The Radiolysis of Mono-, Di- and Trimethylamine in the Gas Phase

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(Received September 24, 1964)

The photolysis of methylamine has been extensively studied during the past twenty years.[1-5] Although the mechanism whereby methylamine decomposes is not completely understood, the most recent study[5] has shown that the primary process is the formation of hydrogen atoms; there may also be a small degree of molecular detachment of hydrogen, which is well known in the fields of the vacuum ultraviolet photochemistry and radiation chemistry of hydrocarbons, as well as a dissociation to methyl and amine radicals.

On the other hand, the radiolysis of aliphatic amines in the gas phase has received little attention.[6,7] Hydrogen and N,N'-tetramethylethylenediamine were observed as the main products in the radiolysis of trimethylamine by Schindler and Krivak.[7] However, much, has been unknown with regard to the primary process.

We, therefore, hoped to clarify the mechanism of the radiolysis of amines and compare the results with those of the photolysis. The present study was undertaken in order to obtain information on the primary process in the radiolysis of methylamines in the gas phase. The methylamines used were mono-, di-, and trimethylamines; the radical scavenger technique was employed to estimate the mechanism of hydrogen formation.

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1) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York (1941), p. 382.

2) C. C. Wetmore and H. A. Taylor, *J. Chem. Phys.*, **12**, 61 (1943).

3) C. I. Johnson and H. A. Taylor, ibid., **19**, 613 (1951).

4) J. S. Watson and B. deB. Darwent, ibid., **20**, 1041 (1952).

5) J. V. Michael and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 1228 (1963).

6) J. Collin, *Bull. soc. chim. Belg.*, **67**, 549 (1958).

7) R. N. Schindler and T. G. Krivak "Quarterly Report," Mellon Institute, Radiation Research Laboratories (Jan.—March, 1963), p. 9.

Experimental

Materials. — Methylamine was prepared from hydrochloride which had been purified by recrystallization several times with water and dried in a vacuum desiccator. The hydrochloride was treated with a nearly-saturated solution of potassium hydroxide at atmospheric pressure. The methylamine evolved was dried by passing it through a column of potassium hydroxide and then collected in a trap in liquid nitrogen, attached to a convenient vacuum line. The amine was kept in a storage bulb after trap-to-trap distillation. The infrared analysis of the sample showed that ammonia was not present as an impurity. The preparation of di- and trimethylamine was similar to that of methylamine mentioned above.

Propane was obtained from the Takachiho Chemicals Co., Tokyo, and was purified by treatment with concentrated sulfuric acid in order to remove olefins and by several trap-to-trap distillations.

Irradiation Procedure.—γ-Irradiation was carried out in a 500 ml. cylindrical reaction vessel fitted with graphite-coated electrodes, a guard ring and a breakable seal. This reaction vessel was similar to that described by Back.[8] The vessel was thoroughly baked in a vacuum before each experiment and filled with sample by conventional vacuum techniques. Irradiations were carried out at room temperature with a 1600 curie cobalt-60 source, applying absolute dosimetry.[8] An electric field, up to 2 kV., was applied to the central anode in order to measure the saturation ion current during irradiation. Saturation ion currents were usually measured at the beginning and the end of the irradiation; the time for the measurements was negligible compared to the total time of irradiation. Several runs were also carried out with pure propane in order to compare the results of amines with those of hydrocarbon.

Analysis.—After irradiation the reaction vessel was attached to a convenient vacuum line, a breakable seal was broken, and the contents of the cell were transferred to the analytical system, which consisted of the following parts: a mercury cut-off, four liquid nitrogen traps (−196°C), a mercury diffusion pump, and a Toepler pump - gas burette. The non-condensable gas collected contained hydrogen and a small amount of methane, the hydrogen in which was removed by diffusion through a palladium thimble heated at 300°C; the amount of the residual methane was then measured.

Their ion pair yields (M/N) were obtained by relating the product yields to the saturation ion currents measured in the radiolysis

Results and Discussion

Saturation Ion Current.—The ion currents are plotted against the field strength for mono-, di-, and trimethylamine at different pressures in Fig. 1. Good saturation curves were observed with these amines, and the saturation ion currents thus obtained were proportional to the gas pressure, up to 300 mmHg, as is shown in Fig. 2. From these results it is clear that the ions produced by γ-irradiation were quantitatively collected at the electrode under these experimental conditions and that the saturation ion current were satisfactory for calculating the ion-pair yields of the products. The differences in the saturation ion currents of these amines were due to the difference in their electron densities. After a suitable correction of their electron densities, almost the same saturation ion currents were observed.

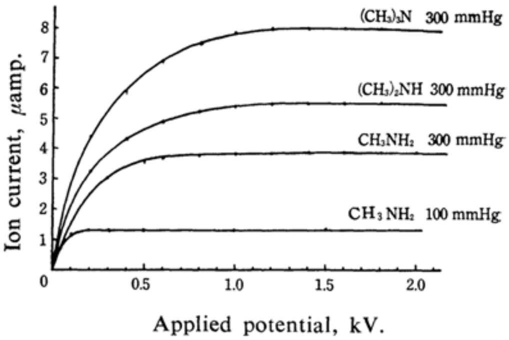

Fig. 1. Ion currents in the γ-radiolysis of amines.

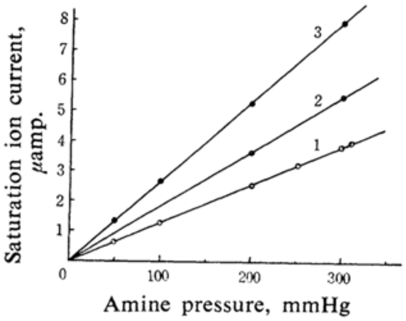

Fig. 2. Saturation ion current as a function of amine pressure.
1: Methylamine, 2: Dimethylamine
3: Trimethylamine

The Radiolysis of Pure Amine.—The results of the radiolysis of amines at 300 mmHg are shown in Table I. The major volatile products are hydrogen, methane and ammonia. The conversion of amines shown in Table I is based on the yield of hydrogen ($2\times H_2$/amine). Hydrogen was the main product, and the yield was relatively high for methylamine, while it decreased for di- and trimethylamine. On the other hand, the yield of methane was very low for methylamine, and increased about four times for di- and trimethylamine.

On the basis of the mechanism elucidated

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[8] R. A. Back, T. W. Woodward and K. A. McLauchlan, *Can. J. Chem.*, **40**, 1380 (1962).

TABLE I. γ-RADIOLYSIS OF AMINES AND PROPANE (Gas pressure, 300 mmHg)

Compound	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	C_3H_8
Saturation ion current (μamp.)	3.70	5.50	7.90	6.07
Conversion (%)	0.09	0.14	0.13	0.08
$(M/N)_{H2}$	3.10	2.78	1.78	1.55
$(M/N)_{CH4}$	0.10	0.45	0.41	0.26

for the photolysis of methylamine, the following possible primary dissociations of methylamine may be considered:

$$CH_3NH_2 \rightsquigarrow H + CH_3NH\cdot \qquad (1)$$
$$\rightsquigarrow H + \cdot CH_2NH_2 \qquad (2)$$
$$\rightsquigarrow \cdot CH_3 + \cdot NH_2 \qquad (3)$$
$$\rightsquigarrow CNH_3 + H_2 \qquad (4)$$

These primary reactions are followed by the secondary reactions:

$$H + CH_3NH_2 \rightarrow H_2 + CNH_4 \qquad (5)$$
$$\cdot CH_3 + CH_3NH_2 \rightarrow CH_4 + CNH_4 \qquad (6)$$
$$2\ CNH_4 \rightarrow NH_3 + C_2NH_5 \qquad (7)$$

Since methane and ethane formations were very little, reaction 3, which should give methane by secondary reaction 6 and ethane by the recombination of the methyl radicals, seemed to be unimportant. The ammonia formation, therefore, may not be due to the hydrogen abstraction of the NH_2 radical produced by reaction 3 but to secondary reaction 7, involving two radicals of the empirical formula CNH_4, which was proposed in the photolysis of methylamine.[5]

Hydrogen-forming reactions, for which several mechanisms are possible, must be the principal primary processes. The decision between 1 and 2 must be based on the results with isotopic compounds CH_3ND_2 and CD_3NH_2, while the processes combining reaction 1 with 2, which are called radical process for hydrogen formation, may be elucidated by a radical scavenger technique, as will be described later. The importance of the amino-hydrogen atom may be pronounced, because the hydrogen yield decreased as the hydrogen atom was replaced with the methyl group, as Table I shows.

Ion-pair yields of hydrogen and methane were measured as a function of the amine pressure, as is shown in Fig. 3. They were independent of the pressure within the range of experimental error, but there was a slight decrease in hydrogen yield at pressures less than 100 mmHg in mono- and trimethylamine. This effect could be due to the wall effect. The neutralization of ions produced by primary processes may occur in the gas phase leading to dissociation, or at the surface of the vessel with deactivation. Low pressure should favor the latter and so lower the hydrogen yield.

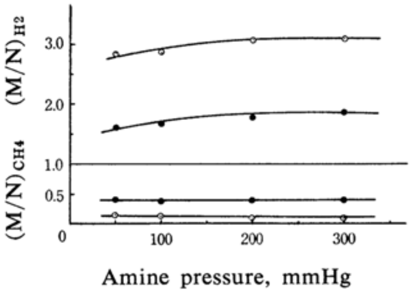

Fig. 3. Ion pair yields of hydrogen and methane as a function of amine pressure.
○ : Methylamine, ● : Trimethylamine

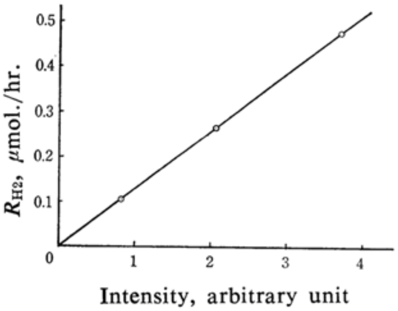

Fig. 4. Hydrogen yields as a function of intensity. (Methylamine 300 mmHg)

In Fig. 4, the hydrogen yield is plotted against the irradiation intensity for the radiolysis of methylamine. A linear function was observed. This may be simply interpreted as indicating that the hydrogen atom produced in reactions 1 and 2 reacted with methylamine by reaction 5, and that the back reactions of 1 and 2, and the recombination reaction 8 of the hydrogen atom were not important in these experimental conditions:

$$H + H + M \rightarrow H_2 + M \qquad (8)$$

The Effect of the Radical Scavenger. — In order to determine the contribution of the

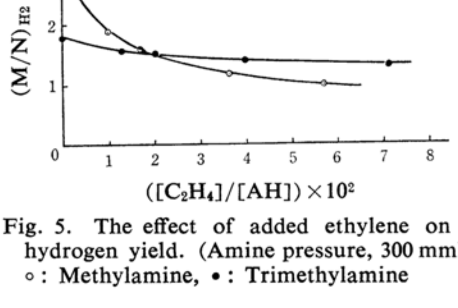

Fig. 5. The effect of added ethylene on the hydrogen yield. (Amine pressure, 300 mmHg)
○ : Methylamine, ● : Trimethylamine

radical process to hydrogen formation, a radical scavenger technique, first developed by Back[9] and Hardwick[10] for hydrocarbons, was employed. The presence of a radical scavenger such as ethylene in the radiolysis of amines reduced the hydrogen yield, shown in Fig. 5, by the following reaction:

$$AH \rightsquigarrow H_2 + \text{Residue} \qquad (9)$$

$$\rightsquigarrow H + \text{Residue} \qquad (10)$$

$$H + AH \rightarrow H_2 + \text{Residue} \qquad (11)$$

$$H + C_2H_4 \rightarrow C_2H_5\cdot \qquad (12)$$

where AH shows the amine. When AH is methylamine, reaction 9 corresponds to reaction 4; reaction 10, to reactions 1 and/or 2, and reaction 11, to reaction 5. If a steady-state kinetic treatment of hydrogen atom production is made for the amine system with and without ethylene present, the following expression is obtained:

$$\frac{1}{\Delta(M/N)_{H_2}} = \frac{1}{(M/N)_{H_2(10)}} \times \frac{k_{11}[AH]}{k_{12}[C_2H_4]} + \frac{1}{(M/N)_{H_2(10)}} \qquad (I)$$

where $\Delta(M/N)_{H_2}$ is the difference in the ion-pair yield of hydrogen, without and with ethylene, and $(M/N)_{H_2(10)}$ is the ion-pair yield of hydrogen by reaction 10. In Fig. 6, the values of the left-hand side of Eq. I are plotted against $[AH]/[C_2H_4]$. From these straight lines, $(M/N)_{H_2(10)}$ and k_{11}/k_{12} were calculated; they are summarized in Table II.

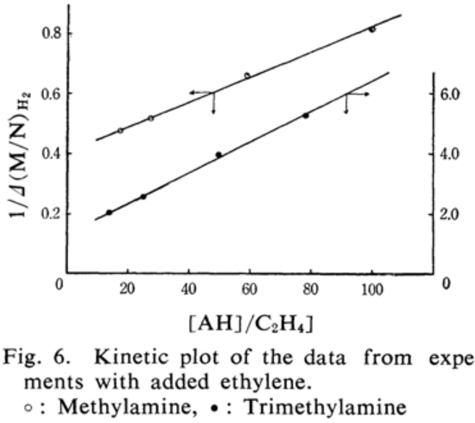

Fig. 6. Kinetic plot of the data from experiments with added ethylene.
○ : Methylamine, ● : Trimethylamine

TABLE II. HYDROGEN YIELD BY RADICAL PROCESS AND k_{11}/k_{12}

Compound	CH_3NH_2	$(CH_3)_3N$	C_3H_8
$(M/N)_{H_2(10)}$	2.50	0.73	1.12
Radical (%)	81	41	72 (75)[9]
Molecular (%)	19	59	28 (25)[9]
$(k_{11}/k_{12})\times 10^2$	1.05	3.56	0.13

These results showed that 81% of the hydrogen produced in the radiolysis of methylamine was scavengable by ethylene, indicating that the non-radical process (19%) were more important than in the photolysis. The hydrogen formed by the latter process was estimated to be less than 10% in the photolysis of methylamine, although the kinetic treatment was not carried out.[5] In the case of trimethylamine, which has no amino-hydrogen atoms, the radical process (41%) became inferior to the non-radical process. Reaction 1. therefore, seemed to be very important for the thermal hydrogen atom formation in the radiolysis, as was pointed out by Michael and Noyes[5] in the photolysis of methylamine. However, it is hoped that, by experiments with the isotopic compounds CH_3ND_2 and CD_3NH_2, it will be possible to clarify these primary processes with more certainty. At this stage of experiment, it can not be decided whether the non-radical process is a molecular process or a process involving hot hydrogen atoms.

Relatively high k_{11}/k_{12} values were observed with these amines compared with that of propane, showing that the rate of the abstraction of the hydrogen atom from the amine may be estimated to be faster than that from propane.

Summary

The γ-radiolysis of methylamines in the gas phase has been investigated, applying the absolute dosimetry involving the measurement of saturation ion currents in the gases during irradiation. The major volatile products are hydrogen, methane and ammonia. Ion-pair yields of hydrogen for mono-, di- and trimethylamine are 3.10, 2.78 and 1.78 respectively. Those of methane are 0.10, 0.45 and 0.41 respectively. The yields of hydrogen and methane are independent of the pressure up to 300 mmHg, but at pressures less than 100 mmHg there are slight decreases in hydrogen yields. The rate of hydrogen formation from methylamine is proportional to the radiation intensity, and the yield decreases in the presence of a small amount of ethylene. By kinetic analyses of the results with an added scavenger, it has been observed that 81% of the hydrogen formed from methylamine is caused by a radical process, while the value is 41% for trimethylamine.

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[9] R. A. Back, *J. Phys. Chem.*, **64**, 124 (1960).
[10] T. J. Hardwick, ibid., **65**, 101 (1961).