[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE REACTION BETWEEN NITROGEN AND HYDROGEN IN THE PRESENCE OF MERCURY VAPOR AND THE RESONANCE RADIATION OF MERCURY

BY W. ALBERT NOYES, JR.

RECEIVED APRIL 24, 1930 PUBLISHED JUNE 6, 1930

In a previous article[1] some experiments on the reaction between nitrogen and hydrogen in the presence of mercury vapor and the resonance radiation of mercury were described. It was pointed out that formation of ammonia was not observed either when a flow method was used or with low temperatures and low pressures of nitrogen, hydrogen and mercury vapor. Only at pressures of one atmosphere and higher and at the temperature of boiling mercury was there any observable formation of ammonia. In the article it was assumed that the important step was the formation of atomic hydrogen through the agency of excited mercury. A reconsideration[2] made it seem possible that the walls of the vessel may have exerted some influence on the reaction. Positive results, obtained under different conditions, have been reported by Hirst[3] and Willey and Rideal.[4]

Subsequently, Taylor and Marshall[5] have shown that monatomic hydrogen produced through the agency of excited mercury will not react with nitrogen to form ammonia under different experimental conditions. Bonhoeffer[6] has also shown that monatomic hydrogen produced by Wood's method[7] will not react with nitrogen to form ammonia.

All of these researches may be interpreted as showing that the production of monatomic hydrogen is not sufficient to initiate the reaction between hydrogen and nitrogen.[8] Recently, however, articles by Gaviola[9] and Beutler and Rabinowitsch[10] have given a possible explanation for the formation of ammonia under the conditions of the previous experiments.[1]

In Gaviola's experiments[9] the NH band at 3360–3370 Å. was observed in a mixture of N_2 and H_2 in the presence of excited mercury. The intensity of this band was proportional to the square of the intensity of the exciting light, a fact which led him to propose the primary mechanism $N_2 + 2Hg' = 2N + 2Hg$. The maximum energy available from two mercury atoms in

[1] Noyes, THIS JOURNAL, **47**, 1003 (1925).

[2] Noyes and Kassel, *Chem. Reviews*, **3**, 199 (1926).

[3] Hirst, *Proc. Cambridge Phil. Soc.*, **23**, 162 (1926).

[4] Willey and Rideal, *J. Chem. Soc.*, 671 (1927).

[5] Taylor and Marshall, *J. Phys. Chem.*, **23**, 1140 (1925); Taylor, THIS JOURNAL, **48**, 2840 (1926).

[6] Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

[7] Wood, *Proc. Roy. Soc.* (London), **102A**, 1 (1923).

[8] See B. Lewis, THIS JOURNAL, **50**, 27 (1928).

[9] Gaviola, *Nature*, **122**, 313 (1928); *Phys. Rev.*, **34**, 1373 (1929).

[10] Beutler and Rabinowitsch, *Z. physik. Chem.*, **6B**, 233 (1930).

the 2^3P_1 state corresponds to 9.8 volts, so that the heat of dissociation of nitrogen must represent a value lower than this amount. The heat of dissociation of nitrogen has been revised downward during the past few years and is now fixed at a probable value in the neighborhood of 9 volts.[11] Beutler and Rabinowitsch propose a mechanism involving two metastable mercury atoms (2^3P_0) each possessing an energy of 4.64 volts. This mechanism they give as follows: 2Hg (4.64 v.) = Hg (9.1 v.) + Hg + 0.18 v. and 2Hg (4.64 v.) + N_2 = N + N + 2Hg + 0.18 v. The production of monatomic nitrogen and the undoubted production of monatomic hydrogen should lead to the formation of some ammonia.[8] The first step may be N + H = NH (by triple collision or on the walls) or N + H_2 = NH + H, followed by NH + H_2 = NH_2 + H and NH_2 + H_2 = NH_3 + H or by other processes involving triple collisions. It is not improbable that all of these reactions are possible energetically.

We may now inquire as to whether this mechanism agrees at all with the previously found facts.[12] The increase in total pressure would have the effect of broadening the absorption line of mercury, thereby increasing the amount of radiation absorbed and increasing the chance of reaction. Another effect would be the conversion of excited 2^3P_1 atoms into metastable 2^3P_0 atoms by collision. Since these have a longer life, the process described by Beutler and Rabinowitsch would become somewhat more probable. In addition the absorption would take place in a region nearer the walls, thereby effecting an increase in concentration of energy-rich atoms in a small region and increasing the probability of processes involving two of them.

It is to be noted that only small amounts of ammonia were formed, approximately the amount required at thermodynamic equilibrium. This is to be expected, since the excited mercury is known to cause the decomposition of this substance.[13] Hence a steady state would be expected under a given set of conditions with the amount of ammonia at a low value.

Summary

Possible explanations for the previously reported formation of ammonia from nitrogen and hydrogen in the presence of mercury vapor and the resonance radiation of mercury have been discussed.

PROVIDENCE, RHODE ISLAND

---

[11] See, for example, Birge, *Phys. Rev.*, **34**, 1062 (1929).

[12] A series of experiments was carried out subsequent to the publication of the previous article;[1] they gave results similar to those published.

[13] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); Taylor and Bates, *ibid.*, **12**, 714 (1926); Bates and Taylor, THIS JOURNAL, **49**, 2450 (1927).