

THE REACTIONS OF METHYL RADICALS WITH
AMINES

A Thesis

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Master of Science

by

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To My Wife

ABSTRACT

The activation energies for the abstraction of hydrogen atoms by methyl radicals, from triethylamine, ethylenimine, N-methyl-ethylenimine, N-ethyl-ethylenimine were found to be 6.7 kcal./mole, 4.8 kcal./mole, 6.7 kcal./mole and 5.4 kcal./mole respectively.

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INTRODUCTION

The reaction kinetics of organic substances have been the subject of a considerable amount of work during the last few decades. Almost always the homogeneous gas phase reactions of these compounds have been found to be complex. The formation of free radicals has often been proven and chain mechanisms have often been proposed to account for the observed rates of reaction.

The evidence that has accumulated for the existence and detection of short lived free radicals is substantial and some of it is worthy of consideration. In 1900 Gomberg (1) first demonstrated the existence of free radicals in solution by the identification of the triphenyl methyl radical. It was left to Paneth and co-workers (2), however, to show that free radicals could be detected by their reaction with a metallic mirror. This metallic mirror was deposited on the inside wall of a tube through which was passed organic vapour previously heated at elevated temperatures in a furnace to produce alkyl radicals. The removal of the mirror and the production of metal alkyls gave evidence of free radical formation. In the case of methyl radicals their half-life was estimated to be about 0.006 seconds.

A second method of detecting free radicals was discovered by Hinshelwood and Stavely (3). By introducing nitric oxide into the reaction system where free radical reactions were suspected the net effect was to greatly inhibit those reactions which were believed to proceed via free-radical mechanisms. Hence according to them the effect of the nitric oxide was to react with, and in some manner destroy the free radicals in the system. This

view has received considerable support as a result of a study by Herzberg and Shoosmith (4). Producing methyl radicals by the flash photolysis technique they determined the absorption spectrum of this radical in the vacuum ultraviolet where strong absorption was expected.

Since the source of methyl radicals for this work was acetone exposed to ultraviolet radiation, a photochemical process, it would be advantageous to consider the various possible processes which a molecule may undergo when it absorbs radiation. Keeping in mind that the effect will depend on the wave-length and intensity of the radiation, as well as the type of bonds in the molecule, at least one of the following will occur:

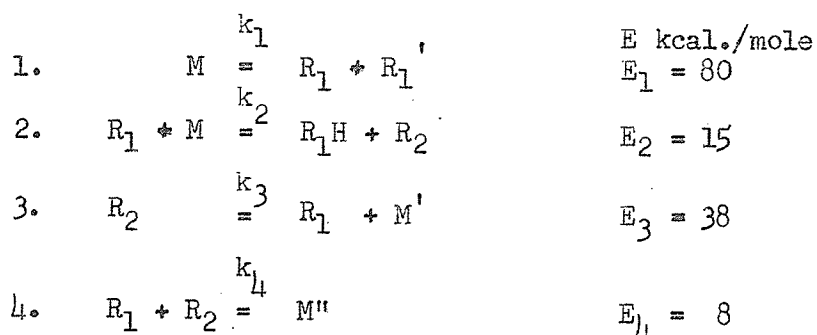
- 1) The energy absorbed may be retained for a short time and then be re-emitted as fluorescence.
- 2) The energy absorbed may be completely or partially transferred to another molecule during a collision.
- 3) The excited molecule can, on collision with another molecule, dissociate into two or more fragments prior to losing this energy via fluorescence.
- 4) The molecule absorbing the energy may dissociate into two or more fragments, thus yielding free radicals.

The last two possibilities are the ones which are chemically important. The absorption of a single photon of light by one of the molecules participating in the reaction is known as a primary process. Once free radicals are formed their reactions, provided the difference between incident radiation energy and bond dissociation energy is small, are simple thermal reactions. These reactions leading to the formation of stable products are known as

secondary processes.

At one time it was assumed that since many organic reactions obey simple kinetic laws, the reactions must be simple elementary processes. However, Rice and Herzfield (5) pointed out that complex radical mechanisms could lead to simple overall kinetics. In order to provide an adequate theoretical explanation their suggested mechanism had to be consistent not only with the apparent contradiction already mentioned but also with the fact that an activation energy of less than the 80 kcal./mole required to rupture a carbon-carbon bond was actually required for the overall reaction.

In keeping with these requirements, Rice and Herzfield suggested several complex reaction schemes, each of which led to free radical decomposition of a hydrocarbon leading to a first order rate.



The first step was assumed to be the dissociation of the reacting molecule M into two radicals and involves the rupture of a carbon-carbon bond. The radical R_1' plays no part in further reactions. R_1 then initiates the steps 2-4 by abstracting a hydrogen atom to form a stable compound RH and a new radical R_2 . This radical then dissociates to give R_1 plus an additional molecule M' . Steps 2 and 3 constitute a chain process which is broken when the two radicals R_1 and R_2 meet to form a third molecule M'' . Assuming long chains and steady state concentrations of R_1 and R_2 and since k_1 is small

(E_1 large) compared to k_2 , k_3 and k_4 , the overall rate of decomposition is given by

$$\frac{-d[M]}{dt} = \frac{(k_1 k_2 k_3)^{\frac{1}{2}} [M]}{(2k_4)}$$

The reaction is therefore first order. The activation energy for the overall process is then

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

By substituting what seemed to them to be reasonable values for the activation energies Rice and Herzfield found the overall activation energy to be considerably less than 80 kcal./mole. At the time when Rice and Herzfield proposed their mechanisms detailed investigations of many of the reactions had not been done. It was therefore necessary to do a considerable amount of speculation in order to estimate the activation energies of the individual steps. Subsequent investigations have given support to the general conclusions though a revision of the details of many of their reaction schemes has been necessary.

Due to the work of Rice and Herzfield the attention of investigators has turned to free radical mechanisms in order to elucidate the rates and energies of elementary reactions. One of the difficulties associated with free radical mechanisms is the measurement of the concentration of free radicals which have a half-life considerably smaller than a second. Hence it has been necessary to compare ratios of rates or to use some other indirect means as a measure of the free radical concentration. Prior to the advent of the rotating sector technique the evaluation of individual specific rate

constants was also impossible. This technique, based upon the comparison of rates under steady and intermittent illumination, has eliminated this difficulty.

Elementary Free Radical Reactions.

The main types of elementary free radical reactions in the gas phase are as follows:

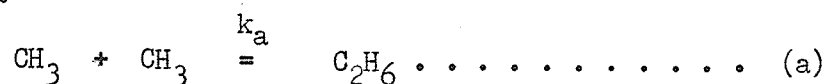
1. Recombination and disproportionation of two free radicals to form stable molecules.
2. Abstraction reactions in which a free radical removes an atom from a stable molecule to produce a molecule and a free radical. The most common type is one in which a hydrogen atom is transferred.
3. Decomposition of a free radical to form a molecule and a smaller radical.
4. Addition of a free radical to a stable molecule to form a larger radical.
5. Free radical displacement or inversion reactions.

Since the reactions of methyl and ethyl radicals have been investigated more thoroughly than those of any other radicals the ensuing discussion will be restricted to these two radicals. The reactions of larger simple free radicals would be expected to be similar in type though rate constants, activation energies and other related details will differ.

a) Recombination and Disproportionation

Whenever two identical organic radicals collide and react to form products they may do so either by simple recombination to form one molecule or by disproportionation to form two smaller molecules, one of which is unsaturated.

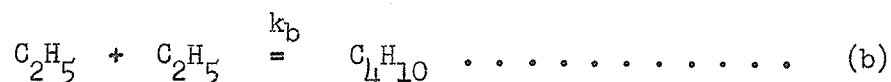
For methyl radicals only one of these reactions is possible, recombination.



This reaction has been studied by Gomer and Kistiakowsky (6) using the rotating sector technique in order to determine the specific rate constant k_a . They found the rate constant for recombination of methyl radicals (k_a) to be $4.5 \times 10^{13} \text{ (moles/cc)}^{-1} \text{ sec}^{-1}$ at 125°C , and the activation energy of the reaction to be $0 \pm 700 \text{ cal/mole}$ independent of the source of methyl radicals.

For ethyl radicals both disproportionation and recombination reactions are possible. Both of these reactions have been studied by Ivin and Steacie (7) and later by Shepp and Kutschke (8) as well. The former authors did their investigation by studying the photolysis of mercury diethyl, which for reasons to be mentioned, is not as reliable as diethyl-ketone as a source of ethyl radicals. Not only does the high extinction coefficient of mercury diethyl and the presence of a thermal reaction require a correction but also the photolysis mechanism of mercury diethyl is not established. In contrast, the photolysis of diethyl-ketone is well understood and hence the values of Shepp and Kutschke (9), who utilized this compound as a source of ethyl radicals, are preferred.

For the recombination reaction -



they found k_b the rate constant, using the rotating sector technique was $1.5 \pm 1 \times 10^{13}$, $2.0 \pm 0.5 \times 10^{13}$, and $4.2 \pm 0.8 \times 10^{13} \text{ cc moles}^{-1} \text{ sec}^{-1}$ at 50°C , 100°C , and 150°C , respectively. An Arrhenius plot of their results indicated the activation energy of reaction (b) to be $2.0 \pm 1 \text{ kcal./mole}$.

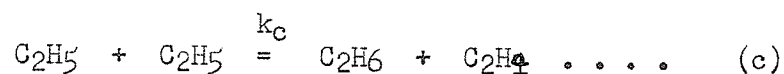
It is a well known fact that when atoms or free radicals recombine energy is liberated equal to the energy of the bond formed.

For a carbon-carbon bond we associate an energy of 80 kcal./mole and hence the recombination of two methyl or two ethyl radicals requires little energy and one would therefore expect the rate constants for the two reactions to be of the same order of magnitude. According to Shepp and Kutschke (8) the small activation energy of 2.0 ± 1 kcal./mole for reaction (b) is due to the unfavourable orientation of ethyl radicals resulting in mutual repulsion of the C-H bond orbitals as the radicals approach "head to head" close enough to allow overlap of the orbitals of the bonding electrons. The somewhat lower activation energy for reaction (a) is explained as due to a sterically more favourable reaction. The similarity of k_a and k_b in the light of the difference in activation energy of reaction (a) and (b) is somewhat inexplicable.

The manner in which reactions (a) and (b) are written would seem to indicate that both methyl and ethyl radical recombinations proceed by a simple two body collision. This is not correct. When energy is liberated due to the formation of bonds the energy must be dissipated either by a three body collision or by the vibrational modes within the product. The larger the number of possible vibrational modes the less one would expect the reaction to be dependent on the presence of a third body. Thus one would expect the recombination of ethyl radicals to be less dependent on the presence of a third body than the recombination of methyl radicals. Experimentally this has been shown to be the case. Dodd and Steacie (9) have shown that the kinetics of the photo-decomposition of acetone at low pressures (20 - 0.2 mm) are consistent with the participation of a third body in the recombination of methyl radicals. They were able to show that below a limiting concentration of efficient third body molecules the frequency

of deactivating collisions was insufficient to sustain the reaction rate. Similarly Brinton and Steacie (10) showed that, to a somewhat smaller extent, the recombination of ethyl radicals was favoured by the presence of a third body at low pressures.

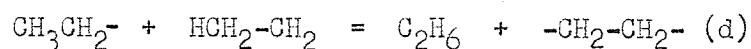
From a consideration of the ethyl radical disproportionation reaction



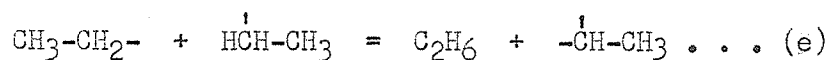
it is evident that this reaction is of the general hydrogen-abstraction type. As such, one might expect it to have an activation energy between 4.5 - 8.0 kcal./mole. Actually it is considerably more exothermic due, probably, to the formation of a double bond in one of the products.

An activation energy can be postulated for reaction (c) on the basis of the work of Ivin and Steacie (7) and Shepp and Kutschke (8). Ivin and Steacie made an Arrhenius plot of k_c/k_b and obtained $E_c - E_b = 0.8 \pm 0.2$ kcal./mole. Taken with Shepp and Kutschke's value of 2.0 ± 1 kcal./mole for E_b one obtains a value of 1.6-4.0 kcal./mole for E_c the activation energy of disproportionation.

The mechanism of the disproportionation reaction was further elucidated by the work of Wijnen and Steacie (11). They analyzed the products from the disproportionation of CH_3CD_2 radicals. When two ethyl radicals disproportionate they may do so by a "head to tail" mechanism

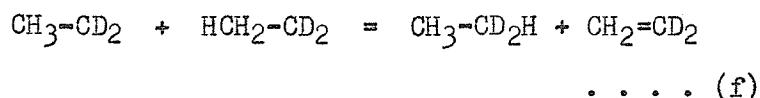


resulting in the formation of bimethylene radical, or they may do so by a "head to head" mechanism



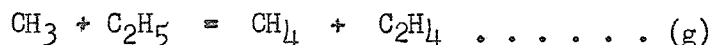
resulting in the formation of the ethylidene radical. If the

biradicals were long lived the activation energy would be of the order of 7-10 kcal./mole. If the biradicals isomerize to C_2H_4 immediately the disproportionation reaction will have an activation energy of approximately zero, as found. Since reaction (r) involves a hydrogen transfer to form ethylene, reaction (d) or the "head to tail" mechanism seems to be the more likely. This was found to be the correct reaction since more than 90% of the ethylene found using CH_3CD_2 radicals was $H_2C=CD_2$.



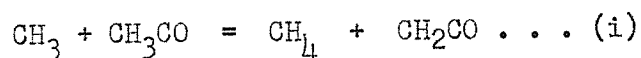
Thus the possibility that the ethylene was being formed by the dissociation of an excited butane molecule seemed to be eliminated.

When both methyl and ethyl radicals are present there is, of course, no reason why mixed disproportionation and recombination reactions should not occur. The occurrence of both reactions was shown by Ausloos and Steacie (12). They found that in the photolysis of methyl ethyl ketone in which both methyl and ethyl radicals were produced the following reactions took place.



From their work they concluded that the ratio of disproportionation to recombination for an ethyl and a methyl radical is of the order of 0.04 ± 0.02 . The ratio of disproportionation to recombination for two ethyl radicals in the same system is considerably larger, about 0.125 ± 0.01 .

In a study of the photolysis of biacetyl Ausloos and Steacie (13) proposed a disproportionation reaction between methyl and acetyl radicals.

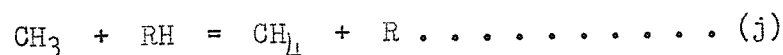


This step was postulated in order to account for the large quantities of methane formed at low temperatures.

b) Abstraction Reactions

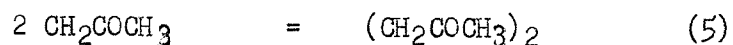
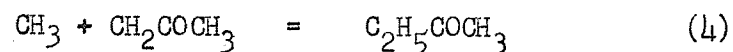
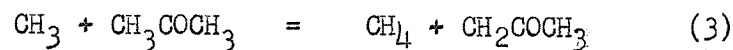
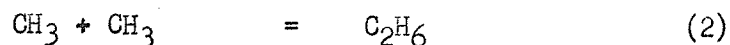
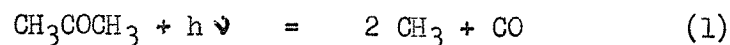
i) Methyl Radicals

The abstraction reactions of the type

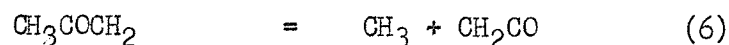


where RH is any hydrogen-containing compound, have been studied extensively. One of the earliest studies of this type of reaction was conducted by H. S. Taylor and co-workers (14,15). It was found, however, by Trotman-Dickenson and Steacie (16) that their quantitative results were in error though the general pattern of the results was apparently correct. In their work on hydrocarbons Taylor and Smith (15) used dimethylmercury as a source of methyl radicals. This compound is not, for reasons mentioned before, the most reliable. Secondly in their calculation of activation energies for the reactions comparable to (j) their method depended upon the validity of the assumption that the rate of formation of ethane is much greater than the rate of formation of methane. Since only the rate of the latter was followed it is easy to see why an error in their assumption was not recognized at the time. Nevertheless, the work of Taylor and Smith did establish, and was confirmed by Trotman-Dickenson and Steacie, that the activation energy for reaction (j) is greater when RH is a hydrocarbon containing only primary hydrogen atoms than where RH is a hydrocarbon containing primary and secondary hydrogen atoms which in turn has a greater activation energy than the reaction where RH has primary, secondary, and tertiary hydrogen atoms.

Since the reactions of methyl radicals have been and still are of considerable interest it has been found convenient by most investigators to use acetone as a source of photochemically produced methyl radicals. Other compounds which have been successfully used as a source of methyl radicals, though with some limitations, are azomethane, dimethylmercury and di-*t*-butyl peroxide. These compounds have been especially important in studying reaction (j) where the compound RH does not itself absorb radiation in a convenient spectral range. The photolysis of acetone has been the subject of a large number of investigations and as a result its use and kinetics has become fairly well established over a considerable range of temperature. Allen (17) was the first to use acetone as a source of methyl radicals though his work was only of an exploratory nature. The work of Noyes and co-workers was confined primarily to temperatures below 100°C, and does not effect this study. It was later extended by Trotman-Dickenson and Steacie (18) to temperatures between 100-300°C using light of wavelength 2537 Å. The principal products of the vapour phase reaction have been shown to be methane, ethane, and carbon monoxide. Under some conditions biacetyl, methyl ethyl ketone (MEK), biacetylonyl, ketene, ethylene and acetaldehyde are also formed. Since, however, these products are minor, little quantitative work had been done to interpret their production in terms of mechanism until only very recently. It has been conclusively demonstrated by Steacie (19) that the reaction proceeds entirely by a free radical mechanism. According to him the photolysis between 100-300°C (the temperature range to which this study was limited) may be fully described by the following scheme:



and above 250°C a sixth reaction must be taken into account in order to explain ketene formation.



Assuming E_2 to be zero Trotman-Dickenson and Steacie (18) obtained a value of 9.7 kcal./mole for E_3 .

The more recent work on minor products referred to above was done by Brinton (20). This study on the photolysis of acetone was conducted in the temperature range 300-475°C and quantitative determinations of the rate of production of minor as well as major products were made. Methane formation was found to be consistent with step (3).

However, the ratio $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} \sqrt{[\text{AC}]}$ was found to be strongly dependent on light intensity and acetone concentration at high temperatures (R refers to rate of formation and $\sqrt{[\text{AC}]}$ is the concentration of acetone.)

It was believed that this dependence did not exist since, prior to the work of Brinton, it had not been observed at temperatures below 300°C and above very low pressures. Outside these conditions reaction (2) satisfactorily represents the formation of ethane. Since the ratio

$R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} \sqrt{AC}$ is lower for low intensities Brinton suggested an additional process favoured at high intensities to form methane or one at low intensities to form ethane.

The first of these postulates can be tested by considering reactions (3), (4), and (5). If these are the only processes leading to formation of methane (CH_4), methyl ethyl ketone (MEK), and 2,5 - hexanedione (AC_2) respectively then

$$R_{\text{CH}_4} = \frac{k_3 k_5^{\frac{1}{2}}}{k_4} \frac{R_{\text{MEK}}}{R_{\text{AC}_2}^{\frac{1}{2}}} \sqrt{AC}$$

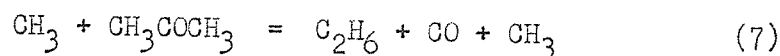
Taking the slope of the R_{CH_4} vs. $\frac{R_{\text{MEK}}}{R_{\text{AC}_2}^{\frac{1}{2}}} \sqrt{AC}$ plot in order to make an

Arrhenius plot of $\frac{k_3 k_5^{\frac{1}{2}}}{k_4}$, Brinton found $E_3 + E_5 - E_4 = 12.0 \text{ kcal./mole}$.

Since the difference between this value and the value of $E_3 = 9.7 \text{ kcal./mole}$ of Trotman-Dickenson and Steacie (18) is relatively small (2.3 kcal./mole), Brinton concludes that $E_3 + \frac{E_5}{2} - E_4 = 12.0 \text{ kcal./mole}$ is probably

a high value of E_3 . In other words step (3) fully accounts for methane formation and the anomalous behaviour of the ratio $(R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}) \sqrt{AC}$ is probably due to an additional process producing ethane in the low intensity region. Further evidence for the validity of this assumption is given when one assumes steps (2), (4) and (5) to be the only reactions producing ethane (C_2H_6), methyl ethyl ketone, and 2,5 - hexanedione respectively. Then according to Brinton's calculations based on collision theory the ratio $R_{\text{MEK}}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} R_{\text{AC}_2}^{\frac{1}{2}} = k_4/k_2^{\frac{1}{2}} k_5^{\frac{1}{2}}$ should be about 2. Since the value is in fact much lower and since R_{MEK} and R_{AC_2} behave in a manner consistent with reactions (4) and (5) it is obvious that $R_{\text{C}_2\text{H}_6}$ is high. Hence he postulates an additional reaction

to account for the increase in ethane formation at high temperatures.



Then

$$R_{\text{C}_2\text{H}_6} \frac{(\text{AC})^2}{R_{\text{CH}_4}^2} = k_2/k_3^2 + (k_7k_4/k_3^2k_5^{\frac{1}{2}}) (R_{\text{AC}_2})^{\frac{1}{2}} \sqrt{\text{AC}}/R_{\text{MEK}}$$

A plot of this function indicated that $k_3/k_2^{\frac{1}{2}}$ was such that $E_3 - E_2/2 = 15.6$ kcal./mole and $E_7 + E_4 - (2E_3 + E_5/2) = -8.6$ kcal./mole. Coupled with the value of $E_3 + E_5/2 - E_4 = 12.0$ kcal./mole one obtains a value of $E_7 - E_3 = 3.4$ kcal./mole. This gives an activation energy for reaction (7) of about 15.4 kcal./mole.

The establishing of reaction (7) though an apparent digression from the range of 120°-260°C, in which the present study was conducted, is important to an understanding of this work. The inclusion of an additional ethane producing step is considered necessary at a temperature where the ethane formation from reaction (2) has become very small. Hence a slight increase in $R_{\text{C}_2\text{H}_6}$ will increase the expected rate several times and will disrupt any plot in which $R_{\text{C}_2\text{H}_6}$ is a factor.

If, however, one supposes that at moderate temperatures the photolysis of acetone proceeds so that the formation of ethane and methane is accounted for completely by reactions (2) and (3) then one can write:

$$R_{\text{CH}_4} = k_3(\text{CH}_3)(\text{AC})$$

where (CH_3) is the concentration of methyl radicals.

$$R_{\text{C}_2\text{H}_6} = k_2(\text{CH}_3)^2$$

Hence

$$k_3/k_2^{\frac{1}{2}} = R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}(\text{AC})$$

According to collision theory one can then say that the specific rate constant k is given by:

$$k = PZ \exp (-E/RT)$$

where P = steric factor

Z = collision no.

E = activation energy

R = gas constant

T = abs. temp.

hence one can write:

$$k_3/k_2^{\frac{1}{2}} = (P_3Z_3/(P_2Z_2)^{\frac{1}{2}}) \exp (E_3-E_2/2) /RT \quad \text{and}$$

from an Arrhenius plot one can obtain $E_3-E_2/2$. Assuming E_2 to be approximately equal to zero one can thus obtain a value for E_3 .

In this way Trotman-Dickenson and Steacie found $E_3 = 9.7$ kcal./mole.

If now a foreign gas RH is introduced having abstractable hydrogen atoms, methane will be formed by the reaction



Provided methane and ethane are produced by no method other than reactions (2), (3), and (8) then

$$R_{CH_4} = k_3(CH_3) (AC) + k_8(CH_3) (RH)$$

$$R_{C_2H_6} = k_2 (CH_3)^2$$

and rearranging

$$R_{CH_4}/R_{C_2H_6} = (k_3/k_2^{\frac{1}{2}}) (AC) + (k_8/k_2^{\frac{1}{2}}) (RH)$$

$$k_8/k_2^{\frac{1}{2}} = 1/(RH) [R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}} - (k_3/k_2^{\frac{1}{2}}) (AC)]$$

Thus all quantities on the right hand side are found experimentally except $k_3/k_2^{\frac{1}{2}}$ which can be determined from the experimental results of Trotman-Dickenson and Steacie, and hence $k_8/k_2^{\frac{1}{2}}$ can be found at

any temperature. Utilizing the former relationship for rate constants one can write:

$$\log (k_8/k_2^{\frac{1}{2}}) = \text{const} - \frac{(E_8 - E_2/2)}{2.303 RT}$$

Plotting $\log k_8/k_2^{\frac{1}{2}}$ vs. $1/T$ one obtains a straight line of slope

$$-(E_8 - E_2/2)/2.303R = -E_8/2.303R$$

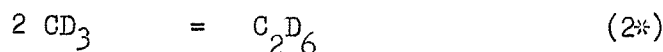
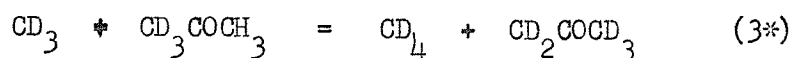
The most important feature of acetone as a source of methyl radicals is that over a wide temperature range ethane is produced only by reaction (2) and methane only by reaction (3). However acetone has many intrinsic advantages over other sources of methyl radicals.

- a) Between 100-250°C it has a quantum yield which within experimental error is unity. Hence the formation of carbon monoxide according to reaction (1) provides a convenient internal actinometer and check on the number of radicals released.
- b) The acetonyl radicals is stabilized by resonance, and when it does decompose it forms ketene and a methyl radical and does not provide an alternative source of methane or ethane.
- c) Acetone is convenient experimentally because it is thermally stable, chemically inert, has a vapour pressure of about 15-20 cm. at room temperature and does not attack stop cock grease.
- d) Acetone has a broad absorption band in the ultraviolet and has a moderate extinction coefficient. Therefore corrections for the effective reaction volume being smaller than the size of the cell are much less important than if mercury alkyls were used.

An alternative approach to determine the activation energy of reaction (8) utilized by Trotman-Dickenson and Steacie (21) was to

photolyze mixtures of deuterioacetone in the presence of hydrocarbons. It was used to determine the activation energy of the hydrogen abstraction reaction (j) where RH was an amine. This was done by the same authors (22) and their results are recorded in Table I.

This method depends on the use of a mass spectrometer. In this case the reactions producing ethane and methane are:



where the asterisk differentiates between deuterated and normal acetone and products. In the absence of the foreign gas RH one can write:

$k_3^* / k_2^* = R_{\text{CD}_4} / R_{\text{C}_2\text{D}_6}^{\frac{1}{2}} (\text{AC}^*)$. From an Arrhenius plot it is then a simple matter to find E_3 . In the presence of a foreign gas RH

$$k_8^* / k_3^* = R_{\text{CD}_3\text{H}} (\text{AC}^*) / R_{\text{CD}_4} (\text{RH})$$

Determining the ratio of $R_{\text{CD}_3\text{H}} / R_{\text{CD}_4}$ mass spectrometrically it is possible to evaluate k_8^* / k_3^* and thus find E_8^* .

Considering the activation energies of only the hydrocarbons listed in Table I, a definite classification into three groups is possible on the basis of their structure. When the methyl radical reacts with a compound containing only primary hydrogen atoms, the activation energy is about 10 kcal./mole; primary and secondary hydrogen atoms - about 8.2 kcal./mole; primary, secondary and tertiary hydrogen atoms - less than 8 kcal./mole.

The interpretation of the results obtained with alcohols and amines was more difficult according to the authors (22) because of some doubt as to which hydrogen atom was being removed. When it was

TABLE I

THE ABSTRACTION OF HYDROGEN ATOMS BY METHYL RADICALS

Compound	E Kcal./mole	Compound	E Kcal./mole
Ethane	10.4	Methylamine	8.4
2,2, - Dimethyl propane	10.0	Dimethylamine	7.2
2,2,3,3, - Tetramethyl- butane	9.5	Trimethylamine	8.8
n - Butane	8.3	Ammonia	10.0
n - Pentane	8.1		
n - Hexane	8.1	Methyl ether	9.5
2, Methyl Propane	7.6	Isopropyl ether	7.3
2,3 - Dimethyl butane i)	6.9	1 - Butyne	9.1
ii)	7.8	2 - Butyne	8.6
2,3,4 - Trimethyl pentane	7.9	Acetone	9.7
Ethene	10.0	Benzene	9.2
Propene	7.7	Toluene	8.3
2 - Butene	7.7	Methanol	8.2
2 - Methyl propene	7.3	Ethanol	8.7
2,3, Dimethyl - 2 - butene	7.8	Isopropanol	7.3
1 - Pentene	7.6		
1 - Butene	7.6		
3 - Methyl - 1 - butene	7.4		
Cyclopropane	10.3		
Cyclobutane	9.3		
Cyclopentane	8.3		
Cyclohexane	8.3		

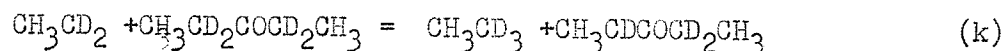
doubtful whether a radical abstracted a hydrogen atom by the rupture of an O-H or C-H bond as in alcohols, or an N-H or a C-H bond as in amines, it was supposed that the C-H bond was preferentially ruptured. This has been shown to be incorrect in some cases at least. The matter will be considered in greater detail when the reactions of amines are discussed.

According to McNesby and Gordon (23) there should be no difference between the activation energies determined using CH_3 or CD_3 radicals. They did, however, find an activation energy difference of 1.64 ± 0.08 kcal./mole for the abstraction of deuterium and hydrogen atoms from acetone by CD_3 radicals.

ii) Ethyl Radicals

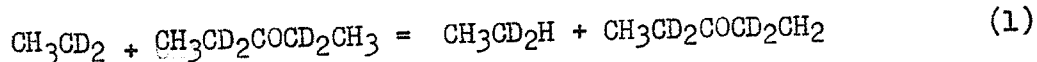
The fact that there was comparatively little quantitative information about the reactions of ethyl radicals was due to two reasons, the difficulty of finding a satisfactory source of ethyl radicals, and the increased complexity of their reactions compared to methyl radicals even at low temperatures (24,25). More recently these difficulties have been overcome.

The work of Kutschke, Wijnen and Steacie (26) has fairly well established the kinetics of the diethylketone photolysis. Utilizing these results to explain the mechanism of the photolysis of diethylketone Wijnen and Steacie (11) in studying the photolysis of 2,2',4,4' tetradeuteriodiethyl ketone ($\text{CH}_3\text{CD}_2\text{COCOD}_2\text{CH}_3$) found that the activation energy for the abstraction of a secondary deuterium atom, in the reaction



was 8.7 kcal./mole. The activation energy for the abstraction of a primary hydrogen atom in the reaction

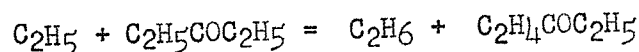
(20)



was found to be 11.7 kcal/mole.

Since the bond dissociation energy for $\text{C}_2\text{H}_5 - \text{H}$ is about 3-4 kcal/mole. less than for $\text{CH}_3 - \text{H}$ one would expect hydrogen abstraction reactions with ethyl radicals to be about 3-4 kcal./mole. less exothermic than the corresponding reactions with methyl radicals.

The work of Ausloos and Steacie (27, 12) confirms the fact that hydrogen abstraction by ethyl radicals does require more energy than by methyl radicals. In order to compare the activation energies they studied the reactions of methyl and ethyl radicals with the same compound RH under similar experimental conditions. In the one case they utilized azomethane, and azoethane as a photochemical source of methyl and ethyl radicals respectively. For the reactions



they found activation energies of 7.0 and 7.6 kcal./mole. respectively.

In a later work on the photolysis of methylethylketone (12) in which both methyl and ethyl radicals were formed they found activation energies for the abstraction of hydrogen atoms from the ketone by methyl radicals of 7.4 ± 0.1 kcal./mole, and for ethyl radicals 8.0 ± 0.1 kcal./mole. Thus they found a difference of 0.6 ± 0.2 kcal./mole in both cases.

Only very recently have ethyl radical abstraction reactions been studied in some detail by Boddy and Steacie (28,29). The photolysis of 3 - pentanone - d_{10} was used as a source of deuterated ethyl radicals. The activation energies of their hydrogen abstraction

reactions with neo-pentane, n-butane and iso-butane were then determined to be 12.6 ± 0.7 , 10.4 ± 0.75 and 8.9 ± 0.6 kcal./mole respectively. The results obtained when compared with the analogous reaction with methyl radicals indicated that there was a change in reactivity of about an order of magnitude as one goes from primary to secondary to tertiary hydrogen atoms. Also in each case the ethyl radical abstraction reaction had a higher activation energy than the methyl radical reaction.

In the second part of their work Boddy and Steacie (29) reacted CD_3 radicals with hydrogen, n-hexane and cyclohexane and found activation energies for H atom abstraction to be 11.5, 10.1, and 10.4 ± 0.5 kcal./mole respectively. Though somewhat disturbing, it is interesting to note that ethyl radicals seem to react relatively faster with hydrogen than with hydrocarbons when compared to the methyl radical reactions with the same reactants. The rate constant per secondary hydrogen atom as obtained from the work on n-hexane, when corrected for the presence of the six primary hydrogen atoms, is in excellent agreement with the rate constant per secondary hydrogen atom obtained from the work on n-butane at the same temperature. The rate constant for the reaction of ethyl radicals with cyclohexane under comparable conditions agrees with the comparable methyl radical results giving a value typical of secondary paraffinic hydrogen atoms.

c) Decomposition of Free Radicals

Radicals larger than methyl can decompose into smaller radicals and atoms even at moderate temperatures. This is of considerable importance to an understanding of the reaction mechanisms of many chain reactions.

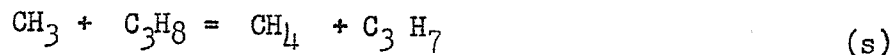
Bywater and Steacie (30,31,32) have been responsible for the most extensive investigations on the decomposition of free radicals. From a study of the mercury photosensitized reactions of ethane, propane, n-butane, and isobutane they determined the decomposition reactions of the ethyl, propyl, n-butyl, and isobutyl radicals. On the basis of their work they obtained the activation energies for the following reactions.

			E. kcal./mole
C_2H_5	$= C_2H_4 + H$	(m)	39.5
C_3H_7	$= C_2H_4 + CH_3$	(n)	20.0
C_3H_7	$= C_3H_6 + H$	(o)	38
iso $-C_4H_9$	$= C_4H_8 + H$	(p)	40
n $-C_4H_9$	$= C_2H_4 + C_2H_5$	(q)	23
n $-C_4H_9$	$= C_3H_6 + CH_3$	(r)	23

The ethyl radical was found (30) to be stable up to temperatures of about 400°C. Above this temperature an increase in hydrogen production gave quantum yields above unity and suggested a chain mechanism. An elementary reaction which regenerated a chain carrying hydrogen atom met the requirement.

Experiments with propyl radicals at high pressures indicated that the propyl radicals were stable up to 300°C. Above 300°C appreciable amounts of methane were formed and a large increase in hydrogen production occurred. The latter result was best explained by postulating a chain reaction with hydrogen atoms as chain carriers. Since the production of methane was accompanied by a roughly equivalent amount of ethylene, reaction (n) was postulated as the source of methane

when followed by



The work on the various butyl radicals indicated that these radicals were stable up to 250°C. In the case of the n-butyl radical appreciable amounts of methane, ethane, ethylene, and propylene were formed above 250°C. in addition to hydrogen and a heavy fraction produced at all temperatures. The reactions (q) and (r) adequately explain the appearance of the additional products when the ethyl and methyl radical formation are followed by hydrogen abstraction reactions. For the iso-butyl radical no C₂ fraction was observed though a sharp rise in hydrogen formation was obtained. Since the two possible branched chain radicals produced by the decomposition of the isobutyl radical could not split to form C₂ products without extensive rearrangement their absence is not unexpected. The increase in hydrogen formation to give quantum yields above unity is explained by including the decomposition reaction of the isobutyl radical (p).

From a consideration of the various radical decomposition reactions Trotman-Dickenson (33) pointed out that the majority of unimolecular decompositions of free radicals fall into two classes. The first class comprises those decompositions in which the radicals lose methyl radicals and have activation energies of 15-35 kcal./mole (n, q, r). The second class is composed of those reactions in which a hydrogen atom is lost and have activation energies around 40 kcal./mole (m, o, p). The difference in activation energy for these two classes of decompositions is of the same order as the difference between the strengths of the C-C and C-H bonds.

One of the difficulties encountered in studying the free radical decompositions is due to the fact that they occur only at high temperatures when other side reactions tend to complicate the interpretation of data. It appears that, other things being equal, the larger the radical the lower the temperature at which decomposition begins.

An additional radical decomposition reaction which has received considerable attention is the decomposition of radicals formed by hydrogen abstraction or formed by the rupture of a bond following a primary step in a photolysis (32). Depending upon the radical undergoing decomposition the activation energy for these type of radicals varies from 10-20 kcal/mole.

d) Addition Reactions

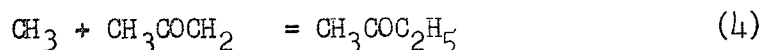
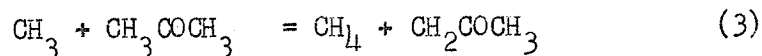
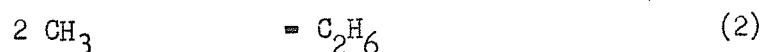
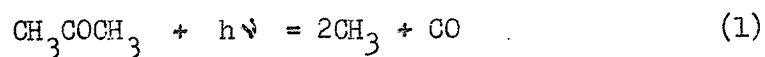
This type of reaction is one of the most difficult to investigate. In the presence of an unsaturated compound, in a reaction system containing atoms or free radicals, addition reactions such as the following occur.



The reason for the difficulty in investigating such reactions is due to the many additional reactions which become possibilities when a large radical is the product of the addition reaction. Thus in the above example in addition to methyl radical recombination, and hydrogen abstraction reactions the following reactions may also occur; the propyl radicals may dimerize to hexanes, disproportionate to propylene and propane, decompose to either a methyl radical and ethylene or to a hydrogen atom and propylene, or add to ethylene to form a pentyl radical, which also may react in many ways. Then also methyl radicals may abstract a

hydrogen atom from ethylene to form vinyl radicals leading to other reactions. In addition the tendency of unsaturated hydrocarbons to polymerize further complicates the determination of kinetic details. In many cases a study of the addition type reaction is simplified by keeping the concentration of unsaturated hydrocarbon at a minimum so that side reactions are effectively eliminated. Rate constants for the addition type reaction have been determined for the addition of methyl and ethyl radicals to unsaturated compounds.

Mandelcorn and Steacie (34) have studied the addition of methyl radicals to unsaturated hydrocarbons. Utilizing acetone as a source of methyl radicals they found the rate of addition by three different methods: the first two depending on obtaining a material balance for the methyl radicals and third depending upon measuring the consumption of the unsaturated reactant. All the methyl radicals produced in the photolysis of acetone can be accounted for by the following four reactions (35).



Hence to within 3% (35) $(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R_{\text{MEK}})/R_{\text{CO}} = 1.90$

In the presence of an olefin addition also occurred and therefore,

$$(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R_{\text{MEK}} + R_{\text{A}}')/R_{\text{CO}} = 1.90$$

where R_{A}' is the rate of formation of propyl radical if the olefine is ethylene and where the other rates are those in the presence of the

olefine and are not the same as the rates in its absence. Since it is possible to measure all the rates except R_A' , the rate of addition can be calculated from the above relationship. This method, however, ignores the consumption of methyl radicals by the combination with propyl radicals and hence would lead to an activation energy somewhat lower than the true activation energy for the addition reaction.

The second method is based on the assumption that most of the methyl radicals released form either ethane or methane and a negligible amount of methyl ethyl ketone. The same relationship utilized in the first method was used again neglecting only R_{MEK} . This method would result in a higher activation energy for the addition reaction than the first.

The third method is based on the assumption that one and only one molecule of olefine is converted into a higher boiling hydrocarbon for each methyl radical which reacts with an olefine. Since there are other reactions such as further polymerization and reaction with acetyl radicals leading to removal of unsaturated molecules, this method will give an upper limit for the rate of addition and hence a lower limit for the activation energy of the addition reaction.

Since the last method is independent of the other two the extent to which the results agree is an indication of their validity. In studies that have been conducted thus far, agreement is quite good. The activation energies for the addition of methyl radicals to ethylene, propylene, acetylene and butadiene were found to be 7.0, 6.0, 5.5, and approximately 2.5 kcal./mole respectively.

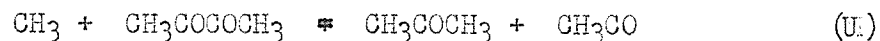
More recently James and Steacie (36) have extended the

knowledge of addition type reactions by conducting study of the rate of addition of ethyl radicals to unsaturated hydrocarbons. They used a method similar to the first of the above three methods. The problem with which they were mainly concerned was the correlation between the structure of an olefine and energy of activation for the addition of the radical to that olefine. Selecting hydrocarbons as representatives of the classes: 1 - alkyne, 1 - alkene, and 2-methyl, 1 - alkene they found activation energies of 8.8 ± 0.4 , 7.0 ± 0.2 , and 5.7 ± 0.9 kcal/mole respectively. The absolute value for the addition rate constant for 1- heptene was found to be $k = 3.2 \times 10^{-13}$

$$(\exp(-8000 \pm 700)/RT \text{ cc}^3 \text{ mole}^{-1} \text{ sec}^{-1}).$$

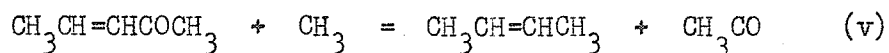
e) Free Radical Displacement Reactions

Usually vapour phase free radical reactions had been classified as one of abstraction, disproportionation, recombination, addition or decomposition. Some good evidence has been obtained by Blacet and Bell (37) for another type of free radical process. A free radical abstracts a portion of the molecule rather than only an atom, to form a stable molecule and a free radical. In a study of the photolysis of biacetyl Blacet and Bell proposed the following reaction in order to explain the large yields of acetone above 80°C.



The activation energy for this unusual reaction was determined as 5.6 kcal/mole. Below 80°C this reaction did not take place. The mechanism has been confirmed in an indirect manner by Ausloos and Steacie (13).

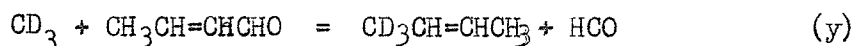
A more extensive study conducted by Pitts and co-workers (38,39) has given direct proof for the occurrence of such reactions. Using acetone as a source of methyl radicals they postulated the following reaction sequence when reacted with trans-methyl propenyl ketone.



Such a sequence would obviously have chain properties. This accounted for two anomalous experimental facts; a) the yield of 2 - butene was increased seven fold when the photolysis of trans-methyl propenyl ketone was conducted in the presence of acetone (CH_3 radical source); b) a quantum yield of carbon monoxide of 1.43 obtained in the photolysis of the mixture of acetone and trans-methyl propenyl ketone as compared to a quantum yield of 1.00 and 0.5 respectively for the pure ketones.

In the absence of a chain mechanism the quantum yield of carbon monoxide would be expected to fall somewhere between 1.00 and 0.5.

In order to test the mechanism of these unusual "free radical displacement or inversion" reactions (40) Pitts and co-workers (39) reacted CD_3 radicals with methyl propenyl ketone and other α - β unsaturated compounds. Under those conditions which resulted in high yields of 2 - butene (high acetone - d_6 conc.) they expected large amounts of $\text{CD}_3\text{CH}=\text{CHCH}_3$ when CD_3 radicals reacted with trans-methyl propenyl ketone if their mechanism was correct. A 2-butene product consisting of 78% $\text{CD}_3\text{CH}=\text{CHCH}_3$ conclusively established the free radical displacement reaction. A further test of the mechanism led to additional evidence when the free radical displacement reaction



was found by analysis to produce C_4 olefine which was solely



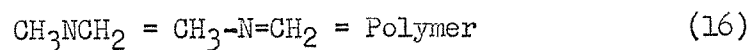
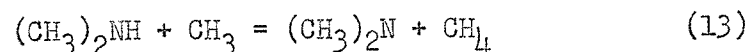
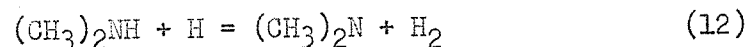
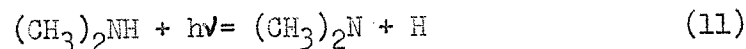
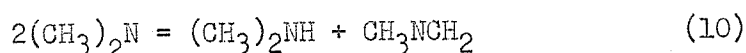
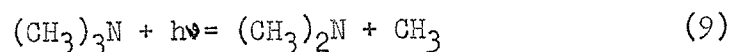
In an electron bombardment study on some aliphatic amines and alcohols by Collin (41, 42), bond breakage probabilities were calculated. The results indicated that the $C_1 - C_2$ bond adjacent to the functional group was the weakest. Hence it was postulated by Kozak and Gesser (43) that aliphatic amines and alcohols could possibly undergo free radical displacement reactions at high temperatures with the cleavage occurring at the $C_1 - C_2$ bond. In some unpublished work by Dr. Gesser in this laboratory methyl radicals reacted with ethyl alcohol did not lead to an increase in ethane formation at high temperatures as would be expected if the free radical displacement reaction occurred. On the other hand this does not mean that the $C_1 - C_2$ bond is not weak but rather that conditions were not extreme enough to result in breakage. The work on amines shall now be considered in greater detail.

GAS PHASE REACTIONS OF AMINES

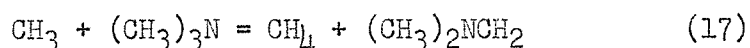
Though relatively little work has been done on the reactions of amines an increasing amount of literature has been accumulating. Among the earliest investigations of the photochemical decompositions of amines was a study of ethyl and methyl amine conducted by Emeleus and Jolly (44). The principal gaseous products found were hydrogen, methane, nitrogen, and small amounts of ethane. No attempt was made to propose a mechanism for their formation. A further study by Emeleus and Taylor (45) established ammonia as a product of the photochemical decompositions of both methyl and ethyl amine. They also suggested a mechanism in which the primary step was production of hydrogen atoms followed by hydrogen abstraction to form diatomic hydrogen gas and decomposition of the amine radical to yield ammonia. In a more recent

investigation by Johnson and Taylor (46) the primary process was confirmed and the possibility of ethylene diamine as an intermediate was considered. They suggested that this intermediate would undergo further photolysis as well as react with hydrogen atoms, thus leading to an unstable polymer formed by two radicals of ethylene diamine less a hydrogen atom. This would then decompose to yield ammonia. No positive proof for the ethylene diamine was found. Following the work of Emeleus and Taylor (45) a more extensive study was conducted by Bamford (47) to elucidate the nature of the primary act as well as the secondary processes for all three types of aliphatic amines. For primary and secondary amines the primary act was the production of hydrogen atoms and alkylamino or dialkylamino radicals respectively. Tertiary amines on irradiation split off an alkyl group. The primary process for primary and secondary amines was later confirmed by Booth and Norrish (48) by an examination of the photochemical reactions undergone by both ammonia and the amines. In both cases the rupture of an N-H bond leading to formation of H atoms was consistent with this mechanism.

For the photolysis of trimethylamine Bamford (47) suggested the following reaction scheme to account for the observed products from which ammonia was absent.

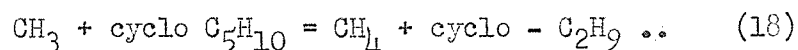


The photolysis of trimethylamine was studied recently by Gesser, Mullhaupt and Griffiths (49). They pointed out that since the activation energy of reaction (13) $E_{13} = 7.2$ kcal./mole (22), the possibility of a reaction

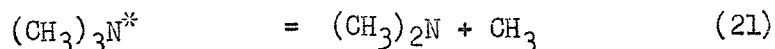
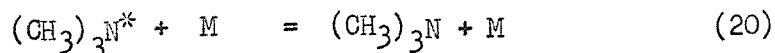
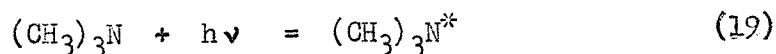


could not be neglected since $E_{17} = 8.8$ kcal./mole was not much higher. The probability of reaction (17) occurring compared to the probability of reaction (13) occurring is enhanced when one considers the comparatively high concentration of trimethylamine as compared to the much lower concentration of dimethylamine produced as the result of a secondary process.

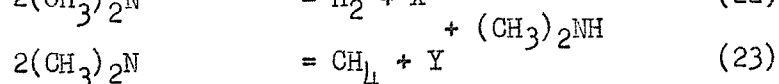
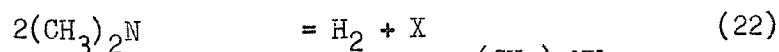
The presence of a subsidiary primary act leading to formation of H atoms was also shown to be extremely doubtful. If reaction (11) was correct then addition of a hydrocarbon having a low activation energy for H abstraction should have increased the rate of formation of hydrogen gas. Using cyclopentane as such a hydrocarbon Gesser and co-workers found the rate of formation of hydrogen actually decreased on addition of cyclopentane. Hence they argued that if hydrogen is produced by a molecular decomposition process of an excited trimethylamine molecule this unusual behaviour can be explained, since the number of excited molecules would decrease on addition of a foreign gas. Also since methane and ethane were found to be products methyl radicals must have been present. In the presence of cyclopentane methyl radicals would form methane by the reaction



They found E_{18} to be 14.4 kcal./mole which was about 6.0 kcal./mole too high thus signifying an incomplete reaction mechanism. Again a reaction sequence involving an excited intermediate seemed to account for the results. Thus they proposed the following scheme:



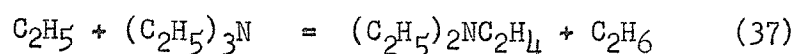
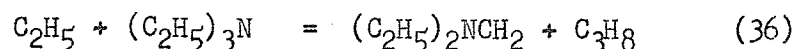
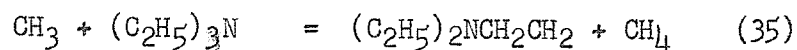
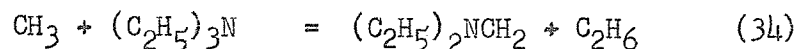
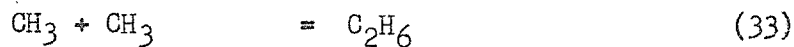
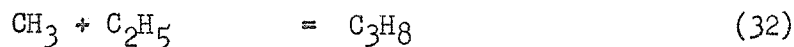
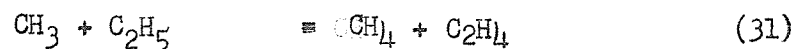
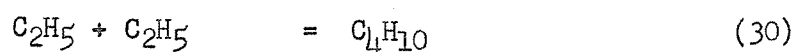
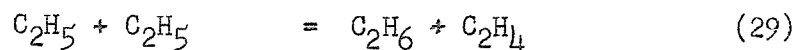
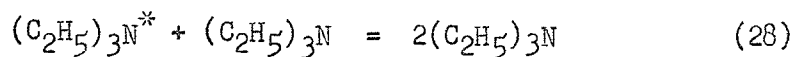
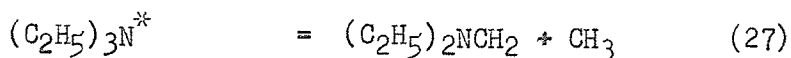
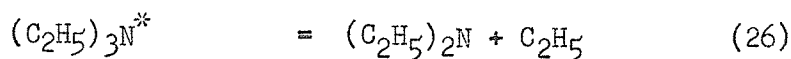
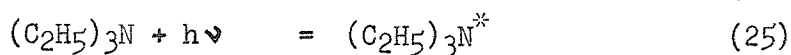
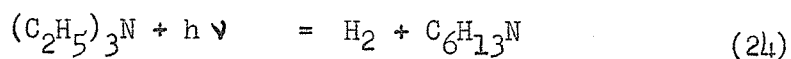
Since it seemed reasonable to assume that reaction (17) would not occur at low temperatures all methane and hydrogen would be formed by disproportionation of the dimethylamino radical while ethane was formed by methyl radical recombination. Hence Gesser and co-workers proposed that (19), (20), and (21) were followed by:



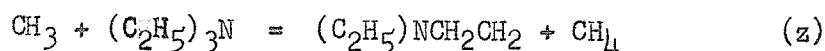
where X and Y are liquid products.

In order to see whether these reactions were common to tertiary amines a study of triethylamine was undertaken, by Kozak and Gesser (43). In order to explain these results a further study was initiated by reacting methyl radicals with triethyl and diethylamine.

In the photolysis of triethylamine the gaseous products were identified as hydrogen, methane, ethane, ethylene, propane, and butane. At low temperatures the rate of formation of products, with the exception of molecular hydrogen, in general decreased with increasing pressure of the reactant. This is analogous to the results obtained for trimethylamine and indicated that the products, except for hydrogen, were formed by dissociation of an excited triethylamine molecule which could be pressure quenched. When the photolysis was conducted in the presence of nitric oxide the rate of formation of all products except hydrogen was decreased. Hence they concluded that hydrogen was formed via a molecular process whereas the hydrocarbon products were formed by free radical reactions involving probably both methyl and ethyl radicals. In keeping with these facts the following sequence was postulated:

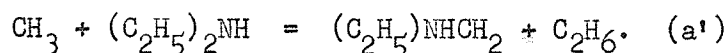


The study on the reaction of methyl radicals with triethylamine and dimethylamine was begun for three reasons: 1) Since the hydrogen abstraction reaction has fairly low activation energy one would expect the following reaction to occur,



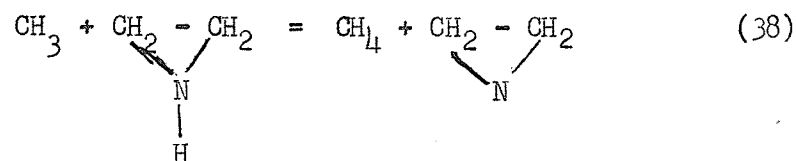
thus yielding the triethylamino radical. If hydrogen was formed by the decomposition of this radical then the same source would have to be taken into account in the triethylamine photolysis since the same radical was thought to be a product (note reactions (35) and (37)). No hydrogen was found in the methyl radical study and hence the only

source of hydrogen in the triethylamine photolysis would be reaction (24). 2) The study of diethylamine with methyl radicals was undertaken in order to see whether the methyl radical in the photolysis of triethylamine was produced by the decomposition of the diethylamino radical. 3) The diethylamine with methyl radical study was also to lend support to the free-radical displacement reactions (34) and (36). If they did occur one would expect a reaction such as



at high temperatures. An Arrhenius plot of $\log k_{\text{CH}_4}/k_{\text{C}_2\text{H}_6}^{1/2}$ vs. $1/T$ would then dip at high temperatures due to an increase in ethane formation. That the curve did dip seemed to indicate that reactions (34) and (36) did occur. Some later unpublished work by Dr. Gesser in this laboratory in which ethyl radicals were reacted with triethylamine seemed to disprove this since no propane was found. Add to this the aforementioned work on ethyl alcohol with methyl radicals and one must conclude that the free radical displacement reaction probably does not occur under the conditions of the studies.

Some interesting work arose from this work as well as the work of Brinton and Volman (50). The latter authors found that on reacting methyl radicals with ethylenimine they obtained an activation energy of 4.8 kcal./mole for the reaction



They assumed that the nitrogen-hydrogen was being abstracted as shown. Gesser and co-workers on their work (43,49) with methyl radicals obtained activation energies for the reactions:

	E kcal./mole
$\text{CH}_3 + (\text{CH}_3)_3\text{N} = \text{CH}_4 + (\text{CH}_3)_2\text{NCH}_2$ (b')	8.0
$\text{CH}_3 + (\text{C}_2\text{H}_5)_3\text{H} = \text{CH}_4 + (\text{C}_2\text{H}_5)_2\text{NC}_2\text{H}_4$ (c')	5.3
$\text{CH}_3 + (\text{C}_2\text{H}_5)_2\text{NH} = \text{CH}_4 + \text{C}_2\text{H}_5\text{NHC}_2\text{H}_4$ (d')	5.7

Since the energy of activation for the abstraction reaction by methyl radicals with triethylamine was of the same order as that for dimethylamine and ethylenimine Gesser and Kozak suggested that the same type of hydrogen atom was being abstracted in each case. This would seem to indicate that the nitrogen hydrogen in ethylenimine was not the one being abstracted but rather one of the hydrogens attached to a carbon atom.

In a more recent work by Brinton (51) it was established that the nitrogen hydrogen was indeed the active one in ethylenimine. Using t-butyl ethylenimine the rate of abstraction of H atoms by methyl radicals was reduced to about 10% of the rate using ethylenimine. Also an activation energy of 6.6 kcal./mole for the hydrogen abstraction from t-butyl ethylenimine by methyl radicals indicated that a different hydrogen atom was abstracted from t-butyl ethylenimine than from ethylenimine. Using di-tert-butyl peroxide as a source of methyl radicals over the limited temperature range of 124 - 157°C Brinton (51) obtained activation energies for hydrogen atom abstraction for the following compounds:

	E kcal./mole
Methylamine	7.6
Ethylamine	7.1
Dimethylamine (DMA)	7.2
Diethylamine (DEA)	7.2
Diisopropylamine (DIA)	7.8
Ethylenimine	4.8
t-butyl ethylenimine	6.6

Trotman-Dickenson and Steacie (22) found that the activation energy for hydrogen abstraction reactions in hydrocarbon systems were quite sensitive to the type of carbon attached to the abstractable hydrogen. Thus comparing hydrocarbons having six, four, and two abstractable hydrogen atoms to amines having a like number, one would expect any trends in the former to be similar to the latter compounds. Thus for ethane, 6 abstractable hydrogens (primary) $E=10.4$ kcal./mole, n-butane 4 abstractable hydrogens (secondary) $E=8.3$ kcal./mole and 2,3 dimethyl butane, 2 abstractable hydrogens (tertiary) $E=6.9$ kcal./mole. However, for the analogous amines DMA, 6 abstractable hydrogens (primary), DEA, 4 abstractable hydrogens (secondary) and DIA, two abstractable hydrogens (tertiary), Brinton found activation energies which were almost identical for the three amines. He therefore concluded that the similarity in activation energies was due to all three amines being secondary ones and that the N-H bond was the active one. A consideration of the rate of abstraction of hydrogen atoms per "active" hydrogen also indicated that the side chain hydrogens of the amines do not participate in the abstraction process.

From the data of Brinton given above and those of Kozak and Gesser (43) it is evident that a wide discrepancy exists between their values for the activation energy for hydrogen abstraction by methyl radicals from DEA. Kozak and Gesser found a value of 5.7 kcal./mole as compared to 7.2 kcal./mole as determined by Brinton, who in this work (51) made an effort to correlate the two values. He suggested that the free radical displacement reaction (a') would occur at low temperatures as well as at high temperatures. Since both studies neglected the effect of reaction (a') the one in which experimental conditions maximize the

probability of the occurrence of this reaction will be in error by the greater amount. An increase in methyl radical concentration will favour the formation of ethane via recombination of methyl radicals and hence minimize the relative contribution of reaction (a'). An increase in diethylamine concentration will increase the probability of reaction (a') and decrease the formation of ethane via recombination. Thus the latter effect would be to increase the error. Brinton showed that the concentration of methyl radicals did lead to an error for both studies though in opposite directions. Since the concentration of DEA was about ten times as great for Kozak and Gesser the error in neglecting reaction (a') will be about ten times as great in their work. This explanation of the discrepancy is of course in error, for reasons mentioned before, and is included only for the sake of completeness.

EXPERIMENTAL

Apparatus and Materials

a) Apparatus

The apparatus (see Figure I) was of conventional high vacuum design and gave a limiting pressure of 10^{-6} mm. of mercury. The apparatus was constructed of pyrex brand glass except for the reaction cell, which was made of quartz. Mercury float valves and stopcocks were used to separate different portions of the apparatus. A high vacuum was produced by means of a two stage mercury diffusion pump and a mechanical fore-pump operating in series.

Reaction Cell

The reaction cell (see Figure II) was a cylindrical quartz vessel with a radius of 2.5 cm. and a length of 10 cm., with plane quartz windows at either end. It was joined to the system by two quartz to pyrex graded seals. The cell was enclosed in a cylindrical brass block open at both ends. The brass block was about 2 cm. longer than the reaction cell at each end so as to minimize the heat loss at the windows. Heating wires were enclosed in an asbestos mat around the brass block. The temperature of the cell was controlled manually to $\pm 1^\circ\text{C}$ by means of a variable transformer. The temperature of the reaction cell was measured by means of a thermometer, set in a well in the brass block, and was checked occasionally by three copper-constantan thermocouples. These thermocouples were placed between the cell wall and the brass block at either end and in the middle of the reaction cell. Voltage measurements for these and other thermocouples were made on a Leeds and Northrup Portable Precision Potentiometer (No. 2745). The volume of the reaction cell was 196 cc. and the volume of the connecting tubing and stirrer

FIGURE I
APPARATUS - ANALYTICAL LINE

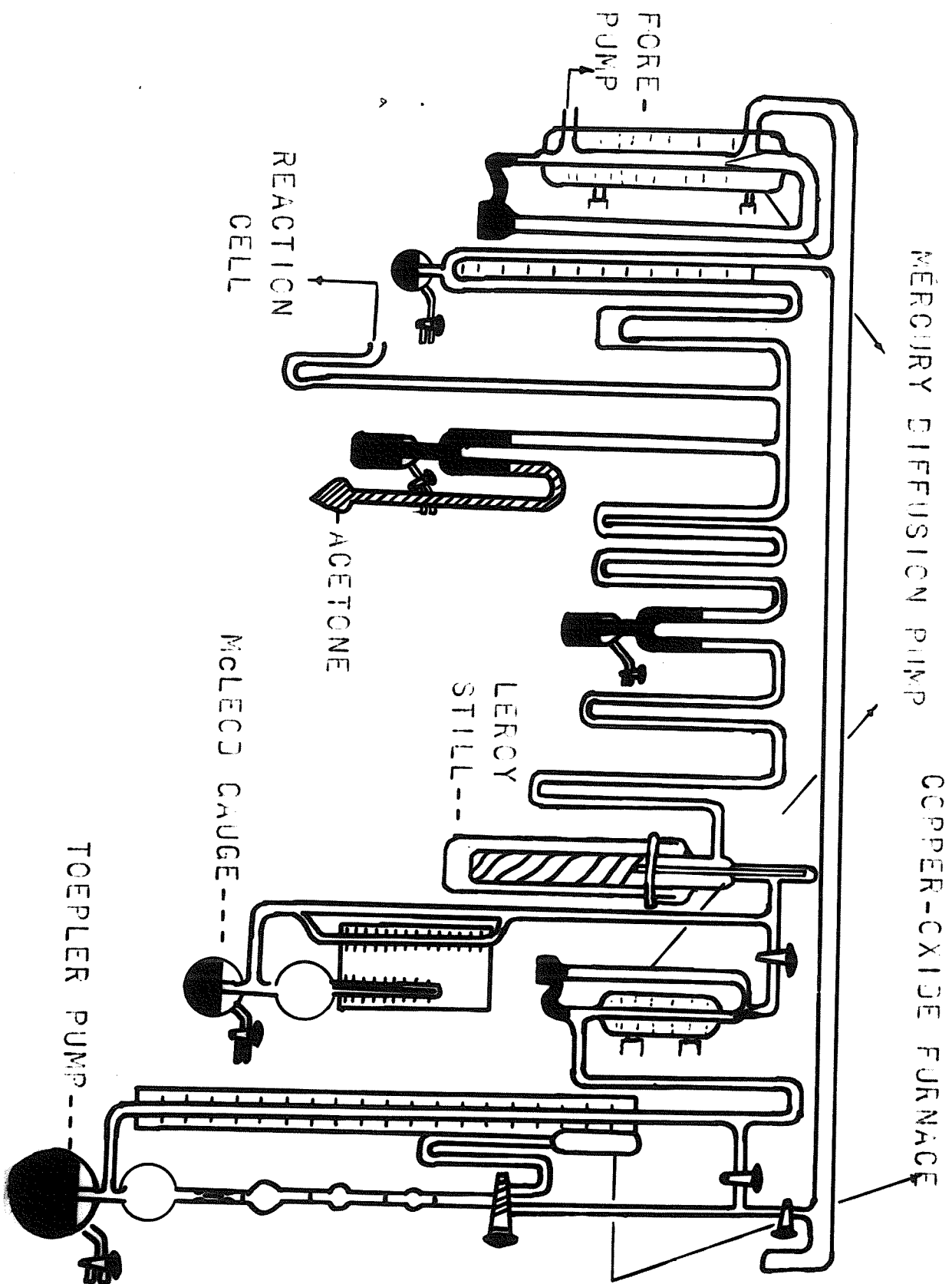
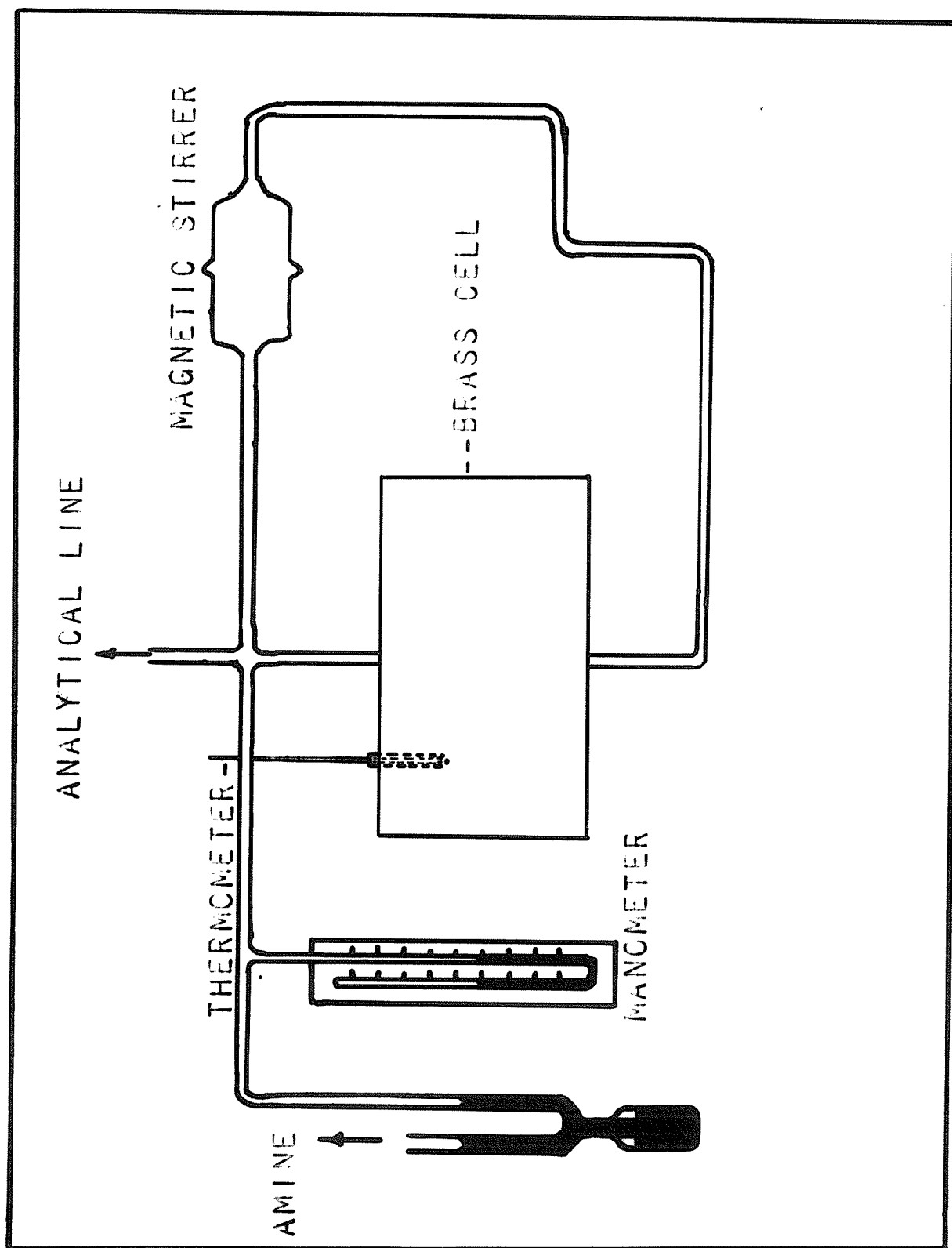


FIGURE II
APPARATUS - REACTION CELL



was 100 cc. A small manometer joined to the connecting tubing, was used to determine the pressure of the reactants in the reaction cell to an accuracy of ± 0.5 mm. The reaction cell assembly was enclosed in a box made of fiberboard. A heater was used to control the temperature of the air surrounding the reaction cell, stirrer and connecting tubing in those cases where pressures of reactants, greater than their vapour pressures at room temperatures, were used. A small glass stirrer was placed between the cell and the connecting tubing and was used to mix the reactants prior to the reaction.

The source of radiation was a Hanovia S-500 medium pressure mercury arc. The light was collimated with a quartz lens and a stop. The almost parallel beam filled the cell. A Corning pyrex filter (No. 7740) was employed to prevent photolysis of the amines and limit the effective light to $3130\text{\AA}$. The intensity of the lamp was controlled manually by keeping the current constant in the primary circuit at 9.0 ± 0.5 amps.

Analytical System

The analytical system consisted of cold traps used for the separation of the gaseous products from the reactants and liquid products; a LeRoy still (52) used for the separation of non-condensables from the other gaseous products and for the fractional distillation of the gaseous products condensable in liquid nitrogen; a McLeod gauge; and a small mercury diffusion pump used for transferring the gases to a combined Toepler pump and gas buret. For analysis of the various components of the gaseous products, a copper - copper-oxide furnace (53) and a micro-hydrogenation unit (54) were used.

b) MaterialsAcetone

Acetone was obtained from Eastman Organic Chemicals and was of "spectro" grade. It was previously (55) redistilled from anhydrous copper sulfate through about thirty theoretical plates at a reflux ratio of 10:1. A middle portion boiling at 56.5°C was collected and stored in a brown ground glass stoppered bottle over anhydrous copper sulfate. After subjecting the acetone to a bulb to bulb distillation the middle fraction was retained. It was stored in a blackened bulb behind a mercury cut-off.

Ethylenimine

Ethylenimine was obtained from Matheson, Coleman, and Bell and was 98-100% pure. It was distilled from reagent grade sodium hydroxide pellets through about thirty theoretical plates at a reflux ratio of 10:1. A middle fraction boiling at $55.5 \pm 0.1^{\circ}\text{C}$ was collected and stored over sodium hydroxide pellets. The first and last fractions were discarded. The imine was subjected to one bulb to bulb distillation and then stored over sodium hydroxide pellets behind a mercury cut-off.

N - Methyl Ethylenimine

The imine was obtained from Monomer Polymer Laboratories. It was distilled from reagent grade sodium hydroxide pellets through about thirty theoretical plates at a reflux ratio of about 10:1. A middle fraction boiling at $24.0^{\circ} \pm 0.2^{\circ}\text{C}$ was collected and stored over sodium hydroxide pellets. Discarding the first and last fractions the imine was subjected to a bulb to bulb distillation and stored over sodium hydroxide pellets at dry ice - acetone temperatures behind a mercury cut-off.

N - Ethyl Ethylenimine

The imine was obtained from BIOS Laboratories. The imine was taken as obtained, subjected to one bulb to bulb distillation. The middle fraction was taken and stored at dry ice - acetone temperatures behind a mercury cut-off.

Triethylamine

Triethylamine was obtained as a 25% aqueous solution from Eastman Organic Chemicals and was of the "white label" grade. It was distilled from anhydrous barium oxide through about thirty theoretical plates (55) at a reflux ratio of about 10:1. A middle portion boiling at 89°C was collected and stored in a brown ground glass stoppered bottle over anhydrous barium oxide. After one bulb to bulb distillation with the retention of the middle fraction the amine was stored behind a mercury cut-off.

EXPERIMENTAL PROCEDURE

The same type of experiment was performed with all the amines or imines. Methyl radicals produced by photolysis of acetone were reacted with ethylenimine, n-methyl ethylenimine, n-ethyl ethylenimine, and triethylamine. In order to check the apparatus and the validity of the results of Trotman - Dickenson and Steacie (18) a few experiments on the photolysis of acetone alone were conducted.

Before any of the reactants were introduced, the apparatus was evacuated to a pressure of 10^{-6} mm. of mercury. In each case the nitrogen containing compound was introduced into the cell first in the following manner. The compound was condensed with liquid nitrogen and the mercury float was lowered. The compound was then allowed to expand slowly into the reaction cell. The pressure in the cell was measured by the small

manometer adjoining the cell. When the pressure of the amine reached the desired value the cell was closed off by raising the mercury float valve. The acetone was then expanded slowly into the line in the same manner as the amine was allowed to expand into the cell. The temperature and pressure of the acetone on the line were recorded. Both the acetone and amine were then condensed with liquid nitrogen in the line and cell respectively. The mercury float valve connecting the line and the cell was then lowered. The acetone was then allowed to expand into the cell where it was condensed with the amine. The two reactants were degassed together by three bulb to bulb distillations at -155°C and then returned to the cell. On expanding the two reactants, a reading of the pressure of both gases permitted a simple calculation of the pressure of acetone in the cell. A knowledge of the effective volume ratio, determined for each cell temperature, between the line and cell permitted a check of the pressure of reactants after the reaction period.

The non-condensable products of the reaction were separated from the condensable products at liquid nitrogen temperatures by five liquid nitrogen traps in series. The gaseous products were separated from the reactants and any liquid products by subjecting them to two trap to trap distillations at a temperature of -155°C .

The gaseous products volatile at -155°C were pumped through the analytical system by the small mercury diffusion pump. Products volatile at -196°C (methane and carbon monoxide) were pumped into the combined Toepler pump and gas buret, and measured as such. They were then introduced into the copper - copper-oxide furnace, maintained at a temperature of 210°C , where carbon monoxide was oxidized to carbon dioxide. The remaining gas was withdrawn at a temperature of -196°C and measured as methane. The liquid nitrogen was replaced by a bath

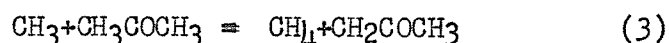
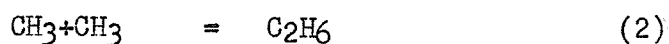
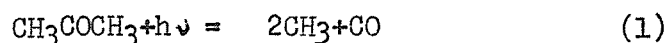
at -100°C and the carbon dioxide withdrawn and measured as the volume of carbon monoxide introduced. A balance with the first measurement of non-condensibles indicated the absence of hydrogen. The liquid nitrogen trap holding back condensibles was then removed and the LeRoy still was set at -180°C . The ethane then distilled over into the combined gas buret and Toepler pump and was measured as such. When the presence of ethylene was suspected the analysis for it was conducted in the following manner. A known amount of hydrogen was introduced into the catalytic chamber followed by the C_2 mixture. After sufficient time had elapsed for complete hydrogenation, generally one-half hour, the ethane was condensed in liquid nitrogen and the excess hydrogen was pumped back into the gas buret and measured. The contraction in the volume of hydrogen was a measure of the quantity of ethylene in the mixture.

In order to check for the presence of C_3 and C_4 hydrocarbons the temperature of the LeRoy still was then set at -155°C and -145°C respectively.

RESULTS AND DISCUSSION

Acetone Photolysis:

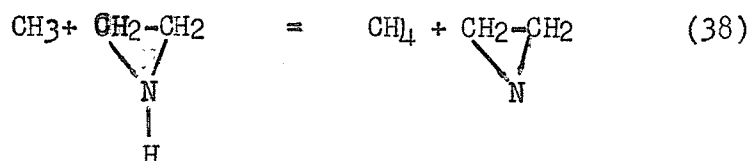
The results of the photolysis of acetone alone are recorded in Table II. As suggested earlier the products of the photolysis of acetone between the temperatures of 100-260°C can be accounted for by the following 3 reactions:



The variation of $k_3/k_2^{\frac{1}{2}}$ with temperature was determined by Trotman-Dickenson and Steacie (18,21) and a plot of their results is reproduced along with the present results in Figure III. The values of $k_3/k_2^{\frac{1}{2}}$ so obtained were compared with the results of Trotman-Dickenson and Steacie. From Figure III it can be seen that the agreement is quite good.

Methyl Radicals with Ethylenimine

The results of the reaction of methyl radicals with ethylenimine are given in Table III. Up to temperatures around 210°C the gaseous products can be accounted for by the three reactions already given for photolysis of acetone plus one additional reaction leading to formation of methane.



Since the rate of formation of methane in the presence of a compound

TABLE II
THE PHOTOLYSIS OF ACETONE

Run	Temp. °C.	Conc. of Acetone	R_{CH_4}	$R_{C_2H_6}$	R_{CO}	$k_3/k_2^{\frac{1}{2}}$	Time (sec.)
1	120	17.8	29.5	18.4	19.1	3.83	3600
10	225	16.5	20.6	8.20	24.5	43.6	1800
14	150	17.6	5.82	13.9	18.7	8.85	3600
32	210	13.1	10.5	6.00	15.0	32.6	3600
41	120	11.7	1.41	8.70	16.3	4.08	3600
42	120	11.4	1.26	8.00	8.93	3.90	3600

The concentration of acetone is expressed as molecules/cc.
 $\times 10^{-17}$; the rates of formation as molecules/cc./sec. $\times 10^{-12}$ and
 $k_3/k_2^{\frac{1}{2}}$ is multiplied by a factor of 10^{13} .

FIGURE III
THE PHOTOLYSIS OF ACETONE
 $\text{LOG } k_3/k_2^{\frac{1}{2}} \text{ VS } 1/T$

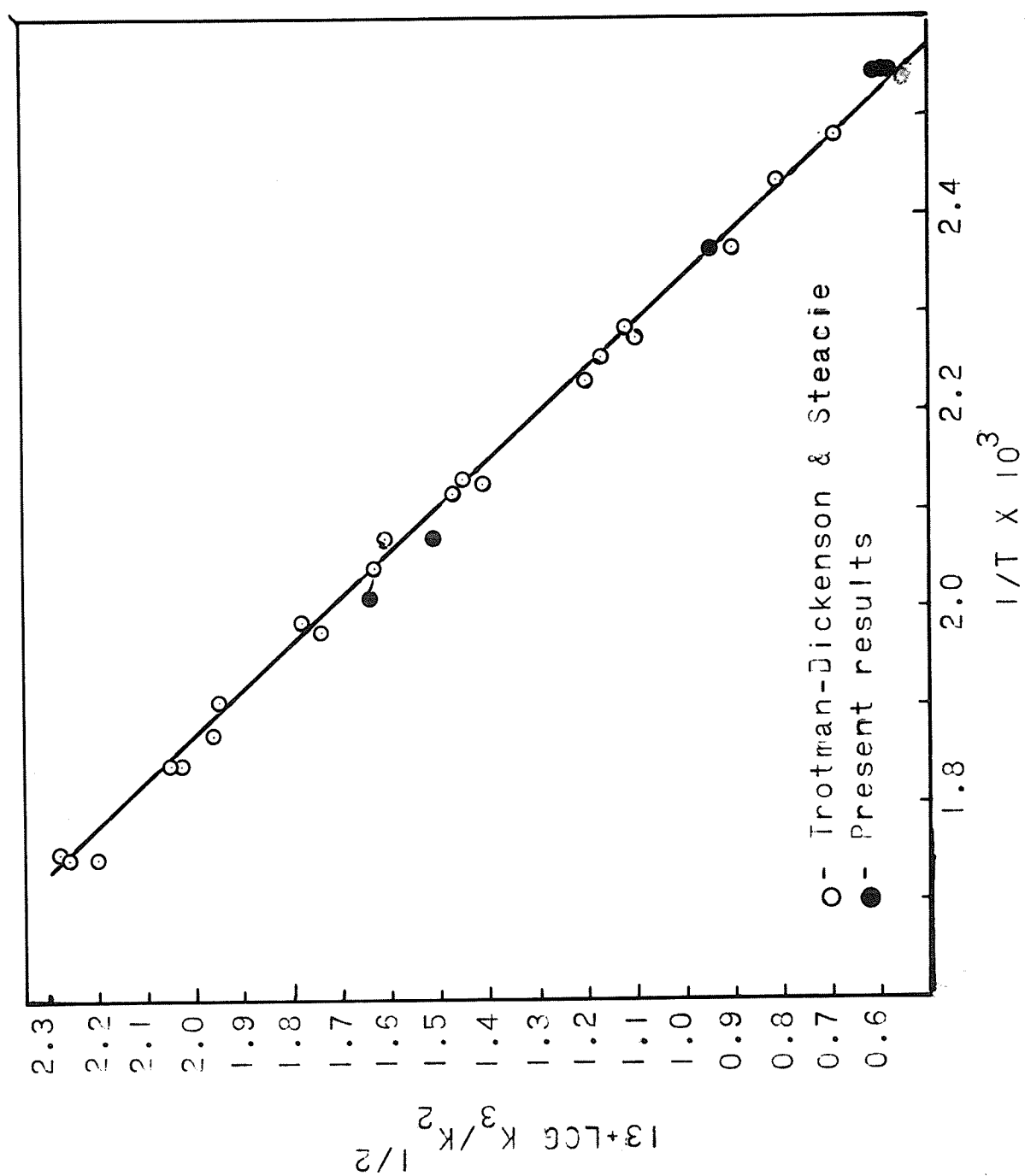


TABLE III
REACTION OF METHYL RADICALS WITH
ETHYLENIMINE

Run	Temp. °C.	Conc. EI	Conc. Acet.	R_{CH_4}	$R_{C_2H_6}$	R_{CO}	$k_3/k_2^{\frac{1}{2}}$	$k_{38}/k_2^{\frac{1}{2}}$	Time (sec.)
2	120	14.7	16.8	26.7	1.72	16.1	3.83	1.32	3600
3	148.5	8.00	16.6	32.5	3.02	21.0	8.40	2.24	3600
4	180	7.00	15.3	38.2	2.50	24.1	18.2	3.03	1800
5	200	7.00	17.0	57.4	2.17	11.8	35.1	4.69	1800
6	250	dark reaction found to be less than 1/10 %							
7	250	6.20	11.6	36.8	1.24	20.2	78.5	3.87	1800
8	260	6.30	14.7	44.6	1.03	24.6	94.3	4.80	1800
9	225	6.40	16.4	42.8	1.80	23.8	49.0	3.75	1800
11	225	6.40	16.2	41.7	1.86	11.6	49.0	3.55	1800
12	150	7.00	16.9	28.5	2.26	18.8	8.40	2.52	1800
13	240	4.50	16.2	40.0	2.14	23.0	66.4	3.68	3600

The concentration of ethylenimine and acetone is expressed as molecules/cc. $\times 10^{-17}$; the rates of formation as molecules/cc./sec. $\times 10^{-12}$; $k_3/k_2^{\frac{1}{2}}$ is multiplied by a factor of 10^{13} and $k_{38}/k_2^{\frac{1}{2}}$ by a factor of 10^8 .

containing an abstractable hydrogen is the sum of reactions (3) and (38) one can obtain $k_{38}/k_2^{\frac{1}{2}}$ as indicated in the introduction:

$$k_{38}/k_2^{\frac{1}{2}} = \left[R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}} - (k_3/k_2^{\frac{1}{2}}) (Ac) \right] / (EI)$$

where (EI) is the concentration of ethylenimine. In this manner $k_{38}/k_2^{\frac{1}{2}}$ could be calculated at various temperatures at which an experiment was conducted. A plot of $\log k_{38}/k_2^{\frac{1}{2}}$ vs $1/T$ is shown in Figure IV. The activation energy for reaction (38), calculated from the slope of this curve is 4.8 ± 0.5 kcal./mole if one assumes the activation energy for the recombination reaction is zero with $\log A_{38} = 10.4$. This value is the same as that obtained by Brinton and Volman (50). At temperatures above 210°C results were erratic. The dip in the plot of $\log k_{38}/k_2^{\frac{1}{2}}$ vs $1/T$ does seem to indicate an additional reaction leading to C_2 hydrocarbon. An analysis of the C_2 fraction for ethylene was negative and hence the increase was taken to be due to formation of additional ethane. It should be pointed out that only a small amount of C_2 hydrocarbon was produced at high temperatures. Hence a small absolute error would result in a relatively large percentage error. A study consisting of several experiments conducted at constant temperature and varying imine pressure should be undertaken to establish whether the high temperature points are real points or whether the error due to experimental difficulties in measuring small amount of gas is the cause of the erratic results.

Methyl Radicals with N-Methyl Ethylenimine

The results of the reaction of methyl radicals with N-methyl ethylenimine are recorded in Table IV. Up to temperatures around 190°C

FIGURE IV

THE REACTION OF METHYL RADICALS WITH ETHYLENIMINE

 $\text{LOG } k_{38}/k_2^{\frac{1}{2}} \text{ vs } 1/T$

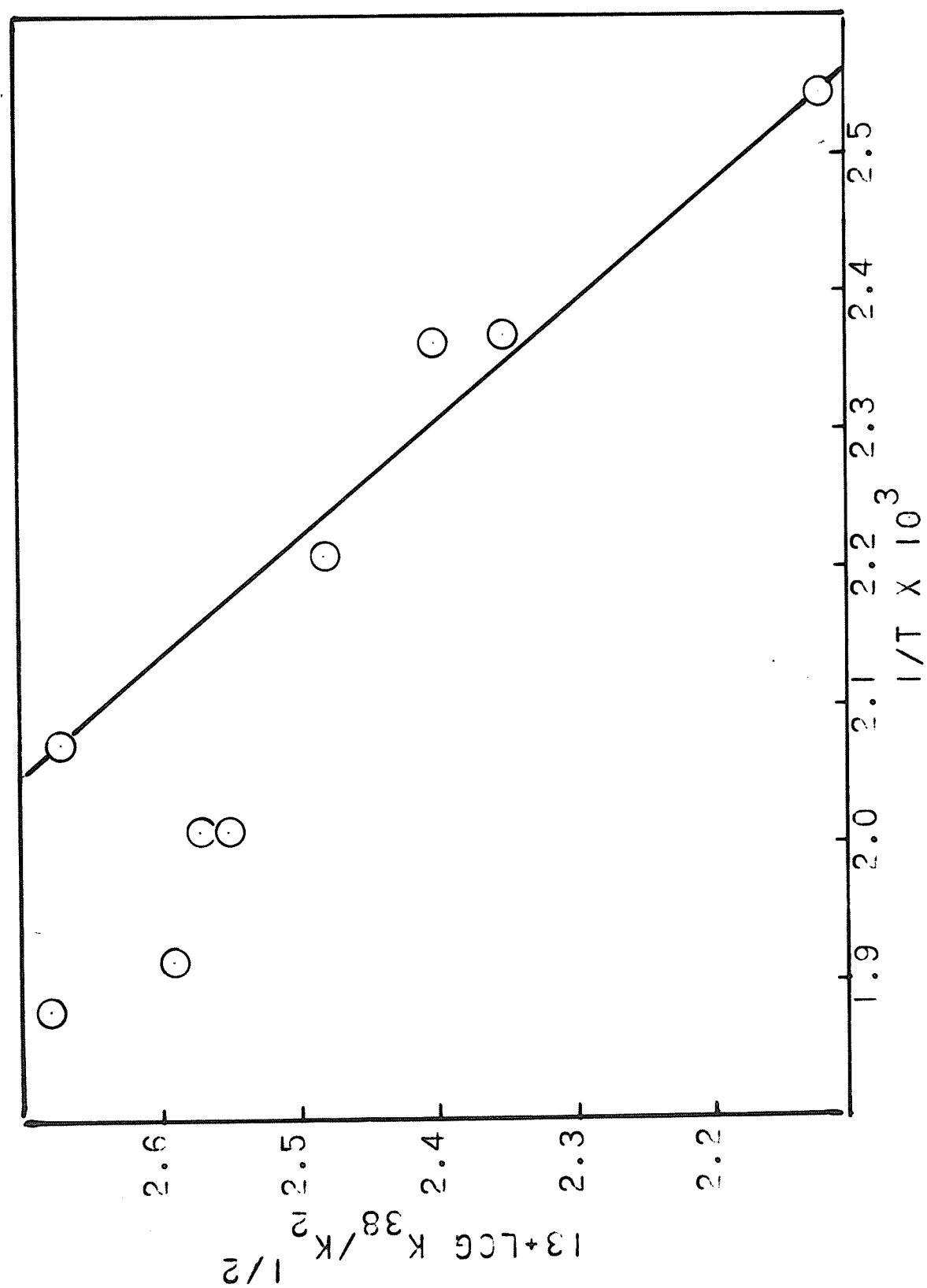
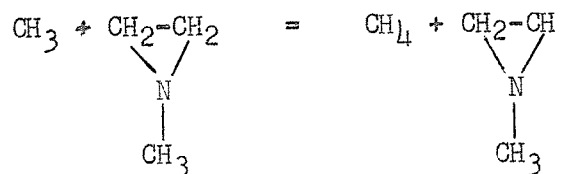


TABLE IV
REACTION OF METHYL RADICALS WITH N-METHYL ETHYLENIMINE

Run	Temp. °C.	Conc. N-MEI	Conc. Acet.	R_{CH_4}	$R_{C_2H_6}$	R_{CO}	$k_3/R_2^{\frac{1}{2}}$	$k_{39}/k_2^{\frac{1}{2}}$	Time (sec.)
15	150	6.50	17.0	6.80	13.4	18.5	8.60	6.15	3600
16	120	15.7	16.8	4.00	13.2	15.4	3.65	3.05	3600
17	180	12.8	14.7	11.9	11.5	17.5	15.7	9.45	3600
18	210	12.0	13.6	17.1	9.50	17.9	36.4	5.26	1800
19	195	12.7	14.0	15.7	9.40	16.9	26.0	10.7	3600
20	135	14.1	16.0	4.70	12.8	16.3	5.62	2.84	3600
21	135	14.2	16.5	4.90	13.0	16.5	5.62	2.96	3600
22	135	14.3	16.1	3.00	11.9	16.5	5.62	-ve	3600
23	210	11.8	13.9	15.0	8.80	17.3	36.4	2.46	3600
25	120	11.7	15.8	2.70	11.6	13.7	3.65	1.53	3600
26	150	14.1	15.2	5.10	11.5	15.6	8.40	2.86	3600
27	165	10.0	13.8	7.00	10.6	15.5	12.7	3.90	3600
28	135	13.4	16.6	4.50	12.4	16.0	5.62	2.54	3600
29	180	13.5	14.2	10.6	10.5	16.9	15.7	4.52	3600
30	210	10.3	13.1	14.6	8.90	16.2	36.4	1.46	3600
31	120	10.9	18.6	1.20	3.70	12.0	3.65	1.48	3600
33	210	9.30	12.8	13.1	6.70	18.4	36.4	4.50	1800

The concentration of N-MEI and acetone is expressed as molecules/cc. $\times 10^{-17}$; the rates of formation are expressed as molecules/cc./sec. $\times 10^{-12}$; $k_3/k_2^{\frac{1}{2}}$ and $k_{39}/k_2^{\frac{1}{2}}$ is multiplied by a factor of 10^{13} .

the gaseous products can be accounted for by the three reactions listed for the photolysis of acetone plus one additional reaction leading to formation of methane.



As before the ratio of $k_3/k_2^{\frac{1}{2}}$ is determined from the experimental results of Trotman-Dickenson and Steacie (Fig. III). Then as with ethylenimine one can obtain $k_{39}/k_2^{\frac{1}{2}}$ from the relationship:

$$k_{39}/k_2^{\frac{1}{2}} = \left[R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} - (k_3/k_2^{\frac{1}{2}}) (\text{AC}) \right] / \text{N-MEI}$$

where (N-MEI) is the concentration of N-methyl ethylenimine. In this manner $k_{39}/k_2^{\frac{1}{2}}$ could be calculated at various temperatures. A plot of $\log k_{39}/k_2^{\frac{1}{2}}$ vs $1/T$ is shown in Figure V. The activation energy for reaction (39) calculated from the slope of this curve is 6.7 ± 1.0 kcal./mole if one assumed the activation energy for the recombination reaction is zero with $\log A_{39} = 9.6$. This is in excellent agreement with Brinton's work (49) of 6.6 kcal./mole for abstraction of hydrogen atoms from t-butyl ethylenimine by methyl radicals. The dip in the curve at temperatures above 190°C again suggests an incomplete mechanism for ethane formation since no unsaturated C_2 fraction was found.

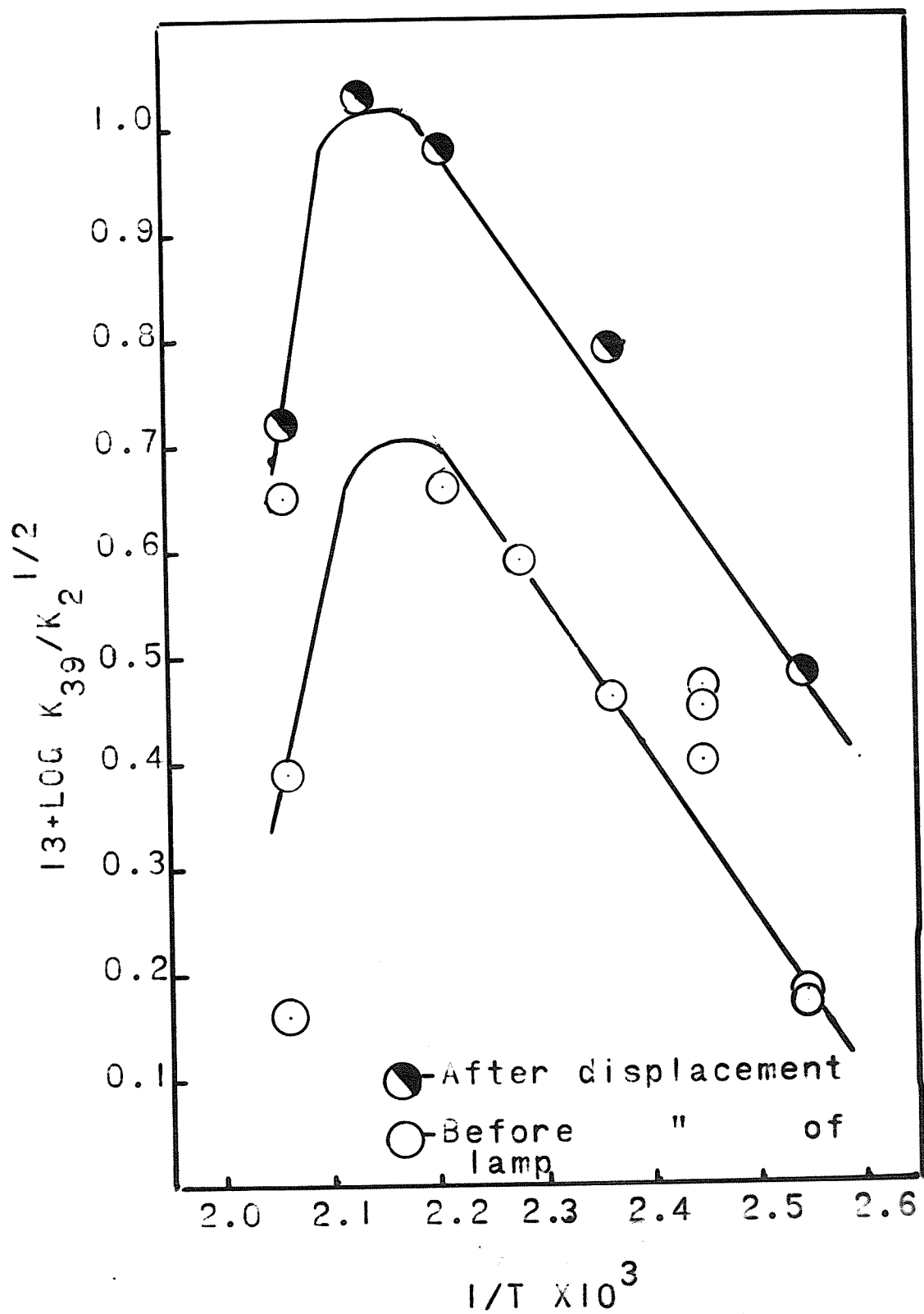
The manner in which reaction (39) is written makes it evident that the hydrogen abstracted is thought to be attached to a carbon atom of the ring. This postulate will be justified later.

From the plot of $\log k_{39}/k_2^{\frac{1}{2}}$ vs $1/T$ it can be seen that two parallel lines have been drawn. The justification for doing this is

FIGURE V

THE REACTION OF METHYL RADICALS WITH N-METHYL ETHYLENIMINE

 $\text{LOG } k_3/k_2^{\frac{1}{2}} \text{ vs } 1/T$



based on two observations. After a certain experiment all points lay above a line drawn previously. These points could be used to form an almost exactly parallel line when the best straight line was drawn through them. It is possible that the lamp was displaced somewhat between experiments thus resulting in a change in the effective reaction volume of the cell. Whereas the light beam was nearly parallel prior to such a displacement, thus almost utilizing the whole cell, this would not be the case after the lamp was disturbed.

It might be pointed out that these observations could not be made at the time of the experiments since no trend could be observed until several experiments had been performed.

The results of the work on n-methyl ethylenimine also confirms the conclusions made by Brinton (51) as to the type of hydrogen abstracted from ethylenimine. Since the ring hydrogens were equally exposed in both ethylenimine and N-methyl ethylenimine one would expect identical activation energies for hydrogen abstraction from either compound by methyl radicals, provided the ring hydrogens were the ones being abstracted in both cases. The difference of 1.9 kcal./mole between 4.8 kcal./mole and 6.7 kcal./mole is substantially greater than the experimental error and hence forces one to conclude that the nitrogen hydrogen is abstracted from ethylenimine.

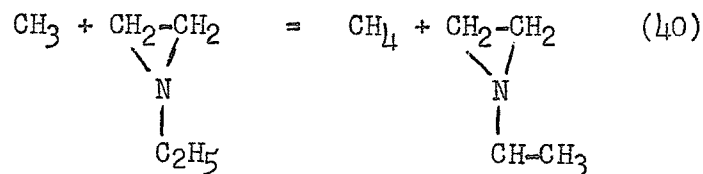
Methyl Radicals with N-Ethyl Ethylenimine

The results of the reaction of methyl radicals with N-ethyl ethylenimine are given in Table V. Up to temperatures of around 170°C the gaseous products could be accounted for by the three reactions given for the photolysis of acetone plus an additional reaction leading to formation of methane.

TABLE V
REACTION OF METHYL RADICALS WITH N-ETHYL ETHYLENIMINE

Run	Temp. °C.	Conc. N-EEI	Conc. Acet.	R_{CH_4}	$R_{C_2H_6}$	R_{CO}	$k_3/k_2^{\frac{1}{2}}$	$k_{40}/k_2^{\frac{1}{2}}$	Time (sec.)
35	120	12.8	14.0	3.76	8.67	9.61	3.65	6.02	3600
36	135	12.6	13.6	5.50	7.91	10.6	5.62	9.41	3600
37	150	13.3	13.6	7.81	9.31	11.4	8.40	10.6	3600
38	165	11.7	13.6	9.54	9.03	12.1	12.7	12.4	1800
39	180	11.6	12.9	12.5	6.90	12.8	18.2	21.0	3600
40	195	11.6	14.9	16.1	10.5	13.3	26.0	9.57	1800

The concentration of N-EEI and acetone is expressed as molecules/cc. $\times 10^{-17}$; the rates of formation are expressed as molecules/cc./sec. $\times 10^{-12}$ and $k_3/k_2^{\frac{1}{2}}$ as well as $k_{40}/k_2^{\frac{1}{2}}$ are multiplied by a factor of 10^{13} .



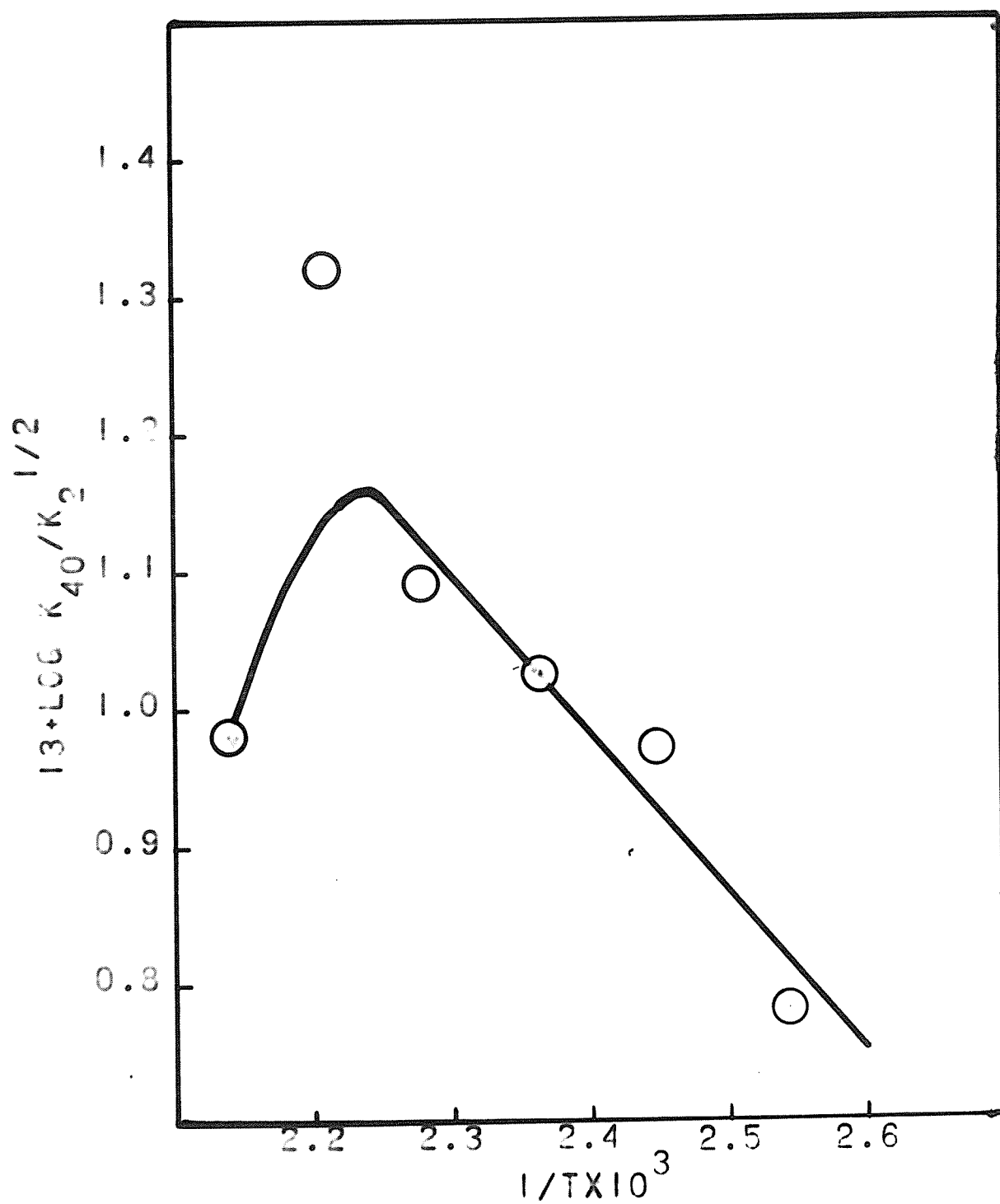
As before the value of $k_3/k_2^{\frac{1}{2}}$ is determined from Fig. III. Then

$$k_{40}/k_2^{\frac{1}{2}} = \left[R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} - (k_3/k_2^{\frac{1}{2}}) (\text{Ac}) \right] / (\text{N-EEI})$$

where (N-EEI) is the concentration of N-ethyl ethylenimine. A plot of $\log k_{40}/k_2^{\frac{1}{2}}$ vs $1/T$ is shown in Figure VI. The activation energy for reaction (40) calculated from the slope of this curve is 5.4 ± 1.0 kcal./mole if one assumes the activation energy for the recombination reaction is zero with $\log A_{40} = 9.5$. According to the results of Trotman-Dickenson Table I this value is not unexpected. They show that for hydrocarbons where all hydrogens are attached to carbon atoms, the activation energy for hydrogen abstraction is less for secondary hydrogens than for primary. Hence the similarity between the activation energy for hydrogen abstraction from ethylenimine and N-ethyl ethylenimine is entirely coincidental and not due to removal of similar hydrogens. The unusually low value of 4.8 kcal./mole for the former is due to the removal of a nitrogen hydrogen while the value of 5.4 ± 1.0 kcal./mole for the latter is explained on the basis of hydrocarbon structure. In this case a secondary hydrogen influenced by the proximity of the nitrogen atom is being abstracted.

The activation energy for hydrogen abstraction by methyl radicals from t-butyl ethylenimine is reported by Brinton as 6.6 kcal./mole. If the hydrogen being abstracted is attached to one of the methyls to the nitrogen atom, then one would expect a substantial lowering of

FIGURE VI
THE REACTION OF METHYL RADICALS WITH N-ETHYL ETHYLENIMINE
 $\text{LOG } k_{10}/k_2^{\frac{1}{2}} \text{ vs } 1/T$



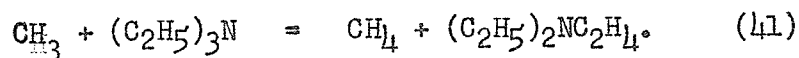
the activation energy for the same reaction with N-methyl ethylenimine where the methyl radical is $\propto$ to the nitrogen atom.

(Note E_{abs} from n-pentane is 8-1 kcal./mole). Since the abstraction of hydrogen atoms by methyl radicals requires 6.7 kcal./mole it appears that in this comparison similar hydrogens are being removed. This means that a ring hydrogen is being removed since these are the only hydrogens which are similiar in the two compounds.

Since abstraction of a ring hydrogen requires an activation energy of 6.7 kcal./mole, and since abstraction of a secondary hydrogen requires a smaller energy of activation than abstraction of a primary hydrogen the hydrogen attached to the carbon $\propto$ to the nitrogen atom but not in the ring is being removed when methyl radicals abstract hydrogens from N-Ethyl ethylenimine.

Methyl Radicals with Triethylamine

The results of the reaction of methyl radicals with triethylamine are given in Table VI. Over the limited temperature range of 120°-140°C. the gaseous products can be accounted for by the three reactions given for the photolysis of acetone plus an additional reaction leading to formation of methane.



As before the value of $k_3/k_2^{\frac{1}{2}}$ is determined from the results of Trotman - Dickenson and Steacie Fig. I.I.I.

Then

$$k_{41}/k_2^{\frac{1}{2}} = \left[\frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}} - (k_3/k_2^{\frac{1}{2}}) (\text{Ac}) \right] / (\text{TEA})$$

where (TEA) is the concentration of triethylamine.

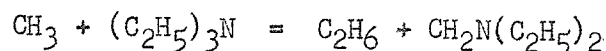
TABLE VI
REACTION OF METHYL RADICALS WITH TRIETHYLAMINE

Run	Temp. °C	Conc. TEA	Conc. ACET.	R_{CH_4}	$R_{C_2H_6}$	R_{CO}	$k_3/k_2^{\frac{1}{2}}$	$k_{41}/k_2^{\frac{1}{2}}$ (Fig. VII)	Time (sec.)
43	120	5.29	11.3	5.66	1.21	5.93	3.65		3600
44	120	10.1	12.1	6.05	0.54	4.80	3.65	84.9	3600
45	120	15.4	11.3	5.49	0.17	3.92	3.65		3600
46	130	5.31	12.2	6.80	1.27	6.48	4.68		3600
47	130	9.36	12.2	7.53	0.55	5.73	4.68	96.5	3600
48	130	16.1	12.4	7.35	0.21	4.86	4.68		3600
49	130	2.64	12.6	5.82	2.48	4.30	4.68		3600
50	120	2.58	12.8	5.00	2.10	6.48	3.65		3600
51	140	4.80	12.8	8.35	1.40	7.63	6.30		3600
52	140	9.85	13.4	9.20	6.02	6.65	6.30	136.0	

The concentration of TEA and acetone is expressed as molecules/cc $\times 10^{-17}$; the rates of formation are expressed as molecules/cc/sec. $\times 10^{-12}$ and $k_3/k_2^{\frac{1}{2}}$ as well as $k_{41}/k_2^{\frac{1}{2}}$ are multiplied by a factor of 10^{13} .

In this manner $k_{41}/k_2^{\frac{1}{2}}$ could be calculated for various temperatures. However, another method was utilized in this work and used to check the above mechanism.

The linearity of the $R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}(Ac)$ vs $(TEA)/(Ac)$ shows that the reaction



does not occur at 120-140°C and confirms the contention made earlier that Brinton's effort to reconcile the results of Kozak and Gesser (43) and Brinton (51) is not valid.

For each temperature several experiments at approximately constant acetone pressure were conducted at varying triethylamine pressure. Simply rearranging the expression for $k_{41}/k_2^{\frac{1}{2}}$ one obtains

$$(k_{41}/k_2^{\frac{1}{2}}) (TEA)/(Ac) + k_3/k_2^{\frac{1}{2}} = R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}(Ac)$$

A plot of $(TEA)/(Ac)$ vs $R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}(Ac)$ was then made Fig. VII. If the above equation is correct the slope of this curve would be $k_{41}/k_2^{\frac{1}{2}}$ and its intercept $k_3/k_2^{\frac{1}{2}}$. The value of the intercept should compare to the results of Trotman-Dickenson and Steacie Fig. 3. For each temperature a reasonably straight line could be drawn. Utilizing the values of $k_{41}/k_2^{\frac{1}{2}}$ thus found a plot of $\log k_{41}/k_2^{\frac{1}{2}}$ vs. $1/T$ was made Figure VIII. From the slope of this curve the activation energy for hydrogen atom abstraction by methyl radicals from triethylamine was determined as 6.7 ± 1.0 kcal./mole (with $\log A_{41} = 7.4$) as compared to 5.5 kcal./mole found by Kozak and Gesser. In the light of the results of the present study and the lower activation energy for hydrogen abstraction from DEA by Kozak and Gesser it would appear that their results may be consistently low. If one then considers the activation

FIGURE VII

THE REACTION OF METHYL RADICALS WITH TRIETHYLAMINE

$$10^{-13} \times R_{\text{CH}_4} / R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}(\text{Ac}) \text{ vs. } (\text{TEA})/(\text{Ac})$$

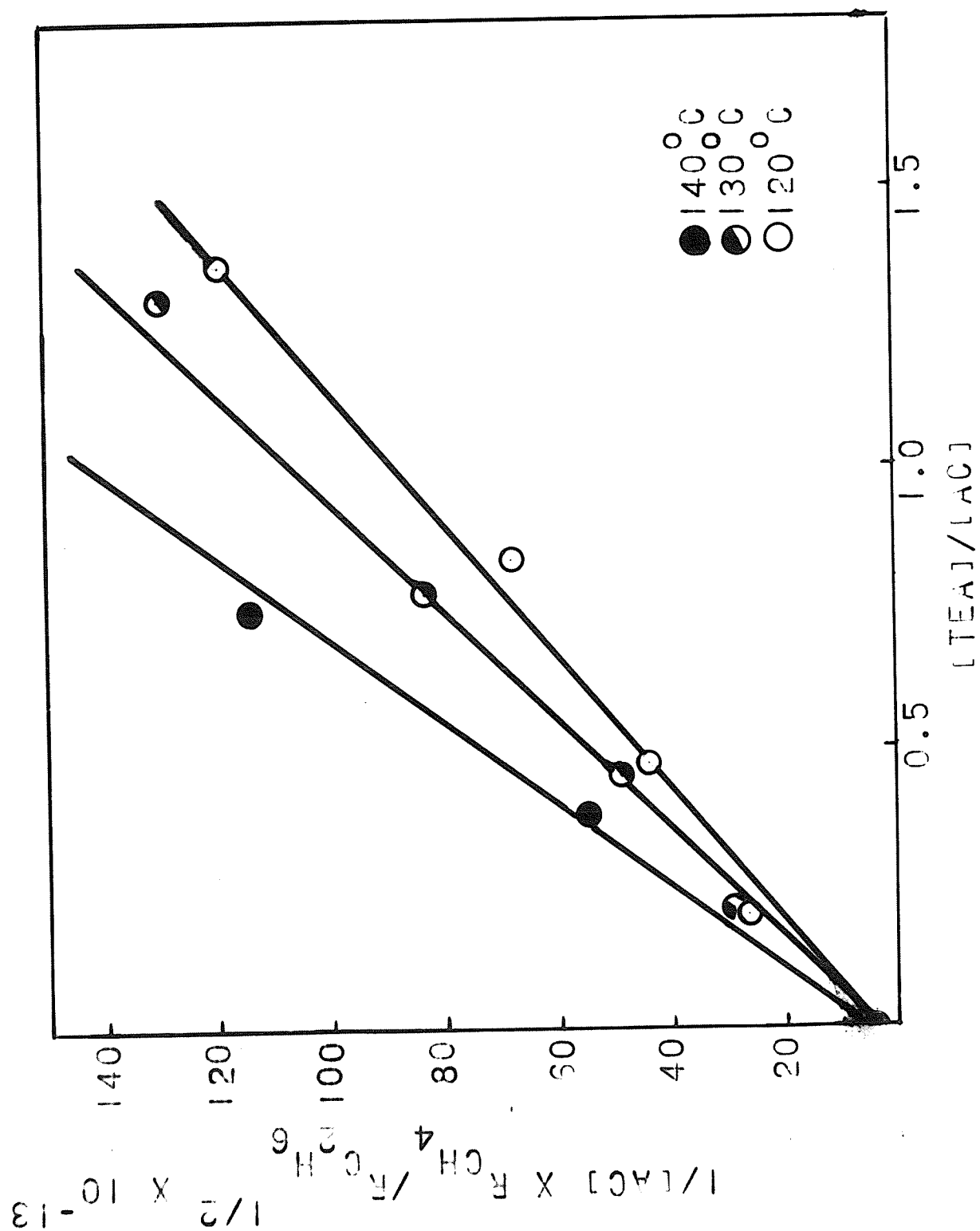
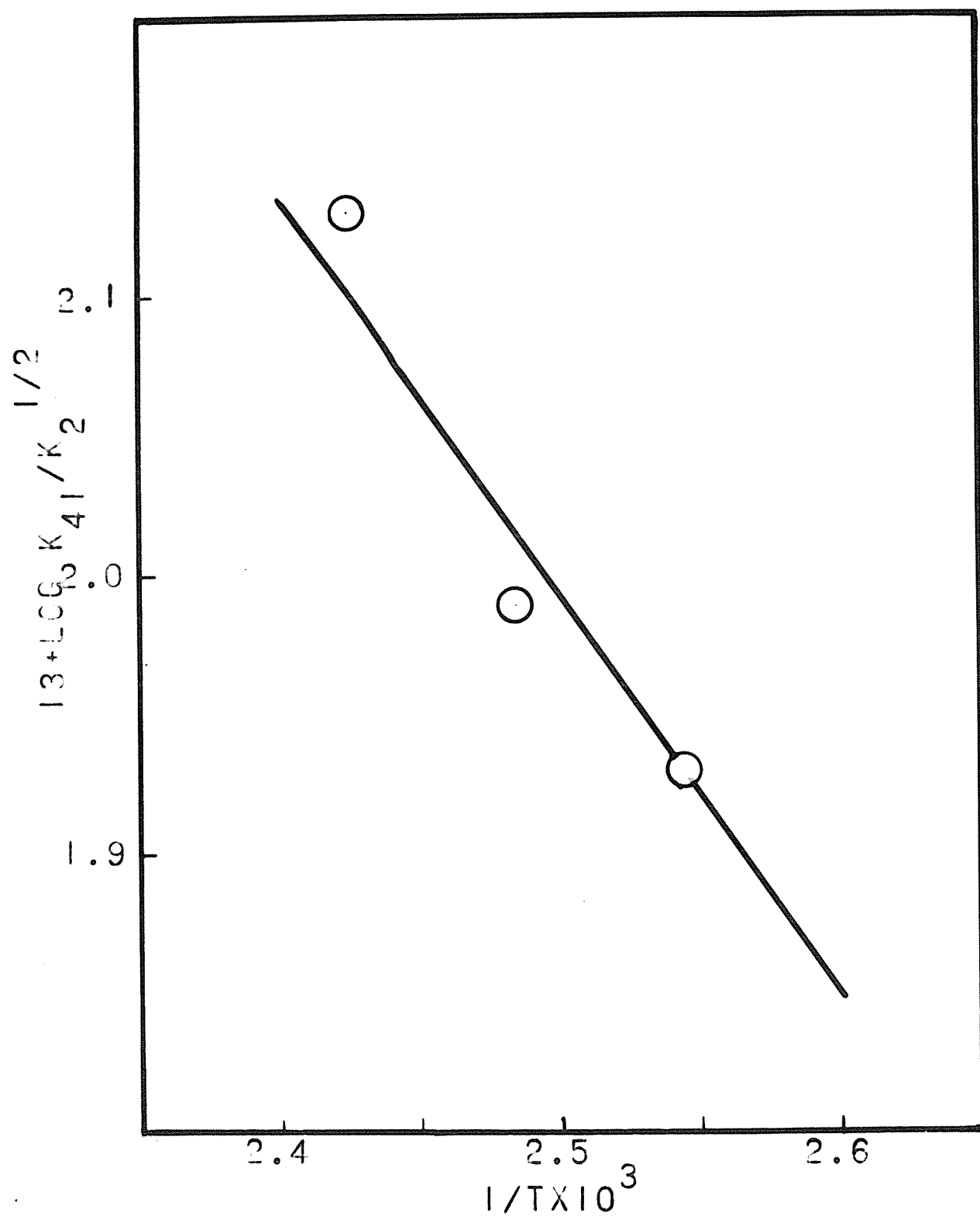


FIGURE VIII
REACTION OF METHYL RADICALS WITH TRIETHYLAMINE

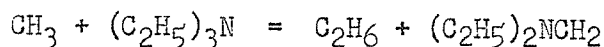
$$\text{LOG } k_{41}/k_2^{\frac{1}{2}} \text{ vs. } 1/T$$



energy for the hydrogen atom abstraction by methyl radicals from trimethylamine of 8.0 kcal./mole it appears that the general trend predicted by Trotman - Dickenson and Steacie (22) is obeyed by amines as well as hydrocarbons provided comparable hydrogens are being abstracted.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1. The activation energy for the abstraction of hydrogen atoms from ethylenimine by methyl radicals was determined as 4.8 ± 0.5 kcal./mole. The hydrogen abstracted was the nitrogen hydrogen.
2. The activation energy for the abstraction of hydrogen atoms from n-methyl ethylenimine by methyl radicals was determined as 6.7 ± 1.0 kcal./mole. The hydrogen abstracted was one of the ring hydrogens.
3. The activation energy for the abstraction of hydrogen atoms from n-ethyl ethylenimine by methyl radicals was determined as 5.4 ± 1.0 kcal./mole. The hydrogen abstracted was a secondary hydrogen on the ethyl side chain attached to the nitrogen.
4. The activation energy for the abstraction of hydrogen atoms from triethylamine by methyl radicals was determined as 6.7 ± 1 kcal./mole. The free radical displacement reaction



does not occur between $120^\circ - 140^\circ\text{C}$.

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