The Photolysis of Methylamine

Orville C. Wetmore and H. Austin Taylor

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equation

$$\Delta pK = \frac{\epsilon^2}{kTD_E(\bar{r^2})^{\frac{1}{2}}},$$ (13)

where $(\bar{r^2})^{\frac{1}{2}}$ is the root mean square intercharge distance, assuming free rotation and taking (except for glycine and β-alanine), as before, the negative charge of each carboxylate group as being midway between the oxygen atoms. The values of $1/(\bar{r^2})^{\frac{1}{2}}$ may be approximated by

$$\bar{r^2} = 4.75d + 2.56 \text{ (in } A^2).$$ (14)

These calculations are shown in columns (5) and (6). The values of D_E in column (7) are calculated from columns (2) and (5), using Eq. (13). We may combine the two expressions $\Delta pK = 2.00/d$ and Eq. (14), and find, as an approximate empirical equation giving D_E as a function of d at 25°C,

$$D_E = 76d/(1.86d+1)^{\frac{1}{2}}.$$ (15)

This equation is used in obtaining column (8) of Table V.

The Photolysis of Methylamine*

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The photolysis of methylamine has been shown to proceed essentially by two consecutive first-order reactions, the first to produce hydrogen, ammonia, and $CH_2 : NCH_3$; the second a dehydrogenation of the latter at a rate approximately double the first. A mechanism involving hydrogen atoms has been postulated. These have been shown experimentally to be present and also have been shown by discharge-tube experiments to react with methylamine.

THE reactions of atomic hydrogen and azomethane studied by Henkin and Taylor[1] yielded at 27°C only an addition compound, symmetrical dimethyl hydrazine. At 110°C, in addition to the hydrazine formation, methane and methylamine were obtained along with traces of ammonia. At 195°C the yield of methylamine increased but without a corresponding increase in methane or ammonia. It was concluded that methane production involved a rupture of the $C-N$ bond in azomethane while methylamine production resulted from an $N-N$ rupture in the hydrazine. The possibility also existed of a $C-N$ rupture in methylamine. The photolysis of methylamine by Eméleus and Jolley[2] gave hydrogen and ammonia as the

only gaseous products accompanying the molecule $CH_2 : NCH_3$, methyl methyleneimine. The photo-reaction is accompanied by a pressure increase. Since, however, the stable form of the imine is a trimer, a liquid of very low vapor pressure, the over-all reaction

$$2CH_3NH_2 = \tfrac{1}{3}(CH_2 : NCH_3)_3 + H_2 + NH_3$$
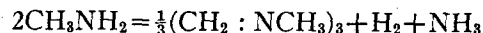
should not be accompanied by a pressure change. To resolve this difficulty and if possible, further elucidate the mechanism, the photolysis of methylamine was re-examined. This has also necessitated a study of the effect of hydrogen atoms introduced both by mercury sensitization and from a discharge tube.

EXPERIMENTAL

Photolysis Apparatus

The light source was a quartz spiral, low pressure mercury resonance arc operated at 5000 volt from a transformer carrying 6.3–6.4 amp. in the

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* Abstract from a dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, 1943.

[1] H. Henkin and H. A. Taylor, J. Chem. Phys. 8, 1 (1940).

[2] H. J. Eméleus and L. J. Jolley, J. Chem. Soc., p. 1612 (1935).

TABLE I. Initial CH_3NH_2 200 mm. Temp. 100°C.
Volumes in cc at N.T.P.

Time (min.)	Init. CH_3NH_2 obs.	NH_3 obs.	NH_3 calc.	Residual CH_3NH_2	H_2	CH_4	H_2 formed / CH_3NH_2 dec.	x in C_2H_xN	ΔP (mm)
1.0	15.1	2.2	2.6	9.9	2.5	0.2	0.48	4.8	10.0
5.0	15.0	3.5	3.9	7.6	4.7	0.4	0.64	4.1	26.0
10.0	15.1	3.3	5.0	5.4	6.9	0.3	0.71	3.9	39.0
10.0	15.1	4.7	5.6	4.4	7.2	0.3	0.67	4.0	39.5
15.0	15.4	4.6	5.6	4.8	7.3	0.4	0.69	4.0	43.5
22.5	15.2	5.8	6.3	3.1	8.9	0.5	0.74	3.5	53.5
22.5	15.0	—	6.0	3.4	8.8	0.4	0.76	3.7	52.5
30.0	15.2	7.1	6.3	3.2	9.2	0.6	0.77	3.6	64.0
50.0	15.0	7.1	7.0	1.4	11.5	0.4	0.85	3.4	72.5
70.0	14.9	7.5	7.4	0.6	12.2	0.5	0.85	3.3	81.5
90.0	14.9	—	7.7	0.0	12.4	0.6	0.83	3.3	82.5

primary. The spiral surrounded the quartz re- action vessel, 2.5 cm in diameter, 11.5 cm in length, and 57.0 cc in volume. In the early experiments the reaction vessel and lamp were submerged in a water bath at 75°C. In later experiments this was replaced by a steam jacket. The necessity for constant temperature so far as the lamp is concerned is the necessity for constant intensity of the light. Some difficulty was experienced in achieving this, since, if the lamp before striking the arc was at 100°C, the temperature would rise upon striking the arc. Despite adjustment based on preliminary trials, the results show evidence of a high reaction rate during the first minute or so. A correction, how- ever, can be applied for this as is shown later.

The methylamine was prepared from the hy- drochloride by treatment with moist potassium hydroxide in vacuum and dried over barium oxide. Hydrogen and propylene used in several runs were taken from tanks. Hydrogen was purified by passage over hot platinized asbestos followed by drierite. Propylene was not further purified.

For a run, methylamine was introduced at the desired pressure into the reaction vessel which was already heated. The lamp was turned on and pressure readings taken at chosen time inter- vals. At the conclusion of the experiment the products were drawn through a trap in liquid nitrogen by means of a Toepler pump. The un- condensed gases were analyzed in a Fisher gas analyzer. The material condensed in the liquid nitrogen trap was subjected to a distillation from −119°, using melting ethyl bromide, to liquid nitrogen temperature to separate ammonia from methylamine. Finally the fraction volatile at dry

ice temperature was drawn off and measured as methylamine.

Hydrogen Discharge Apparatus

A Wood's discharge tube of the conventional type was used as the source of hydrogen atoms. The tube, 10-mm inside diameter, was water cooled over its length of 50 cm between the electrodes, which were of sheet aluminum, 1.5 mm thick bent into cylinders 23 cm long and 3 cm in diameter. A 2-kva transformer operated on 220 volts in the primary furnished the excita- tion for the discharge. Hydrogen was introduced near each electrode and removed at the center of the discharge. It passed thence about 30 cm to the reaction vessel of 500-cc volume, entering through a constricted nozzle to impede back diffusion into the arc. Concentrated sulfuric acid was used as a poisoning agent to prevent atom recombination on the walls. The flow system for the atom experiments used hydrogen at 0.5– 0.8-mm pressure as read on a McLeod gauge and methylamine drawn from a reservoir at −78°C, where the vapor pressure is 7–8 mm, through a capillary flow meter under a pressure difference of 5–7 mm as read on a sloping manometer. The partial pressure of methylamine in the reaction vessel was always less than that of the hydrogen. In all runs the reaction vessel was maintained at 100°C.

EXPERIMENTAL RESULTS

Methylamine

Table I contains a summary of the information obtained from the study of the photolysis of methylamine. The pressure change is that ob- served when the contents of the reaction vessel were again at room temperature after comple- tion of the run. The initial pressure under similar conditions was ~200 mm in all runs. Hydrogen and methane were determined by combustion in oxygen to water and carbon dioxide. No nitrogen was found in any of the work. Am- monia, identified using Nessler's reagent, was separated from undecomposed methylamine as already described. Experiment with known mix- tures of methylamine and ammonia showed that the method is not too satisfactory in that methylamine has a small vapor pressure even

at $-119°C$. A 10–15-min. distillation was found to be reasonably reliable.

Since no nitrogen was found and since hydrogen, ammonia, and methane were the only gaseous products, it is probable that the carbon to nitrogen ratio in the residual products must be 2 : 1. If we assume this, the ammonia and methylamine volumes can be calculated from the total volume of the mixture. Thus since each contains one nitrogen, knowledge of the initial methylamine and the final methylamine plus ammonia gives the residual nitrogen in the residue. Twice this is then the carbon in the residue. This latter plus the carbon in the methane corresponds to the methylamine decomposed. The difference between the undecomposed methylamine and the total ammonia plus methylamine gives the ammonia. Comparison between ammonia values calculated in this way and those obtained by the distillation method show good agreement and whereas the distillation values for the ammonia produced as a function of the time of photolysis are somewhat scattered, the values calculated by the above method lie on a smooth curve that averages the scattered experimental values. The assumption is therefore justified. After some ten such runs with distillation separation of the products, the total volume of ammonia and methylamine alone was measured and the individual volumes obtained by the calculation. A brownish deposit which appeared to be liquid was always observed in the reaction vessel after the longer runs.

In all the experiments reported in Table I the reaction vessel was separated from the rest of the system by plugs of gold foil and gold sponge in the inlet tubing.

Methylamine and Mercury

Since the lamp used as a source of radiation was a resonance lamp and since considerable quantities of hydrogen are produced in the

TABLE II. Effect of mercury at 75°C.

Run	Hg press. mm	CH_3NH_2 P_0 in mm	1 min.	3 min.	5 min.	10 min.	15 min.	20 min.	30 min.
25	0	101.5	9.5	20.5	27.5	37.5	—	46.0	47.5
23	$\sim2\times10^{-3}$	100.0	9.5	22.5	29.0	39.0	43.0	44.0	45.0
24	$\sim7\times10^{-2}$	100.0	8.0	19.5	27.0	37.0	42.5	45.5	47.5

TABLE III. Effect of propylene at 75°C.

CH_3NH_2 cc	C_3H_6 cc	ΔP in mm 1 min.	3 min.	5 min.	10 min.	cc C_3H_8 after 60 min.	cc C_6H_{14} after 60 min.
7.5	0.0	8.0	19.5	27.0	37.0	0.0	0.0
0.0	23.8	4.5	−1.5	−7.5	−21.5	0.9	2.6
7.5	22.9	−3.0	−18.5	−33.5	−59.5	2.3	1.6
ΔP calc.		7.5	17.0	26.0	38.0		

methylamine photolysis, the effect of mercury vapor on the rate of the reaction was studied. Table II summarizes the results obtained. For run number 25 methylamine was passed through plugs of gold foil and gold sponge in the lines connecting the reaction vessel with the mercury manometer. For run number 23 the gold was not present and the system was saturated with mercury vapor at room temperature. For number 24 several drops of mercury were present in the reaction vessel which in all these runs was at 75°C. It will be observed that the rate of pressure increase is in no way altered by the presence of mercury in the reaction vessel. This might be interpreted that hydrogen atoms have no part in the reaction. To test for the presence of hydrogen atoms during the methylamine photolysis the following runs were made in presence of propylene.[3]

Methylamine and Propylene

Table III shows the data obtained in some typical runs. The volume of propane was determined by slow combustion of the gas pulled off dry ice after removal of methylamine, ammonia, and residual propylene. The volume of the hexanes was estimated from the pressure exerted by the residue from dry ice when vaporized in a known volume.

Since propylene polymerizes in the radiation used, a pressure decrease is observed. With methylamine and propylene a larger pressure decrease is found and the difference is seen in the table to be entirely comparable with the pressure increase found with methylamine alone. The volumes of the hydrocarbons obtained after sixty minutes of irradiation show a marked increase in propane and decrease in hexane when methylamine is present. It must be concluded

[3] C. H. Bamford, J. Chem. Soc., p. 17 (1939).

that hydrogen atoms are present during methylamine photolysis and also that the excess of propylene has no great effect on the rate of the photolysis.

Methylamine and Hydrogen

To test the effect of the hydrogen produced during the photolysis on the course of the reaction several runs were made in which hydrogen was added to the methylamine before irradiation commenced. Table IV gives these data in a manner similar to that in Table I.

It will be seen that the general course of the reaction is identical with that in the absence of added hydrogen both from the point of view of the amount of methylamine decomposed, from the rate of pressure change, as also from the formula of the residual product.

Methylamine and Hydrogen Atoms

Since the experiments with propylene show that hydrogen atoms are present and, furthermore, that the general course of the reaction is unaffected, it is necessary to test specifically for the effect of hydrogen atoms on methylamine. To this end hydrogen atoms from a Wood's discharge tube were led into a stream of methylamine at 100°C as already described. No attempt was made to measure the atom concentration though preliminary experiments with chlorine showed a relatively high concentration must be present. The extent of reaction of the hydrogen atoms with methylamine was measured by the amount of ammonia produced as given by the distillation separation from methylamine. In view of the poor reliability of the separation a direct comparison was made between two runs in which the arc was operating and two runs, otherwise identical, but without the arc. The

TABLE IV. Effect of hydrogen. Temp. 100°C.
Volumes in cc at N.T.P.

Time (min.)	Init. CH_3NH_2	Init. H_2	Residual CH_3NH_2	NH_3 calc.	H_2 obs.	CH_4 obs.	x in C_2H_xN	ΔP (min.)
5.0	15.0	16.7	6.8	4.2	22.7	0.2	3.9	26.0
10.0	15.2	15.2	5.2	5.1	22.7	0.2	3.9	39.0
22.5	14.9	16.2	3.1	6.1	25.9	0.4	3.5	51.5
50.0	15.0	15.6	1.8	6.7	27.1	0.2	3.4	63.0
90.0	14.9	15.8	0.3	7.4	29.0	0.2	3.3	73.5

TABLE V. Effect of hydrogen atoms. Temp. 100°C.

Run number →		10 min.			15 min.	20 min.		
	1	*2A	2B	Av. %	1	1	2	Av. %
Arc CH_3NH_2	1.1	0.9	1.1		0.7	1.0	0.4	
on NH_3	2.4	3.2	3.0		2.8	2.5	3.7	
Apparent % NH_3	69	78	73	73	78	72	90	81
Arc CH_3NH_2	5.5	3.5	3.5		4.6	2.5		
off NH_3	0.6	0.7	0.7		1.5	1.7		
Apparent % NH_3	10	17	17	15	25	40		40

* 2A and 2B are duplicate distillations on the same sample after refreezing in liquid nitrogen.

distillation separation was performed on the products collected in liquid nitrogen in each run, to give what is termed "apparent" ammonia but what in the absence of the arc must be methylamine. Table V gives the comparative data and leaves no doubt that ammonia is produced in considerable quantity from hydrogen atoms and methylamine at 100°C. It should also be mentioned here that examination of the gases not condensed by liquid nitrogen showed unreacted hydrogen and small amounts of methane comparable in terms of the methylamine decomposed with those found in the photolysis. No nitrogen was observed.
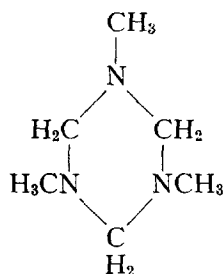
$C_6H_{15}N_3$ Photolysis

For reasons which will appear in the discussion the trimer of methylmethyleneimine, that is, trimethyltrimethylene triamine, was prepared and subjected to photolysis. The preparation employed the method given by Henry[4] of treating aqueous methylamine with aqueous formaldehyde at 0°C. The triamine is salted out with potassium hydroxide as a light oily layer which is dissolved in absolute ether and dried with potassium hydroxide pellets. After removing the ether on a steam bath, distillation at 22 mm gave the product at 64–65°C in good agreement with the value reported in Beilstein 68.3°C at 26 mm. A picrate of the product, without recrystallization, melted at 119–122°C; the value reported by Duden and Scharff[5] is 127–128°C. The refractive index to the sodium D lines was 1.4600 at 19°C; Beilstein reports 1.4632.

[4] L. Henry, Bull. Acad. Roy. Belg. 26, 200 (1893); 28, 359, 360 (1895); 29, 26 (1896).
[5] P. Duden and M. Scharff, Ann. d. Chemie 288, 251 (1895).

Travers and co-workers[6] studying the thermal decomposition of the methylamines report the presence of methylmethyleneimine monomer in the gas phase. To investigate the possible depolymerization of the trimer a vapor pressure-temperature study was made. The data are given in Table VI. A plot of the logarithm of the vapor pressure against the reciprocal temperature is not perfectly straight but shows a small decrease in slope with increase in temperature. The slope of the best straight line corresponds to a molar heat of vaporization of 11,750 cal. Application of Trouton's rule gives a value of 9600 cal. Now a calculation of the molecular refraction for the trimer from atomic refraction equivalents, assuming the structure to be

$$
\begin{array}{c}
CH_3 \\
| \\
N \\
\diagup \quad \diagdown \\
H_2C \qquad CH_2 \\
| \qquad\qquad | \\
H_3CN \qquad NCH_3 \\
\diagdown \quad \diagup \\
C \\
H_2
\end{array}
$$

is 39.5. The refractive index value found, when used in the Lorenz-Lorentz relation, gives a molecular refraction of 38.4. This agreement shows that the liquid is essentially trimer. The relatively high value of the heat of vaporization and its excess over the Trouton figure would seem to indicate some dissociation to the monomer with increase in temperature.

Because of the low vapor pressure of the trimer the photolysis was carried out in a liter quartz reaction vessel at room temperature. The data are presented in Table VII. The formula of the

TABLE VI.

Vap. press. mm	Temp. °C
4.0	26.0
32.0	58.0
33.0	58.5
150	89.5
154	90.0
344	114.0
349	115.0
351	117.0

6 A. G. Carter, P. A. Bosanquet, C. G. Silcocks, M. W. Travers, and A. F. Wilshire, J. Chem. Soc., p. 495 (1939).

TABLE VII. $C_6H_{15}N_3$ photolysis. Temp. 28°C.

Time hr.	$C_6H_{15}N_3$ cc init.	H_2 cc init.	NH_3 cc obs.	H_2 cc obs.	CH_4 cc obs.	Residue formula
4.00	3.5	—	0.5(?)	2.0	0.5	$C_{2.2}H_{3.3}N_{1.0}$
15.75	6.3	—	1.0	1.9	1.8(?)	$C_{2.0}H_{3.3}N_{1.0}$
4.00	3.5	11.2	0.2	12.8	0.8	$C_{1.9}H_{3.2}N_{1.0}$

residue is calculated from a carbon, hydrogen, and nitrogen balance and then expressed with one atom of nitrogen. The 0.5-cc ammonia in the first run did not give a good test with Nessler's reagent and may have been contaminated with the residue from the run. Since in the second run, for 15.75 hr., methane production appears to have increased at the expense of the hydrogen, a third run with hydrogen present initially was made. Here, however, the results again parallel those in the absence of added hydrogen and the high methane in the second run must be considered unreliable.

DISCUSSION

Inspection of the results in Table I shows that hydrogen production increases steadily per unit of methylamine decomposed. Initially two methylamines give one hydrogen but towards the completion of the decomposition the results approach one hydrogen for one methylamine. The ratio of ammonia produced to methylamine decomposed, on the other hand, remains constant throughout the decomposition at 0.5. Such results may be interpreted by a primary decomposition of methylamine to give hydrogen, ammonia, and a residue which undergoes further dehydrogenation. Eméleus and Jolley have suggested as the over-all reaction:

$$2CH_3NH_2 \rightarrow H_2 + NH_3 + CH_2 : NCH_3.$$

The probable existence of the methylmethyleneimine was shown when a Schryver's test for formaldehyde was obtained in an aqueous solution of the non-volatile liquid from a run and also by forming a phenylhydrazone. In the present work positive formaldehyde tests were obtained with Schiff's reagent. The test was found to be less pronounced, however, with the longer runs. In one experiment after irradiation for twelve hours, a weak positive test with Schiff's

reagent only appeared after 20–30 minutes standing. This might be attributed either to a smaller amount of the residue or more probably to a slower hydrolysis of the residue to formaldehyde. Finally, the calculated formula of the residue as shown in Table I appears for short runs to approximate C_2H_5N but for long exposures to approach C_2H_3N.

Travers and co-workers in the pyrolysis of the three methylamines report that the formula of the non-volatile residue from both di- and tri-methylamine approximated C_2H_5N but that for longer runs the hydrogen content was lower. Using data reported in their paper for the two longest runs the residues may be calculated to be $C_{2.0}H_{4.2}N_{1.0}$ and $C_{2.0}H_{4.1}N_{1.1}$. It seems probable that had the length of the run been further increased the residues would have approached C_2H_3N as found here.

The increased production of hydrogen over that of ammonia was observed by Emeléus and Jolley but no explanation was offered for it. If the above equation were to represent the true over-all reaction, then, since the stable form of the imine is the trimer, a saturated triamine, a stable liquid of low vapor pressure, no pressure change should occur. Actually a marked pressure change is observable even in the shortest runs and seems to approach, though falling somewhat short of a fifty percent pressure increase on completion. It is apparent that the over-all reaction should better be represented as

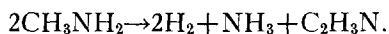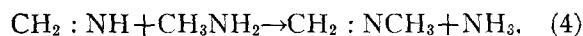$$2CH_3NH_2 \rightarrow 2H_2 + NH_3 + C_2H_3N.$$

Table VI actually shows that the vapor pressure of the trimer is far too high at the temperature of the experiments to account for the observed pressure change. It is not now possible to say what C_2H_3N represents. It is probable that it is a polymer of $CH_3N : C$ or CH_3CN. Many such polymers are known but all contain carbon-carbon bonds and none even vaguely resembles the triamine $C_6H_{15}N_3$. This would suggest that even if the triamine is formed it is probably the monomer $CH_2 : NCH_3$ that dehydrogenates to the isonitrile which subsequently polymerizes.

The results from the photolysis of the triamine show that a dehydrogenation can occur under the experimental conditions. However, in order to obtain comparable amounts of decomposition

as with methylamine very long exposures were necessary which again indicate that it is the monomer which reacts rather than the trimer. One further point is significant from the triamine photolysis, namely, that traces of ammonia and methane were also found. It would seem, then, that the source of the traces of methane found in the methylamine photolysis is the imine rather than from an alternative carbon-nitrogen rupture of the methylamine molecule.

The photolysis in presence of mercury vapor shows that hydrogen atoms have no appreciable effect on either the products of reaction or on the rate of the decomposition. That hydrogen atoms are present during the photolysis even in the absence of mercury vapor is seen from the results with propylene. It must be concluded, therefore, that reactions both producing and consuming hydrogen atoms are present and an internal balance of these is maintained despite additional reactions which would produce or would consume these atoms. One such hydrogen atom consuming reaction, namely, that with methylamine itself has been tested and shown to occur readily at 100°C to yield ammonia in considerable amounts and traces of methane.

These facts are consistent with the following mechanism:

$$CH_3NH_2 \xrightarrow{h\nu} CH_3NH + H, \tag{1}$$

$$CH_3NH + H \rightarrow CH_3NH_2, \tag{2}$$

$$CH_3NH \rightarrow CH_2 : NH + H, \tag{3}$$

$$CH_2 : NH + CH_3NH_2 \rightarrow CH_2 : NCH_3 + NH_3. \tag{4}$$

$$CH_3NH_2 + H \rightarrow CH_3NH + H_2, \tag{5}$$

$$CH_2 : NCH_3 \rightarrow C_2H_3N + H_2. \tag{6}$$

Reaction (1) seems to accord best with the absorption data on ammonia and the amines as an excitation of an electron localized in the amine group. It is consistent with the results for other amines[3] as also for dimethyl hydrazine.[7] Emeléus and Jolley express the fate of the methylamino radical, CH_3NH, by the reaction:

$$2CH_3NH \rightarrow CH_2 : NCH_3 + NH_3.$$
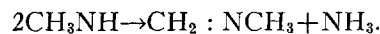
[7] W. L. Kay and H. A. Taylor, J. Chem. Phys. 10, 497 (1942).
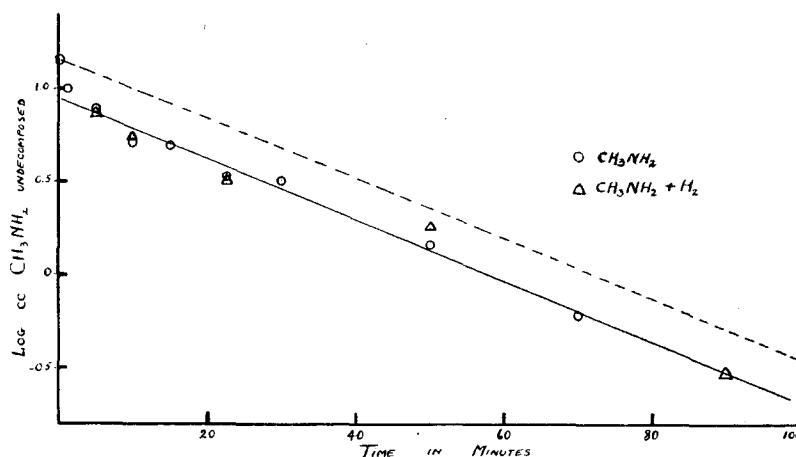
FIG. 1.

Such a reaction between two radicals must be of rare occurrence unless the equation is merely to be taken as an over-all reaction. It appears plausible to offer a mechanism for the production of the imine through reactions (3) and (4). Reaction (3) as a unimolecular decomposition of a radical could conceivably be quite slow. Methyleneimine $CH_2 : NH$, on the other hand, should be as relatively stable as ketene. Its postulation permits a parallelism to be drawn between methylamine photolysis and pyrolysis in that in the latter the high temperature could cause decomposition of the methyleneimine to hydrogen and hydrogen cyanide, which are found, before it could react with methylamine to produce ammonia which is found only in small amounts in the thermal decomposition.

Reaction (5) between hydrogen atoms and methylamine leading to the methylamino radical and hydrogen accounts for the similarity of the results found here from the photolysis and from the discharge-tube experiments. Reactions (3) and (5), however, form a chain series and hence a large quantum yield would be expected for the over-all reaction. Eméleus and Jolley have estimated the quantum yield from a comparison between methylamine and ammonia decompositions and although the reported value ~ 0.7 cannot be considered exact, it seems nevertheless certain that no long chains can be present. Reaction (2), the reverse of (1), will account for the low quantum yield and a simple calculation will show that a difference between the energies of

activation of reactions (2) and (3) of 10–15 kcal. would give a quantum yield of unity. Such a value is at least plausible.

Reaction (6) is intended as an over-all reaction rather than one describing a mechanism. It does not seem possible from the following analysis, however, that it could involve hydrogen atoms and it may very well be a simple dehydrogenation.

Evaluation of the stationary concentrations of hydrogen atoms and methylamino radicals, assuming, in view of the observed rapid ammonia production, that reaction (4) follows rapidly on (3), that is, that methyleneimine does not build up appreciably in the system, gives

$$[CH_3NH] = (k_1k_5/k_2k_3)^{\frac{1}{2}}[CH_3NH_2]$$

and $\quad [H] = (k_1k_3/k_2k_5)^{\frac{1}{2}}.$

The rate of the over-all reaction is then given by:

$$-d[CH_3NH_2]/dt = 2(k_1k_3k_5/k_2)^{\frac{1}{2}}[CH_3NH_2],$$

which is also twice the rate of production of ammonia. These, then, should be of first order in terms of methylamine. The data in Tables I and IV are plotted in Fig. 1 as the logarithms of undecomposed methylamine against time. The plot is linear in agreement with the first-order requirement and the slope of the line gives a value for the velocity constant of 0.036 min.$^{-1}$. It will be noted, however, that the line does not pass through the point corresponding to the initial concentration nor to the data from the

TABLE VIII. Calculated pressure change.

Corr. time min.	ΔP obs. mm	ΔP calc. mm
10	10	9.5
20	26	27.0
30	43.5	44.5
35	53	53.0
40	—	59.0
45	64	64.0
50	—	70.5
60	—	79.0
65	72.5	82.5
80	82	89.5

one-minute run. This has been attributed to a temporary high initial intensity in the lamp. If the dotted line in Fig. 1 be drawn parallel to the "observed" line but passing through the zero time value it is possible to correct the observed times of reaction to discover what times would have been required had the lamp intensity remained constant. This is tantamount to a calculation of the velocity constant from point to point during the course of the reaction when a steady state in the lamp had been achieved and an interpolation for the early stages. The correction amounts to about 10–15 min.

It is now possible to treat the observed pressure changes at these corrected times as due to two consecutive first-order reactions:

$$2CH_3NH_2 \xrightarrow{k_A} H_2 + NH_3 + CH_2 : NCH_3,$$

$$CH_2 : NCH_3 \xrightarrow{k_B} H_2 + C_2H_3N,$$
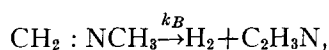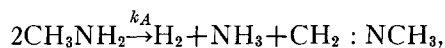
on the assumption that the net pressure change measures the C_2H_3N production. The rate of disappearance of methylamine, 0.036 min.$^{-1}$, measures k_A. Hence k_B may be calculated. The value is found to be 0.075 min.$^{-1}$. Using these velocity constants the pressure changes for 200-mm methylamine may be calculated and are compared with the observed values after various times in Table VIII. The agreement during the first 45 min. which corresponds to about 80 percent reaction is excellent. The low observed values, as compared with those calculated, later in the reaction are to be associated with an alternative loss of the methyl methyleneimine

other than that accounted for in the above scheme, for example, as the polymer, the tri-amine, or in the methane-producing reaction. In any event, it is apparent that the rate of pressure change is a reliable measure of the rate of reaction and hence that the conclusions drawn earlier that the presence of mercury, of hydrogen, and of propylene has little if any effect on the rate of reaction is justified. It is possible, of course, that in all these cases the change in the hydrogen atom concentration was too small to have a noticeable effect. From the experiments with hydrogen atoms it would seem this must be the case. Thus approximately 2.5 cc ammonia were produced from 7 cc of methylamine during a discharge-tube run. These 7 cc passed through the system in 60 min. At a pressure of 0.2 mm this would be 440 cc per min. The hydrogen rate was 1520 cc per min. at 0.6-mm pressure. This total rate of flow, 1960 cc per min., for a reaction vessel of 500-cc capacity means a contact time of $\sim$0.25 min. From the rate constant of the photolysis, 0.036 min.$^{-1}$, the amount of methyl-amine decomposed in 0.25 min. from an initial 7 cc would be only 0.06 cc or half this amount of ammonia produced. The discharge-tube rate is thus some eighty times larger due undoubtedly to the relatively high atom concentration. It must be emphasized, however, that this increased ammonia production in the discharge-tube experiments is not accompanied by a corresponding increase in alkane production. It is therefore unlikely that methyl radicals are present. Hence reaction (5) probably represents the initial step under these conditions.

On the basis of the proposed mechanism the low quantum yield is to be traced essentially to the slowness of reaction (3), the decomposition of the CH_3NH radical. This would probably mean a fairly high activation energy for this reaction, which in turn should be reflected in an over-all activation energy for the photolysis. The sensitivity to temperature early in the runs reported may be due in part to this source as well as to variation in lamp intensity. It is proposed to measure the quantum yield more accurately and also the effect of temperature over-all in order to test these points.