4. *A Study of the Photolysis of Organic Nitrogen Compounds. Part II. Aliphatic Amines.*

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The photolysis of a number of aliphatic amines in the vapour phase has been studied, in order to elucidate the nature of the primary act and of secondary processes which occur. From primary and secondary amines, the primary act produces hydrogen atoms and alkylamino- or dialkylamino-radicals respectively. Both these radicals undergo a disproportionation reaction—the latter exclusively, while the former also participate in a reaction producing a Schiff's base and ammonia. The hydrogen atoms were detected by means of their reaction with propylene. Tertiary amines on irradiation split off an alkyl group; the resulting dialkylamino-radicals then react as above. The reactions occurring in irradiated mixtures of nitric oxide and secondary and tertiary amines are discussed, and attention is directed to the interaction of methyl groups and nitric oxide.

In the photolysis of dimethylnitrosoamine, considerable quantities of hydrogen appear among the products if irradiation with the full light of the mercury arc is prolonged (preceding paper). One of the main products is dimethylamine, and experiment showed that hydrogen is the chief volatile product obtained on irradiation of this substance. It was therefore decided to undertake a more complete study of the photochemistry of the amines.

The spectra of the alkylamines have been studied by Herzberg and Kölsch (*Z. Elektrochem.*, 1933, **39**, 572), Henri and Lasareff (*Compt. rend.*, 1935, **200**, 829), and Emeléus and Jolley (J., 1935, 1612). In all cases absorption commences at 2300—2500 A., and extends in a series of diffuse bands to shorter wave-lengths. The intensity and diffuseness increase as the wave-length decreases; with dimethylamine and trimethylamine the bands eventually give place to a continuum. In general, the spectra of the amines closely resemble the bands of ammonia, and may be attributed to a similar cause, *viz.*, excitation of a non-bonding electron associated with the nitrogen atom (Mulliken, *J. Chem. Physics*, 1935, **3**, 506). Banov and Prileshaeva (*Compt. rend. Acad. Sci. Russ.*, 1934, **3**, 487) report the existence of a fluorescence between 2300 and 2500 A. for ethylamine, but the amines studied in the present work show no fluorescence in the visible region; the possibility of an ultra-violet fluorescence must remain open.

The only work on the photolysis of gaseous amines is that of Bates and Taylor (*J. Amer. Chem. Soc.*, 1927, **49**, 2438), Taylor and Emeléus (*ibid.*, 1931, **53**, 3370), and Emeléus and Jolley (*loc. cit.*). Bates and Taylor examined the direct and the mercury-sensitised photolysis of ethylamine, and found that hydrogen was the main product, being accompanied by small quantities of nitrogen. The other workers studied methylamine and ethylamine, Emeléus and Jolley recording the following reactions for methylamine:

$$\left.\begin{array}{lll} CH_3{\cdot}NH_2 + h\nu & \longrightarrow CH_3{\cdot}NH{\cdot} + H & (a) \\ H + CH_3{\cdot}NH_2 & \longrightarrow CH_3{\cdot}NH{\cdot} + H_2 & (b) \\ 2CH_3{\cdot}NH{\cdot} & \longrightarrow CH_2{:}N{\cdot}CH_3 + NH_3 & (c) \end{array}\right\} \quad . \quad . \quad . \quad (1)$$

hydrogen and ammonia being obtained in comparable quantities. It is reasonable to assume a similar process in the case of dimethylamine, a hydrogen atom being split off, and dimethylamino-radicals formed:

$$\left.\begin{array}{ll} (CH_3)_2NH + h\nu & \longrightarrow (CH_3)_2N{\cdot} + H \\ H + (CH_3)_2NH & \longrightarrow (CH_3)_2N{\cdot} + H_2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

leading to a decrease in volume and the formation of 1 vol. of hydrogen from 2 vols. of amine. It was found, however, that photolysis takes place with very little change in volume, and with no formation of ammonia. Further, 1 vol. of amine produces approximately 1 vol. of hydrogen. These facts may be explained in a number of ways. If (2) is correct, there are the possibilities of: (i) reaction between dimethylamino-radicals, producing hydrogen, (ii) a disproportionation reaction between dimethylamino-radicals, producing dimethylamine:

$$2(CH_3)_2N{\cdot} \longrightarrow (CH_3)_2NH + CH_3{\cdot}\dot{N}{\cdot}\dot{C}H_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a reaction which has been shown to occur in the previous paper. If (2) is not correct, a third possibility (iii) is that the primary act yields directly molecular instead of atomic hydrogen:

$$(CH_3)_2NH + h\nu \longrightarrow CH_3{\cdot}\dot{N}{\cdot}\dot{C}H_2 + H_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The alternative (i) is probably not the explanation, since dimethylamino-radicals produced by photolysis of dimethylnitrosoamine do not react to form hydrogen. It remains then to decide between (ii) and (iii). Emeléus and Jolley (*loc. cit.*) found that photo-oxidation of methylamine produces little hydrogen, but a yield of ammonia which is only slightly less than that obtained in the direct photolysis. They attribute this to the reaction between atomic hydrogen and oxygen molecules. Presumably, a similar method could be used to distinguish between the alternative reactions (2) and (4). However, propylene, which cannot readily form active intermediaries or participate in a chain reaction, was used to detect hydrogen atoms, and on irradiation of a mixture of dimethylamine and propylene a reduced yield of hydrogen was obtained, together with propane and a hexane. These results are in agreement with the reactions :

$$\left.\begin{array}{l} H + C_3H_6 \longrightarrow C_3H_7\cdot \\ C_3H_7\cdot + H \longrightarrow C_3H_8 \\ 2C_3H_7\cdot \longrightarrow C_6H_{14} \end{array}\right\} \quad \ldots \ldots \quad (5)$$

and the primary act of the dimethylamine photolysis is the formation of hydrogen atoms by reaction (2).

Other amines studied were *n*-butylamine, *n*-amylamine, and trimethylamine. With the first two the main problem was similar to that described above, *viz.*, whether the primary act produces atomic or molecular hydrogen. Irradiation with propylene showed that, in fact, hydrogen atoms are formed. With trimethylamine, the primary process is shown to be the scission of a methyl group. Since both dimethylamine and trimethylamine produce dimethylamino-radicals on irradiation, it seemed possible that, when these compounds were irradiated in the presence of nitric oxide, dimethylnitrosoamine would be formed by the reaction $(CH_3)_2N\cdot + NO \longrightarrow (CH_3)_2N\cdot NO$. This was not confirmed, however, but the experiments are described, since they throw some light on the reactions of methyl groups and hydrogen atoms with nitric oxide, and also upon the mechanism of the trimethylamine photolysis.

EXPERIMENTAL.

I. *Photolysis of the Amines.*

The apparatus and method employed were exactly as described in the preceding paper, the vapours of the amines being irradiated by the full light of a mercury arc running hot and consuming about 300 watts. In the experiments on the simple photolysis of the amines, the volatile products were divided into two fractions, usually removed at − 196° and − 100° severally. The residues were composed of polymers and unchanged amine. It was frequently possible to distil off the latter in a vacuum at room temperature and examine the reactions of the polymer. The vapour density of the amine so removed was determined as described in the previous paper, to ascertain whether any of the polymer had also distilled.

When propylene was used, this gas was first introduced into the evacuated apparatus, its pressure measured, and its volume at *N.T.P.* calculated from the known volume of the system. The propylene was condensed into the reaction vessel by cooling the latter in liquid air, and the amine then distilled in a vacuum. The liquid air was removed, the total pressure measured, and after time had been allowed for the vapours to mix by diffusion, irradiation was started. At the conclusion of the run, the products were separated into three fractions, removed at − 196°, − 120°, and 0°. The first two fractions contained only permanent gases, but the third was a liquid which on addition of water produced two layers. The upper one was identified as a hydrocarbon (C_6H_{14}), and it was separated and estimated by cooling the whole to about − 30°, and distilling off the hydrocarbon in a vacuum into a weighed tube.

The procedure when nitric oxide was employed was similar, except that the amine was first introduced into the system, followed by the nitric oxide (since this has an appreciable vapour pressure at liquid-air temperature). In this case the products were separated into two fractions, volatile at − 196° and − 120°, and a comparatively non-volatile residue. The last was distilled under atmospheric pressure in a micro-distillation apparatus, and then treated as described below.

Permanent gases were in all cases analysed by standard methods in a Bone and Wheeler apparatus.

Results.—(i) *Dimethylamine.* (a) Products of photolysis. Two experiments gave the results shown in Table I. Volumes are expressed in c.c. of vapour at *N.T.P.* Fraction II contained no portion soluble in water; ammonia was therefore absent. During the experiments a brown viscous liquid was deposited in the lower portion of the reaction vessel. The weights of polymer and dimethylamine present at the conclusion of the irradiation were estimated as follows. After removal of fraction II at − 120°, the residual dimethylamine was distilled off in a vacuum at room temperature into a tube, and weighed. Vapour-density measurements upon this portion showed that the polymer was slightly volatile, and that a small quantity had distilled over with the amine. The weight of volatile polymer present in the latter was calculated from the vapour density [the polymer being assumed to be $(\mathrm{CH_3{\cdot}\overset{|}{N}{\cdot}\overset{|}{C}H_2})_2$]. The liquid which collected in the reaction vessel was withdrawn by a micropipette and weighed. The vessel was then rinsed with pure ether, and the ether slowly evaporated from the extract in a vacuum at about − 30°. The residue was weighed. From these figures the total weights of polymer and dimethylamine present could be estimated. The weights of dimethylamine decomposed in Expts. (i) and (ii) were 59·2 and 30·1 mg. respectively. The weights of polymer formed should be less than these by the weights of volatile products, and thus would be expected to be 54·3 and 27·1 mg. respectively. These figures are in good agreement with the actual weights obtained (54 and 28 mg.). The polymer was soluble in dilute acids, had a marked basic reaction, and gave on microanalysis C, 55·0; H, 12·1; N, 32·9 [Calc. for $(C_2H_5N)_n$: C, 55·9; H, 11·5; N, 32·6%].

TABLE I.

Expt.	Period of irradiation (hrs.).	$NHMe_2$ decomposed.	H_2.	CH_4.	C_2H_6.	Wt. of polymer (mg.).
i	4½	29·5	21·4	4·4	0·2	54
ii	2	15·0	13·8	2·0	0·1	28
iii	1	8·3	7·9	0·4	—	—

Table I shows that dimethylamine on photolysis produces approximately its own volume of hydrogen. The pressure changes during photolysis were very small, approximately 4% of the pressure of dimethylamine decomposed. These facts are in agreement with the mechanism expressed in equations (2) and (3). The free radical produced in (3) mainly polymerises: similar behaviour for this radical was recorded in the preceding paper. Probably a reorganisation to form the Schiff's base $CH_2{:}N{\cdot}CH_3$ occurs, and is followed by the polymerisation of the latter. The small quantities of methane and ethane may arise from a subsidiary primary act producing methyl groups, most of the latter being hydrogenated at the expense of the dimethylamine, or by combination with hydrogen atoms, while some combine to form ethane.

(b) Experiments with dimethylamine and propylene. Two experiments (see Table II) were performed on the irradiation of mixtures of dimethylamine. The hydrocarbon C_6H_{14} was identified by its complete inertness to reagents and its molecular weight (85). It had b. p. 64—69°; *n*-hexane has b. p. 68°, so the hydrocarbon probably contains an isomeric hexane, *e.g.*, 2-methylpentane (b. p. 60°) or di*iso*propyl (b. p. 58°). The formation of propane and hexane can only be accounted for by the attack of hydrogen atoms on propylene molecules, producing propyl or *iso*propyl radicals, which may either combine with each other to form a mixture of hexanes, or be hydrogenated to propane by further combination with hydrogen atoms [equation (5)]. According to this mechanism, the volume of propylene which disappears in the course of an experiment should equal the volume of propane produced plus twice that of the hexane. In Expts. (i) and (ii) the volumes of propylene reacting were respectively 14·5 and 40·0 c.c., whereas the volumes of propane plus twice that of hexane were 13·7 and 37·9 c.c., respectively.

TABLE II.

Expt.	Time of irradiation (hrs.).	Total pressures, mm. Initial.	Total pressures, mm. Final.	Vol. of C_3H_6 introduced, c.c. at *N.T.P.*	Vols. removed after irradiation, c.c. at *N.T.P.* H_2.	CH_4.	C_3H_6.	C_3H_8.	C_6H_{14}.
i	8	291	178	23·6	11·9	3·3	9·1	4·1	4·8
ii	8	390	194	60·0	4·5	2·0	20·0	6·1	15·9

A comparison of Expts. (i) and (ii) further supports the scheme of equation (5). In each case the initial pressure of dimethylamine was about 200 mm., but in (ii) the initial propylene pressure was about 2·5 times that in (i). The result of this would be expected to be a much more complete combination between the hydrogen atoms and propylene, with formation of a higher stationary concentration of $C_3H_7{\cdot}$ radicals in (ii) but a lower stationary concentration of hydrogen atoms. The rate of the reaction $2C_3H_7{\cdot} \longrightarrow C_6H_{14}$ would thus be very considerably increased relative to that of $C_3H_7{\cdot} + H \longrightarrow C_3H_8$ in experiment (ii). This is in fact the case. Table II shows that in (ii) as compared with (i) there is a greatly increased yield of hexane, and the yield of propane is increased only to a much smaller extent. These experiments thus show conclusively that hydrogen atoms, and not molecules, are the chief products of the primary act. The reactions between hydrogen atoms and olefins given above agree with recent results reported by Jungers and Taylor (*J. Chem. Physics*, **1938**, **6**, 325).

(c) Experiment with dimethylamine and nitric oxide. A mixture of equal volumes of dimethylamine and nitric oxide at a total pressure of 209 mm. was irradiated for 3⅔ hrs. The gaseous products were: nitrogen, 3·3 c.c. (25%); hydrogen, 8·5 c.c. (64%); methane, 0·8 c.c. (6%); ethylene, 0·6 c.c. (4%), and the final pressure was 164 mm. During photolysis a brown viscous liquid was deposited in the lower part of the reaction vessel. This was shown by tests with anhydrous copper sulphate to contain some water. On distillation in a micro-apparatus as described on p. 19, a colourless aqueous liquid with an ammoniacal smell came over first, and was followed by a pale yellow fraction. The latter gave only a very feeble Liebermann reaction, so the formation of dimethylnitrosoamine in any significant quantity appears doubtful. The production of nitrogen and small quantities of ethylene are in agreement with reactions (6) and (7), which have already been suggested as secondary reactions occurring to a small extent in the photolysis of dimethylnitrosoamine (preceding paper, p. 14):

$$\left.\begin{array}{lll} NO + H & \longrightarrow NOH\cdot & (a) \\ (CH_3)_2NH + NOH\cdot & \longrightarrow N_2 + H_2O + 2CH_3\cdot & (b) \end{array}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

$$(CH_3)_2N\cdot + NO \longrightarrow C_2H_4 + N_2 + H_2O \quad . \quad . \quad . \quad . \quad (7)$$

Since the yield of ethylene is much smaller than that of nitrogen, reactions (6) must be responsible for most of the latter.

(ii) n-*Butylamine.* (a) Products of photolysis. Table III gives the results of a number of experiments with this amine. In all experiments except (iv) liquid butylamine was refluxed gently in the reaction vessel, and the vapour irradiated. Expt. (iv) was performed in the absence of liquid to ascertain whether there was any change of pressure on photolysis.

TABLE III.

		Products (c.c. at *N.T.P.*).				
Expt.	Time of irradiation (hrs.).	CH_4.	H_2.	NH_3.	C_3H_8.	Ratio $\frac{H_2}{NH_3}$.
(i)	2	0·1	5·6	2·9	0·3	1·95
(ii)	18	0·5	35·3	19·2	2·7	1·84
(iii)	18¾	0·5	36·2	19·6	4·0	1·84
(iv)	2¾	0·1	4·6	2·6	0·3	1·84
(v)	1	0·1	3·0	1·6	0·1	1·87
						Mean 1·87

Fraction II, containing the ammonia and propane, was distilled off at − 100°. On treatment with water in the gas burette, the major portion dissolved very rapidly, and the solution had the smell and reactions of ammonia. The small quantity of residual gas was identified as propane by explosion with oxygen. In Expt. (ii) the volatile products were removed from the reaction vessel at intervals of 8 hours (except for the last interval of 2 hours). The object of this was to prevent any considerable decomposition of the ammonia, and also to facilitate the refluxing of the butylamine (which, of course, occurs less readily the higher the pressure in the system). The operation was carried out by cooling the liquid in the reaction vessel to − 80° and removing Fraction I with the Toepler pump, through two liquid-air traps. During this process some butylamine which remained uncondensed in the reaction vessel was collected in the traps; the latter were therefore allowed to warm to room temperature, and the contents (butylamine, ammonia) condensed into the reaction vessel cooled in liquid air. Finally, the reaction vessel was maintained at − 80°, and the ammonia distilled off into a trap. The butylamine was then refluxed, and irradiation continued. The whole process was repeated after 8 hours, and again at the end of the experiment. Similarly, in Expt. (iii) volatile products were removed at intervals of 4 hours (except for the final interval of 2¾ hours). It will be seen from Table III that the hydrogen and ammonia are not equivalent, as was found by Emeléus and Jolley (*loc. cit.*) in the photolysis of methylamine. This does not appear to be due to the secondary decomposition of ammonia, for the following reasons: (1) The ratio H_2/NH_3 is constant for different periods of irradiation from 1 to 8 hours (Table III). This would certainly not be so if there was any appreciable photolysis of the ammonia [contrast, *e.g.*, the ratio H_2/CH_4 (Table VI) in the photodecomposition of trimethylamine: in this case the hydrogen is due to a secondary decomposition, and the ratio varies from 1·4 for 11½ hours' irradiation to 0·19 for ½ hour]. (2) No nitrogen was ever detected in the photolysis of *n*-butylamine. (It is of course possible to photolyse ammonia without any formation of nitrogen, but only under carefully chosen conditions.) (3) It is shown below that the primary act in the photodecomposition of *n*-butylamine produces hydrogen atoms; the latter, however, are known to have a very strong inhibiting effect on the photolysis of ammonia (Melville, *Trans. Faraday Soc.*, 1932, **28**, 885). In order to test this point further, the experiments of Emeléus and Jolley on methylamine were repeated. 70 Mm. of the amine were irradiated for 8 hours; after removal of hydrogen at − 196°, a second fraction, containing ammonia and methylamine, was distilled off at − 120°. The ammonia was estimated by vapour-density measurement. The volumes of hydrogen and ammonia obtained were 11·0 and 10·8 c.c. (*N.T.P.*) respectively. No appreciable secondary decomposition therefore occurred in this experiment, and it may be concluded that all the evidence and reasoning points to the absence of secondary decomposition of ammonia during the photolysis of *n*-butylamine.

A mechanism similar to that proposed for methylamine by Emeléus and Jolley is given below:

$$\left.\begin{array}{lll} CH_2Pr{\cdot}NH_2 + h\nu & \longrightarrow CH_2Pr{\cdot}NH{\cdot} + H & (a) \\ H + CH_2Pr{\cdot}NH_2 & \longrightarrow CH_2Pr{\cdot}NH{\cdot} + H_2 & (b) \\ 2CH_2Pr{\cdot}NH{\cdot} & \longrightarrow CHPr{:}N{\cdot}CH_2Pr + NH_3 & (c) \end{array}\right\} \quad . \; . \; . \; (8)$$

Since the hydrogen is in excess of the ammonia, not all the butylamino-radicals formed in 8(*a*) and (*b*) react according to 8(*c*). Now in Expt. (iii) (Table III) the weight of butylamine introduced initially into the apparatus was 183·2 mg. This was decomposed nearly completely (only a trace of amine could be detected in the residue after photolysis). The maximum yield of hydrogen from this weight of butylamine, on the basis of 8(*a*) and (*b*), is 28·1 c.c., whereas 36·2 c.c. were obtained. Hence, those butylamino-radicals which do not react according to 8(*c*) probably either (1) react together giving hydrogen or (2) undergo disproportionation regenerating butylamine:

$$2CH_2Pr{\cdot}NH{\cdot} \longrightarrow CH_2Pr{\cdot}NH_2 + CH_2Pr{\cdot}N{:} \quad . \; . \; . \; . \; . \; (9)$$

The similarity between equations (9) and (3) is at once apparent, and this suggests strongly that the second alternative is the correct one. A further possible explanation of the high yield of hydrogen is that molecular instead of atomic hydrogen results from the primary act, but this is excluded, since the next experiment shows that irradiation actually produces atoms. On the basis of equations (8) and (9) the maximum yield of hydrogen from the above weight of amine is 36·7 c.c.

Since, in Expt. (iv) no liquid was present, and the initial and the final pressure were 58·0 and 59·6 mm., respectively, there is no appreciable volume change during photolysis, in agreement with the scheme of equations (8) and (9), irrespective of the relative probabilities of (8)(*c*) and (9). Actually the ratio of these probabilities is $[NH_3]/([H_2]-[NH_3])$ or about 1 : 0·9.

During the irradiation, a viscous brown polymer was deposited in the lower part of the reaction vessel. On treating this with dilute hydrochloric acid, the characteristic smell of higher aldehydes at once became apparent. When the liquid was nearly neutralised with sodium hydroxide and Schiff's solution added, an immediate pink colour was developed, showing the presence of aldehyde. This behaviour would be expected from the polymer produced by (8)(*c*), the N:C bonds being broken by treatment with acid, with formation of a carbonyl compound and a primary amine. Examination showed that the polymer consists of at least two substances. One may be fairly completely removed by very prolonged distillation in a vacuum, the other remaining behind. The former has a characteristic fragrant odour, and gives the reaction with hydrochloric acid mentioned above, but the other is odourless and inactive. The latter polymer appears to be the substance formed by the polymerisation of the $CH_2Pr{\cdot}N{:}$ radicals produced by reaction (9). The small quantities of propane are probably due to the occurrence of the reaction

$$CH_2Pr{\cdot}N{:} \longrightarrow C_3H_8 + HCN \quad . \; . \; . \; . \; . \; . \; . \; (10)$$

Traces of cyanide were detected in the residue after the removal of fraction II in Expt. (iv).

(b) Experiments with *n*-butylamine and propylene. An experiment in which butylamine vapour was irradiated in the presence of 130 mm. of propylene gave the results shown in Table IV, from which it appears that *n*-butylamine behaves very similarly to dimethylamine when irradiated with propylene, the latter being partly converted into propane and hexane. Some of this propane is produced from the amine; Table III shows that the amount of propane is rather variable, but its volume may be taken as about one-tenth of that of the ammonia. Hence, in Table IV about 0·8 c.c. of propane arises from direct photolysis, the remainder (2·7 c.c.) coming from the hydrogenation of the propylene. As stated on p. 20, the mechanism of equation (5) predicts equality between the volume of propylene which is used up and the sum of the volumes of propane and twice the hexane. This sum is 9·7 c.c., whereas the volume of propylene used is 10·5 c.c. The quantitative agreement is thus satisfactory. Further, the total hydrogen which would have been formed in the absence of propylene is $[H_2] + [C_3H_8] + [C_6H_{14}]$, *i.e.*, 14·9 c.c. The ratio H_2/NH_3 is therefore 1·86, in good agreement with the mean value (1·87) for the experiments recorded in Table III.

TABLE IV.

Time of irradiation (hrs.).	Vol. of C_3H_6 introduced (c.c. at *N.T.P.*).	Vols. removed after irradiation (c.c. at *N.T.P.*).					
		CH_4.	H_2.	C_3H_6.	C_3H_8.	NH_3.	C_6H_{14}.
8¼	26·7	0·5	8·7	16·2	3·5	8·0	3·5

The present experiments thus show that the primary act in the photolysis is the formation of hydrogen atoms by equation (8)(*a*), the other reactions occurring being represented by (8)(*b*),(*c*) and (9).

(iii) n-*Amylamine.* The results of two experiments on the photodecomposition of this amine are recorded in Table V. Volumes of products are expressed in c.c. at *N.T.P.*

TABLE V.

Expt.	Time of irradiation (hrs.).	Products (c.c. at *N.T.P.*).				Ratio $\frac{H_2}{NH_3}$.
		H_2.	CH_4.	NH_3.	C_4H_{10}.	
i	2	4·5	0·1	1·8	0·2	2·5
ii	8	16·0	0·2	6·1	0·6	2·6

In its main features the photolysis resembles that of *n*-butylamine very closely. The ratio H_2/NH_3 is approximately the same in the two experiments, suggesting that there is little secondary decomposition of the ammonia. As with *n*-butylamine, a viscous polymer was formed which appeared to consist of two substances; the more volatile produced an aldehyde when treated with hydrochloric acid, but the other was inert. The reactions which occur on irradiation are thus completely analogous to those expressed in equations (8) and (9).

(iv) *Trimethylamine.* (a) Products of photolysis. The results of a series of experiments are in Table VI. Fraction II was distilled off at − 130°, at which temperature trimethylamine is not appreciably volatile. It contained no portion soluble in water. Ammonia was therefore absent.

TABLE VI.

Expt.	Period of irradiation (hrs.).	Press. (mm.).		Products (c.c. at *N.T.P.*).		
		Initial.	Final.	H_2.	CH_4.	C_2H_6.
i	11½	197	194	9·3	6·6	4·3
ii	1	168	165	0·4(7)	1·1	0·7
iii	½	190	189	0·1(3)	0·8	0·9

Table VI shows that there is a remarkable variation in the relative yields of the products as the period of irradiation is altered: with a period of 11½ hours, hydrogen constitutes 46% of the total gaseous products, whereas with a ½ hour period the proportion has fallen to 9%. This can be explained if the primary act is the splitting of a methyl group from the molecule:

$$(CH_3)_3N + h\nu \longrightarrow (CH_3)_2N\cdot + CH_3\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The dimethylamino-radicals then react in the usual way according to equation (3), producing dimethylamine, some of which undergoes photolysis with formation of hydrogen atoms. Polymerisation of the radical $CH_3\cdot\overset{|}{N}\cdot\overset{|}{C}H_2$ produced by (3) accounts for the formation of a brown viscous liquid during photolysis. This substance is identical with the polymer produced by the irradiation of dimethylamine. The methane (Table VI) may result either from the hydrogenation of methyl groups at the expense of the amine, or by the combination of methyl and hydrogen atoms. There is some evidence that the latter process occurs when irradiation is prolonged. From Table VI it appears that a short period of irradiation increases the ratio of ethane to methane. This is what would be expected, since under such conditions there is less secondary decomposition of dimethylamine and thus a smaller formation of hydrogen atoms. More methyl groups therefore combine with each other and fewer with hydrogen atoms, *i.e.*, the yield of ethane relative to methane is increased.

(b) Experiments with trimethylamine and nitric oxide. Table VII summarises the results of two experiments. A white cloud was formed in the reaction vessel immediately irradiation was started, the effect being very much more pronounced in Expt. (ii) with a higher pressure of nitric oxide. In both experiments a brown liquid was deposited in the lower part of the reaction vessel. This was shown to contain a considerable quantity of water. On distillation in a micro-apparatus, as described on p. 19, a colourless aqueous liquid came over first with a strongly basic smell, and was followed by a yellowish portion. This liquid gave only an extremely feeble Liebermann reaction, so dimethylnitrosoamine (which might possibly have been formed by the union of Me_2N + NO) was present only in traces, if at all. Indeed, so far as could be ascertained the original liquid seemed to be identical with an aqueous solution of the polymer formed when trimethylamine (or dimethylamine) is irradiated. However, in both experiments a considerable volume of nitric oxide disappears; only a relatively small portion of the nitrogen content of this appears in the free state or as a nitroso-compound. The nitric oxide is clearly removed by reaction with methyl groups. On testing a portion of the residue for cyanide after removal of fraction II, an extremely strong positive Prussian-blue test was obtained. These facts are in agreement with the following reaction between methyl groups and nitric oxide:

TABLE VII.

Expt.	Period of irradiation (hrs.).	Press. (total), mm. Initial.	Press. (total), mm. Final.	NO introduced, c.c. at *N.T.P.*	Vols. removed after irradiation (c.c. at *N.T.P.*). H_2.	CH_4.	N_2.	C_2H_6.	C_2H_4.	NO.
i	20	305	223	50·0	16·5	5·8	3·2	1·5	0·3	18·1
ii	10	353	258	69·9	8·3	1·3	7·7	0·2	0·6	20·9

$$CH_3\cdot + NO \longrightarrow HCN + H_2O \quad . \ . \ . \ . \ . \ . \ . \ . \quad (12)$$

(cf. Davis, Jahn, and Burton, *J. Amer. Chem. Soc.*, 1938, **60**, 10). No cyanide could be detected among the products of the simple photolysis of trimethylamine. The union of trimethylamine and hydrogen cyanide may be responsible for the cloud observed at the beginning of the experiments. If all the nitric oxide which disappears reacts with methyl radicals, each of the latter fixing one molecule of nitric oxide, then the total number of c.c. of methyl groups liberated during photolysis will be $[NO] + [CH_4] + 2[C_2H_6]$. In this way the "yields of methyl groups" are seen to be 2·0 and 5·1 c.c./hr. in Expts. (i) and (ii) respectively. Increasing the concentration of nitric oxide thus appears to increase the efficiency of the primary process, and it may well do this by removing methyl groups, and thus impeding the reverse reaction $Me_2N\cdot + Me \longrightarrow Me_3N$.

The nitrogen and ethylene formed (see Table VII) probably arise from reactions (6) and (7).

II. *Absence of Fluorescence.*

The apparatus used to test the fluorescence was described in the preceding paper. Experiments were performed at pressures in the range 0·1—50 mm. (except in the case of amylamine, which has a saturation vapour pressure of about 20 mm. at room temperature). The full light of the hot mercury arc was employed, stray light being carefully excluded. No fluorescence was visible at any pressure for any of the amines. In order to ensure that this was not due to faulty observation, some acetone was introduced into the apparatus, and its characteristic fluorescence was easily visible.

DISCUSSION.

The foregoing experiments show that the primary act in the photolysis of the primary and secondary amines studied is the splitting off of a hydrogen atom from the molecule:

$$\left.\begin{array}{l} R\cdot NH_2 + h\nu \longrightarrow R\cdot NH\cdot + H \\ {}^{R}_{R'}{>}NH + h\nu \longrightarrow {}^{R}_{R'}{>}N\cdot + H \end{array}\right\} \quad . \ . \ . \ . \ . \ . \ . \quad (13)$$

The resulting alkylamino- or dialkylamino-radicals then undergo a disproportionation reaction, with formation of the original amine and a bivalent radical which subsequently polymerises, *e.g.*,

$$\left.\begin{array}{ll} \mathrm{2CH_2Pr{\cdot}NH{\cdot} \longrightarrow CH_2Pr{\cdot}NH_2 + CH_2Pr{\cdot}N\colon} & (a) \\ \mathrm{2N(CH_3)_2 \longrightarrow NH(CH_3)_2 + CH_3{\cdot}\dot{N}{\cdot}CH_2{\cdot}} & (b) \end{array}\right\} \quad . \quad . \quad (14)$$

Whereas (14)(*b*) appears to be the only reaction undergone by the dialkylamino-radicals from the secondary amines, the alkylamino-radicals from the primary amine can also react thus:

$$\mathrm{2R{\cdot}CH_2{\cdot}NH{\cdot} \longrightarrow R{\cdot}CH_2{\cdot}N\colon CHR + NH_3} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

It appears that the probability of (14)(*a*) compared to that of (15) increases as the length of the hydrocarbon chain increases. With methylamine the former reaction does not occur, since the hydrogen and ammonia obtained are equivalent. With *n*-butylamine and *n*-amylamine the ratios of the probabilities (14)(*a*) : (15) are 0·87 and 1·6 respectively. The hydrogen atoms produced by the primary process may either recombine by a three-body collision, or attack a further amine molecule according to equations (1)(*b*) and (8)(*b*). As far as the final products are concerned, these reactions are indistinguishable, but the latter appears more probable since the recombination process would be very slow. In the case of trimethylamine, the primary process is the scission of a methyl group, which may subsequently hydrogenate or dimerise. The resulting dimethylamino-radicals disproportionate in the usual way according to (14)(*b*), so that some dimethylamine is formed.

The similarity between the spectra of ammonia and the alkylamines suggests that the latter undergo a predissociation reaction on irradiation. As mentioned in the preceding paper, however, there may be no close correlation between the lifetime of the excited state and the diffuseness of the spectrum in the case of these polyatomic molecules.

These higher amines show no reaction corresponding to the type II decomposition found for long-chain carbonyl compounds by Norrish and his collaborators (see, *e.g.*, Norrish and Appleyard, J., 1935, 1504). This type of reaction consists in a rupture of the hydrocarbon chain between the α- and the β-carbon atoms with formation of an olefin and a simpler carbonyl compound. A similar process would entail the formation of propylene and methylamine from *n*-butylamine, and neither of these compounds was identified.

The reactions occurring during the photolysis of the amines in the presence of nitric oxide are, in general, complex. Nitrogen appears among the products, and is probably formed mainly by the reactions (6)(*a*), (*b*). It would not seem that reaction (6)(*a*) is very efficient, since the hour yield of hydrogen in the photolysis of dimethylamine is not appreciably altered by the presence of nitric oxide. The values of the hour yield in the presence and absence of nitric oxide are 2·3 and 3·3 c.c./hr. respectively. On the other hand, reaction (12) appears to be efficient, addition of nitric oxide to trimethylamine during photolysis causing the rapid removal of methyl groups, and a consequent increase in the quantum yield by the suppression of the back reaction (see p. 24). A comparison of Tables I and VI shows that the rate of production of hydrogen atoms by the primary act in the case of dimethylamine is about 6—7 c.c./hr., whereas that of methyl groups produced by the primary process in trimethylamine is only 3—4 c.c./hr. The absorption spectra are such that trimethylamine absorbs a number of strong mercury lines, to which dimethylamine is transparent. The quantum yield for the secondary amine is thus considerably higher than that for the tertiary. This may be attributed to the more frequent occurrence of the recombination reaction ($\mathrm{Me_2N{\cdot} + Me \longrightarrow Me_3N}$) with trimethylamine, due perhaps to a larger stationary concentration of methyl groups during the trimethylamine photolysis than hydrogen atoms during the photodecomposition of dimethylamine.

Finally, it may be noted that the occurrence of reaction (12) would explain the observation of Mitchell and Hinshelwood (*loc. cit.*) in the photolysis of acetone in the presence of nitric oxide. These authors recorded that no product was detectable which did not appear in the photolysis of acetone alone, except a little carbon dioxide formed by oxidation of carbon monoxide. This is probably due to the fact that the hydrogen cyanide formed by the action of methyl groups on nitric oxide (12) would form an addition compound with acetone, and thus escape detection.

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