

## A Comparison of the Photosensitized Reaction of Hydrogen and Oxygen, and Deuterium and Oxygen

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## A Comparison of the Photosensitized Reaction of Hydrogen and Oxygen, and Deuterium and Oxygen

MEREDITH GWYNNE EVANS, *Frick Chemical Laboratory, Princeton University*

(Received July 17, 1934)

The rates at which hydrogen-oxygen and deuterium-oxygen mixtures react when illuminated in the presence of mercury vapor, have been measured. There is found to be very little difference between the rates under these conditions and the temperature coefficients of the two reactions are, to within the accuracy of this work, equal. Various mechanisms are discussed in the light of this experimental observation.

### INTRODUCTION

IN a recent communication Bates<sup>1</sup> has reviewed and discussed critically the several theories which have been advanced to account for the kinetics of the mercury photosensitized reaction between hydrogen and oxygen. Since the reaction is photosensitized the discussion is concerned with the fate of the hydrogen atoms which are produced as a first step in the reaction.

The atomic hydrogen is formed by the "quenching" of excited mercury atoms in the <sup>3</sup>P<sub>1</sub> state by molecular hydrogen; this however, will not be the only deactivating process and oxygen will also quench the excited mercury atoms bringing about a deactivation of the mercury and an excitation of the oxygen molecules.

The fate of the hydrogen atoms so produced is now generally conceded to be a reaction between hydrogen atoms and oxygen molecules, H + O<sub>2</sub> → HO<sub>2</sub>. The HO<sub>2</sub> complex so formed may react in the following ways:

1. HO<sub>2</sub> + H<sub>2</sub> → H<sub>2</sub>O + OH,
2. HO<sub>2</sub> + H<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + H  $k_2$ ,
3. HO<sub>2</sub> + HO<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>  $k_3$ .

The reaction scheme proposed by Bates involves the use of reactions 2 and 3 and leads to an expression for the rate of hydrogen peroxide formation of the form

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{k_2}{k_3^{\frac{1}{2}}} [\text{H}_2] \left\{ \frac{k_{\text{H}}[\text{H}_2]I}{k_{\text{H}}[\text{H}_2] + k_0[\text{O}_2]} \right\}^{\frac{1}{2}} + \frac{k_{\text{H}}[\text{H}_2]I}{k_{\text{H}}[\text{H}_2] + k_0[\text{O}_2]}, \quad (1)$$

<sup>1</sup> Bates, J. Chem. Phys. 1 (7), 457 (1933).

where the expression  $k_{\text{H}}[\text{H}_2]I/(k_{\text{H}}[\text{H}_2] + k_0[\text{O}_2])$  is a measure of the ratio of the quenching of excited mercury atoms by hydrogen to the total quenching by the mixed hydrogen and oxygen.

Bates has demonstrated that the above equation is adequate in explaining the known facts concerning the rate of hydrogen peroxide production from hydrogen and oxygen. It has sometimes been assumed that in cases where a large percentage of the products was not found to be hydrogen peroxide that under such experimental conditions hydrogen peroxide was first formed and that it subsequently decomposed into water and oxygen.

The above expression does not, however, explain the observed experimental facts when hydrogen and oxygen photosensitized by mercury vapor and illuminated by mercury resonance light are allowed to react in a static system at relatively low temperatures. Barak and Taylor<sup>2</sup> studied the reaction under such conditions and made the following observations: (a) The rate curves obtained by plotting decrease in pressure against time of illumination were slightly autocatalytic in form. The increase in reaction rate as the reaction proceeded being more marked as the proportion of hydrogen in the mixture was increased. (b) Analysis of the reaction mixture during the course of the reaction always showed a 2 : 1 ratio of disappearance of hydrogen to oxygen and no peroxide could be detected in the reaction system. (c) The average rate of reaction was greatest for the 2 : 1 ratio of hydrogen to oxygen and decreased as the proportion of either constituent was increased.

Bates points out that his expression leaves the

<sup>2</sup> Barak and Taylor, Trans. Faraday Soc. 28, 569 (1932).

results of Barak and Taylor "entirely unexplained" and suggests that in this case of a static system the mechanism is complicated by diffusion processes. The present research was carried out over a temperature range of 20°C to 50°C and using both hydrogen and deuterium-oxygen mixture in the hope that a comparison of the rates of reaction in both cases might give some clue to the mechanism of reaction under these conditions.

## EXPERIMENTAL

### 1. Apparatus

The experiments were carried out in a circulatory system shown in Fig. 1. The reaction vessel

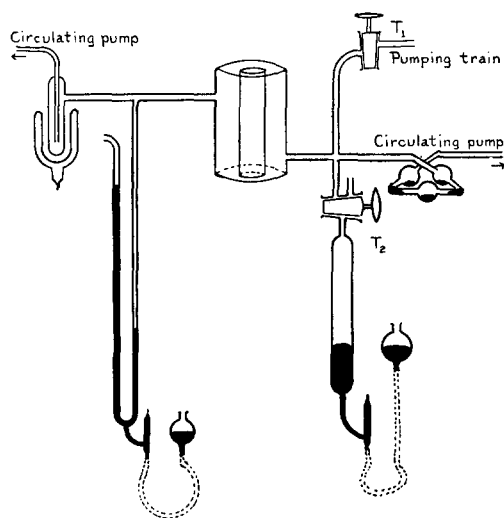


FIG. 1.

was an annular quartz cylinder connected on one side to a manometer and trap and on the other side to the pumping train and gas train. The reaction vessel was so constructed that the mercury arc could be inserted through the center of the cylinder and hence the maximum amount of light was incident upon the reaction vessel. The gases which were circulated through the system passed through mercury bubblers before entering into the reaction vessel. These mercury bubblers were maintained at a constant temperature slightly higher than that of the reaction vessel in order to saturate the gases with mercury vapor. The gases leaving the quartz reaction

vessel passed through a trap which was cooled in liquid air and here any condensible products of reaction were removed. Tap  $T_1$  led to the pumping train which consisted of a mercury vapor pump backed by an oil pump and by means of tap  $T_2$  the gases could be admitted to the apparatus. The reaction vessel and arc were bathed in a thermostat which was maintained at a constant temperature to 0.1°C during the course of an experiment.

### 2. The arc

The arc employed was a Hanovia resonance lamp run off 5000 volts and 30 milliamp. This lamp was exceedingly rich in the resonance line 2537Å as was indicated by a spectrum analysis of the light which showed it to be almost exclusively the resonance line. During the course of the work it was found that the intensity of the light remained exceedingly constant and reproducible results could be obtained under identical experimental conditions of pressure and temperature even after many running hours of the arc.

### 3. Propagation of the gases

In all these experiments the ratio of hydrogen to oxygen was 2 : 1 and the electrolytic gas was prepared by the electrolysis of caustic potash solution. This solution was electrolyzed in a glass cell with nickel electrodes and the cell cooled in ice. Before the preparation of any gas the cell was evacuated and then the first gas evolved was allowed to escape before a sample was collected. The gases so prepared were passed over several tubes containing phosphorus pentoxide and then admitted to a storage bulb.

The deuterium oxygen mixture was prepared by electrolysis of heavy water of the greatest density available; a little sodium metal was added to the pure heavy water to confer conducting properties upon the solution.

### 4. Experimental procedure

The gases were introduced into the apparatus and with the bath, mercury bubblers and the liquid air cooled trap at steady temperatures the gases were circulated by means of a circulation pump until constant pressure readings were obtained on the manometer. It was necessary, in order to avoid fortuitous fluctuations in pressure,

to maintain a constant level of liquid air round the condensation trap. The circulating pumping system caused merely a very small oscillation of the mercury columns in the manometer limbs, the amplitude of the rise and fall of the mercury meniscus being of the order of 0.2 to 0.3 mm. It was possible to estimate the mean position of the mercury level to an accuracy of about 0.2 mm. When under the conditions of the experiment constant readings of the pressure of electrolytic gas in the system had been obtained over a period of half an hour, the mercury resonance arc was switched on and pressure readings taken every minute.

### EXPERIMENTAL RESULTS

The early experiments were carried out at temperatures of about 15–20°C and some of these results are shown graphically in Fig. 2. These curves show an induction period and the general shape of the curve is one of increasing rate as the reaction proceeds. These observations are in agreement with the work of Barak and Taylor who obtained similar curves under comparable conditions in a static system. It was suggested at the time that this form of curve was due to the static system which these workers used and that

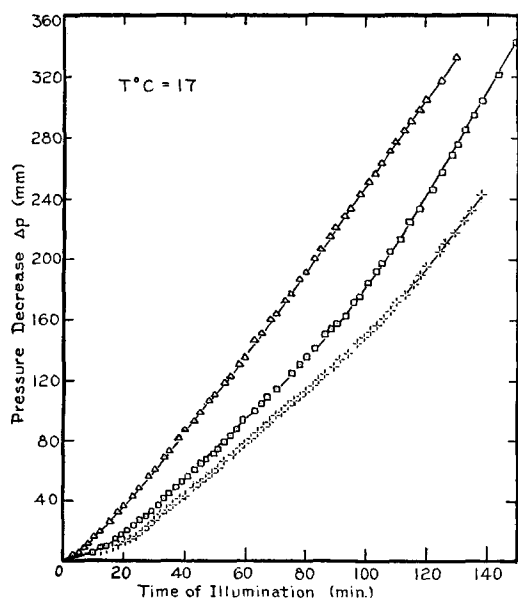


FIG. 2. The increased induction period on successive experiments without removing mercuric oxide. Pressure of electrolytic gas, 520 mm.

the complex diffusion processes which were entering in would disappear when the reaction was carried out in a circulating system. This explanation cannot account, therefore, for these results.

During the course of reactions carried out at temperatures between 15–20°C it was observed that large amounts of mercuric oxide were formed and deposited on the walls of the reaction vessel where the gases entered the illuminated zone and also on the surface of liquid mercury present in the reaction vessel.

If then further experiments were carried out without first removing the mercuric oxide the subsequent reactions showed increasingly longer periods of induction and the overall reaction rate was much slower. The coating of mercuric oxide could be removed by illuminating the vessel with mercury resonance light while circulating hydrogen through the system when the atomic hydrogen produced removed the oxide of mercury. If this cleaning procedure were adopted between experiments it was possible to obtain fairly reproducible results.

The comparisons between the rates of hydrogen-oxygen and deuterium oxygen mixtures were carried out over a higher temperature range 30–50°C and in this range practically no induction period was observed; the vessel was cleaned of mercuric oxide between experiments but the amount of mercuric oxide found at these higher temperatures was considerably smaller than between 15–20°C.

Fig. 3 shows typical reaction curves for hydrogen-oxygen and deuterium-oxygen mixtures in which the pressure decrease  $\Delta p$  in millimeters is plotted against the time of illumination in minutes. It will be observed that the rates of reaction whether for hydrogen or deuterium-oxygen mixtures are under these conditions practically constant from the start of the reaction and show a slight falling off from linearity only towards the end of the reaction.

One also observes both from Fig. 3 and Table I that there exists very little difference between the rates of reaction for the hydrogen or deuterium-oxygen mixture. In order to establish the reality of these small differences it was necessary to obtain a degree of reproducibility for the hydrogen-oxygen reaction which was very much

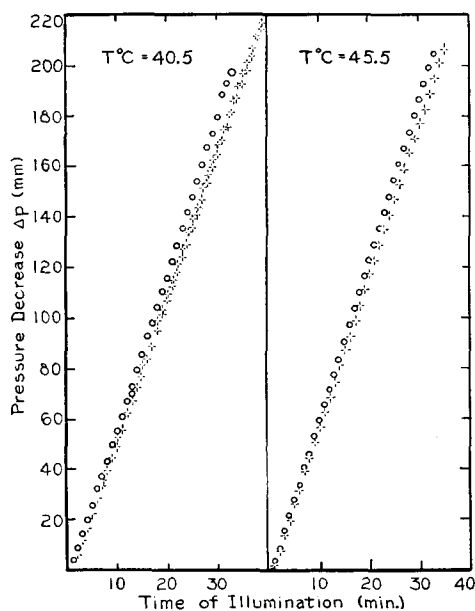


FIG. 3. Typical examples of the difference in rate between hydrogen-oxygen and deuterium-oxygen mixtures. Circle dot, hydrogen oxygen 2 : 1; plus, deuterium oxygen 2 : 1.

TABLE I.

Gas mixture	Temp. °K	Slope $\frac{dp}{dt}$ mm min. <sup>-1</sup>	Gas mixture	Temp. °K	Slope $\frac{dp}{dt}$ mm min. <sup>-1</sup>
Hydrogen + oxygen 2 : 1	303.5	5.25	Deuterium + oxygen 2 : 1	303.5	5.03
	308.5	5.50		308.5	5.19
		5.43			5.27
		5.52			
		5.57			
		5.50			
	313.5	5.94		313.5	5.64
		5.98			5.67
	318.5	6.30		318.5	6.05
	323.0	6.76		323.0	6.37

greater than these differences between the hydrogen and the deuterium reaction. In Table I the results for the temperature 308.5°K indicate the reproducibility which could be obtained. When comparisons between hydrogen and deuterium were being made the experiments were carried out alternately each experiment being repeated at least three times under the same conditions. Moreover the constancy of the light

intensity of the mercury resonance lamp was frequently tested by repeating the hydrogen and oxygen reaction under definite conditions and at the first working temperature 30°C.

From the change in slope of the rate curves with temperature it is possible to obtain the temperature coefficient for the reaction over the restricted temperature range studied. The data for this determination are shown in Table II and

TABLE II.

log <sub>10</sub> rate hydrogen	0.7202	0.7419	0.7740	0.7998	0.8301	Energy of activation for both systems <i>E</i> = 2500 cal.
		0.7460	0.7773			
log <sub>10</sub> rate deuterium	0.7016	0.7150	0.7513	0.7818	0.8041	
		0.7220	0.7540			
1/ <i>T</i> × 10 <sup>-3</sup>	0.3305	0.3252	0.3200	0.3150	0.3096	

to within the experimental accuracy of this work the temperature coefficients of the two reactions with hydrogen or with deuterium are the same and lead to an energy of activation of the process of 2500 cal., a value which is comparable to the value of 3000–5000 obtained by Taylor and Salley<sup>3</sup> for the low temperature range of their investigation. Under these experimental conditions the product of reaction was water as in the work of Barak and Taylor.

## DISCUSSION OF RESULTS

Although the kinetic expression developed by Bates is not applicable to these experiments it is of interest to speculate upon the possible differences between hydrogen and deuterium which one might expect under experimental conditions where Bates' expression is applicable. The differences we should expect to observe between the rates would depend upon the following factors. (a) A difference in the quenching of excited mercury in the <sup>3</sup>P<sub>1</sub> state by hydrogen and deuterium, *k*<sub>H<sub>2</sub></sub>. The author has shown that hydrogen and deuterium have apparently the same quenching efficiency for excited mercury atoms so that no difference in rates of reaction could arise from this factor.<sup>4</sup> (b) The value of *k*<sub>2</sub> which is associated with the reaction HO<sub>2</sub> + H<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + H. One would expect this constant to be sensitive to the change from hydrogen to

<sup>3</sup> Taylor and Salley, J. Am. Chem. Soc. **55**, 96 (1933).

<sup>4</sup> Evans, J. Chem. Phys. **2**, 445 (1934).

deuterium since this reaction involves the breaking of the H—H or D—D bond. Neglecting the possible differences in zero-point energy in the activated state this would introduce a difference in activation energy which would be the full difference in zero-point energy between hydrogen and deuterium, 1.8 kg cal. and also a very much smaller change in activation energy due to the difference in energy level of the HO<sub>2</sub> and DO<sub>2</sub> molecules. Hence we should expect a much smaller value of the constant  $k_2$  when deuterium is employed instead of hydrogen. (c) The value of  $k_3$  for the reaction  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ . It is difficult in this case to assess the difference one would expect due to the difference in zero-point energy of the H—O<sub>2</sub> and D—O<sub>2</sub> bond. The HO<sub>2</sub> or DO<sub>2</sub> molecule has been formed by a bimolecular association reaction and contains in all probability the energy of reaction distributed between the various degrees of freedom in the molecule. If the newly formed HO<sub>2</sub> were to react very soon after its formation it is probable, because of the large amount of energy which the molecule possesses, that the H—O bond would be in a high vibrational level, and since the difference due to the isotope mass effect decreases with increasing vibrational quantum number, we should not expect in comparing the hydrogen and deuterium reactions the full difference due to zero-point energy between the H—O and the D—O bonds to be made manifest. If however the HO<sub>2</sub> or DO<sub>2</sub> suffers a stabilizing collision before entering into reaction, we should then expect the full difference in zero-point energy to be made manifest.

Any mechanism advanced for the reaction must be able to account for (1) the constant rate against time of illumination for experiments carried out at moderate temperatures; (2) the induction period which is made manifest at ordinary temperatures; (3) the close similarity between the rates of reaction by using hydrogen or deuterium.

The large amounts of mercuric oxide which were formed on the surface of the mercury and the walls of the reaction vessel during the course of the experiments at ordinary room temperatures inclines one to the belief that under these conditions the mechanism of reaction is one which involves the alternate oxidation and

reduction of mercury and mercuric oxide,<sup>5</sup> and that the induction period is in some way connected with the formation of a critical concentration of mercuric oxide which at the ordinary temperatures takes an appreciable time to build up.

We will now discuss the reactions which may take part in such a scheme of alternate oxidation and reduction. (1) The production of excited oxygen molecules by the quenching of excited mercury atoms by normal oxygen molecules.  $\text{Hg}' + \text{O}_2 \rightarrow \text{Hg} + \text{O}_2'$ . The evidence is strongly in favor of this reaction occurring by virtue of the excitation of the oxygen molecule from a  $^3\Sigma$  level to a  $^1\Sigma$  level, the conservation of spin momentum being maintained. Zemansky<sup>6</sup> has suggested that the quenching process may be due to the production of mercuric oxide. The excited oxygen molecules will now undergo several reactions probably producing ozone to some extent. If, however, an excited oxygen molecule were to collide with mercury atoms there would be ample energy available to bring about the formation of mercuric oxide.  $\text{Hg} + \text{O}_2' \rightarrow \text{HgO} + \text{O}$ . This reaction may not be brought about directly by the excited oxygen atoms but may be formed from the ozone which is produced when oxygen is illuminated in the presence of mercury vapor by 2537 resonance light.<sup>7</sup> If the rate of oxide formation is the rate governing process then we naturally would not expect to observe any difference between the rates of reaction when hydrogen or deuterium were present. Such a mechanism would not be in accordance with the observation that the maximum rate of reaction is given by the 2H<sub>2</sub>:1O<sub>2</sub> mixture but would imply that the rate should increase with increasing oxygen concentration. The other process which may occur is the reduction of the mercuric oxide by the atomic hydrogen, a process which may occur in two steps, the first being the reduction of the mercuric oxide to the hydroxide  $\text{HgO} + \text{H} \rightarrow \text{HgOH}$  and secondly the further reduction of the hydroxide to mercury and water

<sup>5</sup> Bates came to a similar conclusion in J. Chem. Phys. **1**, 457 (1933).

<sup>6</sup> Zemansky, Phys. Rev. **36**, 919 (1930).

<sup>7</sup> Dickinson and Sherrill, Proc. Nat. Acad. Sci. **12**, 175 (1926). These workers observed that the production of ozone was accompanied by the formation of mercuric oxide.

$\text{HgOH} + \text{H} \rightarrow \text{Hg} + \text{H}_2\text{O}$ . If such reactions do take part in the mechanism as rate determining reactions they will be of great interest.

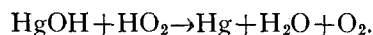
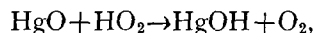
It has been pointed out by Polanyi<sup>8</sup> that in the case of reactions occurring with an activation and involving atomic hydrogen or deuterium the deuterium atoms may react faster than the hydrogen atoms due to the difference in zero-point energy at the top of the activation barrier favoring the deuterium atoms. In the initial state since both hydrogen and deuterium are in the atomic form there will be no zero-point energy difference and hence any differences in the activated state will enter in to their full value. It was in the hope that this reaction might furnish an example of this case that this reaction was studied. The other possibility which has to be considered in this connection is that of "tunnelling." If the reduction of mercuric oxide by hydrogen or deuterium atoms is a rate determining step in this reaction one would expect large differences between the rates of the hydrogen and deuterium reaction if tunnelling were an important factor<sup>9</sup> since a deuterium atom will have a very much smaller probability of tunnelling than an atom of hydrogen.

The fact that no such large difference is observed between the rates would indicate that if this is the mechanism then no tunnelling occurs in this particular case.

Assuming a mechanism in which the rate determining process is the reduction of mercuric oxide one is led to an equation for the rate of water formation which qualitatively is in agreement with the experimental facts, and since the quenching efficiencies of hydrogen and deuterium are the same any difference in the rates of reaction will be dependent upon the velocity constant of the reaction  $\text{H} + \text{HgO} \rightarrow \text{HgOH}$  or  $\text{HgOH} + \text{H} \rightarrow \text{Hg} + \text{H}_2\text{O}$ . This velocity constant will involve the collision frequency between atomic hydrogen or deuterium and the reacting mercuric oxide or hydroxide and whether we imagine this reaction to occur in the vapor phase or on the solid surface of mercuric oxide formed on the walls of the vessel or on the surface of the liquid mercury present, we should

expect a difference in collision frequency between hydrogen and deuterium. On the kinetic theory basis the hydrogen should react faster than the deuterium atoms in approximately the ratio of 1.4 : 1. The observed results indicate that hydrogen reacts faster than deuterium in the ratio of 1.05 : 1. This may imply that the simple mechanism we have advanced is not operative in this work or on the other hand that the discrepancy may be due to a smaller activation energy for the deuterium atom reaction because of a smaller zero-point energy of the deuterium in the activated state. This difference would imply an activation energy for deuterium of  $\sim 200$  calories smaller than that for the hydrogen and such a difference could not be detected in the calculation of activation energy over the limited temperature range of this work.

There is, however, the possibility that the hydrogen atoms would rarely react as hydrogen atoms and that because of the high concentration of oxygen molecules would form  $\text{HO}_2$  complexes and that the reduction would be carried on by these molecules.



This mechanism would lead to an equation for the rate of reaction which would be formally the same as that for reduction by hydrogen atoms alone. But if the velocity constant of the reduction reaction entered into the equation we would expect a difference in the rate of reaction when hydrogen and deuterium were compared. This difference would arise because the breaking of the  $\text{H}-\text{O}_2$  or  $\text{D}-\text{O}_2$  bond is involved and since this reduction is suspected of being a surface reaction the  $\text{HO}_2$  or  $\text{DO}_2$  would have suffered stabilizing collisions by the time the complex reached the mercuric oxide and we would suppose that the full zero-point energy would enter into the activation energies.

Since this communication was written a letter has appeared in *Nature* by Melville<sup>10</sup> in which he gives results which are in agreement with the results discussed here. He finds, however, a decrease in the rate of reaction with deuterium as

<sup>8</sup> Polanyi, *Nature* **132**, 819 (1933).

<sup>9</sup> Bawn and Ogden, *Trans. Faraday Soc.* **30**, 432 (1934).

<sup>10</sup> Melville, *Nature* **133**, 947 (1934).

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.<sup>4</sup> 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  $\text{HO}_2$  complexes which took part in the subsequent changes. The difference in zero-point energy between the  $\text{HO}_2$  and  $\text{DO}_2$  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

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

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(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 Taylor<sup>1</sup> 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 Mitchell<sup>2</sup> and Melville.<sup>3</sup> 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-

<sup>1</sup> Jungers and Taylor, *J. Chem. Phys.* **2**, 373 (1934).

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

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