# THE ABSTRACTION OF HYDROGEN ATOMS FROM AMINES AND RELATED COMPOUNDS<sup>1</sup>

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#### ABSTRACT

The reaction of methyl radicals with a group of amines and amine-like compounds has been investigated in the temperature range 125° to 157°C. The abstraction activation energies of hydrogen atoms from these compounds, the corresponding pre-exponential factors, and the actual reaction rates indicate that the N—H hydrogen atoms are more labile than the C--H atoms in these compounds.

#### INTRODUCTION

The abstraction of hydrogen atoms by methyl radicals from various compounds has been studied in detail by Trotman-Dickenson and Steacie (1). In the case of those compounds with hydrogen atoms attached only to the carbon atom skeleton, they were able to correlate the abstraction activation energies, pre-exponential factors, and actual rates of reaction with the structure of the molecules. Compounds such as amines and alcohols having hydrogen atoms attached to nitrogen or oxygen as well as carbon atoms were found more difficult to evaluate, and they made no attempt to assess the effect of structural factors or the relative importance of the N—H and O—H hydrogen as compared with the C—H hydrogen in the over-all contribution to methane formation.

A little more information on this problem was furnished by the work of Brinton and Volman (2), who reported the activation energy for the methyl radical abstraction of hydrogen from ethylenimine to be 4.8 kcal/mole, a value much lower than any C--H type abstraction found by Trotman-Dickenson and Steacie. Brinton and Volman felt that these data indicated a greater lability of N-II hydrogen than C-H hydrogen in this compound. However, their tacit assumption that the N-H hydrogen was the active species in the abstraction was not founded on any experimental evidence.

Recently Kozak and Gesser (3) investigated the photolysis of triethylamine. In the course of the study they determined the activation energies of methane formation in the reaction of methyl radicals with trimethylamine, triethylamine, and diethylamine by a technique similar to that of Trotman-Dickenson and Steacie. The values obtained, 8.0, 5.3, and 5.7 kcal/mole respectively, led them to conclude that the hydrogen attached to carbon was being abstracted in all of these compounds, and that this was probably the case for ethylenimine also.

Confirmation of Kozak and Gesser's mechanism is to be found in the course of a number of condensations between the  $\alpha$ -carbon of an amine and a 1-olefin occurring in the liquid phase (4). These reactions are induced by peroxides or light so a radical process may be inferred, and it is probable that an abstraction similar to that postulated by Kozak and Gesser is responsible for the type of products found.

The present study was initiated in an attempt to clarify the kinetics of the reaction of methyl radicals with amines. It was hoped that if a clear difference between the ease of hydrogen abstraction from carbon and nitrogen atoms does indeed exist, sufficient data could be obtained so predictions could be unequivocally made concerning the course of the abstraction reactions for amine-type compounds.

Manuscript received April 4, 1960.

Contribution from the Department of Chemistry, University of California, Davis, California.

Can. J. Chem. Vol. 38 (1960)

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#### EXPERIMENTAL

The apparatus and experimental technique have been described previously (5). In the present study the methane and ethane fractions were separated at  $-215^{\circ}$  (solid nitrogen) and  $-185^{\circ}$  (liquid oxygen). Mass spectrometric analyses were made of both fractions. The  $-185^{\circ}$  fraction was in all cases more than 99% ethane. The  $-215^{\circ}$  fraction was 70–99% methane, depending on the sample size. Very small samples (<1  $\mu$  mole) contained appreciable amounts of nitrogen produced from the residual air left in the rather large (3 liters) reaction system.

Di-*t*-butyl peroxide was kindly supplied by the Shell Development Co.; it was purified by bulb-to-bulb distillation *in vacuo*. A center fraction was used in the pyrolysis experiments.

Methylamine and ethylamine were generated from the hydrochloride salts with saturated KOH solution. The amines were dried over KOH pellets, degassed, and distilled *in vacuo*.

Dimethylamine, diethylamine, and diisopropylamine were Eastman White Label products. They were used without further purification except for the degassing procedure. *t*-Butyl ethylenimine was supplied by Dr. Albert Bottini (6).

*t*-Butyl acetaldimine was prepared according to the method of Hurwitz (7) from *t*-butylamine and acetaldehyde. The fraction of boiling range  $78.0-78.1^{\circ}$  (uncorr.) from a 20-plate helice column was collected for the pyrolyses.

The acetaldazine sample used was that employed in previously described work from this laboratory (8).

The pyrolyses were carried out at two temperatures:  $156.73^{\circ}$  C at which a 4-minute reaction period was used, and  $124.82^{\circ}$  where 2 to 4 hours were required for sufficient reaction. The DTBP concentration was about the same in all experiments,  $4.6 \times 10^{-7}$  mole cm<sup>-3</sup> (ca. 11 mm). The pressure of the added compound was adjusted, insofar as it was possible, to produce comparable and significant amounts of methane and ethane so that the analyses of these gases were of good precision. Approximately 3.5% of the DTBP was decomposed at  $156.73^{\circ}$  and from 2 to 4% at  $124.82^{\circ}$ . In most trials the percentage of the added compound reacting was from 0.3 to 2%. In two experiments (dimethylamine and diethylamine at  $124.82^{\circ}$ ) the percentage reacted was about 6%. The average concentration of the added compound was used in all calculations.

#### RESULTS AND DISCUSSION

The pyrolysis of DTBP has been frequently used as a source of methyl radicals in this laboratory (2, 5, 9, 10, 11). The important reactions are:

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO$$
 [1]

$$(CH_3)_3CO \xrightarrow{\kappa_2} CH_3COCH_3 + CH_3$$
[2]

$$2CH_3 \xrightarrow{\kappa_3} C_2H_6$$
[3]

$$CH_{3} + (CH_{3})_{3}COOC(CH_{3})_{3} \xrightarrow{k_{4}} CH_{4} + (CH_{3})_{3}COO(CH_{3})_{2}CH_{2}$$

$$[4]$$

If another hydrogen-containing source, RH, is present additional methane is formed by the process

$$CH_3 + RH \xrightarrow{k_5} CH_4 + R.$$
 [5]

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In the present study the total rate of  $CH_4$  production,  $R_{CH_4}^{total}$ , the summation of [5] and [4], was corrected for the  $CH_4$  formed by [4] in order to evaluate the rate of  $CH_4$  formed in process [5] only,  $R_{CH_4}$ . This correction was made by the following formula:

$$R_{\rm CH_4} = R_{\rm CH_4}^{\rm total} - R_{\rm CH_4}^{\rm DTBP} [R_{\rm C_2H_6} / R_{\rm C_2H_6}^{\rm DTBP}]^{1/2}.$$

Here  $R_{CH_4}^{DTBP}$  and  $R_{C_2H_6}^{DTBP}$  are the rates of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> production in a pyrolysis containing only DTBP. The quantity  $R_{C_{2H_6}}$  is the rate of C<sub>2</sub>H<sub>6</sub> production in a pyrolysis containing RH as an additive. As the concentration of DTBP was about identical in all trials, the ratio of rates of methane formation by process [4] of any two pyrolyses would be expected to be equal to the half power of the ratio of the corresponding rates of ethane formation in the same two experiments. In most of the experiments the correction calculated from  $R_{CH_4}^{DTBP}$  was relatively small, 3–15% of the  $R_{total}^{CH_4}$ . However, the *t*-butyl acetaldimine reacted so slowly that the corrections in these pyrolyses were approximately equal to the methane formed by the hydrogen abstraction from acetaldimine itself.

The values of  $R_{CH_4}/R_{C_{2H_6}}^{1/2}$  [M] =  $k_5/k_3^{1/2}$  have been calculated for the listed concentration, [M], of various amine and amine-like additives. These quantities as well as the activation energies,  $E_5$ , and the log  $A_5$  are listed in Table I. Gomer and Kistiakowsky's (12) values of  $E_3 = 0$  and  $A_3 = 4.5 \times 10^{13}$  for the combination of methyl radicals were used to calculate the individual  $E_5$  and log  $A_5$  in the table. For most compounds, determinations were made at two temperatures only. The previous studies with ethylenimine (2) showed the Arrhenius plot to be a straight line at least over the rather limited temperature range imposed by the use of DTBP as a methyl radical source. Pyrolyses using dimethylamine and diethylamine were made at 138.6° C as well as for the two temperatures shown in Table I. The values of  $k_5/k_3^{1/2}$ , 12.05 and 15.31 respectively, gave good straight lines in the Arrhenius plots of these two compounds.

The data of Table I give strong indication that the N—H hydrogen is active in the formation of methane in the methyl radical abstraction process rather than the hydrogen on the carbon alpha to the nitrogen. This evidence is most easily demonstrated by considering certain groups of Table I separately.

	124.8° C		156.73° C			
Reactant (M)	[M]×10 <sup>7</sup>	$R_{\rm CH_4}/R_{\rm C_2H_6}^{1/2}[{ m M}]$	[M]×107	$R_{\rm CH_4}/R_{\rm C_2H_6}^{1/2}[{ m M}]$	$E_5$ , kcal	$\log A_{i}$
Methylamine	2.73	0.944	2.73	1.92 5.45	7.6	10.9
Dimethylamine	0.982	8.77	1.68	17.30	$\frac{7.1}{7.2}$	11.7
Diisopropylamine	1.00	8.70	1.89 0.755	$\frac{22.20}{18.02}$	7.8	$11.8 \\ 12.0$
Ethylenimine <i>t</i> -Butyl ethylenimine	3.0 8.38	$16.6^{a}$ 0.14	10.78	0.26	$\frac{4.8}{6.6^{b}}$	${10.7 \atop 9.6^b}$
<i>t</i> -Butyl acetaldimine Acetaldazine	$\frac{8.62}{5.89}$	$egin{array}{c} 1.09\ 2.26 \end{array}$	$\begin{array}{c} 10.66 \\ 5.33 \end{array}$	$egin{array}{c} 2,26\ 3,99 \end{array}$	7.8 $6.1$	$\frac{11.1}{10.5}$

TABLE .	L
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The reaction of methyl radicals with amines and related compounds

NOTE: All rates and concentrations are expressed in units of moles, cm<sup>3</sup>, and sec.

<sup>a</sup>Data on ethylenimine are from ref. 2.

<sup>b</sup>These calculated values are of low accuracy because of the very low  $R_{CH_4}$  and the relatively large correction,  $R_{CH_4}^{DTBP}$ , used in the  $R_{CH_4}$  calculation.

#### 1. Dimethylamine (DMA), Diethylamine (DEA), and Diisopropylamine (DIA)

These compounds, all secondary amines, have quite different structures of the two

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aliphatic side chains. All six of the aliphatic group hydrogens of DMA are on primary carbons, four of the 10 hydrogens of DEA are on secondary carbons, and two of the 14 hydrogens of DIA are on tertiary carbons. Table I indicates that all three of these compounds have very similar abstraction activation energies,  $E_5$ , and pre-exponential factors  $A_5$ . Trotman-Dickenson and Steacie (1) and Trotman-Dickenson (13) found the analogous reactions in hydrocarbon systems to be quite sensitive to the type of carbon containing the abstractable hydrogen. If the side-chain hydrogens were being abstracted from the amines, it would be expected that the three amines being considered would show a similar trend, say to the analogous series ethane, n-butane, and 2,3dimethyl butane, which have respectively the abstraction energies 10.4, 8.3, and 6.9 kcal/mole (1). In addition, if DMA is assumed to have six abstractable hydrogen atoms (primary), DEA four (secondary), and DIA two (tertiary) the actual values of  $R_{CH_4}/R_{C_{2H_6}}$  [M] at 124.8° per "active" hydrogen are in the ratios of 1:1.9:3.0. The corresponding ratios for ethane, n-butane, and 2,3-dimethyl butane found by Trotman-Dickenson and Steacie (1) are 1:7.5:51.7 at 182° C. Thus neither the abstraction activation energies nor the rates of abstraction indicate that the side-chain hydrogens of the amines are participating in the abstraction process. It must be inferred rather that the amine hydrogen is active in the reaction and the similarity of activation energy, preexponential factors, and the actual rates of abstraction may be attributed to their being secondary amines.

## 2. Ethylenimine and t-Butyl Ethylenimine

The abstraction activation energy for ethylenimine given previously (2) is considerably lower than others reported for H-atom abstraction by methyl radical from organic compounds. In this former investigation it was assumed that the N-H bond was the active participant in the reaction. It is proposed in the present study to test the validity of such a mechanism by reacting the methyl radicals with *t*-butyl ethylenimine wherein the N—H hydrogen has been replaced by the *t*-butyl group. Table I shows the rate of abstraction from the t-butyl ethylenimine to be less than 10% of the analogous reaction from ethylenimine itself at 124.8°. Inasmuch as the ring hydrogens are available to an equal degree from both these compounds, a strong argument can be made to eliminate these H atoms as sources of methane production and to establish the N-H hydrogen as the principal reactant with the methyl radicals. The activation energy and preexponential factor for t-butyl ethylenimine are shown bracketed in Table I. The very low rate of methane production for this compound at both experimental temperatures introduces considerable error into these calculated quantities. They should be considered as approximations only and no significance can be attributed to their values relative to the values of the corresponding constants for ethylenimine.

## 3. t-Butyl Acetaldimine and Acetaldazine

*t*-Butyl acetaldimine  $(CH_3)_3C-N=CH-CH_3$  and acetaldazine  $CH_3CH=N-N=CHCH_3$  have been included to show the behavior of compounds which do not have N-H hydrogens available. Again it is not certain which hydrogen is entering into reaction, those of the terminal  $CH_3$  group or the H atoms on the carbon of N=C bond. However, it is quite significant that the rate at 124.8° for the acetaldazine abstraction is almost exactly twice that for *t*-butyl acetaldimine. Two hydrogens on the C=N carbon and six hydrogens on  $CH_3$  groups are available in acetaldazine, and one hydrogen on C=N carbon and 12 hydrogens on  $CH_3$  groups are contained on the *t*-butyl acetaldimine. Thus the

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abstraction rates of the two compounds are compatible with the interpretation that the C—N carbon atom furnishes the hydrogen for the abstraction although the evidence is not extensive enough to justify a definite conclusion.

## 4. Methylamine and Ethylamine

The data in Table I for these two compounds do not furnish further confirmation for the thesis that the N—H hydrogen is active in the abstraction process. On the other hand the evidence is not necessarily contradictory. The similarity in the abstraction activation energies does tend to support the idea of N—H hydrogen abstraction but it is not clear why the abstraction rate at 124.8° for ethylamine is about three times that of methylamine.

The conclusions reached in the preceding discussion as well as some of the experimentally determined data differ markedly from those of Kozak and Gesser's study (3). Their conclusion that low and similar abstraction energies for triethylamine and diethylamine probably indicate a labile C—H rather than N—H hydrogen is reasonable on basis of this evidence alone. However, their value for the abstraction constant of diethylamine (log A = 10.9, E = 5.7) is somewhat different from that shown in Table I (log A = 11.8, E = 7.2). Reasons for this difference are speculative as the experimental methods used in both investigations have proved to be reliable in a large number of previously tested cases. It should be pointed out that the data of Trotman-Dickenson (13) for methylamine (log A = 11.3, E = 8.4) and dimethylamine (log A = 11.3, E = 7.2) are in good agreement with the corresponding quantities shown in Table I, and in addition their value for trimethylamine (log A = 11.8, E = 8.8) agrees reasonably well with Kozak and Gesser's result (log A = 12.6, E = 8.0) for this same compound. Thus all three studies show conformity between at least some compounds that were mutually tested.

A possible clue to the wide difference in abstraction activation energies for diethylamine between the present study and Kozak and Gesser's work may be seen in their Arrhenius plots for diethylamine and triethylamine. In both curves there is a pronounced falling off in the values of  $k_{abs}/k_{comb}^{1/2}$  at the higher temperature. Their explanation for this curvature, the growing importance of the reaction,

$$CH_3 + (C_2H_5)_2NH \rightarrow C_2H_5NHCH_2 + C_2H_6,$$
[6]

as temperature is increased is compatible with the experimental evidence. However, their assumption that the straight lines drawn through the limited low-temperature points truly represent the behavior of reaction [5] only is open to considerable doubt. It seems reasonable that the effect of reaction [6] is active to a degree, at least, over the whole temperature range and that the slopes of the Arrhenius lines should be somewhat steeper, thereby yielding higher activation energies for triethylamine and diethylamine. Whether both curves would be affected in a similar fashion is not predictable, but it is not unlikely that the relative magnitude of the two activation energies might shift so that different conclusions could be drawn concerning the role of the various hydrogens in the abstraction process.

The argument in the previous paragraph would apply equally as well to the present study if reaction [6] were taking place even to a limited extent in the lower temperature range. As the total rate of ethane production would then be the sum of processes [3] and

\*The values calculated by Kozak and Gesser for this corresponding quantity for diethylamine,  $A_{19}/A_8^{1/2} = 9 \times 10^{-5}$  is in error. The value should be  $1.4 \times 10^{-8}$  molecule<sup>-1/2</sup> cm<sup>3/2</sup> sec<sup>-1/2</sup>. Similarly their value of  $A_{11}/A_8^{1/2}$  for triethylamine shown as  $3 \times 10^{-5}$  should be  $6.8 \times 10^{-9}$ .

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[6], the error made by using the total  $R_{C_{2H_6}}$  in place of  $R_{C_{2H_6}}$  by [3] would depend on the relative rates of the two ethane-producing reactions. It can be shown that

$$\frac{R_{\rm CH_4}}{R_{\rm C_{2H_6}}^{1/2}[\rm M]} = \frac{k_5}{k_3^{1/2}} \left[ 1 + \frac{k_6[\rm M]}{k_3[\rm CH_3]} \right]^{-1/2}.$$

Thus the effect of process [6] on the value determined for  $k_5/k_3^{1/2}$  will be minimized by low concentrations of additive, [M], as well as high methyl radical concentrations,  $[CH_3]$ .

It is significant that there is appreciable difference between the magnitude of both these variables in the two studies under comparison. The diethylamine concentrations used by Kozak and Gesser in their photolyses  $(12.4 \times 10^{-7} \text{ to } 16.9 \times 10^{-7} \text{ mole cm}^{-3})$ were about 10 times those used in the DTBP pyrolyses. Clearly in this case the effect of the additive term in the above expression will be only about 1/10th as great for this study as for Kozak and Gesser's work.

The consequence of using an appreciably higher methyl radical steady-state concentration at 156.7° in the peroxide work than in the photolyses is not so easily evaluated. In the present work on diethylamine  $R_{c_{2H_0}}$  is approximately  $3.0 \times 10^{-12}$  and  $115 \times 10^{-12}$  mole cm<sup>-3</sup> sec<sup>-1</sup> at 124.8° and 156.7° respectively. The lower temperature rate is about conparable to that of Kozak and Gesser's 123° experiment  $(2.5 \times 10^{-12})$ , but the higher temperature rate is about 50 times the rate of their 155° photolysis  $(2.1 \times 10^{-12})$ . From the above expression it may be seen that for a constant [M] the activation energy measured by the change in  $R_{CH_4}/R_{C_{2H_6}}$  [M] as a function of temperature will be exactly that of  $E_5$  if  $k_6/[CH_3]$  is maintained constant over the range of temperature variation. Kozak and Gesser's Arrhenius curves for diethylamine and triethylamine indicate that  $E_6$  is considerably higher than  $E_5$ , perhaps of the order of 15 kcal/mole, and therefore  $k_6(156.7^\circ)/k_6(124.8^\circ) \cong 4$ . In order for  $k_6/[CH_3]$  to maintain its constancy the ratio  $R_{C_{2H_6}}(156.7^{\circ})/R_{C_{2H_6}}(124.8^{\circ})$  must be of the order of 16. If this estimate of  $E_6$  is valid and if  $R_{C_2H_5}^{1/2}$  may be taken as being proportional to [CH<sub>3</sub>], the experimental technique of Kozak and Gesser in which  $[CH_3]$  was about constant would yield a value somewhat too small for  $E_5$  while that of the present work would give too large an activation energy. The magnitude of the error of course depends on the size of the additive term within the bracketed expression of the above formula. Determination of the absolute magnitude of the effect of [6] on ethane formation and thus on the value of  $E_5$  is perhaps possible by a detailed study of diethylamine variation at constant temperature in the case of the DTBP pyrolyses. In a like manner investigation of the effect of intensity and diethylamine variation at constant temperature for the photolyses of Kozak and Gesser should produce similar information.

#### ACKNOWLEDGMENTS

The author wishes to thank the National Science Foundation for financial assistance in carrying out this study. He is also indebted to Dr. Amos Newton and Mr. Aldo Sciamanna of the Lawrence Radiation Laboratory, University of California, Berkeley, California, for some of the mass spectrometric analyses.

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