151. *Hydrazine Formation in the Synthesis and Decomposition of Ammonia. Part II. The Photochemical Decomposition of Ammonia.*

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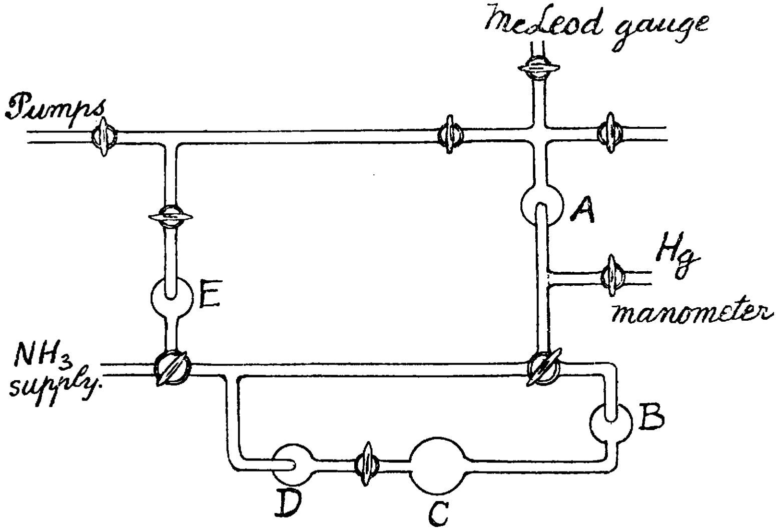
THE formation of hydrazine in the decomposition of ammonia by cathode rays (Gedye and Allibone, *Proc. Roy. Soc.*, 1931, *A*, **130**, 346) suggested the probability of its formation in the photochemical decomposition. While this work was in progress, Koenig and Brings (*Z. physikal. Chem.*, Bodenstein Festband, 1931, 541) reported the formation of hydrazine in the photochemical decomposition of ammonia. The present work confirms their results and contributes further information on the conditions under which hydrazine is formed.

EXPERIMENTAL.

The apparatus (see fig.) could be evacuated by means of a mercury diffusion pump, backed alternatively by a Töpler or a " Hyvac " pump. The quartz reaction vessel, *C*, was illuminated by means of a vertical quartz–mercury lamp which could be run either hot or water-cooled. The taps were greased with Shell " Apiezon L " grease, and the apparatus thoroughly out-gassed before use. Ammonia, prepared by reducing the pressure over an aqueous solution, was passed over soda–lime and phosphoric anhydride, and condensed in the trap *E* by liquid air, at the temperature of which its vapour pressure is immeasurably small. Any permanent gases were then pumped off and the ammonia further purified by repeated fractional distillation between the traps *E* and *A*, according to the following method. The traps *D* and *B* were cooled in solid carbon dioxide and acetone (— 78°). The liquid air, around the trap *E* which contained the ammonia initially, was then replaced by carbon dioxide and acetone, and *A* cooled in liquid air. The appropriate taps being opened, ammonia then distilled slowly from *E* to *A*, *via D*, *C*, *B*, the impurities condensing in traps *D* and *B*



and the last fraction remaining in *E* being rejected. The process was repeated until no trace of condensable impurity such as water or hydrazine remained behind in the traps cooled to − 78°.

The experimental procedure was as follows : Ammonia, initially in *E*, was distilled into *A*, which was cooled in liquid air, through the illuminated reaction vessel *C* and the trap *B*, which was cooled to − 78° to freeze out hydrazine. Under these conditions the ammonia in *E* remained at its m. p., at which temperature its vapour pressure is 4·4 cm., until almost the whole had distilled over. The nitrogen and hydrogen formed during the exposure passed on, and were pumped off continuously and collected for measurement. The light was then switched off and the ammonia again distilled three times through the trap cooled to − 78°. On removal of the cooling mixture from *B*, a condensable product could be seen as a white deposit on the sides of the trap. It was found that under the conditions practically the whole of the condensable product was frozen out. Experiments could also be carried out by cooling *D* to − 78°, and distilling in the reverse direction.

The condensable product was proved to be hydrazine by a determination of the percentage composition and molecular weight by the following method. It was distilled into *A*, and freed from ammonia by removing the cooling mixture, allowing it to warm to room temperature, freezing it again and pumping off the uncondensed ammonia. This process had to be repeated two or three times in order to remove all the ammonia. Observations of the difference in levels of the mercury columns in the McLeod gauge then showed the product to have 12—15 mm. vapour pressure at room temperature, *i.e.*, about the same as water. The pressure of the product was read on the mercury manometer, and, the volume of the apparatus having been separately determined, the volume at *N.T.P.* was known. It was then distilled into *B* and decomposed by irradiation from the mercury lamp. The products were collected, measured, and analysed. From the data obtained the percentage composition and molecular weight were calculated, the results being as follows.

Pressure by Hg manometer 3·1 mm.; corrected vol. 0·663 c.c.
Analysis of gas after photochemical decomposition (c.c.) :
H_2, 1·013; N_2, 0·598; NH_3, 0·255; total, 1·866.

Thus the composition of the original product is :

H = 1·396 c.c., N = 0·726 c.c., or H = 65·7%, N = 34·3%; and the molecular weight is 36·4.

The ammonia was separated from the permanent gases by liquid air and measured separately. The above results agree satisfactorily with the composition N_2H_4. The apparent error in the molecular weight is outside the limits of experimental error, but this is not unexpected, since it is doubtful whether Boyle's law holds accurately for hydrazine at 3 mm. pressure at ordinary temperatures. Percentage compositions obtained in two other cases in which the initial volume was not measured were 67·8 and 63·6% hydrogen (by vol.). The production of three volumes of permanent gas from one of the condensable products was also confirmed in a number of experiments.

Tests were also made with gold chloride as described in Part I (this vol., p. 1158), and a violet colour obtained.

Further tests were made by the thermal decomposition method (*ibid.*). A rather surprising result was obtained in a vessel thoroughly out-gassed by an electric discharge. Instead of four volumes of ammonia and one of nitrogen, the products were condensable and permanent gases in equal volumes, as required by the equation $2N_2H_4 = 2NH_3 + N_2 + H_2$. This is the type of decomposition which occurs on a platinum or tungsten filament (Askey, *J. Amer. Chem. Soc.*, 1930, **52**, 970). The vessel in which this decomposition was observed was then cut out and replaced, and the hydrazine now decomposed normally into four volumes of ammonia and one of permanent gas : $3N_2H_4 = 4NH_3 + N_2$. Apparently out-gassing by an electric discharge alters the catalytic activity of the glass surface.

In the following experiments the hydrazine was determined by measuring the gases formed in its photochemical decomposition, which was practically complete normally in about 4 hours. Water was not decomposed under these conditions, and hence any error due to its possible presence was excluded. The probable error in the determination of hydrazine due to incomplete freezing out, incomplete decomposition, and errors in measurement is considered to be not more than 10%. It was not expedient to increase the accuracy beyond this limit in view of the extra time required and the difficulty of control of other factors such as flow-rate and pressure. All volumes have been corrected to *N.T.P.*

When ammonia was distilled from *E* to *A* the capillary exit of the reaction vessel was water-cooled, *i.e.*, the outflowing gases were rapidly cooled to room temperature.

No detectable trace of condensable product could be obtained in a static system, when ammonia at 4·4 cm. was illuminated for 15 mins. with the hot lamp. A careful analysis of the permanent gases formed during photochemical decomposition of ammonia by the hot lamp gave 75·4% of hydrogen. This does not differ by

TABLE I.

					Yield.		
Expt. No.	Time of flow, mins.	Mean rate of flow, c.c./min.	Direction of distillation.	Mercury vapour.	Permanent gas, c.c.	Hydrazine, c.c.	N_2H_4, as % of NH_3 decomp.
(*a*) Lamp water-cooled. Approximate temperature of reaction vessel 45°.							
8	125	80	*A* to *E*	Excluded	18·72	0·707	13·6
9	100	80	,,	,,	12·7	>0·325	>9·6
34	68	43	*E* to *A*	,,	4·40	0·284	21·6
36	48	63	,,	,,	3·58	0·250	23·1
38	28	89	*A* to *E*	Present	5·09	0·111	8·7
39	27	93	,,	,,	2·30	0·043	7·5
44	120	8	*E* to *A*	Excluded	14·0	0·0319	0·9
(*b*) Lamp hot. Approximate temperature of reaction vessel 120°.							
40	33	76	*E* to *A*	—	4·82	0·0543	4·8
41	34	74	,,	—	4·72	0·0514	4·4
42	38	64	*A* to *E*	—	6·09	0·032	2·1
43	32	76	,,	—	3·87	0·0229	2·3
47	90	8	*E* to *A*	—	11·05	0·0107	0·40

more than the experimental error from the proportion $3H_2 : N_2$, and is in agreement with the low yield of hydrazine obtained. The hydrazine yield is greatly reduced by a lowering of the flow rate.

Effect of Temperature.—The relative hydrazine yields in Table I (*a*) are consistently higher than those in Table I (*b*), which indicates that hydrazine formation is favoured at lower temperatures. Much higher yields were obtained on cooling the reaction vessel by flowing water, thus:

Lamp hot. Reaction vessel water-cooled.

					Yield.		
Expt. No.	Time of flow, mins.	Mean rate of flow, c.c./min.	Direction of distillation.	Temp. of reaction vessel.	Perm. gas, c.c.	Hydrazine, c.c.	N_2H_4, as % of NH_3 decomp.
52	24	80	*E* to *A*	11°	1·55	0·39	55·7
53	55	8	,,	11	4·02	0·41	31
54	35	70	,,	2	1·04	0·264	57·2

In expt. 52 the permanent gases formed were analysed and gave 81% hydrogen, in good agreement with the observed hydrazine yield.

The relative hydrazine yield is greatly increased by lowering the temperature of the reaction vessel, and is far less dependent on the rate of flow when the reaction vessel is cooled. It would appear, therefore, that the principal effect of high flow-rate is due to the rapid removal of the products of reaction into colder parts of the apparatus. The effect of rapid cooling is also demonstrated by the relatively high yields in expts. 34 and 36, in which the exit of the reaction vessel was water-cooled, and also by the following experiments, in which the conditions were as in expts. 40—43, but the capillary exit of the reaction vessel was cooled in solid carbon dioxide and acetone :

			Yield.		
Expt. No.	Time of flow, mins.	Rate of flow, c.c./min.	Permanent gas, c.c.	Hydrazine, c.c.	N_2H_4, as % of NH_3 decomp.
45	30	68	2·53	0·0523	7·8
46	25	82	2·37	0·0523	8·3

It was observed that rates of decomposition of ammonia and hydrazine under similar conditions were of the same order of magnitude. Since, with the rate of flow normally employed, the amount of decomposition of ammonia was only about 0·1% of that flowing through the reaction vessel, it is clear that the photochemical decomposition of hydrazine cannot seriously affect the relative yields. Further, the thermal decomposition of hydrazine cannot appreciably affect the results, since this does not become measurable below 200°.

Preliminary experiments were carried out on the mercury-sensitised reaction. A 25% solution of acetic acid was used as a filter to cut out the short-wave radiation which decomposes ammonia directly. The gas was passed over mercury, electrically warmed to about 40°, to ensure saturation. Observation with a spectroscope and fluorescent screen revealed the 253·7 μμ line in the reaction vessel when mercury only was present. On admission of ammonia, its intensity decreased, and was completely suppressed by 1·0 cm. pressure of the gas. The result obtained was as follows :

Temp. of reaction vessel ...	18°	Yield of permanent gases (c.c.)	1·00
Time of flow (mins.)	89	Yield of hydrazine (c.c.)	0·0053
Mean rate of flow (c.c./min.)	101	Yield of N_2H_4 as % of ammonia decomp.	2·0

The value for the yield of hydrazine may be slightly low, for decomposition was not carried quite to completion in its determination. The relative yield is very much smaller, however, than under comparable conditions in the direct reaction. It is significant that Dickinson and Mitchell (*Proc. Nat. Acad. Sci.*, 1926, **12**, 692) found 87% hydrogen in the products of the direct photochemical reaction and 70% in the mercury-sensitised reaction, indicating the formation of a nitrogen-rich compound (hydrazine) in the direct reaction. The low value in the photosensitised reaction was ascribed to clean-up of hydrogen.

Discussion.

The decompositions of ammonia by cathode rays and by light show certain similarities, and a comparison of the two reactions affords information on the mechanism of the photochemical reaction.

In the decomposition of ammonia by cathode rays the intermediate formation of NH is proved by the observation of its characteristic bands when an electric discharge is passed through ammonia, as already pointed out by one of us (Gedye, *Trans. Faraday Soc.*, 1931, **27**, 474). Bartlett's analysis of the positive ions formed by electron bombardment of ammonia (*Physical Rev.*, 1928, **33**, 169) reveals the presence of $NH_3^{\cdot}$ and $NH_2^{\cdot}$ at very low pressures, the ion $NH^{\cdot}$ appearing at higher pressures. The lowest energies at which the three types of ion appeared were (in electron-volts): $NH_3^{\cdot}$, 11·2; $NH_2^{\cdot}$, 12·0; $NH^{\cdot}$, 11·2, the value for $NH_3^{\cdot}$ being in good agreement with that obtained by other workers. No negative ions, and few if any $H^{\cdot}$ ions, were obtained. This led to the conclusion that $NH^{\cdot}$ ions are provided by collision of ammonia molecules with the primary products, $NH_3^{\cdot}$ and $NH_2^{\cdot}$. Further dissociation might be expected to occur on recombination of the ions. It is to be noted, however, that 11·2 volts provide insufficient energy to give complete dissociation according to the equation $NH_3 = N + 3H$. We may, therefore, conclude that the products formed on ionic recombination are NH, atomic hydrogen, and possibly NH_2.

The formation of hydrazine from ammonia in the discharge can be almost quantitative with a high flow-rate and low pressure at − 75° (Koenig and Brings, *loc. cit.*), and Gedye and Allibone (*loc. cit.*) found yields of over 40%, at low pressures in a static system, under cathode ray bombardment, at room temperature. It is probable that hydrazine formation is due mainly to the reaction

$$NH + NH_3 = N_2H_4 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which will probably require three-body collision for stabilisation of the molecule of hydrazine.

The preferential formation of hydrazine at low pressure and temperature indicates that an alternative reaction resulting in direct production of nitrogen and hydrogen, presumably

$$NH + NH_3 = N_2 + 2H_2 \quad . \quad . \quad . \quad . \quad (2)$$

is favoured by higher pressure or temperature. This mechanism would result in a maximum efficiency of two molecules of ammonia decomposed per ion-pair, provided no reaction occur between atomic hydrogen and ammonia. This is in agreement with the observations of Gedye and Allibone (*loc. cit.*). The value of 1·2 given in that paper was based on the total ionisation in ammonia relative to air being 0·95. Using the more reliable value of 0·90 (Laby, *Proc. Roy. Soc.*, 1907, *A*, **97**, 206), and applying a more accurate cooling correction to our calorimetric experiments, we now obtain 1·3. The earlier suggestion that negative ions may participate to an important extent must be withdrawn, as not being in accordance with the experimental data. Reaction occurring between atomic hydrogen and ammonia at high temperatures would lead to a maximum efficiency of 4 molecules decomposed per ion-pair in accordance with the results of Wourtzel (*Le Radium*, 1919, **11**, 289). The reaction

$$NH_3 + H = NH_2 + H_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is almost certainly accompanied by only a small energy change and would be favoured by rise of temperature.

If we now compare these results with those of the photochemical reaction, we notice certain similarities. Hydrazine is produced in both cases, and the same factors—low temperature and high flow-rate—favour its formation. The quantum and ion-pair efficiencies possess similar temperature coefficients. On the other hand, the quantum efficiency at ordinary temperatures, *viz.*, 0·23 (Warburg, *Sitz. Preuss. Akad. Wiss.*, 1911, 746), is much less than the ion-pair efficiency.

The work of Bonhoeffer and Farkas (*Z. physikal. Chem.*, 1928, **134**, 337) shows that the photochemical reaction in the range of wave-lengths investigated is a case of predissociation. The only primary processes possible for a quantum corresponding to the wave-lengths employed are :

$$NH_3 = NH_2 + H \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or

$$NH_3 = NH + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The similarity found by Haber, Farkas, and Harteck (*Naturwiss.*, 1930, **18**, 443) between the effects of illuminated ammonia on the explosion temperature of hydrogen–oxygen mixtures and those of hydrogen atoms indicates that the principal reaction occurring is (4). This is not quite conclusive, for an active radical such as NH might be expected to produce a similar effect. If, however, (5) were the principal primary reaction, it would be difficult to account for the lower efficiency of the photochemical reaction. The results of our investigation show that if (4) is the primary reaction, two secondary reactions are possible, *viz.*,

$$NH_2 + NH_2 = N_2H_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or

$$NH_2 + NH_2 = N_2 + 2H_2 \quad . \quad . \quad . \quad . \quad (7)$$

(7) being favoured by rise of temperature.

Since hydrazine is decomposed by ultra-violet light according to the equation $2N_2H_4 = 2NH_3 + N_2 + H_2$, the expected quantum efficiency as determined by the ultimate nitrogen and hydrogen produced should be between 0·33 and 1·0, depending on the relative hydrazine yield, or might be somewhat lower if the reaction $NH_2 + H = NH_3$ occurs to an important extent. Reaction between atomic hydrogen and ammonia should predominate at higher temperatures and would lead to a *maximum* quantum efficiency of 2. It will be interesting, therefore, to know whether Kuhn's value of 3·3 at 500° (*Compt. rend.*, 1924, **178**, 708) can be confirmed. The inhibiting effect of hydrogen at high temperatures observed by Kuhn, not occurring at ordinary temperatures, may be due to the reverse of reaction (3). It is significant that Kassel and Noyes (*J. Amer. Chem. Soc.*, 1927, **49**, 2495) found a quantum efficiency of 0·7 at ordinary temperatures in the range 160—190 $\mu\mu$. The reaction $NH_3 = NH + 2H$ becomes possible below 170 $\mu\mu$ and provides a possible explanation of the higher efficiency at short wave-lengths.

In the union of nitrogen and hydrogen, Caress and Rideal (*Proc. Roy. Soc.*, 1927, *A*, **115**, 684, 1927) and Brett (*ibid.*, 1930, *A*, **129**, 319) have shown that the reaction in the low-voltage arc is due mainly to $N_2^{\cdot}$ and $N^{\cdot}$ ions. Caress and Rideal showed that in the presence of atomic hydrogen, some reaction occurred (at 13 volts) below the ionisation potential of nitrogen. This would probably be due to the hydrogen ion formed at this potential. Normal hydrogen atoms did not react with nitrogen except on a catalytic surface. According to Lewis (*J. Amer. Chem. Soc.*, 1928, **50**, 27), active nitrogen which contains metastable molecules and atoms reacts with atomic hydrogen to give ammonia, but no reaction was observed between active nitrogen and normal hydrogen or between normal nitrogen and atomic hydrogen. No hydrazine was detected in any case. Steiner (*Z. Elektrochem.*, 1930, **36**, 807), on the other hand, found that reaction between active nitrogen and active hydrogen yielded ammonia, and reaction between active nitrogen and molecular hydrogen gave hydrazine. No reaction was observed between atomic hydrogen and normal nitrogen, in agreement with Caress and Rideal. In the mercury-sensitised reaction, Hirst (*Proc. Camb. Phil. Soc.*, 1926, **23**, 162) obtained traces of ammonia, and a reducing substance which he believed to be hydrazine, in the presence of liquid mercury. Gaviola and Wood (*Phil. Mag.*, 1928, **6**, 1191), showed that NH bands appeared when nitrogen was mixed with a small quantity of hydrogen and illuminated by the line 253·7 $\mu\mu$ in the presence of mercury vapour. They concluded that the formation of NH required dissociation of the nitrogen molecule by two collisions with excited or metastable mercury, the improbability of this occurrence accounting for the low efficiency of the reaction, and that excess hydrogen removed NH by formation of ammonia, the reaction $H + N_2 = NH + N$ being impossible on thermochemical grounds. Under the action of high-velocity electrons it is certain that both atomic nitrogen and atomic hydrogen would be formed, since the ions $H^{\cdot}$, $H_3^{\cdot}$ (Brasefield, *Physical Rev.*, 1928, **31**, 52), and N' (Hogness and Lunn, *ibid.*, 1925, **25**, 786) are known to be formed by electron bombardment in hydrogen and nitrogen respectively. In the discharge tube the NH bands have been observed for all mixtures of nitrogen and hydrogen (Lewis, *Astrophys. J.*, 1914, **40**, 154).

All investigations agree, then, that in the presence of atomic hydrogen and nitrogen, reaction occurs according to the equations $N + H = NH$, $NH + H_2 = NH_3$, three-body collisions being presumably required. The formation of hydrazine observed by Hirst, Steiner, and ourselves in each case occurred in the presence of atomic nitrogen, and the most probable mechanism is that suggested by Steiner, *viz.*, $N + H_2 = NH_2$, $2NH_2 = N_2H_4$. To this we may add that our results on the photochemical decomposition show that only a part of the NH_2 molecules react to form hydrazine, and the yield should fall off very rapidly with rise of temperature.

Summary.

(1) The photochemical decomposition of ammonia by the total radiation from a quartz–mercury arc has been investigated by a flow method.

(2) The formation of hydrazine has been proved by a determination of the percentage composition and molecular weight of the condensable product formed.

(3) The relative yield of hydrazine is favoured by low temperature of the reaction vessel, high flow-rate, and rapid cooling of the gases leaving the reaction vessel. Under the optimum conditions the yield may represent over 50% of the decomposed ammonia. Very little hydrazine is obtained in the mercury-sensitised decomposition.

(4) The decompositions of ammonia by light and ionising radiations are discussed and compared.

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