The Mechanism of the Photolysis of DeuteroAmmonia

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# The Mechanism of the Photolysis of Deutero-Ammonia

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In order to avoid theoretical objections to the mechanism previously suggested for the photolysis of ND_3, a new mechanism is proposed involving competition between two spontaneous predissociation processes in the discrete region. The relative amounts dissociating by the two paths, one yielding atomic hydrogen and the other molecular hydrogen, are shown to be in the approximate ratio 19 : 1 in the primary act. In the diffuse region, the time of decomposition is so short that the reaction is exclusively by the first path.

ACCORDING to Wiig,[1] the photolysis of deutero-ammonia is distinguished in a rather unusual way. The quantum yield in the discrete region at $\lambda2138A$ is greater than that in the diffuse region at $\lambda2100A$. Although the quantum yields in the two regions vary with pressure, their difference remains constant. A mechanism, of which the following are essential parts, was suggested to explain these results,

$$ND_3 + h\nu \rightarrow ND_3^* \qquad (1)$$

$$ND_3^* + ND_3 \nearrow ND_2 + D + ND_3 \qquad (2)$$
$$\searrow N_2 + 3D_2 \qquad (3)$$
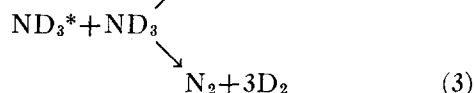
Reaction 2 may be recognized as an induced predissociation reaction; this part of the mechanism can be subjected to simple tests such as a search for variation in fluorescence with pressure.[2] Reaction 3 is particularly interesting. If true it is one of the few cases in which there is still reason to believe in a photoactivated molecule entering into a reaction with a nonactivated molecule. One by one such cases (e.g. in the photolysis of hydrogen iodide) have been eliminated. Furthermore, there is theoretical objection to reaction 3. On the basis of the principle of microscopic reversibility, any reaction involving four product molecules seems extremely improbable. It is worth while, therefore, to determine whether the results obtained by Wiig can be explained in some simpler way.

In the first place, it must be emphasized that the discrete absorption at $\lambda2138A$ is no indication that an induced predissociation process is occurring. Just as in the case of ammonia, whose absorption bands all appear diffuse, a spontaneous process may be involved. However, whereas the spontaneous process in NH_3 (and in ND_3 in the blurred region at 2100A) is rapid, in ND_3 at 2138A it is slow.[3] The slowness of the predissociation process introduces possibilities which might not otherwise occur.

In a determination of the mechanism of the photolysis of NH_3 it is necessary to consider two possible primary processes

$$NH_3^* \rightarrow NH_2 + H \qquad (4)$$

$$NH_3^* \rightarrow NH + H_2. \qquad (5)$$
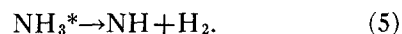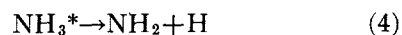
In that case only reaction 4 occurs.[4] The diffuseness of the bands indicates that it takes place in less than 10^{-11} sec. Reaction 5, which is a predissociation by rearrangement, takes a longer time (say 10^{-10} to 10^{-9} sec.) and consequently does not occur. In deutero-ammonia, however, there seem to be conditions (whose nature we need not examine) which make the reaction analogous to 4

$$ND_3^* \rightarrow ND_2 + D \qquad (6)$$
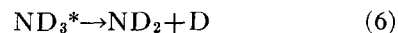
a slow process, requiring, say 10^{-10} to 10^{-9} sec. Since the reaction
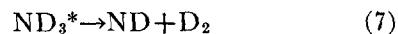
$$ND_3^* \rightarrow ND + D_2 \qquad (7)$$

[1] Wiig, J. Am. Chem. Soc. **59**, 955 (1937).
[2] Cf. Burton and Rollefson, J. Chem. Phys. **6**, 416 (1938).

[3] In this respect the behavior of ammonia is analogous to that of formaldehyde in the discrete region above 2750A. See ref. 2.
[4] Wiig, J. Am. Chem. Soc. **59**, 827 (1937).

actually requires less energy than reaction 6,[5] it will proceed whenever the proper configuration is attained and there will in many molecules be time for the attainment of that configuration before reaction 6 can occur.

The next step suggested is

$$ND + ND \rightarrow N_2 + D_2. \qquad (8)$$
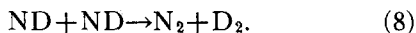
The assumption is made that ND does not react readily with any of the other substances present, i.e., ND_3, N_2, D_2 and the assumed intermediates.[6] It follows that the quantum yield in that fraction of the ND_3 molecules in which decomposition occurs via reaction 7 is unity and independent of the pressure. In the portion decomposing via reaction 6 the quantum yield is low due to the various possible back reactions and varies with the pressure. However, the fraction entering into step 6 is unaffected by the pressure.

The fraction of ND_3 molecules decomposing via step 7 may be presumed equal to the difference between the quantum yields at $\lambda2138$ and $\lambda2100A$, i.e., ~0.05. The total yield at $\lambda2138A$ is then

$$\gamma_{2138} = 0.05 + 0.95\phi(p), \qquad 1$$

where $\phi(p)$ is a function which indicates the effect of pressure on quantum yield via reaction 6. If it be assumed that there is no loss either by fluorescence or collisional deactivation at either $\lambda2100$ or $\lambda2138A$, $\phi(p)$ will have the same form

at both wave-lengths and will be no greater than ~0.27, the value for the maximum quantum yield at $\lambda2100A$. But

$$\gamma_{2100} = 1.0\phi(p), \qquad 2$$

which value therefore differs from the second term of Eq. 1 by only 0.05×0.27 or ~0.01 at a maximum, well within the experimental error of the method. The constancy of the difference between the quantum yields is thus accounted for.

It may also be seen from Eq. 1 that the rates of the two primary reactions 6 and 7 are in the ratio 19 : 1 at $\lambda2138A$. At $\lambda2100A$, of course, reaction 7 occurs not at all or in negligible amount.

DISCUSSION

It has been shown by Rollefson and Burton[7] that in those cases where there is competition between decomposition into free radicals and into ultimate molecules in the primary act, the former is favored by decrease in wave-length. In acetone,[7] for example, only the former takes place at shorter wave-lengths.[8] In NH (as contrasted with NH_2) all the electrons are paired.[9] In the parallel case of CH_2, Pearson, Purcell and Saigh[10] have concluded, on the basis of mirror experiments, that methylene behaves more like a very reactive molecule than like a free radical. It consequently appears justifiable to treat NH as a molecule and to say that reaction 7 involves a decomposition into ultimate molecules in the primary act. It may be seen that this case of deutero-ammonia is but another illustration of the general behavior to be expected in the case of polyatomic molecules.[7]

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[5] The reaction $NH_3 \rightarrow NH_2 + H$ requires $\geqq101$ kcal. (cf. Ellis, Phys. Rev. 33, 27 (1929)). The reaction $NH_3 \rightarrow NH + H_2$ requires 45–57 kcal. (cf. Bates, Zeits. f. physik. Chemie. Bodenstein-Festband, 329 (1931)). The latter values are estimated on the basis of 249.85 kcal. as the heat of formation for NH_3 from its atoms (Bichowsky and Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corp., New York, 1936)).

[6] It should, however, be noted that in explaining the Hg-photosensitized synthesis of NH_3 from its elements at high pressures, Noyes, J. Am. Chem. Soc. 52, 2418 (1930) suggested such reactions as $NH + H_2 \rightarrow NH_2 + H$.

[7] Rollefson and Burton, J. Chem. Phys. 6, 674 (1938).
[8] Cf. Spence and Wild, J. Chem. Soc. 352 (1937).
[9] Cf. Kronig, *The Optical Basis of the Theory of Valency* (Cambridge University Press, 1935), p. 134.
[10] Pearson, Purcell and Saigh, J. Chem. Soc. 409 (1938).