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THE MERCURY PHOTOSENSITIZED REACTIONS
OF PROPANE

by

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GENERAL INTRODUCTION

Although the study of reaction kinetics really originated when Guldberg and Waage enunciated the Mass Law in 1867, little progress was made for many years. Early workers investigated whether a reaction would or would not go and what yield of products it would give but they gave little consideration to the mechanism of the reaction. Much of their work on thermal decomposition reactions consisted of passing the compound to be investigated through a hot tube under conditions which resulted in almost complete decomposition of the original substance. In many cases, moreover, the products of the primary decomposition would also decompose so that the final products gave little information about the primary processes.

The great interest taken in this subject during the last fifteen years is due largely to the discovery by Hinshelwood in 1926 that the thermal decompositions of a number of simple organic materials followed a first-order mechanism. Subsequent investigations have shown that this is the case for a large number of reactions and it seems probable that at least the primary step in most organic decompositions is a unimolecular change.

As a result of these investigations, many new

kinetic theories have been hypothesized. Outstanding among these is the Rice Free Radical Theory. This branch of kinetics, which grew up with the discovery of free radicals by Paneth and the proof of their importance by F. O. Rice, deals with reactions involving atoms, radicals, and simple molecules.

The industrial importance of the hydrocarbons has aroused great interest in their thermal decomposition mechanisms. Unfortunately, however, the thermal decomposition reactions of these compounds generally involve a great many steps that are extremely hard to untangle and the choice of a mechanism, in many cases, becomes one of pure speculation. Consequently, attempts have been made to supplement the information obtained from thermal studies by independent methods.

The present investigation is concerned with the applicability of the free radical theory to hydrocarbon decompositions. Information is obtained by an independent method: mercury photosensitization. However, since contemporary knowledge of the subject comes from a variety of sources, it will be advantageous to review the theory of free radicals and to point out the information that can be obtained by the various independent methods before proceeding to specific reactions.

INTRODUCTION

The Kinetics of Unimolecular Reactions.

Hinshelwood's discovery (1) and its subsequent confirmation that most organic substances decompose by a first-order mechanism have led to the general conclusion that the stability of gaseous organic molecules is really determined by the size of the unimolecular velocity constant. This is usually expressed in terms of the integrated form of the Arrhenius equation:

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

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

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

The first problem in this theory was to explain the mechanism of activation. Perrin (2) and others (3,4)

suggested that the molecule obtained the necessary activation energy by absorption of "black body" radiation. This idea, however, met with severe obstacles and did not survive many tests.

The modern theory of unimolecular reactions is based on the hypothesis, first suggested by Lindemann (5), that activation occurs by collisions but that a time

lag exists between activation and reaction. Consequently, most activated molecules are deactivated before they have a chance to react. Hence there exists a stationary concentration of activated molecules, which is calculable from the Maxwell-Boltzmann distribution, and the rate of reaction is proportional to the first power of the concentration of the reacting substance. At low pressures, however, the diminished number of collisions will no longer be able to replace the activated molecules destroyed by reaction. Thus the stationary concentration will fall and the rate of reaction will diminish with decreasing pressure.

In the general case the process may be represented by

In the steady state an equilibrium exists between the activating and deactivating mechanisms. Thus

$$-\frac{d}{dt}(A^*) = \frac{d}{dt}(A^*)$$

$$\text{or} \quad 2k_1(A)^2 - k_3(A^*) - k_2(A)(A^*) = 0$$

$$\text{whence } (A^*) = \frac{2k_1(A)^2}{k_3 + k_2(A)}$$

The overall rate of reaction is entirely governed by reaction (3), or in other words by $k_3(A^*)$. Hence

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

At high pressures $k_2(A) \gg k_3$ and the above equation reduces to

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

which is the characteristic form of a first-order reaction.

At sufficiently low pressures, however, deactivation is slower on account of the decrease in the number of collisions and finally $k_3 \gg k_2(A)$. The rate expression is then

$$-\frac{d}{dt}(A) = 2k_1(A)^2$$

and the reaction becomes of the second order. In the intermediate range, the rate constant will gradually fall off and the order of the reaction will have a value between 1 and 2.

On the basis of the Lindemann hypothesis various theories have been proposed, especially to account for that portion of the rate-pressure curve where the

The preceding derivation and other sections of the introduction have been adapted from Steacie: Kinetics of Reactions of Hydrocarbons, Chem. Reviews 22, 311 (1938).

velocity ceases to conform to the unimolecular law. In the development of such theories it is necessary to be more specific about the nature of the energy of activation. The older type of theory, of which Hinshelwood (6) was the chief exponent, assumes that if a molecule has an energy equal to or greater than E , it has a definite probability of reacting, independent of its excess energy over and above E . Although this is the simplest form of theory, it does not agree well with experimental facts. The other form of theory assumes that for reaction, energy must be concentrated in one particular degree of freedom or in one vibrational bond of the molecule. Hence the chance of getting energy $\geq E$ into one bond will be a function of the total energy of the molecule and will increase rapidly with the excess of the energy over E in the activated molecule. This type of theory gives results which are in good agreement with experiments. There are a number of forms of this theory (7) (8) but all are essentially the same. That of Kassel (7) is the one which is usually employed.

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

the purpose of predicting the products of decomposition reactions, it becomes of prime importance to discover any possible relation between the activation energy of a reaction and the strength of the bonds formed and broken in it.

Free Radicals in Organic Decomposition Reactions

The mechanism by which many organic compounds decompose at high temperatures is still a matter of controversy. The various theories proposed, however, fall into two main classifications.

The first and classical theory is termed the molecular mechanism. It assumes that the rupture of a molecule to form two or more new molecules occurs in a single step. It is obvious that the activation energy of such a process will bear no very simple relation to the bond strengths.

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

step, the activation energy should be a direct measure of the strength of the ruptured bond.

The existence of such unsaturated radicals has already been proved by experiment. In 1929, Paneth and Hofeditz (9) and Paneth and Lautsch (10) showed that methyl and ethyl radicals from the decomposition of organic products could be detected in rapidly flowing gas streams by their reaction with lead mirrors. Using this technique, F. O. Rice and his co-workers (11-20) made a comprehensive study of organic decomposition reactions. They found that free radicals could be detected in the decomposition of almost all organic substances, and this led them to postulate a general free radical theory for hydrocarbon decomposition reactions.

Rice points out that if two reactions have activation energies differing by 4 Kcal., then the relative rates at 600° C. are in the ratio of $e^{-400/2 \times 873}$ to 1, or approximately 9 to 1. Similarly for a difference of 10 Kcal., the ratio is 500 to 1. Trusting then in the basic assumption that the activation energy is intimately connected with bond strength, we may conclude that if there are two or more ways of accomplishing a primary break in the molecule, and if one of these has an activation 10 Kcal.

or more lower than that of any of the others, it alone will occur to any appreciable extent.

Though there is considerable disagreement about the absolute bond strengths, it is definite that the C = C and C $\equiv$ C bonds are very much stronger than the other bonds in the molecule. Indirect evidence (21) indicates further that the C-H bond is about 10-15 Kcal. stronger than the C-C bond. One may therefore conclude that, if the thermal decomposition takes place by a free radical mechanism, it will always split at a C-C bond and never at a C-H or a double or triple bond.

Only methyl and ethyl radicals can be detected by the Paneth technique (22) presumably because the higher radicals are unstable at high temperatures and break down before detection into ethyl and methyl groups. It should be noted, however, that Pearson and Purcell (23) have detected higher radicals by photolysis at room temperature.

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

and this would be followed by the series of reactions

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

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

Thus, using Rice's mechanisms, it is possible to predict the products of reaction. To be fully successful, however, the theory must also account for the kinetics of the reaction. For instance, it must explain why the

overall mechanism of an organic decomposition appears to be of the first order though the mechanism is really a complex series of steps. Secondly, if most reactions occur by the rupture of a C-C bond as postulated, it must explain why the experimental activation energies for such reactions are usually far smaller than the C-C bond strength.

Rice and Herzfeld (17) answered these questions by devising mechanisms on a free radical basis which would lead to a first-order overall rate. Furthermore, by a suitable choice of activation energies of the part reactions, they were able to make the overall activation energy agree quite well with the experimental value. As an example, consider the following artificially simplified scheme for the decomposition of an organic molecule (20):

E in Kcal.

The molecule M_1 decomposes initially into a radical R_1 and a smaller molecule M_2 . The radical R_1 then reacts with a fresh molecule of reactant M_1 , abstracts a hydrogen atom, and forms the stable compound R_1H and the free radical R_2 . R_2 then breaks up into the radical R_1 and a molecule M_3 .

Thus a chain process is set up since steps (2) and (3) can repeat over and over again until the radical R_1 is destroyed to form a stable molecule M_4 .

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

$$\frac{d}{dt}(R_1) = 0 = k_1(M_1) - k_2(R_1)(M_1) + k_3(R_2) - k_4(R_1)(R_2) \quad (5)$$

and

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

The overall decomposition of M_1 may be expressed as

$$-\frac{d}{dt}(M_1) = k_1(M_1) + k_2(R_1)(M_1) \quad (7)$$

By solving equations (5) and (6) for R_1 and substituting in (7), we obtain:

$$-\frac{d}{dt}(M_1) = k_1(M_1)(1 + \sqrt{k_2 k_3 / 2k_1 k_4}) = (M_1) \sqrt{\frac{k_1 k_2 k_3}{2k_4}} \text{ approx.}$$

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

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

so that substituting the assigned values of E , we obtain:

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

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

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

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

the overall order would be 1.5, while

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

is much faster than the other two possible recombinations.

Such mechanisms are admittedly highly speculative. Furthermore, it should be noted that experiments using the Paneth technique to prove the existence of free radicals were, of necessity, carried out at temperatures 200-300°C. above the normal thermal decomposition range. Thus, while these experiments prove that free radicals are present at high temperatures, they do not necessarily prove that free radicals are present or of importance in the usual temperature range.

Striking support for the fundamental concept of free radical chain reactions was soon forthcoming. Frey (24) was able to initiate chains in the decomposition of n-butane at temperatures below the normal decomposition range by the addition of methyl radicals (from the decomposition of dimethyl mercury). Similarly Allen and Sickman (25),(26), Fletcher and Rollefson (27), Echols and Pease (28), and Heckert and Mack (29) produced sensitized chain decompositions of a number of organic substances.

Evidence for the presence of chains was also obtained from photochemical investigations. Leermakers (30) showed that the photolysis of acetaldehyde is a chain reaction above 80°C. and his results are in agreement with Rice and Herzfeld's predicted mechanisms. Leermakers (31) also found that chains are set up in the decomposition of dimethyl and diethyl ether induced by admixed acetone.

Further evidence for the chain character of some decompositions is furnished by Stavely and Hinshelwood (32) and others (33),(34),(35),(36). From a study of the effects of different amounts of nitric oxide on reactions, they calculated chain lengths ranging from two to fifteen for a number of reactions. This is definite evidence for the presence of chains, but, in most cases, the chain lengths

are far too small to be in accord with the Rice-Herzfeld mechanisms. Recent work, however, (37),(38) indicates that in certain cases there may be a few long chains rather than a large number of short ones, i.e., that the Rice-Herzfeld mechanisms may hold for a small fraction of the total reaction, the remainder decomposing by a molecular mechanism.

It may therefore be said that, in general, the evidence supports the free radical theory and that a great deal of data can be correlated on this basis. However, when the specific Rice-Herzfeld mechanisms for a number of reactions are tested, the situation is entirely different. To date three general methods have been used as tests for the scheme. The stationary hydrogen atom concentration has been measured and compared with the theoretical value. Secondly, the activation energy of one of the proposed part reactions is measured independently. Thirdly, deuterio compounds are used as indicators of the mechanism.

The results of these investigations throw much doubt on the validity of the Rice-Herzfeld mechanisms.

Photochemical Reactions

From the preceding discussion, it is evident that the kinetics of the thermal decomposition are hard to unravel and it becomes of utmost importance to find independent methods of studying the "elementary reactions" that make up these decomposition mechanisms. Until we have further knowledge about the individual reactions, no great confidence can be placed in any one theory.

Such information is often obtained from photochemical investigations. To activate a molecule photochemically, it is only necessary for it to absorb a light quantum of energy equivalent to its activation energy. It is true that the method of activation is different to that of ordinary thermal reactions which takes place by collisions. However, once the primary steps have occurred, the following stages of a photochemical process are thermal reactions which often involve atoms and radicals. Unfortunately, however, very little information is available from the photodecomposition of the simple hydrocarbons since these compounds are transparent down to the extreme ultra-violet and the difficulties involved in working in the Schumann region are very great.

Photosensitized Reactions

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

Cadmium resonance radiation is also being employed in photochemical studies. Steacie and Potvin (40) (41), following the pioneer work of Bates and Taylor (39), have developed a powerful source of cadmium resonance radiation which they have used in their studies of the photosensitized reactions of the simple hydrocarbons. The first

cadmium resonance line is at 3261 A.U., which corresponds to 87 Kcal.

At the present time, zinc photosensitized reactions are being studied in this laboratory (42). The purpose of using zinc or cadmium resonance radiation is the attainment of greater selectivity than that allowed by mercury photosensitization.

Atomic Reactions

Photosensitization can also be used to study reactions involving hydrogen atoms. This was first demonstrated by the classical work of Taylor and his co-workers (43) (44). In the presence of hydrogen and a reacting substance, we have:

or possibly

Recent work by Olsen (45) indicates that the formation of HgH is due to secondary reactions of hydrogen atoms and excited mercury atoms so that reaction (2) is more probable than (2a).

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

Reactions involving hydrogen atoms can also be investigated by the Wood-Bonhoeffer technique (46) (47). This is accomplished by pumping hydrogen atoms out of a hydrogen discharge tube and allowing them to react with other gases in a reaction chamber. By such a method, it is possible to obtain a very high hydrogen atom concentration, but the experiments can be carried out only at very low pressures (between 0.1 and 1 mm.). However, a large number of reactions have been investigated in this way.

The Photochemical and Atomic Reactions of
the Aliphatic Hydrocarbons

Having reviewed the free radical theory in general, and discussed the chief methods of investigating its applicability to the decomposition of simple organic molecules, it would be of interest to consider the results obtainable by such investigations. Accordingly, the available data on the photochemical and atomic reactions of the simple hydrocarbons will be reviewed in the following sections.

Methane

The Photo- and Photosensitized Decomposition

Spectroscopic observations on the photodecomposition of methane have been made by Leifson (48) and Scheibe and his co-workers (49-51). They found that diffuse bands appear in the neighbourhood of 1600 A.U. On the basis of their work, Bonhoeffer (52) suggests that the primary reaction is

followed by the formation of ethane and hydrogen.

Leighton and Steiner (53) made a direct investigation of the photolysis of methane using a hydrogen lamp near the lower limit of fluorite. They obtained

hydrogen and unsaturated hydrocarbons in the approximate mole ratio of 4:1 and estimated the quantum yield to be approximately unity.

Groth and Laudenklos (54), using a Harteck xenon lamp (1469 A.U. and 1295 A.U.), found hydrogen and acetylene as the main decomposition products although they obtained also ethane and traces of C_2H_4 and C_3 to C_5 hydrocarbons. They suggested the following mechanism to account for the decomposition:

A brief investigation of the photolysis of methane, using the shorter wave length of a mercury lamp, ($\lambda \sim 1850$ A.U.) led Kemula and Dyduszyński (55) to conclude that the first step is

Early investigators (44) (56) (57) have reported that methane is stable in the presence of mercury atoms excited by resonance radiation. Recently, however, Morikawa, Benedict, and Taylor (58) have shown that the reaction

has a low activation energy and Steacie and Phillips (59) have found that the reaction proceeds at a measurable rate. They found that the quantum yield for the production of hydrogen was roughly 0.04 at 195°C. and 0.25 at 350°C.

The Reaction of Hydrogen Atoms with Methane

The reaction of hydrogen atoms with various hydrocarbons was first investigated by Bonhoeffer and Harteck (60) using a Wood's tube. They found that methane was surprisingly stable. The inertness of methane was confirmed by similar work by von Wartenberg and Schultze (61) and Chadwell and Titani (62).

Geib and Harteck (63) extended the experiments over a range of temperatures and found that no reaction occurred up to 183°C. They concluded that the reaction

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

proceeds more rapidly than other reactions such as

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

occurred with a low enough activation energy. Since estimates of the activation energy of reaction (2) vary from 8 to 23 Kcal. (12)(64-67), the issue is somewhat in doubt.

Geib and Steacie (68)(69) investigated the reaction of deuterium atoms with methane using the Wood-Bonhoeffer method. They found no detectable reaction up to 100°C., indicating an activation energy for the exchange reaction of not less than 11 Kcal. Their work indicates that the reaction is the analogue of the ortho-para hydrogen conversion

rather than

Preliminary work on the thermal exchange reaction by Farkas (70) served to support this suggestion.

The reaction has been studied by other investigators and the results obtained for the activation energy are tabulated below.

Investigators		Method.	Result
Steacie and Phillips	(71)	Mercury photosensitization	11.7 Kcal.
Farkas and Melville	(72)	Wood-Bonhoeffer	13 Kcal.
Morikawa, Benedict, and Taylor	(58)	Mercury photosensitization	12.5-14 Kcal.
Steacie	(73)	Wood-Bonhoeffer	12.9 ± 2 Kcal.
Trenner, Morikawa, and Taylor	(74)	Wood-Bonhoeffer	> 15.6 Kcal.

There is considerable disagreement as to whether the mechanism of the reaction is reaction (a) or (b). In general, however, the evidence favors an activation energy of about 12-13 Kcal. for the reaction

and a somewhat greater value of E for the reactions

Ethane

The Photo- and Photosensitized Decomposition

So far, very little work has been done on the ethane photodecomposition. The very meagre spectroscopic evidence (52) indicates that the absorption is probably by the C-H bond.

The recent investigation of the photolysis of ethane, propane, and butane led Kemula and Dyduszynski (55) to the general equation

It is difficult, however, from this evidence, to say just what the primary step may be.

Taylor and Hill (56) were the first to study the mercury photosensitized decomposition of ethane. They observed that ethane and higher hydrocarbons were found in ethylene--hydrogen mixtures. Anomalous pressure changes after the ethylene-hydrogen reaction was over led them to suspect that the ethane formed was being attacked both by hydrogen atoms and excited mercury atoms. They verified this and suggested that the reaction involved radicals.

Kemula, Mrazek, and Tolloczko (75), following

earlier work by Tolloczko (57), carried out a more detailed investigation of the photosensitized reaction. They circulated the reaction mixture through a trap at -80°C . to remove products of high molecular weight and thus prevent secondary processes. The gaseous products consisted entirely of hydrogen and methane, the ratio of hydrogen to methane being about 3:1 when the trap was kept at -80°C . and approaching infinity when the trap was kept at 20°C . Rough fractional distillations indicated that the condensable products consisted mainly of butane and octane. This points to a C-H rupture for the first step. The investigators therefore suggested

They concluded that the higher hydrocarbons resulted from the secondary reactions of butane

The mercury photosensitized decomposition was re-investigated by Steacie and Phillips (76) using a circulating system. They found that by maintaining the trap in the system at a lower temperature than $-80^{\circ}\text{C}.$, it was possible to remove higher boiling-point hydrocarbons more efficiently and thus avoid the occurrence of secondary reactions. Their products contained considerable amounts of hydrogen, methane, propane, and butane, and some higher hydrocarbons, the relative amounts of each depending on the trapping temperature. At lower trapping temperatures, the formation of hydrogen was almost entirely inhibited. This indicated that hydrogen was not a product of the ethane decomposition and that the initial split was in the C-C bond.

Later, Steacie and Phillips investigated the reaction using a "single pass" flow system (77). By this arrangement, the ethane was subjected only once to the action of the lamp. Analysis of the products showed a large yield of hydrogen and made it no longer necessary to rule the C-H bond split out. Steacie and Phillips, therefore, decided that the best mechanism for the decomposition was the following:

The inclusion of the second step was rendered necessary by the high quenching efficiency of hydrogen. This series of reactions explains the experimental results providing that reaction (3) is at least four times as fast as reaction (4). The assumption that reaction (3) would occur, however, is contrary to the general postulates of the Rice mechanisms. In order to account for the production of methane, but at the same time to avoid postulating chain splitting reactions similar to reaction (3), Taylor (78) has suggested that methane is formed by

At the present time, Steacie and Cunningham (79) are continuing the work on the "single pass" system over a wide temperature and pressure range to find out

whether temperature and pressure changes alter the course of the reaction.

Steacie and Potvin (41) have investigated the decomposition by cadmium photosensitization and obtained hydrogen, methane, propane, butane, plus higher hydrocarbons (mainly hexane). They found that in the early stages of the reaction the hydrogen produced was very large while the methane produced was very small. They therefore concluded that the primary step involves a C-H bond split as in the case of the mercury photosensitized experiments

and that the formation of methane occurs by

followed by

as suggested by Taylor.

The Reaction of Hydrogen Atoms with Ethane

Bonhoeffer and Harteck (60) and von Wartenberg and Schultze (61) found that luminescence occurs on mixing hydrogen atoms and ethane, bands due to C-H and C-C being observed. They recovered most of the ethane unchanged, but found no methane as they had no means of trapping it out. Chadwell and Titani (62) in a preliminary investigation reported the finding of about 4% methane and small amounts of ethylene.

Steacie and Phillips (71) studied the reaction of deuterium atoms with ethane using the Wood-Bonhoeffer technique. They found that an exchange reaction was taking place which appeared to have an activation energy of 6.3 Kcal. They concluded that the correct mechanism for the exchange was

Trenner, Morikawa, and Taylor (74) reinvestigated the reaction using the same technique. They concluded that at room temperature the main reaction was

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

as reported by Steacie and Phillips. There is, however, a considerable discrepancy in the activation energy between the two investigations (6.3 and 11.7 Kcal.). This is partly accounted for when it is realized that separate products were not isolated in Steacie and Phillips' investigation, it being assumed from the work of Chadwell and Titani that the formation of methane was negligible. Recently, Steacie (80) has confirmed the production of methane, finding about 10% decomposition. This, however, is not enough to bring the two activation energies into line.

Several qualitative investigations (44)(81) of the reaction of ethane with hydrogen atoms produced by mercury photosensitization have been made. Steacie and Phillips (76) have done some quantitative work along this line. They found that methane, propane, and butane, but no higher hydrocarbons were produced and that hydrogen was consumed. In a typical experiment using a trapping temperature of -125°C., the following stoichiometric

equation expresses the results

They suggested that the mechanism is

followed by various radical recombination reactions.

The mercury photosensitized reactions of ethane-deuterium mixtures were also studied by Steacie, Phillips, and Alexander (82). They found that the methane produced was highly deuterized but the residual ethane was only slightly deuterized. They therefore concluded that the reactions

do not occur to any great extent.

The reaction has also been studied by Steacie and Potvin (41) using cadmium photosensitization. Using a 1:1 hydrogen-ethane mixture, they found a large production of methane. Hydrogen was still produced, however, although

in smaller quantities. They concluded that the mechanism of the reaction was

followed by

which would account for the hydrogen produced, and by

which would account for the methane formed.

Propane

The Photo- and Photosensitized Decomposition

Kemula and Dyduszyński (55) investigated the photolysis of propane using the shorter wave-length of a mercury lamp ($\lambda \sim 1850$ A.U.). They concluded that the main reaction of propane is

The Reaction of Hydrogen Atoms and Propane

Taylor and Hill (43)(44) investigated the reaction of hydrogen atoms with ethane, propane, and butane, using mercury photosensitization. They reported that the speed of reaction increases with higher molecular weight, a finding that is reported by the large decomposition of pentane by hydrogen atoms observed by Frankenburger and Zell.

Trenner, Morikawa, and Taylor (74), in the course of another investigation, made two runs with propane and deuterium atoms by the Wood-Bonhoeffer method. They found that the products of the reaction were mainly methane and small amounts of ethane. The ethane and methane were highly deuterized but the propane was not exchanged. Propane, on this basis, is much less reactive than ethane.

Steacie and Parlee (83)(84) investigated the reaction by the Wood-Bonhoeffer technique over a temperature range from 30° to 250°C. They found methane, ethane, ethylene, but no hydrocarbons heavier than propane in the products. At 30°, methane was the only product but the ethane production increased rapidly and the ethylene formation more slowly as the temperature was raised. The activation energy of the primary step

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

Butane

The Photo- and Photosensitized Decomposition

Little work has been done on the photochemical reactions of butane. In the course of another investigation, Steacie and Phillips (76) made one run on the mercury photosensitized decomposition of butane. They found that hydrogen and higher hydrocarbons were produced in large amounts. The quantum yield at room temperature was 0.55.

The Reaction of Hydrogen Atoms with Butane

Taylor and Hill (43)(44), as already reported, found that butane reacts faster with hydrogen atoms produced by mercury photosensitization than does propane, and propane in turn reacts faster than ethane.

Recently Trenner, Morikawa, and Taylor (74) have made one run with n-butane and deuterium atoms using the discharge-tube method. They found about 11% decomposition at 110°C . to give methane, ethane, and propane. At

the present time, Steacie and Brown (85) are investigating the reaction by the same method.

Higher Hydrocarbons

The Photo- and Photosensitized Decomposition

Klemenc and Patat (86) investigated the mercury photosensitized decomposition of n-pentane. They found that both decomposition and polymerization occurred; hydrogen, methane, and other hydrocarbons being formed. Similar results led Frankenburger and Zell (87) to conclude that the primary process involved the splitting of both C-H and C-C bonds.

A brief investigation of the mercury photosensitized decomposition of n-hexane was made by Taylor and Bates (88). Much hydrogen and some methane were formed in the reaction.

THE MERCURY PHOTSENSITIZED REACTIONS OF PROPANE

As the foregoing summary shows, comparatively little work has been done on the photosensitized reactions of propane. Consequently, it was considered profitable to make a study of the mercury sensitized reactions over a series of temperatures. For purposes of comparison with the results of Steacie and Parlee for the reaction of hydrogen atoms with propane by the Wood-Bonhoeffer method (83) (84), it was decided to employ the same series of temperatures in this investigation.

There are, as we have already mentioned, two dynamic methods of investigation namely, the "single pass" and the circulating systems. In the "single pass" system, as the name implies, the gas is subjected only once to the lamp radiation. By passing the gas through the reaction chamber at a rapid rate, secondary reactions can be cut out to a large extent and the primary step can be ascertained. Such a process, however, is very inefficient and it is difficult to analyze accurately for reaction products in the presence of large amounts of undecomposed reactant gas.

The alternative method is to circulate the reaction mixture through a trap at a temperature low enough to remove the products of higher molecular weights as fast

as formed and thus prevent secondary processes. Such a method, of course, will not remove any hydrogen formed so that the reaction of hydrogen atoms with the gas must also be considered. In spite of this drawback, the method is widely used because of its much greater efficiency and consequent greater ease of analysis.

Preliminary experiments on the mercury photosensitized decomposition of propane by Steacie using a "single pass" system yielded chiefly hydrogen and high-boiling compounds. It was decided, therefore, to complete the investigation by using the circulating system.

Experimental

Apparatus

The apparatus employed in this investigation is shown diagrammatically in Figure 1.

The mercury saturator (S) supplied the necessary mercury vapor to saturate the reactant gas. It provided a mercury surface of about 30 cm.² and was heated electrically to 60°C.

A desaturating trap (D) filled with iron pellets removed any excess mercury at room temperature.

FIGURE I

Apparatus employed

The circulating pump (P) consisted of a brass tube 40 cm. long and 4 cm. diameter, inside of which was a close-fitting steel cylinder. 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 380 cc.

The circulating pump was connected to a series of mercury valves(V). These valves were so arranged that the gas in the line always flowed in the one direction, i.e., through the saturator to the reaction vessel.

The condensable reaction products were collected in a product trap (T) which was filled with iron pellets and was kept at a temperature of -80°C .

The fused quartz reaction vessel (C) was annular in form to utilize the largest possible fraction of light from the lamp. The vessel was 10 cm. long by 8 cm. in diameter with a hole 4 cm. in diameter through the middle. Its volume was 320 cc.

The reaction vessel was illuminated by a Hanovia Sc. 2537 mercury resonance lamp which was filled

FIGURE II

Spectrogram of Light Source A

<u>Row</u>	<u>Exposure Time</u>
# 1-4	2 sec.
# 5-8	4 sec.
# 9-12	6 sec.

with a drop of mercury and with argon at a low pressure. The lamp (later referred to as light source A) was in the form of a double-U and was run at 100 milliamperes with a 5000 volt sign transformer. The radiation from the lamp was used directly without filtering as spectroscopy (Figure II) showed that the 2537 line was essentially the only line emitted.

As the Hanovia lamp was unsuitable for high temperature investigations, a new combined lamp source and reaction vessel (Figure III) was employed in later work. The design of the lamp (light source B) was similar to that of Steacie and Phillips (89) except that the emitting portion was a quartz tube in the form of a double-U. The quartz tube was joined to the pyrex electrode chambers (E) by graded seals (G), and was filled with neon at a pressure of 8 mm. and a droplet of mercury. Electrodes were coated and supplied by the Claude Neon Eastern Limited, Montreal and the filling and bombarding were done by the usual neon sign technique.

The lamp source was sealed in a pyrex jacket (P) with a volume of 870 cc., which served as the reaction chamber. The reaction chamber was equipped with gas inlet and outlet tubes and was provided with a thermocouple well

FIGURE III

Light Source B

(T) for measuring the temperature of the reaction vessel. The temperature was measured by a chromel-alumel thermocouple in conjunction with a potentiometer. For high temperature work, the reaction vessel was enclosed in an electrically heated furnace and the lamp electrodes were air-cooled or water-cooled to prevent reversal of the mercury resonance radiation.

The main portion of the apparatus had a total volume of about 1680 cc. when light source A was employed and of about 2220 when light source B was used. It was connected to a pumping system, a McLeod gauge, gas reservoirs, a Toepler pump, gas holders, etc.

The Intensity of the Light Sources

The intensity of the radiation emitted by the lamps was determined by measuring the rate of hydrolysis of monochloroacetic acid (90). The acid used was 0.5 N. and the procedure employed was that used by Steacie and Phillips (76). Recent work (91) has shown that low values are obtained by this method but it was used to facilitate comparison with the ethane decomposition.

Experimental Procedure

All runs were carried out at the vapor pressure of propane at -80°C . (about 14 cm.). A sufficient quantity of gas (or gases if hydrogen was one of the reactants) was allowed to enter the system and the excess was condensed out when the trap (T) was brought to a temperature of -80°C . The mercury saturator was then heated, the circulating pump started, and the gas illuminated for a definite period of time.

This procedure had to be modified for high temperature runs in order to obtain better temperature control. Before making a run, the lamp and furnace were heated up to the required temperature for several hours. The lamp was then turned off, a sufficient quantity of gas admitted to the system, and the excess rapidly condensed out while the mercury saturator was heating. The circulating was then started and the gas illuminated for a definite time as before.

Analysis of the Gaseous Products

At the conclusion of a run, the gaseous products were pumped by a Toepler pump into a portable gas-holder.

The gas was then analyzed in a low temperature fractional distillation apparatus of the Podbielniak type (92). The hydrogen-methane fraction was further analyzed by combustion in the usual way. Occasional tests on fractions were made for unsaturated hydrocarbons in a Burrell gas analysis apparatus.

Analysis of the Liquid Products

The condensate, which consisted of high boiling hydrocarbons, was weighed and saved for future analysis. Analysis of the combined condensates of similar runs was made in a fractional distillation apparatus (Figure IV) designed for high temperature distillations. This apparatus was similar in construction to the Podbielniak still. For high temperature work, however, an air blast (A) replaced liquid air as the cooling agent for the column and all portions of the apparatus except the receivers (R) were heated electrically. This heating enabled the fractions to be taken off as gases and not as liquids as in other semi-micro methods of analysis.

In making a run with this apparatus, the sample was condensed in the small bulb (B) with liquid air. It was then heated slowly by a small flame or electric furnace

FIGURE IV

High Temperature Distillation Apparatus

until the column pressure was atmospheric and the liquid was refluxing over the thermcouple (T). The gas was then allowed to leak through the filed stopcock (S) and be collected in the receivers which were cooled in ice. The apparatus was standardized by the distillation of samples of acetone, pentane, hexane, heptane, etc., of reagent grade (Eastman Kodak).

Fractions from the distillation were at first further analyzed by combustion and by testing for unsaturates with bromine solution. Later fractions, however, were analyzed by determining their melting-points and refractive indices. These later analyses were carried out by Mr. J. R. Maillet of the staff of the National Research Council.

Materials

Propane was obtained in cylinders from the Ohio Chemical and Manufacturing Company. It was stated to be 99.8% pure and no appreciable impurities were detected in Podbielniak analyses. The gas was consequently used without further purification.

Hydrogen was obtained from commercial cylinders. It was purified by passage over platinized asbestos at 600°C. and through a liquid air trap. The purified gas was then stored in resevoirs attached to the apparatus.

Experimental Results

The Mercury Photosensitized Decomposition of Propane

The results obtained for the mercury photosensitized decomposition of propane at room temperature using light source A are given in Tables I and II. The initial and final pressures of the gas given in columns (3) and (4) mean the pressures of the gas at room temperature. The quantum yield, expressed in terms of hydrogen and methane formed, is given in column (6).

The experiments in Table II were carried out in the same way as those in Table I except that different initial propane pressures were used. The results show that when the quantity of propane used is insufficient, the quantum yield of the reaction falls off.

The liquid condensate is expressed in column (7) as " C_6H_{14} " since the main fraction of the distillate analyzed to C_6H_{14} on combustion. The condensate also contained some hydrocarbons of higher boiling point than the boiling point of the C_6H_{14} fraction and small traces of lower boiling material so that this method of reporting is somewhat in error. However, as the C_6H_{14} fraction was

TABLE I

The Mercury Photosensitized Decomposition of Propane

Volume of system 1680 cc. Propane vapor pressure 14 cm.
 Volume of reaction cell 320 cc. Trap temperature -80°C.
 Arc current 0.100 amp. Reaction temperature 24-27°C.

Resonance radiation absorbed 4×10^{-6} einsteins/sec.

Circulating rate 1900 cc./min.

RUN NO.	TIME in Min.	GAS PRESSURE		DECOMP. RATE Moles $\times 10^{-6}$ /sec.	QUANTUM YIELD ($H_2 + CH_4$)	PRODUCTS in Moles $\times 10^{-4}$			PRODUCTS Mole Percentage		
		INIT.	FINAL			H_2	CH_4	" C_6H_{14} "	H_2	CH_4	" C_6H_{14} "
A-1	180	364	301?	0.73	0.18	78.5	0.9	65.1	54.3	0.6	45.1
2	180	367	319	.70	.17	73.4	1.9	65.3	52.2	1.4	45.1
3	180	365	325.5	.68	.17	73.6		--	--	--	--
4	180	365	323	.72	.18	76.6	0.9	70.6	51.7	0.6	47.6
5	180	405	370	.71	.18	76.2		67.0	53.2		46.8
6	150	414.5	--	.78	.19	67.5	1.1	61.4	51.9	0.8	47.2
7	180	397	--	.74	.18	76.9	2.7	59.3	55.3	1.9	42.8

TABLE II

The Mercury Photosensitized Decomposition of Propane

Operating conditions as in Table I

RUN NO.	TIME in Min.	GAS PRESSURE		DECOMP. RATE Moles $\times 10^{-6}$ / sec.	QUANTUM YIELD ($H_2 + CH_4$)	PRODUCTS in Moles $\times 10^{-4}$			PRODUCTS Mole Percentage		
		INIT.	FINAL			H_2	CH_4	" C_6H_{14} "	H_2	CH_4	" C_6H_{14} "
P-1	150	165.5	142.5	0.64	0.16	45.5	12.0	47.0	43.5	11.5	45.0
2	180	162	142.7	.53	.13	56.6	0.4	45.7	55.1	0.4	44.5
3	180	161.3	139	.56	.14	60.4		--	--	--	--
4	180	261	220	.68	.17	70.8	3.0	49.5	57.4	2.4	40.2
5	180	261	211.5	.70	.17	72.8		--	--	--	--

over 80% by volume of the total condensate in all cases, the error is not serious.

The results of runs at 100°, 175°, 250°, and one run at 323°C. using light source B are given in Tables III, IV, and V. The method of reporting is the same as for Tables I and II.

The Reaction in the Presence of Added Hydrogen

The results of the decomposition of propane in the presence of added hydrogen using light source A are given in Table VI. In this table, the moles of hydrogen in the products are the moles of hydrogen formed during the reaction and the quantum yield is expressed in terms of hydrogen and methane formed.

Condensate Analysis

The results of the condensate analysis are given in Table VII. The high boiling products are expressed in volume percent of the total condensate. The results show that the liquid products are essentially the same in all cases.

TABLE III

The Mercury Photosensitized Decomposition of Propane

Volume of system 2215 cc. Circulating rate 1900 cc./min.
 Volume of reaction cell 870 cc. Trap temperature -80°C.
 Arc current 0.090 amp. Propane vapor pressure 15 cm.
 Resonance radiation absorbed 9.5 x 10⁻⁶ einsteins/sec.

RUN NO.	TEMP.	TIME	PRESS.	DECOMP.	QUANTUM	PRODUCTS			PRODUCTS		
	in °C.	in Min.	in Mm.	RATE Moles x 10 ⁻⁶ /sec.	YIELD (H ₂ +CH ₄)	in Moles x 10 ⁻⁴			Mole Percentage		
						H ₂	CH ₄	"C ₆ H ₁₄ "	H ₂	CH ₄	"C ₆ H ₁₄ "
N-1	76	180	280	1.62	0.17	175.0	0.0	127.0	57.9	0.0	42.1
2	103	90	370	1.78	.19		96.3	82.3	53.8		46.2
3	107	60	350	1.56	.16	56.2	0.0	48.0	53.9	0.0	46.2
4	105	75	380	1.36	.14		61.3	--	--	--	--
5	107	75	360	1.26	.13	56.3	0.2	58.5	49.0	0.2	50.8
6	107	75	360	1.51	.16	65.7	2.4	56.8	52.6	1.9	45.5

TABLE IV

The Mercury Photosensitized Decomposition of Propane

Operating conditions as in Table III

RUN NO.	TEMP in °C.	TIME in Min.	PRESS. in Mm.	DECOMP. RATE Moles x 10 ⁻⁶ /sec.	QUANTUM YIELD (H ₂ +CH ₄)	PRODUCTS in Moles x 10 ⁻⁴			PRODUCTS Mole Percentage		
						H ₂	CH ₄	"C ₆ H ₁₄ "	H ₂	CH ₄	"C ₆ H ₁₄ "
N11	175	75	250	2.28	0.24	95.7	6.5	82.0	51.9	3.5	44.6
12	175	75	360	2.37	.25	102.5	4.2	72.7	57.1	2.3	40.6
13	175	75	360	3.34	.35	150.0		--	--	--	--
14	175	37½	350	3.72	.39	83.6	0.0	67.5	55.3	0.0	44.7
15	175	75	300	3.33	.35	149.8		119.7	55.6		44.4
16	176	60	350	3.35	.35	118.8	2.1	70.2 [#]	61.4	1.8	36.8
17	173	60	320	3.10	.33	111.7		91.7	54.8		45.2

Portion of condensate lost

TABLE V

The Mercury Photosensitized Decomposition of Propane

Operating conditions as in Table III

RUN NO.	TEMP.	TIME	PRESS.	DECOMP. RATE	QUANTUM YIELD	PRODUCTS			PRODUCTS		
	in °C.	in Min.	in mm.	Moles $\times 10^{-6}$ /sec.	($H_2 + CH_4$)	in Moles $\times 10^{-4}$			Mole Percentage		
						H_2	CH_4	" C_6H_{14} "	H_2	CH_4	" C_6H_{14} "
N-20	255	60	160	0.0	0.0	0.0	0.0	0.0	Blank run Lamp off		
21	248	60	250	2.28	.24	79.5	2.5	63.7	54.5	1.7	43.8
22	249	66	360	2.42	.26	95.1	0.5	77.3	55.0	0.3	44.7
23	249	60	320	2.56	.27	89.3	3.0	81.7	51.3	1.7	47.0
24	253	6	300	--	--	15.0	0.7	--	--	--	--
25	250	60	300	2.68	.28	96.8		83.4	53.7		46.3
31	323	61	320	1.39	0.15	50.7		48.0	51.4		48.6

TABLE VI

The Decomposition of Propane in the Presence of Added Hydrogen

Volume of system 1680 cc. Reaction temperature 24-27°C.
 Volume of reaction cell 320 cc. Trap temperature -80°C.
 Arc current 0.100 amp. Propane vapor pressure 14 cm.
 Resonance radiation absorbed 4.0×10^{-6} einsteins/sec.
 Circulating rate 1900 cc./min.

RUN NO.	TIME in Min.	GAS PRESSURES in mm.			DECOMP. QUANTUM REACTION PRODUCTS RATE				REACTION PRODUCTS			
		C_3H_8	H_2	FINAL	Moles $\times 10^{-6}$ /sec.	YIELD $(H_2 + CH_4)$	H_2	CH_4	" C_6H_{14} "	H_2	CH_4	" C_6H_{14} "
H-1	180	265.5	10	242.7	0.64	0.16	67.3	2.0	62.2	51.2	1.5	47.3
2	180	257.5	50	267	.64	.16	68.8		57.0 [#]	54.7		45.3
3	180	268.5	49.5	277	.67	.17	72.1	0.0	66.0	52.2	0.0	47.8
4	180	278	50	284	.67	.17	72.3	0.1	66.5	52.1	0.1	47.8
5	180	274	53	282	.70	.17	75.3		--	--	--	--

Portion of condensate lost

TABLE VIIAnalysis of the CondensateA

RUNS	MAIN FRACTION		HIGH BOILING	
	B. P. in °C.	ANALYSIS	FRACTION	
<u>Steacie</u>				
Rough analysis	60--62	---	< 20%	
"Single pass" runs	57.5	{ C ₆ H ₁₄ # 5% unsat- urates	10%	C ₉ #
<u>Dewar</u>				
Runs A 1-7	58.0-58.5	C ₆ #	present	

determined by combustion

B

RUNS	MAIN FRACTION			HIGH BOILING FRACTIONS	LOW
	M. P. in °C.	B. P.	n _D		
P 1-5 } H 1-5 }	-154	58.8-59.4	1.37349 (20.4°)	present	---
N 1-7	-169	(a) 59.2-59.7 (b) 60.2-61.0	1.37359 (20.5°) 1.37327 (20.7°)	~ 10%	trace
N 11-17	-167 -169	(a) 58.6-59.9 (b) 61.0-61.2	1.37359 (20.8°) 1.37343 (20.3°)	## 10-15%	trace
N 21-25	-167	58.8-59.4	1.37247 (21.0°)	< 20%	---

n_D of fraction 1.400262 (21°)

DISCUSSION

The Mercury Photosensitized Decomposition of Propane

As the above tables show, the products of the mercury photosensitized decomposition of propane are almost exclusively hydrogen and hexane(s) at all the temperatures studied. This evidence indicates that the mechanism for the decomposition is

There is also a possibility, particularly at high temperatures, that the formation of hexane occurs by the reaction

Only traces of methane are found, possibly from secondary reactions of the propyl radical

These results must be contrasted with those obtained by cadmium photosensitization. Recently Steacie and Potvin (41), in the course of their investigation of

the ethane decomposition using the 3261 Å.U. cadmium resonance line, made a run on the propane decomposition at 280°C. They obtained

Gaseous products $\text{H}_2 = 6.4\%$

$\text{CH}_4 = 67.4\%$

$\text{C}_2\text{H}_4 = 0.6\%$

$\text{C}_4\text{H}_{10} = 25.6\%$

Liquid products 28.1% by weight of total products

and concluded that the mechanism was

When these results were compared with those of the mercury photosensitized decomposition at room temperature, it was concluded that the difference arose from the different operating temperatures. The propyl radical is known to be unstable at high temperatures and to decompose

and it was thought that this instability would explain the divergent results. Investigations of the mercury photosensitized decomposition at higher temperatures, however, show that there is no material change in products when the temperature is increased to 250°C. Consequently, the instability of the propyl radical at high temperatures is not a sufficient explanation of the divergence.

At first sight, it would appear that the different results obtained are due to the great difference in the excitation energies of the two metal atoms--112 Kcal. for mercury and 87 Kcal. for cadmium. Estimates of the C-H bond strength range from 92 to 108 Kcal. On this basis, a C-H bond split can occur in the case of mercury photosensitization but is not likely in the cadmium experiments. Bender (93), however, has shown that the formation of CdH occurs in the presence of hydrogen so it is obviously possible for it to be formed in these experiments. CdH has a heat of dissociation of 15.5 Kcal. Consequently, if the reaction takes place as follows

the C-H bond split is quite possible. Moreover, the results of the cadmium photosensitized decomposition of ethane

furnish further evidence that the decomposition takes place by a C-H rather than by a C-C split.

The divergent results, of course, may be due to differences in experimental conditions. The mercury lamp, being more intense than the cadmium, should give a higher concentration of propyl radicals and hydrogen atoms. Consequently, we would expect the following reactions

if the propyl radical were present at all and had a reasonable lifetime. With the smaller radical concentration produced by the cadmium lamp, the propyl radical is more likely to decompose

before meeting and uniting with another C_3H_7 radical. The fact that the decomposition produces a large quantity of methane but also a small amount of hexane(s) makes this explanation appear reasonable. The low concentration of ethylene in the products is explained, as Steacie and Potvin found, by the rapid hydrogenation of ethylene

Another difference in operating conditions is the relatively high vapor pressure employed in the cadmium experiments (0.01-0.02 mm.). Consequently, a large fraction of the resonance radiation will be absorbed near the wall and wall effects may be responsible for the differences in products.

This divergence in the products obtainable by the two methods is also seen in the case of butane. Thus, in a run on the cadmium photosensitized decomposition of butane, Steacie and Potvin obtained

gaseous products	H_2	=	0.6%
	CH_4	=	24.2%
	C_2H_6	=	28.8%
	C_3H_8	=	46.4%

liquid products 58.2% by weight of total products

while Steacie and Phillips (76) using mercury photosensitization obtained hydrogen and liquid products. Similar products for the mercury photosensitized decomposition have recently been found in the preliminary investigations of Winkler and Hay (94).

It is also of value to compare the present results with those obtained by Steacie and Parlee (83)(84) for the reaction of hydrogen ~~of hydrogen~~ atoms with propane

by the Wood-Bonhoeffer method. The products in the latter case are methane, ethane, ethylene, but no hexane.

This divergence in results, however, is not surprising. In the present research, propane pressures are high while the hydrogen atom concentration is low. These conditions favor radical recombination reactions. Consequently, as we have already shown, we would expect to find hexane(s) if the propyl radical had a reasonable lifetime. Under the high hydrogen concentration (both atomic and molecular) employed in the Wood-Bonhoeffer method, on the other hand, collisions between propyl radicals would be very scarce and, consequently, there would be little chance of hexane being formed. The propyl radical is more likely to undergo the reactions

In general, there is a definite parallelism between reactions of hydrocarbons and hydrogen atoms when the results of the mercury photosensitization and the Wood-Bonhoeffer methods for ethane and propane are compared. In both cases, large amounts of higher paraffins are obtained by mercury photosensitization (propane and butane from ethane and hexane from propane) while only lower paraffins

are obtained by the discharge-tube method. The current results on the reaction of hydrogen atoms with butane obtained by Steacie and Brown (85) using the Wood-Bonhoeffer technique show that this is also the case for butane.

The Reaction in the Presence of Added Hydrogen

Neither the products nor the efficiency of the reaction are materially altered by the presence of added hydrogen. This would suggest that the mechanism is practically the same in both cases. Since hydrogen is more efficient than propane in quenching the resonance radiation, we would expect the primary step in the reaction to be

and the following steps to be the same as reactions (2), (3), (4), (5), and (6).

Condensate Analysis

The results of the condensate analysis are of unusual interest. The main fraction of the distillate analyzed to C_6H_{14} on combustion. This, however, is not sufficient to identify the fraction as there are five different hexanes. The following table lists the melting-points, boiling-points, and refractive indices of the five hexanes.

TABLE VIIIPhysical Constants of the Hexanes #

NO.	HEXANE	M. P. °C.	B. P. °C.	REFRACTIVE INDEX at 20°C.
(1)	n-Hexane	-94	68.8	1.37506
(2)	2-Methylpentane	-153.7	60.2	1.37149
(3)	2-3-Dimethylbutane	-128.8	58.0	1.37499
(4)	3-Methylpentane	(-118)	63.2	1.3765
(5)	2-2-Dimethylbutane	-98.2	49.7	1.36887

The above table is based on values given in

Egloff: Physical Constants of Hydrocarbons, Vol. I
Reinhold Publishing Corporation 1939.

It is fairly definitely established by this and other investigations (75)(77) that the first step in the mercury photosensitized decomposition of the lower paraffins is a C-H split. In the case of propane, however, the C-H split can occur in two ways: a primary hydrogen can be removed to leave a n-propyl radical, $\text{CH}_3\text{CH}_2\text{CH}_2\cdot$, or a secondary hydrogen can be split off to give the isopropyl radical, $(\text{CH}_3)_2\text{CH}\cdot$. On the basis of pure chance, we would expect both propyl radicals to be formed. These two radicals would then react to give

n-hexane	(n-propyl + n-propyl)
2-3-dimethylbutane	(isopropyl + isopropyl)
2-methylpentane	(isopropyl + n-propyl)

The formation of the other two hexanes cannot be explained by any simple free radical mechanism.

If the above reasoning is correct, the results of the condensate analysis show that the liquid product is not n-hexane but rather 2-methylpentane or 2-3-dimethylbutane or possibly a mixture of both. The fact that no n-hexane is obtained indicates that the isopropyl radical is favored in the C-H split and subsequent radical recombinations.

The very good agreement of the analytical results of the different condensates indicates that the liquid

product is a very definite substance. This is further confirmed by recent work on the cadmium photosensitized decomposition of propane. Using the 3P_1 cadmium resonance line, Steacie and Potvin (95) obtained a liquid product, the main fraction of which (75%) analyzed to

M. P.	B. P.	n_D
-164°C.	59°C.	1.37385 (20°C.)

The main liquid products obtained by the two methods are thus in good agreement

The high boiling fraction is probably nonane, occurring by

The very small amount obtained each run, however, makes analysis very difficult.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1 The mercury photosensitized decomposition of propane has been studied for the first time over a temperature range from 25° to 250°C. using a circulating system to further test the applicability of the Rice free radical postulates to the decomposition reactions of the lower paraffins. The radiation employed was the 3P_1 mercury resonance line (2537 A.U.) and this was obtained from intense light sources similar to those used in this laboratory for the mercury photosensitized decomposition of ethane.

The products of the decomposition have been found to be almost exclusively hydrogen and hexane(s) at all the temperatures studied. This indicates that the primary step in the process is a C-H split as in the case of the ethane decomposition. The postulated free radical mechanism for the decomposition is

Traces of methane have been found in the products, arising possibly from secondary reaction of the propyl radical

The present results have been contrasted with those obtained by cadmium photosensitization and reasons for the divergence have been discussed. The results are also compared with those obtained from investigations of the reaction of hydrogen atoms with propane by the Wood-Bonhoeffer method.

2 The mercury photosensitized decomposition of propane in the presence of added hydrogen has also been studied in the same apparatus. The products have been found to be the same as those of the mercury photosensitized decomposition, indicating that the mechanisms of the two are essentially the same. The high quenching power of the hydrogen has made it necessary to postulate that the first step is

The subsequent steps, however, are the same as those of the mercury photosensitized decomposition.

3 The liquid products of the above decomposition reactions have been studied in considerable detail. A fractional distillation apparatus of the Podbielniak type specially designed for high temperature work has been employed for boiling-point determinations. This apparatus has made possible the analysis of small quantities of liquid products. Distillate fractions have been further analyzed by combustion, and by melting-point and refractive index determinations.

Combustion has shown that the main fraction of the liquid products ($\sim 80\%$ by volume) is C_6H_{14} . Boiling-point, melting-point, and refractive index determinations, however, have shown that the hexane is not n-hexane but rather 2-3-dimethylbutane or 2-methylpentane or possibly a mixture of both. This indicates that the isopropyl radical is favored in the original C-H split and subsequent recombination reactions.

CHEMICAL WARFARE RESEARCH

In January 1940, the investigation of the mercury photosensitized reactions of propane was discontinued in favor of special research in chemical warfare. With the permission of the McGill authorities, this latter work has been carried out in the laboratories of the National Research Council under the supervision of Drs. E. W. R. Steacie, O. Maass, and E. A. Flood. Reports on the progress of this work have been submitted from time to time to the above-mentioned supervisors for their approval. As the work is confidential, however, such reports cannot be included in this thesis.

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