Deuterium as an Indicator of Mechanism in the PhotoDecomposition of Ammonia

Hugh S. Taylor and Joseph C. Jungers

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By studying the photolysis of ammonia-deuterium mixtures it has been experimentally demonstrated that the reaction $NH_2+H=NH_3$ is an important feature of the overall photo-decomposition and provides one reason for the low quantum yield observed in the photo-process. It has further been shown that the interaction of hydrogen atoms with ammonia molecules is a process of low efficiency at room temperatures.

IN all recent studies[2] of the photolysis of ammonia in ultraviolet light it has been assumed that the initial process on absorption of light is

$$NH_3+h\nu=NH_2+H$$
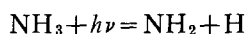
and that this is followed, among other processes which lead to nitrogen and hydrogen, by a back reaction $NH_2+H=NH_3$ which may or may not be a three-body process. This reverse reaction is used to account for the low quantum yield (0.25 or less at room temperatures) of a predissociation process which might have been expected to give a quantum yield of unity. Melville[2b] obtained strong evidence in support of this view by showing that the ammonia decomposition was markedly suppressed when atomic hydrogen, produced by means of excited mercury atoms, was simultaneously present in the reaction system.

By making use of deuterium in place of hydrogen in the experiment of Melville we have decisively demonstrated the marked existence of the reverse reaction. In a previous communication[3] on the deutero-ammonias we have shown that they are readily distinguishable from ammonia by means of their ultraviolet absorption spectra, and that semi-quantitative estimates of their respective concentrations can be deduced from such spectra. Accordingly, we have illuminated in a quartz reaction vessel suitable for the spectroscopic measurements,[3] a mixture of 160 mm of ordinary ammonia and 600 mm of pure deuterium gas in the presence of a little mercury. As source of illumination we employed the Hanovia Sc-2537 quartz mercury vapor rare gas discharge tube already described.[3] Of this light source we know that there is light emitted of wave-length around 2100A, adequate to effect photochemical decomposition of ammonia. It is also a rich source of resonance radiation, $\lambda=2536.7$A.

The gas pressures were so chosen as to give satisfactory absorption spectra of the ammonias and to ensure, due to the high concentration of deuterium, that the decomposition of ammonia would not be very rapid. From time to time, after intervals of illumination, the absorption spectra of the mixture were photographically recorded. There was revealed a progressive change in the absorption spectra from that of pure NH_3 to that of an equilibrium mixture of NH_2D, NHD_2 and ND_3. After 48 hours illumination we estimate that the ammonia present contained 70 percent of the hydrogen as the deuterium isotope.

The possibility that these deutero-ammonias arose from interaction of atomic deuterium with molecular ammonia was tested by a second experiment in which the short wave-length light, instrumental in dissociating the ammonia, was reduced by surrounding the light source with a filter of 25 percent acetic acid solution 1.5 cm in thickness. The light source was so disposed as to give a somewhat larger intensity of resonance radiation than in the first experiment. Under these conditions we found a very much reduced production of the deutero-ammonias, about 10 percent of the deuterium compounds being formed in 72 hours illumination. It is not possible
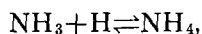
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[2] (a) Wiig and Kistiakowsky, J. Am. Chem. Soc. **54**, 1806 (1932); (b) Melville, Trans. Faraday Soc. **28**, 885 (1932); (c) Ogg, Leighton and Bergstrom, J. Am. Chem. Soc. **56**, 318 (1934).

[3] Jungers and Taylor, J. Chem. Phys. **2**, 373 (1934).

to say whether even this change did not arise from photo-decomposition of the ammonia and the reverse reaction since the action of the light-filter is possibly not completely efficient and also the photosensitized decomposition of ammonia by excited mercury must have occurred to some extent even in the presence of such an excess of deuterium. The experiment, however, is decisive to this extent, that it indicates that any reactions such as $NH_3 + D = NH_2D + H$ or $NH_3 + D = NH_2 + HD$, followed by a reverse reaction, $NH_2 + D = NH_2D$, are processes of low probability in comparison with the reverse process following photo-decomposition. This conclusion is a direct experimental check of the early observation of Bonhoeffer[4] that atomic hydrogen, produced in a Wood's discharge tube, did not interact with ammonia molecules.

Note added June 5, 1934. This last experiment is of importance also in view of the paper by L. Farkas and Harteck,[5] just issued, on the mechanism of photo-decomposition of ammonia as revealed by studies of the stationary hydrogen atom concentration in illuminated ammonia-hydrogen systems. They measured the atom concentration by its influence on the para-hydrogen conversion and are led to the postulate of an equilibrium between hydrogen atoms and ammonia and an intermediate product, NH_4. They assume a kinetic equilibrium

$$NH_3 + H \rightleftharpoons NH_4,$$

which is practically on the NH_4 side at room temperatures and on the $NH_3 + H$ side at 300°C. They assume a binding energy of 10 kilocals. Our experiment with resonance radiation and deuterium indicates that the NH_4 cannot be a complex in which each of the four hydrogen atoms are equivalent, since if this were so the kinetic equilibrium should yield concentrations of deutero-ammonias equally as well as decomposition of ammonia. Our experiment indicates that the complex, if it exists, is rather of the nature $NH_3 - D$, with the atom bound by the polarization forces of the ammonia molecule and that it decomposes into NH_3 and D. Whether under these circumstances the Farkas-Harteck mechanism is anything other than a three-body recombination of H and NH_2 with NH_3 as the third body, coupled with an alternative decomposition process

$$H + NH_2 + NH_3 = NH_3 + NH + N_2,$$
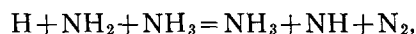
the ratio of which recombinations and decompositions are 3 : 1, to give the observed quantum yield of 0.25, is indeed problematical. The difficulties which attend their proposal when it is applied to the definite results of Melville on the suppression of photolysis by increased concentration of hydrogen atoms, are inherent also in this latter interpretation. It is doubtful, therefore, whether their proposals, even in the modified form suggested by our experiment, are superior to those mentioned in our introductory paragraph.

We are indebted to Dr. W. S. Benedict for his assistance in interpreting the spectrographic measurements.

[4] Boehm and Bonhoeffer, Zeits. f. physik. Chemie **119**, 385, 474 (1926).

[5] Farkas and Harteck, Zeits. f. physik. Chemie **B25**, 257 (1934).