# 152. *Hydrazine Formation in the Synthesis and Decomposition of Ammonia. Part III. A Note on the Synthesis of Hydrazine at Catalytic Surfaces.*

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THE formation of hydrazine from its elements by gaseous ionisation raises the question whether it is also formed as an intermediate product in the thermal synthesis of ammonia.

Preliminary experiments were carried out with palladised copper as catalyst, prepared by cleaning copper turnings with dilute nitric acid and treating them with palladium nitrate, and rendered active by alternate oxidation and reduction down to below 200°. The mixed gases, prepared as described in Part I (this vol., p. 1158), were purified by passage through pyrogallol, sulphuric acid, and then successively over caustic potash, catalyst, potash, and phosphoric anhydride. Any ammonia and hydrazine formed were removed from the gases by cooling in liquid air, the former being determined by pressure measurements over solid carbon dioxide and ether. No condensable products were obtained in the liquid-air trap when the catalyst was used cold. With an active catalyst, ammonia was detectable at 200°, with a flow-rate of the gases over the catalyst of 40 c.c./min., $0{\cdot}95 \times 10^{-3}$ c.c. being obtained per litre of gas. No measurable trace of any substance remained after pumping off the ammonia with the catalyst below 400°. A condensable vapour with vapour pressure about 15 mm. at room temperature and capable of reducing gold chloride solution was obtained on raising the temperature to 480°. The gold chloride reduction is also given by hydroxylamine, but the latter possesses only a small vapour pressure at room temperature. After activation of the catalyst by successive oxidations and reductions down to 160°, with a high rate of flow (*ca.* 150 c.c./min.) yields could at first be obtained at 480° as high as $2$—$3 \times 10^{-3}$ c.c. per litre of gas. After several hours at this temperature, or immediately at 610°, no further detectable quantities could be obtained until the catalyst had been reactivated, a process which occupied several days.

The palladised copper was accordingly replaced by the usual iron catalyst promoted with the oxides of aluminium and potassium obtained from the Fixed Nitrogen Research Laboratory, Washington, D.C., to whom our thanks are due. To reduce any oxide to iron and remove adsorbed gases, the catalyst was heated to 550° alternately in hydrogen and in a vacuum, the process being continued for about 32 hours after reduction was apparently complete.

*Purification of Gases.*—In order to eliminate the possibility of production of hydroxylamine, it was essential to purify the gases carefully from oxygen and water. The procedure adopted was as follows : The mixed gases were bubbled slowly through (i) alkaline sodium hyposulphite (to remove oxygen and carbon dioxide) and (ii) 50% sulphuric acid (to remove alkaline impurities such as ammonia), then over (iii) solid caustic potash (to trap sulphuric anhydride and water), (iv) heated non-active copper (to remove the last traces of oxygen), (v) phosphoric acid (to remove any ammonia or hydrazine formed on the heated copper), and (vi) phosphoric anhydride (to remove traces of water). They were then stored in a large reservoir.

From this, they passed through a heated combustion-glass tube containing the catalyst, and then through a liquid-air trap to condense hydrazine or ammonia formed by synthesis. The whole apparatus as far as the potash tube was tested and found to be vacuum-tight. No attempt was made to ensure complete absorption of the condensable products in liquid air, since it was more important to employ a high rate of flow, which, in each experiment, was the maximum possible for the pumping system employed. 5 Litres of gas were used in each case, and 99% of the gas passed over the catalyst in 6 minutes. Temperatures were recorded by means of a copper–constantan thermocouple. The absolute values are probably correct to about 10°, and the differences over the range employed to 2—3°.

Before each experiment 1—2 litres of gas were passed over the catalyst, the products not being collected, and the catalyst was baked out in a high vacuum between exposures.

The temperature of the catalyst fell when the gas was passed over, the recorded temperatures being the minimum observed during gas flow. The method of detecting hydrazine by its thermal decomposition was described by Gedye and Allibone (*Proc. Roy. Soc.*, 1930, *A*, **130**, 346).

The following results were obtained :

| Expt. No. | Mixture. | Temp. | Yield of $NH_3$, c.c. at *N.T.P.* | Hydrazine. |
|---|---|---|---|---|
| 1 | $N_2 : 3H_2$ | 528° | 0·59 | See note A |
| 2 | $N_2 : 2H_2$ | 565 | 0·31 | ,, B |
| 3 | $N_2 : 2H_2$ | 475 | 0·052 | ,, C |
| 4 | $N_2 : 2H_2$ | 437 | 0·17 | ,, D |
| 5 | $N_2 : 2H_2$ | 580 | 0·23 | ,, E |

A. Thermal decomposition gave the following results :
Pressure of products (total) 0·015 mm.
,, ,, (non-condensable in liquid air) 0·012 mm.
Residue gave distinct positive test with gold chloride.

B. Half product gave very faint positive test with gold chloride. Colour was only appreciable after 2 days' standing.

C. Product gave distinct positive test with gold chloride. Appreciable colour developed in 40 mins.

D. Successive readings for thermal decomposition method gave :

| | (*a*). | (*b*). | (*c*). | Total. |
|---|---|---|---|---|
| Permanent gases (mm. Hg) ... | 0·0061 | 0·0052 | 0·0054 | 0·0167 |
| Condensable ,, ,, ... | 0·0042 | 0·0041 | 0·0039 | 0·0122 |

Residue gave very faint positive test with gold chloride.

E. Faint positive test with gold chloride.

These results demonstrate quite clearly the formation of hydrazine, the relative yield being greater at lower temperatures. The thermal decomposition experiments both agree with the equation, $3N_2H_4 =$

$4NH_3 + N_2$, within the limits of experimental error for the small quantities available for the test.

The results of expt. 4 enable an approximate calculation of the relative yield to be made. The yield of hydrazine calculated from the thermal decomposition is 0·0031 c.c. which will be somewhat low owing to a trace remaining undecomposed. This corresponds to approximately 2% of the total yield by volume, or nearly 4% by weight. It is known that hydrazine is formed during the catalytic oxidation of ammonia (Hofmann and Korpiun, *Ber.*, 1929, **62**, *B*, 3000), but it seems improbable that traces of oxygen which might have survived the rigorous system of purification could be responsible for the formation of this amount of hydrazine.

The irregularity of the yields of ammonia is to be expected, since the effective rate of flow over the catalyst cannot be reproducible under the conditions employed.

Two blank experiments were carried out with the catalyst cold. In both cases less than 0·0002 c.c. of any product condensable in carbon dioxide and ether was obtained from 3 litres of gas.

## *Summary.*

Hydrazine, as well as ammonia, is formed by the union of nitrogen and hydrogen on the surface of a catalyst of iron, promoted by oxides of aluminium and potassium. The relative yield of hydrazine is greater at lower temperatures. At 437° with a very high flow-rate, it was approximately 4% by weight.

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