

THE PHOTOLYSIS OF TRIETHYLAMINE AND  
REACTION OF METHYL RADICALS WITH  
DIETHYLAMINE AND TRIETHYLAMINE

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by  
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April 1958



To My Wife

## ABSTRACT

The photolysis of triethylamine was investigated over a temperature range from 0°C. to 250°C. The products found were methane, hydrogen, ethane, ethylene, propane and butane. A mechanism is proposed to account for these products. The activation energies for the abstraction of hydrogen atoms by methyl radicals, from triethylamine and diethylamine were found to be 5.5 kcal./mole and 5.7 kcal./mole respectively, assuming that the recombination of methyl radicals has zero activation energy. The upper limit for the activation energy of the free radical displacement reaction of methyl radicals with diethylamine was determined as 16.2 kcal./mole.

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## INTRODUCTION

It is a well known fact that in the photolysis of a large number of gaseous substances free radicals are formed as intermediate products. When a molecule absorbs a quantum of light, several processes may occur. In most cases the increase in energy of the molecule results in the rupture of one or more bonds, thus yielding two or more fragments of the molecule or free radicals. The bond that is broken depends upon the energy of the radiation and the strength of the bond. Another process that may occur is the formation of an excited molecule. The excited molecule could then be deactivated by collision with another molecule or the walls of the containing vessel; re-emit all or part of its energy of excitation as fluorescence; or it could dissociate into two or more fragments, thus yielding free radicals. Hence the primary step in a photolysis will be dependant upon the substance being irradiated, and the temperature and pressure of the gas.

However, once free radicals are formed, their reactions will be simple thermal reactions leading to the formation of stable products. Hence a brief discussion of the thermal reactions of free radicals would not be out of order.

The existence of short-lived alkyl free radicals was first demonstrated some twenty five years ago by Paneth (1)



and his co-workers. In the subsequent decade investigators were primarily concerned with the detection of free radicals in reacting systems. Paneth showed that when organic vapors were passed through a furnace at elevated temperatures and then over a metallic mirror, the mirror was removed and metal alkyls were formed. It was thus shown that aliphatic free radicals are intermediates in a large number of pyrolysis and photolysis reactions.

The theory necessary to explain the existence of free radicals in organic decompositions was provided by Rice and Herzfeld (2). They showed that mechanisms could be derived on a free radical basis which would lead to a first-order rate, as had previously been observed. The theory also showed that by a suitable choice of activation energies for the various steps, an over-all activation energy could be found which agreed with the experimental results. The application of spectroscopy to flash photolysis, where free radical concentrations are high, has essentially verified many of the basic assumptions made in the theory.

Another method of demonstrating the presence of free radicals was developed by Hinshelwood (3). In 1936 he showed that the addition of small quantities of nitric oxide to the reacting system greatly inhibited the pyrolysis of many organic vapors. The inhibition was explained by the suppression of the free radical chains by the nitric oxide.

During the last decade the interest of most investigators has shifted from the qualitative study of complex systems to the quantitative study of elementary processes occurring in pyrolysis, photolysis and polymerization reactions.

Free radicals and their behaviour have therefore become increasingly important in explaining the mechanism of gas phase reactions. Free radicals, produced by both pyrolysis and photolysis reactions, have been the subject of many investigations; and have been used to elucidate the rates and energies of elementary reactions. A thorough knowledge of such elementary free radical reactions is required before a complete mechanism can be obtained which will explain the quantitative distribution of the products of many free radical reactions.

It is usually impossible to determine free radical concentrations directly, and it is, therefore, necessary to compare ratios of rates or to use some other indirect means as a measure of the free radical concentrations. Hence it was impossible to determine the rate constants for individual reactions. Recently it has become possible to evaluate rate constants by using the rotating sector technique. By comparing the rates of reaction under steady and intermittent illumination it is possible to determine the rate of a single elementary reaction.

### 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 different molecule and a free radical. The most common type is that in which a hydrogen atom is transferred.
3. Decomposition of a free radical to form a molecule and a smaller radical.
4. Addition of free radicals to stable molecules to form larger radicals.
5. Free radical displacement or inversion reactions.

### Recombination and Disproportionation

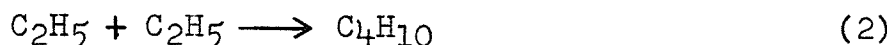
The free radicals which have been most thoroughly investigated are methyl and ethyl radicals. Most of the discussion will be concerned with these two radicals, keeping in mind that the reactions of other simple free radicals will be similar.



Reaction 1 was studied by Gomer and Kistiakowsky (4). Using the rotating sector technique, they found the value of

the rate constant for the recombination of methyl radicals ( $k_1$ ) to be  $4.5 \times 10^{13}$  (moles/cc.)<sup>-1</sup> sec.<sup>-1</sup> at 125°C., and the activation energy of the reaction to be  $0 \pm 700$  cal./mole regardless of the radical source.

The recombination of ethyl radicals

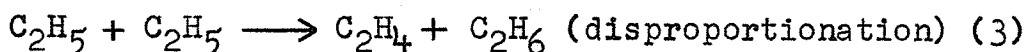


was studied by Shepp and Kutschke (5), who applied the theory of the rotating sector to the photolysis of diethyl ketone. They obtained the rate constant for the recombination of ethyl radicals ( $k_2$ ) as  $1.5 \pm 1 \times 10^{13}$ ,  $2.0 \pm 0.5 \times 10^{13}$ , and  $4.5 \pm 0.8 \times 10^{13}$  cc. moles<sup>-1</sup> sec.<sup>-1</sup> at 50°C., 100°C. and 150°C. respectively. The activation energy for  $k_2$  was found to be  $2.0 \pm 1$  kcal./mole.

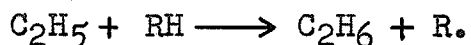
All atoms or free radicals recombine with the liberation of energy corresponding to the energy of the bond formed. This energy must be dissipated either by a third body or by the vibrational modes within the molecule formed. Reactions 1 and 2 as written imply that no third body is necessary to remove the excess energy when two free radicals combine. However, Dodd and Steacie (6) have shown that in the photolysis of acetone at low pressures (20 - 0.2 mm.) a third body is necessary for the recombination of methyl radicals. Brinton and Steacie (7) have shown that a third body is necessary for the recombination of ethyl radicals in the photolysis of diethyl ketone at pressures of 0.01 mm.

to 30 mm. However, they found that the third body effect in ethyl radicals to be smaller than with methyl radicals.

When two identical radicals interact and disappear from a system with the formation of products, they may do so either by recombination or disproportionation reactions. For methyl radicals there is only one possibility, that of recombination. For ethyl radicals and all other larger radicals, the following reactions may take place.



Reaction 3 is of the general hydrogen-abstraction type, and might by analogy be expected to have an activation energy of 5 to 8 kcal./mole. However, because of the formation of a double bond in the ethylene, the process is far more exothermic than the usual reaction of the type



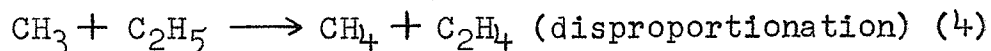
It is, therefore, quite possible that reaction 3 may have a very low activation energy.

Most of the knowledge regarding disproportionation comes from the work done on ethyl radicals. Both Ivan and Steacie (8), and Shepp and Kutschke (5) have studied the recombination and disproportionation of ethyl radicals. The ratio of  $k_3/k_2$  from the work of Ivin and Steacie, on the photolysis of diethyl ketone, was taken to be 0.12; and Shepp and Kutschke indicate that the activation energy for  $k_2$  was

$2.0 \pm 1$  kcal./mole. Ivin and Steacie made an Arrhenius plot of  $k_3/k_2$  and obtained  $E_3 - E_2$  equal to  $0.8 \pm 0.2$  kcal./mole. Taken with the result of Shepp and Kutschke for  $E_2$ , this indicated that the activation energy for the disproportionation reaction was from 2.6 to 4.0 kcal./mole.

The question of which hydrogen was transferred in the disproportionation reaction was solved by Wijnen and Steacie (9). They analyzed the products from the disproportionation of  $\text{CH}_3\text{CD}_2$  radicals, released by the photolysis of 2,2',4,4'-tetradeuterodiethyl ketone. They found that the ethylene was more than ninety per cent  $\text{H}_2\text{C} = \text{CD}_2$ , so that the radicals must have reacted when head-to-tail, that is  $\text{CH}_3\text{-CD}_2\text{-H-CH}_2\text{-CD}_2$ . This result eliminated the possibility that the disproportionation was taking place through an excited butane molecule.

There is no reason why mixed disproportionations, such as the reaction of a methyl with an ethyl radical, should not occur. The occurrence of both recombination and disproportionation reactions for an ethyl with a methyl radical was shown by Ausloos and Steacie (10). In the photolysis of methyl ethyl ketone, they found that the following reactions occurred.



In the temperature range from  $78^\circ\text{C.}$  to  $130^\circ\text{C.}$ , it was found

that the ratio  $k_4/k_5$  remained approximately constant with an average value of about  $0.04 \pm 0.02$ .

Another disproportionation reaction which has received some attention is the reaction between methyl radicals and acetyl radicals.



Ausloos and Steacie (11) in studying the photolysis of biacetyl proposed the above reaction to account for the anomalous quantities of methane formed and the formation of ketene.

#### Abstraction Reactions

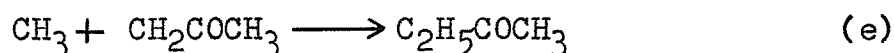
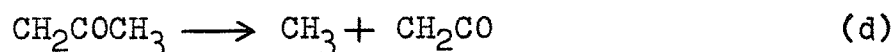
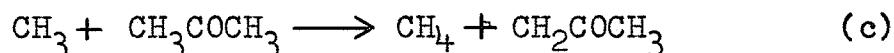
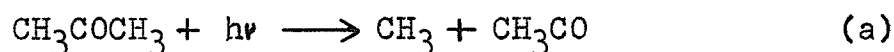
The abstraction reaction which has been the subject of a large number of investigations is one of the type:



where RH is any hydrogen-containing compound. The first extensive study of reaction 6 was performed by H. S. Taylor and co-workers (12, 13). It has been shown by Trotman-Dickenson and Steacie (14) that, in the majority of cases, very little reliance could be placed on the quantitative results obtained. However the general pattern of the results was undoubtedly correct. Taylor found that for reaction 6 in which RH is an alkane containing only primary, secondary and tertiary hydrogen atoms respectively, the activation energy followed the general trend; primary > secondary > tertiary.

Since the work of Taylor a considerable number of

reactions of this type have been investigated using photochemically produced methyl radicals. In most of the work, the source of methyl radicals was the high temperature photolysis of acetone. The photolysis of acetone has been the subject of a large number of investigations, and Steacie (15) in his review of the literature gives the following mechanism for the photolysis at high temperature.



Trotman-Dickenson and Steacie (16, 17) investigated the production of methane and ethane at high temperatures. They found the value of  $E_c - \frac{1}{2}E_f$  to be 9.7 kcal./mole. Since  $E_f$  was assumed to be zero, the value of  $E_c$  was taken as 9.7 kcal./mole.

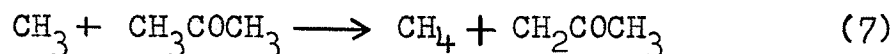
Since no generally applicable method has yet been developed for the determination of the methyl radical concentration, the usual method has been to use the reaction



as a yardstick for the radical concentration. At high



temperatures, ethane and methane are produced by reactions 1 and 7.



In the presence of a hydrogen-containing substance, RH, methane will also be produced by reaction 6.



In most cases it is very unlikely that either methane or ethane is produced in any other way.

When acetone is photolysed alone the rate of formation of methane and ethane is given by the following expression.

$$R_{\text{CH}_4} = k_7 [\text{CH}_3] [\text{CH}_3\text{COCH}_3]$$

$$R_{\text{C}_2\text{H}_6} = k_1 [\text{CH}_3]^2$$

Where  $R_{\text{CH}_4}$  and  $R_{\text{C}_2\text{H}_6}$  are the rates of production of methane and ethane. The ratio of the rate constants is given by the following expression.

$$\frac{k_7}{k_1^{\frac{1}{2}}} = \frac{R_{\text{CH}_4}}{(R_{\text{C}_2\text{H}_6})^{\frac{1}{2}} [\text{CH}_3\text{COCH}_3]}$$

The quantities on the right hand side of this equation may be found experimentally, and the values of  $k_7/k_1^{\frac{1}{2}}$  at any temperature may be determined.

When a mixture of acetone and the substance RH, present as a source of abstractable hydrogen atoms, is photolysed the rates of formation of methane and ethane are given by the following expressions.

$$R_{CH_4} = k_7 [CH_3] [CH_3COCH_3] + k_6 [RH] [CH_3]$$

$$R_{C_2H_6} = k_1 [CH_3]^2$$

The ratio of the rate constants now becomes,

$$\frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}} = \frac{k_7 [CH_3COCH_3]}{k_1^{\frac{1}{2}}} + \frac{k_6 [RH]}{k_1^{\frac{1}{2}}} .$$

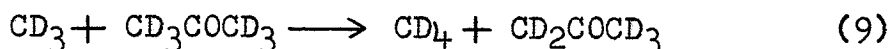
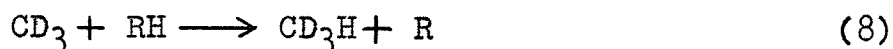
The first term on the right hand side can be evaluated at any temperature from experiments on the photolysis of acetone alone, and it is possible, knowing RH, to find the value of  $k_6/k_1^{\frac{1}{2}}$  at any temperature.

The advantages of using acetone as a source of methyl radicals are as follows.

1. The mechanism at high temperatures is well known.
2. The ratio  $k_7/k_1^{\frac{1}{2}}$  appears to be independent of the intensity over a wide range, at constant temperatures.
3. The use of the ratio  $k_7/k_1^{\frac{1}{2}}$  and its temperature coefficient to determine activation energies of hydrogen abstraction reactions will be justified provided: (i) the temperature is greater than 100°C., (ii) the acetone pressure is high, (iii) the light beam fills the cell.

An alternative approach to the determination of the activation energy of reaction 6 is to photolyse mixtures of deuterioacetone in the presence of hydrogen-containing compounds (RH). Methane and ethane are formed by the reactions:

(12)



The ratio of the rate constants for acetone alone is

$$\frac{k_9}{k_{10}^{\frac{1}{2}}} = \frac{R_{\text{CD}_4}}{R_{\text{C}_2\text{D}_6}^{\frac{1}{2}} [\text{CD}_3\text{COCD}_3]},$$

and in the presence of RH

$$\frac{k_8}{k_9} = \frac{R_{\text{CD}_3\text{H}} [\text{CD}_3\text{COCD}_3]}{R_{\text{CD}_4} [\text{RH}]}.$$

Thus it is possible to evaluate the ratio  $k_8/k_9$  by determining the ratio  $R_{\text{CD}_3\text{H}}/R_{\text{CD}_4}$  by means of a mass spectrometer.

By either of the above methods it is thus possible to evaluate  $E_6 - \frac{1}{2}E_1$  and since  $E_1$  is very nearly equal to zero,  $E_6 - \frac{1}{2}E_1$  is equal to  $E_6$  to a very good approximation.

Recently Trotman-Dickenson and Steacie (18), using ordinary and deuterated acetone, obtained the activation energies for the abstraction reactions of  $\text{CH}_3$  and  $\text{CD}_3$  radicals with various hydrocarbons and amines. The values are given in Table I.

From an examination of the values of  $E_6 - \frac{1}{2}E_1$  given in Table I for the hydrocarbons, it is seen that the activation energies fall into three groups. When the methyl radicals react with only (1) primary hydrogen atoms the

TABLE I  
THE ABSTRACTION OF HYDROGEN ATOMS BY METHYL RADICALS

Compound	$E_6 - \frac{1}{2}E_1$ (kcal./mole)	Number of "active" H atoms
Ethane	10.4	6
2,2-Dimethyl propane	10.0	12
2,2,3,3-Tetramethyl butane	9.5	18
n-Butane	8.3	4
n-Pentane	8.1	6
n-Hexane	8.1	8
2-Methyl propane	7.6	1
2,3-Dimethyl butane (i)	6.9	2
(ii)	7.8	2
2,3,4-Trimethyl pentane	7.9	3
Ethene	10.0	4
Propene	7.7	3
2-Butene	7.7	6
2-Methyl propene	7.3	6
2,3-Dimethyl-2-butene	7.8	12
1-Butene	7.6	2
1-Pentene	7.6	2
3-Methyl-1-butene	7.4	1

TABLE I (continued)

Compound	$E_6 - \frac{1}{2}E_1$ (kcal./mole)	Number of "active" H atoms
Cyclopropane	10.3	6
Cyclobutane	9.3	8
Cyclopentane	8.3	10
Cyclohexane	8.3	12
Benzene	9.2	6
Toluene	8.3	3
Methanol	8.2	3
Ethanol	8.7	2
Isopropanol	7.3	1
Methylamine	8.4	3
Dimethylamine	7.2	6
Trimethylamine	8.8	9
Ammonia	10.0	3
Methyl ether	9.5	6
Isopropyl ether	7.3	2
1-Butyne	9.1	2
2-Butyne	8.6	6
Acetone	9.7	6

activation energy is about 10 kcal./mole; (2) primary and secondary hydrogen atoms - about 8.2 kcal./mole; (3) primary and tertiary hydrogen atoms - less than 8 kcal./mole.

The interpretation of the results obtained with alcohols and amines was difficult because of some doubt as to which hydrogen atom was removed in the reaction.

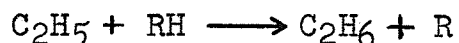
The activation energies which were determined using  $\text{CD}_3$  radicals should be no different from those determined by using ordinary methyl radicals, according to McNesby and Gordon (19). Their results on the photolysis of deuterated and normal acetones, indicated that there was no activation energy difference for the abstraction of a hydrogen atom from acetone by  $\text{CH}_3$  and  $\text{CD}_3$  radicals. However they found an activation energy difference of  $1.64 \pm 0.08$  kcal./mole for the abstraction of deuterium and hydrogen atoms from acetone by  $\text{CD}_3$  radicals.

Brinton and Volman (20) have studied the reaction of methyl radicals, formed in the thermal decomposition of di-t-butyl peroxide, with ethylenimine. They found the activation energy for the reaction



to be 4.8 kcal./mole, assuming that the activation energy for the recombination of two methyl radicals to be zero. Their results seem to indicate that the hydrogen removed was the one bonded to the nitrogen atom.

For reactions of the type



relatively little information is available. In view of the fact that the bond dissociation energy for ( $\text{C}_2\text{H}_5 - \text{H}$ ) is about 3 to 4 kcal./mole less than that for ( $\text{CH}_3 - \text{H}$ ), hydrogen abstraction reactions with ethyl radicals will be about 3 to 4 kcal./mole less exothermic than the corresponding reactions with methyl radicals. Hence a slightly higher activation energy would be expected.

Most of the work has been done on the abstraction of hydrogen atoms from diethyl ketone. Wijnen and Steacie (9) 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

$$\text{CH}_3\text{CD}_2 + \text{CH}_3\text{CD}_2\text{COCOD}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CD}_3 + \text{CH}_3\text{CDCOCOD}_2\text{CH}_3,$$

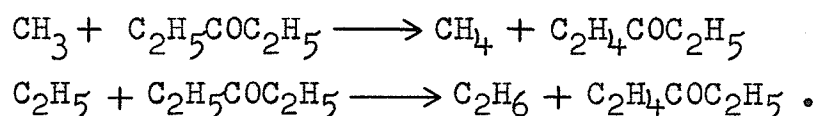
was 8.7 kcal./mole. The activation energy for the abstraction of a primary hydrogen atom, in the reaction

$$\text{CH}_3\text{CD}_2 + \text{CH}_3\text{CD}_2\text{COCOD}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CD}_2\text{H} + \text{CH}_2\text{CD}_2\text{COCOD}_2\text{CH}_3$$

was found to be 11.7 kcal./mole.

To compare the activation energies for the abstraction reactions of methyl and ethyl radicals, Ausloos and Steacie (21, 10) studied their reactions with the same hydrogen-containing compound and under similar experimental conditions. In the first case, they studied the reactions

of methyl and ethyl radicals, produced by the photolysis of azomethane and azoethane, with diethyl ketone. The activation energies were found to be 7.0 and 7.6 kcal./mole respectively, for the reactions



In the photolysis of methyl ethyl ketone (10), in which both methyl and ethyl radicals were formed, the activation energy for the abstraction of hydrogen atoms from the ketone by methyl radicals was  $7.4 \pm 0.1$  kcal./mole, and for ethyl radicals was  $8.0 \pm 0.1$  kcal./mole. In both cases the difference in activation energies was equal to  $0.6 \pm 0.2$  kcal./mole.

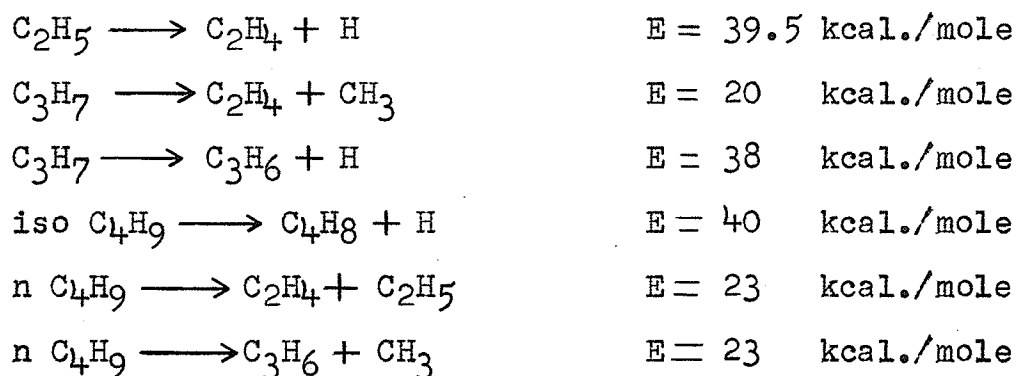
#### Decomposition of Free Radicals

The reactions in which free radicals decompose are of considerable importance in reaction mechanisms. The majority of free radical decompositions fall into two classes (22). The first class comprises those decompositions in which the radicals lose methyl radicals and have activation energies of 15 to 35 kcal./mole. The second class is composed of those in which a hydrogen atom is lost and these reactions have activation energies around 40 kcal./mole. The difference in activation energies is of the same order as the difference between the strengths of the C--C and the C--H bonds. The difficulties which are associated with the study of these reactions are those which are usually



encountered in the study of large radicals, but they are also more difficult because most of the decompositions only take place at conveniently measureable rates above 300°C. At this temperature many other side reactions take place.

The most extensive investigations on the decomposition of free radicals were those of Bywater and Steacie (23, 24, 25). From a study of the high temperature mercury-photosensitized reactions of ethane, propane, n-butane and iso-butane they obtained the activation energies for the following reactions.

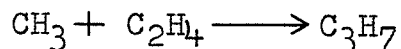


Another type of radical decomposition which has received considerable attention, is the decomposition which occurs after the primary step in a photolysis or after a hydrogen atom has been abstracted from a molecule (22). It has been found that the activation energy for this type of reaction varies from 10 to 20 kcal./mole, depending upon the radical undergoing decomposition.

#### Addition Reactions

When unsaturated hydrocarbons are present in a

reaction system containing atoms or free radicals, addition reactions such as the following will occur.



This type of reaction is difficult to investigate because of the complications arising from the various other reactions in which the reactants also participate, and since the product formed in the reaction is a free radical. The main difficulty lies in the tendency for the unsaturated hydrocarbons to polymerize, which may obscure the fate of the free radicals in the system, and often prevents the quantitative study of any single process.

Mandelcorn and Steacie (26) have studied the addition of methyl radicals, produced by the photolysis of acetone, to unsaturated hydrocarbons. The rate of the addition reaction was studied by two methods. All the methyl radicals produced in the photolysis of acetone at high temperatures can be accounted for by four thoroughly investigated reactions. The rate of addition of methyl radicals to an unsaturated hydrocarbon will be equal to the rate of disappearance of methyl radicals which cannot be accounted for by the four reactions. The other method uses the rate of disappearance of the unsaturated hydrocarbon as a measure of the rate of the addition reaction. The concentration of unsaturated hydrocarbon was kept as low as possible to prevent the occurrence of any reactions other than the

addition reaction. The activation energies for the addition of methyl radicals to ethylene, propylene, acetylene, and butadiene was found to be 7.0, 6.0, 5.5, and  $\sim 2.5$  kcal./mole.

### Free Radical Displacement or Inversion Reactions

Another type of metathetical reaction is one in which a free radical abstracts a portion of the molecule rather than an atom to form a stable molecule and a free radical. This type of reaction has been called both an inversion reaction (27) and a free radical displacement reaction. Blacet and Bell (28) in their study of the photolysis of biacetyl proposed the following reaction as part of the overall mechanism.



The activation energy of the reaction was determined as 5.6 kcal./mole, and the reaction only takes place at temperatures above 80°C. Ausloos and Steacie (11) in their investigation of the photolysis of biacetyl confirmed the mechanism proposed by Blacet and Bell.

In later work by Pitts and Co-workers (29, 30) more confirmatory evidence was presented for this type of reaction. They studied the reactions of methyl radicals with  $\alpha, \beta$ -unsaturated ketones. In all cases the methyl radicals extracted an alkene radical from the ketone.

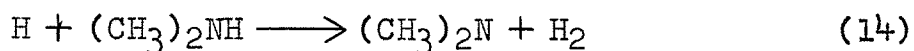
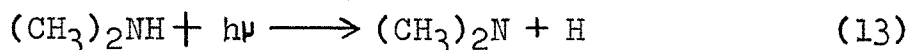
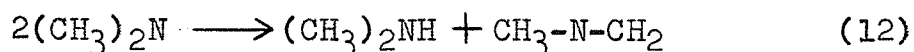
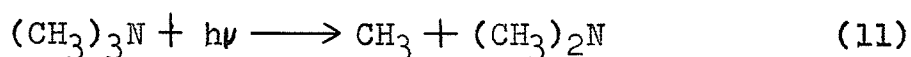
It has recently been shown by Collin (31, 32) that for aliphatic amines and alcohols, the bond with the highest

probability of breaking is the  $C_1 - C_2$  bond adjacent to the functional group. Hence it is possible that aliphatic amines and alcohols can undergo free radical displacement reactions with the cleavage occurring at the  $C_1 - C_2$  bond.

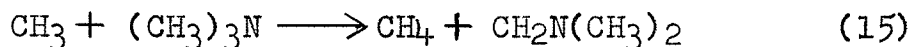
#### Gas Phase Reactions of the Amines

Relatively little work has been done on the photolysis of the amines and there is no evidence in the literature that the photolysis of triethylamine has been studied before. One of the first investigations of the photochemical decomposition of the amines was by Emeleus and Taylor (33), who investigated the photolysis of methylamine and ethylamine. The gaseous products were found to be hydrogen, methane, nitrogen and small amounts of ethane. Later work by Emeleus and Jolley (34) established that ammonia was one of the products of the photochemical decomposition of both methylamine and ethylamine. In a recent investigation of the photolysis of methylamine by Johnson and Taylor (35), the possibility of ethylenediamine as an intermediate was considered. They suggested that this intermediate underwent further decomposition or polymerization involving ammonia. Bamford (36) studied the photolysis of aliphatic amines and found that for primary and secondary amines, the primary process was the production of hydrogen atoms and alkylamino or dialkylamino radicals respectively. Tertiary amines on irradiation were found to split off an alkyl group.

The photolysis of trimethylamine was recently investigated by Gesser, Mullhaupt and Griffiths (37). They found the gaseous products to be hydrogen, methane and ethane. The formation of methyl radicals was postulated as the primary process. There appears to be some uncertainty as to the mechanism of the hydrogen formation. Bamford (36) stated that this occurred by the following mechanism.



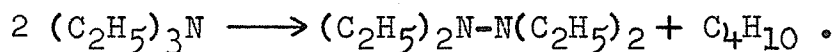
Gesser and co-workers showed that this could not be the mechanism since when cyclopentane was added to the reaction mixture, the rate of formation of hydrogen was decreased. This would indicate that atomic hydrogen was not present and that the decrease in the rate of formation of hydrogen was due to the quenching effect of cyclopentane on an excited trimethylamine molecule. They found that the activation energy for the reaction



was a minimum of 7.2 kcal./mole.

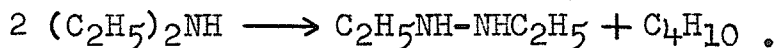
The thermal decomposition of triethylamine was studied by Taylor and Juterbock (38) over a pressure range of 15 to 400 mm. and at temperatures from 450 to 500°C. When the experiments were performed in a bomb and the

reactant thoroughly decomposed at a temperature of 500°C., the products were found to be methane, ethane, ammonia and unsaturated hydrocarbons but no hydrogen and nitrogen. With experiments at 400°C., some primary amine, a hydrazine, ammonia, unsaturated hydrocarbons, butane, nitrogen and less than one per cent hydrogen and methane were found in the products. They also found that butane was present in considerable quantities at the start of the reaction. To account for this and the hydrazine, the primary process proposed was



The hydrazine and the butane then decomposed to give the observed products.

The thermal decomposition of diethylamine was studied by Taylor and Herman (39). Decompositions were carried out for 18 to 24 hours at 400°C. The initial reaction was postulated as



The hydrazine was then postulated to have decomposed to give the observed products.

The thermal decompositions of the alkyl hydrazines were studied by Westphal and Eucken (40). They found that the stability of a hydrazine increased with the number of alkyl groups added. The primary step in the decomposition was the rupture of the nitrogen-nitrogen bond to form two

dialkylamino radicals. These radicals then recombined to reform the original product or disproportionated to give a dialkylamine and a Schiff's base. These two products were not decomposed any further. This was proved by introducing the products, prepared by a different method, into the reaction cell at the same temperature as used for the decomposition of the hydrazines. The products were recovered unchanged.

## EXPERIMENTAL

### Apparatus and Materials

Two apparatuses were used in this investigation. These were of conventional high vacuum design and gave a limiting pressure of  $10^{-6}$  mm. of Hg. The apparatuses were constructed of pyrex brand glass except for the reaction vessels, which were 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 forepump operating in series. The essential difference between the two apparatuses was that apparatus I was designed for low temperature studies, whereas apparatus II was designed for studies at high temperatures. Apparatus I was identical to that used by Gesser, Mullhaupt, and Griffiths (37). Apparatus II will be described in more detail later.

### Acetone

Acetone was obtained from Eastman Organic Chemicals and was of the "spectro" grade. It was redistilled from anhydrous copper sulfate through about 30 theoretical plates at a reflux ratio of 10:1. A middle portion boiling at  $56.5^{\circ}\text{C}$ . was collected and stored temporarily in a ground glass stoppered bottle over anhydrous copper sulfate. After thorough outgassing in the vacuum line at the temperature of



dry ice, the acetone was subjected to two bulb to bulb distillations with the retention of the middle fraction in each case. It was stored in a blackened bulb 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 30 theoretical plates at a reflux ratio of 10:1. A middle portion boiling at 89°C. was collected and stored temporarily in a ground glass stoppered bottle over anhydrous barium oxide. After thorough outgassing in the vacuum line at the temperature of dry ice, the triethylamine was subjected to two bulb to bulb distillations with the retention of the middle third fraction in each case. It was stored in a bulb behind a mercury cut-off.

### Hydrogen

Hydrogen was obtained from a cylinder of commercial grade. The hydrogen was purified by passing it through a heated palladium thimble. It was stored in a large bulb behind a stopcock.

### Oxygen

Oxygen was prepared by heating C. P. potassium permanganate. The potassium permanganate was first degassed

by heating in a vacuum. It was then heated and the non-condensable gases collected. The oxygen was purified by passing it through a number of traps immersed in liquid nitrogen. The oxygen was stored in a large bulb behind a stopcock.

#### Nitric Oxide

Nitric oxide was prepared as follows: a mixture of potassium nitrite, potassium iodide, and water in a weight ratio of 2:1:6, was first repeatedly degassed in the high vacuum line. A 50% solution of sulfuric acid, also degassed in the high vacuum line, was added slowly, allowing the evolved gases to pass into a trap cooled in liquid nitrogen. These gases were degassed repeatedly and the nitric oxide was distilled from liquid oxygen into a trap cooled in liquid nitrogen and stored in a large bulb behind a mercury stopcock. Samples of nitric oxide were distilled from the storage bulb, at the temperature of liquid oxygen, into the line as required.

#### Cyclohexane

Cyclohexane was obtained from Eastman Organic Chemicals and was of the "spectro" grade. It was degassed in the high vacuum line at the temperature of Dry Ice, and then subjected to two bulb to bulb distillations with the retention of the middle third fraction in each case. It was

stored in a bulb behind a mercury cut-off.

### Diethylamine

Diethylamine was obtained from Eastman Organic Chemicals and was of the "white label" grade. It was dried by storage over anhydrous barium oxide. After thorough degassing in the vacuum line, it was subjected to two bulb to bulb distillations with the retention of the middle third fraction in each case. It was stored in a bulb behind a mercury cut-off.

### Trimethylamine

Trimethylamine was identical to that used by Gesser et al (37). It was subjected to two bulb to bulb distillations with the retention of the middle third fraction in each case. It was stored in a large bulb behind a mercury cut-off.

### The Reaction Cell

The reaction cell in apparatus I has been described (37). The reaction cell in apparatus 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 by three copper-constantin 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 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  $\pm 0.5$  mm. The reaction cell assembly was enclosed in a box made of fiberboard. This was used to control the temperature of the air surrounding the reaction cell, stirrer, and connecting tubing. This was particularly useful when pressures of reactants greater than the vapor pressure at room temperature were used. The temperature inside the box was regulated by means of two light bulbs and a glow heater to  $\pm 1^{\circ}\text{C}$ . A small all-glass stirrer was placed between the cell and the connecting tubing and was used to mix the gases. The

gases were stirred for a period of fifteen minutes prior to the start of the reaction. The thoroughness of the mixing was tested by reacting trimethylamine with methyl radicals produced by the photolysis of acetone. The activation energy for the reaction of methyl radicals abstracting hydrogen atoms from trimethylamine was compared with the result obtained by Trotman-Dickenson and Steacie (18). From Figure 2 it may be seen that the results obtained agree within experimental error.

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. In the photolysis of triethylamine the unfiltered beam was employed. For the photolysis of acetone in the presence of triethylamine (experiments A1 - A9), a Corning pyrex filter No. 7740 was employed to prevent the photolysis of triethylamine. For the photolysis of triethylamine in the presence of an inert gas (cyclohexane) and nitric oxide (experiments B1 - B7), a Corning filter No. 9863 was used to prevent the photolysis of the added gases. In the photolysis of acetone in the presence of diethylamine and trimethylamine (experiments D1 - D9), a Corning pyrex filter No. 7740 was employed to prevent the photolysis of the amines. The intensity of the lamp was controlled manually by keeping the current constant in the primary circuit at  $9 \pm 0.5$  amps.

### Analytical System

The analytical system on apparatus I and II consisted of cold traps used for the separation of the gaseous products from the reactants and liquid products; a pump-down liquid nitrogen trap used to separate the non-condensibles from ethane and ethylene; a LeRoy still (41) used 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 the analysis of various components of the gaseous products, a copper-copper oxide furnace (42), a micro hydrogenation unit (43), and a platinum wire combustion furnace were used. Each of the above analytical units were equipped with a Toepler pump which delivered the gases to the unit from the gas buret. Mercury float valves separated each unit and the fractionation system from a common return line connected to the main Toepler pump and gas buret.

### Experimental Procedure

Three different types of experiments were performed which were as follows: (1) the photolysis of triethylamine alone, (2) the reaction of methyl radicals produced by the photolysis of acetone, with triethylamine, diethylamine, and trimethylamine, (3) the photolysis of triethylamine with an inert gas (cyclohexane) and nitric oxide present in the

reaction mixture.

Before any of the reactants were introduced, the apparatus was exhausted to a pressure of  $10^{-6}$  mm. Hg. For the photolysis of triethylamine alone the sample was introduced into the cell as follows: the reaction vessel and the tubing connecting it to the storage bulb of the amine was separated from the rest of the apparatus by means of stopcocks or float valves, depending upon which apparatus was used. The amine was condensed with liquid nitrogen and the mercury float valve lowered. The gas was allowed to expand slowly into the line. On line I the pressure of the gas was determined by a Bourdon gauge in conjunction with a silicone oil manometer, while on line II it was measured by the small manometer adjoining the cell. The cell was closed off when the pressure of the amine reached the desired value and the excess gas was then returned to the storage vessel. The pressure and temperature of the gas in the cell was then recorded. The amine was degassed by subjecting it to four bulb to bulb distillations at a temperature of  $-135^{\circ}\text{C}$ . The amine was then returned to the reaction cell where it was subsequently photolysed.

For the introduction of a second reactant, a knowledge of the effective volume ratio, determined for each cell temperature, between the line and the cell was used. The first reactant was introduced as described above. The

second reactant was allowed to expand into the line only, and its temperature and pressure was recorded. The pressure of the reactant in the cell was then calculated using the effective volume ratio. The two reactants were degassed together at a temperature of  $-150^{\circ}\text{C}$ . when their vapour pressures were of the same order of magnitude. Nitric oxide was degassed by pumping on it at liquid nitrogen temperatures. It was then distilled into the line from liquid oxygen temperatures.

The gaseous products were separated from the reactants and liquid products by subjecting them to four trap to trap distillations at a temperature of  $-135^{\circ}\text{C}$ . The reactants and some liquid products were then pumped out of the apparatus.

The analytical procedures employed in this work were similar to those described by Marcotte and Kutschke (42). The gaseous products volatile at  $-135^{\circ}\text{C}$ . were pumped through the analytical system by the small mercury diffusion pump. They were passed through three traps; one immersed in liquid nitrogen at a temperature of  $-196^{\circ}\text{C}$ ., a pump-down liquid nitrogen trap at  $-215^{\circ}\text{C}$ . and the LeRoy still. Products volatile at  $-215^{\circ}\text{C}$ . (hydrogen, 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 hydrogen and carbon monoxide were oxidized to water and carbon dioxide respectively. 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. The volume of hydrogen was determined by difference. Combustion of the methane in the platinum wire furnace indicated the absence of nitrogen.

The liquid nitrogen and pump-down liquid nitrogen traps were removed and the gases allowed to warm up and pass into the LeRoy still. The temperature of the LeRoy still was then set at -185°C. and the ethane and the ethylene distilled over into the combined gas buret and Toepler pump and measured. The method used for the analysis of unsaturates was an adaptation of that of Shepp and Kutschke (43). A known amount of hydrogen was introduced into the catalytic chamber followed by the C<sub>2</sub> 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. When experiments were performed on apparatus II, which did not contain a hydrogenation unit, the C<sub>2</sub> fraction was transferred to apparatus I and the amount of ethylene

was determined there.

The temperature of the LeRoy still was set at  $-155^{\circ}\text{C}$ . and  $-145^{\circ}\text{C}$ . and the  $\text{C}_3$  and  $\text{C}_4$  hydrocarbons respectively, were distilled and measured. The  $\text{C}_3$  and  $\text{C}_4$  hydrocarbons were found to be free of unsaturated hydrocarbons.

## RESULTS AND DISCUSSION

The results of the photolysis of triethylamine alone are given in Table II. These experiments were performed on apparatus I. The concentration of triethylamine and other reactants in the reaction cell was calculated from the temperature and pressure of the gases. The extent of decomposition was usually one per cent and never greater than five per cent. These results were not used in any of the calculations, but are given for the sake of completeness and the use of future workers.

The results of the photolysis of triethylamine alone, performed on apparatus II, are given in Table III.

The results of the reaction of methyl radicals, produced by the photolysis of acetone, with triethylamine are given in Table IV. In experiments A<sup>4</sup> and A<sup>10</sup>, acetone was photolysed alone and the results obtained were compared with those of Trotman-Dickenson and Steacie (16, 17). Hydrogen was not detected as a product in any of the experiments.

The results of the photolysis of triethylamine in the presence of an inert gas (cyclohexane) are given in Table V. In experiment B<sup>1</sup> the methane and hydrogen were not measured. In experiment B<sup>2</sup> the photolysis was not conducted long enough, hence the yield of products was very small and some might have missed detection.

TABLE II  
THE PHOTOLYSIS OF TRIETHYLAMINE ON APPARATUS I

Run	Temp. °C.	Conc. of TEA <sup>†</sup>	RCH <sub>3</sub>	RH <sub>2</sub>	RC <sub>2</sub> H <sub>4</sub>	RC <sub>2</sub> H <sub>6</sub>	RC <sub>3</sub> H <sub>8</sub>	RC <sub>4</sub> H <sub>10</sub>
Molecules/cc./sec. X 10 <sup>-11</sup>								
31	30	13.90	8.80	42.4		36.65	17.03	
32	30	13.90	5.50	30.6		27.85	7.86	
33	30	15.62	7.44	35.55	6.36	21.30	7.70	
34	29	13.10	4.04	29.4	6.74	21.75	7.08	
37	28	6.30	3.35	24.0	6.86	20.43	12.08	
38	29	3.19	3.97	22.7	7.64	23.95	15.82	
39	28	4.12	3.85	19.8	7.32	23.45	18.37	
40	27	1.85	3.85	15.61	7.34	23.40	22.5	
41	27	14.80	2.85	26.20	5.27	17.38	13.55	
42	0	5.38	2.12	18.50	5.48	16.00	13.03	
43	0	3.74	1.95	16.02	8.12	11.53	6.15	6.27
44	28	15.33	2.78	22.20		24.75	2.95	3.86
45	25	6.61	2.32	19.62		47.8	4.06	4.86
46	26.5	1.62	2.72	12.18	NIL	19.80	6.57	10.88
47	0	1.70	2.68	12.35	4.32	13.38	6.57	8.83
48	27	15.43	2.20	19.60	3.76	9.97	2.60	3.88
49	27	6.62	1.95	16.90	3.58	10.95	3.22	4.13
50	26.5	1.96	1.99	11.90	3.96	13.14	5.54	5.83

<sup>†</sup>The concentration of triethylamine (TEA) is expressed as molecules/cc. X 10<sup>-17</sup>.

TABLE III  
THE PHOTOLYSIS OF TRIETHYLAMINE ON APPARATUS II

Run	Temp. °C.	Conc. of TEA <sup>†</sup>	RCH <sub>4</sub>	RH <sub>2</sub>	RC <sub>2</sub> H <sub>4</sub>	RC <sub>2</sub> H <sub>6</sub>	RC <sub>3</sub> H <sub>8</sub>	RC <sub>4</sub> H <sub>10</sub>
Molecules/cc./sec. X 10 <sup>-11</sup>								
51	76	8.23	25.75	133.0	45.05	188.3	58.8	20.55
52	120	8.35	35.15	154.8	56.71	260.5	67.6	21.50
53	28	7.06	18.18	89.7	30.35	167.8	49.9	18.30
54	76	8.31	21.75	127.8	47.00	164.5	54.4	18.58
55	169	8.51	52.87	138.7	60.1	319.5	73.6	15.62
56	208	8.43	97.3	129.3	93.0	491.0	77.4	30.95
57	254	8.24	355.5	114.6	122.0	1052	136.8	55.8
58	253	8.44	373	120	140.2	1155	144.8	65.7

<sup>†</sup>The concentration of triethylamine (TEA) is expressed as molecules/cc. X 10<sup>-17</sup>.

TABLE IV  
THE REACTION OF METHYL RADICALS WITH TRIETHYLAMINE

Run	Temp. °C.	Conc. of TEA†	Conc. of Acet.†	$RCH_3$	$RC_2H_5$	$RC_2H_5$	$RC_3H_7$	$RC_4H_9$
					Molecules/cc./sec. $\times 10^{-11}$			
A1	123	8.72	17.48	139	20.4	NIL	NIL	NIL
A2	169	8.35	19.70	298	45.26	2.26	NIL	NIL
A3	213	8.31	23.60	511	209.5	13.18	45.3	12.2
A4	260	0.00	19.55	490	75.8	0.00	0.0	0.0
A5	263	8.34	19.9	714	966	32.0	61.2	38.2
A6	151	8.57	19.3	225	27.9	NIL	NIL	NIL
A7	143	8.31	18.8	184	23.55	NIL	NIL	NIL
A8	126	8.85	19.2	141.5	22.0	NIL	NIL	NIL
A9	132	8.42	17.55	145.4	23.0	NIL	NIL	NIL
A10	120	0.00	18.50	37.5	224	0.00	0.0	0.0

†The concentration of triethylamine (TEA) and acetone (Acet.) is expressed as molecules/cc.  $\times 10^{-17}$ .

TABLE V  
THE PHOTOLYSIS OF TRIETHYLAMINE IN THE PRESENCE OF  
CYCLOHEXANE

Run	Temp. °C.	Conc. of TEA†	Conc. of C <sub>6</sub> H <sub>12</sub> †	R <sub>CH<sub>3</sub></sub>	R <sub>H<sub>2</sub></sub>	R <sub>C<sub>2</sub>H<sub>4</sub></sub>	R <sub>C<sub>2</sub>H<sub>6</sub></sub>	R <sub>C<sub>3</sub>H<sub>8</sub></sub>	R <sub>C<sub>4</sub>H<sub>10</sub></sub>
Molecules/cc./sec. X 10 <sup>-11</sup>									
B1	189	8.74	0.00	14.5	74.0	19.2	119.0	3.66	12.2
	189	8.74	8.74	73.6		16.8	118.0	2.74	13.1
B2	30	10.7	0.00	NIL	38.2	1.22	2.44	NIL	NIL
	31	10.7	11.13	NIL	31.6	1.78	1.94	NIL	NIL

†The concentration of triethylamine (TEA) and cyclohexane (C<sub>6</sub>H<sub>12</sub>) is expressed as molecules/cc. X 10<sup>-17</sup>.

The results of the photolysis of triethylamine in the presence of nitric oxide are recorded in Table VI. The pressure of the nitric oxide was measured in the line and the pressure in the reaction cell was then calculated from the knowledge of the volume ratio between the line and the cell at the temperature of the experiment. In experiments B3 and B4 insufficient nitric oxide was added, since no excess was observed at the end of the experiments. The non-condensable fraction believed to be methane was found to be nitrogen by combustion in the platinum wire furnace. The "propane" fraction was found to be nitrous oxide. In some unpublished work performed in this laboratory by Gesser and Griffiths, nitrous oxide was found to be one of the products of the photolysis of nitric oxide. The nitrous oxide was identified by comparing the vapor pressure curves of the fraction thought to be nitrous oxide with that obtained by Gesser and Griffiths in the photolysis of nitric oxide. The hydrogen fraction was shown to contain only hydrogen and not oxygen, which might have been formed in the photolysis of nitric oxide. This was shown by oxidizing the hydrogen in the copper-copper oxide furnace and the water so formed was recovered and measured. The amount of water corresponded to the hydrogen introduced to within experimental error.

The results of experiments conducted on the reaction of methyl radicals, produced by the photolysis of acetone,



TABLE VI  
THE PHOTOLYSIS OF TRIETHYLAMINE IN THE PRESENCE OF  
NITRIC OXIDE

Run	Temp. °C.	Conc. of TEA†	pNO†	R <sub>N2</sub>	R <sub>H2</sub>	R <sub>C2H4</sub>	R <sub>C2H6</sub>	R <sub>N2O</sub>	R <sub>C4H10</sub>
Molecules/cc./sec. X 10 <sup>-11</sup>									
B3	30	10.7	1	NIL	54.5	NIL	5.3	NIL	NIL
B4	190	8.74	1	35.5	48.9	8.31	7.89	3.61	2.82
B5	187	8.82	21	342	70.7	NIL	1.57	87.5	NIL
B6	30	10.7	8	21.45	40.0	NIL	1.59	149.0	NIL
B7	31	8.73	6.2	18.9	37.6	NIL	1.50	NIL	NIL

†The concentration of triethylamine (TEA) is expressed as molecules/cc. X 10<sup>-17</sup> and the pressure of nitric oxide in the reaction cell as mm. Hg.

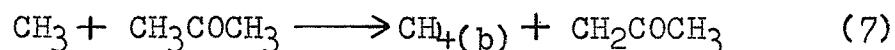
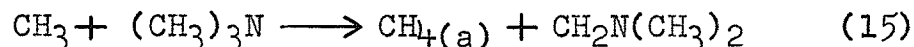
with diethylamine are given in Table VII.

The results of experiments conducted on the reaction of methyl radicals, produced by the photolysis of acetone, with trimethylamine are given in Table VIII. No hydrogen was detected among the products in any of the experiments.

The reaction of methyl radicals with trimethylamine was studied to see if a fifteen minute mixing period was sufficient to thoroughly mix the reactants.

This series of experiments was also performed to see if hydrogen, one of the products in the photolysis of trimethylamine (37), was formed by the decomposition of the  $\text{CH}_2\text{N}(\text{CH}_3)_2$  radical, formed when a methyl radical abstracts a hydrogen atom from trimethylamine. Since hydrogen was not observed as a product in the reaction of methyl radicals with trimethylamine, it may be concluded that hydrogen does not come from the decomposition of this radical.

The gaseous products formed in the reaction of methyl radicals with trimethylamine may be accounted for by the following reactions. Carbon monoxide was formed in the primary step of the photolysis of acetone and need not be considered here.



The ratio of  $k_7/k_1^{\frac{1}{2}}$  is given by the expression

TABLE VII

## THE REACTION OF METHYL RADICALS WITH DIETHYLAMINE

Run	Temp. °C.	Conc. of DEA†	Conc. of Acet.†	$RCH_3$	$RC_2H_5$	$RC_2H_5$	$RC_3H_7$	$RC_4H_9$
Molecules/cc./sec. X $10^{-11}$								
D1	123	7.54	7.54	98.4	15.23	NIL	NIL	NIL
D2	155	8.35	8.22	166.8	12.52	NIL	NIL	NIL
D3	175	8.84	8.84	216	12.52	NIL	NIL	NIL
D4	204	9.93	10.72	330	36.0	NIL	NIL	NIL
D5	249	10.15	11.07	500	235.5	10.5	15.3	30.6
D6	140	9.35	9.35	146	12.1	NIL	NIL	NIL

†The concentration of diethylamine (DEA) and acetone is expressed as molecules/cc. X  $10^{-17}$ .

TABLE VIII

## THE REACTION OF METHYL RADICALS WITH TRIMETHYLAMINE

Run	Temp. °C.	Conc. of Trimethyl- amine†	Conc. of Acetone†	$RCH_3$	$RCO$	$RC_2H_5$
Molecules/cc./sec. X $10^{-11}$						
D7	132	10.01	10.01	75.2	117	43.6
D8	208	10.03	10.03	254.5	197.6	19.94
D9	269	11.78	11.78	468.7	256	6.75

†The concentration of trimethylamine and acetone is expressed as molecules/cc. X  $10^{-17}$ .

$$\frac{k_7}{k_1^{\frac{1}{2}}} = \frac{R_{\text{CH}_4(b)}}{R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} [\text{Acetone}]} .$$

The variation of  $k_7/k_1^{\frac{1}{2}}$  with temperature was determined by Trotman-Dickenson and Steacie (16, 17) and a plot of their values is reproduced in Figure 1. From the value of  $k_7/k_1^{\frac{1}{2}}$  at any temperature it was possible to calculate the rate of formation of methane formed in reaction 7. The rate of formation of methane coming from the abstraction of a hydrogen atom from trimethylamine was obtained by subtracting  $R_{\text{CH}_4(b)}$  from the total rate of methane formation. Using this value of the rate of formation of methane,  $R_{\text{CH}_4(a)}$ , it was possible to determine the ratio  $k_{15}/k_1^{\frac{1}{2}}$  at various temperatures,

$$\frac{k_{15}}{k_1^{\frac{1}{2}}} = \frac{R_{\text{CH}_4(a)}}{R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} [\text{TMA}]} ,$$

where  $[\text{TMA}]$  is the concentration of trimethylamine. A plot of  $k_{15}/k_1^{\frac{1}{2}}$  vs  $1/T$  is shown in Figure 2. The values obtained by Trotman-Dickenson and Steacie are also shown for comparison. The activation energy calculated from the slope of this curve was 8.0 kcal./mole, assuming that the activation energy for the recombination reaction was zero. This result is slightly lower than the value of 8.8 kcal./mole obtained by Trotman-Dickenson and Steacie (18), and higher than the

FIGURE 1  
THE PHOTOLYSIS OF ACETONE  
 $\text{LOG } k_7/k_1^{\frac{1}{2}} \text{ VS } 1/T$

- - Results of Trotman-Dickenson and Steacie
- - Present Results

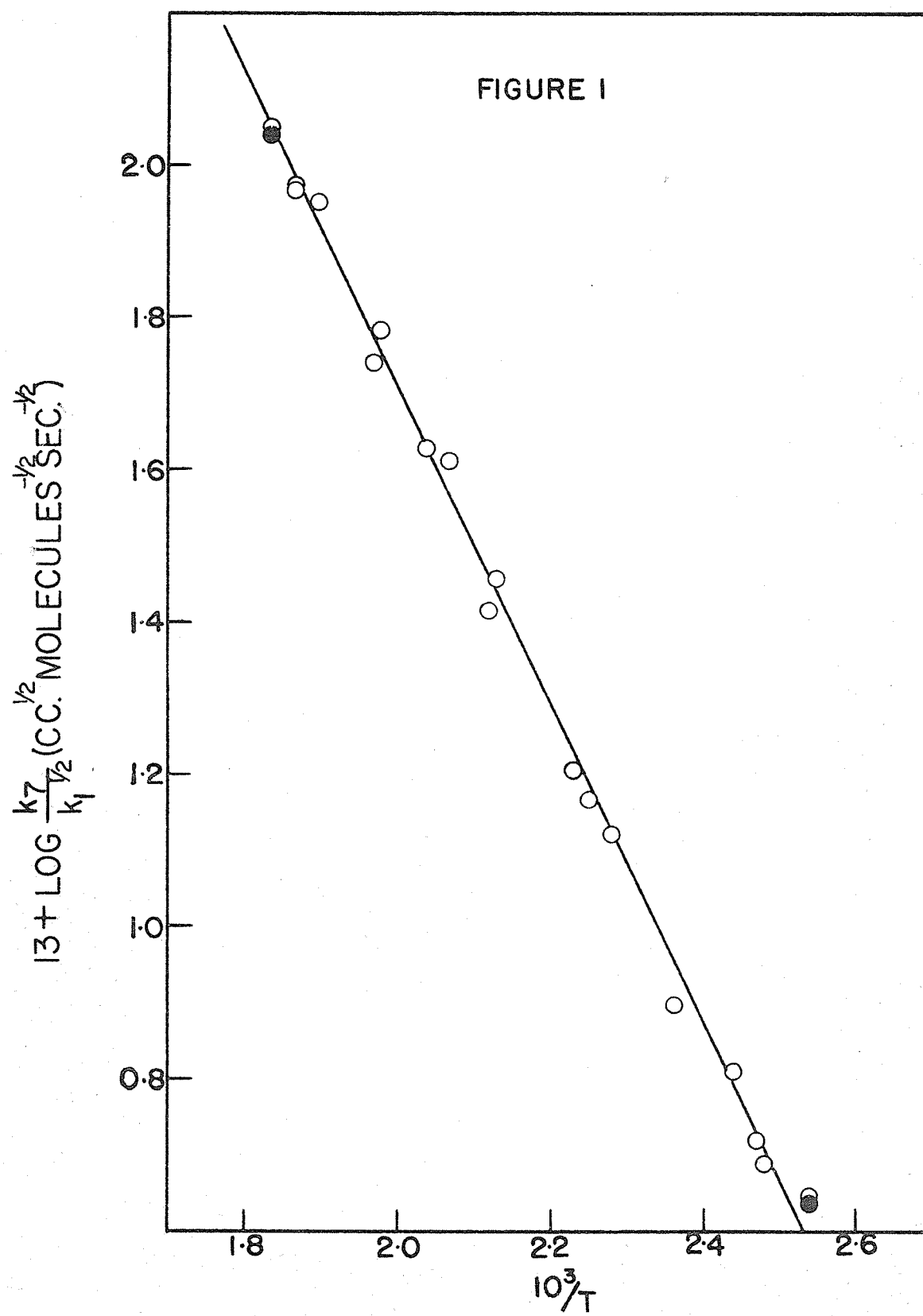
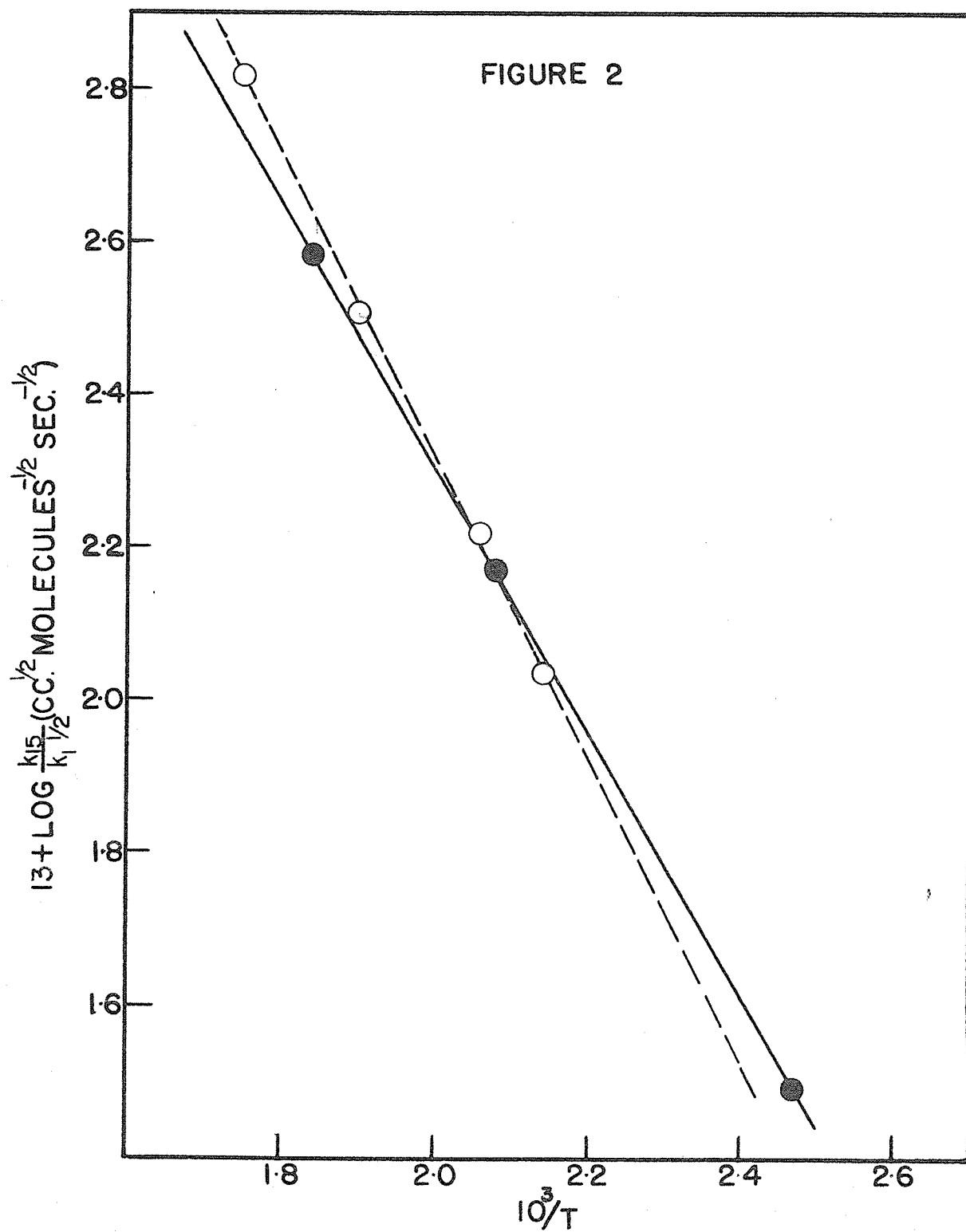


FIGURE 2  
THE REACTION OF METHYL RADICALS WITH TRIMETHYLAMINE  
 $\text{LOG } k_{15}/k_1^{\frac{1}{2}} \text{ VS } 1/T$

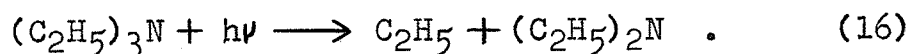
- Results of Trotman-Dickenson and Steacie
- Present Results





value of 7.2 kcal./mole obtained by Gesser, Mullhaupt and Griffiths (37). The possible reasons why the value of 8.0 kcal./mole differed from the value obtained by Trotman-Dickenson and Steacie might be experimental error or the fact that they used deuterated acetone as a source of methyl radicals. However, McNesby and Gordon (19) have shown that there is no activation energy difference for the abstraction of a hydrogen atom from acetone by  $\text{CH}_3$  and  $\text{CD}_3$  radicals. Hence the difference of 0.8 kcal./mole is probably due to experimental error. It was concluded that a fifteen minute mixing period was sufficient to thoroughly mix the reactants.

According to Bamford (36) the primary process in the photolysis of tertiary amines was the splitting off of an alkyl group. Hence in triethylamine the probable primary process is



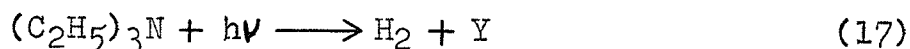
The presence of ethyl radicals in the reaction mixture accounts qualitatively for ethane, ethylene and butane. The presence of methane and propane in the products shows that there must be another primary process. The latter set of products could be formed by either a molecular or free radical mechanism. In a free radical mechanism the methane could be formed by methyl radicals abstracting hydrogen atoms from triethylamine, and the propane could be formed by the combination of methyl and ethyl radicals. The

presence of hydrogen as a product of the reaction indicates that there is a further complication in the primary process. The hydrogen could have come either from the recombination of hydrogen atoms or from a molecular mechanism.

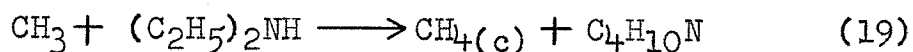
To differentiate between the products coming from a free radical mechanism and those coming by a molecular mechanism, triethylamine was photolysed in the presence of nitric oxide. It is well known (3) that in the presence of nitric oxide all free radical mechanisms are eliminated because of the removal of the free radicals from the reaction system by the nitric oxide. From an examination of the results in Table VI, excluding experiments B3 and B4 in which there was insufficient nitric oxide, it is seen that all products except hydrogen are eliminated. In the experiment B2 triethylamine was photolysed using filter No. 9863. In this experiment the rate of formation of hydrogen was  $38.2 \times 10^{11}$  molecules/cc./sec. In experiment B6, at the same pressure and temperature and with the same filter but with nitric oxide present, the rate of formation of hydrogen was  $40.0 \times 10^{11}$  molecules/cc./sec. Since these two values agree to within experimental error, all the hydrogen must be formed directly in the primary process. The small amount of  $C_2$  hydrocarbon measured was probably nitric oxide which was not completely pumped out of the system, since the vapor pressures at  $-185^\circ C.$  are similar. Since the formation of

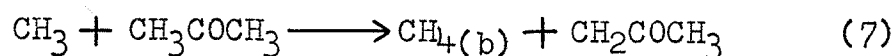
all other products was inhibited by the nitric oxide, they must have been formed by a free radical mechanism. Therefore methyl and ethyl radicals are the source of the hydrocarbon products.

In the results listed in Table V, in experiment B1, the rate of formation of hydrogen and methane was less when cyclohexane was present in the reaction mixture. Also in experiment B2 there was less hydrogen when cyclohexane was present. Hence it is possible that the hydrogen was formed by the decomposition of an activated triethylamine molecule which was deactivated by the cyclohexane. Along with reaction 16 the two other possible primary processes are as follows:



The reaction of methyl radicals with diethylamine (Table VII) was studied to investigate the possibility of the formation of methyl radicals by the decomposition of the diethylamine radical,  $(\text{C}_2\text{H}_5)_2\text{N}$ , produced in reaction 16. There was no evidence of a chain reaction and it was concluded that methyl radicals could not be coming from the decomposition of the diethylamine radical. The methane and ethane formed at low temperatures was accounted for by the following reactions.





The value of  $k_7/k_1^{1/2}$  at any temperature was obtained from Figure 1. The rate of formation of methane from acetone,  $R_{\text{CH}_4(\text{b})}$ , was calculated in the same manner as in the study of trimethylamine. The rate of formation of methane from diethylamine,  $R_{\text{CH}_4(\text{c})}$ , was obtained by subtracting  $R_{\text{CH}_4(\text{b})}$  from the total methane. The value of the ratio  $k_{19}/k_1^{1/2}$  is given by the expression

$$\frac{k_{19}}{k_1^{1/2}} = \frac{R_{\text{CH}_4(\text{c})}}{R_{\text{C}_2\text{H}_6}^{1/2} [\text{DEA}]},$$

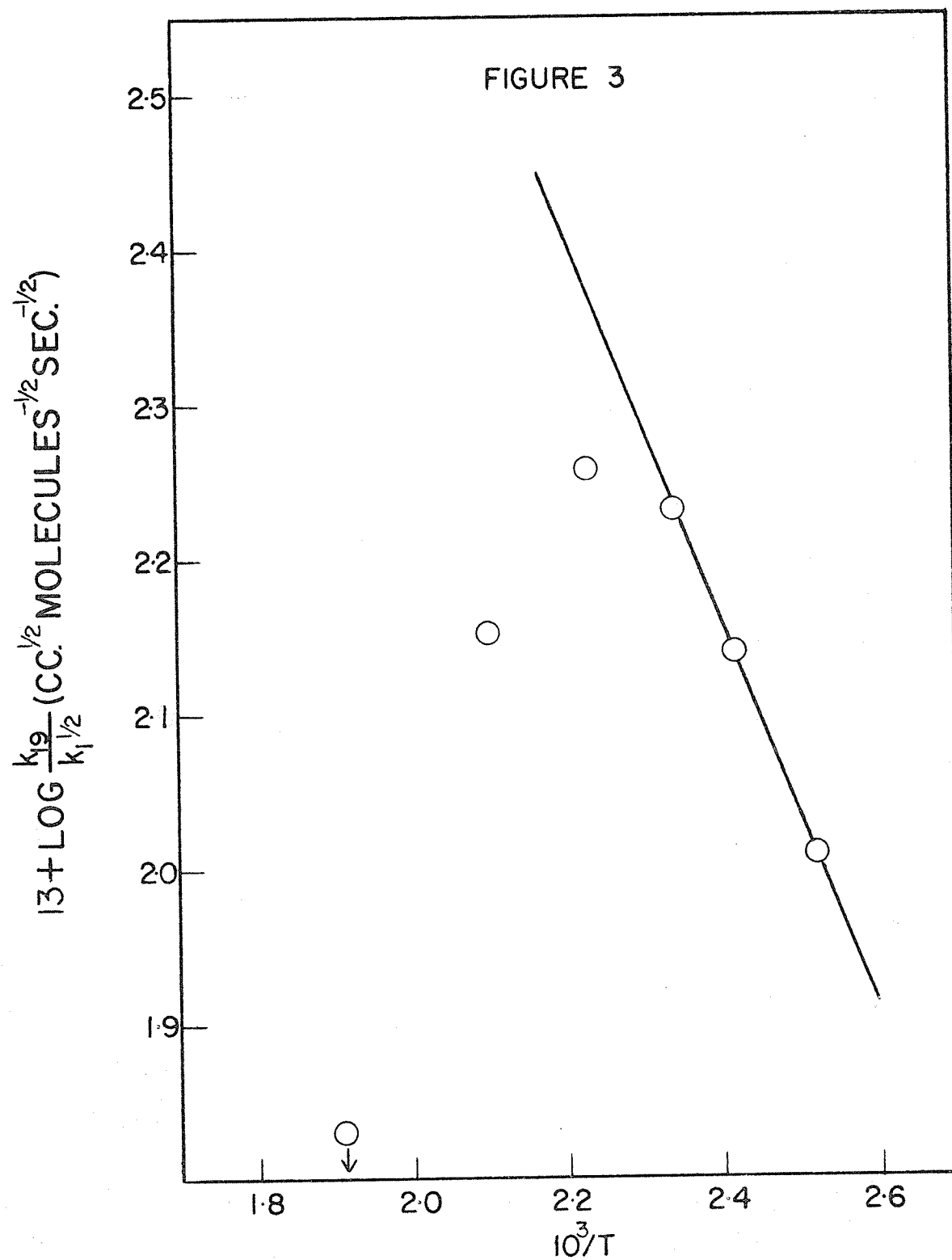
where  $[\text{DEA}]$  is the concentration of diethylamine. The calculated values of  $k_{19}/k_1^{1/2}$  at different temperatures are tabulated in Table IX. A plot of  $k_{19}/k_1^{1/2}$  vs  $1/T$  is shown in Figure 3. The activation energy calculated from the slope of the straight line drawn through the points at low temperatures, was found to be 5.7 kcal./mole. The curve deviates from a straight line at higher temperatures. At the highest temperature (experiment D5) ethyl radicals are formed in some manner because ethylene, propane and butane are found as products. However for the other two points at lower temperatures that are not on the straight line, there are no ethyl radicals formed since ethylene, propane and butane are not detected as products. Therefore, at these

TABLE IX  
RESULTS OF CALCULATIONS ON DIETHYLAMINE

Run	10 <sup>3</sup> /T	Conc. of DEAT <sup>†</sup>	Conc. of Acet. <sup>†</sup>	RCH <sub>3</sub> Total	RCH <sub>3</sub> (b)	RCH <sub>3</sub> (c)	RC <sub>2</sub> H <sub>6</sub> Total	k <sub>19</sub> /k <sub>1</sub> <sup>1/2</sup> <sup>†</sup>	k <sub>19</sub> /k <sub>7</sub>	RCH <sub>3</sub> (b) Extr.	RC <sub>2</sub> H <sub>6</sub> Rec.	RC <sub>2</sub> H <sub>6</sub> Reac. (20)	k <sub>7</sub> /k <sub>20</sub>
D1	2.52	7.54	7.54	98.4	3.62	94.8	15.23	101.8	26.2	--	--	--	--
D2	2.34	8.35	8.22	166.8	8.74	158.1	12.52	169.7	17.8	--	--	--	--
D3	2.23	8.84	8.84	216.0	16.1	200	12.52	202.5	12.4	13.9	9.32	3.20	1.49
D4	2.10	9.93	10.72	330	63.1	266.9	36.0	142	4.58	29.4	7.83	28.2	0.965
D5	1.91	10.15	11.07	500	424	76	235.5	15.4	.20	64.5	5.32	232	0.256
D6	2.42	9.35	9.35	146	6.58	139.4	12.1	137	21.2	--	--	--	--

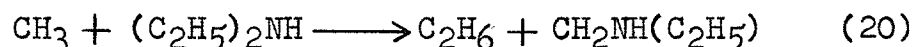
<sup>†</sup>The concentration of diethylamine and acetone is expressed as molecules/cc. X 10<sup>-17</sup>; the rates of formation are expressed as molecules/cc./sec X 10<sup>-11</sup> and k<sub>19</sub>/k<sub>1</sub><sup>1/2</sup> is multiplied by a factor of 10<sup>13</sup>.

FIGURE 3  
THE REACTION OF METHYL RADICALS WITH DIETHYLAMINE  
 $\text{LOG } k_{19}/k_1^{1/2} \text{ VS. } 1/T$



two points (experiments D3 and D4) there must have been a method of production of ethane other than the recombination of methyl radicals. The ethane could not be formed by the abstraction of hydrogen atoms by ethyl radicals, since these were not present.

The carbon-carbon bond next to the nitrogen atom in diethylamine has the greatest probability of breaking (31, 32), and hence ethane might be produced by the following reaction.



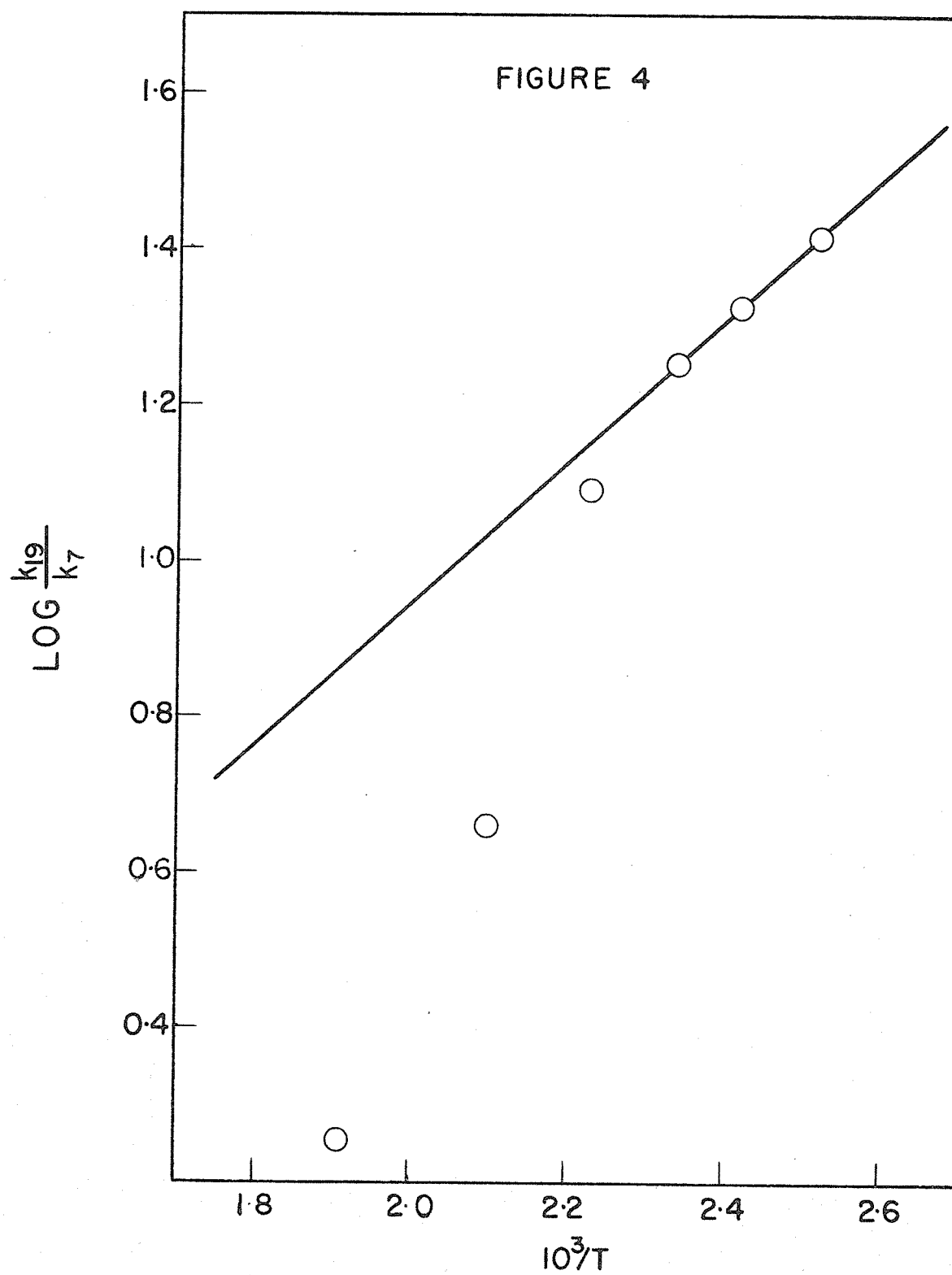
For the points not on the straight line, the methane coming from the abstraction of a hydrogen atom from acetone, could not be calculated by the method used for trimethylamine, since the total ethane measured included that formed by reaction 20. However the ratio of methane formed in reaction 19, to that formed in reaction 7 was obtained from the following expression.

$$\frac{k_{19}}{k_7} = \frac{R_{\text{CH}_4(c)} [\text{CH}_3\text{COCH}_3]}{R_{\text{CH}_4(b)} [\text{DEA}]}$$

The values of  $k_{19}/k_7$ , calculated from the experiments at the three lower temperatures, are given in Table IX, and the values so obtained were plotted against  $1/T$  in Figure 4. The straight line obtained was extrapolated to higher temperatures, since the difference in activation energy should be constant. When the ratio at higher temperatures was



FIGURE 4  
THE REACTION OF METHYL RADICALS WITH DIETHYLAMINE  
LOG  $k_{19}/k_7$  VS  $1/T$



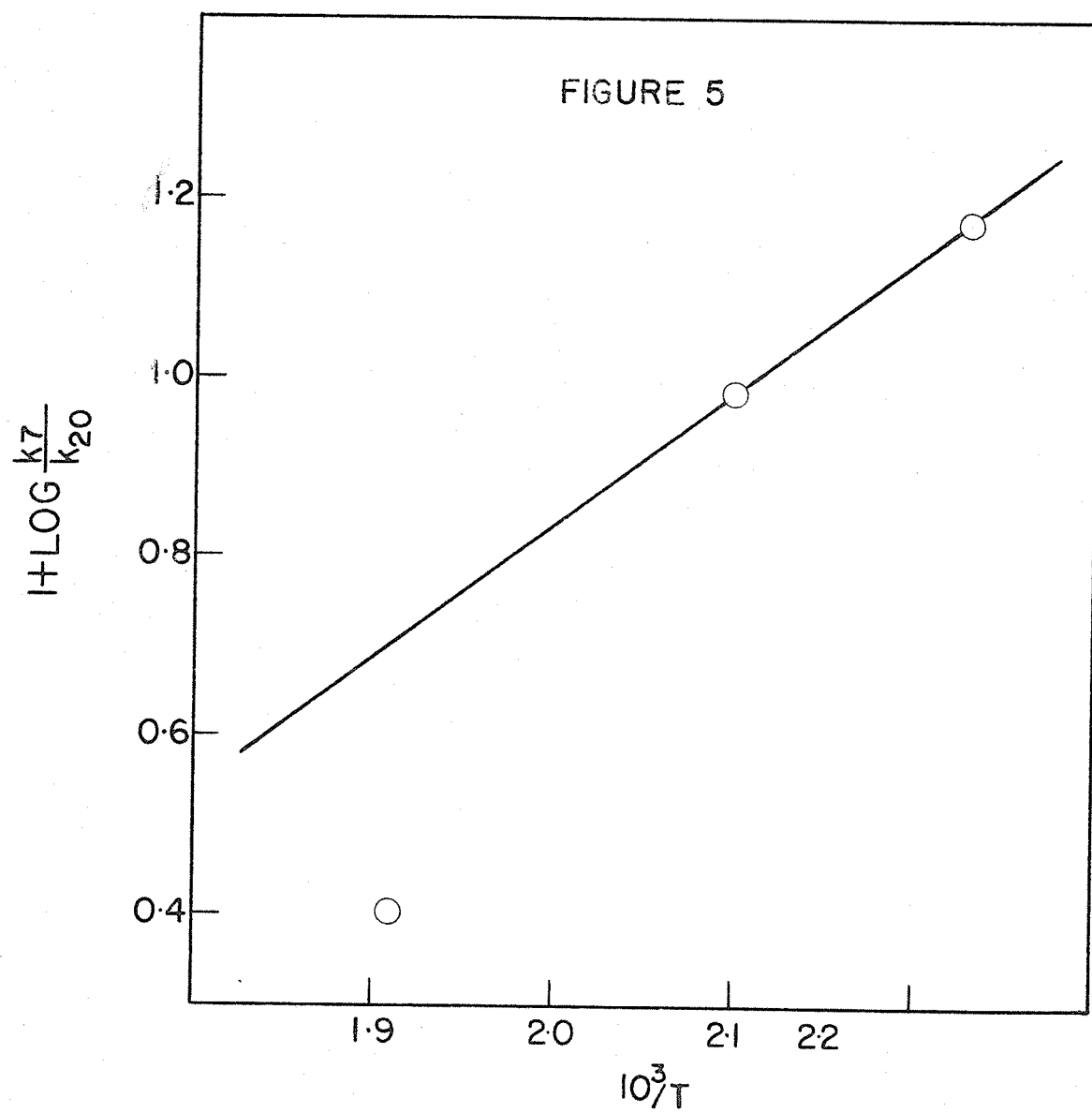
calculated assuming the total amount of ethane came from reaction 1, the points did not lie on the straight line, indicating that the mechanism is incomplete. From the slope of the straight line the difference in activation energies,  $E_{19} - E_7$ , was found to be  $-4.1$  kcal./mole. Taking the value of  $E_7$  as  $9.7$  kcal./mole from the results of Trotman-Dickenson and Steacie (16, 17), the value for  $E_{19}$  is  $5.6$  kcal./mole.

In experiments D3, D4 and D5, the rate of formation of methane coming from acetone,  $R_{CH_4(b)}$ , was calculated using the values of  $k_{19}/k_7$  obtained from Figure 4. The calculations are shown in Table IX. From the values of  $R_{CH_4(b)}$  so obtained the rate of formation of ethane, formed by reaction 1 was calculated using the values of  $k_7/k_1^{1/2}$  obtained from Figure 1. By subtracting this ethane from the total ethane, the rate of formation of ethane from reaction 20 was obtained. These results are shown in Table IX. The plot of  $k_7/k_{20}$ , given by the expression,

$$\frac{k_7}{k_{20}} = \frac{R_{CH_4(b)} [DEA]}{R_{C_2H_6} [CH_3COCH_3]}$$

against  $1/T$  is shown in Figure 5. The activation energy difference,  $E_7 - E_{20}$ , was calculated as  $-6.5$  kcal./mole, and since  $E_7$  is  $9.7$  kcal./mole (16, 17),  $E_{20}$  is  $16.2$  kcal./mole. The point for the highest temperature does not fall on the straight line but this can be readily explained, since the

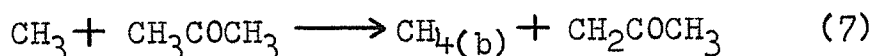
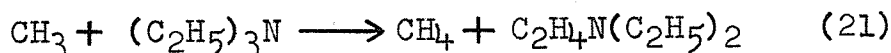
FIGURE 5  
THE REACTION OF METHYL RADICALS WITH DIETHYLAMINE  
LOG  $k_7/k_{20}$  VS  $1/T$



ethane is now being formed by the reaction of ethyl radicals abstracting a hydrogen atom from diethylamine. This ethane was not subtracted from the total ethane because there is no information on this reaction, and the ratio  $R_{\text{CH}_4(b)}/R_{\text{C}_2\text{H}_6}$  is therefore low.

The results of the reaction of methyl radicals with triethylamine are given in Table IV. In experiments A4 and A10 pure acetone was photolysed to check the technique and the accuracy of the apparatus. The values of  $k_7/k_1^{1/2}$  so obtained were compared with the results of Trotman-Dickenson and Steacie (16, 17) and from Figure 1 it can be seen that the agreement is very close.

At low temperatures the only products of the photolysis of acetone in the presence of triethylamine were methane, ethane and carbon monoxide. Neglecting carbon monoxide, the ethane and methane were formed by the following reactions.



By assuming that at all temperatures the ethane found was formed by reaction 1, the value of  $k_{21}/k_1^{1/2}$  may be calculated for each experiment by the method previously used. The results of the calculations are given in Table X. A plot of the ratio  $k_{21}/k_1^{1/2}$  against  $1/T$  is given in Figure 6. The

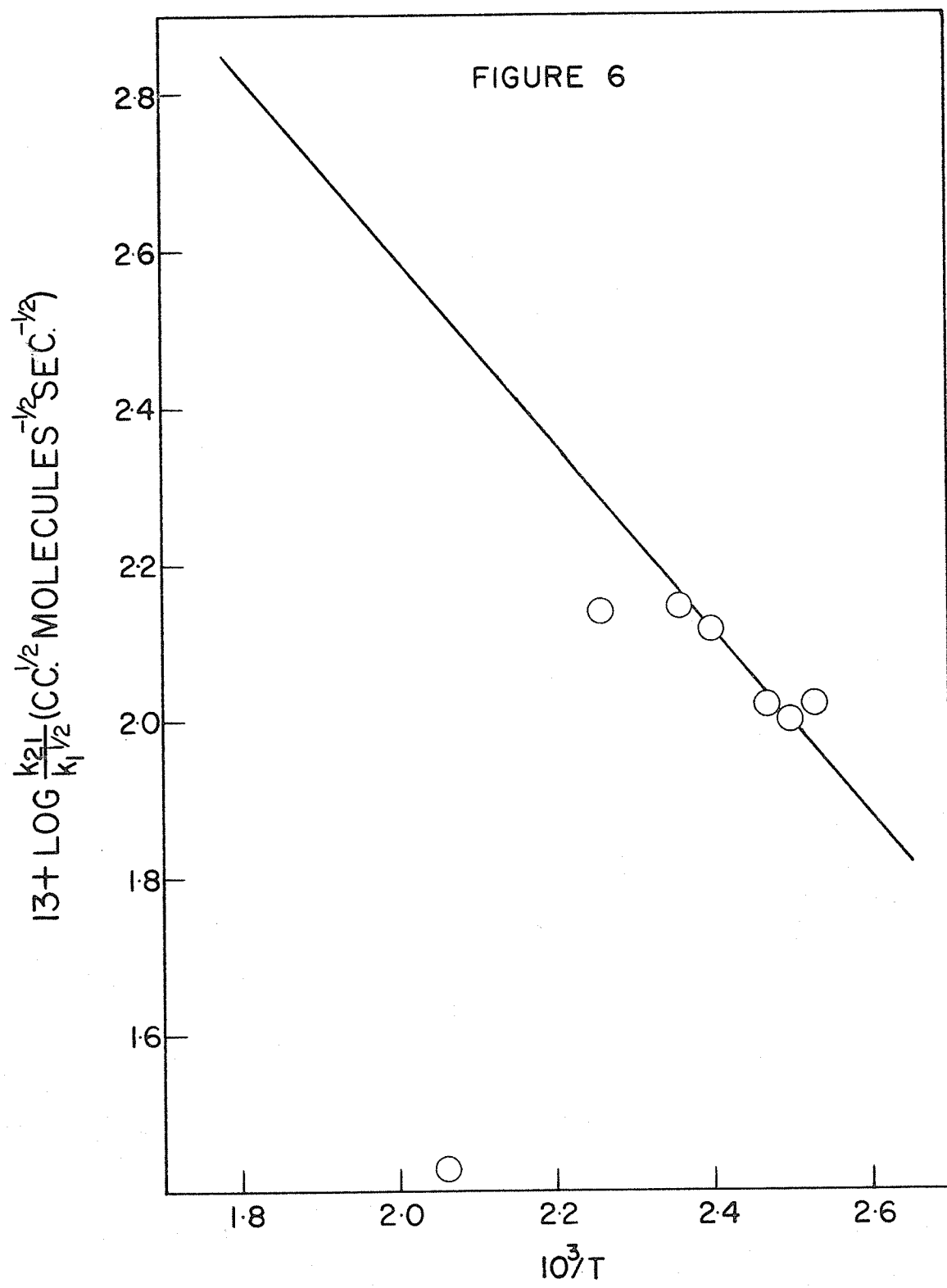
TABLE X  
CALCULATIONS OF  $k_{21}/k_1^{1/2}$  AT VARIOUS TEMPERATURES

Run	10 / T	Conc. of TEA*	Conc. of Acetone*	$R_{CH_4}$ Total	$R_{C_2H_6}$	$R_{CH_4(b)}$	$R_{CH_4}$ Tea	$k_{21}/k_1^{1/2}$
				Molecules/cc. X $10^{-11}$		X $10^{-11}$		X $10^{13}$
A1	2.52	8.72	17.48	139	20.4	9.73	129.3	104
A2	2.26	8.35	19.70	298	45.26	58.6	239.4	135.0
A3	2.06	8.31	23.60	511	209.5	408	101.2	26.8
A5	1.87	8.34	19.90	714	966	--	--	--
A6	2.36	8.57	19.30	225	27.9	27.7	197.3	138
A7	2.40	8.31	18.80	184	23.55	20.2	163.8	128.5
A8	2.50	8.85	19.20	141.5	22.0	12.2	129.3	98.9
A9	2.47	8.42	17.55	145.4	23.0	13.3	132.1	103.7

\*The concentration of triethylamine and acetone is expressed as molecules/cc. X  $10^{-17}$ .

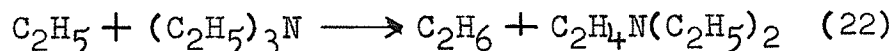
FIGURE 6  
THE REACTION OF METHYL RADICALS WITH TRIETHYLAMINE  
 $\text{LOG } k_{21}/k_1^{1/2} \text{ VS } 1/T$



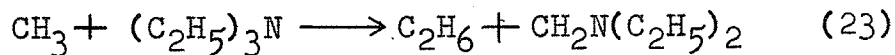


points at higher temperatures did not lie on the straight line indicating that ethane was formed by another process. From the slope of the line drawn through the points at lower temperatures, where the mechanism was consistent, the activation energy for reaction 21 was calculated as 5.5 kcal./mole, assuming that the activation energy for reaction 1 was zero. The energy of activation for the abstraction reaction of methyl radicals with triethylamine is of the same order as that for diethylamine and ethylenimine (20). This would seem to indicate that the same type of hydrogen atom was abstracted in all cases. Hence it is doubtful if the hydrogen that was abstracted in the case of ethylenimine, was the one bonded to the nitrogen.

The presence of ethylene, propane and butane amongst the products in the experiments at higher temperatures indicated that ethyl radicals were present, probably formed by the decomposition of some radical. Therefore ethane must have been formed at high temperatures by the following reaction.



It is also very likely that methyl radicals were undergoing a free radical displacement reaction with triethylamine similar to the reaction with diethylamine.

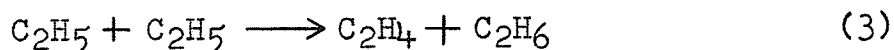


It is impossible to estimate the amount of ethane

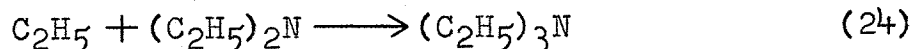
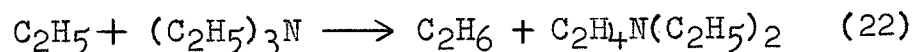
formed by reaction 22 or 23 since neither the rate constants nor any ratio of the rate constants is known. However the activation energy for reaction 23 will be of the same order as reaction 20 but the steric factors will be different. The value of  $k_{23}/k_7$  at any temperature will be different from  $k_{19}/k_7$  because even if the line has the same slope as in Figure 5 it will be displaced. For this reason it was not possible to make a correction for the ethane formed by reaction 23 and the activation energy of reaction 22 could not be calculated.

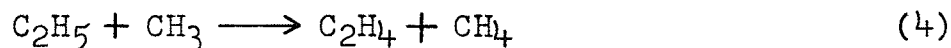
When an attempt was made to calculate the activation energy of reactions 22 and 23 from the results on the photolysis of triethylamine alone the same difficulty was encountered.

The mechanism proposed for the photolysis of triethylamine consists of the three reactions written for the primary process (reactions 16, 17, 18) and the thermal reactions of the free radicals produced in the primary process. The interactions of the free radicals and their reactions with triethylamine may be written as follows.

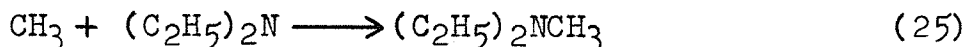
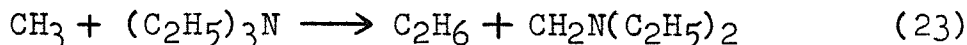


The ratio of  $k_3/k_2$  is known to be 0.12 (8).

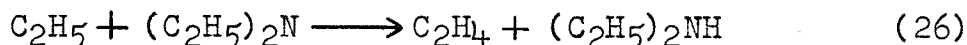




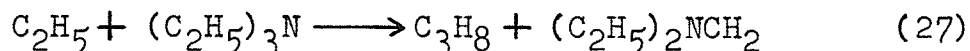
The ratio of  $k_4/k_5$  is known to be  $0.04 \pm 0.02$  (10).



It was found that the rate of formation of ethylene calculated from the ratio  $k_3/k_2$  did not account for all of the ethylene found experimentally (Table XI), even at low temperatures. This indicates that ethylene was formed by another reaction, which takes place readily at low temperatures. The following reaction is proposed to account for this.



The propane could also be formed by a free radical displacement reaction similar to reaction 23.



The large yields of propane at high temperatures (Table III) substantiate this proposed reaction.

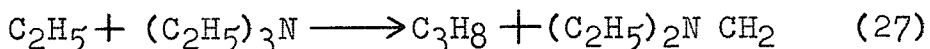
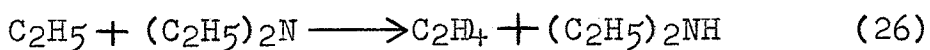
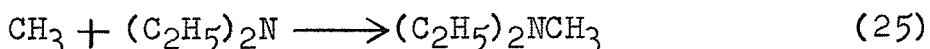
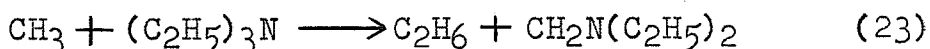
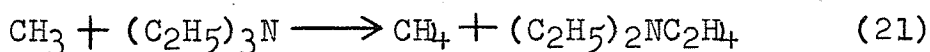
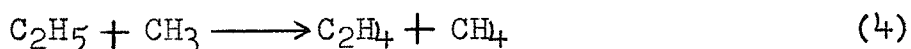
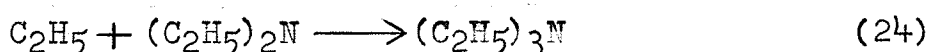
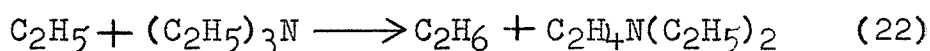
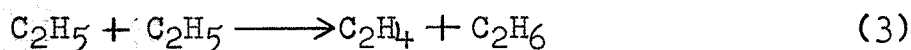
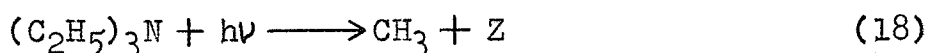
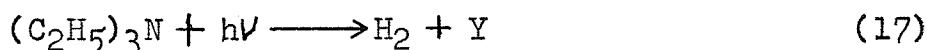
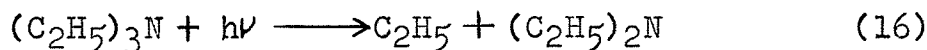
The source of the ethyl radicals found at higher temperatures when methyl radicals react with triethylamine and diethylamine, might be the decomposition of the radical formed after a hydrogen atom is abstracted from the stable molecule.

TABLE XI  
RATE OF FORMATION OF ETHYLENE IN EXCESS OF THE  
DISPROPORTIONATION OF ETHYL RADICALS

Run	RC <sub>2</sub> H <sub>4</sub> Total Molecules/cc./sec. X 10 <sup>-11</sup>	RC <sub>2</sub> H <sub>4</sub> from Reaction 3	RC <sub>2</sub> H <sub>4</sub> from Reaction 4	RC <sub>2</sub> H <sub>4</sub> Excess
47	4.32	1.10	0.26	2.96
48	3.76	0.49	0.10	3.17
49	3.58	0.52	0.13	2.93
50	3.96	0.73	0.22	3.01
51	45.05	2.57	2.35	40.13
52	56.71	2.69	2.71	51.31
53	30.35	2.29	2.00	26.06
54	47.00	2.32	2.18	41.50
55	60.01	1.95	2.95	55.11
56	93.0	3.87	3.10	86.03
57	122.0	6.98	5.47	110.55
58	140.0	8.22	5.80	126.2

## SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1. The photolysis of triethylamine was investigated and the following mechanism is proposed to account for the gaseous products.



2. The activation energy for the abstraction of hydrogen atoms from triethylamine by methyl radicals was determined as 5.5 kcal./mole. The accuracy of this and other activation energies was estimated as  $\pm 1$  kcal./mole.

3. The activation energy for the abstraction of hydrogen atoms from diethylamine by methyl radicals was determined as  $5.7 \pm 1$  kcal./mole.
4. The similarity of activation energies for the abstraction of hydrogen atoms from triethylamine and diethylamine indicates that the same type of hydrogen atom was abstracted in all cases.
5. The upper limit for the activation energy of the free radical displacement reaction of methyl radicals with diethylamine was determined as 16.2 kcal./mole. This result is of a preliminary nature and more work will have to be done to determine it with any degree of accuracy.

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