusion. On simplification of the steady state expression we get

$$\frac{[H_2]}{[C_2H_6]} = \frac{ef}{2r(1-f)}$$

where $r = \dfrac{\sigma_1^{\,2}\,\mu_1^{\,1/2}}{\sigma_2^{\,2}\,\mu_2^{\,1/2}} = 60$

Now in the experiments performed at the lower trapping temperatures, as in runs 7, 8 and 9 of Table VI, the pressure of ethane in the reaction system was only about 1/10 of the total gas pressure due to condensation in the traps. Then if we assume in the extreme case that $e = 1$ and f say $= 0.9$ then the percentage of hydrogen which should be found in the products of the reaction would be 0.75. This would be two or three times the sensitivity of the analytical method used. If $e = 0.5$ and $f = 0.5$ then $H_2 = 0.04$ percent, a value much below that possible to detect by the methods employed here. It is therefore quite possible that the decomposition can take place by a C-H bond split mechanism.

The above analysis although indicating that a C-H bond split mechanism is possible offers no direct proof that (3) is the primary step. It was to establish this point with certainty that the experiments in the continuous flow system were performed. By this method the concentration of H_2 (if formed) would be kept low and so the back reaction by (5) would be diminished. The results showing a quantum yield of 0.08 in the production of hydrogen demonstrate with certainty that the primary reaction is (3) and establish the mechanism as outlined above.

In discussing the results obtained at higher temperatures it seems that the obvious explanation lies in an increase in the rate of (6) with respect to (7) as would be expected from its higher activation energy. This is in accord with the results of Trenner, Morikawa and Taylor (68) who found that above 100°C or so (6) predominated over (7). This process would also lead to an increased production of ethyl radicals. The higher yields of butane relative to propane confirm this idea.

The Reaction at High Trapping Temperatures.

Under these circumstances the reaction is complicated by secondary processes, and the results are thus only of minor importance. Since the addition of hydrogen to ethane at low trapping temperatures leads to hydrogen consumption rather than production, it is apparent that the production of hydrogen from ethane alone at high trapping temperatures is not "autocatalytic", and must be due to secondary decomposition of butane. Also, the low methane production relative to the butane and higher products formed must be due to the presence of butane. It thus appears that the butane decomposition leads to the formation of higher products from ethane in some manner not involving the production of methane.

The Decomposition of Butane.

Since these experiments were made merely to confirm the production of hydrogen, no discussion is necessary.

A New Field of Quantitative Investigation.

The results obtained for ethane, though far from constituting an exhaustive study, indicate that the mercury photosensitized method is a powerful tool for studying the primary processes of hydrocarbon decompositions. Now that the experimental technique has been developed, and the products of a decomposition need no longer be reported as "hydrogen and a non-volatile oil," results should be rapidly forthcoming on the various reactions of the other hydrocarbons. This will constitute an important step in unravelling the complexities of organic decomposition.

F. SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1. The reaction of deuterium atoms with methane has been investigated, the atoms being produced by photosensitization with mercury. The activation energy of the reaction

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

is found to be not far from 11 kcal.

2. The reaction of deuterium atoms with ethane was studied, the atoms being produced by the discharge tube method. The activation energy of the process is found to be 6.3 kcal.

3. The mechanism of the latter reaction was analyzed and it is concluded that the measured activation energy is that of the reaction

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

Hence the reaction

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

must have approximately the same energy of activation.

4. The effect of this value on the Rice-Herzfeld mechanism for the decomposition of C_2H_6 has been examined, and it is concluded that although a value of 6.3 kcal. for the above reaction would give calculated values of $[H]$ in agreement with the experimental results of Sachsse,

the scheme would no longer predict a first order rate or the experimental value of the overall activation energy.

5. An arrangement has been devised making it possible to utilize, in a photochemical reaction, 10^{19} quanta per second of mercury resonance radiation (λ2537).

6. The mercury photosensitized decomposition of ethane has been studied both in a continuous flow and in a circulatory system.

7. In the circulatory system by employing improved trapping methods it is possible to remove propane and butane from the system as fast as formed and thus further reactions of these hydrocarbons are entirely inhibited. Under these circumstances the products of the reaction (at near room temperature) consist exclusively of methane, propane, and butane, the hydrogen and higher hydrocarbons found in previous investigations being secondary products of the propane and butane decompositions. The quantum yield at 35°-75°C (in terms of ethane disappearing) is approximately 0.2 .

8. On the other hand in the continuous flow system at rates of flow identical to those used in the circulatory system hydrogen was found to be produced in large quantities the quantum yield for its production being 0.08 at 65°C.

9. The reaction of H and D atoms with ethane was investigated, the atoms being produced by photosensitization with mercury. Higher products were removed from the system

by circulating the gases through cooled traps. Under these conditions hydrogen and deuterium were consumed and large amounts of methane formed. Propane and butane were also formed but in much lesser quantities. In the reaction in the presence of deuterium, methane, propane, and butane were found to be considerably more exchanged than the residual ethane. The quantum yield at 35°-75°C in terms of ethane disappearing is 0.15.

10. A detailed consideration of the reactions shows that the decomposition of ethane with or without the initial presence of hydrogen can be adequately expressed by the following steps:

$$
\begin{array}{lll}
Hg(6^3P_1) + C_2H_6 & \longrightarrow & C_2H_5 + H + Hg(6^1S_0) \\
Hg(6^3P_1) + C_2H_6 & \longrightarrow & C_2H_6 + Hg(6^3P_0) \\
Hg(6^3P_1) + H_2 & \longrightarrow & 2H + Hg(6^1S_0) \\
H + C_2H_6 & \longrightarrow & CH_3 + CH_4 \\
H + C_2H_6 & \longrightarrow & C_2H_5 + H_2 \\
2H & \longrightarrow & H_2 \text{ (wall)} \\
2CH_3 & \longrightarrow & C_2H_6 \\
2C_2H_5 & \longrightarrow & C_4H_{10} \\
CH_3 + C_2H_5 & \longrightarrow & C_3H_8
\end{array}
$$

11. The reaction $H + C_2H_6 \rightarrow CH_3 + CH_4$ has an activation energy roughly 1 kcal. less than the reaction $H + C_2H_6 \rightarrow C_2H_5 + H_2$.

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APPENDIX

Two experiments were made on the mercury photosensitized decomposition of methane in a circulatory system. The experimental conditions with the exception of the cell and trapping temperatures were the same as in run No. 9 Table VI. The methane used was obtained from The Ohio Chemical and Manufacturing Co. and was purified by distillation in an apparatus of the Podbielniak type. The trapping temperature was -183°C. The quantum yield for the production of hydrogen was roughly 0.04 at 195°C and 0.25 at 350°C.