A. The Mercury Photosensitized Decomposition

of n-Butane.

B. The Kinetics of the Factors Influencing

the Stability of "S".

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Chemistry

Ph. D.

Alden W. Hay

A. The Mercury Photosensitized Decomposition of n-Butane.

B. The Kinetics of the Factors Influencing the Stability of "S".

PART A

The mercury photosensitized decomposition of n-butane was investigated at 100, 175 and 250°C. Hydrogen, octanes and dodecanes were the main products found. The mechanism of the reaction was concluded to be a C-H bond split followed by radical combination reactions.

PART B

The reactions of N, N^{I} -di-(3-chloroethyl)methyl amine ("S") in absolute methanol were investigated at 0, 25, and 41.5°C by following the rate at which it disappeared and the rate at which chloride and hydrogen ions formed. Analytical methods used were shown to be valid.

It was concluded that the principal reaction involved is dimerization by a unimolecular S_n mechanism. The reaction was found to have an activation energy of about 9.6 Kcal.

Part A

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The Mercury Photosensitized Decomposition

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INTRODUCTION

Certain simple bimolecular reactions, such as the thermal decomposition of hydrogen iodide have been shown to conform to the rate equation

$$k = Ze^{-L/\kappa T}$$

developed by Lewis in 1919 (1). In the above equation, k is the rate constant, Z the collision frequency, R the gas constant, T the temperature and E is the energy of activation obtained by substituting experimental values of k and T into the Arrhenius equation

$$\frac{d \ln K}{dt} = E/RT^2$$

Values of k calculated from the experimental value of E and the kinetic theory value of Z are frequently of the same magnitude as those obtained by experiment and, in some cases, the numerical agreement is reasonably good. The dependence of the rate of these bimolecular reactions on the collision frequency obviously establishes the mode of activation to be collisions between molecules.

The theory of unimolecular reactions developed much more slowly, owing mainly to the lack of experimental evidence, the thermal decomposition of nitrogen pentoxide being the only known reaction up until 1926. Obviously, the mode of activation of unimolecular reactions was a problem. Perrin (2) and others (3, 4, 5), difficulties which it did not survive.

The modern theory of activation of unimolecular reactions was originally proposed by Lindemann (6) in 1922 and later elaborated by Hinshelwood (7) and others (8, 9, 10, 11). They suggested that activation occurs by collisions between molecules, but that a time lag exists between activation and reaction. By virtue of the internal motions, molecules must pass through maxima and minima of stability and it is quite conceivable that a molecule activated by collision will decompose only when it passes through its next minimum of stability, provided it is not deactivated by a second collision before it reaches that minimum of stability. Then if the average interval between activation and transformation is large compared with the interval between collisions, most of the molecules will lose their energy by collision before they have a chance to react. Thus we have -

normal molecules \rightleftharpoons activated molecules (a) activated molecules \rightleftharpoons products of reaction (b) The processes indicated in (a) take place very rapidly compared with that indicated in (b) and a stationary state is thus set up in which a constant fraction of the mole-

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cules present possess the necessary energy for reaction. The majority of these molecules will be deactivated by collision, but a small constant fraction of them will get a chance to decompose. The chemical reaction therefore disturbs the concentration of activated molecules very little. Since the fraction of the molecules activated is constant and only a small fraction of these activated molecules react, and since the fraction of the molecules is nearly proportional to $e^{-\frac{E/kT}{kT}}$ (Boltzmann distribution), the number of molecules reacting per unit time is independent of the pressure and all the conditions of a unimolecular reaction are realized.

If, however, the rates of the processes indicated in (a) are decreased (by a decrease in pressure), eventually the rate of activation, becoming equal to or less than the rate of reaction, will become the rate determining process and the reaction will become second order. Thus with a decrease in pressure the unimolecular rate constant should eventually drop off and we should get a gradual transition from first to second order.

Evidence to support the above hypothesis was soon forthcoming. In 1926 Hinshelwood and his co-workers (12, 13) found that propionic aldehyde and acetone decompose in a unimolecular manner over a range of pressures and that these decompositions tended to become second order with a sufficient decrease in pressure. However, the rates of these decomposition reactions were

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found to be from 10^2 to 10^5 times those predicted by the Lewis equation. Following this work a large number of organic decomposition reactions were found to exhibit the same behaviour and it is now generally conceded that nearly all organic thermal decomposition reactions conform to a rate expression of the form of the classical unimolecular equation.

Various theories have been proposed to explain the abnormally fast rates of these reactions. Christiansen and Kramers (14) suggested that a first order process might take place by a chain mechanism in which the energy of activation augmented by the heat liberated in the reaction itself was handed on from the products to fresh molecules of reactants. The objection to this "energy chain" is that inert gases, including the products of the reaction themselves, should help to dissipate the energy and thus retard the change. Such retardation is not generally observed.

Hinshelwood (15) and others (16, 17) suggested that the numerous internal degrees of freedom were involved in the activation of complex molecules. If the various degrees of freedom can contribute to the activation energy then the possible rate of activation may be up to a million times greater than that expected from the Lewis equation. By making reasonable assumptions as to the number of degrees of freedom involved, Hinshel-

wood was able to account for the rates of a large number of reactions. However, the theory cannot account for the rate of the nitrogen pentoxide decomposition at low pressures and gives no explanation of the products formed in the type of reaction under consideration.

The work of Paneth and his co-workers (18, 19) on free radicals, contributed to place the chain theory in a new light. F. O. Rice and his co-workers (20 - 28) using the Paneth technique were able to detect free methyl and ethyl radicals in a number of organic thermal decomposition reactions. This led Rice to suggest that nearly all organic decomposition reactions proceed by a free radical chain mechanism.

Rice points out that if two reactions have activation energies differing by 4 Kcal., then the relative rates at 600° C are in the ratio of $e^{-400/2 \times 873}$ to 1, or approximately 9 to 1. Similarly for a difference of 10 Kcal., the ratio is 500 to 1. Assuming that the activation energy is intimately connected with bond strength (17), we may conclude that if there are two or more ways of accomplishing a primary break in the molecule, and if one of these has an activation energy 10 Kcal., or more, lower than that of any of the others, it alone will occur to any appreciable extent.

Though there is considerable disagreement about the absolute bond strengths, it is definite that the CIC and CIC bonds are very much stronger than the

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C-C or C-H bonds in a molecule. Moreover indirect evidence (29) indicates that the C-H bond is about 10 - 15 Kcal. stronger than the C-C bond. One may therefore conclude that, if the thermal decomposition takes place by a free radical mechanism, a molecule will always split at a C-C bond and never at a C-H, or a double or triple bond.

Only methyl and ethyl radicals can be detected by the Paneth technique (30) presumably because the higher radicals are unstable at high temperatures and break down before detection into ethyl and methyl groups. Pearson and Purcell (31), however, have detected higher radicals by photollysis at room temperature.

The primary reactions of the butane decomposition (32) according to the Rice scheme would be:-

$$C_4H_{10} = CH_3 + CH_3CH_2CH_2 \qquad (1a)$$

$$C_4H_{10} = 2CH_3CH_2$$
 (1b)

Followed by the secondary reaction

$$CH_3CH_2CH_2 = C_2H_4 + CH_3$$
 (2)

and the chain reactions

$$C_{4}H_{10} + R = RH + CH_{3}CH_{2}CH_{2}CH_{2} \qquad (3a)$$

$$= KH + C_{2}H_{4} + CH_{3}CH_{2}$$

$$C_{4}H_{10} + R = KH + CH_{3}CH_{2}CH_{2} \qquad (3b)$$

$$KH + C_{1}H_{3}CH_{2}CH_{3}CH_{3}$$

where R denotes a methyl or ethyl radical. This scheme assumes reactions (3a) and (3b) to have activation energies much smaller than that of (1). On the basis of accessibility, reaction (3a) would be faster than reaction (3b) in the ratio of 3:2 since there are six primary hydrogen atoms and only four secondary hydrogen atoms. There is evidence, though, that secondary hydrogen atoms are less strongly bound. On this assumption Rice estimates reaction (3a) is to reaction (3b) as 6:8. Thus the overall reaction may be represented by

or $14C_{4}H_{10} = 8C_{3}H_{6} + 6C_{2}H_{6} + 6C_{2}H_{4} + 8CH_{4}$

Although this scheme does not predict the formation of butenes and hydrogen, which are actually found in the thermal decomposition products of butane, (33), it is reasonably successful in predicting the products of most of the hydrocarbon decompositions especially for the lower members.

By making suitable assumptions Rice and Herzfeld (26) showed that free radical mechanisms of the above type can lead to a first order overall rate. Furthermore, by a suitable choice of activation energies, they were able to make the overall activation energy agree quite well with the experimental value, thus explaining why the experimental activation energies for such reactions are usually

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far smaller than the C-C bond strength. As an example, consider the artificially simplified scheme for the decomposition of an organic molecule (32):

E in Kcal.

м		=	R ₁ +	M ₂	80	(1)
RI	+ M	=	R ₁ H ∔	^R 2	15	(2)
^R 2		=	R _I ∔	м ₃	38	(3)
RI	+ R ₂	Ξ	M ₄		8	(4)

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

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

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

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

and the overall decomposition of M₁ may be expressed as

$$-\frac{d}{dt}(M_{1}) = k_{1}(M_{1}) + k_{2}(R_{1})(M_{1})$$
(7)
By solving equations (5) and (6) for R_{1} and substituting
in (7) we obtain:

$$-\frac{d}{dt}(M_{1}) = k_{1}(M_{1})(1 + \sqrt{k_{2}k_{3}/2k_{1}k_{4}}) = (M_{1})\sqrt{\frac{k_{1}k_{2}k_{3}}{2k_{4}}}$$
or,

$$-\frac{d}{dt}(M_{1}) = K(M_{1})$$
i.e., the reaction is of the first order. Furthermore,
E overall = $1/2$ (E + E₂ + E₃ - E₄)
so that substituting the assigned values of E we obtain
E overall = $1/2$ (80 + 15 + 38 - 8) = 62.5 Kcal.,
which is well below the strength of the C-C bond.
The method by which the chains are ter-

minated determines the order of the reaction. The above scheme assumes they end by radical recombination

$$R_1 + R_2 = M_4$$

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

$$2 R_{1} = M_{5}$$

the overall order would be 1.5 while

$$2 R_{2} = M_{6}$$

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

$$R_1 + R_2 = M_4$$

is much faster than the other two possible recombinations.

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Although mechanisms of this sort are, to a considerable extent, based on conjecture, impressive support for the fundamental idea of free radical chains soon made its appearance. Frey (34) was able to start chains in butane below its normal decomposition range by adding methyl radicals formed by the decomposition of dimethyl mercury. Similarly, Allen and Sickman (35), Fletcher and Rollefson (36) and Echols and Pease (37) produced the sensitized chain decomposition of a number of organic substances. All these observations prove that radicals can cause chain decomposition, but they do not necessarily prove that such free radical chains occur in the normal pyrollysis of the substances concerned.

Evidence for the presence of chains was also obtained from photochemical investigations. Leermakers (38) showed that the photolysis of acetaldehyde is a chain reaction above 80°C and his results are in agreement with the mechanism predicted by Rice and Herzfeld. Leermakers also found that chains are set up in the decomposition of dimethyl and diethyl ether induced by admixed acetone (39).

Further evidence for the chain character of some decompositions is furnished by Staveley and Hinshelwood (40) and others (41, 42, 43, 44). While these investigations indicated that large amounts of added nitric oxide would catalyse the reactions investigated, small amounts

caused some inhibition. Assuming that maximum inhibition corresponds to a complete suppression of chains normally present, these investigators calculated chain lengths of from two to fifteen for a number of reactions. This is definite evidence for the presence of chains, but in most cases the chain lengths are far too small to be in accord with the Rice-Herzfeld mechanisms. There are, however, indications (45, 46) that in certain cases there may be a few long chains rather than a large number of short ones, i.e., that the Rice-Herzfeld mechanisms may hold for a small fraction of the total reaction, the remainder decomposing by a molecular mechanism. Recent work (47) suggests that nitric oxide may be a "selective" inhibitor and thus maximum inhibition by nitric oxide may not correspond to complete suppression of all the chains present which would lend further support to the Rice-Herzfeld mechanism.

It may therefore be said that, in general, the evidence supports the free radical theory. A great deal of data can be correlated on this basis and the theory has pointed the way to a great deal of fruitful work. However, when the specific mechanisms for a number of reactions are tested, the situation is quite different. To date the methods used for this purpose are:

(a) The stationary hydrogen atom concentration is measured and compared with the theoretical value.

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(b) The activation energy of one of the proposed part reactions is measured independently.

(c) Deutero-compounds are used as indicators of the mechanism.

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

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PHUTUSENSITIZATION

From the foregoing discussion it is evident that more information concerning the elementary processes in thermal decomposition reactions is necessary and that no great confidence can be placed in any one theory until we have further knowledge about the individual reactions. Information regarding the reactions of radicals, particularly when confirmed by independent methods, is of utmost importance. The chief methods used are photochemical reactions and reactions with hydrogen atoms.

Straight photochemical decomposition is seldom used in the investigation of the reactions of the simple hydrocarbons since they are transparent down to the extreme ultra-violet, and work of this nature in the Schumann region involves considerable experimental difficulty. These difficulties are avoided, however, if photosensitization technique is employed. In this a metal vapor is mixed with the reactant gas and the mixture illuminated by resonance radiation of that metal. Upon illumination the atoms of the metal vapor absorb the radiation and the energy thus gained is imparted by collision to the molecules of reactant gas.

Photosensitized reactions present a much closer analogy to thermal processes than do direct photolyses, since the reactant molecule receives the energy necessary for reaction by collision. Furthermore, the situation is much simpler in a photosensitized reaction than in a thermal reaction in that the reactant molecules receive a rather definite amount of energy instead of the Boltzmann distribution. Mercury, cadmium and zinc metals have been used for this purpose. The resonance lines available through the use of these metals together with the energies associated with the excited atoms etc., are summarized in Table I (48).

TABLE I.

EXCITATION, ENERGIES, ETC.

				Heat of	"Maximum energy
			Energy	iation	split off H atom
	0		of	of	assuming inter-
S., b	Reson-		excited	hydride,	mediate hydride
stance		Trancition	arom	Kcal.	tormation
<u>si an</u> ce	LineA		NCGI.		
Mercury	I 8 49	6 ¹ 5 ₀ -6 ¹ P ₁	153.9	8.5	162.4
	2537	6 ¹ S ₀ -6 ³ P I	112.2	8.5	120.7
Cadmium	2288	5 ¹ S ₀ -5 ¹ P ₁	124.4	15.5	139.9
	3261	5 ¹ S ₀ -5 ³ P ₁	87.3	15.5	102.8
Zinc	2139	4 S ₀ -4 P	133.4	23.1	156.5
	3076	4 ¹ s ₀ -4 ³ P ₁	92.5	23.1	115.6

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From the above table we see that the energies involved are in most cases greater than the activation energies of most reactions and thus with efficient transference of energy a wide variety of reactions is possible.

At the present time there is some doubt as to the mechanism of the primary act in photosensitized reactions and consequently, some doubt regarding the energy involved. For example, with hydrogen we have

	М	÷	h v	=	М			()
Followed by	М	ŧ	н ₂	=	М	ŧ	2H	(2a)
or	Μ	ŧ	н ₂	=	MH	Ŧ	н	(2b)

If the mechanism of the primary act is (2a) then the energy involved will be that of the excited atoms plus a little kinetic energy. If equation (2b) represents the primary act, the heat of formation of the metal hydride must also be taken into consideration.

In the case of mercury, Olsen (49) found it was not possible to produce resonance excitation of HgH bands in a mercury-hydrogen mixture. This seems to indicate that the primary act in mercury photosensitization occurs according to equation (2a). In the case of cadmium-hydrogen mixtures, however, Bender (50) has observed strong resonance excitation of the CdH bands suggesting that mechanism (2b) occurs in cadmium photosensitizations.

Taylor and his co-workers (51, 52) first demonstrated that mercury photosensitization is applicable to the study of hydrogen atom reactions. In the presence of hydrogen and a reacting substance we have

Hg	()	's _o)	ŧ	hν	=	Hg (2 ³ P ₁)	(1)
Hg	(2	³ P ₁)	Ŧ	н ₂	=	Hg (S _O) + 2H	(2)
		Н	Ŧ	Х	=	Products	(3)
2H	+ a	a thir	d b	ody	=	H ₂	(4)

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

A more direct method of investigating the reactions of hydrogen atoms involves the use of the Wood-Bonhoeffer technique (53, 54) in which hydrogen atoms are pumped from a discharge tube and allowed to react with other gases in a reaction chamber. Although high hydrogen atom concentrations are obtained by this method, experiments can only be carried out at very low pressures (between O.I and I mm.). However, a large number of reactions have been investigated in this way.

THE ATOMIC AND PHUTUCHEMICAL REACTIONS OF THE ALIPHATIC HYDROCARBONS

METHANE

Hydrogen Atom Reaction using Wood-Bonhoeffer Technique.

Early investigators (55, 56, 57) of the reaction of methane with hydrogen atoms found methane to be quite stable. Geib and Harteck (58), extending the experiments over a range of temperatures found no reaction occured up to 183° C. They concluded that the reaction

 $CH_4 + H = CH_3 + H_2$ (1) had an activation energy of at least 17 Kcal. An alternative suggestion was that this reaction occurs readily but the back reaction

 $CH_3 + H + M = CH_4 + M$

proceeds more rapidly than other reactions such as

 $2CH_3 = C_{26}H_{26}$

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

 $CH_{3} + H_{2} = CH_{4} + H$ (2)

occured with a low enough activation energy. Since estimates of the energy of reaction (2) vary from 8 to

23 Kcal. (59, 60, 61, 62, 63) the issue is somewhat in doubt.

Geib and Steacie (64, 65) investigating the reaction of deuterium atoms and methane found no detectable reaction up to 100°C indicating an activation energy for the exchange reaction of not less than II Kcal. Their work also indicates that the reaction is the analogue of the ortho-para hydrogen conversion

 $CH_4 + D = CH_3D + H \qquad (a)$

rather than

 $CH_4 + D = CH_3 + HD$ (b)

Steacie (66) investigated the reaction up to 500°C and obtained an activation energy of 12.9 + 2 Kcal., the value calculated from the temperature coefficient and the collision yield being in good agreement. Preliminary work on the thermal exchange reaction by Farkas (67) served to support this suggestion. The reaction has been studied by other investigators and the results obtained for the activation energy are tabulated as follows:-

INVESTIGATOR		RES	ULT	_	
Farkas and Melville	(68)	13 K	cal.		
Steacie	(66)	12.9	· +	2	Kcal.
Trenner, Morikawa,	(69)	15.6	6 Kcal	•	-
and Taylor.					

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

 $CH_4 + D = CH_3D + H$

and a somewhat larger value of E for the reactions

$$CH_{A} + D = CH_{3} + HD$$

and

Photo-Decomposition:

Spectroscopic observation on the photo decomposition of methane have been made by Leifson (70) and Scheibe and his co-workers (71, 72, 73). They found that diffuse bands appear around 1600 A.U. On the basis of their work, Bonhoeffer (74) suggests that the primary reaction is

 $CH_4 = CH_3 + H$

followed by the formation of ethane and hydrogen.

Leighton and Steiner (75), using a hydrogen lamp near the lower limit of Fluorite, made a direct investigation of the photolysis of methane. They obtained hydrogen and unsaturated hydrocarbons in the approximate mole ratio of 4:1 and estimated the quantum

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yield to be in the order of unity. They suggested the mechanism

$$CH_4 + hv = CH_2 + H_2$$

2 $CH_2 = C_2H_2$

Subsequent to a preliminary note by Groth and Laudenklos (76), Groth (77) reported the results of a thorough investigation using a Harteck xenon lamp (78) which produces strong lines at 1469 A.U. and 1295 A.U. Hydrogen and acetylene were found to be the main decomposition products along with some ethane and traces of ethylene and higher hydrocarbons. Their results are in good agreement with those of Leighton and Steiner and they suggest a somewhat similar mechanism

$$CH_4 + hv = CH_3 + H$$

 $CH_3 + H = CH_2 + H_2$
 $2 CH_2 = C_2H_2 + H_2$

A brief investigation of the photolysis of methane with the shorther wave length of a mercury lamp - 1850 A.U.) led Kemula and Dyduszynski (79) to conclude (that the first step is

$$CH_4 + hv = CH_2 + H_9$$

Thus it appears that Bonhoeffer's mechanism is not valid.

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Mercury Photosensitized Reactions:

Early investigators (51, 52, 80) reported that methane was stable to mercury photosensitization but, in a preliminary note, Taylor, Morikawa and Benedict (81) using a deuterium-methane mixture found the reaction to have a low energy of activation. Steacie and Phillips (82) found the reaction to proceed at a measurable rate with a quantum yield, for the production of hydrogen, of roughly 0.04 at 195° C and 0.25 at 350° C. Farkas and Melville (68) investigated the reaction over a wide range of temperatures using ortho-deuterium-methane mixtures and measuring the rate of ortho-para conversion as well as the exchange. These investigators concluded that the reaction occuring is

 $CH_4 + D = CH_3D + H$

rather than

 $CH_{A} + D = CH_{3} + HD$

In a later paper Morikawa, Benedict and Taylor (83) working with the systems $CH_4 + D_2$, $CD_4 + H_2$ and $CH_4 + CD_4$ obtained deutero-methanes and some ethane which led them to conclude that the primary reaction is largely

Hg $({}^{3}P_{1} \text{ or } {}^{3}P_{0}) + CH_{4} = CH_{3} + H + Hg ({}^{1}S_{0})$ followed by

 $CH_3 + D = CH_3D = CH_2D + H$

The activation energies obtained in the above investigations are as follows:

22	
	KESULT
(82)	II.7 Kcal.
(68)	13 Kcal.
(83)	2.5 - 4 Kcal
	(82) (68) (83)

and Taylor.

ETHANE

Hydrogen Atom Reaction Using Wood-Bonhoeffer Technique.

Bonhoeffer and Harteck (84) and von Wartenberg and Schultze (56) found that luminescence occurs on mixing hydrogen atoms and ethane. Bands due to C-H and C-C were observed and the major part of the ethane was recovered unchanged. These investigators had no means of trapping methane and therefore, did not report it. Chadwell and Titani (57) in a preliminary investigation reported the finding of small amounts of methane and ethylene.

Steacie and Phillips (82) studying the reaction of deuterium atoms with ethane found an exchange reaction was taking place which appeared to have an activation energy of 6.3 Kcal. They concluded the correct mechanism for the exchange was

> $C_{2}H_{6} + D = C_{2}H_{5} + HD$ $C_{2}H_{5} + D = C_{2}H_{5} D$

Trenner, Morikawa and Taylor (69) also investigated this reaction and concluded (a) that at room temperature the main reaction was

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 $C_2H_6 + D = CH_3 + CH_3D$ (E = 7.2 Kcal.) and (b) that the exchange reaction

 $C_2H_6 + D = C_2H_5 + HD$ (E = 11.4 Kcal.) was only appreciable at temperatures of 100° C and upwards.

There is considerable discrepancy in the activation energy between the two investigations. Steacie and Phillips in their investigation assumed from Chadwell and Titani's work that methane formation is negligible. Steacie, however, finding about ten percent decomposition has confirmed the production of methane, but this is not enough to bring the two activation energies into line.

Photodecomposition:

Very little work has been done on the photo-decomposition of ethane. The very meagre spectroscopic evidence (80) indicates that the absorption is probably in the C-H bond.

An investigation by Kemula and Dyduszynski (79) led them to the equation

 $C_2H_6 + hv$ (1850 A.U.) = $C_2H_4 + H_2$ but it is difficult to infer just what the primary step may be.

Mercury Photosensitized Reactions:

Taylor and Hill (51) were the first to study the mercury photosensitized decomposition of ethane. They observed in ethylene-hydrogen mixtures that ethane and higher hydrocarbons were formed. Anomalous pressure changes after the ethylene-hydrogen reaction was over led them to suspect that the ethane formed was being attacked by both hydrogen atoms and excited mercury atoms. Verifying this, they suggested the reaction involved radicals. Kemula (85) also showed that ethane could be decomposed by excited mercury atoms.

Kemula, Mrazek and Tolloczko (86) following earlier work by Tolloczko (80), carried out a more detailed investigation of the photosensitized reaction. They circulated the reaction mixture through a trap at -80° C to remove products of high molecular weight as soon as they were formed and thus prevent secondary processes. The gaseous products consisted entirely of hydrogen and methane in the ratio of about 3:1. If the trap was maintained at 20° C they found the ratio of hydrogen to methane approached infinity. Since -80° C is not sufficiently low a temperature to remove butane efficiently. their prevention of secondary changes was only partially successful. They found that the decrease in pressure as the reaction proceeded was accompanied by an exactly parallel increase in the volume of the liquid condensate. Rough fractional distillations indicated that these condensable products were mainly butane and octane. This points to a C-H rupture for the first step. The investigators therefore suggested

$$\begin{array}{rcrcrc} & --- & 25 & --- \\ & C_{2}H_{6}^{*} & = & C_{2}H_{5}^{*} + H \\ & 2 & C_{2}H_{5}^{*} + M & = & C_{4}H_{10}^{*} + M \\ & & 2H + M & = & H_{2}^{*} + M \\ & & 2H + M & = & H_{2}^{*} + M \\ & & C_{2}H_{6}^{*} + H & = & C_{2}H_{5}^{*} + H_{2} \\ & C_{2}H_{6}^{*} + H & = & CH_{3}^{*} + CH_{4} \end{array}$$

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

$$C_{4}H_{10} = C_{4}H_{9} + H$$

2 $C_{4}H_{9} + M = C_{8}H_{18} + M$

where M is a third body.

Steacie and Phillips (88) made a more complete investigation of the mercury photosensitized reactions of ethane. They observed the reaction both in a "multiple pass" flow system and in a "single pass" flow system (89).

In the multiple pass system trapping temperatures below -80° C gave efficient removal of the higher hydrocarbons formed and thus prevented secondary reactions. The products thus obtained consisted of methane, propane and butane. The hydrogen formed was reported as the product of the decomposition of propane and butane. The suggested mechanism follows

$$C_{26}^{H} + H_{9}^{H} (6^{3}P_{1}) = 2 CH_{3}^{H} + H_{9}^{H} (6^{1}S_{0}^{H})$$

 $CH_{3}^{H} + C_{2}H_{6}^{H} = CH_{4}^{H} + C_{2}H_{5}^{H}$
 $2CH_{3}^{H} = C_{2}H_{6}^{H}$

$$2C_{2}H_{5} = C_{4}H_{10}$$

 $CH_{3} + C_{2}H_{5} = C_{3}H_{8}$

Using a single pass flow system, Steacie and Phillips found a considerable production of hydrogen and concluded that the primary step in the reaction must be the rupture of a C-H bond instead of a C-C bond as postulated above. Furthermore, the rate of formation increased with temperature. Thus they suggested the following mechanism

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$$C_{2}H_{6} + H_{g} (\delta^{3}P_{1}) = C_{2}H_{5} + H + H_{g} (\delta^{1}S_{0})$$
 (1)

$$H_2 + H_g (6^3 P_1) = 2H + H_g (6^1 S_0)$$
 (2)

$$H + C H = CH + CH$$
 (3)
26 4 3

$$H + C H = C H + H$$
 (4)
26 25 2

$$2CH_3 = C_2H_6$$
 (5)

$$CH_3 + C_2H_5 = C_3H_8$$
 (6)

$${}^{2}C_{2}H_{5} = C_{4}H_{10}$$
 (7)

$$2H = H_{2}$$
 (8)

The inclusion of the second step was rendered necessary by the high quenching efficiency of hydrogen. Providing that reaction (3) is at least four times as fast as reaction (4) this series of reactions explains the experimental results. To account for the production of methane, but at the same time to avoid postulating chain splitting mechanisms similar to (3) Taylor (90) has suggested that methane is formed by

$$H + C_2H_5 = C_2H_6^{\#} = 2CH_3$$

 $H + CH_3 = CH_4$

Steacie and Cunningham (91) also investigated the mercury photosensitized decomposition over a wide range of temperatures and pressures with a "single pass" flow system. Their results are entirely compatible with the above mechanism as modified by Taylor. We thus have

$$C_{2}H_{6} + H_{9}({}^{3}P_{1}) = C_{2}H_{5} + H_{1} + H_{9}({}^{1}S_{0})$$

$$H_{2} + H_{9}({}^{3}P_{1}) = 2H + H_{9}({}^{1}S_{0})$$

$$H + C_{2}H_{6} = C_{2}H_{5} + H_{2}$$

$$H + C_{2}H_{5} = 2CH_{3}$$

$$2 CH_{3} = C_{2}H_{6}$$

$$CH_{3} + C_{2}H_{5} = C_{3}H_{8}$$

$$2 C_{2}H_{5} = C_{4}H_{10}$$

$$CH_{2} + H = CH_{4}$$

Several qualitative investigations (52, 85) of ethane hydrogen mixtures by mercury photosensitization have been made. Steacie and Phillips (88) have done some quantitative work along this line. They found methane, propane and butane produced and hydrogen consumed. No higher hydrocarbons were formed. In a typical experiment using a trapping temperature of -125° C the following stoichiometric equation expresses the results

$$I C_{2}H_{6} + 0.5 H_{2} = 1.34 CH_{4} + 0.17 C_{4}H_{10} + traces of C_{3}H_{8}$$

They suggested that the mechanism is

$$H_{g} ({}^{3}P_{1}) + H_{2} = H_{g} ({}^{1}S_{0}) + 2H$$

$$H + C_{H} = CH_{4} + CH_{3}$$

$$H + C_{H} = H_{2} + C_{4} + CH_{3}$$

followed by various radical recombination reactions. The mercury photosensitized reactions of ethane-deuterium mixtures were also studied by Steacie, Phillips and Alexander (92). They found the methane produced to be highly deuterized, while the residual ethane was only slightly deuterized. They therefore concluded that the reactions

$$C_{2}H_{5} + H = C_{2}H_{6}$$

and

$$C_{2}H_{5} + H_{2} = C_{2}H_{6} + H$$

do not occur to any great extent.

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Cadmium Photosensitized Reactions:

Steacie and Potvin (93) have investigated the ethane decomposition by cadmium photosensitization and obtained hydrogen, methane, propane, butane and some higher hydrocarbons. The quantum yield is of the same order of magnitude as that obtained with mercury and qualitatively the products are the same. Hydrogen production in the early stages was large, while that of methane was small. They therefore concluded that the primary step involves a C-H bond rupture as in the case of the mercury photosensitized experiments and in the light of spectroscopic measurements on Cd-H₂ mixtures they favored as the primary act

 $C_{26} + Cd(^{3}P_{1}) = C_{25} + CdH$

rather than

$$C_{26}^{H} + Cd(^{3}P_{1}) = C_{25}^{H} + H + Cd(^{1}S_{0})$$

They proposed methane formation by the reaction

$$H + C_{2}H_{5} = 2CH_{3}$$

followed by

$$CH_3 + H = CH_4$$
$$CH_3 + H_2 = CH_4 + H$$

The other products were accounted for by radical recombination reactions.

Steacie and Potvin (98) also worked

with photosensitized ethane hydrogen mixtures. Using a I:I hydrogen methane mixture they found a large production of methane. Hydrogen was still produced, however, although in smaller quantities. They concluded the mechanism of the reaction was

> $C_{d}({}^{3}P_{1}) + H_{2} = CdH + H$ $Cd({}^{3}P_{1}) + H_{2} = Cd({}^{1}S_{0}) + 2H$

followed by

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$$H + C_{2}H_{6} = C_{2}H_{5} + H_{2}$$

which would account for the hydrogen produced, and

 $H + C_{2}H_{5} = 2 CH_{3}$ $H + CH_{3} = CH_{4}$ $CH_{3} + H_{2} = CH_{4} + H_{3}$

which would account for the methane formed.

PKOPANE

Hydrogen Atom Reaction Using Wood-Bonhoeffer Technique.

The first investigation of the reaction of hydrogen atoms with propane was made by Bonhoeffer and Harteck (84). They observed that the recombination of atomic hydrogen was accelerated by the presence of propane.

Trenner, Morikawa and Taylor (69) using hydrogen and deuterium atoms showed the products were mainly methane, with a small amount of ethane. The
methane and ethane were found to be highly deuterized while the propane was not exchanged. Thus propane seems to be much less reactive than ethane. They found no evidence for the catalytic recombination of hydrogen atoms observed by Bonhoeffer and Harteck.

Steacie and Parlee (94, 95) investigated the same reactions over a temperature range from 30° to 250° C. They found methane to be the sole product at low temperatures with some ethane and ethylene also formed at higher temperatures.

They concluded the results can only be explained on the assumption that the reaction

$$H + C_{25} = 2 CH_{3}$$

is of importance. The main steps in the postulated mechanism are

 $H + C_{3}H_{8} = C_{3}H_{7} + H_{2}$

followed by the secondary reactions

 $H + C_{3}H_{7} = CH_{3} + C_{4}H_{2}$ $H + C_{2}H_{5} = 2 CH_{3}$ $H + CH_{3} = CH_{4}$

at low temperatures. In addition to the above they postulate the following secondary reactions at higher temperatures.

$$C_{37}^{C} = C_{24}^{C} + CH_{3}^{C}$$

 $2 CH_{3}^{C} = C_{2H_{6}}^{C}$

With deuterium the methane and ethane produced were found to be highly deuterized while the propane was not appreciably exchanged.

Photodecomposition:

Kemula and Dyduszynski (79) investigated the photollysis of propane using the mercury ^IP₁ line. They concluded the main reaction of propane is

$$C_{3}H_{8} + hv (1850 A.U.) = C_{3}H_{6} + H_{2}$$

Mercury Photosensitized Reactions:

Steacie and Dewar (96) investigated the photosensitized decomposition of propane over a temperature range from 25° to 325° C and found the products to be hydrogen and hexanes with a trace of methane, thus indicating the primary step is a C-H bond split as in the case of ethane. They postulated the following free radical mechanism

$$C_{3}H_{8} + H_{9} ({}^{3}P_{1}) = C_{3}H_{7} + H + H_{9} ({}^{1}S_{0})$$

$$H + C_{3}H_{8} = C_{3}H_{7} + H_{2}$$

$$2 C_{3}H_{7} = C_{6}H_{14}$$

$$C_{3}H_{7} + C_{3}H_{8} = C_{6}H_{14} + H$$

$$H + H = H_{2}$$

and suggested the traces of methane were formed from decomposition of the propyl radical.

Steacie and Dewar also investigated the photosensitized reaction of propane-hydrogen mixtures postulating as the primary act

 $H_{g}({}^{3}P_{1}) + H_{2} = 2 H + H_{g}({}^{1}S_{0})$

The subsequent steps, however, were found to be the same as the straight mercury photosensitized decomposition.

The hexanes were found to be mainly isomers of n-hexane, thus indicating the primary act involves mainly secondary hydrogen atoms.

Cadmium Photosensitized Reactions:

Steacie, Leroy and Potvin (97) have investigated the cadmium photosensitized reactions of propane and propane-hydrogen mixtures at 310°C. The products of the reaction and the reaction rates were found to be practically identical. Hydrogen and hexanes along with smaller amounts of methane, butane, pentanes and heptanes were found. The formation of these products indicates the main process to be a C-H rupture along with some C-C bond splitting. The investigators favor the following mechanism

 $Cd ({}^{3}P_{1}) + C_{3}H_{8} = CdH + C_{3}H_{7}$ $CdH = Cd ({}^{1}S_{0}) + H$ $H + C_{3}H_{8} = C_{3}H_{7} + H_{2}$ $2 C_{3}H_{7} = C_{6}H_{14}$

Methane and butane production are accounted for by

 $H + C_{3}H_{7} = C_{2}H_{5} + CH_{3}$ $CH_{3} + C_{3}H_{8} = CH_{4} + C_{3}H_{7}$ $CH_{3} + C_{3}H_{7} = C_{4}H_{10}$ $2 C_{2}H_{5} = C_{4}H_{10}$

and pentane production by

 $C_{2}H_{5} + C_{3}H_{7} = C_{5}H_{12}$

in the presence of hydrogen an additional primary process

$$Cd (^{3}P_{1}) + H_{2} = CdH + H$$

is postulated.

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As in the mercury photosensitized

reactions the hexanes formed are mainly isomers again indicating that a secondary hydrogen is involved in the primary act.

The above reaction establishes a maximum value of 102.8 Kcal. for the strength of a secondary C-H bond.

BUTANE

Hydrogen Atom Reaction Using Wood-Bonhoeffer Technique.

Trenner, Morikawa and Taylor (69) made one run with n-butane and deuterium atoms. They found about II percent decomposition at **IIO^O C.,** to give methane, ethane, and propane. While the methane was highly exchanged, they found the recovered butane was not at all exchanged. Steacie and Brown (98) studied the reaction with hydrogen atoms over a range of temperatures trom 35° to 250° C. They found the products consisted solely of methane at temperatures below 100° C; above this temperature ethane was found in considerable amounts. They concluded that the results indicate a mechanism in which a series of "atomic cracking" reactions play the main role. The main steps in the postulated mechanisms are:

 $H + C_4 H_{10} = C_4 H_9 + H_2$

with

$$H + C_{4}H_{9} = C_{3}H_{7} + CH_{3}$$
$$= 2C_{2}H_{5}$$
$$H + C_{3}H_{7} = C_{4}H_{5} + CH_{3}$$
$$H + C_{2}H_{5} = 2CH_{3}$$
$$H + C_{2}H_{5} = 2CH_{3}$$
$$H + CH_{3} = CH_{4}$$

as secondary processes at low temperatures and at high temperatures, the following additional secondary reactions

$$C_{4}H_{9} = C_{2}H_{4} + C_{2}H_{5}$$

$$H + C_{1}H_{2} = C_{1}H_{2}$$

$$C_{1}H_{7} = C_{1}H_{4} + CH_{3}$$

$$H_{2} + C_{2}H_{5} = C_{2}H_{6} + H$$

$$H_{2} + CH_{3} = CH_{4} + H$$

Photodecomposition:

Using the Pj mercury line, Kemula

and Dyduszynski (68) found butane and hydrogen to be the main products

 $C_{4|0} + hv (1850 A.U.) = C_{4|8} + H_2$

From this evidence, it is hard to tell what the primary act may be.

Mercury Photosensitized Reactions:

Very little work has been done on the mercury photosensitized reactions of butane. Taylor and Hill (52) found that reaction proceeds more quickly in butane-hydrogen mixtures than in propane-hydrogen mixtures which in turn react more quickly than ethane-hydrogen mixtures.

Steacie and Phillips (88) in the course of another investigation did one run with n-butane and obtained hydrogen and higher hydrocarbons.

Cadmium Photosensitized Reactions:

Steacie and Potvin (99) made one run on the cadmium photosensitized decomposition of n-butane and obtained the gaseous products

> $H_2 = 0.6\%$ $CH_4 = 24.2\%$ $C_2H_1 = 28.8\%$ $C_3H_8 = 46.4\%$

and liquid products 58.2% by weight of the total products.

HIGHER HYDRUCARBUNS

The Photo and Photosensitized Decomposition:

Klemenc and Patat (100) investigated

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

A brief investigation of the mercury photosensitized decomposition of n-hexane was made by Taylor and Bates (102). Much hydrogen and some methane were formed in the reaction.

THE PHOTUSENSITIZED DECUMPUSITION OF n-BUTANE

As the foregoing summary shows, comparatively little work has been done on the photosensitized reactions of butane. Consequently, it was considered profitable to make a study of the photosensitized decomposition over a range of temperatures using the 2537 mercury resonance line. For purposes of comparison with the results of Steacie and Dewar (96) and Steacie and Brown (98) it was decided to employ, as far as practicable, the same series of temperatures as were used in their investigations.

There are two dynamic methods used in this type of investigation; namely, the "single pass" and "multiple pass" systems. In a "single pass" system, as the name implies, the reactant gas is subjected only once to the lamp radiation. By passing the gas through the reaction chamber at a rapid rate, secondary reactions can be eliminated to a large extent. Such a process is very inefficient and as a result, it is difficult to attain sufficient product for accurate analysis in the presence of large amounts of undecomposed reactant.

In a multiple pass system the reactant gas is circulated through the reaction vessel at a low enough temperature to remove the products of higher molecular weights as fast as they are formed. Such a method, of course, will not remove any hydrogen formed so the reaction of hydrogen atoms with the reactant gas must also be considered. Obviously, greater quantities of products may be obtained in a "multiple pass" system and consequently, the analysis of these products will be more accurate and more easily accomplished. For these reasons a "multiple pass" system was used in this investigation.

EXPERIMENTAL

Apparatus:

The apparatus employed in this investigation is shown diagramatically in Figures I, II, and III. The corresponding parts in these diagrams are indicated by the same letters.

The mercury saturator 5 supplied the mercury vapor necessary to saturate the gas. It provided a surface area of about thirty square centimetres and was heated electrically to 60° C. Any excess mercury at 20° C was removed by an iron coil in trap D. Thus at all times a constant amount of mercury vapor passed through F into the reaction vessel.

The circulating pump, P, consisted of a brass tube 35 centimetres long and 4 centimetres 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 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.



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The pump was connected by R and C to a set of mercury valves V (Figure I) which is shown in detail in Figure II. If the pump delivers to C, from Figure II, it is apparent that valve I prevents the gas from going into B, valve 2 allows the gas to bubble through and out A, valve 4 prevents the gas from going back to the other side of the piston, while the vacuum created by the pump will cause gas to bubble through valve 3 into the cylinder. If the pump delivers to R then valve 4 delivers to A, valves 2 and 3 prevent the gas from going backwards and valve I allows gas into the pump cylinder. Thus the gas in the system can only flow one way, i.e., through the saturator to the reaction vessel.

Since an ordinary Hanovia lamp is unsuitable for work at elevated temperatures a combined light source and reaction vessel (Figure III) was employed. The design of the lamp was similar to that of Steacie and Dewar (96). The emitting portion of the lamp was a quartz tube in the form of a double U. The pyrex electrode chambers, E, were joined to the quartz tube by means of the graded seals G. The electrodes were supplied and coated by the Claude Neon Eastern Limited, Montreal, and the bombarding and filling were done by the usual Neon sign technique. The finished lamp contained a drop of mercury and three millimetres of neon at room temperature.

The light source was sealed in a pyrex

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jacket, P, with a volume of eight hundred and seventy cubic centimetres, which served as the reaction vessel. This chamber was equipped with a gas inlet, connected to F on trap D (Figure 1.), and a gas outlet which was connected to inlet K above trap M (Figure 1.). A thermo-couple well T was provided for measuring the temperature of the reaction vessel with chromel-alumel thermo-couples in conjunction with a potentiometer. The reaction vessel was enclosed in an electrically heated furnace.

Owing to the proximity of the electrodes to the reaction vessel they became quite hot, thus increasing the vapor pressure of the mercury in the lamp. With an increase in pressure the collision frequency of excited and normal atoms and the chance of fluorescence before collision accordingly decreased. Thus the energy involved was shared by a larger number of atoms and the longer wave lengths of the mercury emission spectrum were produced at the expense of the intensity of the 2537 line. By equipping the electrodes with copper cooling coils and controlling the rate of flow of cold water through these coils this reversal of the 2537 line was controlled.

The condensable products of the reaction were collected in traps M and L (Figure 1), which were provided with ground glass joints and spirals so they might be removed and weighed. In early runs at 100° C the combined light source and reaction vessel was in a horizontal position and the products were collected in trap L which was maintained at -40° C by cooling acetone with dry ice. However, on elevating the oven temperature to 175° C comparatively large amounts of liquid distilled out of the reaction vessel and condensed in the adjoining glass tubing. This made necessary the reinvestigation of all the work previously done by the author with the reaction vessel and oven in a vertical position directly above trap M maintained at 0° C by ice-water. In view of the above it was not practical to attempt runs at room temperature.

Trap M was connected to the system by K (Figure I). The total volume of the main portion of the apparatus was 1786 cubic centimetres. It was connected by U (Figure I) to a trap containing liquid butane at -78°C, by H to a manometer, by T to a McLeod gauge, mercury diffusion pump and rotary "Hy-vac" pump. A Toepler pump and gas holder were connected to the system by N.

The Intensity of the Light Source.

It was shown by Steacie and Phillips (89) that the radiation from the type of lamp employed in this investigation is essentially composed of one wavelength, namely the ${}^{3}P_{1}$ mercury line at 2537 A.U., the ${}^{1}P_{1}$ line being quite efficiently absorbed by the quartz walls of the emitting tube. The intensity of this radiation was determined by measuring the rate of hydrolysis of monochloracetic acid. Half normal acid was illuminated at ${}^{35}{}^{\circ}C$ for a definite period of time. Aliquot samples of the illuminated solution were then analyzed by the addition of an excess of half normal AgNO₃ solution and back titrating with KLIND using terric alum as an indicator. Identification of the end point was facilitated by the addition of diethyl ether to the solution, thus creating an interface at which the precipitated AgSNC and AgCl collected. The mean of a number of measurements gave for the total resonance radiation entering the reaction vessel a value of 3.16×10^{-6} Einsteins/sec. based on Rudberg's value of one for the quantum yield (103). Although recent work (104) has shown that low values are obtained by this method, it was used to facilitate comparison with other work.

<u>General Procedure</u>

All runs were carried out at the vapor pressure of butane at -40° C (about 12.5 cm Hg). With the lamp on the oven temperature was raised to about twenty degrees above the temperature at which the run was to proceed. A sufficient quantity of butane was allowed to enter the system and the excess was condensed out when the trap L was brought to -40° C. While this excess butane was condensing the mercury saturator was heated and the circulating pump started. During this period the oven temperature was gradually falling and a few degrees before the reaction temperature the furnace was turned off. When the reaction temperature was reached the lamp was turned on and the gas illuminated for a definite period of time (5 hrs.). The initial heating effect of the lamp balanced out the cooling of the oven, which, after appropriate adjustment of the rhoestats controlling the current, was turned on to maintain the reaction temperature.

Analysis of the Reaction Mixture

The initial pressure of butane was taken with traps L and M at O^oC. Preliminary work indicated that the liquid products formed were octanes and dodecanes. Thus by maintaining traps L and M at O^oC by means of ice water for a short while at the end of a run the pressure of the gaseous products and unused butane could be determined. Then maintaining trap M at O^oC and cooling trap L with liquid air, the gaseous products were circulated till the manometer gave concordant readings on stopping the pump. Thus all possible gaseous products with the exception of methane and hydrogen were removed from the system and the pressure of hydrogen and methane (if present) could be determined. Trap L in liquid air was then removed from the system and liquid air placed around trap M. The oven temperature was then raised to ensure the trapping out of all high boiling products which might have condensed on the walls of the reaction vessel. After a period of five hours the "hydrogenmethane fraction" was removed with a Toeppler pump into a gas holder in which it was transferred to a combustion apparatus. To ensure the absence of traces of higher hydrocarbons in the combustion bulb the gas was first distilled in a Podbelniak type low temperature still (105). , This also provided a check on the efficiency of the trapping

which proved to be quite high.

After pumping off the hydrogen in trap L the contents were analyzed by fractionation in the low temperature still and combustion apparatus. The high boiling fraction left in this trap and the liquid collected in trap M were weighed and saved for further analysis. Tests for unsaturates were made from time to time by the usual absorption method.

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Analysis of Liquid Products:

Unfortunately the high boiling points of the products found precluded the use of a Podbelniak type high temperature still so a typical semi-micro still was used to fractionate the products. Owing to the small amount of liquid produced the products from a series of runs at a particular temperature were combined before fractionation. After weighing, the fractions with corresponding boiling points were combined and separated by distillation into three portions. The boiling point determinations had to be carried out under total reflux so the liquid would not boil away before the thermometer reached an equilibrium.

Material

Normal butane was obtained in cylinders from the Ohio Chemical Company. Although it contained no impurities detectable by the analytical methods employed, a rough fractionation was done to ensure its purity. This entailed the condensation of a large sample of butane in a trap, pumping off the first fraction, saving the middle fraction and pumping off the last fraction. --- 46 ---

EXPERIMENTAL RESULTS

The results obtained for the mercury photosensitized decomposition of n-Butane at 100, 175 and 250° are given in Table II. The quantum yield given, based on the hydrogen produced is the over all quantum yield of several reactions and has no direct connection with the amount of butane decomposed. The liquid condensate is expressed as ${}^{n}C_{8}$ H₁₈ⁿ and ${}^{n}C_{12}$ H₂₆ⁿ since boiling point determinations indicate octanes and dodecanes to be the main components of the condensate.

The material balance given in Table III is not particularly good. From Table III it is evident that the amount of liquid products found is too large. Expressing the products in terms of butane decomposed magnifies the discrepancy in the hydrogen balance. A similar behaviour has been observed in previous work done with the apparatus used by the author. Small amounts of stopcock grease dissolved by the condensate accounts for part of the above discrepancy and, in view of the number of operations involved in a material balance, the agreement is satisfactory.

The results of the condensate analysis are given in Tables IV and V. From Table IV it is seen that the boiling points obtained for the "light" fractions at all temperatures studied are definitely in the boiling range of the octanes. The boiling point of the "heavy" fraction from the runs at 100°C. is definitely in the dodecane boiling range. In the absence of methane, ethane and propane, the "heavy" products of the runs at 175°C boiling within the dodecane range are in all probability also dodecanes. However, in the runs^250°C the formation of small amounts of methane does not preclude the presence in small amounts of pentanes, heptanes, nonanes and undecanes. That these are actually present in small amounts is shown in Table V which gives the results of further distillation of the combined fractions of corresponding boiling points (Table IV). From the boiling points and the nature of the gaseous products it appears that isomers of normal octane and dodecane are the main liquid products formed. This will be further discussed in the next section.

Inasmuch as some hydrocarbons between C_4 and C_{12} other than C_8 are formed at 250°C the material balance at 250°C (Runs 6 - 9) in Table III should be slightly high since it was assumed that the liquid condensate from runs at this temperature was exclusively C_8 H₁₈ and C_{10} H₂₆.

TABLE II

Vol. of System 1786 cc. Butane Vapor Pressure 12.5 cm. Vol. of Reaction Cell 683 cc. Trap Temperature -40°C Arc Current - 89 milliamps. Circulating rate - 2.67 litres/min. Resonance Radiation absorbed 3.16 x 10° Einsteins/sec.

(x: See middle of next page)

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		Decom- position Pate Moles	Overall Quantum Vield	 Mo	P & ODU(I e s	×10 ⁻²	
Run No•	Temp. °C.	$\times 10^{-6}$ /sec.	of H ₂ .	H ₂	CH 4	C ₈	C ₁₂
I	100	.764	.19	1.06		.359	.529
2	100	.825	.19	1.11		.351	.518
3	99	.787	.19	1.09		•342	.500
4	175	1.28	.25	.44		.386	.641
5	174	1.31	.26	1.46		.394	.653
6	250	2.03	•29	1.65 0	.01	•939	.737
7.	249	2.06	.28	1.61 0	.011	.951	.741
8×:	249	5.81	.29	1.89	.042	1.01	.694
9 ^{x‡}	250	6.08	• 30	1.90	. ³ 044	1.01	.759

x: A new lamp with an intensity of 7.33x10⁻⁶ Einsteins/sec. was used in these runs.

		TABLE	111	
Run No•	C4 ^H 10 equivalent to C8 ^H 18 and C H 12 26 formed.	C4 ^H 10 decomposed.	H ₂ equivalent to C ₈ H and C ₁₂ H ₂₆ formed.	H ₂ produced.
I	2.31	1.38	1.42	1.06
2	2.26	1.49	1.39	1.11
3	2.18	I.42	1.34	1.09
4	2 .7 0	2.31	1.67	1.44
5	2.75	2.36	1.70	1.46
6	3.99	3.64	2.36	1.65
7	3.93	3.68	2.43	1.62
8	4.10	4.18	2.40	1.89
9	4.29	4.37	2.53	1.90

TABLE IV

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LIQUID CONDENSATE ANALYSIS

	B	oiling		
Prots. o	f Runs. Po	ints C.	Remarks	Weight %
1 - 3	(Fraction	115.5	Octanes	31.6
	(Fraction 2	195-200	Dodecanes	68.4
4 - 5	(Fraction	115.5	Octane	28.7
	(Fraction 2	160.	Dodecanes	71.3
6 - 7	(Fraction {	109.	Octanes and lower.	46.2
	IFraction 2	160.	Dodecanes and lower.	53.8
8 - 9	(Fraction (110.	Octanes and lower.	49.2
	(Fraction 2	160.	Dodecanes and lower.	50.8

TABLE V

CONDENSATE ANALYSIS

		Boiling Po MaintFrac	int of tion	Dom a sko
·		••	· ·	Kemdrks.
Combined	Light	Fraction	6- 20	Also trace of lower bolling fraction.
Comb i n e d	Heavy	Fractions	184	Traces of lower and higher boil- ing fractions.

--- 50 ---DISCUSSION

From the above tables it is apparent that the main products of the mercury photosensitized decomposition of n-butane are hydrogen, octanes and dodecanes at all temperatures studied.

The formation of octanes indicates the primary step to be the production of butyl radicals by the reaction

or

$$C_{4}H_{10} + Hg ({}^{3}P_{1}) = C_{4}H_{9} + Hg ({}^{1}S_{0}) \quad (1).$$

$$C_{4}H_{10} + Hg ({}^{3}P_{1}) = C_{4}H_{9} + Hg H \quad (2).$$

$$= C_{4}H_{9} + Hg + H$$

followed by

$$2C_{49} = C_{818}$$
 (3).

Since hydrogen is a product of the reaction which is not trapped out, the formation of hydrogen atoms by the reaction

$$H_{2} + H_{g} ({}^{3}P_{1}) = 2H + H_{g}$$
 (4).

٥r

$$H_2 + H_3 ({}^{3}P_1) = H_3 H + H . (5).$$

= H + H + Hg

in the latter part of a run cannot be precluded. Formation of butyl radicals may therefore take place by

$$H + C_4 H_{10} = C_4 H_9 + H_2$$
 (6).
However, the contribution of butyl radicals from this reaction
is probably not large since the hydrogen atom concentration in
systems of this type is generally low.

The reaction

$$C_{49}^{H} + C_{410}^{H} = C_{818}^{H} + H$$
 (7).

cannot be considered a source of octanes. This reaction is of the same general type as

$$CH_3 + CH_4 = C_{4} + H_{26}$$
 (8).

which is estimated to have an activation energy of from 40 to 50 Kcal. (97).

The formation of dodecanes indicates the formation, in the presence of butyl radicals, of octyl radicals by the reaction

$$C_{8}H_{18} + Hg(^{3}P_{1}) = C_{8}H_{17} + H + Hg(^{1}S_{0})$$
 (9).

٥r

$$C_{8}H_{18} + H_{9}({}^{3}P_{1}) = C_{8}H_{17} + H_{9}H$$
 (10).
= $C_{8}H_{17} + H + H_{9}$.

followed by

$$\begin{array}{cccc} C H & + C H & = C H \\ 8 & 17 & 4 & 9 & 12 & 26 \end{array}$$
(11).

The reaction

$$C_{4}H_{9} + C_{8}H_{18} = C_{12}H_{26} + H$$
 (12).

is again of the same type as reaction (8) and cannot be suggested as a source of dodecanes. However, the preponderance of dodecanes over octanes in the runs at 100°C and 175°C suggests the formation of octyl radicals at these temperatures by

$$C_4H_9 + C_8H_{18} = C_4H_{10} + C_8H_{17}$$
 (13).

in addition to reaction (9) or (10). Reaction (13) is of the same general type as

$$CH_3 + C_4H_{10} = CH_4 + C_4H_9$$
 (14).

This is known to occur at these temperatures from the work of Smith and Taylor (106). The formation of octyl radicals by

$$H + C_8 H_{18} = H_2 + C_8 H_{17}$$
 (15).

cannot be excluded, but again the low concentration of hydrogen atoms rules out this reaction as an important source of octyl radicals.

The reversal of the octane-dodecane ratio at 250°C is probably due to the decomposition of octyl radicals by

$$C_{8|7}^{H} = C_{4|9}^{H} + C_{4|8}^{H}$$
 (16).

followed by

 $H + C_{H} = C_{H}$ (17).

The above mechanism suggested for the

decomposition of octyl radicals is the only one which will not produce considerable amounts of methane, ethane and propane. If these were formed in considerable quantities, the formation of more than traces of liquids other than those boiling in the octane and dodecane ranges should occur. This was not observed. The lack of unsaturates in both the gaseous and liquid products indicates that any butylene formed is hydrogenated. This makes necessary the inclusion of reaction (17).

The mechanism of the n-butane decomposition is, in certain respects, similar to that of the mercury photosensitized decomposition of propane. Steacie and Dewar (96) concluded the main reactions of importance in the propane decomposition to be --- 53 ---

$$H_{g} ({}^{3}P_{I}) + C_{3}H_{8} = H_{g} ({}^{1}S_{0}) + C_{3}H_{7} + H \quad (18).$$

$$H_{g} ({}^{3}P_{I}) + H_{2} = H_{g} ({}^{1}S_{0}) + 2H \quad (19).$$

$$H + C_{38} = C_{37} + H_{2}$$
 (20).

$$2 C_{H} = C_{H}$$
 (21).

$$2 H = H_2$$
 (22).

With both propane and butane the primary act involves the removal of a hydrogen atom which is followed by radical combination. However, Steacie and Dewar report only small amounts of higher hydrocarbons, mainly nonanes, which presumably arise from the combination of hexyl and propyl radicals. While this reaction is relatively unimportant in the propane decomposition, its counterpart, reaction (II), in the n-butane decomposition is considerably more prominent.

The results of this investigation are in no way incompatible with the results of the reaction of n-butane with hydrogen atoms obtained by Trenner, Morikawa and Taylor (69) and Steacie and Brown (98). They suggested reaction (6) as the primary step in their investigation. They accounted for the formation of large amounts of methane and ethane (which are not found here) by reactions of the general type.

H. +
$$C_4H_9 = C_3H_7 + CH_3$$
 (23).

and

$$H_2 + C_3 H_7 = C_3 H_8 + H.$$
 (24).

In the case of the photosensitized decomposition the high pressure of butane will favor radical recombination reactions and the relatively low concentration of hydrogen atoms renders unimportant reactions similar to (23) and (24).

The formation of small amounts of methane at 250°C may possibly occur by reactions of the same type as (23) and (24) or by C-C bond splitting in the sensitized butane molecules. If the C-C bond splitting involves the breaking off of only one carbon atom the same products will result from both types of reaction. The situation is quite complex and in view of the relatively small amounts of methane formed further discussion seems to be unwarranted.

The octanes formed in the reaction appear from their boiling points to be mainly isomers of n-octane. Of the many isomers of n-octane, those falling in the boiling range found are listed in Table VI.

It is apparent that n-Octane, 3-Methyl heptane and 3, 4 - Dimethyl hexane are the only products that could result from the combination of n-butyl and/or isobutyl radicals. It is therefore concluded that the octanes formed are mainly 3, 4-Dimethyl hexane and/or 3-Methyl heptane. This indicates that the radicals formed are mainly isobutyl rather than n-butane, which is in accord with the results of other investigators.

x: From Egloff, Physical Constants of the Hydrocarbons (New York, 1939), Vol. 1.

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TABLE VI

somer	B.Pt. @ 760 mm.	Carbon Skeleton
n-Octane	125.6	c-c-c-c-c-c-c-c
3-Methyl heptane	119	c-c-c-c-c-c l c
3,4-Dimethyl hexane	1 7.8	c-c-c-c-c c c
2-Methyl heptane	117.2	c-c-c-c-c-c c
4-Methyl heptane	118.0	c-c-c-c-c-c c .
2, 3-Dimethyl hexane	115.7	c-c-c-c-c c c
3-Methyl, 3-Ethyl pentane.	118.4	c c-c-c-c c-c

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Part 8.

The Kinetics of the Factors Influencing

the Stability of "S".

(In collaboration with A. L. Thompson).

INTRODUCTION

Methyl bis-g-chloroethylamine, generally designated by "S", has been found to produce pronounced physiological effects of such nature that it is regarded as an outstanding weapon for chemical warfare. However stabilization of the compound has been tound difficult. Freshly distilled, this compound is a colorless oily liquid with a marked tendency towards supercooling at low temperatures. Although the melting point of the solid is around -63°C.(1), the liquid is frozen with difficulty at -78° C. It has a b.p. of 59° at 2 mm., 64° at 5 mm., 75° at 10 mm.(2), is sparingly soluble in water but readily soluble in the usual organic solvents. The redistilled liquid, on standing at room temperature over a period of time, deposits a fluffy mass of small white crystals, the rate of formation of which increases with an increase in temperature or when a solvent such as methanol or ethanol (1) is present.

In analogy to the dimerization of other β -chloroethylamines (3,4) it was suggested (2) that this precipitate might be a piperazinium chaboride of the type

resulting from the dimerization of "S".

That this white precipitate does contain * the piperazinium chloride

$$CH_{3} + CH_{2} - CH_{2} + CH_{3}$$

$$CI CH_{2} - CH_{2} - N = CH_{2} - CH_$$

is indicated by molecular weight determinations (5), by analyses on "purified polymer" and its picrate (6) and by the fact that the "polymer" possesses two ionizable chlorines, which may be determined in aqueous solution by precipitation with silver nitrate (6). This dimer shrinks at 310°C. giving off hydrogen chloride and the residue melts at 325°C.(6). The di-picrate formed by the elimination of two moles of hydrogen chloride melts at 208°C (6,8). It thus appears that liquid "S" itself slowly dimerizes on standing and the rate of dimerization is accelerated by an increase in temperature or by solution in methanol or ethanol.

In an attempt to find a "stabilizing agent" for "S", Burns, Eastwood and McAlpine (7) carried out a large number of tests with a variety of substances. Most of the materials used were found to have little or no effect on the rate of dimerization. Among these were aluminum, cadmium, nickel, tin and cobalt metals. Iron

Although the evidence is not conclusive, the indications (8) are that the dimer of "S" does possess the above structure and in further references made by the author to the dimer this structure will be assumed.

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appeared to have a definite stabilizing effect while copper and silver appeared to increase the rate of dimerization. Anti-oxidants in general were also found to increase the rate of dimer formation. Formamide gave an unidentified precipitate which Burns et al. suggest might be a salt of "S".

In nitro-benzene, they observed slow deposition of a solid, which from the melting point of its picrate, appeared to be a complex involving "S" and nitro-benzene. Dimerization was also found to occur in nitro-methane, since the precipitate formed yielded a picrate of the same melting point as that of dimer picrate. Chlorobenzene, carbon tetrachloride, chloroform and dioxane were found to have a marked stabilizing effect, chlorobenzene being the most effective and dioxane the least effective of the four solvents.

Marion (6,8) found solutions of "S" in 87% formic acid were clear at the end of forty days provided that the concentration of "S" in the solution was not over 40% by weight. When, however, 10 g. of "S" and 2 g. of 87% formic acid were combined,: a precipitate formed almost immediately, with the evolution of heat. The picrate of this precipitate melted at 225° C.(dimer picrate m.p. 208° C.) and analysis of this picrate indicated it to be dimer picrate. Marion suggests this might be a case of dimorphism, but there is also the possibility of isomerism. --- 65 ---

in agreement with Burns, Eastwood and McAlpine, Marion found hydroquinone accelerated dimerization. Ammonium chloride was found to have no effect while thio-urea did exhibit a stabilizing influence but not as marked an influence as benzene. A solution of 93% "S" in benzene dimerized to the extent of 2.3% in 15 days at room temperature while "S" itself was found to be 6% dimerized in the same time. Thus benzene would appear to be a good stabilizing agent. In agreement with this it was found (9) that only .29% of the "S" in a 50% "S"-benzene solution had dimerized on standing for seven days at 100°C. This determination was made by weighing the filtered precipitate after washing it with ether.

It is to be noted that precipitation of a solid was used as the criterion of stability in all of "" the above work." However, reaction to give a soluble product cannot be disregarded, and since chloride ion is produced in almost any reaction in which "S" might participate, it would seem that a test with silver nitrate would be a more suitable criterion and more indicative of the relative stability of "S" in various solvents. From the above it appears that non-ionizing solvents favor stabilization but, due to the lack of quantitative information and due to possible solubility effects, the relative merits of the various stabilizing agents mentioned above cannot be judged.

Marion does not state in his report how he determined the amount of dimerization in benzene.
The hydrochloride of "S" is quite stable when dry and provides a means of storing "S" in the laboratory over long periods of time. Sandin and Nichol (10) found no increase in the chloride content of a solution of "S"-hydrochloride ("S-HCl") in pyridine at the end of three hours. The stability of the dry hydrochloride and that of a pyridine solution of the hydrochloride would seem to indicate that the formation of quaternary nitrogen in the "S" molecule prevents further reaction.

In water, the hydrochloride appears to be subject to change. Robinson (11) followed the production of chloride ion in an aqueous solution of "S-HCI" by precipitation with acidified silver nitrate solution and found 19.25% of the total chlorine ionizable in 72 hours. This would correspond to an increase of .37% in the ionizable chlorine in 72 hours. Sandin and Nichol (12) found 1% "hydrolysis" in 2 days at 24°C. and 40% "hydrolysis" in 10 minutes at 90°C. Marion (6,13) followed the reaction with silver nitrate and sodium hydroxide (indicator not statëd) and reported 1.3% hydrolysis in 20 days and 3.4% hydrolysis in 47 days. In determining the amount of chloride ion present at the end of 47 days he found an acidified silver

nitrate solution gave 2.6% reaction when the precipitate was coagulated by letting the solution stand over night, while coagulating the precipitate by boiling the solution for 5 minutes gave 11.5 to 12.5% ionizable chlorine. It is apparent that the results of the above investigations do not agree at all and from Marion*s work doubt arises

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regarding the validity of chloride determinations in the presence of "S"-HCI.

Also, while Sandin and Nichol conclude the main reaction is hydrolysis, Robinson concludes from his results that the course of the reaction is dimerization followed by hydrolysis of the dimer (14). Maxima concluded from his results: (at that no ionizable chlorine was determinable in "S"-HCI solutions by precipitation with silver nitrate, 4b) that the normal hydrolysis reaction occurs very slowly, (c) that the dimer if formed at all is present in negligible quantity only. Thus these three investigations are in violent disagreement.

Since the structure of "S"-HCl is analagous to that of NH_4Cl , it is probable that in aqueous solution the following equilibrium is set up

 $SH^{+} + CI^{-} \implies S + H^{+} + CI^{-}$ and as Robinson indicates (14) a number of reactions are possible, namely - hydrolysis of "SH⁺", hydrolysis of "S", dimerization of "S", hydrolysis of "S" dimer and possibly iminization, making the reaction of "S"-HCI in aqueous solution quite complicated. The discrepancies in the results of the above investigations, in view of Marionts work may well be due, in part at least, to the analytical procedure used in the determination of chloride ion.

Robinson (11) also followed the production of chloride ion in a solution of "S"HCI which was 3N with respect to NAOH. He concluded that bases decompose "S"HCI fairly rapidly. Sandin and Nichol (12) followed the production

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of chloride ion in a 7.5 N NH₄OH solution of "S-HCl" and reported practically 100% "hydrolysis" in 3 hours at room temperature. In 1% sodium bleate solution, they found 80% of the "S-HCl" "hydrolysed" in 3 hours at 24°C. and 70% "hydrolysis" in 10 minutes at 90°C. The results of these investigations indicate that "S" itself is quite unstable in alkaline aqueous solution.

Measurements made by Dixon (15) on the conductivity of a fresh .001 molar solution of "S" in a 30% alcohol water mixture indicate "S" to be quite unstable in water alone. The conductivity increased rapidly and reached a constant value in six minutes. No appreciable hydrogen ion formation was observed in this time but it was possible to follow the production of chloride ion by precipitation with silver nitrate. He reported the conductivity value reached to be "about what would be expected, if one CI per molecule of "S" became ionic", and that hydrogen ion formation occured to some extent after a period of time." From this he concluded that in aqueous solution "S" undergoes very rapid dimerization which is followed by hydrolysis of the dimer.

Young, Miller and Hopewell (16) followed the production of chloride ion in the two phase system of "S" and water. They found only 50% of the total chlorine became ionizable even on standing and that the rate of formation of chloride ion increased when the mixture was stirred. From this they concluded that dimer formation was the main process

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occurring and that the solution of "S" in water occurred mainly by dimerization.

These authors followed the effect of pH on the rate of production of chloride in "S" water mixtures. Their results are briefly summarized in Table VII

		-
рH	BUFFER	RATE OF CI FORMATION
		(% lonizable Chlorine)
3.3	Formic Acid	Trace Cl after 3 hours
4	Tartaric Acid	2.24% after 3 days
4	Clark and Lubs Buffer	41% atter 26 hours
5	Clark and Lubs Buffer	65% after 24 hours
6	Clark and Lubs Buffer	51.2% after 24 hours
. 7	Clark and Lubs Buffer	68% after 24 hours
8	Clark and Lubs Buffer	96% after 22 hours
8	Boric Acid	45% after 72 hours
2N NaOH		94% after 24 hours

TABLE VII

Young et al. concluded from their results that "S" in water is stabilized at pH 3.5 or less, forms dimer (or higher polymer) at pH values between 4 and 7 and that the dimer undergoes hydrolysis above pH 8.

Ogston (17) studied the rate of formation of chloride ion and hydrogen ion with "S" in a 5% ethanolwater mixture at 25⁰C.over a range of pH. The chloride ion formation was followed by titrating excess AgNO₃ with

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KCNS and hydrogen ion formation by titrating the whole solution with small portions of N/10 NaOH and measuring the time required for the pH to reach a definite value (indicators). The rate of formation of chloride ion was found to be the same at pH 9-10 as at pH 6-8. The relative rates of hydrogen and chloride ion production found by Ogston are given in Table VIII (17).

	TABLE VIII
рН	RATE OF H / RATE CI
9 - 10	0.016
6.5- 7	0.067
4.5- 5	va. 1.0

In thiosulphate solution Ogston found the formation of chloride ion to be independent of the thiosulphate concentration and to proceed smoothly to the "total" end at 2 equivalents of chlorine ion per mole of "S", with the production of

$$s_2O_3 - CH_2 - CH_2$$

N - CH₃
 $s_2O_3 - CH_2 - CH_2$

From these results he concluded the chief mechanism of "S" disappearance in water to be of the unimolecular SNI type (18) but that the reaction is complicated by the dimerization of "S" and the formation of a variety of quaternary compounds among which are imines.

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Thus while Robinson, Dixon and Young, Miller and Hopewell, are of the opinion that the main course of the reaction is dimerization followed by dimer hydrolysis, Ogston concludes the main reaction to be the hydrolysis of "S" which is complicated by dimerization and the formation of quaternary products such as imines. Both Ogston and Young and his co-workers have crystallized dimer picrate out of their reaction mixtures; the fundamental difference in opinion is the relative rates at which the dimerization and hydrolysis of "S" take place. These investigators also disagree on the effect of pH on the **teaction** rate. As in the case of the hydrochloride, this discrepancy in the rates at pH 6-7 and at pH: 9-10 may be due to the analytical procedures used.

In view of the confusion indicated above, and in view of the apparent complexity of the reactions of "S" and "S-HCI" in aqueous solution, it was decided to undertake a study of the kinetics of the formation of chloride and hydrogen ions by "S" in various organic solvents.

EXPERIMENTAL

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Attempts were made to study the reactions of "S" in carbon tetrachloride and in acetone solutions. Reaction in these solutions was found to proceed very slowly at 25°C. At 100°C. a rust colored precipitate was formed in the carbon tetrachloride solutions while acetone solutions at this temperature turned orange-yellow in color with the deposition of only a small amount of white precipitate. In view of these complications, studies with carbon tetrachloride and acetone were discontinued and methanol substituted as a solvent.

Solutions were prepared by adding pre-cooled methanol to a weighed quantity of "S" at -78°C. (dry iceacetone bath). Since no reaction was observed, the pure compound and its solutions were stored at this temperature. The "S" was prepared from recrystallized "S-HCI" by neutralizing it with NH4OH and extracting with chloroform. The chloroform solution was subjected to a vacuum distillation and the fraction having a boiling point corresponding to that of "S" was redistilled. The methanol was dried over CaO for 36 hours, at the end of which time it was distilled over fresh CaO, the boiling point of the final product being 64.5°C.

Aliquot portions of solutions prepared in the above manner were sealed in pyrex bulbs at -78 ^OC., due allowance being made for expansion of the solution in coming to the reaction temperature. The transfer of solution to these bulbs was made with a pipette connected to a water suction pump through a scratched stop-cock. It was necessary to enclose the body of the pipette and the graduated stem in a glass jacket containing CaCl₂ to prevent condensation of moisture on the walls of the pipette. The smooth surface of the rubber stopper constituting the bottom of the pipette jacket fitted the neck of the stock solution container quite closely preventing moisture from condensing into the solution. Ice formed on the stem of the pipette[†] while it was draining. To keep this ice from contaminating the stock solution, it was allowed to melt and the stem of the pipette was dried carefully after the transfer of each sample.

A mixture of ice and water was used as a constant temperature bath at 0° C. Other thermostats were controlled to $.05^{\circ}$ C. by the conventional methods with thermoregulators, relays and heating coils.

Since it was reported that ferric ion catalysed dimerization (1), determination of chloride ion by the Volhard method was considered unsuitable, although the method apparently has been used with success by Ogston (17). Moreover, "S" is unstable in neutral solution. The production of chloride ion was followed therefore by precipitation with AgNO₂ in 4N. HNO₂.

The liquid in a bulb was transferred to a beaker containing approximately 10 ml. of the acid, after which the precipitate was washed out of the bulb into the beaker with separate portions of the acid, the volume of

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the resulting solution being about 60 ml. After the white precipitate dissolved, 15 ml. of 10% AgNO3 solution was added and the AgCl precipitate coagulated by heating over a steam bath for one hour. The precipitate was then filtered by means of a pyrex sintered Gooch crucible, washed with .02 N. HNO3 and with acetone, dried for one hour at 100°C. and weighed. Determinations on solutions of known chloride content in the presence of various concentrations of "S" (Table IX) indicate the above procedure to give results accurate to .0015 grams of AgCl.

The hydrogen ion production was followed by titrating the contents of bulbs at 0° C. to a pH of 8.5 with standard base. The samples were immediately back titrated with standard acid to a pH 4.0 to check the total amount of "S" lett in the solution (Fig.1). The end points were obtained with a Beckman pH-meter. Determinations on solutions of known "S" concentration (Table X) indicated that, although titration with standard acid gives low values for the "S" present, the application of a constant correction factor was quite in order. With the correction applied the estimation of "S" by this method gives results accurate to within 1%.

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EXPERIMENTAL RESULTS

The results of this investigation are tabulated in Tables IX to XVIII and in the accompanying graphs. Data in the tables marked with the superscript x are not actual experimental values but are taken from experimental rate curves. The figures in the left hand column of Tables XI to XVI are obtained by substracting the amount of hydrogen ion produced from the amount of chloride ion produced.

TABLE IX

Validity of Chloride Determinations in "S" Solutions.

Conc. of "S" Moles/Litre	Weight of AgCi Calc. (g.)	Weight of AgCl found (g.)
0.000	0.1435	0.1415
0.000	0.1435	0.1408
0.000	0.1435	0.1420
0,000	0.1435	0.1399
0.069	0.1435	0.1436
0.069	0.1435	0.1410
0.138	0.1435	0.1440
0.138	0.1435	0.1400
0.367	0.1435	0.1440
0.\$50	0.1435	0.1440

Average of above determinations = .1421 grams. Average Deviation = .0015 grams.

TABLE X

I. Titration of free or combined acid in the presence of "S".

Milliequivalents of "S" present in sample = 2.89

Milliequivalents of HCl present

_Calculated	Analysed
2.89	2.90
2.89	2.89

2. Back titre of above samples to pH 4.0 with standard HCI.

Milliequivalents of "S" present

Calculated	Analysed	Correction Factor
2.89	2.69	I •075
2.89	2.71	1.065

Average Correction factor = 1.070

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Milliequivalents



Titration Curves

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TABLE XI

"S" in Methanol - Reaction Temperature = 0° C. Initial "S" concentration = .5668 moles/litre at -78°C.

Time (hours)	"S" Reacted -2 Moles x 10	Total CI Produced Moles x 10=2	H ⁺ Produced -2 Moles x 10	CI Formed by Dimerization Moles x 10
14		•090	Negligible	.090
	.120			
24		• 1 20	Negligible	.120
48	and the second	•254	Negligible	.254
51	.200		.001	
98		.304		
131	.380		•006	
194		.431		

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TABLE XII

"S" in Methanol - Reaction Temperature = $0^{\circ C}$. Initial "S" concentration = 1.148 moles/litre at -78°C.

Time (hours)	"s" Reacted -2 Moles x 10	Total CI Produced Moles x 10=2	H Produced -2 Moles x 10	Cl Formed by Dimerization Moles x 10 ⁻²
	• • •	• • • *	• • •	• • • • • •
12	•072	•058	•002	•056
17	.106	•088	.003	.085
29.5	.178	.146	.004	.142
41.5	• 248	.194	.004	•190

Except for the data given in the above table and in Figure VI, results obtained are in close agreement. The significance of this discrepancy cannot be assessed without further work at 0°C with the concentration of "S" indicated.



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TABLE XIII

"S" in Methanol - Reaction Temperature = 25° C. Initial "S" concentration - .570 moles/litre at -78°C.

Time (hours)	"S" Reacted Moles x 10	Total CI Produced Moles x 10 ⁻²	H [‡] Produced Moles x 10 ⁻²	Cl Formed by Dimerization Moles x 10 ⁻²
1	** *	*109		
2	• 202	.172	•002	.170
3	•262	•273	.008	.265
6	.360	.396		
9	. 424	• 450	.019 .019	. 431
11.5	***	• 473		
13	• 452	~~~		
17	.470	.476	.021	• 455
18	***	• 477		

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at 25°C. Initial "S" concentration = .570 M at -78°C.

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TABLE XIV

"S" in Methanol – Reaction Temperature = 25° C. Initial "S" concentration = 1.148 moles/litre at -78°C.

Time (hours)	"S" Reacted Moles x 10 ⁻²	Total Cl Produced Moles x 10 ⁻²	H [‡] Produced -2 Moles x 10 ⁻²	Cl Formed by Dimerization Moles & 10 ⁻²
•2		.062		
1	•088	•089	•004	.085
2	.193	•200	•006	.194
3	. 28 7	•264	•008	.256
4	.341	.317	.009	.308
8	.447	• 471	.013	• 458
12	• 480	. 482	.016	.466
19	•••	.509		

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TABLE XV

"S" in Methanol - Reaction Temperature = 41.5° C. Initial "S" concentration = .572 moles/litre at -78°C.

Time (Hours)	"S" Reacted Moles x 10 ⁻²	Total CI Produced _2 Moles x 10	H- Produced Moles x 10 ⁻²	CI Formed by Dimerization Moles x 10
± ₽	•224	.217	•005	•212
I.	.298	.307	•015	•292
2	.396	. 401	.023	.379
3		. 457		·
3.5	• 459	• 4 70 ×	•035	• 435
4		• 480		
6.25	• 491	• 505 ×	•054	.449
8		.518		
9	• 492	•513 ×	.055	• 458
14		.518		
17	. 492	• 525	.060	. 465
48		.547		



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Fig. IX

Rate curves obtained in absolute methanol at 41.5° C. Initial concentration of "S" = .570 M at -78°C. --- 88 ---

TABLE XVI

"S" in Methanol - Reaction Temperature = 41.5° C. Initial "S" concentration = 1\$48 moles/litre at -78°C.

Time (hours)	"s" Reacted -2 Moles x 10	Total CI Produced Moles x 10-2	H ^t Produced -2 Moles x 10	Cl Formed by Dimerization Moles x 10 ⁻²
•5	•239	•278	.014	•264
i	.371	.335	•017	.318
2	• 45 5	.456	•021	. 435
3	. 468	• 488	•026	• 462
4	.501	.512	•029	.483
8	.521	.540	.037	• 503
12	.526	•542	•039	• 503

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TABLE XVII

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Data for Arrhenius Line

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Temp. A	I/Tx10 ⁻³	I.148M."S" soin.		•570M•"S" sola•	
<u></u>		k initial (unimol)	in(kxlO)	k(initial) (unimol)	In(kxIO)
314.5	3.19	1.30	10.262	•925	9.92
298	3.36	2.04×10-1	8.40	2.09×10 ⁻¹	8.44
273	3.67	.90×10 ⁻²	5.39	1.02×10 ⁻²	5.40



Fig. XI.

Arrhenius Line from initial unimolecular rate constants of the reaction of "S" in absolute methanol.

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DISCUSSION

Validity of the Analytical Methods.

Doubt exists as to the validity of gravimetric determinations of chloride ion with slightly acidified AgNO3 in "S" or "S-HCI" solutions. Marion's results (6) indicate that chloride ion production occurs quite readily at 100°C in the dilute acid solution. The results given in Table IX indicate that reasonable stabilization is obtained by the addition of 50 ml. of 4 N. HNO_3 to a IO ml. sample of a .550 molar solution of "S" in methanol, and that determinations with AgNO2 by the previously described procedure, may be carried out in "S" and/or "S-HCI" solutions, the accuracy being about 1.5 milligrams of AgCl. Thus, in the above results the maximum error arising from the analytical method used for chloride determinations would be 2% and the method therefore is quite suitable for following the rate of chloride ion production in this investigation.

The titration curves of "S" and "S-HCI" given in Figure IV show that the end points, obtained in the hydrogen ion and "S" determinations with standard base and standard acid, are quite sharp. The data in Table X indicate that titration values for "S" are low by a factor of 1.070 and, that, with the application of the indicated correction, determinations of "S" by this method are accurate to with the Titrating at 0°C with standard base and standard acid therefore Face suitable method for following the rate of formation of H⁴ and the rate of disappearance of "S" in the reactions investigated.

Reactions of "S" in Methanol Solution.

The variety of reactions that might possibly occur in a methanol solution of "S" are given below:



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must be included. To this list should be added the formation of ethylene imines by the products of reactions (3) and (4) in the following manner:



where X is a CH₃O group, or a Cl. Again if X is a Cl the possibility of imine formation requires the inclusion of the reaction



and

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Iminization might also occur by the reaction



Of the above possible reactions (1), (5), (6), (9) and (11) would produce chloride ion alone while (2), (7), (8), and (10) would produce equal quantities of hydrogen and chloride ions. From the data in Tables XI: to XVI and from Figures V: to X it appears that the production of chloride ion is practically the only process occurring in the initial stages of the reaction at the temperatures indicated. The reaction or reactions producing hydrogen ion do not become prominent until 30 to 40% reaction has occurred.

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Since practically no hydrogen ion formation occurs in the initial phases of the reaction it would appear that reaction (2) does not occur to any appreciable extent. This eliminates the possibility of the occurrence, to any appreciable extent of reactions (4), (5) and (6). The low initial concentration of hydrogen ion renders the production of chloride ion by (9) quite improbable and the marked stability of "S-HCI" in pyridine solution (10) indicates reactions (9) and (10) do not occur at all.

Reactions (7) and (8) obviously cannot be the source of the large amount of chloride ion produced in the initial phases of the reaction. Thus it would appear that reactions (1) and (11) are the only processes that could occur in the initial phases of the reaction. From the work of Marion (6), who obtained dimer from methanol solutions of "S" it would appear that reaction (1), which would be bimolecular, is the principal process occurring in the early stages of the reaction. However, from Figures V to X it is apparent that doubling the initial concentration of "S" does not appreciably affect the rate of chloride ion production. Since dimer is the principal product obtained by Marion, its rate of formation appears to be controlled by a unimolecular process.

Reaction (11) would be unimolecular and, therefore, it would appear that the rate of imine formation by (11) governs the rate of dimer formation and that dimer formation does not occur by reaction (1) but by the reaction.

CH3-N-CH2-CH2-CI

(12)

=

2

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Thus it is concluded that the principal reaction occurring in the initial stages of the reaction is the unimolecular S_n formation of dimer.

From Figures V to X it is seen that, although the rate of dimerization and the rate of "S" disappearance appear to have dwindled almost to zero in the latter part of the reaction, the total amount. of chloride ion and hydrogen ion present in the solution continues to increase. Moreover the slopes of the total chloride ion curves and the hydrogen ion curves appear to be the same. This indicates the presence of a process in the latter phase of the reaction in which equivalent amounts of hydrogen and chloride ion are formed. Since some hydrogen ion is formed in the intermediate phase of the reaction and, since "S" is a weak base, it appears that the small amount of hydrogen ion formed would immediately combine with "S" by reaction (3). Thus at the point where the rate of "S" disappearance falls off, it would appear that the "S" originally present in the solution is dimerized or stabilized by formation of the hydrochloride.

Since hydrogen and chloride ion are formed in equivalent amounts after all the "S" in the solution has dimerized or formed hydrochloride, their production presumably involves a product formed in the earlier part of the reaction. While dimer formation is

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the main reaction taking place, slight alcoholysis of "S" by reaction (2) might produce the initially small amounts of hydrogen ion found. The two products present in appreciable amounts are dimer and "S"-HCI" either of which may react with solvent to produce hydrogen and chloride ions.

The presence of an induction period in the production of hydrogen ion is difficult to detect under the experimental conditions employed, owing to the slow rate at which hydrogen ion is produced. Only further data on the relative rates of dimer hydrolysis and the hydrolysis of "S"-HCI can determine which of the products is the source of the equivalent amounts of hydrogen and chloride ion.

Thus the course of the reaction appears to be the unimolecular S_n l dimerization of "S" accompanied by a slight amount of alcoholysis. The products of these reactions are then further alcoholized. The calculation of rate constants for the dimerization process is complicated by the occurrence of reaction (3). However, initial rate constants (Table XVII) give a suitable Arrhenius line which indicates this reaction to have an activation energy of about 9.6 Kcal.

The results of this investigation and the conclusions arrived at in the above discussion compare quite favorably with work done by Mason and Block (13). They investigated the polymerization of β -4-morpholinoethyl chloride and found that 34% of the com pound was converted to N, N- β dispiromorpholino-piperaznium dichloride when an ethanol solution containing 5 grams of the compound was refluxed for 24 hours. Evaporation of the alcohol after the removal of the solid piperazinium dichloride gave them a solid which they indentified as β -4-morpholinoethyl ether.

Since "S" contains a second β -chloroethyl group it is to be expected that the dimerization of "S" would proceed much more quickly than the dimerization of β -4-morpholinoethyl chloride.

NOTE:

Porton Report No. 2384 which became available immediately prior to submission of this thesis is in agreement with the conclusions from the present study. In this report it is concluded that iminization is the rate controlling process in the reaction of "S" with water and that dimer is the principal product formed when high concentration of "S" (11% by weight) are used.

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Summary and Contribution to Knowledge

Part A.

The mercury photosensitized decomposition of butane has been investigated at 100°C, 175°C and 250°C. Hydrogen, octanes and dodecanes are the main products at all the temperatures studied.

It is concluded that the primary step is a C-H bond split:

 $C_{4}H_{10} + H_{3}(^{3}P_{1}) = C_{4}H_{9} + H_{3} + H_{1}$

or

$$G_4H_{10} + Hg(^3P_1) = G_4H_0 + HgH$$

= $G_4H_0 + Hg + H_1$

The main secondary reactions are

$$2 C H = C H
4 9 8 18,$$
Hg $({}^{3}P_{1}) + C_{8}H_{18} = C_{8}H_{17} + Hg + H$

or

΄.

$$= C_8H_{17} + Hg + H_{17}$$

and

$$C_{H} + C_{H} = C_{H} + C_{H}$$

4 9 8 8 8 7

Followed by

$$C_{H} + C_{H} = C_{H} + C_{H}$$

8 17 4 9 12 26

and

$$H + H = H_2.$$

The octanes formed appear to be mainly 3, 4-dimethyl hexane and/or 3-methyl heptane. --- 103 ---

Bart B.

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The reaction of N, N-di-(s-chloroethy) methyl amine ("S") in absolute methanol were investigated at 0, 25 and 41.5°C by following the rate at which it disappeared and the rate at which chloride and hydrogen ions formed. Analytical methods used were shown to be valid.

It was concluded that the principal reaction involved is dimerization by a unimolecular $S_n!$ mechanism. The reaction was found to have an activation energy of about 9.6 Kcal.

APPENDIX

The results given in the following tables were obtained in the course of the above investigation. Further work is necessary to demonstrate their significance.

	TABLE XVIII					
"S" in Methanol-water Solutions.						
Reaction Ter	np. = 0°C	6 1. 0				
Initial "S"	Concentration	= .573 mo	les/litre at -78°C.			
· · · · · · · · · · · · · · · · · · ·	<u>Chloride l</u>	on_Producti	ion (moles x10 ⁻²)			
Time [hours]	0.0M.H ₂ 0	7M.H ₂ 0	14M.H20			
2	-	•036	-			
3	-		•078			
4	-	.066	-			
10	-	•111	•203			
12		-	•247			
14	•090	-	-			
15	-	.166				
24	•120	.241	• 3 78			
36	-	-	• 451			
48	.254	.384	-			
98	.304	-	-			
194	• 431	-	-			

y.

<u>д М.</u>

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TABLE XIX

"S" in Methanol-water Solutions.

Reaction Temp. = 25°C.

Initial "S" Concentration = .573 Moles/Litre at -78°C.

Time (hours)	<u>Chloride Ion Production (moles x10⁻²)</u>			
	0.0M.H ₂ 0	7м.H ₂ 0	I 4M.H_0	
1/2	-	. 44	.213	
1	.109	•223	.340	
2	•172	.328	.449	
3	•273	.398	• 489	
6	•396	-	-	
7	- -	_	.534	
9	• 450	•506	-	
11.5	• 473	-	-	
14	-	.526	-	
1.7	• 476 [×]	-	-	
18	• 477	-	-	
22	.486	-	-	
24	-	-	.562	
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