150. *Hydrazine Formation in the Synthesis and Decomposition of Ammonia. Part I. Synthesis of Hydrazine and Ammonia by Cathode Rays.*

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IN a previous communication (*Proc. Roy. Soc.*, 1931, *A*, **130**, 346), the effects observed in the decomposition of ammonia by cathode rays were described. The number of molecules decomposed per ion pair agreed with that obtained in the corresponding reaction with α-particles, and the intermediate formation of hydrazine was noted. The combination of nitrogen and hydrogen has been investigated under the action of α-particles and in the glow discharge, and a definite synthesis of ammonia observed. Lind and Bardwell (*J. Amer. Chem. Soc.*, 1928, **50**, 745) found that the number of molecules of ammonia formed per ion pair (M/N) corresponded to a mean value of 0·2, variability being ascribed to incomplete absorption at the low concentrations employed. Ponsaerts (*Bull. Soc. chim. Belg.*, 1929, **38**, 110) obtained $M/N = 0{\cdot}3$ by a static method. Brewer and Westhaver (*J. Physical Chem.*, 1930, **34**, 153), using the glow discharge, on certain assumptions, obtained $M/N = 0{\cdot}25$. On the other hand, Busse and Daniells (*J. Amer. Chem. Soc.*, 1928, **50**, 3271) obtained such small and inconsistent yields in the corresponding reaction due to cathode rays that they considered their results not worth recording.

We have therefore investigated this reaction and find that small yields of ammonia and hydrazine are obtainable. The long range of the cathode rays in a mixture of the composition $3H_2 : N_2$ and the low efficiency of the reaction render the method somewhat less suitable for the investigation of this reaction than for the decompositions of ammonia and of nitrous oxide previously described. We have therefore confined our investigation to the initial stages of the reaction and particularly to formation of hydrazine, which has not been previously detected in the reaction due either to α-particles or to high-velocity electrons.

EXPERIMENTAL.

The electrical apparatus and reaction vessel were as previously described (*loc. cit.*, and J., 1931, 3016). The chemical apparatus was unchanged except for the substitution of quill-tubing spirals for the type of liquid-air trap previously employed.

Hydrogen was prepared by the electrolysis of a solution of sodium and barium hydroxides, and mixed with nitrogen in a large aspirator. The gases were purified by passing over copper at about 550°, solid

potash and phosphoric anhydride, and finally through two spirals immersed in liquid air. The second spiral lay between the mercury manometers and the reaction vessel, thus assuring the absence of mercury vapour.

After exposure to cathode rays, the gases were drawn slowly at reduced pressure through a spiral immersed in liquid air to freeze out condensable products, and under these conditions it was shown that absorption of such products was practically complete. Preliminary out-gassing of the vessel by electron bombardment was most important, for otherwise considerable quantities of condensable substances were liberated from the surface. Blank experiments showed that the gases after purification contained no ammonia detectable by Nessler's solution.

Readings on the McLeod gauge with the spiral at room temperature showed that the vapours formed did not obey Boyle's law, but if the spiral were cooled in carbon dioxide and acetone, measurements could be made. The product uncondensed at −78° was proved to be ammonia by tests with Nessler's solution. These were carried out by freezing this product in a side tube, sealing it off, and opening it under ammonia-free water. The colorimetric estimations agreed closely with the quantity of ammonia calculated from the readings of the McLeod gauge. The ammonia having been pumped off, the residual product was shown by McLeod-gauge readings to have a vapour pressure of about 15 mm. at room temperature. Its quantity could not, therefore, be measured on the gauge. It was shown to be hydrazine by a number of tests as follows: (1) It reduced a solution of gold chloride, giving a violet colour due to colloidal gold. (2) It reduced iodine and potassium permanganate. (3) On being heated in a sealed tube it gave ammonia, detected by Nessler's solution. (4) It underwent thermal decomposition in a glass vessel into a permanent and a condensable gas in the proportion 1 : 4 by volume, according to the equation $3N_2H_4 = 4NH_3 + N_2$. The following readings were obtained for the pressure (in mm.):

	NH_3.	N_2.	Total.	Ratio, NH_3/N_2.
(1)	0·028	0·006	0·034	4·6
(2)	0·034	0·008	0·042	4·2

It is thus clear that nitrogen and hydrogen combine under the influence of cathode rays to form, not only ammonia, but also hydrazine.

A large number of qualitative experiments were made both in Pyrex-glass and silvered vessels. Tests for hydrazine and ammonia were always positive. The following quantitative measurements were made, the maximum voltage being 220 kilovolts.

Mixture.	No.	Initial pressure (cm. Hg).	Time (mins.).	Current (micro-amps.).	Ammonia. C.c. at N.T.P.	Ammonia. Mols. per electron.
$3H_2 : N_2$	1	75·0	5	2·5	0·027	155
	2	74·0	10	1·3	0·025	138
	3	30·0	5	2·3	0·011	71
	4	14·8	10	2·1	0·016	57
	5	5·4	10	2·3	0·008	26
$H_2 : N_2$	6	75·0	4′ 20″	2·2	0·014	105
	7	75·0	6′ 20″	2·5	0·035	156

No accurate determinations of hydrazine were made, but rough estimations by comparison of the effects produced with gold chloride, and by measurement of the volume of the products of thermal decomposition, showed that they were of the same order of magnitude as the ammonia yields. The low efficiency of the reaction, combined with the long range of cathode rays in the $3H_2 : N_2$ mixture, shows that it is not worth while attempting to work under conditions of complete absorption with a Tesla transformer. An approximate calculation of the amount of energy per molecule of ammonia formed is, however, possible. Calorimetric experiments described in our previous communication (*loc. cit.*) show that the mean energy utilised per electron at 75 cm. pressure is of the order 30—50 kv. This gives about 300 electron volts per molecule of ammonia formed, and an ion-pair efficiency of about 0·1. Hydrazine being regarded as an intermediate product in the formation of ammonia, the agreement with the values obtained by other methods of investigation may be considered satisfactory.

Summary.

Small yields of ammonia and hydrazine were obtained by the action of high-velocity electrons on mixtures of nitrogen and hydrogen. Owing to the long range of such electrons in a $N_2 : 3H_2$ mixture, the method is not very suitable for the quantitative investigation of this reaction.

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