THE MERCURY PHOTOSENSITIZED REACTIONS OF 2-METHYLPROPANE (ISO-BUTANE)

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A. INTRODUCTION

I - The Kinetic Aspect of Chemical Reactions.

From the expression for the distribution of energy in Maxwell-Boltzmann statistics, it may be shown that the exponential factor in the Arrhenius rate equation[1],

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

measures the fraction of molecules with energy equal to or greater than E. The factor A may be identified with the collision number Z.

Following the discovery, by Hinshelwood and Thompson[2], that the reaction type in the decomposition of propionic aldehyde changed from first to second order with decreasing pressure, and with the subsequent acceptance of Lindemann's hypothesis[3], it became evident that activation, in all thermal reactions, was the direct result of collision.

Accepting the collision mechanism of activation, kineticists then concerned themselves with the elucidation of the behaviour of the molecule subsequent to activation. It was evident that for a bond to break, the amplitude and frequency of vibration of this degree of freedom must be increased to a certain definite point at which the component atoms can no longer be regarded as linked together.

Hinshelwood's early suggestion[4] that the rate of reaction, which is proportional to the probability of breaking a particular bond, was independent of any energy contained by the molecule in excess of E was soon found to be only an approximation to experimental fact. A more mathematical treatment led O.K. Rice and Ramsperger[5] and Kassel[6] to propose theories in which the velocity of the reaction was shown to depend on the energy in excess of E contained by the molecule. The rate of decomposition of compounds of simple structure was found to agree satisfactorily with the results predicted by the above theories. Some reactions were found, however, in which the rates were several powers of ten greater than that predicted by the above equations. Two theories were proposed to account for these fast reactions, based on the contribution of energy[7,9,12] from all numerous internal degrees of freedom of the molecule and on the occurrence of self-repeating stages leading to a chain reaction[8,11,].

Hinshelwood[7] suggested that the molecule could store up energy acquired in small increments, in the various internal degrees of freedom and that all of this energy could, by surging into a particular bond, cause the bond to break. He accordingly modified the Arrhenius equation to

$$k = Z e^{-E/RT} \frac{(E/RT)^{(\frac{1}{2}n-1)}}{(n/2 - 1)!}$$

by the inclusion of a factor giving the probability of a molecule containing energy in excess of E in ½n degrees of freedom. In most cases the value of n necessary to account for the observed results is in fair agreement with the known size of the molecules involved.

The conception of chain reactions was initially proposed by Christiansen and Kramers[8]. Their mechanism required a highly specific transfer of energy for propagation of the chains and has therefore been discredited except in a few reactions involving very short chains.

After Paneth and his co-workers[10] had shown existence of free radicals in the products of the pyrolysis of some organic compounds by the removal of metallic mirrors, F.O. Rice[11] suggested that all organic decomposition reactions proceeded by a free radical mechanism and that these radicals could propagate a chain in much the same way as did the atoms in Bodenstein and Nernst's theory.

A major difficulty in the path of the Rice theory was that, by their mechanism, the initial step in many reactions would require a larger activation energy than that experimentally found. Thus acetaldehyde has been found to decompose:-

$$CH_3.CHO \longrightarrow CH_4 + CO$$

with an activation energy of about 47 kcal. However, the primary split in the Rice mechanism

$$CH_3.CHO \longrightarrow CH_3 + CHO$$

would require approximately 80 kcal. to break the C-C bond. Rice and Herzfeld[13] then showed how, by plausible assumptions as to the values of E for the various links in the chain, the overall E could be made to agree with experiment.

Some of the evidence supporting the Rice theory may be summarised briefly:

(a) Paneth's Mirror Experiments: A strong indication of the presence of free radicals at very high temperatures. The conditions used, however, are very different from those under which reactions normally are investigated so that the results of mirror experiments need not necessarily apply.

(b) Initiation of chain processes by the artificial introduction of free radicals[14,15]: This shows that free radicals are capable of accelerating reactions but is no sure proof that these radicals actually do partake normally in the reaction under consideration.

(c) Inhibition by Nitric Oxide[16]: There is some doubt as to whether NO is specific in chain breaking since its inhibitive effect seems to be very variable. There is also some doubt as to the catalytic effect of NO on some reactions.

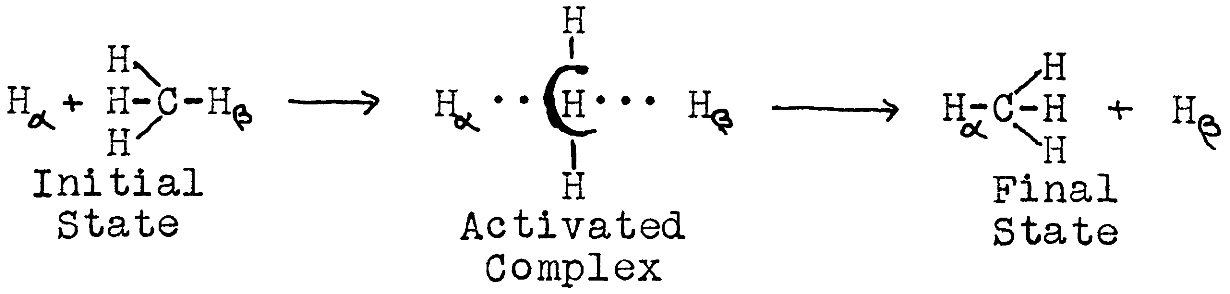
(d) Ortho-para Hydrogen Conversion[17]: The results obtained give definite indication of the presence of radicals but the concentrations of radicals as indicated by this method are much too small for good agreement with the Rice theory.

The most searching test of the Rice theory will be provided when the individual steps in a proposed chain have been investigated and activation energies assigned to them. Smith and H.S. Taylor[18] have made a start along these lines and have investigated the reactions between methyl radicals and some of the lower paraffin hydrocarbons. This aspect of the problem will be discussed in connection with the elementary reactions of the paraffins in section 3 of this introduction.

An effort is being made by several workers in the fields of chemical kinetics and quantum mechanics to determine the relations existing between reactants at all stages in the process of reaction. The most modern conception of the problem is embodied in the "Transition State" theory developed by Eyring and his co-workers[19]. The essential point of this theory is that, at some stage of the reaction, a configuration is established the properties of which are intermediate between those of the reactants and products. This configuration is known as the "activated complex". The activated complex is then regarded as crossing an energy barrier in the reaction co-ordinate between products and reactants. The height of the energy barrier is equivalent to the activation energy of the reaction.

In the photosensitized reactions of the hydrocarbons it is assumed generally that the primary act after activation is a C-H split although the C-C bond is known to be considerably weaker than the C-H bond. The application of the transition state theory is of interest in that it affords a possible explanation of this apparently anomalous behaviour.

Eyring[19] has made use of the semi-empirical method of Eyring and Polanyi[20] and adopted the views of London[21] on the "adiabatic" character of many reactions to construct the potential energy surface for the reaction between hydrogen atoms and methane, that is, representing the variation in potential energy with interatomic distance. From this plot Eyring has found that the activated complex may be represented as CH_5 and that it is stable to the extent of about 10 kcal. Gorin, Kauzmann, Walter and Eyring[22] have calculated the relative probabilities of the hydrogen exchange and abstraction in the above reaction. The exchange is regarded as proceeding through the following steps:-



The problem was solved by the use of integrals proposed by van Vleck[23] and by the use of Morse curves to evaluate the binding energy of the C-H and H-H bonds for varying interatomic distances. The activation energy was found to be 37 kcal. per mole.

The

hydrogen abstraction was treated as involving the following steps:-

$$H_{\alpha} + H_{\beta}\text{—}CH_3 \longrightarrow H_{\alpha}\cdots H_{\beta}\cdots CH_3 \longrightarrow H_{\alpha}H_{\beta} + CH_3$$

and, by treating the problem as one of three electrons, the dimensions of the activated complex was determined and the activation energy calculated to be 9.7 kcal. From the above investigation it is evident that the dehydrogenation will predominate.

The aim of Eyring's treatment of reaction rates is to predict the behaviour of systems under given conditions by the use of known atomic constants and of relations derived from the quantum mechanical conception of matter. Due to the inadequacy of mathematics to treat problems involving complex systems this method has been applied only to comparatively simple reactions.

II - Photosensitization and the Quenching of Resonance Radiation.

The phenomenon known as photosensitization was first reported by Cario and Franck[24] who investigated the photochemical reduction of metallic oxides by hydrogen. They found that, to cause reduction of the oxide at 45°C., it was necessary for the reaction chamber (quartz) to contain mercury and for it to be illuminated by the radiation from a cooled mercury arc. No reaction was obtained if mercury was absent or if the arc was allowed to run hot. Marshall[25] investigated the mercury photosensitized reaction between oxygen and hydrogen, taking precautions to filter out any light of wave length greater than 2537Å, and so showed that the $Hg(6^3P_1)$ was alone responsible for the activation. The primary reactions were therefore assumed to be:-

$$Hg(6^1S_0) + h\nu(2537\text{Å}) \longrightarrow Hg(6^3P_1) \quad \ldots\ldots\ldots\ldots(1)$$

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

Reaction (2) is energetically possible since the energy associated with $Hg(6^3P_1)$ is 4.89 ev. and the energy required to break the H-H bond is only 4.46 ev.. The difference of 0.46 ev. was assumed to be taken up as relative kinetic energy of the particles.

Further examples of photosensitized reactions were then reported. Dickinson[26], Mitchell[27], Taylor[28], Marshall[29,30] and several others investigated the mercury photosensitized reaction between hydrogen and oxygen while the similar reaction between hydrogen and ethylene was reported by Marshall[25]. Several other substances such as ammonia[31,32], hydrazine[33] and water[34] were found to be decomposed by the action of excited mercury atoms. These reactions are strictly analogous to the photosensitized reactions of the hydrocarbons which will be considered in the next section of this introduction.

The above account of the phenomenon of photosensitization has been adapted largely from Mitchell and Zemansky's book "Resonance Radiation and Excited Atoms" ref. 35.

It is of interest to consider the fate of a quantum of 2537Å radiation in a mixture of Hg(6^1S_0) atoms with for example hydrogen and iso-butane molecules. It is well known that hydrogen and the paraffin hydrocarbons are both transparent to the 2537Å line, hence the quantum will be unaffected by encounters with these molecules. The quantum will be absorbed by the mercury in the ground state according to reaction (1) and the course of the reaction will then depend on the fate of the Hg(6^3P_1). Two possibilities are open to the Hg(6^3P_1) atom, either to radiate the 2537Å or to hand on its energy to a reactant molecule by a collision of the second kind. If the atom radiates, the quantum either will be reabsorbed by another mercury atom or lost to the reaction. Hence the probability of absorption of the quantum will depend on the concentration of mercury in the reactor and the efficiency with which this quantum is utilised in the reaction will depend on the number and efficiency of the collisions between the excited mercury atoms and the reactant molecules. The transfer of energy by collisions of the second kind between reactants and mercury is known as "Quenching" of the radiation. For any one hydrocarbon the efficiency of quenching per collision will be constant under constant conditions and the overall efficiency will depend therefore on the number of collisions i.e. the pressure of the compound in question. To compare the efficiencies of different hydrocarbons it is usual to base the comparison on the apparent diameter of the molecule in the process under consideration. This is called the "Quenching Diameter" of the molecule.

By reference to the Grotrian diagram for the energy levels in mercury (Fig. I) it will be seen that there are two transitions whereby the Hg(6^3P_1) atoms may lose energy. In these transitions they revert to either the ground (6^1S_0) state or to the (6^3P_1) level. In the latter state the mercury atoms still possess enough energy to cause the H-H or the C-H bond to break; this state is known as a metastable level as the transition from 6^3P_0 to the ground state is one of the forbidden transitions of mercury. Meyer[36] has found that the metastable (6^3P_0) atoms, produced by the action of nitrogen on the 6^3P_1 atoms, were still capable of activating hydrogen, and that the addition of nitrogen increased the velocity of reduction of metallic oxides by hydrogen at low pressure. This

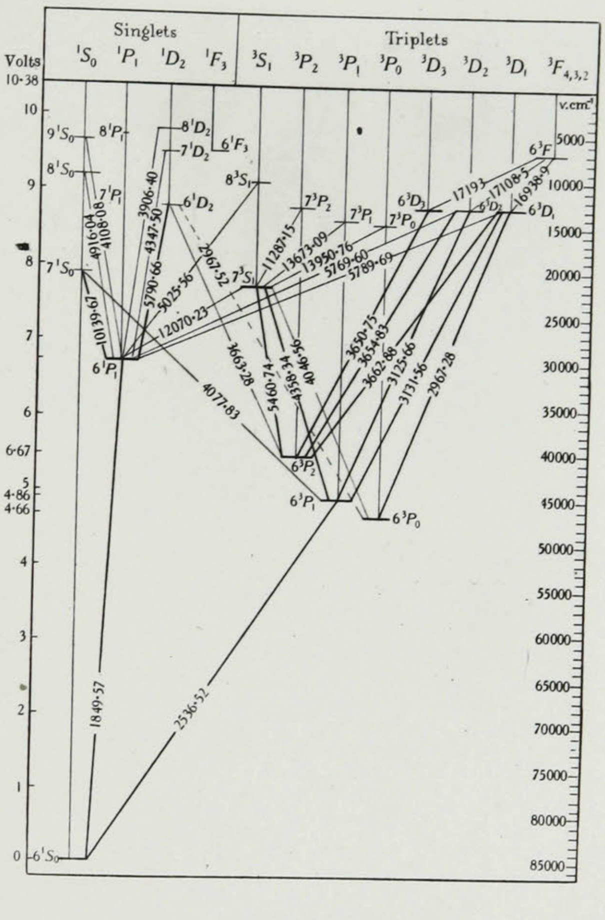


FIGURE I

Energy levels of mercury (Grotrian)

(From Mitchell and Zemansky Ref. 35)

is because the metastable atoms have longer life than the 6^3P_1 atoms, so that the probability of quenching is increased.

In the quenching of the resonance radiation by hydrogen there are two possible mechanisms:-

$$Hg^* + H_2 \longrightarrow Hg + 2H \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(a)$$

$$Hg^* + H_2 \longrightarrow HgH + H \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(b)$$

Either of the above mechanisms is energetically possible. The decision as to which of the mechanisms actually occurs is a point of great importance, not only from the energetic standpoint, but as an aid to the elucidation of the actual primary step of the reaction. In (a) the energy available for reaction is that associated with the Hg(6^3P_1) atom, whereas in (b) there will be a little extra energy available, equivalent to the heat of dissociation of HgH. Proof of the formation of HgH would also give added support to the theory of a directed collision between Hg and hydrocarbon molecules.

The evidence for the formation of HgH in the quenching of the mercury 2537 line by hydrogen is rather contradictory. Compton and Turner[37] report the formation of bands corresponding to HgH in a low voltage arc in hydrogen and mercury. This has been substantiated by the results of Gaviola and Wood[38]. On the other hand Olsen[39] has been unable to produce resonance excitation of the HgH bands in a mercury-hydrogen mixture.

On the theoretical side Compton and Turner[37] have pointed out that the reverse of reaction (a) would require the simultaneous collision of two hydrogen atoms and one mercury atom. This is very improbable. They therefore conclude, from the principle of microscopic reversibility, that reaction (a) must also be very improbable. A similar result has been achieved by Beutler and Rabinowitsch[40] by considering the conservation of energy and of angular momentum on collision between an excited mercury atom and a hydrogen molecule.

The above analysis of the relevant evidence together with the fact that resonance bands corresponding to CdH and ZnH have been obtained in experiments on the quenching by hydrogen of the cadmium [41] and zinc[42] resonance lines, makes it probable that HgH is formed in the case of mercury.

The energies associated with the chief resonance lines used in the investigation of photosensitized reactions are given in Table I.

Table I

Energies associated with resonance lines

Substance	Resonance Line Å	Transition	Energy of Excited Atom (kcal.)	Heat of Dissocn. of Hydride (kcal.)	Maximum Energy Available (kcal.)
Mercury	(1849	6^1S_0- 6^1P_1	153.9	8.5	162.4
	(2537	6^1S_0- 6^3P_1	112.2	8.5	120.7
Cadmium	(2288	5^1S_0- 5^1P_1	124.4	15.5	139.9
	(3261	5^1S_0- 5^3P_1	87.3	15.5	102.8
Zinc	(2139	4^1S_0- 4^1P_1	133.4	23.1	156.5
	(3076	4^1S_0- 4^3P_1	92.5	23.1	115.6

Apart from the quenching of the resonance radiation, by which its energy is made available to the activation of the reactants, there are other processes, commonly grouped together as "broadening processes" which reduce the effectiveness of the radiation. The various types of processes by which a line may be broadened are as follows:-

(a) Natural broadening due to the finite lifetime of the excited state.

(b) Doppler broadening due to the motion of the atoms at the instant of emission.

(c) Lorentz broadening due to collisions with foreign gases.

(d) Holtmark broadening due to collisions with other atoms of the same kind.

(e) Stark effect broadening due to collisions with electrons and ions.

Both Lorentz and Holtmark broadening are grouped together as "pressure" broadening.

It is evident therefore, that there are several agencies which are capable of affecting the transfer of resonance energy in photosensitized reactions. Because of these effects it is always necessary to exercise care and judgement in comparing the quantum efficiencies of photosensitized reactions, especially if they are carried out under radically different conditions.

III - The Elementary Reactions of the Lower Paraffin Hydrocarbons.

In proposing a mechanism to account for the general characteristics of a reaction it is necessary to consider not only the results of the immediate investigations but also the results of past work on the same or on strictly similar reactions. Hence, to interpret the kinetics of the mercury photosensitized reactions of iso-butane, it is necessary to review the results obtained by previous investigators from similar studies of reactions of the lower paraffins and their corresponding radicals.

It is known that, in photosensitized reactions, the initial act may be brought about by H atoms, produced by photosensitization, as well as through the agency of excited metal atoms. Hence it will be necessary to consider also reactions between paraffins and H atoms, produced by methods other than photosensitization. The usual method for producing H atoms, other than by photosensitization, is by the electric discharge, a method originated by Wood[42] and by Bonhoeffer[43].

In the Wood-Bonhoeffer method hydrogen is passed at low pressure, about 0.3 mm., and at high velocities through an electric discharge and mixed with the hydrocarbon in a suitable reaction vessel under conditions such that the hydrocarbon itself is not subjected to the action of the electric discharge.

Photosensitized reactions have been investigated either in a static or in a flow system. The results obtained in static systems may be of difficult interpretation since the products are not removed from the zone of reaction and will therefore undergo subsequent reaction. These secondary reactions may be minimised by the choice of suitable conditions in a flow system. There are two types of flow system, the single pass system in which the reactant is subjected to only one passage through the reactor, and the multiple pass system in which the reactant is made to circulate repeatedly through the reactor. In single pass systems the contact time may be reduced to such an extent that the primary products may be isolated with fair certainty. The results therefore permit reliable deductions to be drawn concerning the primary act. The disadvantages of the single pass system lie in the small yields of product which make subsequent analysis difficult and tedious. In multiple pass systems the reactant may be circulated through a trap the temperature of which may be adjusted so as to remove, more or less completely, the higher boiling products of the reaction. The degree of precision obtained with this method depends on the thoroughness with which the products are removed.

In comparing the results obtained by the Wood-Bonhoeffer method with those obtained by photosensitization it must be remembered that the conditions of the reaction differ widely in the two techniques. The Wood-Bonhoeffer method is characterised by a very low pressure and a high H atom concentration; conditions which favour subsequent reaction between H atoms and the products. In photosensitization experiments, on the other hand, the pressure is of the order of 10 cms. and the stationary atom concentration is very low; conditions which favour radical recombination reactions. The products of the Wood-Bonhoeffer method usually consist of lower paraffins, methane being prevalent, whereas polymers of the original paraffin are usually produced by photosensitization.

METHANE.

Early investigations[44,45,46,47] of the reaction between methane and H atoms produced by the Wood-Bonhoeffer method indicated the absence of any reaction up to 183°C. As a result Geib and Harteck[47] concluded that the reaction:-

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

must have an activation energy of at least 17 kcal. A suggestion that reaction(1) does occur but that the effects are nullified by the occurrence of

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

was discounted by Geib and Harteck because this would cause an increased consumption of H atoms whereas the presence of methane causes no alteration in the concentration of H atoms, and also because it was unlikely that this reaction would occur to the complete exclusion of reactions such as:-

$$2CH_3 \longrightarrow C_2H_6$$

The only reaction which could be postulated to account for the apparent inertness of methane is:-

$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (3)$$

which was tested by Geib and Steacie[48] using D atoms produced by the discharge tube method. They found no detectable reaction up to 100°C indicating that the activation energy of either

$$D + CH_4 \longrightarrow CH_3D + H \qquad (4)$$

or $$D + CH_4 \longrightarrow CH_3 + HD \qquad (5)$$

is not less than 11 kcal.

Farkas[49] investigated the reaction between methane and D atoms produced thermally at about 1000°C. Although he did not determine the temperature coefficient of the reaction he postulated an activation energy of 11 to 12 kcal. and considers that the reaction was of the true exchange type (4) rather than hydrogen abstraction.

Further investigations of this reaction, using the Wood-Bonhoeffer method were made by Trenner, Morikawa and Taylor[50] and by Steacie[51]. The values proposed by various investigators for the activation energy of this reaction may be summarised:-

INVESTIGATOR	E
Geib and Harteck[47]	17 kcal.
Farkas[49]	11 - 12 kcal.
Geib and Steacie[48]	11 kcal.
Trenner, Morikawa and Taylor[50]	15.6 kcal.
Steacie[51]	12.9 2 kcal.
Farkas and Melville[52]	13 kcal.

From the above discussion it seems that the values given by Steacie and by Farkas and Melville of about 13 kcal. are probably near the truth.

Taylor, Morikawa and Benedict[53] used mercury photosensitization to produce deuterium atoms in an investigation of the reaction between these atoms and methane. They reported a low activation energy for the reaction. Steacie and Phillips[54] reinvestigated the reaction using essentially the same technique and reported an activation energy of 11.7 kcal. assuming a steric factor of 0.1. Farkas and Melville[52] worked over a wide temperature range and used ortho-deuterium-methane mixtures. They determined the atom concentration by measuring the rate of the ortho-para conversion as well as that of the exchange. They concluded that the reaction occurring was an exchange rather than a hydrogen abstraction.

The above authors all assumed that the only reaction that occurred was between methane and deuterium atoms. Morikawa, Benedict and Taylor[55], however, showed that methane itself was attacked by active mercury atoms. They then suggested that the reaction:-

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

also occurred and that some of the exchange found by earlier investigators using the photosensitization method occurred by

$$CH_3 + D + M \longrightarrow CH_3D + M \qquad (7)$$

as well as by the true exchange reaction (4).

The work of Gorin, Kauzmann, Walter and Eyring[22] has shown that the hydrogen abstraction is more probable than the exchange reaction. This paper received support from the results of Morikawa, Benedict and Taylor and the exchange reaction is now regarded as being of little importance as compared to the abstraction of hydrogen.

ETHANE

Early investigators[44,45] of the reaction between ethane and hydrogen atoms produced by the Wood-Bonhoeffer method found indications that some reaction occurred when they observed luminesence on mixing the reactants. They were, however, unable to isolate the products of the reaction although bands due to C-H and C_2 were observed. Cha~~l~~dwell and Titani[46] reported small amounts of methane and ethylene as products of this reaction.

Steacie and Phillips[54] used deuterium atoms produced by the same technique and found that some reaction did occur, with an apparent activation energy of 6.3 kcal. They conclude that the exchange occurred by the following mechanism:-

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

$$C_2H5 + D \longrightarrow C_2H5D \qquad (2)$$

Trenner, Morikawa and Taylor[50] repeated the investigation and found that a large amount of methane, which was up to 50% deuterised, was formed and that the ethane recovered was entirely light when the reaction occurred below 100°C. They concluded that, below 100°C, the main reaction was:-

$$C_2H_6 + D \longrightarrow CH_3 + CH_3D \qquad (3)$$

which had an activation energy of 7.2 kcal. To account for the high deuterisation of the methane they postulated:-

$$CH_3 + D \longrightarrow CH_3D^* \longrightarrow CH_2D + H \qquad (4)$$

They objected to the mechanism of Steacie and Phillips for the reaction below 100°C on the basis of the work of Taylor and Hill[56] on the mercury photosensitized hydrogenation of ethylene. To account for the small deuterisation of the ethane above 100°C they suggested that reactions (1) and (2) occur to some extent with an activation energy of 11.2 kcal. The large discrepancy in activation energy for the exchange reaction as reported by Steacie and Phillips and by Taylor et al. may be due, in part, to the fact that the former did not realise that methane was produced. This, however, could not account entirely for the large discrepancy reported. Steacie[57] later confirmed the occurrance of methane in the products.

The first indication that ethane is unstable to excited mercury atoms was provided by the investigations of Tolloczko[58]. This was confirmed by the work of Taylor and Hill[56] on the mercury photosensitized hydrogenation of ethylene and by Kemula[59]. A more detailed investigation was then carried out by Kemula, Mrazek and Tolloczko[60] who used a circulatory system and analysed the products obtained at varying trapping temperatures. They found that at all trapping temperatures down to -80°C, the gaseous products consisted entirely of methane and hydrogen and that the ratio of hydrogen to methane, which was about 3:1 at -80°, approached infinity at 20°C. The liquid products were found to consist mainly of butane and octanes. On the basis of this evidence they proposed the following mechanism to account for the principal characteristics of the reaction:-

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

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

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

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

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

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

and that the higher products were the result of secondary reactions of butane:-

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

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

The above investigation was then repeated in greater detail by Steacie and Phillips[61] who used essentially the same technique but extended the range of trapping temperature down to -132°C. Their results confirmed those of Kemula, Mrazek and Tolloczko at trapping temperatures of -80°C and higher and also showed that at still lower trapping temperatures the production of hydrogen and of butane decreased and that propane was present in increasing amounts the lower the temperature. At low trapping temperatures they found that the reaction could be represented by the following relation:-

$$1.00\ C_2H_6 \longrightarrow 0.59\ CH_4 + 0.24\ C_3H_8 + 0.17\ C_4H_{10}$$

When the reaction was repeated in the presence of added hydrogen at low trap temperatures it was found that hydrogen was consumed in the process and that the yield of methane was increased. The reaction under these conditions conforms to the equation:-

$$1.00\ C_2H_6 + 0.35\ H_2 \longrightarrow 1.1\ CH_4 + 0.11\ C_3H_8 + 0.12\ C_4H_{10}$$

They concluded from these results that the primary act was a C-C bond split followed by radical recombination reactions. The ethyl radicals were assumed to be formed by the following reaction:-

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$

Hydrogen was regarded as being formed, not as a result of the decomposition of ethane, but from the decomposition of butane and/or propane which were incompletely removed at the higher trapping temperatures.

The reaction was then repeated by the same author[62] using a "single pass" system. In these experiments they found that hydrogen was produced under all conditions and that it must therefore be regarded as a primary product of the ethane decomposition. They therefore revised their original mechanism to postulate a C-H split as the initial act:-

$$C_2H_6 + Hg(6^3P_1) \longrightarrow C_2H_5 + H + Hg(6^1S_o) \qquad (1)$$

$$H_2 + Hg(6^3P_1) \longrightarrow 2\ H + Hg(6^1S_o) \qquad (2)$$

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

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

with radical recombination reactions to produce the final products. This series of reactions accounts for the experimental results if (3) is at least four times as fast as (4). Taylor[63] objected to the chain-splitting reaction (3) and suggested instead that methane was produced by a reaction between H atoms and ethyl radicals:-

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

a proposal which has received support from Rice and Teller[64] and from Gorin, Walter, Kauzmann and Eyring(22) from purely theoretical considerations, as well as considerable support on the experimental side from work on H atom reactions[65,66,67,68,69]. The above mechanism, with Taylor's modification, is now generally accepted. A continuation of this work by Steacie and Cunningham[70], who studied the reaction up to 475°C, showed that the above mechanism is applicable over a wide range.

The cadmium photosensitized decomposition of ethane has been investigated by Steacie and Potvin[71]. The products and quantum yield of this reaction were found to be essentially idenrical with those obtained in the mercury sensitized reactions. In the presence of added hydrogen the same authors[72] obtained results which were also essentially similar to those obtained in the corresponding reaction with mercury. The mechanism proposed for these reactions was similar to that proposed by Steacie and Phillips for the reactions with mercury.

PROPANE

The main information on the reaction between propane and H and D atoms produced by the Wood-Bonhoeffer method comes from the work of Trenner, Morikawa and Taylor[50] and Steacie and Parlee[66,67]. The former made two runs using deuterium atoms and found that at room temperature the products were roughly 85% methane and 15% ethane and 65% methane and 35% ethane at 109°C. The reaction was found to be slower than with ethane. The methane and ethane were found to be highly deuterised but the propane was recovered unexchanged. Steacie and Parlee made a much more detailed study of the reaction. They found that methane was the sole product of the reaction below 100°C at which temperature ethane made its appearance. The proportion of ethane in the products increased steadily with reaction temperature and, at 250°C, was more than double the amount of methane. They confirmed the results of Taylor et al on the deuterisation of the fractions. They concluded that the initial act was the abstraction of hydrogen:-

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

rather than one of the chain splitting reactions:-

$$H + C_3H_8 \longrightarrow C_2H_5 + CH_4$$

$$H + C_3H_8 \longrightarrow C_2H_6 + CH_3$$

The mercury photosensitized reactions of propane and of propane and hydrogen were investigated by Steacie and Dewar[73] who found that over the range of reaction temperatures from 25°C. to 32°C., the products were hydrogen and hexanes with only a trace of methane. This indicated clearly that the primary act was a C-H split:-

$$C_3H_8 + Hg(6^3P_1) \longrightarrow Hg(6^1S_o) + C_3H_7 + H$$

or, in the presence of hydrogen,

$$H_2 + Hg(6^3P_1) \longrightarrow Hg(6^1S_o) + H + H$$

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

The main products were supposed to be formed by radical recombination and the small amounts of methane by "atom cracking" reactions.

The cadmium photosensitized reactions of propane at 310°C were investigated by Steacie, LeRoy and Potvin[74] who found that the main products were hydrogen and hexanes as with the mercury photosensitized reactions. Considerable amounts of methane, butane, pentanes and heptane were found. They postulate that the initial process is the same as in the mercury reaction but indicate that the extent of the atom cracking reaction is much larger with cadmium since the methyl and ethyl radicals, from which the by-products are formed, arise by virtue of this type of reaction.

The analysis of the hexanes produced in these reactions indicate that most of the reaction takes place on the secondary hydrogen atoms.

BUTANE.

Trenner, Morikawa and Taylor[50] found that butane reacted rather more rapidly with deuterium atoms than did propane. They did one run at 110°C. and found that the products consisted of methane, ethane and propane. As with propane, the methane and ethane were highly deuterised while the recovered butane was not exchanged at all.

Steacie and Brown[68] reinvestigated the reaction over the temperature range 35° to 250°C and found results that were similar to those obtained by Steacie and Parlee with propane. The products of the reaction were methane and ethane. The production of methane decreased with temperature while the amount of ethane increased and, at 250°C, more than twice as much ethane as methane was obtained. A significant point in this investigation was that no propane was found in the products. The initial act was again assumed to be the abstraction of hydrogen:-

$$C_4H_{10} + H \longrightarrow C_4H_9 + H_2$$

and the products were ascribed to further reactions, "atomic cracking" of the butyl radical.

Some preliminary work on the mercury photosensitized reactions of butane has been done by Taylor and Hill[56] and by Steacie and Phillips. The most complete investigation, however is that of Hay and Winkler[75] who investigated the reaction from 100° to 250°C. The products of the reaction were found to be almost entirely hydrogen and octanes together with varying amounts of dodecanes. Methane was present in only very small amounts. The dodecane production varied inversely with the reaction temperature. The initial act postulated was the same as that suggested by Steacie and Brown[68]. The dodecanes were regarded as arising from the following series of reactions:-

$$C_8H_{18} + H \longrightarrow C_8H_{17} + H_2$$

$$C_8H_{17} + C_4H_9 \rightarrow C_{12}H_{26}$$

A rough analysis of the liquid products indicated that, as with propane, most of the reaction occurs on the secondary hydrogen atoms.

Secondary Reactions in Atomic and Photosensitized Processes.

In the previous section of this introduction it was shown that the primary act in atomic or photosensitized reactions of the paraffin hydrocarbons has, in all cases, been assumed to be the abstraction of hydrogen thereby producing the corresponding radical. It is now proposed to consider the fate of the radical under different experimental conditions.

(a) Reactions between H atoms and Radicals.

On the basis of the Transition State Theory a "hot" butane molecule is formed as the activated complex in the reaction between a hydrogen atom and a butyl radical. The course of the reaction will depend on the fate of this "hot" molecule. The reaction may be represented:-

$$H + C_4H_9 \longrightarrow C_4H_{10}^{*} \longrightarrow \text{Products.}$$

where $C_4H_{10}^{*}$ represents a molecule of butane containing energy in excess of the average; it is identical with the ordinary butane molecule except that it possesses one less degree of freedom, along the reaction co-ordinate. The main possibilities of reaction of this "hot" molecule are as follows:-

(i) Deactivation:- The chance of the hot molecule being deactivated will depend largely on its average life and the probability and efficiency of the deactivating collisions.

For methyl radicals this reaction has been widely postulated as the source of methane in H atom and photosensitized reactions. In view of the simplicity of the methane molecule it is probable that this reaction will occur only under dreierstoss conditions. Kimball's estimate[76] of a mean life of 3.2×10^{-12} sec. for CH_4 strengthens the dreierstoss restriction on this reaction.

Steacie, Alexander and Phillips[77] have shown that in the reaction between ethane and deuterium atoms the recovered ethane is practically unexchanged and therefore conclude that the reaction:-

$$D + C_2H_5 \longrightarrow C_2H_5D^* \longrightarrow C_2H_5D \quad \text{(third body)}$$

does not occur to any appreciable extent. Kimball[76] has estimated that, in the above reaction, the active complex has a mean life of 2.1 sec. and so should stand a very good chance of being deactivated before it decomposes.

Some information on the reaction between ethyl radicals and hydrogen atoms is provided by the work on the hydrogenation of ethylene[28,79,80,81,82] since the primary act in this case has been shown to be

$$C_2H_4 + H \longrightarrow C_2H_5$$

$$C_2H_5 + H \longrightarrow C_2H_6$$

The possibility that ethane may be formed by disproportionation:-

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4$$

leaves the question still in doubt.

The fact that propane is recovered unexchanged in the reaction with deuterium atoms[50,66,67] indicates that the recombination of propyl radicals and hydrogen atoms is an inefficient process. The production of propane in the mercury photosensitized hydrogenation of propane[65] with the attendant possibility of the disproportionation reaction makes the recombination reaction as uncertain in this case as for ethane.

(ii) Hydrogen Abstraction. - There are two main possibilities of hydrogen abstraction in the reaction between hydrogen atoms and radicals:-

$$H + CH_3 \longrightarrow CH_4^* \begin{array}{l} \longrightarrow CH_3 + H \qquad (a) \\ \searrow CH_2 + H_2 \qquad (b) \end{array}$$

The first was postulated by Trenner, Morikawa and Taylor[50] to account for the very high deuterisation of the methane produced in their investigation of the reaction between deuterium atoms and ethane. A similar reaction with methyl radicals has been accepted by Steacie, Alexander and Phillips[77] and by Steacie and Parlee[26] for the reactions between deuterium atoms and ethane and propane respectively. Eyring et al[22], however, object to this reaction on theoretical grounds and consider that reaction (b) is basically more probable.

Similar considerations apply for ethyl radicals. Steacie, Alexander and Phillips[77] found that, in the mercury photosensitized reaction between deuterium atoms and ethane, the methane, propane and butane formed were highly deuterised. Since the butane was formed from ethyl radicals the deuterisation of the butane must have been due to the deuterisation of the ethyl radicals after they were formed. Eyring et al again object to the reaction:-

$$D + C_2H_5 \longrightarrow C_2H_4D + H$$

and consider that the deuterisation of the ethyl radical is more likely to occur by:-

$$D + C_2H_5 \longrightarrow C_2H_4 + HD$$

followed by:-

$$D + C_2H_4 \longrightarrow C_2H_4D$$

No information is available as to the occurence of these reactions involving propyl or butyl radicals but there seems to be no good reason why similar considerations should not be applicable to these cases as well.

In discussing the relative probabilities of the exchange and dehydrogenation reactions it may be indicated that either of them accounts equally well for the experimental results, since it is known that the reaction between H atoms and olefins

$$H + C_nH_{2n} \longrightarrow C_nH_{2n+1}$$

is very fast. The absence of olefins in the products of H atom reactions with paraffins is not contrary to the Eyring mechanism, but as Eyring's objection to the exchange reaction appears valid, it is probable that dehydrogenation will be much more likely than exchange.

(iii) Atomic Cracking:- This term is used for reactions between hydrogen atoms and radicals in which a C-C bond is broken and two smaller radicals are produced. With the butyl radical two atomic cracking reactions are possible:-

$$C_4H_9 + H \begin{array}{l} \nearrow CH_3 + C_3H_7 \qquad (a) \\ \searrow 2\ C_2H_5 \qquad (b) \end{array}$$

If the activated complex in the above reaction is $C_4H_{10}^{*}$ and if the excess energy is not removed it is probable that the molecule will decompose at the weakest bond and since the C-C bond is known to be about 20 kcal. weaker than the C-H bonds it is evident that the rupture will occur at one of the three C-C bonds in preference to one of the ten C-H bonds in spite of the greater probability of reaction on the latter. It is probable that the structure of the activated complex formed in atomic cracking reactions differs from that in hydrogen abstraction reactions. The following structures may be postulated

$$C_4H_9 + H \rightarrow C_4H_8 - H -- H \rightarrow C_4H_8 + H_2 \quad \text{(abstraction)}$$

$$C_4H_9 + H \rightarrow C_4H_{10}^{*} \longrightarrow CH_3 \quad C_3H_7 \quad \text{(cracking)}$$

The above are based on the structures of the activated complexes in the corresponding reactions of ethane as postulated by Eyring.[19]

The reaction:-

$$H + C_2H_5 \longrightarrow C_2H_6^* \longrightarrow 2\ CH_3$$

was postulated by Taylor[63] and has received theoretical support from Rice and Teller[64] and from Eyring et al[22]. This mechanism has been adopted by Steacie and his students to explain the results of hydrogen atom reactions with ethane[70], propane[66,67] and butane[68] and by White, Winkler and Kennalty[69] in the corresponding reaction of iso-butane. Further support for this reaction comes from the work of Moore and Taylor[65] who found that, in the photolysis of diethylmercury, methane was produced only when the hydrogen was present and when the mixture was irradiated with the 2537Å mercury resonance line. This effect was ascribed to the production of hydrogen atoms:-

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

followed by the subsequent reaction of the atoms with ethyl radicals produced by the photolysis:-

$$Hg(C_2H_5)_2 + h\nu \longrightarrow C_2H_5 + Hg(C_2H_5)$$

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

(b) Reactions between hydrogen molecules and radicals.

The activation energy of the reaction

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

was estimated by von Hartel and Polanyi[82] to be about 8 kcal. They investigated the reaction between methyl chloride and sodium vapour and measured the consumption of hydrogen, which was used as a carrier gas for the sodium vapour, thereby estimating the activation energy of the above reaction.

Sickman and Rice[83] provided indirect evidence of the occurrence of this reaction when they found that hydrogen did not behave as an inert gas in the decomposition of azomethane.

Paneth, Hofeditz and Wunsch[84] found that methyl radicals disappeared more rapidly in hydrogen than in helium, even at room temperature. They concluded that the above reaction occurred with an activation energy of about 15 kcal. Trenner, Morikawa and Taylor[50] estimate an activation energy of 11.1 kcal. and Taylor and Rosenblum[85] a value of 11 ± 2 kcal.

Cunningham and Taylor[86] found that the rate of decomposition of dimethyl mercury, as well as the production of methane, is greatly increased by the presence of hydrogen.

Using the steady state treatment they estimate an activation energy of 8.1 kcal. Smith and Taylor[88] confirm this value from a similar reaction using deuterium atoms.

With ethyl radicals Geddes and Mack[87] found that hydrogen influenced the decomposition rate of germanium tetraethyl but Leermakers[88] found that hydrogen had no influence on the rate of tetraethyl lead decomposition.

A more comprehensive investigation of the reaction was reported by Moore and Taylor[65] using the photolysis of mercury and zinc diethyls. They found that, below 160°C., the rate of decomposition was not influenced by the presence of hydrogen. They concluded that the activation energy of the reaction was about 9 kcal., approximately the same as for methyl radicals. A point of interest in this work was that the production of ethane was increased by the presence of hydrogen even at tempratures below 160°C.

No information is available about the corresponding reactions involving propyl or butyl radicals.

(c) Radical - Hydrocarbon Reactions

Reactions between methyl radicals and paraffin hydrocarbons, of the general type:-

$$CH_3 + C_nH_{2n+2} \longrightarrow CH_4 + C_nH_{2n+1}$$

have been investigated by Smith and Taylor[18]. They produced methyl radicals by the photolysis of dimethyl mercury and allowed them to react with the paraffin in the temperature range 100° to 300°C. They estimated the activation energy by measuring the rate of formation of methane. By plotting log k_{CH_4} vs. $1/T$ they determined the activation energy of the reaction in question. The activation energies reported for the reactions between methyl radicals and various hydrocarbons were as follows:-

Hydrocarbon	Activation Energy kcal
Ethane	8.3
n-Butane	5.5
iso-Butane	4.2
neo-Pentane	8.3

These results indicate that the strength of the primary C-H bond is 2.8 kcal stronger than the secondary and 4.1 kcal. stronger than the tertiary.

(d) Reaction between Radicals.

Reactions of the general type:-

$$R + R' \longrightarrow R\text{-}R'$$

have often been postulated as a chain breaking step and have been suggested as the mechanism by which the final products of photosensitized reactions are produced[53,60,61,62,70,73,75].

The reaction:-

$$CH_3 + CH_3 \longrightarrow C_2H_6$$

has been investigated by Paneth and co-workers[10,84]. It was shown that methyl radicals disappeared rapidly and that the rate of disappearance was unaffected by the presence of inert gas. Since ethane was the main product of the reaction it was evident that the process occurring was the above recombination. By altering the extent of the surface it was shown that the reaction occurred mainly in the presence of a third body or at the surface. The rate of disappearance of the radicals was shown to be increased by the presence of hydrogen and, under these conditions, the average life of the radicals varied inversely with the temperature, the conclusion being that the reaction occurred after adsorption on the surface, the extent of which adsorption was diminished by increasing the temperature. Increasing the pressure of the methyl radicals increased the production of ethane and decreased that of methane in the presence of hydrogen; this is in complete accord with a competition between recombination of methyl radicals and a reaction between these radicals and hydrogen molecules. Allen and Bawn[88] measured the concentration of methyl radicals at varying distances from the reaction zone with the aid of metallic mirors. They found that the concentration of the radicals did not decrease up to that corresponding to 10 collisions between the radicals, and concluded that the recombination reaction occurred with a small activation energy or with a small steric factor.

Taylor and Rosenblum[85] investigated the photolysis of acetone alone and in the presence of hydrogen. They concluded that the recombination occurs at the wall and has a small activation energy. The fact that these reactions have a small activation energy is substantiated by the work of Cunningham and Taylor[86] and of Smith and Taylor[18].

Theoretical explanation of the low activation energy of these reactions was given by Gorin, Kauzmann, Walter and Eyring[22] who consider that in the recombination of radicals the activation energy is really zero but that a small, apparent activation energy may result from the action of opposing polarisation and rotational energies of the radicals.

Kimball's calculation[76] of a mean life of 10^{-12} sec. for the complex C_2H_6 formed in the reaction between methyl radicals indicates that the reaction will, in general, occur only under dreierstoss conditions.

Similar reactions involving ethyl, propyl and butyl radicals have been postulated and have been shown to account very satisfactorily for the products formed in the photosensitized reactions of the corresponding hydrocarbons.

B. EXPERIMENTAL

I Materials.

The iso-butane used was obtained from the Ohio Chemical Co. It was stated to be at least 99 per cent pure, the only likely impurity being n-butane. As no impurity could be detected by the analytical methods available the iso-butane was used after only a simple bulb to bulb distillation.

(a) The Optical System:-

The source of the 2537Å mercury resonance line used in these investigations was in essentials identical with that described by Steacie and Phillips[89] and, as recommended by them, the reaction vessel was sealed directly over the lamp so that the possibility of reflection of the radiation prior to absorption by the reacting gases was eliminated.

The construction of the lamp-reactor unit is illustrated in figure II. The transmitting portion of the lamp was made of clear quartz and was sealed to the electrode chambers and to the reactor, both of which were made of pyrex, by means of two quartz to pyrex graded seals. The lamp was fitted with coated electrodes and

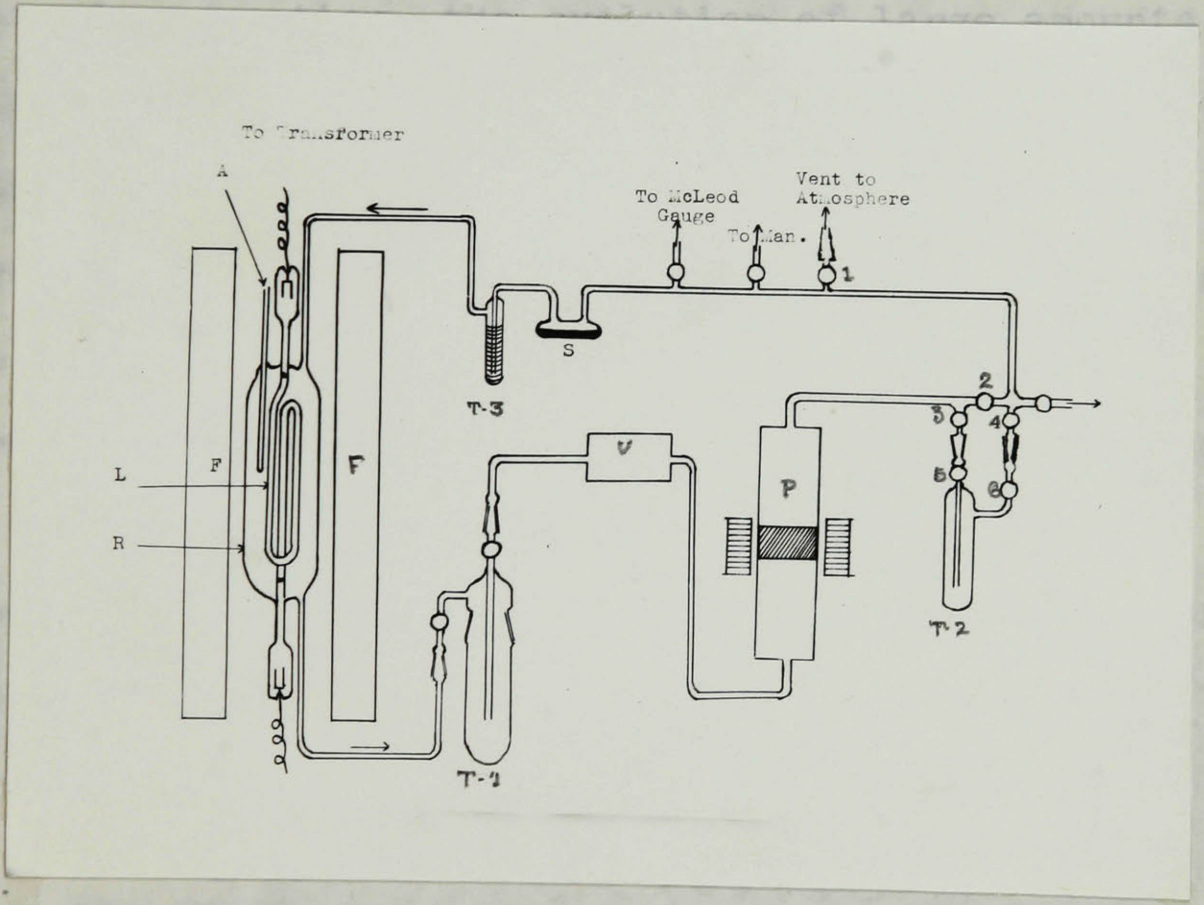


FIGURE II.

Apparatus - Optical, Reaction and Circulatory System.

was filled with 3 mm. of neon and a drop of mercury after the electrodes had been bombarded by the usual neon sign technique[91]. The bombarding of the electrodes and the filling of the lamp were done by the Claude Neon Eastern Ltd., Montreal. Melville[90] has shown that lamps of this type produce a reasonably narrow line and do not suffer from the disadvantage of unsteady operation, the evolution of large amounts of heat and self-reversal of the line usually associated with other types of lamp and especially with the mercury arc. Steacie and Phillips[89] have shown that the type of lamp used is suitable to the study of mercury photosensitized reactions since they obtained no reaction with ethane in the absence of mercury vapour in the reactor. That the reaction in the presence of mercury vapour was due to the 2537Å radiation is fairly certain since the only other resonance line, at about 1850Å, that would be effective in promoting the reaction is known to be efficiently filtered out by the quartz of the transmitting portion of the lamp.

The characteristics of a lamp similar to that used in the present investigation have been reported by Steacie and Phillips[89] who found that the efficiency in the production of the 2537Å radiation increased with decreasing input and reported an efficiency of 80 per cent with an input of 1.8 Watts (713 volts and 2.5 mamps.). They found, however, that there was a corresponding decrease in the total output of the lamp, so that it was decided to run the lamp under conditions that provided a large output rather than a high efficiency.

The lamp was run from a 5000 volt Jefferson sign transformer of the type used for commercial neon signs. The primary current was standardised at 5.7 amps. at 110 volts A.C. which gave an arc current of about 90 mamps.

The lamp was found to be usually very constant in operation. To avoid undue heating of the electrodes in the high temperature runs the electrode chambers were placed about six inches from the ends of the reactor; in this position the electrodes remained cool throughout the runs and the radiation was found to be unreversed even when the reactor was heated to 250°C. With this arrangement, however, some difficulty was experienced in keeping the production of the mercury radiation constant during the low temperature runs. When the electrodes were too cool the mercury vapour pressure was lowered to such an extent that the lamp emitted the neon spectrum and in these runs it was sometimes necessary to run the lamp for a long time, up to 40 mins., before a constant and uninterrupted mercury spectrum was obtained. This difficulty was overcome to some extent by aspirating hot air through a copper coil surrounding the electrodes, although this did not reduce materially the time required for the attainment of the mercury spectrum it did prevent reversion to the neon spectrum once the mercury spectrum had been established.

The quantum output of the lamp was determined by measuring the rate of the hydrolysis of monochloracetic acid. The lamp surface was freed from any adhering film of hydrocarbon polymer by filling the reactor with carbon tetrachloride and allowing the lamp to stand in this solvent overnight; the reactor and lamp were then washed twice with acetone and several times with water. The reactor was then filled with 0.5N monochloracetic acid and illuminated for a definite time. Acid of this strength has been shown by Steacie and Phillips[90] to effect complete absorption of the radiation in question in a vessel of similar dimension to that used here. When the lamp was switched on the temperature rose gradually from about 25°C to about 60°C. The temperature was measured by means of a thermocouple at five minute intervals throughout the illumination and the average temperature during the determination estimated by integrating the curve obtained by plotting time against temperature.

(b) The Reaction System:

The main features of the apparatus are shown in figure II. The lamp-reactor unit R was surrounded by a large electrically heated furnace F the temperature of which was manually controlled by a series of rheostats. It was found that the temperature could be maintained within 5°C of the desired value.

The mercury saturator S supplied the mercury vapour necessary to saturate the reactants. It provided a surface of about thirty square centimetres and was electrically heated to 60°C. Any excess mercury at 20°C was removed by an iron coil in trap T-3. Thus at all times there was a constant supply of mercury to the reaction vessel.

The circulating pump P consisted of a brass tube 35 cms. long and 4 cms. in diameter inside of which was a short close-fitting solid steel cylinder which acted as a piston. A solenoid of about 1000 ampere turns was arranged to slide on the outside of the tube and a reciprocating motion was applied to it by means of a strong cord, a set of pulleys and an eccentric wheel geared to a quarter horsepower electric motor. The displacement of the pump was 312 cubic centimetres.

The pump was connected to a set of mercury valves V which were designed to ensure that the gas in the system flowed only in one direction.

The reaction vessel R had a volume of 870 cc.; it was provided with a gas inlet and outlet and with a thermocouple well which extended to the middle of the reactor. The temperature in the reactor was measured by means of a chromel-alumel thermocouple in conjunction with a potentiometer.

The condensable products of the reaction were collected in the trap T-1 which was maintained at a temperature sufficiently low to prevent any appreciable amount of the solid or liquid product of the reaction condensing in the mercury valves or in the pump. The trap T-2 served as a reservoir for the iso-butane and was maintained at such a temperature that the iso-butane condensed in this trap and provided the desired working pressure. The apparatus was connected to a vacuum system consisting of the usual mercury diffusion pump backed by a Cenco Hyvac, and to a McLeod gauge and a mercury manometer.

III Procedure

Before each run the temperature of the reactor was raised to about 350°C with the apparatus connected to the vacuum system and left in this state overnight.

When the apparatus had been shown to be free from leaks and from traces of heavy hydrocarbons deposited on the wall of the reactor, the temperature of the reactor was adjusted slightly, usually about 20°C, below the value required in the run and a definite amount of iso-butane admitted. Trap T-2 was cooled with solid CO_2 - acetone mixture to a temperature such that the iso-butane condensed and provided the requisite vapour pressure. The trap T-1 was then cooled to a temperature slightly higher than that of T-2 so as to remove the higher boiling products of the reaction as completely as possible from the reaction mixture without causing the iso-butane to condense in this trap. The mercury saturator was now heated to about 60°C and the circulating pump started. The lamp was then switched on, the current to the primary of the transformer adjusted to 5.7 amps., and the gas illuminated for a definite time. The temperature of the traps T-1 and T-2 was maintained within one degree of the desired temperature by the addition of small pieces of solid CO_2.

After illumination trap T-1 was placed in ice-water and T-2 allowed to attain atmospheric temperature and the temperature of the reactor adjusted to that at which the initial pressure of the iso-butane was measured. After the apparatus had attained equilibrium the pressure of the residual iso-butane together with that due to the gaseous products of the reaction and the small vapour pressure of the liquid products was measured. Trap T-1 was then cooled in liquid air and the gases circulated to constant pressure; the pressure of the incondensable gas gave a measure of the amount of hydrogen and methane formed in the reaction. The permanent gas fraction was then removed from the apparatus through the trap, cooled in liquid air, by means of a Toepler pump and stored in a portable gas holder.

IV <u>Analysis</u>: (a) <u>Permanent Gas Fraction</u>.

The permanent gas may be assumed to consist essentially of methane and hydrogen. The methane content of this gas was determined by combustion in excess oxygen, the CO_2 produced being estimated by absorption in standard alkali. The gas was passed slowly through a pyrex spiral immersed in liquid air, to ensure the removal of higher hydrocarbons, and collected in a calibrated flask attached to the combustion unit and to a manometer. The volume of gas used in these analyses usually amounted to about 2.5×10^{-3} moles. The combustion unit consisted of a quartz tube, 1.5 cm. diameter and 90 cm. long, the middle 30 cm. of which was heated electrically 900 to 1000°C. The gas was bled slowly into a rapid stream of tank oxygen and the mixture passed through the heated tube. The effluent gases were passed through a sintered glass disc below the surface of a measured volume of standard, about 0.1N, sodium hydroxide to which had been added two to three drops of butyl alcohol which acted as a neutral foaming agent. With a high gas velocity a fine foam about four inches high was produced; this gave very efficient contact between the gas and the alkaline absorber. The CO_2 produced was estimated by back titration with 0.1N sulphuric acid, phenolphthalein being used as indicator. The CO_2 was equivalent to between one and three cubic centimetres of 1/10 normal alkali. Several blank determinations showed an average correction of 0.12 cc. The analyses were carried out in duplicate and good agreement was obtained in all cases. By the analysis of known mixtures the method was shown to be accurate to about 10 per cent of the methane content for gases containing 10 per cent of methane.

(b) Condensable Gases.

The condensed gases and higher products of the reaction were isolated in the trap cooled in liquid air. This trap was removed from the reaction system and attached to a Podbielniak type low temperature fractional distillation apparatus. The column of this apparatus was packed with a modified Stedman type wire gauze packing as recommended by Bower and Cooke[92]. The column consisted of a pyrex tube 135 cms. long and about 4 mm. I.D.; the packed portion was 83 cms. long. This column was found to possess an efficiency of 23 theoretical plates at total reflux and was found to be capable of an efficient separation of n- and iso-butanes. The temperature at the top of the column was measured by a thermocouple in conjunction with a millivoltmeter. At no time was more than a trace of hydrocarbon boiling below iso-butane found in the condensed gas fraction. Neither was there any indication of the presence of neo-pentane in the products.

(c) Liquid - Solid Product.

The higher boiling products of the reaction were left in the trap at the end of the low temperature distillation. Since these products consisted of a mixture of liquid and solid hydrocarbons it was not feasible to decant them from the trap to a tared capsule for weighing. The volatility of these hydrocarbons was found to be too high to permit decantation after melting and so low as to make transferrence from the trap to the capsule by vacuum distillation a slow and tedious method. Difficulty was experienced in handling these hydrocarbons, owing not only to the proximity of the melting and boiling points of the solid octane produced, but also to the low vapour pressure of the dodecanes formed. Because of these difficulties the trap in question was constructed with a ground glass joint which permitted it to be dismantled and the products to be removed mechanically. It was found that these products could be transferred mechanically, by the aid of a stout copper wire, with negligible loss. The condensed products from individual runs were weighed and stored separately for future analysis.

The analysis of these heavy products presented a further difficulty. Rough distillation showed that the products consisted essentially of octanes with smaller amounts of dodecanes, the separation of which groups could be accomplished with ease. The analysis of the octane fraction, however, presented much greater difficulties since the boiling points of the three isomeric octanes which are probably produced in the reaction lie within a narrow range. Because of the similarity in refractive index and density of two of the isomers, 2,2,4-trimethylpentane and 2,5-dimethylhexane, it was evident that analyses based on these two properties would be unreliable; it would, of course, be necessary to use two properties for the analysis of a three component system. Because of the high melting point of the third isomer, hexamethylethane, it was thought that this body could be removed from the mixture by freezing. This would have afforded a method of estimating this compound and would have left a two component mixture, the composition of which could be determined from the refractive index with moderate accuracy. By reference to the literature on the freezing characteristics of hydrocarbon mixtures, it was found that the isomeric octanes usually formed continuous series of solid solutions. This made it evident that the freezing method could not be used in this case. It was then decided to attempt an analysis of the mixture by an efficient semi-micro fractional distillation and long runs, of about twenty hours duration, were done to obtain sufficient of the liquid product for the distillation. The column that was used for the distillations of the condensed gas fraction was used also in this distillation. It was provided with a small ground glass joint at the bottom, to which a small still pot could be fitted, and with a reflux collector, consisting of a small inverted pear-shaped bulb to which was attached a draw-off tube with a stopcock, and a reflux condenser. The collector had a volume of about o.5 cc. and was designed so that the liquid in it was in contact with the ascending vapours. The column was enclosed in two concentric glass tubes the inner of which was fitted with a heating coil to allow the column to be operated under conditions that were as nearly adiabatic as possible. The reflux collector was also wound with a nichrome heating coil and wrapped with several layers of cotton as lagging. A thermometer was placed in the annular space between the column and the inner, heater wound, jacket; the temperature of the vapour at the top of the column was measured by a thermocouple. The still pot was heated by a well lagged conical "glow coil" resistance. The charge, eight to ten grammes, was placed in the tared stillpot and weighed. The still was clamped in place, a slight upward stress being used to keep the joint tight, and the pot and jacket heaters switched on. The column usually required about four hours before equilibrium could be attained. When the column had been in equilibrium for 30 to 40 mins. the liquid which had collected in the bowl was run off and weighed. No difficulty was experienced with the early fractions which were liquid at room temperature. The middle fractions, however, were rich in hexamethylethane and solidified in the draw-off tube thus making it necessary to apply heat to the reflux collector and outlet. Since the melting and boiling points of this compound are very close together it was evident that there would be large losses incurred in drawing off the fractions. The column was run at the maximum boil-up rate contingent on the avoidance of flooding since this type of column is known to operate most efficiently just below the flood point and, because of the intermittent removal of distillate possible with the type of head used, the distillation was conducted at total reflux except for the few seconds during which the sample was being removed. Because of the small amount of vapour around the thermocouple it was unlikely that the temperature indicated would correspond to the true boiling point of the fraction so it was decided to determine this property on a small sample of the fraction by the Markownikoff method; the melting range of the solid fractions was determined at the same time. From the results obtained it was evident that no reliable analysis of the octane fraction could be obtained from the distillation curve. However, although the fractions obtained were not single component systems it was seen from the melting ranges that the fractions did not contain more than two components, and that it should be possible to obtain an analysis based on the refractive index of each fraction. It was not found possible, with the equipment available, to determine the refractive indices of the solid fractions by operating the refractometer at sufficiently high temperatures to ensure a homogeneous liquid sample, since the film on the prisms evaporated before the reading could be taken. The refractive indices of these fractions were determined from the refractive indices of solutions of known composition of the mixed octanes in n-hexane.

C. RESULTS.

The conditions under which the various runs were performed are given in Table II and the details of the fractionation of the liquid products in Table III. In these tables all percentages are expressed on a weight basis.

The octane fractions may be assumed to consist of hexamethylethane, 2,2,4-trimethylpentane and 2,5-dimethylhexane to the exclusion of the other isomers since these are the only octanes that could be formed if no isomerisation of the butyl radical or of the 2-methylpropane molecule occurred during the reaction. The results of past work have shown that such isomerisation is extremely unlikely.

It was found that a linear relation existed between the refractive index of solutions of hexamethylethane and of 2,2,4-trimethylpentane in n-hexane and the composition of the solution on a weight percentage basis. The data supporting this relation are given in Table IV. Since this relation holds for the above solutions it was assumed that a similar relation would hold also for solutions in which the octane component was 2,5-dimethylhexane. These relations may be expressed

TABLE II.

Experimental Conditions

Volume of Reactor 870 cc. Volume of System 1985 cc.

Arc Current 89 ma. Circulation Rate 2.67 lits/min.

Resonance Radiation absorbed 1.19×10^{-5} einsteins / sec.

SERIES A - Runs at 80°C.

Run No.	Average Time of Run (mins.)	Initial Pressure of Butane (cms. Hg)	Working Pressure of Butane (cms. Hg)	Final Pressure - Cms. Hg Total Prods.	Final Pressure - Cms. Hg Hydrogen Methane	Liquid Products (gms.)
A 1	120	30.5	6.4	26.2	5.2	–
A 2	120	50.5	9.2	45.0	5.3	0.42
A 3	540	60.0	10.7	44.6	18.0	1.90
A 4	593	50.5	11.4	33.1	19.0	2.15
A 5	120	51.3	21.8	44.8	6.3	0.55
A 6	180	60.0	30.6	50.5	10.3	0.95

SERIES B - Runs at 150°C.

Run No.	Average Time of Run (mins.)	Initial Pressure of Butane (cms. Hg)	Working Pressure of Butane (cms. Hg)	Final Pressure - Cms. Hg Total Prods.	Final Pressure - Cms. Hg Hydrogen Methane	Liquid Products (gms.)
B 1	180	50.2	5.0	34.0	16.6	1.53
B 2	300	50.0	10.0	29.8	24.0	–
B 3	150	50.1	11.0	36.9	14.1	1.51
B 4	150	60.3	11.0	42.4	14.6	1.27
B 5	240	51.3	11.0	27.8	24.5	2.20
B 6	90	60.2	31.7	55.3	8.9	–

TABLE II.(cont'd)

Experimental Conditions

SERIES C - Runs at 250°C.

Run No.	Average Time of Run (mins.)	Initial Pressure of Butane (cms. Hg)	Working Pressure of Butane (cms. Hg)	Final Pressure - Cms. Hg		Liquid Products (gms.)
				Total Prods.	Hydrogen Methane	
C 1	300	50.5	6.0	40.6	11.0	1.12
C 2	150	49.8	10.0	35.5	14.4	1.13
C 3	210	70.2	10.8	45.2	21.7	2.12
C 4	180	69.9	12.6	51.0	23.7	1.40
C 5	120	60.8	19.0	49.0	10.5	0.92
C 6	120	60.5	23.8	50.4	11.6	1.10
C 7	90	50.0	27.0	45.3	6.8	-
C 8	120	58.9	27.8	48.0	10.6	-
C 9	150	70.0	32.9	54.3	13.2	1.26
C 10	120	56.9	41.8	48.9	7.9	1.23
C 11	210	54.4	51.4	43.5	11.3	1.81
C 12	120	65.0	61.0	56.0	8.3	1.19

Vol. of system 3190 cc.

TABLE III.

Fractionation of Liquid Products and Properties of Fractions.

SERIES A - Runs at 80°C.

Charge to distillation	9.70	gms.,	100%	of	charge
Distillate	5.83	"	60%	"	"
Residue	1.67	"	17%	"	"
Loss on distillation	2.20	"	23%	"	"

Fraction No.	% of distillate	B.P. °C.	Melting Range °C.	Refractive Index n_D^{20}	Hexane Soln. %C8	Hexane Soln. n_D^{20}
1	10.3	73.6	-78	1.3860	49.7	1.3851
2	10.3	92.1	-78	1.3925	-	-
3	10.1	95.1	-	1.3962	61.2	1.3899
4	10.0	100.0	-	1.4000	45.9	1.3881
5	9.2	103.3	0 to 62	1.4015	48.6	1.3888
6	8.5	105.2	20 " 69	-	28.1	1.3842
7	9.9	104.6	50 " 89	-	38.0	1.3860
8	9.7	104.8	50 " 90	-	31.3	1.3840
9	12.8	105.2	30 " 85	-	47.0	1.3890
10	9.2	106.6	-10 " 68	-		

TABLE III (cont'd)

Fractionation of Liquid Products and Properties of Fractions.

SERIES B - Runs at 150°C.

Charge to distillation	7.99 gms.,	100%	of charge.
Distillate	4.75 "	59%	" "
Residue	0.92 "	12%	" "
Loss on distillation	2.32 "	29%	" "

Fraction No.	% of Distillate	B.P. °C.	Melting Range °C.	Refractive Index n_D^{20}	Hexane Soln. %C_8	Hexane Soln. n_D^{20}
1	9.9	101.5	? to -78	1.3954	61.8	1.3884
2	10.5	105.0	-10 " 45	-	49.4	1.3878
3	7.0	105.0	-10 " 82	-	56.4	1.3904
4	11.2	106.0	5 " 91	-	53.4	1.3901
5	9.3	106.0	65 " 95	-	44.6	1.3881
6	8.0	106.2	75 " 98	-	52.8	1.3906
7	8.2	106.1	92 " 100	-	50.0	1.3899
8	8.6	106.5	93 " 100	-	48.6	1.3891
9	9.5	106.7	25 " 88	-	61.6	1.3951
10	7.3	115.4	5 " 30	-	-	-
11	10.5	-	-	-	-	-

TABLE III (cont'd)

Fractionation of Liquid Products and Properties of Fractions.

SERIES C - Runs at 250°C.

Charge to distillation .... 7.80 gms., 100% of charge.

Distillate .... 5.52 " 70.9 " "

Residue .... 0.34 " 4.4 " "

Loss on distillation .... 1.94 " 24.7 " "

Fraction No.	% of Distillate	B.P. °C.	Melting Range °C.	Refractive Index n_D^{20}	Hexane Soln. %C8	Hexane Soln. n_D^{20}
1	11.1	79.0	-78	1.3885	63.9	1.3880
2	10.5	98.0	? to -78	1.3969	61.7	1.3906
3	9.2	102.5	0 " 15	1.4000	49.0	1.3890
4	14.6	101.0	20 " 49	-	40.9	1.3874
5	9.6	105.7	80 " 93	-	-	-
6	12.7	103.6	96 " 100	-	-	-
7	10.9	105.0	98 " 100	-	41.1	1.3874
8	9.1	103.8	55 " 92	-	50.4	1.3904
9	8.5	104.4	10 " 54	-	31.1	1.3846
10	3.8	-	-	-	-	-

TABLE IV

Relation between Refractive Index and Composition of Solutions of Octanes in n-Hexane.

HEXAMETHYLETHANE		2,2,4-TRIMETHYLPENTANE	
% of C_8 in solution	n_D^{20}	% of C_8 in solution	n_D^{20}
59.4	1.3927	85.0	1.3891
46.5	1.3900	61.3	1.3851
44.9	1.3890	44.4	1.3819
36.1	1.3858	36.4	1.3812
27.5	1.3856	16.2	1.3778
23.9	1.3819		
13.6	1.3800		

by equations of the type:-

$$n = mx + c$$

where n - refractive index (n_D^{20}) of the solution.

x - weight percentage of the octane in the solution.

c - a constant = n_D^{20} for n-hexane = 1.3750

m - a constant.

The constant m was found to have the following values:-

Octane	m
Hexamethylethane	3.34×10^{-4}
2,2,4-trimethylpentane	1.60×10^{-4}
2,5-dimethylhexane	1.64×10^{-4}

To obtain an analysis of the fraction it was necessary to assume that each fraction contained not more than two components one of which was hexamethylethane. Since the column was reasonably efficient and since hexamethylethane, the most prevalent of the octanes, has its boiling point intermediate between those of the other two octanes, it is considered that the above assumption is not unreasonable. Since the constant m has very similar values for 2,2,4-trimethylpentane and for 2,5-dimethylhexane the presence of one of these substances as a third component in a mixture of the other with hexamethylethane would have little effect on the final result.

In addition to the above it is necessary to assume also that in a mixture of two octanes and n-hexane containing a fixed percentage of octanes, the refractive index bears a linear relation to the composition of the octane component. This assumption is not unreasonable in view of the ideality of solutions of isomeric hydrocarbons.

By combining the values of the constants m and c the following expressions were derived:-

% hexamethylethane in mixture with 2,2,4-trimethylpentane

$$= \frac{n - 1.3750 - (1.64x)10^{-4}}{(1.70x)10^{-4}} 100$$

% hexamethylethane in mixture with 2,5-dimethylhexane

$$= \frac{n - 1.3750 - (1.60x)10^{-4}}{(1.74x)10^{-4}} 100$$

The composition of the fractions was determined from the above relations. The analyses are reported in Table V.

No C_2 or C_3 hydrocarbons were detected in the analysis of the gas fractions obtained. The composition of the hydrogen - methane fractions are given in Table VI.

In the estimation of the quantum output the

TABLE V

Analysis of Liquid Products.

PRODUCT FROM RUNS AT 80°C.

Fraction No.	% of total distillate	Hexamethyl ethane	2,2,4-trimethyl pentane	2,5-dimethyl hexane	Hydrocarbons lower than octanes
1	10.3	0.0	50.0	0.0	50.0
2	10.3	23.0	77.0	0.0	0.0
3	10.1	34.0	66.0	0.0	0.0
4	10.0	45.1	54.9	0.0	0.0
5	9.2	71.4	28.6	0.0	0.0
6	8.5	70.9	29.1	0.0	0.0
7	9.9	96.5	3.5	0.0	0.0
8	9.7	72.0	0.0	18.0	0.0
9	12.8	61.1	0.0	38.9	0.0
10	9.2	76.9	0.0	23.1	0.0
Total Distillate	100.0	55.4	29.7	9.8	5.1

Estimated values.

TABLE V (cont'd.)

Analysis of Liquid Products.

PRODUCT FROM RUNS AT 150°C.

Fraction No.	% of total distillate	Hexamethyl ethane	2,2,4-trimethyl pentane	2,5-di methyl hexane	Hydrocarbons lower than octanes
1	9.9	0.0	60.0	0.0	40.0
2	10.5	31.4	68.6	0.0	0.0
3	7.0	56.0	44.0	0.0	0.0
4	11.2	63,4	34.6	0.0	0.0
5	9.3	69.1	30.9	0.0	0.0
6	8.0	76.4	23.6	0.0	0.0
7	8.2	76.4	11.8	11.8	0.0
8	8.6	79.4	0.0	20.6	0.0
9	9.5	74.0	0.0	26.0	0.0
10	7.3	95.6	0.0	4.4	0.0
10(a)	10.5	100.0	0.0	0.0	0.0
Total	100.0	64.6	25.8	5.6	4.0

Estimated values.

TABLE V cont'd.

Analysis of Liquid Products.

PRODUCT FROM RUNS AT 250°C.

Fraction No.	% of total distillate	Hexamethyl ethane	2,2,4-trimethyl pentane	2,5-dimethyl hexane	Hydrocarbons lower octanes
1	11.1	0.0	70.0	0.0	30.0
2	10.5	24.1	75.9	0.0	0.0
3	9.2	52.4	47.6	0.0	0.0
4	14.6	72.1	27.9	0.0	0.0
5	9.6	85.2	17.5	0.0	0.0
6	12.7	100.0	0.0	0.0	0.0
7	10.9	100.0	0.0	0.0	0.0
8	9.1	81.8	0.0	18.2	0.0
9	8.5	83.1	0.0	16.9	0.0
10	3.8	85.2	7.4	7.4	0.0
Total	100.0	67.7	25.9	3.1	3.3

Estimated values.

TABLE VI

Analysis of Hydrogen - Methane Fractions.

RUNS AT 80°C.		RUNS AT 150°C.		RUNS AT 250°C.	
Run No.	%CH4	Run No.	%CH4	Run No.	%CH4
A 1	-	B 1	3.8	C 1	10.6
A 2	-	B 2	4.3	C 2	9.6
A 3	6.3	B 3	4.3	C 3	6.8
A 4	5.3	B 4	3.9	C 4	10.8
A 5	-	B 5	3.8	C 5	-
A 6	-	B 6	-	C 6	-
				C 7	-
				C 8	-
				C 9	11.4
				C 10	6.1
				C 11	7.3
				C 12	-

average temperature in both runs was 37°C and the total time of illumination was 60 mins. The results of these determinations are given below:-

Experiment No.	1.	2.
Moles hydrolysed x 10^3	11.82	13.12
Time to Hg spectrum - mins.	40	26
Average time steady - "	40	47
Rate of hydrolysis - mole. sec^{-1} x 10^6	4.9	4.7

Hence an average rate of hydrolysis of 4.8 x 10^{-6} mole. sec.$^{-1}$ was obtained. Leighton, Smith and Leighton (J.A.C.S. 61, 2299, -1939) have determined the quantum efficiency for the hydrolysis of monochloracetic acid by the 2537Å line at various temperatures. By interpolating their results a figure of 0.404 moles per einstein sec.$^{-1}$ was obtained for the efficiency of the hydrolysis at 37°C. Hence the output of the lamp was taken as being 1.19 x 10^{-5} einstein sec.$^{-1}$.

The analytical data contained in Tables III, V, and VI have been combined to give the final results shown in Tables VII and VIII.

TABLE VII

The Mercury Photosensitized Decomposition of Iso-butane - Results.

(Conditions as in Table I)

Run No.	Average Working Pressure (cms.Hg)	Reaction Rate Moles C_4H_{10} Reacted sec.$^{-1}$	Quantum Yield	PRODUCTS Moles of product per 100 moles C_4H_{10} reacted.			
				H_2	CH_4	C_8H_{18}	$C_{12}H_{26}$
A 1	6.4	1.6 x 10^{-6}	0.14	49.5		-	-
A 2	9.2	1.8 "	0.15	45.0		24.0	3.1
A 3	10.7	1.1 "	0.09	50.5	2.6	40.5	5.6
A 4	11.4	1.1 "	0.09	49.0	2.6	42.0	5.9
A 5	21.8	2.1 "	0.18	45.7		26.7	4.0
A 6	30.6	2.1 "	0.18	49.4		30.5	4.5
Average		1.6 "	0.14	49.8	2.6	32.7	4.6
B 1	5.0	2.9 x 10^{-6}	0.24	46.6	1.9	36.9	3.4
B 2	10.0	2.3 "	0.17	51.7	2.3	-	-
B 3	11.0	2.6 "	0.22	51.9	2.6	50.1	4.3
B 4	11.0	3.2 "	0.27	46.0	1.7	33.9	3.1
B 5	11.0	3.1 "	0.26	48.4	2.0	38.1	3.3
B 6	31.7	2.3 "	0.19	60.0		-	-
Average		2.7 "	0.23	48.9	2.1	39.8	3.5

TABLE VII (cont'd)

The Mercury Photosensitized Decomposition of Iso-Butane - Results.

(Conditions as in Table II)

<table>
<tr><th rowspan="2">Run No.</th><th rowspan="2">Average Working Pressure (cms. Hg)</th><th rowspan="2">Reaction Rate Moles C_4H_{10} Reacted $sec.^{-1}$</th><th rowspan="2">Quantum Yield</th><th colspan="4">PRODUCTS Moles of Product per 100 moles C_4H_{10} reacted.</th></tr>
<tr><th>H_2</th><th>CH_4</th><th>C_8H_{18}</th><th>$C_{12}H_{26}$</th></tr>
<tr><td>C 1</td><td>6.0</td><td>1.0×10^{-6}</td><td>0.09</td><td>49.0</td><td>4.8</td><td>50.6</td><td>1.7</td></tr>
<tr><td>C 2</td><td>10.0</td><td>2.5 "</td><td>0.22</td><td>43.9</td><td>7.4</td><td>40.9</td><td>1.3</td></tr>
<tr><td>C 3</td><td>10.8</td><td>3.1 "</td><td>0.27</td><td>40.9</td><td>3.1</td><td>45.4</td><td>1.5</td></tr>
<tr><td>C 4</td><td>12.6</td><td>3.2 "</td><td>0.27</td><td>47.9</td><td>5.9</td><td>33.1</td><td>1.1</td></tr>
<tr><td>C 5</td><td>19.0</td><td>2.6 "</td><td>0.22</td><td colspan="2">45.0</td><td>41.9</td><td>1.1</td></tr>
<tr><td>C 6</td><td>23.8</td><td>2.6 "</td><td>0.22</td><td colspan="2">50.9</td><td>50.1</td><td>1.6</td></tr>
<tr><td>C 7</td><td>27.0</td><td>1.8 "</td><td>0.15</td><td colspan="2">54.4</td><td>-</td><td>-</td></tr>
<tr><td>C 8</td><td>27.8</td><td>2.5 "</td><td>0.21</td><td colspan="2">47.0</td><td>-</td><td>-</td></tr>
<tr><td>C 9</td><td>32.9</td><td>2.6 "</td><td>0.22</td><td>40.5</td><td>4.3</td><td>45.5</td><td>1.3</td></tr>
<tr><td>C 10</td><td>41.8</td><td>3.1 "</td><td>0.26</td><td>43.7</td><td>2.8</td><td>50.8</td><td>1.4</td></tr>
<tr><td>C 11</td><td>51.4</td><td>2.3 "</td><td>0.19</td><td>42.8</td><td>3.6</td><td>52.6</td><td>1.7</td></tr>
<tr><td>C 12</td><td>61.0</td><td>3.6 "</td><td>0.30</td><td colspan="2">41.0</td><td>38.6</td><td>1.2</td></tr>
<tr><td>Average</td><td></td><td>2.6 "</td><td>0.22</td><td>42.9</td><td>4.6</td><td>45.0</td><td>1.4</td></tr>
</table>

TABLE VIII.

Yield of Products.

Product	Moles of Product per 100 moles of iso-butane reacted. 80°C.	150°C.	250°C.
Hydrogen	49.8	48.9	42.9
Methane	2.6	2.1	4.6
Heptanes and lower	1.7	1.6	1.4
Hexamethylethane	18.2	25.7	30.4
2,2,4- Trimethylpentane	9.7	10.3	11.6
2,5-Dimethylhexane	3.2	2.2	1.4
Dodecanes	4.6	3.5	1.4

D. DISCUSSION.

I The Mercury Photosensitized Reactions of Iso-butane.

The results obtained in the present study of the mercury photosensitized reaction of iso-butane have been given in the previous section and summarised in Tables VII and VIII. The following characteristics of the reaction merit discussion:-

(1) The rate and nature of the products of the reaction are independent of the working pressure of the hydrocarbon at all temperatures investigated.

(2) The reaction temperature has little influence on the rate but does affect the nature of the products.

(3) The products of the reaction are almost entirely hydrogen and polymers of the original hydrocarbon.

(4) Only small amounts of methane and hydrocarbons lighter than octane were detected in the products.

(5) The quantum yield of the reaction has been found to be much smaller than that corresponding to 100 per cent efficiency.

(6) The material balance shows a loss of material at low temperatures. It improves with increasing reaction temperature and is almost perfect at 250°C.

The effect of the working pressure of iso-butane on the course of the reaction is shown in Table VII.

It is seen that neither the nature of the products nor the rate of the reaction are influenced to any appreciable extent by a wide variation in pressure. It may be concluded, therefore,

(a) That none of the major reactions are significantly affected by the dreierstoss restriction,
(b) That quenching of the resonance radiation was essentially complete even at the lowest pressure used and that, even at the highest pressure used, there was no significant increase in the extent of pressure broadening of the resonance line. Although quenching as well as broadening may have been increased by an increase of pressure it is considered very unlikely that these two factors would have altered to the same extent at all pressure so as to exactly compensate one another.
(c) Within the limits encountered, the relative proportions of iso-butane and hydrogen in the reaction mixture do not affect the course of the reaction.

The effect of temperature on the reaction is shown in Tables VII and VIII. It is seen that increasing temperature increases the rate between 80° and 150°C but that an increase from 150° to 250°C causes no further increase in the rate. The following alterations in the products of the reaction with increasing temperature are considered significant:-

(a) Hydrogen:- the yield decreases with increasing temperature above 150°C.

(b) Methane:- the yield increases with increasing temperature above 150°C.

(c) "Dodecanes": - the yield decreases with temperature above 150°C.

(d) Octanes:- the variation in the production of the individual octanes with temperature shows that the initial C-H split apparently occurs on the primary C-H as well as at the tertiary C-H bonds and that the extent of the latter split increases relative to the former with increasing temperature.

The most obvious result of the investigation was the fact that the products of the reaction consisted almost entirely of octanes (and dodecanes) and hydrogen. Very little methane was found. This indicates clearly that the primary reaction of the iso-butane molecule is the production of the corresponding radical:-

$$C_4H_{10} + Hg(6^3P_1) \longrightarrow C_4H_9 + HgH \qquad (1)$$

followed by:-

$$HgH \longrightarrow H + Hg(6^1S_0) \qquad (2)$$

The above reactions are in complete accord with the mechanisms postulated for the photosensitized and H atom reactions of the lower paraffin hydrocarbons.

In the early stages of the reaction the H atom produced in (2) will certainly enter into collision with an iso-butane molecule and the reaction:-

$$H + C_4H_{10} \longrightarrow C_4H_9 + H_2 \qquad (3)$$

has been shown by White, Winkler and Kennalty[69] to occur readily.

As the reaction proceeds and as hydrogen accumulates in the system, the reaction:-

$$H_2 + Hg(6^3P_1) \longrightarrow H + HgH \qquad (4)$$

will assume increasing importance and, owing to the high efficiency with which hydrogen is known to quench $Hg(6^3P_1)$ atoms, will eventually be the major source of H atoms.

The production of H atoms by a reaction between butyl radicals and hydrogen molecules:-

$$C_4H_9 + H_2 \longrightarrow C_4H_{10} + H \qquad (5)$$

would be kinetically probable in the later stages of a run. The indications[65] are, however, that reactions of this type do not occur readily below 160°C. and, as the H atom produced would probably react by (3), the reaction can have little significance in the present investigation.

It is evident that (3) must be the chief source of butyl radicals especially in the later stages of a run. The production of hydrogen molecules by recombination:-

$$H + H + M \longrightarrow H_2 + M \qquad (6)$$

cannot be regarded as important because of the dreierstoss restriction, the small probability of collision and the fact that the reaction in the present type of system is independent of the relative concentrations of paraffin and of hydrogen.

The production of octanes is most easily accounted for as the result of recombination of the butyl radicals:-

$$2\ C_4H_9 \longrightarrow C_8H_{18} \qquad (7)$$

These reactions are known to occur with little or no real activation energy[22] and have been postulated as being responsible for the major products of photosensitized reactions. The only reasonable alternative to this reaction would be:-

$$C_4H_9 + C_4H_{10} \longrightarrow C_8H_{18} + H \qquad (8)$$

Reactions of this type have been estimated[74] to have an activation energy of 40 to 50 kcal. so that (8) would be most improbable and, in any case, could not be postulated from any of the results obtained in the present investigation.

The dodecanes probably are formed by the combination of butyl and octyl radicals, these latter bodies being produced by reactions similar to (1) or (3) involving octane instead of butane molecules. The results of Smith and Taylor[18] show that the octyl radicals may be produced also by

$$C_4H_9 + C_8H_{18} \longrightarrow C_4H_{10} + C_8H_{17} \qquad (8')$$

since they consider that the activation energy of this reaction is less than 10 kcal. The reaction:-

$$C_4H_9 + C_8H_{18} \longrightarrow C_{12}H_{26} + H$$

must be discounted for the same reasons as was (8) and so cannot be regarded as a source of dodecane.

The presence of small amounts of methane in the product requires some explanation. It has been assumed that, in photosensitized[73,75] and in hydrogen atom reactions [66,67,68,69], the methane is produced by a series of "atomic cracking" reactions following the production of the initial radical. In the present case these reactions would be:-

$$C_4H_9 + H \longrightarrow C_3H_7 + CH_3 \qquad (9a)$$

$$C_3H_7 + H \longrightarrow C_2H_5 + CH_3 \qquad (9b)$$

$$C_2H_5 + H \longrightarrow CH_3 + CH_3 \qquad (9c)$$

and the methane would be regarded as being formed from the hydrogen atom reaction with the methyl radical:-

$$CH_3 + H \longrightarrow CH_4 \qquad \text{(Third Body)} \qquad (10)$$

Steacie and Dewar[73] found no ethane in the products of the mercury photosensitized reactions of propane and Hay and Winkler[75] found no propane or ethane in the similar reactions of n-butane. It was therefore concluded that the above series of reactions occurred and that the intermediate radicals in the series did not enter into any reaction, such as

$$R + R'H \longrightarrow RH + R'$$

where R' is an alkyl radical or a hydrogen atom, which would lead to the production of the corresponding paraffin hydrocarbon. In view of the probable high concentration of the initial radical it would seem likely, on kinetic grounds, that radical recombination with one of the intermediate radicals in the atomic cracking series of reactions should occur. Butanes and pentanes then might have been expected in the propane reaction and pentanes, hexanes and heptanes from n-butane in addition to the major products of these reactions. No butanes or pentanes were reported by Steacie and Dewar, Hay and Winkler found only traces of the intermediate hydrocarbons and, as shown in Table VIII, the production of heptanes and lower hydrocarbons in the present investigation is certainly very small. However, the correspondence between the production of methane and of heptanes in the present case indicates that, under the conditions pertaining in photosensitized reactions, the atomic cracking series of reactions does not proceed to any extent beyond the first stage (9a) but that the propyl radicals produced react with the initial butyl radicals. It is probable that, at 250°C, the propyl radicals also suffer thermal or photosensitized decomposition:-

$$C_3H_7 + X \longrightarrow C_2H_4 + CH_3 + x \qquad (11)$$

where x represents an active mercury atom or a quantum of thermal energy. The ethylene then would combine with a hydrogen atom to form an ethyl radical.

In the present investigation a diligent search was made for neopentane in the condensed products; no trace of this compound could be found. Because of this surprising result it must be concluded that one of the reactions:-

$$R + H + M \longrightarrow RH + M \qquad (12a)$$

$$R + H_2 \longrightarrow RH + H \qquad (12b)$$

$$R + C_4H_{10} \longrightarrow RH + C_4H_9 \qquad (12c)$$

occurs much more readily when R is a methyl than when it is a propyl radical with the consequence that all the methyl radicals are hydrogenated before they are given the opportunity to react with a butyl radical. Evidence of the likelihood of the occurrence of these reactions has been given in the introduction to this work. The indications are[24] that (12b) has an activation energy of about 9kcl. and therefore will not be important below 160°C. Reaction (12c) has a low activation energy, about 4.2 kcal[49], and a very high kinetic probability and may be assumed to be responsible for the majority of the methane produced. Owing to the high pressures used in the reaction, the dreierstoss restriction in (12a) will probably not be very serious and, since the activation energy of this reaction is probably very low, it will be responsible for a large proportion of the methane produced.

The decrease in the production of hydrogen with increasing temperature is considered to be the consequence of the increasing production of methane. At 250°C the butyl radical probably becomes slightly unstable and the reaction:-

$$C_4H_9 \longrightarrow C_3H_6 + CH_3$$

or $$C_4H_9 \longrightarrow C_2H_4 + C_2H_5$$

starts to play an important part in the mechanism. The olefin formed then reacts rapidly with hydrogen atoms:-

$$C_3H_6 + H \longrightarrow C_3H_7$$

and the radical formed, which in any case will contain an abnormal amount of energy, also exhibits instability at this temperature and decomposes by an analagous process. This series of reactions is not subject to the same objections as were raised previously to the "atomic cracking" series since the postulated decomposition of the intermediate radicals is not bimolecular and since the chance of survival of the "hot" radicals produced as intermediates, with subsequent reaction with the butyl radicals present, is probably very small. Hence the fact that the production of heptanes does not increase and that ethane and/or propane do not appear in the products at this temperature is not surprising.

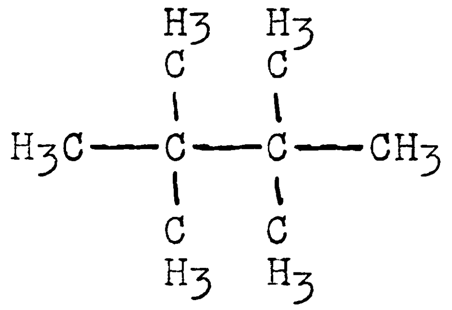
The apparent increase in the relative extent of the tertiary C-H split in the primary act is surprising at first sight, since all estimates show that the tertiary C-H bond is significantly weaker than the primary. One would, therefore, have expected the extent of the primary split relative to that of the tertiary to have increased with increasing temperature. In the face of the above facts it is therefore necessary to postulate some secondary act whereby the production of hexamethylethane relative to that of the other octanes is increased with rise in temperature. The explanation of the above phenomenon is dependent on the negative temperature coefficient of the production of dodecanes.

Working with n-butane, Hay and Winkler[75] found a large amount of dodecane in their product at low temperatures and that the production of dodecanes relative to octanes decreased with increasing temperature. They explained their results by assuming that the octyl radicals were unstable at high temperatures and decomposed, not by the splitting off of a methyl radical, but at the middle of the carbon chain with the production of a butyl radical and a molecule of butene:-

$$C_8H_{17} \longrightarrow C_4H_8 + C_4H_9$$

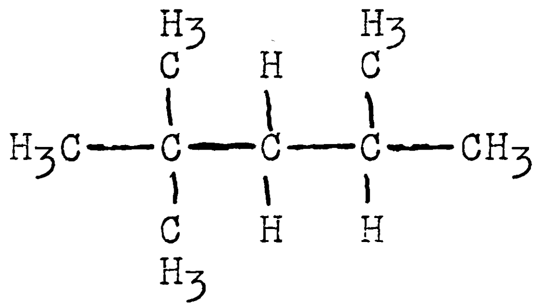
The butene produced is then hydrogenated to a butyl radical. This appears to be the only mechanism which will account for the observed behaviour in their work.

The octanes formed in the iso-butane reaction can have only the following structure:-



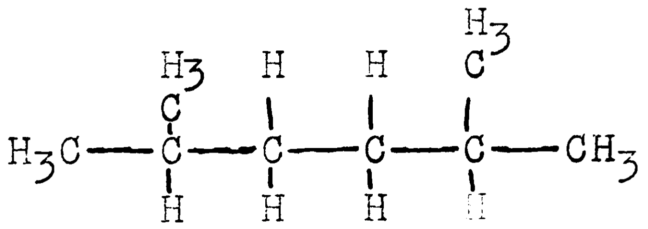
$H_3C-C(CH_3)_2-C(CH_3)_2-CH_3$

(Hexamethylethane)



$H_3C-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

2,2,4-trimethylpentane

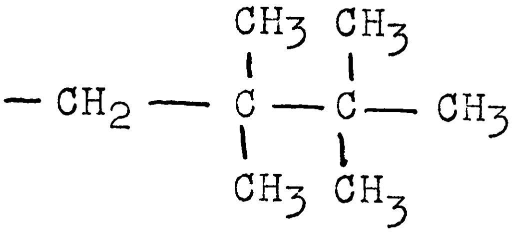


$H_3C-CH(CH_3)-CH_2-CH_2-CH(CH_3)-CH_3$

2,5-dimethylhexane

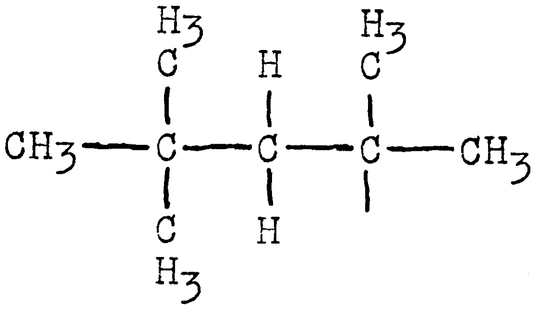
In producing the corresponding radicals it may be assumed that tertiary C-H bonds are broken more easily than the secondary or primary. This assumption is in accord with the results obtained in the present study. The radicals will be formed from the above octanes in the following manner:-

All the methyl groups in hexamethylethane are identical owing to the symmetry of the molecule and the radical can therefore have only one structure:-



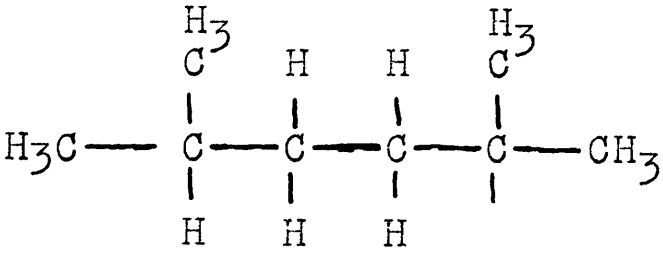
$$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

Assuming a tertiary C-H split only one radical can be produced from 2,2,3-trimethylpentane:-



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{|}{C}}-CH_3$$

Again, from the same assumption, only one radical can be formed from 2,6-dimethylhexane:-



$$H_3C-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{|}{C}}-CH_3$$

If we assume that the free bond in a radical confers unsaturation character to all bonds involving the unsatisfied carbon atom and that this consequently strengthens all those bonds then, since it is known that long carbon chains usually break near the middle,[94,95]. The fragments formed by the decomposition of the above radicals will be:- $CH_2{=\!=}C(CH_3)_2$ from 2,5-dimethylhexane and 2,2,4-trimethylpentane and the radical $(CH_3)_3C-$ from hexamethylethane. The most likely point of addition of a hydrogen atom to an olefin is on the most highly hydrogenated carbon atom. Such a process is in accord with the results obtained in the present investigation since it will invariably produce a tertiary butyl radical. Hence, the above series of reactions explains how a butyl radical which originated from iso-butane by a primary C-H split is converted to a tertiary butyl radical.

The improvement in the material balance obtained with increased temperature, shown in Table VIII, may also be explained by an argument similar to that used above. At low temperatures it has been shown that there is probably little decomposition of the octyl radicals with the consequent large production of dodecanes. It is reasonable to suppose that these compounds will then react further to produce the dodecyl radical which will then react with butyl radicals to produce C_{16} paraffins. These paraffins have sufficiently high boiling points to condense on the walls of the reactor where, under the influence of excited mercury atoms, they would probably be converted to high polymers. The excess of hydrogen in the products at low temperatures tends to confirm this suggestion since it is very likely that the polymers formed would be unsaturated so that the reactions responsible for their formation would produce an excess of hydrogen. The deficiency of hydrogen at 250°C. is probably due to an increase in the amount of radical decomposition, such as (11), at these temperatures with the accompanying increase in the production of methane.

The low quantum yields obtained in these reactions is a point which merits some discussion. For perfect efficiency the quantum yield of these reactions should be 2.0; the figure obtained in the mercury photosensitized reactions of the lower paraffins is about 0.2. Quantum yields have been reported higher than this figure in previous work, but results were based on the value of unity given by Rudberg for the quantum yield for the hydrolysis of monochloracetic acid and are therefore roughly twice the correct value.

Since there is reason to believe that the quenching in these systems is essentially complete it is evident that each quantum of 2537Å radiation will eventually excite a mercury atom to the 6^3P_1 state. In this state the mercury atom possesses ample energy for the breaking of the C-H bond even without assuming the formation of the hydride. The quantum yield of the reaction will depend on two factors:-

(a) - The efficiency with which sufficient energy is transferred from the excited mercury atom to the paraffin molecule to cause reaction.

(b) - The occurrence of back reactions and deactivating processes.

Steacie and Phillips discounted the possibility of the occurrence of back reactions as the cause for the low quantum yield in the ethane reaction because they found that the ethane recovered in the mercury photosensitized reaction between ethane and deuterium atoms was only slightly exchanged. They considered that the cause of the inefficiency lay in the primary act.

There are two possibilities of inefficiency in the primary act:-

(i) Inefficiency in the conversion of the electronic energy of the excited mercury atom to vibrational energy of the paraffin molecule. Disregarding for the present the effect of quenching to the metastable state, the only act that would lead to inefficiency would be some process such as:-

$$\underset{\phantom{112\text{ kcal.}}}{C_4H_{10}} + \underset{112\text{ kcal.}}{Hg(6^3P_1)} \longrightarrow \underset{52\text{ kcal.}}{C_4H_{10}} + \underset{60\text{ kcal.}}{Hg(6^1S_0)}$$

in which the energy transferred to the butane molecule would be insufficient to cause reaction. The energy content of the deactivated mercury atom must then be too small to correspond to any of the electronically excited levels and must therefore by manifest as translational energy. The objections to this process are:-

(a) It is known that the conversion of electronic to translational energy is exceedingly inefficient so that the above process must be inherently unlikely.

(b) The addition of 60 kcal. to the translational energy of the mercury atom would cause a marked rise in temperature in the system; it would, in effect, be equivalent to a conversion of the energy of the 2537Å radiation to heat energy, a most improbable process.

(ii) Quenching to the metastable state:-

$$C_4H_{10} + Hg(6^3P_1) \longrightarrow C_4H_{10} + Hg(6^3P_0)$$

This process has been suggested by Dr. Steacie† as a possible cause of the inefficiency. Since it is known that the metastable mercury atom, because of its long life, is efficient in splitting the hydrogen molecule, the above process would be effective in reducing the quantum yield only if the metastable atom is deactivated at the wall or if it is elevated to an electronic state higher than the 6^3P_1 level from which it returns to the ground state in a stepwise manner, the radiation emitted in the transitions being of too long wave length to cause

† Private communication.

reactivation of the ground state atoms.

For the metastable atoms to be deactivated at the wall it would be necessary either for the metastable atom to be largely unaffected by these collisions or for them to originate at a point so close to the wall that they do not collide with iso-butane molecules.

The work of Bates[97] seems to indicate that, although methane probably quenches the 6^3P_1 atoms to the metastable state and is inefficient in utilising the energy left at this point, ethane either does not quench in the same manner or, if it does, is very efficient in abstracting the energy from the metastable atoms. Since butane quenches even more efficiently than ethane it seems unlikely that the metastable atoms, if they were produced, would survive many collisions with iso-butane molecules. Moreover, it is well known that hydrogen is very efficient in utilising the energy of the metastable mercury atom; since neither the accumulation of hydrogen in the reaction, nor the addition of hydrogen in previous similar experiments, have caused any significant increase in the rate, it seems very unlikely that metastable atoms produced in the body of the reaction mixture could have much influence on the efficiency of the process.

An alternative possibility mentioned above is that the metastable atoms are produced so close to the lamp that they diffuse to the surface without deactivation. It is reasonable to assume that about one half of the output of the lamp is absorbed by ground state mercury atoms at a distance equal to the mean free path of the photon in mercury vapour. If one quarter of the Hg(6^3P_1) atoms so produced are regarded as moving towards the lamp at any one instant then only one eighth of the total output of the lamp would be lost to the reaction. Assuming that the 6^3P_1 atoms are quenched to 6^3P_0 an inefficiency of 12.5 per cent would be possible, if none of these metastable atoms are deactivated by collision with iso-butane. Since the mean free path of the photon is certainly much greater than that of the mercury atom, it is likely that a very large proportion of the metastable atoms would suffer collision with iso-butane molecules and, since these collisions are probably efficient in removing the energy from the mercury atoms, it is likely that the inefficiency due to wall deactivation would amount to only a small fraction of the value given above.

Since the physical processes examined above would appear to be incapable of accounting for more than a small percentage of the inefficiency of the reaction it is necessary to determine as far as possible whether any secondary chemical process could be postulated as being responsible for the observed behaviour.

There are three secondary processes which may be regarded as being responsible for the inefficiency of the reaction. These are:

(1) Deactivating Collisions:- A reaction of the type:-

$$C_4H_{10} + Hg(6^3P_1) \longrightarrow C_4H_{10}^{*} + Hg(6^1S_0)$$

followed by:-

$$C_4H_{10}^{*} + M \longrightarrow C_4H_{10} + M$$

would cause the process to be inefficient. The occurrence of this reaction will depend on the average life of the butane molecule containing roughly 112 kcal. in excess of the normal energy content at the reaction temperature, as well as on the frequency and efficiency of the deactivating collisions. There is no reliable information at present about the life time of the active butane molecule and it is very difficult to make any useful estimate by analogy with other work. Kimball's estimates[36] of 3.2×10^{-12} seconds for CH_4 and of 2.1 seconds for C_2H_6 indicates that loss of efficiency through such deactivating collisions might be important in the photosensitized reactions of ethane, propane and butanes. However, it should be noted that Kassel[96] has raised objections to Kimball's results and if these objections are valid the above considerations are also invalidated. The absence of a pressure effect in these reactions may not be significant since the life of the active molecule may be sufficiently long to permit essentially complete deactivation to occur even at the lowest pressure used.

(2) Recombination:- Evidence for the occurrence of reactions between hydrogen atoms and hydrocarbon radicals have been given in the introduction of this thesis. The main objection to the occurrence of reactions of the type:-

$$R + H \longrightarrow RH$$

in which R is an alkyl radical, is that ethane[50,61] and propane[50,66,67] recovered in the reactions of these hydrocarbons with deuterium atoms produced by the Wood-Bonhoeffer method were largely unexchanged. However, there are obvious objections to the application of results obtained in the Wood-Bonhoeffer type of studies to high pressure systems such as the present. When the deuterium atoms were produced by mercury photosensitization Steacie and Phillips[62] found that the recovered ethane was exchanged to the extent of about 12 per cent and from this result they concluded that recombination between ethyl radicals and deuterium atoms did not occur to any very great extent. The amount of exchange reported represented the percentage deuterisation of the residual ethane. This does not necessarily give a true picture of the reaction since it was stated[77] that only approximately one half of this residual ethane was given the opportunity to react, as the ethyl radical, with deuterium atoms. If the ethane was in reality deuterised to about double the extent indicated then the recombination reaction could account for a large proportion of the inefficiency.

The recombination of hydrogen atoms cannot be postulated as a source of the inefficiency of the reaction. The active hydrogen molecule formed would decompose within one vibration period so that the recombination could occur only by dreierstoss or at the wall. The absence of any pressure effect in these reactions prohibits the postulation of a dreierstoss reaction as the major step.

(3) Disproportionation:- The possible occurrence of reactions of the type:-

$$R + C_4H_9 \longrightarrow C_4H_8 + RH$$

where R represents a hydrogen atom or a butyl radical, have been mentioned in the introduction. This reaction would be effective in reducing the quantum yield if it were followed by:-

$$H + C_4H_8 \longrightarrow C_4H_9$$

The evidence indicated that some reaction of this type occurs in the reaction between ethane and deuterium atoms and is responsible for the high deuterisation of the butane formed. The absence of any unsaturated compounds in the products of the photosensitized reactions of the lower hydrocarbons should not be regarded as adverse evidence for the occurrence of this reaction since the hydrogenation of the olefin under these conditions certainly occurs very rapidly.

It is very difficult to estimate the relative effects of the three reactions discussed above on the inefficiency of the overall process. It seems likely that they all are responsible to varying degrees for this inefficiency but the weight of the evidence appears to favour the disproportionation in preference to the other two reactions.

II. The Photosensitized Reactions of the Lower Paraffin Hydrocarbons.

The present investigation completes a series of photosensitized reactions of the lower paraffins and it seems worthwhile to review the results of these reactions at this time.

As shown in part III of the introduction the mechanisms proposed to account for the characteristics of all of these reactions are similar in all details, consisting as they do of a C-H split as the initial act, the main products being formed by radical recombination, and atomic cracking accounting for the production of methane and methyl radicals. The results show, however, important differences in the type of products formed from ethane on one hand and propane, n-butane and iso-butane on the other. Since these hydrocarbons are all of the same type, it is proposed to discuss this behaviour and to determine whether any reasonable explanation can be given for these differences.

It has been found that hydrogen and polymers of the original hydrocarbon were the principal products of the photosensitized reactions of propane and the butanes; the small amounts of methane found could be accounted for by a reaction between the initial radicals and hydrogen atoms. The products from ethane, however, contained large amounts of methane and propane as well as butane, hexane and hydrogen. The methane and propane were assumed to have been formed by the reactions of methyl radicals with hydrogen atoms or with ethyl radicals. Hence the total production of methane and propane forms a measure of the amount of methyl radicals produced.

Steacie and Phillips[61] found that in a multi-pass system the nature of the products did not change appreciably with the working pressure of the ethane at low trap temperatures, and at trap temperatures below -116°C. an average value for their products is:-

Steacie and Phillips[61]	Products - mole per cent			
	CH_4	C_3M_8	C_4H_{10}	H_2
Average values for runs at low trap temperatures.	59.1	22.5	18.4	0.0
Total CH_3 produced	81.6			

Steacie and Cunningham[70], using a single pass system, got the following average values at reaction temperatures below 250°C; -

	Products - mole per cent		
	CH_4		C_3H_8
Ethane Pressure - 5 cms.	14.5		9.6
Total CH_3		24.1	
Ethane Pressure - 10 cms.	10.1		7.4
Total CH_3		17.5	

These results of Steacie and Cunningham show that there is no significant change in the proportions of the hydrocarbons in the products between reaction temperatures of 100°C. and 250°C. so that it is permissible to base the discussion on the average results for the reaction between these limits.

It seems likely that the difference in the nature of the products in these two investigations is due to the accumulation of hydrogen in the multi-pass system of Steacie and Phillips which caused an increase in the concentration of hydrogen atoms and consequently an increase in the extent of "atom cracking". The results of Steacie and Cunningham, however, show that even in the single pass system, where the concentration of hydrogen, and therefore of hydrogen atoms, is very low, the extent of the "atom cracking" reaction is still much greater than that found with the higher homologues of ethane. This result is surprising since all the work on the higher hydrocarbons has shown that the accumulation of hydrogen in the multi-pass system does not influence significantly the nature of the products. Since the concentration of hydrogen is kept to a very low level in the single pass system, and especially as Steacie and Cunningham have shown that no significant change in the nature of the products is caused by increasing the rate of ethane flow from 0.37 to 2.41 cc/sec., it seems very unlikely that the production of the methyl radical is due entirely to the reaction between hydrogen atoms and ethyl radicals since, especially in the high pressure runs, the fate of the hydrogen atoms produced as the result of the initial act would be to react with an ethane molecule:-

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

The chance of a collision with an ethyl radical would be small.

If the H atom reaction is discredited as the source of the methyl radicals, it will be necessary to postulate some other reaction, which will not apply equally well to propane and the butanes, as the origin of these bodies. The following differences between ethane and the higher paraffins may be responsible for the

the differences in the nature of the products obtained:-

(a) - Ethane is a smaller molecule so that there are fewer vibrational degrees of freedom to absorb the energy in the activated molecule; hence we would expect the activated ethane molecule to decompose more readily then the others. On the other hand the greater length of the propane and butane molecules is accompanied by a progressive weakening of the C-C bonds at the middle of the carbon chain, which would tend to counteract the stabilizing effect of the longer chain.

(b) - Ethane contains only primary C-H bonds whereas both propane and n-butane contain secondary, and iso-butane a tertiary bond. The results show that the decomposition of propane and the butanes occurs almost entirely on the secondary or tertiary bonds. Since the energy added to the hydrocarbon molecule in the mercury photosensitized reactions, about 112 kcal., would correspond to a very high temperature in a thermal reaction, it is surprising that the lack of the primary C-H split in these hydrocarbons is as pronounced as that found.

To account for the occurrence of the C-H split in preference to the C-C split it is necessary to postulate a directed collision between the hydrocarbon and the activating molecule:-

$$R\text{-}H + X \longrightarrow R\text{----}H\text{----}X \longrightarrow R + HX$$

where X represents the activating agent, either $Hg(6^3P_1)$ or a hydrogen atom. In the formation of the active complex X approaches the molecule in the direction of a C-H bond, exerts an attractive force on the hydrogen atom, thus stretching the C-H bond which then breaks to produce the corresponding radical and HX. In this manner it is likely that the C-C bond at the middle of the molecule would be largely unaffected by the collision. This mechanism would thus account for the reaction occurring by a C-H rather than by a C-C split.

The production of methyl radicals in these reactions has been assumed to be due to the reaction:-

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad (1)$$

In the work of Steacie and Cunningham, especially in the runs at 10 cms., it seems very unlikely that the hydrogen produced in the initial act would collide with an ethyl radical because of the high concentration of ethane and the low concentrations of hydrogen atoms and ethyl radicals. It appears, therefore, that some other reaction must be postulated to account for this formation of methyl radicals. The following seem to be the only reasonable possibilities:-

$$X + C_2H_6 \longrightarrow 2\,CH_3 + X \qquad (2)$$

where $X = Hg^*$ or H

$$Hg(6^3P_1) + C_2H_5 \longrightarrow CH_3 + CH_2 + Hg(6^1S_0) \qquad (3)$$

both of which have high kinetic probabilities. Reaction (2) has been suggested by Trenner, Morikawa and Taylor[50] as well as by Steacie and Phillips[61] but, in the face of further evidence, which has been given in the introduction, it was found necessary to discard it as a major step in these reactions and (1) was then accepted as the chief source of methyl radicals. If reaction (2) is rejected then (3) would appear to be the main source of methyl radicals in the experiments of Steacie and Cunningham.

The increase in the production of methane with decreasing ethane pressure in the single pass system of Steacie and Cunningham can be accounted for by the increased probability of (3) under these conditions. The large increase in the production of methyl radicals in the multi-pass reactions of Steacie and Phillips at low trap temperatures must be due to the occurrence of (1) as well as (3) as a result of the accumulation of hydrogen in the system; this also accounts for the consumption of hydrogen in these reactions. The large decrease in the production of the methyl radical at high trap temperatures found by Steacie and Phillips may be due to the much increased pressure of ethane in the system with the result that the hydrogen atoms formed by photosensitization, either from the ethane molecule or from a hydrogen molecule, would have a very small probability of reacting with an ethyl radical. This suggestion is strengthened by the fact that the production of methyl radicals in the high trap temperature runs was similar to that found by Steacie and Cunningham in the single pass system in which reaction (1) is very unlikely to occur, so that in these runs methyl radicals may have been produced entirely by reaction (3).

The fact that methyl radicals are not produced to any comparable extent in the photosensitized reactions of the other paraffins must be ascribed to a marked difference in reactivity of these hydrocarbons in (1) and

(3). Possible differences in the paraffins which may be responsible for the observed differences in behaviour have been mentioned above.

SUMMARY AND CLAIM TO ORIGINALITY.

1. The mercury photosensitized reactions of iso-butane have been investigated in a multiple-pass system at 80°, 150° and 250°C. and at various pressures. This is the first time that this reaction has been investigated.

2. The products of the reaction were found to consist almost entirely of hydrogen and octanes. Fairly large amounts of dodecanes were formed especially at the lower reaction temperatures and small amounts of methane and hydrocarbons boiling below the octanes, classed as "heptanes", were also present in the products at all temperatures.

3. A detailed analysis of the liquid products showed that the octane fraction consisted mostly of 2,2,3,3-tetramethylbutane with smaller amounts of 2,2,4-trimethylpentane. Traces of 2,5-dimethylhexane were also found.

4. The absence of significant amounts of methane, ethane and propane as well as the large production of hydrogen and octanes show that the initial step is a carbon-hydrogen split followed by radical recombination and that the amount of carbon-carbon split is negligible. The large production of 2,2,3,3-tetramethylbutane shows that the majority of the

reaction occurs at the tertiary carbon-hydrogen bond in spite of the large statistical factor in favour of the primary bond.

5. The rate of the reaction was found to be independent of the temperature and the working pressure of the hydrocarbon over the ranges investigated.

6. The following series of reactions account for the observed behaviour:-

$$i\text{-}C_4H_{10} + Hg(6^3P_1) \longrightarrow Hg(6^1S_0) + C_4H_9 + H$$

$$\text{or} \longrightarrow HgH + C_4H_9$$

$$Hg\,H \longrightarrow Hg(6^1S_0) + H$$

$$H + i\text{-}C_4H_{10} \longrightarrow C_4H_9 + H_2$$

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

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

$$H + C_8H_{18} \longrightarrow C_8H_{17} + H_2$$

$$C_4H_9 + C_8H_{17} \longrightarrow C_{12}H_{26}$$

$$H + C_4H_9 \longrightarrow C_3H_7 + CH_3$$

$$H + CH_3 \longrightarrow CH_4$$

$$C_3H_7 + C_4H_9 \longrightarrow C_7H_{16}$$

at higher temperatures the following reactions become increasingly important.

$$C_8H_{17} \longrightarrow C_4H_8 + C_4H_9$$

$$H + C_4H_8 \longrightarrow C_4H_9$$

$$C_4H_9 \longrightarrow C_2H_4 + C_2H_5$$

$$H + C_2H_4 \longrightarrow C_2H_5$$

$$C_2H_5 \longrightarrow CH_3 + CH_2$$

$$H + CH_2 \longrightarrow CH_3$$

7. The quantum yield of the reaction was found to be only about 10% of the theoretical figure. The possible cause of this inefficiency has been examined.

8. A comparison has been made between the results obtained from the mercury photosensitized reactions of ethane on one hand and of propane, n-butane and iso-butane on the other.

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APPENDIX

THE SYSTEM N-HEXANE-METHYLCYCLOPENTANE-ANILINE

FOREWORD

The main reason for the investigation of the system n-hexane-methylcyclopentane-aniline was not the academic interest of the problem but to determine whether solvent extraction of a mixture of the two hydrocarbons with aniline as solvent would be practicable on a commercial scale.

The hydrocarbons in question have very similar boiling points and, in the close fractionation of petroleum, a cut can be isolated which consists essentially of these two compounds. The presence of n-hexane prohibits the use of this fraction as a constituent of aviation fuel because of the poor anti-knock properties of this compound. The separation of these two hydrocarbons would be advantageous as it would permit the use of the high octane number methylcyclopentane as a blending agent for aviation fuel.

A. INTRODUCTION.

The system n-heptane-methylcyclohexane-aniline has been investigated recently at 25.0°C. and the following relations proposed (4):-

(a) The ratio of heptane to methylcyclohexane in the solvent layer bears a constant relation to the same ratio in the hydrocarbon layer. This relation may be expressed:-

$$\frac{y_n}{y_p} = \beta \frac{x_n}{x_p}$$

where y_n = weight fraction of the naphthene in the solvent layer

y_p = weight fraction of the paraffin in the solvent layer

x_n, x_p = similar fractions to the above but in the hydrocarbon layer

β = constant.

(b) The percentage of either of the hydrocarbons in the solvent layer is a definite function of its percentage in the hydrocarbon layer at equilibrium. The following equations were proposed:-

$$y_n = \frac{a_n x_n}{1 + b_n x_n}$$

$$y_p = \frac{a_p x_p}{1 + b_p x_p}$$

where the x and y terms are the same as shown above and a and b are constants.

(c) Linear relationship between the percentage of methylcyclohexane and of n-heptane in either of the layers:-

$$x_p = m_H x_n + b_H$$

$$y_p = m_S y_n + b_S ,$$

the symbols having the same significance as before with m and b constants.

The data obtained for the system n-heptane-methylcyclohexane-aniline at 25.0°C. have been found (1) to give straight consolute lines by applying the method of Sherwood (3) or that given in the International Critical Tables (2).

The present study of the system n-hexane-methylcyclopentane-aniline at 25.0°, 34.5° and 45.0°C. has made it possible to determine whether the above relations, and methods for obtaining straight consolute lines, were applicable generally to systems of this type, independent of temperature. At the same time, it has made possible an assessment of the commercial practicability of separating n-hexane and methylcyclopentane by solvent extraction methods.

EXPERIMENTAL

Normal hexane was prepared from n-hexyl alcohol by dehydration over activated alumina at 400°C., after which the resulting mixture of hexenes was dried and hydrogenated over copper chromoxide or Raney's nickel in a high pressure autoclave at 180°C.[†] The hexane obtained was washed repeatedly with concentrated sulphuric acid until free from olefins, dried and fractionated in a column of 20 to 24 theoretical plates efficiency. The distillate boiling between 68° and 69°C., depending on the atmospheric pressure, and of refractive index $n_D^{20} = 1.3751$ was bulked as pure n-hexane.

Methylcyclopentane was prepared by refluxing cyclohexane with aluminium chloride and a trace of water. The resulting mixture was washed with concentrated sulphur-

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[†] We are indebted to Dr. L. Cooke, of the Department of Industrial and Cellulose Chemistry, McGill University, for carrying out the hydrogenation reactions for us.

ic acid, dried and distilled in a column which had an efficiency of 74 theoretical plates at total reflux. The portion taken as pure methylcyclopentane boiled at 71.7° to 72.5°C., the refractive index of successive small portions of distillate being constant at n_D^{20}= 14099.

Aniline was purified by distillation, and dried over anhydrous sodium sulphate.

The solubilities of mixtures of the two hydrocarbons in aniline were determined by noting the miscibility temperatures of mixtures of known composition. Aniline was pipetted into a test-tube, a measured volume of the hydrocarbon added from a burette and the miscibility temperature noted. Precautions were taken to avoid local overheating, loss by evaporation and contamination by the atmosphere.

Tie lines were determined by shaking mixtures of known composition at constant temperature for 6 to 8 hours, allowing the layers to separate at the same temperature and removing the top layer. The ratio of the two hydrocarbons in the top layer (solvent-free) was determined from the refractive index of the mixture after removal of the aniline by washing with dilute sulphuric acid.

RESULTS AND DISCUSSION

The solubility-temperature relations of mixtures of n-hexane and methylcyclopentane in aniline are given in Table I and shown in fig. 1. From fig. 1 a linear relation was obtained between the composition of the hydrocarbon mixture and the temperature to obtain a given degree of miscibility. This relation is shown in fig. 2.

Using the relations shown in figs. 1 and 2 the phase boundary curves for the system at 25.0°, 34.5°, and 45.0°C. were drawn. These curves are shown in figs. 3,4 and 5 and the experimental data given in Table II.

The data from which the tie lines were drawn are given in Table III and the tie lines shown in figs. 3,4 and 5. One extremity of the tie line was taken as the point where the line joining the apex (solvent) to the point on the naphthene paraffin axis representing the composition of the solvent-free hydrocarbon layer intersects the hydrocarbon portion of the phase boundary curve. The tie line was drawn from this point of intersection to the point representing the total composition of the original mixture, the second extremity

TABLE I

The Solubility-Temperature Relations of Mixtures of n-Hexane and Methylcyclopentane in Aniline

Mole fraction of n-Hexane in Hydrocarbon Mixture

1.000		0.883		0.750		0.674	
T.	H.C.	T.	H.C.	T.	H.C.	T.	H.C.
7.4	.048	10.0	.056	6.7	.058	7.2	.063
33.8	.103	28.9	.096	25.4	.102	25.2	.104
41.2	.140	43.2	.142	40.4	.156	36.1	.144
55.1	.203	54.4	.199	53.3	.241	46.7	.201
62.4	.259	61.5	.284	59.0	.315	54.3	.292
65.0	.309	64.7	.389	61.1	.390	57.7	.394
67.4	.361	64.8	.420	61.3	.402	57.6	.394
67.5	.369	65.1	.474	61.6	.421	58.0	.441
68.3	.402	65.0	.511	61.0	.605	57.8	.552
68.6	.429	64.3	.619	56.8	.730	56.7	.651
68.8	.534	61.0	.715	45.1	.824	53.4	.742
66.0	.675	54.5	.801	28.4	.911	45.8	.824
59.8	.773	43.0	.861	12.8	.957	32.1	.898
49.1	.841	26.8	.918			7.6	.952
30.9	.913	11.0	.965				

0.467		0.266		0.083		0.000	
T.	H.C.	T.	H.C.	T.	H.C.	T.	H.C.
13.4	.086	11.0	.108	5.7	.114	8.3	.137
27.0	.132	22.2	.149	15.6	.153	15.7	.177
35.1	.173	32.3	.209	24.4	.204	21.7	.214
40.1	.205	40.4	.298	31.7	.269	25.7	.251
44.0	.240	43.8	.409	35.1	.332	29.8	.306
47.5	.287	43.7	.411	36.6	.396	32.4	.364
49.5	.337	44.0	.489	37.3	.471	33.6	.419
50.8	.416	43.6	.626	37.4	.579	33.8	.427
51.0	.431	40.0	.746	36.6	.684	34.0	.464
51.0	.529	31.1	.854	33.4	.756	34.4	.516
50.3	.634	16.3	.922	25.7	.864	34.5	.533
48.2	.715			11.9	.930	34.2	.626
43.6	.789					33.6	.690
36.7	.846					31.5	.766
27.8	.892					25.8	.874
8.5	.949					11.0	.926

T. - Temperature of miscibility °C.

H.C. - Mole fraction of hydrocarbon mixture dissolved in aniline.

being obtained by producing this line to meet the portion of the phase boundary curve representing the solvent layer.

The methods (2,3) that were found to yield straight consolute lines for the system n-heptane-methylcyclohexane-aniline at 25.8°C. (1) have been applied to the present system with the results shown in figs. 3,4 and 5. From these graphs it is seen that both methods give reasonably straight lines for mixtures containing large amounts of paraffin and which are far removed from the plait point. For mixtures near the plait point, however, or for mixtures containing only a small concentration of paraffin the consolute line is markedly curved as shown clearly in figs. 4 and 5.

Values of β (Table IV) were calculated from the relation (4)

$$\frac{y_n}{y_p} = \beta \frac{x_n}{x_p}$$

the symbols having the significance given previously except that here the units are mole fractions instead of weight fractions, a change which cannot alter the numerical value of the constant.

TABLE II

System n-Hexane -Methylcyclopentane-Aniline
Data for Phase Boundary Curves

INITIAL HYDROCARBON MIXTURE mole fraction of n-Hexane	TEMPERATURE OF MISCIBILITY - °C					
	25.0 °C.		34.5 °C.		45.0 °C.	
	H.C.	P.	H.C.	P.	H.C.	P.
1.000	.079	.079	.104	.104	.142	.142
0.883	.084	.074	.109	.096	.152	.134
0.750	.084	.076	.133	.100	.181	.136
0.674	.106	.071	.144	.097	.197	.133
0.467	.122	.057	.167	.078	.250	.117
0.266	.166	.035	.226	.049	. -	-
0.083	.208	.017	.303	.025	-	-
0.000	.242	.000	.540	.000	-	-
0.000	.857	.000	.540	.000	-	-
0.083	.868	.072	.750	.062	-	-
0.266	.889	.191	.824	.178	-	-
0.467	.900	.421	.861	.402	.771	.361
0.674	.919	.619	.883	.595	.828	.558
0.750	.921	.691	.886	.663	.833	.625
0.883	.929	.820	.901	.796	.855	.755
1.000	.933	.933	.905	.905	.865	.865

H.C. - Mole fraction of hydrocarbon (paraffin naphthene) in the aniline solution.

P. - Mole fraction of paraffin in the aniline solution.

TABLE III

System n-Hexane-Methylcyclopentane-Aniline
Data for Drawing Tie Lines

Equilibrium Temperature °C.	Total Mixture		H.C. Layer (Solvent-free)	
	P.	N.	n_D^{20}	p.
25.0	.416	.048	1.3780	.902
	.371	.096	1.3812	.798
	.322	.192	1.3861	.646
	.242	.235	1.3901	.528
	.161	.375	1.3978	.310
	.079	.441	1.4037	.154
	.039	.456	1.4063	.088
34.5	.700	.076	1.3780	.902
	.631	.157	1.3811	.801
	.633	.155	1.3810	.803
	.499	.311	1.3871	.616
	.434	.385	1.3900	.530
	.391	.436	1.3920	.473
	.263	.584	1.3978	.311
	.150	.716	1.4030	.173
	.150	.716	1.4030	.173
	.077	.801	1.4063	.088
45.0	.731	.040	1.3766	.948
	.654	.129	1.3801	.835
	.511	.295	1.3865	.634
	.343	.492	1.3942	.411
	.336	.500	1.3945	.402

P. - Mole fraction of paraffin in the total mixture.

N. - Mole fraction of naphthene in the total mixture.

p. - Mole fraction of paraffin in the solvent-free hydrocarbon layer (equilibrium conditions).

Reasonable constancy of β prevails, not only for tie lines at each temperature, but also over the temperature range in this investigation. Hence β appears to be a general constant for the system and to be temperature independent.

The relations between the mole fractions of either of the hydrocarbons in the solvent phase to the mole fraction of the same hydrocarbon in the hydrocarbon phase is shown in figs. 6 and 7. The curves for the system n-heptane-methylcyclohexane-aniline (4), converted to a mole fraction basis, are given for comparison. It is seen that at 25.0°C. the curves for the system n-hexane-methylcyclopentane-aniline and for the system n-heptane-methylcyclohexane-aniline are very similar in shape and that the former system is relatively nearer the critical solution temperature of the naphthene concerned than is the latter system at the same temperature, The equations proposed (4) to express these relations are:-

$$y_n = \frac{a_n x_n}{1 + b_n x_n}$$

$$y_p = \frac{a_p x_p}{1 + b_p x_p}$$

TABLE IV

System n-Hexane-Methylcyclopentane-Aniline - Equilibrium Relations

Equilibrium Temperature °C.	H.C. Layer			Solvent Layer			β
	P.	N.	N/P	N.	P.	N/P	
25.0	.930	.000	-	.082	.000	-	-
	.838	.090	.107	.076	.016	.143	1.34
	.736	.187	.250	.073	.022	.301	1.19
	.535	.326	.604	.060	.055	.917	1.03
	.480	.430	.896	.050	.080	1.600	1.22
	.278	.618	2.223	.037	.117	3.161	1.42
	.136	.744	5.468	.028	.141	5.018	0.92
	.075	.795	10.610	.007	.209	29.860	1.31
	.000	.856	-	.000	.244	-	-
			Average Value of β				1.20
34.5	.906	.000	-	.113	.000	-	-
	.816	.087	.107	.108	.017	.107	1.00
	.718	.174	.242	.099	.038	.394	1.08
	.718	.174	.242	.099	.038	.394	1.08
	.537	.336	.625	.082	.081	.989	1.08
	.460	.405	.881	.074	.106	1.431	1.11
	.409	.451	1.103	.072	.111	1.050	0.95
	.262	.580	2.214	.056	.157	2.802	1.27
	.141	.666	4.720	.037	.228	9.041	1.30
	.141	.666	4.720	.037	.228	9.041	1.30
	.066	.694	10.52	.021	.291	13.85	1.32
	.000	.640	-	.000	.640	-	-
			Average Value of β				1.14
45.0	.860	.000	-	.138	.000	-	-
	.814	.046	.056	.137	.009	.066	1.16
	.716	.140	.196	.130	.056	.431	2.20
	.525	.301	.573	.128	.079	.617	1.08
	.307	.438	1.437	.121	.208	1.72	1.20
	.298	.440	1.477	.120	.211	1.76	1.19
			Average Value of β				1.37

$$\beta = \frac{\text{N/P in Solvent Layer}}{\text{N/P in Hydrocarbon Layer}}$$

It has been found possible to evaluate the constants to obtain close agreement at 25°C. with the curve for the system n-heptane-methylcyclohexane-aniline, but for higher temperatures the equations for the curves become increasingly inaccurate.

The linear function proposed (4) for the relation between the concentrations of paraffin and naphthene in either of the liquid phases is shown in fig. 8 to hold well at low temperatures but at higher temperatures pronounced deviations from linearity are evident. From this it may be concluded that, for the present system, this relation is only approximate even at low temperatures. The similarity in shape of the curves shown in fig. 8 to the corresponding phase boundary diagrams has been noticed. Although no rigid mathematical connection has been obtained between the shapes of these curves, there is a probability that linearity in one case presupposes a similar relation in the other. From fig. 8 it is evident that, except at 25.0°C., the curve for the above relation in one of the phases is a continuation of that representing the same relation in the other phase. Two separate and distinct curves, approximating linearity, are obtained only at low temperatures when the miscibility is such that the phase boundary lines do not form a continuous curve and are approximately linear in form.

By suitable mathematical manipulation of the three equations proposed (4) to describe the system n-heptane-methyl-cyclohexane-aniline at 25.0°C. the following relation may be derived:-

$$x_n = \frac{\frac{b_S}{a_n} - \frac{b_H}{\beta}}{\frac{m_H}{\beta} - M_S - \frac{b_S B_n}{a_n}}$$

in which all of the symbols on the right side of the equation are constant. As x_n is one of the variables the above result is anomalous. This anomaly is probably due to the inadequacy of the relations proposed to account accurately for the system.

As far as the use of this method for separating methylcyclopentane and n-hexane is concerned the above results indicate quite clearly that the efficiency of separation is too small for commercial application.

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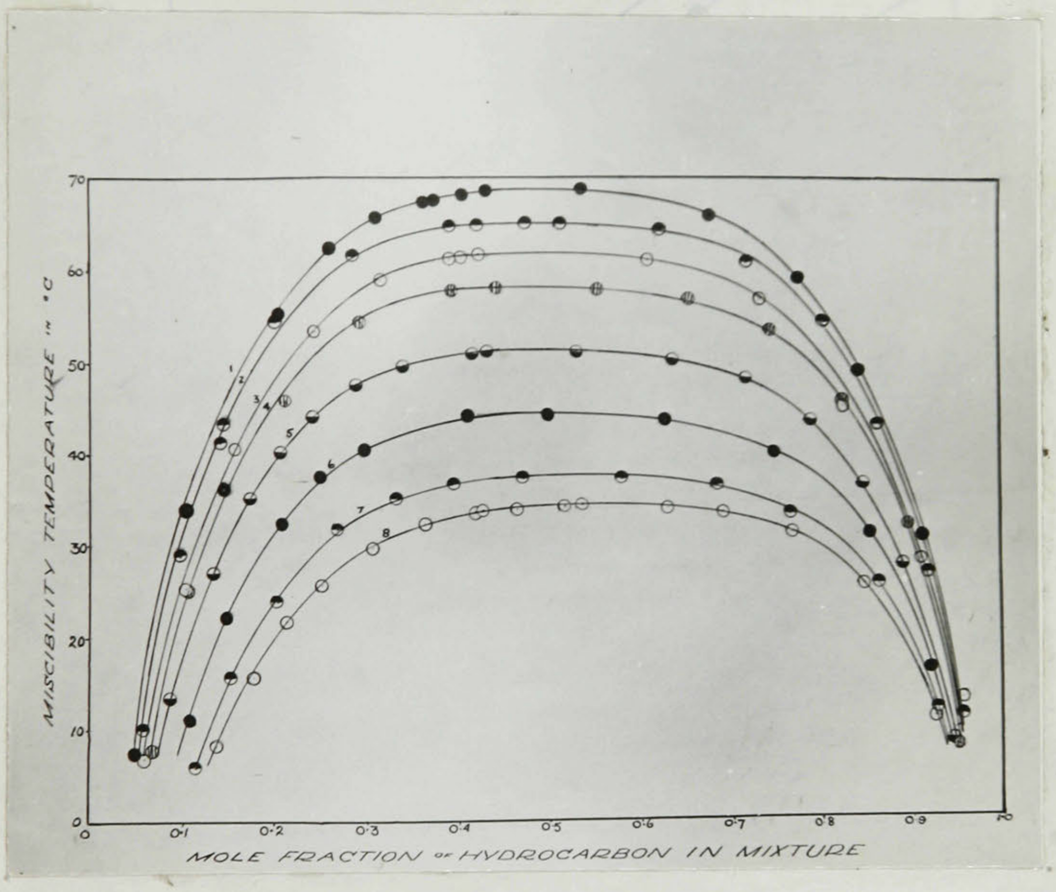

FIGURE I

The Solubility-Temperature Relations for Mixtures of n-Hexane and Methylcyclopentane with Aniline.

Mole per cent n-hexane in hydrocarbon mixture:

Curve 1	- 100;	Curve 5	- 50;
" 2	- 90;	" 6	- 30;
" 3	- 78;	" 7	- 8;
" 4	- 71½	" 8	- 0.

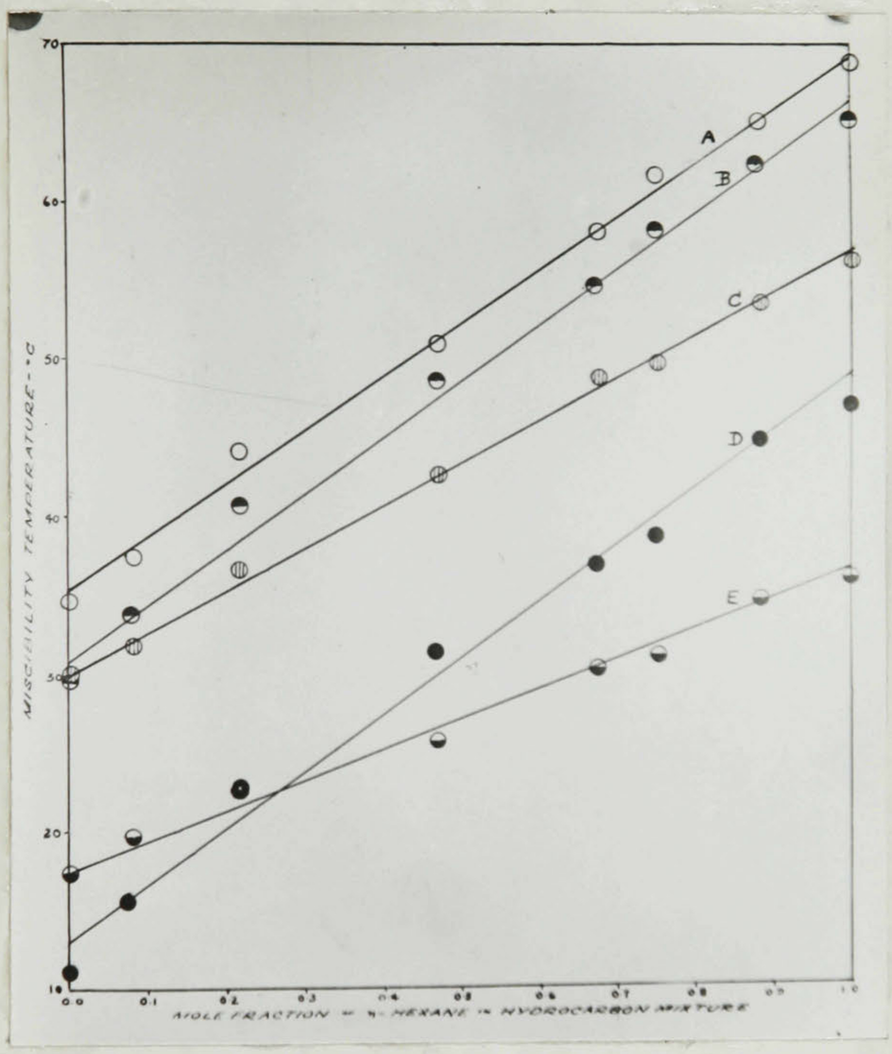

FIGURE 2.

The Relation between the Composition of the Hydrocarbon Mixture and the Temperature Required to Obtain a Given Degree of Miscibility with Aniline.

Curve A, 50 per cent miscibility with aniline;
" B, 30 " " " " " ;
" C, 80 " " " " " ;
" D, 15 " " " " " ;
" E, 90 " " " " " .

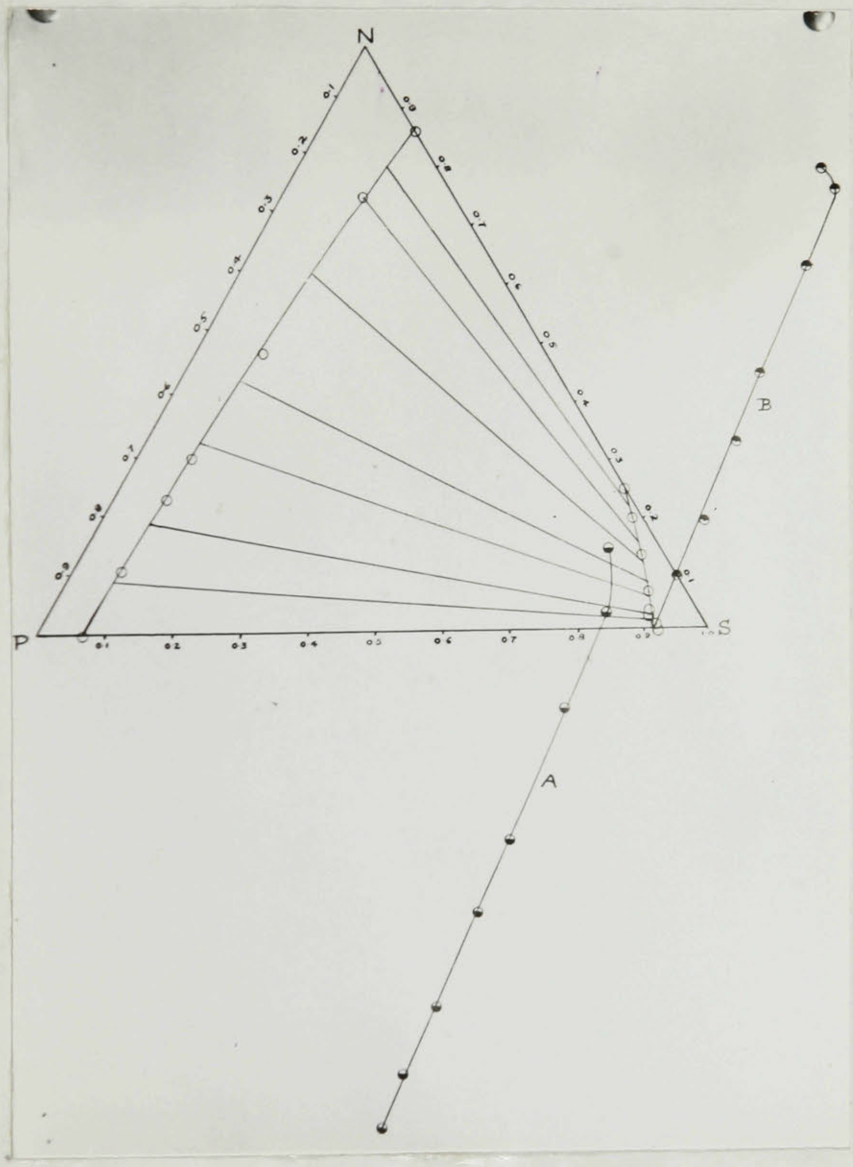

FIGURE 3.

System n-Hexane-Methylcyclopentane-Aniline at 25.0°C.
Phase-Boundary Curves and Tie-Line Relations.

Curve A, conjugate line (Sherwood (3));
Curve B, " " (International Critical Tables(2)).

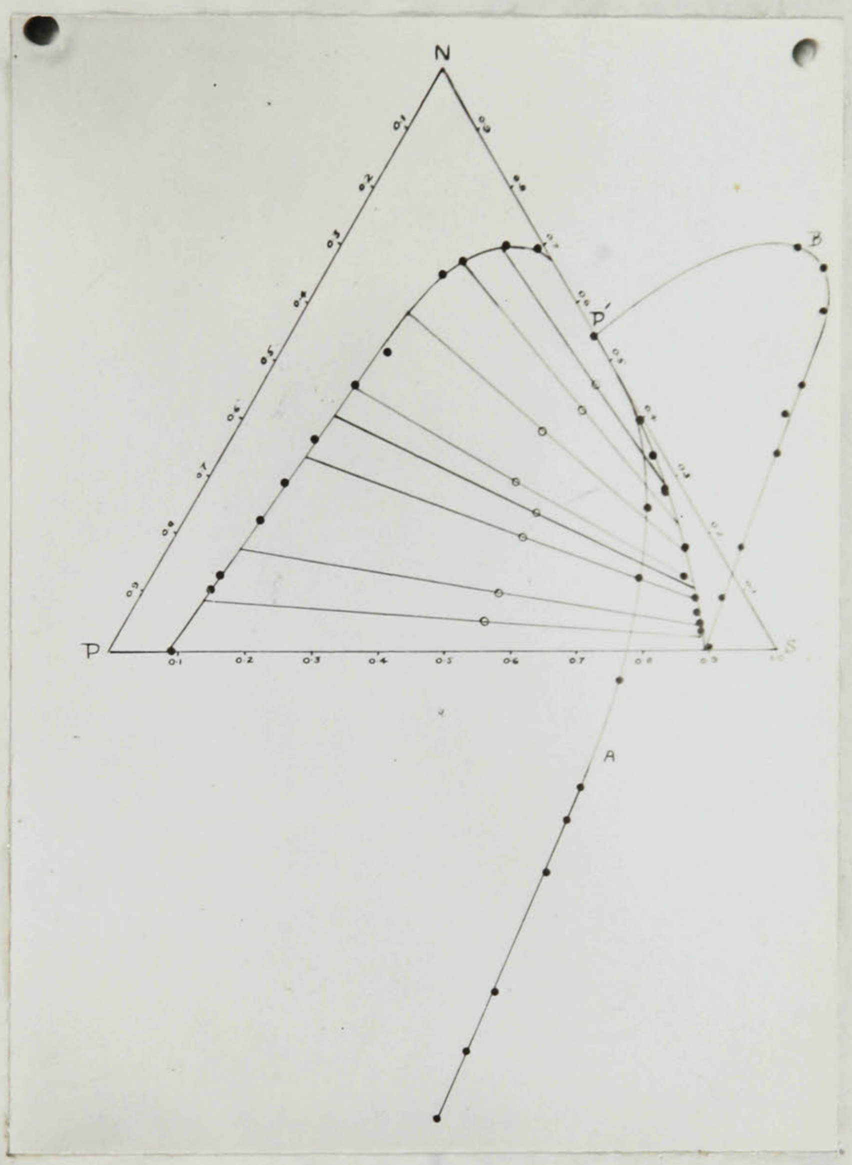

FIGURE 4.

System n-Hexane-Methylcyclopentane-Aniline at 34.5°C.
Phase-Boundary Curves and Tie-Line Relations.

Curve A, conjugate line (Sherwood (3));
" B, " " (International Critical Tables(2)).

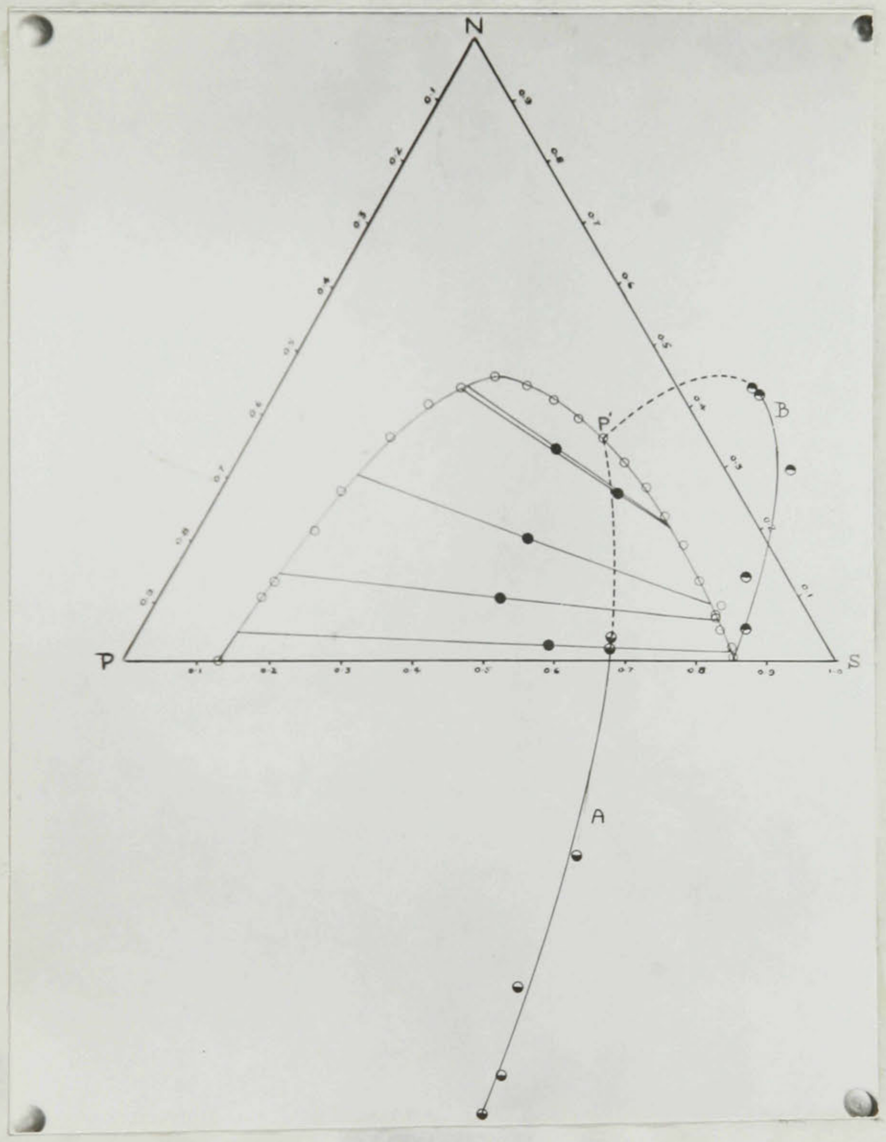

FIGURE 5.

System n-Hexane-Methylcyclopentane-Aniline at 45.0°C.
Phase-Boundary Curves and Tie-Line Relations.

Curve A, conjugate line (Sherwood (3));
" B, " " (International Critical Tables (2)).

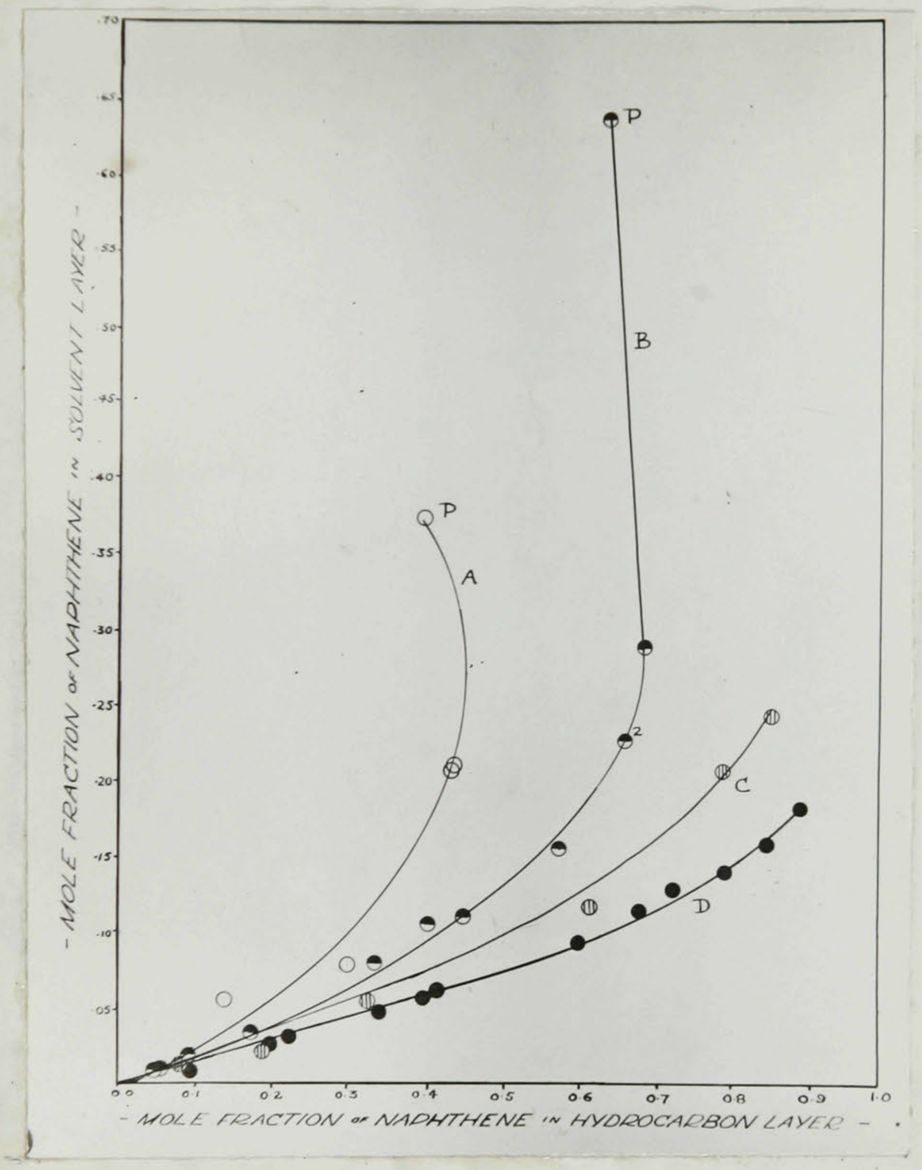

FIGURE 6.

The Relation between the Concentrations of the Naphthene Component in Two Layers at Equilibrium.

Curve A, system n-hexane-methylcyclopentane-aniline at 45.0°C.;
" B, " " " " " 34.5°C.;
" C, " " " " " 25.0°C.;
" D, " n-heptane-methylcyclohexane-aniline " 25.0°C.

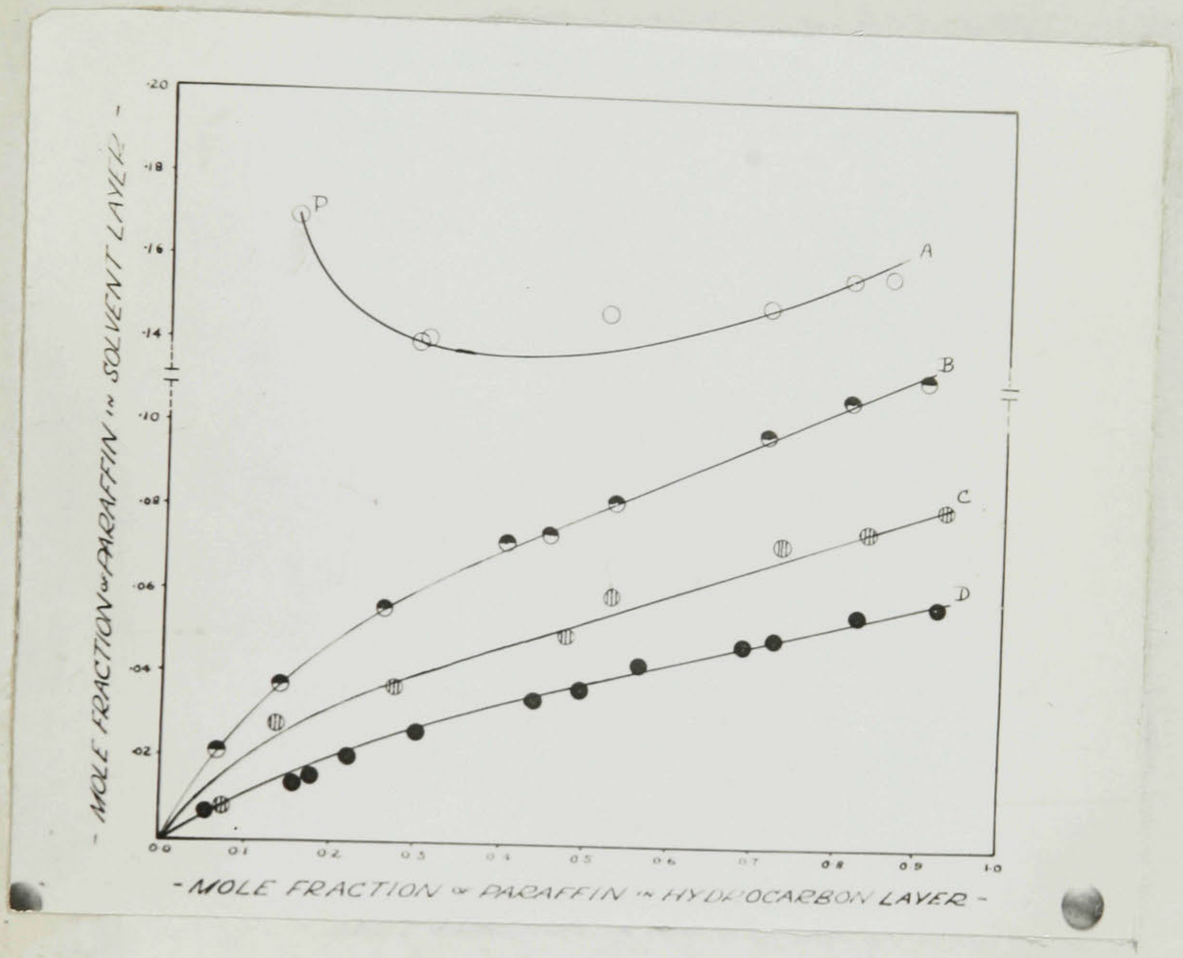

FIGURE 7.

The Relations between the Concentrations of the Paraffin Component in Two Layers at Equilibrium.

Curve A, system n-hexane-methylcyclopentane-aniline at 45.0°C.;
" B, " " " " " 34.5 " ;
" C, " " " " " 25.0 " ;
" D " n-heptane-methylcyclohexane-aniline " 25.0 " .

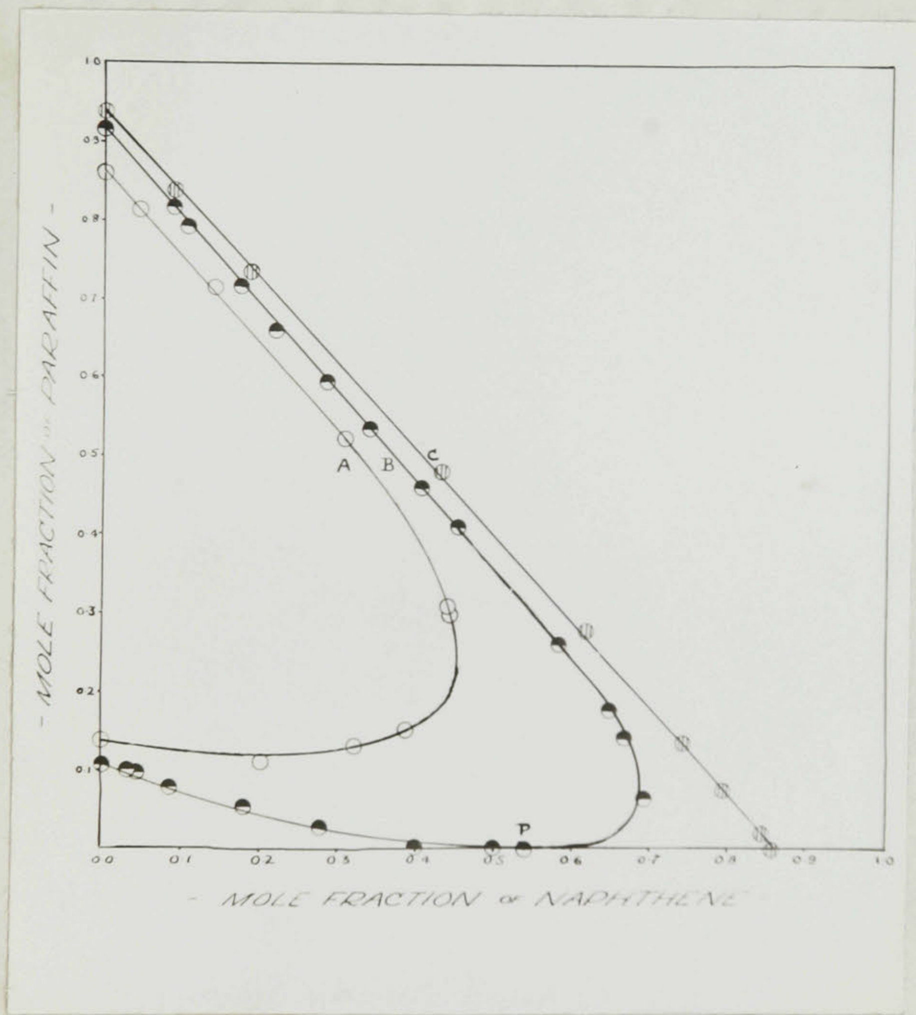

FIGURE 8.

The Relations between the Concentrations of Paraffin and Naphthene Components in the same Layer.

Curve A, 45.0°C;
" B, 34.5 "
" C, 25.0 "