

A Kinetic Expression for the Rate of the Photosensitized Decomposition of Ammonia and Deuteroammonia

Meredith G. Evans and Hugh S. Taylor

Citation: [The Journal of Chemical Physics](#) **2**, 732 (1934); doi: 10.1063/1.1749387

View online: <http://dx.doi.org/10.1063/1.1749387>

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compared with hydrogen at high oxygen concentration. This difference he attributes to a difference in the quenching efficiencies of hydrogen and deuterium. The author is of the opinion that there is no difference in the quenching efficiencies of hydrogen and deuterium.⁴ The results reported by Melville would be explained if, at high oxygen concentration, the hydrogen atoms did not take part in the reaction as such but formed relatively stable HO_2 complexes which took part in the subsequent changes. The difference in zero-point energy between the HO_2 and DO_2 would then be more than adequate to account for the changes observed at high oxygen concentration.

This reaction is probably too complex for any

simple mechanism to represent the experimental results fully and the most that can be said with certainty is that since there is no great difference observed in the rates of reactions of hydrogen and deuterium the process is either one in which the breaking of a $\text{H}-\text{X}$ bond does not enter in as a rate determining step or that the reaction is governed by a step involving hydrogen atoms which we would expect from the considerations discussed above to show little or no difference when deuterium is substituted for hydrogen.

The author wishes to thank Professor Hugh S. Taylor for his interest in this work and for the benefit of many helpful discussions, and also for the great facilities afforded the author in these laboratories.

NOVEMBER, 1934

JOURNAL OF CHEMICAL PHYSICS

VOLUME 2

A Kinetic Expression for the Rate of the Photosensitized Decomposition of Ammonia and Deuteroammonia

MEREDITH G. EVANS AND HUGH S. TAYLOR, *Frick Chemical Laboratory, Princeton University*

(Received August 1, 1934)

A kinetic expression for mercury sensitized ammonia and deuteroammonia decompositions which represents the experimental data is developed empirically and an explanation of the expression in terms of the various kinetic processes is sought. This expression is further modified to include the intrinsic decomposition probability of the ammonia or deuteroammonia molecule. The final expression is able to express the results quantitatively, and yields values for the quenching ratio, $k_{1\text{NH}_3} : k_{1\text{ND}_3} = 4 : 1$ and a decomposition probability after quenching $\phi_{\text{NH}_3} : \phi_{\text{ND}_3} = 5 : 1$.

JUNGERS and Taylor¹ have, in a recent publication, discussed the kinetics of the decomposition of ammonia and deuteroammonia on the basis of a kinetic expression derived by Dickinson and Mitchell² and Melville.³ An examination of the experimental results does not lead to a quantitative agreement with the kinetic expression

$$\frac{1}{R} = \frac{1}{K} \left\{ 1 + \frac{k_2[\text{H}_2] + k_3}{k_1[\text{NH}_3]} \right\}, \quad (1)$$

where K is proportional to the intensity of the

incident light and to the mercury vapor pressure, k_2 and k_1 are the quenching collision factors for hydrogen and ammonia, respectively, and k_3 is the factor for spontaneous loss of energy of excitation of mercury in the 3P_1 state.

The discrepancies which arose in the application of the above expression to the experimental data were: (1) a comparison of the quenching efficiencies of ammonia and deuteroammonia obtained from a comparison of the values of k_3/k_1 in the two cases led to a ratio $k_{1(\text{NH}_3)} : k_{1(\text{ND}_3)} = 4.2 : 1$. If, however, the expression for the hydrogen or deuterium pressure required to reduce the reaction rate to one-half of its initial value were used *viz.*, $k_{2[\text{H}_2]} = k_{1[\text{NH}_3]} + k_3$ a comparison of $k_{1(\text{NH}_3)}/k_{2(\text{H}_2)} : k_{1(\text{ND}_3)}/k_{2(\text{D}_2)}$ led to a ratio of approximately 7 : 1. This would ap-

¹ Jungers and Taylor, *J. Chem. Phys.* **2**, 373 (1934).

² Dickinson and Mitchell, *J. Am. Chem. Soc.* **49**, 1487 (1927).

³ Melville, *Proc. Roy. Soc. A* **138**, 384 (1932); *Trans. Far. Soc.* **28**, 805 (1932).

parently mean that, to bring the ratios of $k_{1(\text{NH}_3)} : k_{2(\text{ND}_3)}$ into agreement, deuterium should be approximately twice as efficient as hydrogen in quenching excited mercury. This, however, has not been found experimentally⁴ to be the case and we are, therefore, led to examine the kinetic expression used.

It was possible from the experimental data to plot $1/R$ against $1/\text{NH}_3$ or $1/\text{ND}_3$ for different constant values of hydrogen or deuterium pressure; this should lead to a series of straight lines with increasing slope as the hydrogen or deuterium concentration is increased, all cutting the $1/R$ axis at the constant value of $1/K$. This however was found not to be the case; a series of straight lines were obtained which did not meet at the intercept of $1/K$ but intersected at a definite value of $1/\text{NH}_3$ approximately 0.017 mm^{-1} . This would lead to an empirical expression of the form

$$\frac{1}{R} = \frac{1}{K} \left\{ 1 + \frac{k_2[\text{H}_2] + k_3}{k_1} \left(\frac{1}{\text{NH}_3} - x \right) \right\}. \quad (2)$$

It was interesting and significant that the empirical value of x for the ammonia and the deuterioammonia data was the same. If this expression is used to determine the ratio of $k_{1(\text{NH}_3)}/k_{2(\text{H}_2)} : k_{1(\text{ND}_3)}/k_{2(\text{D}_2)}$ the value obtained is approximately 4 : 1 and agrees well with the ratio of $k_{1(\text{NH}_3)} : k_{1(\text{ND}_3)}$ of 4.2 : 1 obtained from the k_1/k_3 ratio and, moreover, would indicate that the quenching efficiencies of the hydrogen and the deuterium are approximately the same, as found experimentally.⁴ The introduction of this empirical correction into the expression for the hydrogen or deuterium pressure at the half reaction rate naturally gives the same result for the above ratio; but, it is also significant that whereas the uncorrected expression gave on plotting $[\text{H}_2]_{1/2}$ or $[\text{D}_2]_{1/2}$ against NH_3 or ND_3 , a curve which was convex to the NH_3 or ND_3 axis and which led to a large amount of uncertainty in the value of k_1/k_2 , the corrected expression gives a straight line.

It is of interest to speculate on the theoretical significance of this empirical equation. The experimental results can be represented by a slightly

modified form of the empirical equation

$$\frac{1}{R} = \frac{1}{K} \left\{ 1 + \frac{k_2[\text{H}_2] + k_3}{k_1[\text{NH}_3](1 + x[\text{NH}_3])} \right\}. \quad (3)$$

This equation yields results which are in agreement with those given above. Expressing the significance of these empirical equations in words one can say that the rate of the photosensitized decomposition of ammonia increases more rapidly with increasing ammonia pressure than is indicated by the expression (1) derived from the simpler kinetic considerations. At small ammonia pressures, the kinetic expression (1) is applicable since the $[\text{NH}_3]$ is small compared with unity and the two equations, kinetic and empirical, reduce to the same form. It is only when working at higher pressures, which were enforced in the case of deuterioammonia because of the slow rate of decomposition, that deviations from the kinetic expression are encountered.

We believe that the deviations which are made manifest at these higher pressures are a consequence of the broadening of the absorption line of the mercury vapor. Jablonski⁵ has discussed the Lorentz broadening⁶ on the basis of the Franck-Condon principle. He assumed that a "quasi" molecule was formed between the absorbing atom and the foreign gas, in this case mercury and ammonia. This complex was held together by van der Waals forces and was capable of absorbing energy from the incident radiation and passing into a complex of excited atom plus foreign gas molecule. Further advances which have been made have employed the London theory of van der Waals forces to define the potential energy curves for the two quasi species. If now we consider the fate of such a complex of an excited mercury atom and an ammonia or deuterioammonia molecule such as will exist in the experiments which we are considering, there are several possibilities. The complex $[\text{Hg}'\text{NH}_3]$ may spontaneously radiate and fall back again to the unexcited state, the energy of excitation may be transferred to the ammonia molecule which would constitute a quenching process and lastly the complex may

⁵ Jablonski, *Zeits. f. Physik* **70**, 723 (1931).

⁶ For a discussion of this see Mitchell and Zemansky, *Resonance Radiation and Excited Atoms*, p. 158, Macmillan, 1934.

⁴ Evans, *J. Chem. Phys.* **2**, 445 (1934).

suffer a collision with another ammonia molecule and transfer of energy with or without subsequent decomposition may result. The effect of such complex formation will be to add an extra term to the terms representing the quenching effect of the ammonia, that due to direct quenching being $k_1[\text{NH}_3][\text{Hg}']$, while that due to the "quenching" of a complex by the ammonia being $k_1x[\text{NH}_3]^2[\text{Hg}']$. The factor x will depend upon the probability of such complex formation as we have discussed and since only van der Waals forces or polarization forces are operative in the formation of these complexes we should not expect a large difference in the value of x for ammonia and for deuterioammonia again in agreement with the empirical analysis. It is obvious that the introduction of the term $[\text{Hg}']k_1[\text{NH}_3](1+x[\text{NH}_3])$ into the kinetic expressions instead of the simple quenching term $k_1[\text{NH}_3][\text{Hg}']$ will lead to a kinetic equation of the same form as that obtained empirically. It is not surprising that the $\text{Hg}'\text{NH}_3$ complex should be quenched by collision with another NH_3 molecule since there will probably be very close resonance between the two. It would appear that the chance of the complex being quenched by hydrogen molecules is comparatively small compared with the ammonia quenching process. In the Jungers-Taylor experiments this is doubly true owing to the relatively small concentrations of hydrogen or deuterium present. In experiments at low ammonia pressures the hydrogen concentration may well become important (cf. reference 2). There is a further discrepancy between the theoretical expression and the experimental results in the value of K . This constant should, from the theoretical equation, be dependent only upon the mercury vapor pressure and on the intensity of the incident radiation. This would imply that the value of K should be the same for the photosensitized decomposition of ammonia and deuterioammonia carried out under the same experimental conditions of mercury vapor pressure

and light intensity. In other words, from the kinetic expression, one would expect that, at a sufficiently high ammonia or deuterioammonia pressure, the rates of decomposition of the two should be the same and the value of the initial rate R_0 should be proportional only to the mercury vapor pressure and to the light intensity. This, however, is not found to be the case; when ammonia and deuterioammonia are compared the ratio of the $K_{\text{NH}_3} : K_{\text{ND}_3}$ is approximately 5 : 1.

We consider that this deviation from the kinetic expression is due to the fact that, in the derivation of this equation, it is assumed that every quenching collision leads to decomposition. This is not necessarily the case and in addition to a difference between ammonia and deuterioammonia in the quenching of excited mercury, there will also be a difference in the probabilities of decomposition of the ammonia and deuterioammonia molecules which have received the energy of excitation from the mercury. An example of this difference is shown in the ultra-violet absorption spectra of ammonia and deuterioammonia; whereas ammonia shows no fine structure in the principal absorption band, deuterioammonia shows discrete levels, the deuterioammonia being stable when the ammonia is predissociating.⁷

If we introduce then a factor φ representing the probability of decomposition of an energy-rich ammonia molecule, the kinetic expression becomes:

$$\frac{1}{R} = \frac{1}{\varphi K} \left\{ 1 + \frac{k_2[\text{H}_2] + k_3}{k_1\text{NH}_3(1 + x\text{NH}_3)} \right\}.$$

φ is found to be 5 times greater for ammonia than for deuterioammonia at constant K , a difference which one is inclined to attribute to the difference in zero point energy between the $\text{N}-\text{H}$ and the $\text{N}-\text{D}$ bond.

⁷ For this information the authors are indebted to Dr. Benedict in this laboratory.