# 86. *The Photolysis of Triethylamine, and Reactions of Methyl Radicals with Triethylamine and Diethylamine.*

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The photochemical decomposition of triethylamine has been investigated over the temperature range of 0—254° c. The gaseous products were hydrogen, methane, ethane, ethylene, propane, and butane. The primary photochemical product is hydrogen, with methyl and ethyl radicals produced from triethylamine in an excited state. A mechanism is proposed to account for the products.

Hydrogen-abstraction of methyl radicals with triethylamine and diethylamine was investigated over the temperature range of 123—~260° c and the activation energies of the reactions were found to be about 5·3 and 5·7 kcal./mole respectively.

Evidence is given for the inversion or free-radical displacement reactions

$$CH_3\cdot + (C_2H_5)_3N \longrightarrow C_2H_6 + \cdot CH_2\cdot N(C_2H_5)_2$$
$$CH_3\cdot + (C_2H_5)_2NH \longrightarrow C_2H_6 + \cdot CH_2\cdot NH\cdot C_2H_5$$

Photolysis of trimethylamine has been shown [1] to be complicated by the presence of hydrogen amongst the gaseous products. The primary process postulated was the formation of methyl radicals from an excited trimethylamine molecule. The hydrogen was considered to be formed by secondary reactions of the dimethylamino-radical. Photolysis of triethylamine has now been investigated to see if the above photochemical reactions are common to tertiary amines; and to explain some of the results obtained, a study was made of the reactions of methyl radicals with triethylamine and diethylamine.

## Experimental

The apparatus used was similar to those previously described.[1] The source of radiation was a Hanovia S-500 medium-pressure mercury arc. The light beam was collimated with a quartz lens and a stop. The full unfiltered arc was used in the photo-decomposition of triethylamine. A Corning filter No. 9863 was used when nitric oxide was added to triethylamine and a Corning filter No. 7740 was used when acetone and amine mixtures were photolysed. The quartz cell used at high temperatures was 2·5 cm. in diameter and 10 cm. long and was enclosed in an open-ended brass-block furnace 14 cm. long. The temperature was controlled within 1° c.

The analytical system consisted of a trap for solid nitrogen to separate the non-condensable gases from the ethylene and higher hydrocarbons, a LeRoy still for the fractional distillation of the condensable hydrocarbon products, a micro-hydrogenator [2] for determination of the unsaturated hydrocarbons, a copper–copper oxide furnace at 210° for determination of hydrogen and carbon monoxide, and a platinum-wire combustion furnace for oxidation of hydrocarbons.

Triethylamine (Eastman's White Label grade) was fractionally distilled from anhydrous barium oxide. It was further dried, fractionated, and degassed in the vacuum-line by bulb-to-bulb distillation. Eastman's "Spectrograde" acetone was distilled from anhydrous copper sulphate and further fractionated by bulb-to-bulb distillations in the vacuum-line, the middle third fraction being retained. Trimethylamine was identical with that previously used.[1] Diethylamine (Eastman's White Label grade) was dried over anhydrous barium oxide and fractionated in the vacuum-line.

The mixture of acetone and amine was stirred for 15 min. by an all-glass stirrer before the start of each photolysis.

## Results and Discussion

*Photolysis of Triethylamine.*—The gaseous products from the photolysis of triethylamine were identified as hydrogen, methane, ethane, ethylene, propane, and butane. Nitrogen,

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[1] Gesser, Mullhaupt, and Griffiths, *J. Amer. Chem. Soc.*, 1957, **79**, 4834.

[2] Shepp and Kutschke, *Canad. J. Chem.*, 1954, **32**, 1112.

propene, and butene were shown to be absent within the limits of the analytical techniques employed.

The results of preliminary experiments in the low-temperature cell[1] are recorded in Table 1. They show that the rates of formation of products, with the exception of hydrogen and ethylene, in general increase with decrease in pressure of reactant. The high extinction coefficient for triethylamine[3] means almost complete absorption of the effective mercury lines. This is analogous to the results obtained for trimethylamine and indicates that the products, except hydrogen, are formed by dissociation of an excited triethylamine molecule which can be pressure-quenched.

TABLE 1. *Photolysis of triethylamine.*

Illumination time = 1 hr. Illumination vol. = 130 cm.$^3$.

| Temp. | $[(C_2H_5)_3N]$ (molecules/cm.$^3$) $\times 10^{-17}$ | $R_{CH_4}$ | $R_{H_2}$ | $R_{C_2H_4}$ | $R_{C_2H_6}$ | $R_{C_3H_8}$ | $R_{C_4H_{10}}$ |
|---|---|---|---|---|---|---|---|
| | | | (molecules cm.$^{-3}$ sec.$^{-1}$) $\times 10^{-11}$ | | | | |
| 0° | 3·7 | 2·0 | 16·0 | 8·1 | 11·5 | 6·2 | 6·3 |
| 0 | 1·7 | 2·7 | 12·4 | 4·3 | 13·4 | 6·6 | 8·8 |
| 27 | 15·4 | 2·2 | 19·6 | 3·8 | 10·0 | 2·6 | 3·9 |
| 27 | 6·6 | 2·0 | 16·9 | 3·6 | 11·0 | 3·2 | 4·1 |
| 27 | 2·0 | 2·0 | 11·9 | 4·0 | 13·1 | 5·5 | 5·8 |

TABLE 2. *Photolysis of triethylamine.*

Illuminated vol. = 196 cm.$^3$.

| Temp. | Time (sec.) | $[(C_2H_5)_3N]$ (molecules cm.$^{-3}$) $\times 10^{-17}$ | | $R_{H_2}$ | $R_{CH_4}$ | $R_{C_2H_4}$ | $R_{C_2H_6}$ | $R_{C_3H_8}$ · | $R_{C_4H_8}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | (molecules cm.$^{-3}$ sec.$^{-1}$) $\times 10^{-12}$ | | | | |
| | | | | Full arc | | | | | |
| 76° | 3600 | 8·0 | | 13·3 | 2·6 | 4·5 | 18·8 | 5·9 | 2·1 |
| 120 | 1800 | 8·4 | | 15·5 | 3·5 | 5·7 | 26·1 | 6·8 | 2·2 |
| 28 | 3600 | 7·1 | | 9·0 | 1·8 | 3·0 | 16·8 | 5·0 | 1·8 |
| 76 | 1800 | 8·3 | | 12·8 | 2·2 | 4·7 | 16·4 | 5·4 | 1·9 |
| 169 | 1800 | 8·5 | | 14·0 | 5·3 | 6·0 | 32·0 | 7·4 | 1·6 |
| 208 | 1800 | 8·4 | | 12·9 | 9·7 | 9·3 | 49·1 | 7·7 | 3·1 |
| 254 | 1800 | 8·2 | | 11·5 | 35·5 | 12·2 | 150 | 13·7 | 5·6 |
| 253 | 600 | 8·4 | | 12·0 | 37·3 | 14·0 | 116 | 14·5 | 6·6 |
| | | | | Corning filter No. 9863 | | | | | |
| 30 | 1800 | 10·7 | 0 * | 3·8 | Nil | 0·12 | 0·24 | Nil | Nil |
| 30 | 3600 | 10·7 | 8 * | 4·0 | Nil | Nil | Nil | Nil | Nil |

* Pressure of nitric oxide (in mm.).

When triethylamine was photolysed in the presence of excess of nitric oxide (Table 2) only hydrogen (with small amounts of nitrogen and nitrous oxide formed from the photolysis of nitric oxide) was formed in yields approximately equal to that obtained in the absence of nitric oxide. This seems to indicate that hydrogen is formed by a molecular process, whereas the hydrocarbon products are formed by free-radical reactions probably involving both methyl and ethyl radicals.

The results of the photolysis of triethylamine at approximately constant concentration at elevated temperature are recorded in Table 2 and show that the rate of formation of hydrogen is constant within 10% and that the rates of formation of the hydrocarbon products increase with increase in temperature. This is consistent with the low-temperature results and the requirements of an excited triethylamine intermediate.

The annexed mechanism best explains the results. Recombination of the amino-radicals to form liquid products is expected. Other reactions are required to explain the relative yields of hydrocarbon products at low temperature. Reactions (12) and (14) are required to explain the high yields of propane (and ethane) at high temperatures. Evidence

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[3] Tannenbaum, Coffin, and Harrison, *J. Chem. Phys.*, 1953, **21**, 311.

for a weak αβ carbon–carbon bond in amines has been obtained by Collin.[4] A similar reaction,[5] $H\cdot + C_2H_5\cdot NH_2 \longrightarrow CH_4 + \cdot CH_2\cdot NH_2$, can account for the high yields of methane in the reaction of hydrogen atoms with ethylamine.[6]

$$(C_2H_5)_3N + h\nu \begin{cases} \longrightarrow H_2 + C_6H_{13}N & \dots\dots (1) \\ \longrightarrow (C_2H_5)_3N^* & \dots\dots (2) \end{cases}$$

$$(C_2H_5)_3N^* \begin{cases} \longrightarrow (C_2H_5)_2N\cdot + C_2H_5\cdot & \dots\dots (3) \\ \longrightarrow (C_2H_5)_2N\cdot CH_2\cdot + CH_3\cdot & \dots\dots (4) \end{cases}$$

$$(C_2H_5)_3N^* + (C_2H_5)_3N \longrightarrow 2(C_2H_5)_3N \quad \dots\dots (5)$$

$$C_2H_5\cdot + C_2H_5\cdot \begin{cases} \longrightarrow C_2H_6 + C_2H_4 & \dots\dots (6) \\ \longrightarrow C_4H_{10} & \dots\dots (7) \end{cases}$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \quad \dots\dots (8)$$

$$CH_3\cdot + C_2H_5\cdot \begin{cases} \longrightarrow CH_4 + C_2H_4 & \dots\dots (9) \\ \longrightarrow C_3H_8 & \dots\dots (10) \end{cases}$$

$$CH_3\cdot + (C_2H_5)_3N \begin{cases} \longrightarrow (C_2H_5)_2N\cdot C_2H_4\cdot + CH_4 & \dots\dots (11) \\ \longrightarrow (C_2H_5)_2N\cdot CH_2\cdot + C_2H_6 & \dots\dots (12) \end{cases}$$

$$C_2H_5\cdot + (C_2H_5)_3N \begin{cases} \longrightarrow (C_2H_5)_2N\cdot C_2H_4\cdot + C_2H_6 & \dots\dots (13) \\ \longrightarrow (C_2H_5)_2N\cdot CH_2\cdot + C_3H_8 & \dots\dots (14) \end{cases}$$

*Reaction of Methyl Radicals with Triethylamine and Diethylamine.*—When acetone alone is photolysed above 120° C the following reactions account for the methane and ethane produced:

$$CH_3\cdot CO\cdot CH_3 + h\nu \longrightarrow 2CH_3\cdot + CO \quad \dots\dots (15)$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \quad \dots\dots (8)$$

$$CH_3\cdot + CH_3\cdot CO\cdot CH_3 \longrightarrow CH_4 + \cdot CH_2\cdot CO\cdot CH_3 \quad \dots\dots (16)$$

and the relation $R_{CH_4}/(R_{C_2H_6})^{\frac{1}{2}}[A] = k_{16}/k_8^{\frac{1}{2}}$ is obeyed ($R$ refers to rate of formation, and [A] represents the concentration of acetone). The value of $k_{16}/k_8^{\frac{1}{2}}$ obtained at various temperatures agreed with those reported by Trotman-Dickenson and Steacie[7] (cf. Fig. 1).

In the presence of an added gas with an abstractable hydrogen atom, an additional reaction can occur, namely:

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \quad \dots\dots (17)$$

and the expression $R_{CH_4}/(R_{C_2H_6})^{\frac{1}{2}} = k_{16}[A]/k_8^{\frac{1}{2}} + k_{17}[RH]/k_8^{\frac{1}{2}}$ is then valid.[8] At any temperature, all the values except $k_{17}/k_8^{\frac{1}{2}}$ are known and hence it is possible to calculate

[4] Collin, *Bull. Soc. chim. belges*, 1954, **63**, 500.
[5] Jamieson, Ph.D. Thesis, McGill University, 1956.
[6] Wright, Jamieson, and Winkler, *J. Phys. Chem.*, 1958, **62**, 657.
[7] Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1950, **18**, 1097.
[8] Trotman-Dickenson and Steacie, *ibid.*, 1951, **19**, 329.

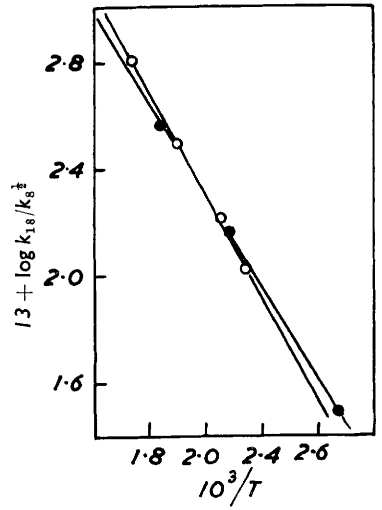
this ratio from the rates of formation of methane and ethane, the concentration of acetone and amine, and from the known values of $k_{16}/k_8^{\frac{1}{2}}$.

Methyl radicals were first caused to react with trimethylamine to check the effectiveness of the stirring and other experimental techniques. The results are recorded in Table 3. The activation energy for the reaction

$$CH_3\cdot + (CH_3)_3N \longrightarrow CH_4 + (CH_3)_2N\cdot CH_2\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

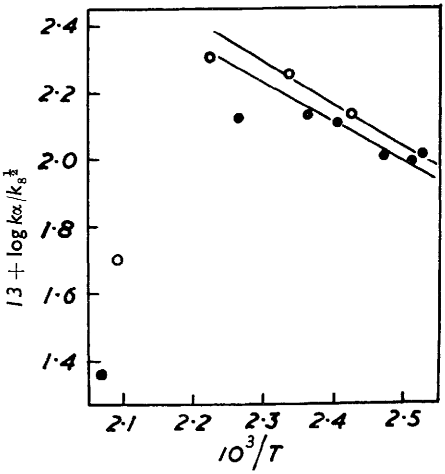
was found to be 8·0 kcal./mole from the Arrhenius plot of $k_{18}/k_8^{\frac{1}{2}}$ against $1/T$ shown in

FIG. 1. *Arrhenius plot of* $k_{18}/k_8^{\frac{1}{2}}$.



● *Present work.* ○ *Results of Trotman-Dickenson and Steacie*

FIG. 2. *Arrhenius plots of* $k_{11}/k_5^{\frac{1}{2}}$ *and* $k_{19}/k_8^{\frac{1}{2}}$.



● $\alpha = 11$. ○ $\alpha = 19$.

Fig. 1, where also comparison is made with the results of Trotman-Dickenson and Steacie [8] who obtained a value of 8·8 kcal./mole. This agreement is considered to be reasonably good.

TABLE 3. *Reaction of methyl radicals with trimethylamine.*

| Temp. | Time (sec.) | $[(CH_3)_3N]$ | [A] | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | $k_{18}/k_8^{\frac{1}{2}}$ |
|---|---|---|---|---|---|---|---|
| | | (molecules cm.$^{-3}$) $\times 10^{-17}$ | | (molecules cm.$^{-3}$ sec.$^{-1}$) $\times 10^{-11}$ | | | (cm.$^{\frac{3}{2}}$ molecules$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$) $\times 10^{13}$ |
| 132° | 1800 | 10·0 | 10·0 | 117 | 75·2 | 43·6 | 31 |
| 208 | 900 | 10·0 | 10·0 | 198 | 255 | 19·9 | 146 |
| 269 | 900 | 11·8 | 11·8 | 256 | 496 | 6·8 | 375 |

The results of the reaction of methyl radicals with triethylamine and diethylamine are recorded in Tables 4 and 5 respectively. Hydrogen was not obtained in any of these experiments, or in those with trimethylamine. Arrhenius plots for the activation energies of reactions (11) and (19) (Fig. 2) give the values of 5·3 kcal./mole for $E_{11}$ and 5·7 kcal./mole for $E_{19}$. A large error of about $\pm 1$ kcal./mole is estimated for these activation energies. The approximate values for $A_{11}/A_8^{\frac{1}{2}}$ and $A_{19}/A_8^{\frac{1}{2}}$ are $3 \times 10^{-5}$ and $9 \times 10^{-5}$ respectively.

$$CH_3\cdot + (C_2H_5)_2NH \longrightarrow CH_4 + C_2H_5\cdot NH\cdot C_2H_4 \quad . \; . \; . \; . \; . \; . \; . \quad (19)$$

The fact that the values of $E_{11}$ and $E_{19}$ are similar seems to indicate that the same type of hydrogen atom is abstracted in each case. For diethylamine this means that hydrogen is abstracted from the carbon atom rather than from the nitrogen atom, though there is no evidence to indicate whether the α- or the β-carbon has the weaker carbon–hydrogen bond.

A similar low value of 4·8 kcal./mole was obtained by Brinton and Volman [9] for the activation energy for methyl-radical abstraction of hydrogen from ethyleneimine. However, these authors assumed that the amine-hydrogen was abstracted, and the possibility of a weak carbon–hydrogen bond in ethylenimine must now be considered.

The break in the slope of the Arrhenius lines at high temperatures indicates the presence of another process for the formation of ethane, which in both reactions is probably the radical-displacement mechanism (12) and (20):

$$CH_3\cdot + (C_2H_5)_2NH \longrightarrow C_2H_6 + C_2H_5\cdot NH\cdot CH_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

The presence of ethylene, propane, and butane at the high temperature can best be explained by assuming that the amine radicals formed in reactions (11), (12), (19), and (20) decompose thermally into ethyl radicals and ethylene. Butene is probably formed by reaction (7). Since $k_6/k_7$ can be taken [10] as 0·12 and $k_9/k_{10}$ as 0·04 (ref. 11), and if ethylene is formed solely by reactions (6) and (9), then $R_{C_2H_4}/(0{\cdot}12R_{C_4H_{10}} + 0{\cdot}04R_{C_3H_8})$ should be unity. However, this ratio is experimentally greater than unity and this implies an additional ethylene-forming reaction, probably the decomposition of the amine radicals.

TABLE 4. *Reaction of methyl radicals with triethylamine.*

| Temp. | Time (sec.) | $[(C_2H_5)_3N]$ (molecules cm.$^{-3}$) $\times 10^{-17}$ | [A] | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | $R_{C_2H_4}$ | $R_{C_3H_8}$ | $R_{C_4H_{10}}$ | $k_{11}/k_8^{\frac{1}{2}}$ (cm.$^{\frac{3}{2}}$ molecules$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$) $\times 10^{13}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | (molecules cm.$^{-3}$ sec.$^{-1}$) $\times 10^{-11}$ | | | | | |
| 123° | 600 | 8·7 | 17·5 | 134 | 139 | 20·4 | — | — | — | 103 |
| 169 | 1800 | 8·4 | 19·7 | 228 | 298 | 45·3 | 2·3 | — | — | 133 |
| 213 | 900 | 8·3 | 23·6 | 327 | 511 | 209 | 13·2 | 45·3 | 12·2 | 23 |
| 263 | 900 | 8·3 | 19·9 | 400 | 714 | 966 | 32·0 | 61·2 | 38·2 | *x* |
| 151 | 900 | 8·6 | 19·3 | 184 | 225 | 27·9 | — | — | — | 136 |
| 143 | 900 | 8·3 | 18·8 | 156 | 184 | 23·6 | — | — | — | 129 |
| 126 | 1200 | 8·9 | 19·2 | 130 | 142 | 22·0 | — | — | — | 99 |
| 132 | 900 | 8·4 | 17·6 | 133 | 145 | 23·0 | — | — | — | 103 |

— signifies an immeasurable amount of product, if any.
*x* represents a negative value.

TABLE 5. *Reaction of methyl radicals with diethylamine.*

| Temp. | Time (sec.) | $[(C_2H_5)_2NH]$ (molecules cm.$^{-3}$) $\times 10^{-17}$ | [A] | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | $R_{C_2H_4}$ | $R_{C_3H_8}$ | $R_{C_4H_{10}}$ | $k_{19}/k_8^{\frac{1}{2}}$ (cm.$^{\frac{3}{2}}$ molecules$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$) $\times 10^{13}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | (molecules cm.$^{-3}$ sec.$^{-1}$) $\times 10^{-11}$ | | | | | |
| 123° | 1800 | 7·5 | 7·5 | 76 | 98·4 | 15·2 | — | — | — | 103 |
| 155 | 1800 | 8·4 | 8·2 | 111 | 167 | 12·5 | — | — | — | 168 |
| 175 | 1800 | 8·8 | 8·8 | 135 | 216 | 12·5 | — | — | — | 202 |
| 204 | 1800 | 9·3 | 10·7 | 190 | 330 | 36·0 | — | — | — | 148 |
| 249 | 900 | 10·2 | 11·1 | 252 | 550 | 236 | 10·5 | 15·3 | 30·6 | 15 |
| 140 | 1800 | 9·4 | 9·4 | 100 | 146 | 21·1 | — | — | — | 135 |

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[9] Brinton and Volman, *J. Chem. Phys.*, 1952, **20**, 25.

[10] Kutschke, Wijnen, and Steacie, *J. Amer. Chem. Soc.*, 1952, **74**, 714; Brinton and Steacie, *Canad. J. Chem.*, 1955, **33**, 1840.

[11] Ausloos and Steacie, *Canad. J. Chem.*, 1955, **33**, 1062.