383. *The Photochemical Decomposition of Methylamine and Ethylamine.*

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METHYLAMINE and ethylamine were shown by Taylor and Emeléus (*J. Amer. Chem. Soc.*, 1931, **53**, 3370) to decompose when irradiated with a mercury arc; the reaction was accompanied by a small pressure increase, hydrogen, a non-volatile liquid, and small amounts of methane, ethane, and nitrogen being formed. It was assumed that any ammonia formed would itself undergo photodecomposition; this has been found to be incorrect, for ammonia constitutes one of the products from both amines. The thermal oxidation and decomposition of methylamine have recently been investigated (Jolley, J., **1934**, 1957; Emeléus and Jolley, this vol., p. 929), and for comparison with these reactions, it was desirable to obtain further data for both the photodecomposition and the photo-oxidation of methylamine. The work described below comprises a re-examination of the products of these reactions, and an approximate determination of the quantum yields.

The absorption spectra of the two amines were photographed as a preliminary to studying the photochemical reactions. Herzberg and Kölsch (*Z. Elektrochem.*, 1933, **31**, 572) have briefly described these spectra, which begin at approximately 2400 Å., and extend to the limit of optical transmission of quartz; the spectra consist of broad bands, resembling those of ammonia (Liefson, *Astrophys. J.*, 1926, **63**, 73), and these authors suggested that the absorption process is localised in the amino-group. Our re-examination of these spectra shows definite evidence of fine structure in some of the absorption bands.

EXPERIMENTAL.

The Absorption Spectra of Methylamine and Ethylamine.—Methylamine and ethylamine were prepared by dropping saturated solutions of their hydrochlorides on solid sodium hydroxide, drying the amines with lime, and purifying them by vacuum fractionation. The gases were stored in glass globes.

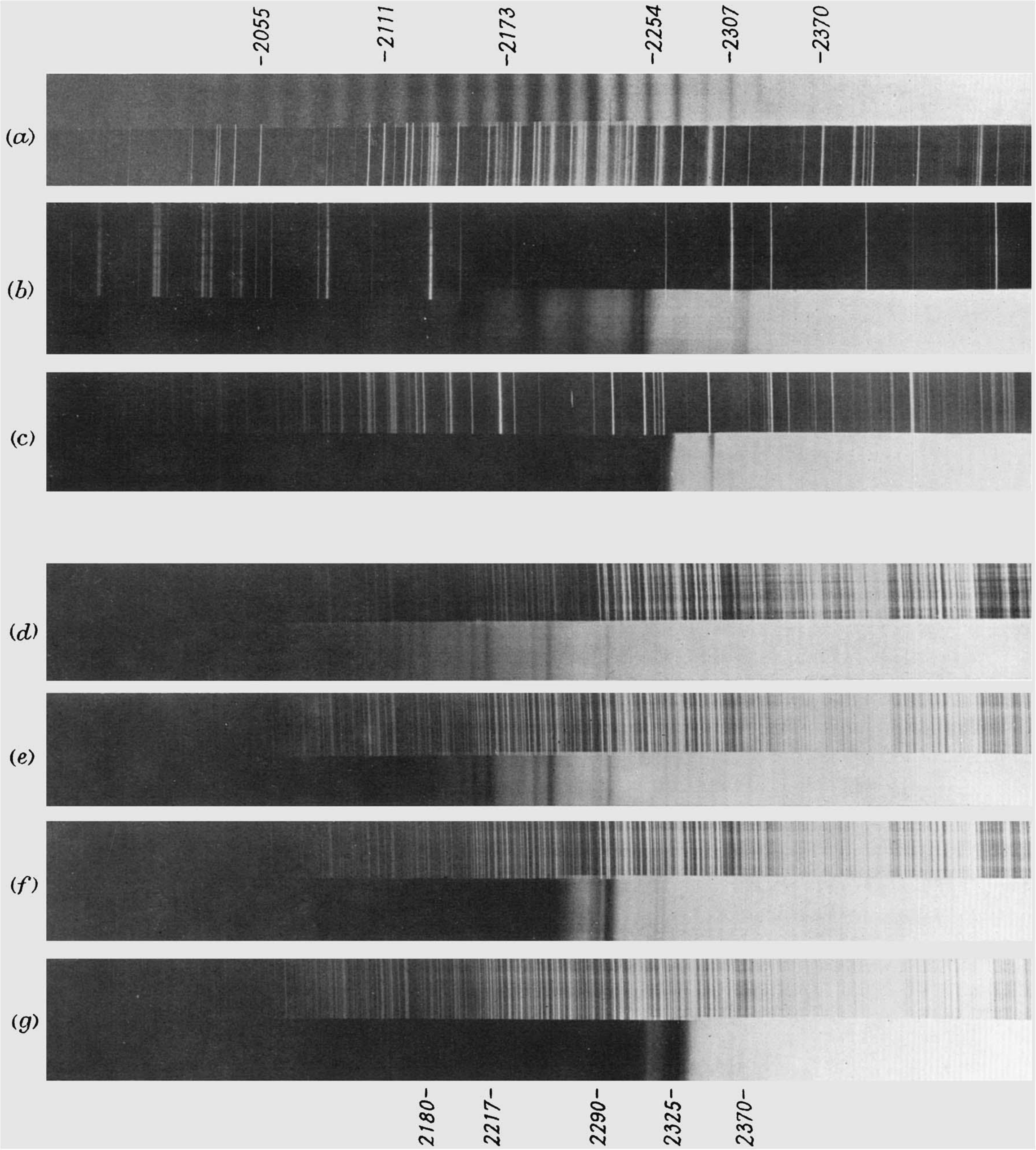
The spectrograph used was a small quartz instrument (Hilger, E.4) giving a dispersion of about 20 Å./mm. at 2400—2200 Å. A number of exposures were also made on a medium quartz instrument (Hilger E.2). The light source was a water-cooled Wood's hydrogen tube with hollow cylindrical aluminium electrodes and a waxed-on quartz window. It was operated from a 5000-volt transformer at 0·25—0·3 amp. Iron or copper arc comparison spectra were superposed on all the absorption spectrum exposures. Ilford ordinary or special "Q" plates were used. In the latter, absorption by gelatin at wave-lengths less than 2350 Å. is minimised.

Absorption Bands of Methylamine.

λ, Å.	1/λ, cm.$^{-1}$.	Δν.
2442	40,951	763
2397	41,714	659
2360	42,373	658
2324	43,031	
2307	43,351	671
2288	43,702	682
2271	44,033	663
2254	44,365	652
2238	44,685	660
2221	45,025	671
2205	45,356	674
2188	45,699	662
2173	46,018	683
2156	46,382	689
2141	46,707	680
2125	47,062	664
2111	47,371	666
2095	47,728	706
(2080)	48,077	626
(2068)	48,354	584
(2055)	48,661	666
(2040)	49,020	

Absorption Bands of Ethylamine.

λ, Å.	1/λ, cm.$^{-1}$.	Δν.
2372	42,158	
2365	42,282	724
2332	42,882	
2325	43,012	786
(2313)	43,236	
2290	43,668	
2280	43,860	697
2274	43,974	
2254	44,365	
2245	44,544	
2237	44,704	745
(2229)	44,867	
2217	45,110	
2209	45,277	
2200	45,455	719
2193	45,597	
2182	45,829	
2176	45,953	
2166	46,166	
(2159)	46,318	



Absorption spectra of methylamine and ethylamine.

$CH_3{\cdot}NH_2$: (*a*) 12 *mm.*, (*b*) 8 *mm.*, (*c*) 200 *mm.*
$C_2H_5{\cdot}NH_2$: (*d*) 3·5 *mm.*, (*e*) 9·5 *mm.*, (*f*) 28 *mm.*, (*g*) 100·5 *mm.*

[*To face p.* 1613.

A cylindrical quartz absorption cell (5 cm. diameter, 5 cm. thick) with plane ends was used. It was connected by a standard ground joint to a mercury manometer, to the vacuum line, and to the amine reservoir. A series of exposures was taken at different pressures. Measurements of the absorption bands were made on an enlargement (× 10) of the negative, the arc lines being used for reference. The positions of the centres of the bands were measured in every case with an estimated accuracy of ±2 Å. The bracketed values refer to weaker bands, for which the error may be greater.

The frequency differences between the second and third and the third and fourth bands measured were 660 and 670 cm.$^{-1}$ respectively. This difference is constant within the limits of experimental error throughout the spectrum, the differences tabulated under $\Delta\nu$ being those of alternate bands after the first three. The divergence shown by the band at 2442 Å. is probably due to the fact that its centre was not measured.

The mean value (669 cm.$^{-1}$) agrees with that given by Herzberg and Kölsch (*loc. cit.*) and attributed by them to a vibrational frequency of the excited amino-group. The corresponding value in the case of ammonia is 900 cm.$^{-1}$.

Photographs of the absorption spectrum of methylamine are shown in the plate. At a pressure of 12 mm. (Fig. *a*) the absorption bands visible extend from 2000 to 2400 Å. The band width is 4—8 Å., and there is no indication of band heads or structure below 2300 Å. Enlargement (Fig. *b*) shows the spectrum at a pressure of 8 mm. on the medium quartz spectrograph. The most prominent bands are those at 2397, 2360, 2324, and 2307 Å., and with the greater dispersion they exhibit sharp heads with degradation towards the violet. At a pressure of 20 cm. (Fig. *c*) only two absorption bands are visible, *viz.*, those at 2397 and 2441 Å., absorption at shorter wave-lengths being continuous. These again show evidence of structure. The measurement of rotational fine structure in the absorption bands of so complex a molecule as methylamine would require a high dispersion, and photographs with a grating spectrograph are to be made. At wave-lengths less than 2300 Å., the absorption bands of methylamine are diffuse and resemble those of ammonia. The few bands at longer wave-length probably have structure, and absorption in this region may result in an excited molecule instead of predissociation.

The absorption bands of ethylamine differ in general appearance from those of methylamine and ammonia in that they are arranged in groups. The tabulated values of the wave numbers show a constant frequency difference of 726 cm.$^{-1}$ (mean) between the first members of each group. This value is repeated for the second, third, and fourth members of the groups. It probably corresponds to the values 670 cm.$^{-1}$ found for methylamine and 900 cm.$^{-1}$ for ammonia, and to a characteristic frequency of the excited amino-group. Photographs of these bands at pressures of 3·5, 9·5, 28, and 100·5 mm. are shown in the plate (Figs. *d*—*g*).

The breadth of the ethylamine absorption bands is 5—8 Å. Those below 2300 Å. appear to be diffuse and to lack sharp edges. At longer wave-lengths the bands show a complex structure (cf. Figs. *f*, *g*). If this is rotational fine structure it will explain the observation of Banov and Prileshaeva (*Compt. rend. Acad. Sci., U.R.S.S.*, 1934, **3**, 497), who reported a fluorescence of ethylamine at low pressures when illuminated with light of wave-length between 2800 and 2300 Å. At short wave-lengths (< 2300 Å.) predissociation may occur, while absorption of light of longer wave-length could cause dissociation in collisions at higher pressures, and give rise to fluorescence at lower pressures.

Photodecomposition of Methylamine.—Convenient rates of decomposition were obtained with a vertical mercury arc (200 watts) placed 1·5 cm. from the wall of the cylindrical quartz reaction bulb (10 cm. long, 2·5 cm. diam.). The latter was connected by 2-mm. capillary tubing to reservoirs containing the reactants, to a constant-volume capillary mercury manometer, and to a Töpler pump for withdrawing gases for analysis in the Bone and Wheeler apparatus. With this arrangement the reaction vessel became heated to 100—150°. Irradiation with an aluminium spark, operated with a 2-kw., 10,000-volt transformer with a large tinfoil–glass condenser in parallel and an auxiliary spark gap in series, also gave convenient rates of decomposition. No appreciable heating of the reaction vessel took place with the spark 5 cm. from the quartz surface. The electrodes were aluminium rods 1 cm. thick; the spark gap was 5—10 mm. and was kept constant during a run by throwing a magnified image on a screen, and adjusting the gap by hand. Reproducibility of reaction rates showed the intensity of illumination to be constant to approximately ±10%.

Products. The non-condensable gases were analysed in a Bone and Wheeler apparatus. The gas condensable in liquid air contained undecomposed methylamine together with ammonia and other products, and was transferred to a vacuum fractionation apparatus (Stock and

Somiesky, *Ber.*, 1916, **49**, 111). It was established in a series of preliminary experiments that ammonia could be separated from methylamine by distilling the mixture in a vacuum from a U-tube cooled to − 118°, and condensing the volatilised gas in a second U-tube cooled in liquid air. This method was applied to the product from the photodecomposition of methylamine. After 10—25 minutes' distillation no further material volatilised. The vapour pressures of the volatile and the non-volatile fraction were then measured at a series of low temperatures, the respective values being in approximate agreement with those of ammonia and methylamine. Finally, each of the fractions was distilled in turn into a small bulb with a manometer attached, in order to determine the relative volumes, and the completeness of absorption in dilute acid was tested by distilling into a bulb containing dilute sulphuric acid. Both fractions were absorbed completely, showing that condensable hydrocarbons were absent. It was also shown by separate tests that the less volatile fraction contained no hydrogen cyanide.

The non-volatile liquid reaction product was soluble in water, the solution being alkaline to methyl-red. A very small and variable titration was obtained with 0·05*N*-hydrochloric acid which was ascribed to dissolved methylamine or ammonia. The solutions gave a strong formaldehyde reaction (Schryver's test). To another portion of the solution, 2 : 4-dinitrophenylhydrazine hydrochloride was added; a small yellow precipitate was formed, probably indicating the presence of $CH_3{\cdot}N{:}CH_2$ in the liquid product.

Table I shows the results of analyses in five experiments. In Expts. 1—3 the aluminium spark at a distance of 5 cm. was used for illumination, but in 4 and 5 the mercury arc at a distance of 1·5 cm. was used. The experiments at room temperature with the aluminium spark show that approximately 1 mol. each of ammonia and hydrogen are formed in the decomposition of 2 mols. of methylamine. The reaction $2CH_3{\cdot}NH_2 = H_2 + NH_3 +$ a non-volatile product would involve no pressure change. Possible reaction mechanisms are discussed later. Expts. 4 and 5 with the hot system show an increased formation of hydrogen, and a total pressure increase corresponding to the extra hydrogen formed. They also show a slightly increased formation of methane, which was even more marked in earlier experiments at 260° (Emeléus and Taylor, *loc. cit.*), and was attributed to the increasing probability of the slightly endothermic reaction $CH_3 + H_2 = CH_4 + H$ with rise in temperature. An alternative mechanism for methane formation is suggested on p. 1617.

TABLE I.

Products of the Photodecomposition of Methylamine.

		Spark.			Arc.	
Expt.		1.	2.	3.	4.	5.
Initial $CH_3{\cdot}NH_2$ pressure (mm.)		148·0	108·0	160	107·4	113·0
Time of illumination (hrs.)		2	5	5·5	2	3
Pressure change (mm.)		+3·5	+9·5	+4·2	+17·4	+22·0
Products (mm.)	H_2	20·8	28·3	30·0	52·3	68·5
	NH_3	15·1	28·2	28·7	36·5	43·3
	CH_4	0·4	1·1	1·2	1·9	3·0
	N_2	1·8	3·4	0·6	0·6	1·0
Residual $CH_3{\cdot}NH_2$ (mm.)		113·4	56·5	103·8	33·5	17·3
$CH_3{\cdot}NH_2$ decomposed (mm.)		34·6	51·5	56·2	73·9	95·7

Quantum Yield of the Decomposition of Methylamine.—An estimate of the quantum yield was made by comparing the rates of decomposition of ammonia and methylamine when illuminated under the same conditions. The rates so observed will be proportional to the quantum yields for the two reactions only if absorption of the effective light is complete in each case, and if the two substances absorb in the same spectral region. The first criterion is satisfied in the measurements at approximately 100 mm. pressure recorded below, since the reaction rates at this pressure have reached a steady value. The second criterion is satisfied only very roughly, since the absorption spectrum of ammonia extends to 2260 Å., and that of methylamine to *ca.* 2450 Å. The most intense lines in the ultra-violet spectrum of the aluminium spark are at wave-lengths less than 2000 Å. and are absorbed by both substances, but there are several lines of moderate intensity which would be absorbed by methylamine and not by ammonia. Accordingly, the quantum yields observed for methylamine will represent an upper limit. They will, however, serve to show whether the photodecomposition of the amine is a reaction with long chains, or whether it is more analogous to that of ammonia.

Data for these experiments which were all of one hour's duration, are tabulated below. The centre of the spark was at 5 cm. from the side of the quartz vessel, and the gap was kept constant.

Relative Rates of Decomposition of Ammonia and Methylamine.

Ammonia.		Methylamine.	
Initial press., mm.	Press. of NH_3 decomp., mm.	Initial press., mm.	Press. of $CH_3{\cdot}NH_2$ decomp., mm.
49·5	10·0	49·5	23·4
101·5	9·2	101·9	32·4
102·5	11·7	106·0	31·4
		295	30·0

At a pressure of approximately 100 mm., corresponding with complete absorption, the decomposition rate for methylamine was three times greater than that for ammonia. If the quantum yield for the decomposition of ammonia is taken as 0·25 (Warburg, *Berl. Akad. Ber.*, **1911**, 746), that for methylamine cannot be greater than 0·75.

This value must be modified owing to differences in light absorption, and also on account of the formation of ammonia in the photo-reaction. Such ammonia would itself absorb part of the active light, but the effect is likely to be small, since little hydrogen is found in the final reaction products. It is concluded from these experiments that the quantum yield of the decomposition of methylamine is less than 0·75, and that the reaction does not involve a chain mechanism.

Photo-oxidation of Methylamine.—Irradiation of a methylamine–oxygen mixture in a quartz bulb produced a relatively large pressure decrease, and the deposition of a dew on the walls of the bulb. Analysis of the non-condensable gas present at the completion of the reaction showed small amounts of carbon monoxide, hydrogen, and nitrogen to have been formed. The liquid reaction product contained a white crystalline solid, which gave a Schryver test after warming with sulphuric acid. It was probably a mixture of condensation products of formaldehyde with ammonia and methylamine.

In the following experiment the methylamine–oxygen mixture was illuminated with the aluminium spark, and the reaction products were analysed. Non-condensable gases were first removed. The residual products were separated as far as possible from water by repeatedly distilling them from a bath at − 100°. After each distillation the residual material was allowed to warm to room temperature and then cooled rapidly. By this means gases dissolved in the water were removed, for, on rapid cooling, they did not redissolve. The ammonia and methylamine in the volatile fraction obtained in this way were separated as already described. The results of this experiment were as follows :

Time of illumination = 3 hrs. Press. decrease = 49·2 mm.
Initial $CH_3{\cdot}NH_2$ press. = 131·5 mm.
,, O_2 ,, = 124·2 ,,

The products (expressed as mm. pressure in the reaction system) were : H_2, 2·7; CH_4, 0·3; N_2, 2·8; CO, 6·5; NH_3, 30·0. The methylamine and oxygen consumed were respectively 83·5 and 28·7 mm. The amount of ammonia and methylamine recovered from the reaction product must be low owing to the reaction with formaldehyde, *i.e.*, the figure for the methylamine used is too high and that for ammonia formed is too low, but these corrections cannot be determined. Two facts emerge from this analysis : (i) there is very little change in the amount of ammonia formed in the oxidation as compared with the decomposition; (ii) very little free hydrogen is formed in the oxidation.

In order to determine if absorption of light by oxygen plays any part in initiating the reaction, mixtures of methylamine and oxygen were illuminated with light from a horizontal mercury arc, with and without the insertion in the light path of a quartz cell, 5 cm. thick, containing a 5% sodium chloride solution. This filter absorbs all light of wave-length less than 2050 Å., *i.e.*, all wave-lengths which would be absorbed by oxygen molecules. There was a decrease in reaction rate from 6 mm./hr. (pressure change) without the filter to 5 mm./hr. with the filter, an effect so small as to be attributable to the change in light available for absorption by methylamine. This observation means that the non-appearance of molecular hydrogen is not due to its direct oxidation, as the oxidation occurs normally when no light is absorbed by oxygen. The hydrogen must result from some intermediate stage in the reaction (*e.g.*, by interaction of CH_3 or H with methylamine), the intermediate product being sensitive to oxygen.

The following experiments were made under identical conditions of illumination with the aluminium spark for the decomposition and oxidation reactions.

	$CH_3·NH_2$ (mm.).	O_2 (mm.).	Time (hrs.).	Δp (mm.).	Products, mm.			O_2 consumed.
					H_2.	CO.	N_2.	
Decomposition ...	367	—	25·5	− 2	47·5	—	1·0	—
Oxidation............	139	229	21	−122	2·0	1·6	4·3	49·5

In these two experiments the difference in initial methylamine pressure is without influence, absorption being complete in either case. In the oxidation experiment the oxygen consumed is approximately equal to the hydrogen formed in the decomposition. It has already been shown that in the oxidation the methylamine oxidised (a maximum value) equals twice the oxygen consumed. In the decomposition the methylamine decomposed is equal to twice the hydrogen formed. It follows that the rate of disappearance of methylamine is uninfluenced by the addition of oxygen, and therefore the quantum yield is the same for the oxidation as for the decomposition. Thus the photo-oxidation of methylamine either is not a chain reaction, or involves very short chains.

Photodecomposition of Ethylamine.—Two experiments were carried out with the vertical mercury arc placed 1·5 cm. from the quartz bulb, the times of illumination being 2 and 3·5 hours. The analytical results are recorded below, pressures being expressed in mm.

$p_{NH_2Et.}$	Δp in reaction.	$\Delta p_{NH_2Et.}$	p_{H_2}.	p_{NH_3}.	p_{CH_4}.	p_{N_2}.	$p_{Hydrocarbon.}$
250·1	24·9	96·5	58·8	51·7	5·7	2·0	3·32
148·0	49·2	109·9	84·5	53·2	9·4	2·2	2·67

Comparing the rate of decomposition with that of methylamine under the same conditions (Expt. 4, Table I), it is seen that in 2 hours 96·5 mm. of ethylamine or 73·9 mm. of methylamine were decomposed. This shows that the quantum yields of the two reactions are of the same order ($< 0·75$). Ammonia is formed in considerable amounts in the photodecomposition of ethylamine. Its separation from undecomposed ethylamine was effected in the same manner as in the case of methylamine, the vapour pressures differing sufficiently to give an almost quantitative separation. The ammonia fraction was not completely absorbed in dilute acid, showing that hydrocarbons (ethane and ethylene) were present. These hydrocarbon residues in the above two experiments were combined, and on analysis in the Bone and Wheeler apparatus were found to contain 93·7% of ethane and 6·3% of ethylene. The liquid reaction product when dissolved in water smelt of acetaldehyde, and gave a yellow precipitate with 2 : 4-dinitrophenylhydrazine, but the amount was not sufficient for a m. p. determination. The gaseous products are similar to those from methylamine, since hydrogen and ammonia again predominate. It is evident that the reaction mechanism is similar to that for the photodecomposition of methylamine.

DISCUSSION.

The foregoing experiments establish that ammonia is one of the products of the photodecomposition both of methylamine and of ethylamine. The quantum yield in the former decomposition has been shown to be less than 0·75, that of ethylamine being of the same order. The chemical changes taking place are probably very complex. It has been shown that the absorption spectrum of methylamine is probably of the predissociation type, which implies that dissociation of the molecule occurs spontaneously on absorption. The weakest link in the molecule is that between carbon and nitrogen (70 kg.-cals.), values for C–H and N–H being 90 and 91 kg.-cals. respectively. The production of a methyl and an amino-group, the initial step assumed by Taylor and Emeléus (*loc. cit.*), will explain the photosensitisation of ethylene polymerisation by methylamine. Recently, Emeléus and Jolley (*loc. cit.*) have suggested a chain mechanism which accounts for the products of pyrolysis of methylamine. The initial process consists of a thermal dissociation into free methyl and amino-radicals, subsequent stages being

$$CH_3 + CH_3·NH_2 = CH_4 + CH_3·NH \longrightarrow CH_4 + CH_2{:}NH + H \quad . \quad . \quad (1)$$

$$NH_2 + CH_3·NH_2 = NH_3 + CH_3·NH \longrightarrow NH_3 + CH_2{:}NH + H \quad . \quad . \quad (2)$$

$$H + CH_3·NH_2 = H_2 + CH_3·NH \longrightarrow H_2 + CH_2{:}NH + H \quad . \quad . \quad (3)$$

$$CH_2{:}NH = HCN + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As calculated from the bond strengths, the first steps in (1) and (2) are almost thermoneutral, the second stages being endothermic to the extent of about 20 kg.-cals.

If the same process were operative in the photo-reaction as in the pyrolysis, methane and ammonia should be formed in comparable amounts. Actually, little methane results unless the temperature is raised. There is no other ready way of accounting for the methyl groups, as they form no ethane. A further difficulty in adopting the pyrolysis mechanism for the photochemical reaction is that no hydrogen cyanide is formed, and that the only clearly exothermic process is that represented by equation (3).

The alternative is that methylamine dissociates into atomic hydrogen and the $CH_3\cdot NH$ residue. This process might occur if the energy absorbed remained within the amino-group, and it would be comparable with the photo-dissociation of ammonia into NH_2 and H (Geib and Harteck, *Z. physikal. Chem.*, 1931, Bodenstein Festband, **861**; Melville, *Trans. Faraday Soc.*, 1932, **28**, 885). On this basis it would be necessary to suppose that molecular hydrogen is formed in the exothermic process $H + CH_3\cdot NH_2 = CH_3\cdot NH + H_2$. Formation of ammonia is best accounted for by the bimolecular process $2CH_3\cdot NH = CH_3\cdot N{:}CH_2 + NH_3$, which, from bond-strength calculations, is exothermic. The exact value is doubtful owing to the unknown factor involved in the formation of a double bond. It is necessary to assume in this case that the $CH_3\cdot NH$ radical will make unfruitful collisions with methylamine and hydrogen molecules. This reaction scheme accounts for the influence of oxygen on the products of photolysis, for atomic hydrogen would react readily with oxygen. The product $CH_3\cdot N{:}CH_2$ should hydrolyse to formaldehyde, in agreement with the observed behaviour of the liquid product of photolysis. The production of atomic hydrogen may well occur in the photolysis of ethylamine also. We hope to apply Pearson's method of detecting free radicals in photochemical reactions (J., 1934, 1718) to obtain further information as to the presence or absence of free methyl and ethyl in the two processes which have been studied.

The authors thank the Government Grants Committee and Messrs. Imperial Chemical Industries Ltd. for grants, and Professor C. L. Fortescue for the loan of transformers.

Imperial College, London, S.W. 7. [*Received, August 22nd*, 1935.]