

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## The Photo-oxidation of Gaseous Hydrogen Iodide

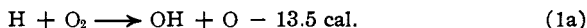
BY JOHN R. BATES AND GEORGE I. LAVIN

In studies<sup>1</sup> of the reaction of hydrogen atoms with oxygen molecules it has been assumed that the first process consists of an associative reaction between these atoms and oxygen molecules.



The molecule  $\text{HO}_2$  then reacts with a hydrogen molecule if a subsequent collision with hydrogen occurs within the lifetime of  $\text{HO}_2$  and has sufficient energy.

The straight bimolecular process



has been ruled out as improbable, due to the high activation energy necessary. If we accept the values for the heat of formation<sup>2</sup> of  $\text{OH}$  and  $\text{O}_2$  of 104 cal. and 117.5 cal., respectively, the reaction is endothermic 13.5 cal. Only one collision in at least  $5 \times 10^{10}$  would be effective at  $0^\circ$ . However, the value of 104 cal. for  $\text{OH}$  is not as definite as might be desired, and it is well to note that this mechanism does not agree with the experimental evidence obtained from quantum yield studies of the reaction.

The value of the quantum yield of hydrogen peroxide formation in the sensitized reaction is of the order of 1.2–2.5 as given by the work of Marshall<sup>3</sup> and of Frankenburger and Klinkhardt.<sup>4</sup> Reaction (1a) would give rise to a maximum of but one hydrogen peroxide molecule per quantum, since oxygen atoms are known<sup>5</sup> not to react with hydrogen molecules.

For a considerable time it was assumed that the quasi molecules such as  $\text{HO}_2$  could only exist for about  $10^{-13}$  to  $10^{-14}$  seconds. More recently it has been suggested by Kassel<sup>6</sup> and demonstrated experimentally by Pease<sup>7</sup> in the hydrogenation of ethylene that these molecules may have greater lifetimes, especially in cases where the molecule is polyatomic. It seemed, therefore, desirable to see if it was not possible to learn something concerning the lifetime of  $\text{HO}_2$  in the reaction of hydrogen atoms with oxygen.

Since hydrogen iodide is known to decompose into atoms<sup>8</sup> on the absorption of a quantum of light it appeared feasible to study the oxidation of hydrogen atoms by the method used in the case of methyl groups<sup>9</sup> and to

(1) Bonhoeffer and Haber, *Z. physik. Chem.*, **137A**, 363 (1928); Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **27**, 431 (1931).

(2) Haber and Bonhoeffer, *Z. physik. Chem.*, **127**, 264 (1928); Bonhoeffer and Reichert, *ibid.*, **129A**, 75 (1928); Herzberg, *ibid.*, **10B**, 189 (1930).

(3) Marshall, *J. Phys. Chem.*, **30**, 1078 (1926); *THIS JOURNAL*, **54**, 4460 (1932).

(4) Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **27**, 431 (1931).

(5) Kistiakowsky, *THIS JOURNAL*, **52**, 1868 (1930).

(6) Kassel, *ibid.*, **53**, 2143 (1931).

(7) Pease, *ibid.*, **54**, 1876 (1932).

(8) Bonhoeffer and Farkas, *Z. physik. Chem.*, **132**, 235 (1928).

(9) Bates and Spence, *THIS JOURNAL*, **53**, 1689 (1931).

obtain from the kinetics of the hydrogen iodide photo-oxidation valuable data concerning the reaction of hydrogen atoms and oxygen molecules.

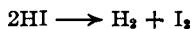
### Experimental

The apparatus was similar to that of Bates and Spence.<sup>9</sup> The same mercury arc and reaction vessel was used, but since hydrogen iodide is corrosive a quartz spiral manometer was substituted for the mercury manometer. Very satisfactory yields of hydrogen iodide<sup>10</sup> were obtained by passing hydrogen over iodine and then over a platinum catalyst. The hydrogen iodide was distilled *in vacuo*, and a pure white product, free from iodine, was obtained. The final product was distilled into a tube which was immersed in liquid air. Oxygen was taken from a tank, dried and stored in a large glass bulb. Since, according to Bodenstein and verified by the present work, hydrogen iodide does not appreciably attack pure vaseline, this was used to lubricate the stopcocks shutting the reaction vessel from the rest of the system.

The quartz reaction vessel was kept at a temperature of 0°. The vessel was connected to the rest of the apparatus by a ground joint so that it could be removed and the reaction products studied.

### Experimental Results

A series of runs showed that with oxygen present the pressure decrease was greater than could be obtained by the decomposition of hydrogen iodide alone. In the straight decomposition process a decrease equal to half the original hydrogen iodide present is to be expected:



In Table I it can be seen that with oxygen present the pressure decrease observed ( $-\Delta P_{\text{obs.}}$ ) is considerably greater than  $-\Delta P$  obtained by dividing the original hydrogen iodide pressure by two.

### Reaction Products

**Iodine.**—By titrating with *N*/10 thiosulfate it was possible to show that practically all of the iodine originally present in the hydrogen iodide could be recovered as free iodine. The titrations of iodine are given by  $-\Delta\text{HI}$  in Table II.

**Hydrogen Peroxide.**—Since all of the mechanisms postulated for the reaction of hydrogen atoms with oxygen involve the formation of hydrogen peroxide efforts were made to identify it in the products. A liquid product, which could be seen in the reaction vessel after a run, was washed out in water and the excess iodine removed with silver nitrate. Such a liquid gave very slight tests for peroxide. A blank run on iodine dissolved in water gave no such test. It is not surprising that hydrogen peroxide should not appear in large quantities, since Abel<sup>11</sup> has shown that liquid

(10) Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

(11) Abel, *ibid.*, **136**, 161 (1928).

TABLE I

HI, mm.	O <sub>2</sub> , mm.	-ΔP <sub>(obs.)</sub>	-ΔP (1/2 P <sub>HI</sub> )
53.0	300	35.5	26.5
50.2	493	39.7	25.1
50.2	302	38.3	25.1
49.9	255	34.6	24.9

TABLE II

No.	Initial pressure		Final total press.	Cor- rected final press.	-ΔHI	Final HI (HI <sub>B</sub> )	% H <sub>2</sub> G. A.	% H <sub>1</sub> -ΔP	Mm. H <sub>2</sub> Final	Mm. H <sub>2</sub> -ΔP	K G. A.	K <sub>2</sub> /K <sub>1</sub> G. A.	K -ΔP	K <sub>2</sub> /K <sub>1</sub> -ΔP
B1	50.4	150.1	168.5	160.0	46.5	3.9	8.3	8.6	13.2	14.0	17.2	0.114	13.2	0.088
B2	50.5	150.5	171.0	162.7	46.8	3.7	8.3	9.6	13.5	15.9	16.5	.110	10.2	.066
B3	50.5	302.3	315.5	309.1	48.7	1.7	4.2	4.1	13.1	12.8	17.8	.059	19.0	.069
B4	50.2	512.5	520.3	512.7	47.2	3.0	1.23, 1.27	1.3	6.3, 6.5	6.7	67.65	0.130, 0.127	61.0	.119
B5	51.0	199.0	218.0	211.1	48.7	2.2	6.4	7.6	13.6	16.2	17.3	0.087	10.2	.051
B6	49.9	255.7	271.0	263.0	46.5	3.4	5.3	4.6	14.0	12.4	14.3	.056	20.0	.078
C-1	112.3	302.0	349.3	329.7	92.7	19.6	9.6		31.9	33.9	26.0	.084	40.0	.134
C-2	101.1	309.0	348.9	329.9	82.1	19.0	10.4, 8.6		34.3, 28.6	27.6	40.0	.130	25.0	.073
C-3	101.8	269.5	313.4	290.3	78.7	23.0	9.6, 11.0		28.0, 31.9	27.1	17.5	.065	25.0	.093
												Av. 0.095	Av. 0.085	

hydrogen peroxide is decomposed in the presence of hydrogen iodide, yielding water and oxygen. The hydrogen iodide acting as a catalyst is not removed by the reaction. Knowing little of the conditions in the liquid phase in our reaction system, we were forced to the assumption that those processes occurring in the liquid phase were without effect upon the gas reactions, an assumption which is perhaps approximate, but which is borne out by the results.

**Hydrogen.**—Since both decomposition and oxidation were taking place simultaneously, it became necessary to determine the hydrogen formed during the course of the reaction. Accordingly gas analyses were carried out upon the gaseous products resulting from various initial concentrations of reactants. In most cases the hydrogen to oxygen ratio was determined by explosion and by absorption of oxygen by pyrogallol. These data are shown in Table II. Also recorded in the same table are the initial concentrations, the final total pressure and the final pressure of hydrogen calculated from the final total pressure and the gas analyses.

**Influence of Oxygen on the Reaction Rate.**—The variations of rate of decrease in pressure with varying oxygen pressures were studied, keeping the hydrogen iodide pressure constant. These results are represented in Table III, column 2.

TABLE III

PO <sub>2</sub>	No.	A	Rate observed	Rate calcd.	$K_2/K_1 = 0.097$	
					Obs. corrected rates	Calcd. corrected rates
300	A-2	0.76	1.35	1.16	1.35	1.16
401.6	A-7	.61	1.25	1.01	1.56	1.26
101.2	A-5	.61	0.75	0.75	0.935	0.935
302.8	A-9	.599	0.87	0.94	1.11	1.19
611.6	A-11	.45	1.13	0.82	1.91	1.61
149.8	A-18 B	1.28	2.08	1.71	1.235	1.015

### Discussion of Results

If we assume that the reaction of hydrogen atoms with oxygen takes place through the formation of the molecule HO<sub>2</sub>, as seems most probable, we may write the steps of the reaction as follows



At stationary concentrations

$$\frac{d[\text{H}]}{dt} = -\frac{d[\text{H}]}{dt} \quad \text{and} \quad \frac{d[\text{HO}_2]}{dt} = -\frac{d[\text{HO}_2]}{dt}, \quad \text{or} \quad (1)$$

$$[\text{HO}_2]K_4 + A = [\text{H}][\text{HI}]K_1 + [\text{H}][\text{O}_2]K_2, \quad \text{and} \quad (1)$$

$$[\text{H}][\text{O}_2]K_2 = [\text{HO}_2][\text{HI}]K_3 + [\text{HO}_2]K_4 \quad (11)$$

Equations I and II can be solved simultaneously to give the stationary concentrations of  $\text{HO}_2$  and  $\text{H}$  in terms of  $[\text{HI}]$ ,  $[\text{O}_2]$ ,  $A$ ,  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$ .

The rate at which hydrogen is produced according to (2) is

$$\frac{d[\text{H}_2]}{dt} = [\text{H}][\text{HI}]K_1 \quad (\text{III})$$

while the total rate of hydrogen iodide decomposition may be represented

$$-\frac{d[\text{HI}]}{dt} = 2[\text{H}][\text{HI}]K_1 + 2[\text{HO}_2][\text{HI}]K_3 \quad (\text{IV})$$

Dividing III by IV we obtain

$$-\frac{d[\text{H}_2]}{d[\text{HI}]} = 1/2 \frac{[\text{H}][\text{HI}]K_1}{[\text{H}][\text{HI}]K_1 + [\text{HO}_2][\text{HI}]K_3} \quad (\text{V})$$

Substituting the values of  $[\text{H}]$  and  $[\text{HO}_2]$  obtained from I and II we obtain

$$[\text{H}_2] = -1/2 \int_{\text{HI}_0}^{\text{HI}_E} \frac{([\text{HI}]K_3K_1 + K_1K_4)d[\text{HI}]}{[\text{HI}]K_3K_1 + [\text{O}_2]K_2K_3 + K_1K_4} \quad (\text{VI})$$

where  $\text{HI}_0$  and  $\text{HI}_E$  are the initial and final pressures of hydrogen iodide. If  $[\text{O}_2] = 0$ , we arrive at the expression

$$[\text{H}_2] = 1/2 \int_{\text{HI}_E}^{\text{HI}_0} d[\text{HI}], \text{ or } [\text{H}_2] = \frac{\text{HI decomposed}}{2} \quad (\text{VII})$$

which is true for straight photochemical decomposition. The same expression is deduced if  $K_4 \gg K_1$ ,  $K_2$  and  $K_3$ , which would indicate that, if  $K_4$  is very much greater than the other constants, no oxidation of the hydrogen atoms will occur.

If, on the other hand, we can neglect  $K_4$  in comparison with the other constants we obtain

$$d[\text{H}_2] = 1/2 \int_{\text{HI}_E}^{\text{HI}_0} \frac{[\text{HI}]K_1}{[\text{HI}]K_1 + [\text{O}_2]K_2} d[\text{HI}] \quad (\text{VIII})$$

Integrating, and taking the limits

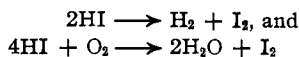
$$\frac{1}{K} = \frac{1}{\text{HI}_0 - \text{HI}_E - 2\text{H}_2} \ln \frac{K + \text{HI}_0}{K + \text{HI}_E} \quad (\text{IX})$$

where  $K = (K_2/K_1)[\text{O}_2]$ .

It appears immediately that  $K_4$  is not sufficiently greater than the other constants to make VII hold. If this were true, we should expect no influence of oxygen on the decomposition of hydrogen iodide, and hydrogen and iodine would be the sole products, which is definitely disproved by the data of Table II.

Equation VI cannot be used in its present form to express the results because of the large number of undetermined constants it contains. It seemed, therefore, most convenient first to attempt to fit the experimental results to IX and then to observe any deviations which might occur in the constancy of  $K_2/K_1$ , which would indicate the relative magnitude of  $K_4$  and the other constants.  $\text{HI}_0$  is the initial pressure of hydrogen iodide, while

$HI_0 - HI_E$  is given by the iodine titration, whence values for both of these can be obtained.  $[H_2]$  can be obtained in two ways. The analysis of the hydrogen and oxygen resulting from the reaction, together with the final total pressures of these gases, gives  $[H_2]$  directly. If we assume that the oxidation product of the reaction is water it is possible to obtain the amount of hydrogen present after reaction from the total decrease in pressure and the iodine titration. If  $\gamma$  is the fraction of the hydrogen iodide reacting to give water,  $1 - \gamma$  produces hydrogen. If, then, we write the two over-all reactions:



it can readily be seen that the following equation holds

$$\frac{(1 - \gamma)(HI_0 - HI_E)}{2} + 5/4 (HI_0 - HI_E)\gamma = - \Delta P + 4.6 \text{ mm.}$$

where 4.6 mm. is the vapor pressure of water at  $0^\circ$ . After solving this for  $\gamma$ ,  $[H_2]$  is obtained from the expression

$$H_2 = \frac{2}{(1 - \gamma)(HI_0 - HI_E)}$$

The values for  $H_2$  obtained from these two sources are found in Table II, columns 7 and 8, labeled  $H_2$  G.A. and  $H_2 \Delta P$ , respectively. Fairly good agreement is obtained between the two values in any one experiment, indicating that water is the final product of the oxidation reaction.

We now have all the values necessary for a determination of  $K$  and  $K_2/K_1$  from equation IX. This equation is easiest solved by a method of trial and error. We put  $1/K = Y = 1/(HI_0 - HI_E - 2H_2)\ln(K + HI_0)/(K + HI_E)$ , and then plot the hyperbola  $Y = 1/K$ , which is independent of the various experimental values. The point at which  $Y = 1/(HI_0 - HI_E - 2H_2)\ln(K + HI_0)/(K + HI_E)$  intersects the hyperbola is the desired solution of  $K$ . The values of  $K$  are given in Table II. From these, and the initial oxygen concentrations,  $K_2/K_1$  are obtained and given in columns 12 and 14. These values agree among themselves within the limits of these experiments and indicate that we are justified in neglecting  $K_4$  and using equation X to express our results.

It can be seen that the rate of the reaction, that is,  $-dP/dt$ , will be given by

$$- \frac{dP}{dt} = \frac{dH_2}{dt} + 2.5 \frac{dH_2O_2}{dt} \quad (X)$$

Eliminating  $[H]$  and  $[HO_2]$  and substituting we have

$$- \frac{dP}{dt} = \frac{A([HI] + 2.5[O_2]K_2/K_1)}{[HI] + [O_2]K_2/K_1} \quad (XI)$$

The value of  $A$  is found by placing  $[O_2] = 0$  and is the rate of decomposition of hydrogen iodide. It is to be pointed out that since it was

impossible to maintain a constant (from day to day) light intensity it was always necessary to make parallel experiments with hydrogen iodide alone and then with oxygen. In this way the variation of the light source was minimized and the necessary modification of  $A$  obtained.

We are now in a position, having evaluated  $K_2/K_1$ , to calculate  $-dP/dt$  assuming  $K_4$  to be small, and to compare the value so obtained to the experimental value. In Table III the values of  $A$  are obtained from the corresponding runs with hydrogen iodide alone; in column 4 the ratio, calculated from equation XI, and using the  $A$  values given in column 2. In the last two columns these values are corrected to an  $A$  value of 0.76, thus showing the rise in absolute rate as the oxygen increased. The corrected experimental values agree with the calculated within 20% and are a further proof that our mechanism is correct.

It becomes of great interest to see what restrictions neglecting  $K_4$  in equation VII places upon the magnitude of this quantity. Suppose  $K_1$ ,  $K_2$  and  $K_3$  are bimolecular constants expressed in millimeters pressure of mercury reacting per second per millimeter pressure of reactants. One atom at one millimeter pressure makes  $\sim 10^7$  collisions per second, so that the total number of bimolecular collisions at 1 mm. pressure of reactants is equal to  $\sim 10^7 \times 10^{16} = \sim 10^{23}$  per cc./sec. at 1 mm. pressure of the gases. Thus our constants  $K_1$ ,  $K_2$ ,  $K_3$  are  $\gtrsim 10^{23}/10^{16} = 10^7$  mm./sec. per mm. of reactants. Their true value will be smaller than this figure by a factor giving the efficiency of collisions, which will depend upon activation energy, and steric factors. They cannot, which is of importance for our considerations, exceed this order of magnitude.

If, using  $K_1 = K_2 = K_3 = 10^7$ , we substitute a value of  $K_4 = 10^{13}$ , which gives an accepted value for the life of a quasi-molecule equal to  $10^{-13}$  sec., and also substitute for  $[HI]$  50 mm. and  $[O_2]$ , 200 mm., we find that the amount of oxidation would be of the order of 2 parts in 100,000. The value of  $-d[H_2]/d[HI]$  would differ from 0.5 by only 0.02%, indicating that hydrogen would be the sole detectable product. This shows us immediately that such a value for  $K_4$  is much too high, since at these concentrations we observe considerable oxidation (Table I).

Before going further it would perhaps be well if we could arrive at more carefully estimated values for our  $k$ 's. Bonhoeffer and Farkas<sup>8</sup> have observed that the relative efficiencies of the reaction of hydrogen atoms with hydrogen iodide and iodine are in the ratio 1:100. This means that  $K_1$  must be less than  $10^5$ . Our results show that  $K_2$ , on this basis, would be  $\sim 10^4$ . These values in the expression  $([HI]K_1K_3 + K_1K_4)/([HI]K_1K_3 + [O_2]K_3K_2 + K_1K_4)$  give the values shown in Table IV, using  $[O_2] = 200$  throughout and the values of  $K_3[HI]$  and  $K_4$  indicated. The fraction under  $K_4 = 0$  are those which agree with our experiments, and deviations from these values for various  $K_4$  values can be read from the table.

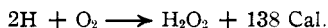
TABLE IV

		O <sub>2</sub> = 200 mm.				
		0	10 <sup>7</sup>	10 <sup>8</sup>	10 <sup>9</sup>	10 <sup>10</sup>
K <sub>4</sub> =						
K <sub>3</sub> = 10 <sup>7</sup>	HI = 50	0.715	0.72	0.75	0.884	0.981
	HI = 10	.333	.354	.500	.925	.990
K <sub>3</sub> = 10 <sup>6</sup>	HI = 50	.715	.75	.884	.981	
	HI = 10	.333	.500	.925	.990	

It can easily be seen that in the most unfavorable circumstances, shown by the top row that  $K_4$  is certainly  $\leq 10^9$ . There the deviation from experiment is  $(0.884 - 0.715)/0.715 = 23.6\%$ . In addition, since our results represent an integration over pressures of hydrogen iodide from 50 to  $\sim 3$  mm., we can safely say that the value of  $K_4$  is probably  $10^3$ .

The usually accepted values for the lifetime of such a quasi-molecule are of the order of  $10^{-13}$  to  $10^{-14}$  seconds, which give rise to a decomposition reaction constant of  $10^{13}$  to  $10^{14}$ . These values are, then,  $10^4$  to  $10^6$  greater than we find in our experiments, and indicate, as suggested by Kassel, that the lifetimes involved in polyatomic quasi molecules are considerably greater than usually accepted. This is of great interest in all cases in which a so-called three-body process is involved, since, when the lifetime increases above a definite value, the reaction loses its three-body characteristics and becomes essentially a straight bimolecular reaction. It also should be recognized that the reverse process of unimolecular decomposition involves considerations which may be affected by this longer lifetime.

It is of interest to discover the significance of these high values of the lifetime of HO<sub>2</sub> in the light of Kassel's considerations. This molecule has a heat of formation from a hydrogen atom and an oxygen molecule of 69 large calories if we take half of the energy of formation of hydrogen peroxide:



Further, having three atoms, its "s" value is three. Using these data we find that for  $K_4 = 10^9$ ,  $n$ , the number of vibration levels, must be  $\sim 50$ . For  $K_4 = 10^8$ ,  $n \sim 100$ . These give us average vibrational quanta of 500  $\text{cm.}^{-1}$  and 250  $\text{cm.}^{-1}$ , respectively, provided 0.1 of the energy continuum is to be filled. *A priori*, these are not at all impossible values. It must be remembered that these are only average values. The most fully worked out example of the relation of such an average value to the fundamental frequency of a molecule is given by the upper electronic level involved in the visible iodine absorption bands. Here 59 vibration levels are known within an energy interval of 4400  $\text{cm.}^{-1}$ ,<sup>12</sup> giving a maximum average separation of 75  $\text{cm.}^{-1}$ . The fundamental frequency of this state is 127.5  $\text{cm.}^{-1}$ . Remembering that the value 75  $\text{cm.}^{-1}$  is obtained by using only the number of measured levels, which is smaller than the actual number,

(12) Ruark and Urey, "Atoms, Molecules and Quanta," The McGraw-Hill Book Co., New York, 1930, pp. 395, 400, 402. The value 4400 is obtained by subtracting the energy of the electronic jump from that of the convergence limit.

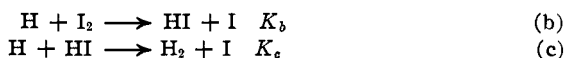


we can readily see that the average separation is considerably smaller than the fundamental frequency. An examination of band spectra data will reveal that this must be fairly universal. In attempting to compare the values of 500 and 250  $\text{cm.}^{-1}$  with those of the  $\text{HO}_2$  molecule, the nearest possible approach are the fundamental frequencies of hydrogen peroxide,<sup>13</sup> 875 and 903  $\text{cm.}^{-1}$ . These are not incompatible with the 500  $\text{cm.}^{-1}$  average value, but perhaps high for the 250  $\text{cm.}^{-1}$  average.

A consideration of the possibility of the reaction



occurring in the light of these data yields an interesting fact which makes this process seem unlikely. As we have said, the ratio of the  $K_b$  and  $K_c$  in the reactions



is 100,  $K_b/K_c = 100$ . Now reaction (b) is supposed to involve little or no activation energy.<sup>14</sup> Hence, reaction (a) would take place in about 1 in every 1000 collisions, which indicates an activation energy of 3.8 cal. If this were true, the heats of formation of  $\text{O}_2$  and OH could not differ by more than this amount, while the difference in the accepted values is 13.5 cal., a discrepancy of 10 large calories.

Since this mechanism seems an unlikely one according to the accepted values for the heats of linkage involved, we are led to the formation of the  $\text{HO}_2$  complex as the only plausible explanation of the reaction. In addition to other evidence already discussed earlier in this work, the formation of high percentages (90%) of hydrogen peroxide in the mercury sensitized hydrogen-oxygen reaction also points to the  $\text{HO}_2$  intermediate. This reaction has been the subject of intensive work in this Laboratory which will be presented shortly in *THIS JOURNAL*. The long life ascribed by us to the  $\text{HO}_2$  molecule is naturally contingent upon its intermediate formation being the correct mechanism for the reaction studied.

The authors wish to thank Professor Hugh S. Taylor for his many constructive criticisms.

### Summary

1. The kinetics of the photo-oxidation of gaseous hydrogen iodide have been studied.
2. The result of the application of simple reaction kinetic theory to the experimental results leads to the conclusion that the quasi molecule  $\text{HO}_2$  can have a life of  $10^{-8}$  to  $10^{-9}$  seconds, which is many orders of magnitude larger than that usually ascribed to such complexes.

PRINCETON, NEW JERSEY

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(13) Kohlrausch, "Der Smekal-Raman Effect," Table XXII.  
(14) Eyring, *THIS JOURNAL*, **53**, 2537 (1931).