



# The Mercury PhotoSensitized Reaction Between Hydrogen and Oxygen David H. Volman

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CH<sub>3</sub>D present. However, parent ions (i.e., those formed by the removal of an electron from the parent molecule) of corresponding molecules have shown the same intensity per unit pressure in all cases observed. Therefore, if it is possible to use only the parent ions as measures of concentration, it should not be necessary to examine the spectrum of the pure isotopesubstituted compound.

No detailed explanation has been developed for these effects. However, the  $\pi$  and  $\Gamma$  deduced here give definite information about a specific type of reacting system. It seems reasonable to suppose that they can be of considerable assistance in extending present methods of making rate and reaction mechanism calculations.

Note added in proof: Since this manuscript was submitted for publication, it has come to our attention (through Dr. D. P. Stevenson) that Bleakney, Condon, and Smith, J. Phys. Chem. 41, 197 (1937), account for the difference in ratio of atomic to molecular ions between H<sub>2</sub> and D<sub>2</sub> on the basis of the difference in zero point amplitudes of vibration and the Franck-Condon principle. This doubtless provides the basis for the explanation of the effects reported above. It seems certain that if sufficiently accurate information were available on ground normal vibrational wave functions and on excited electronic states it would be possible to calculate the  $\pi$  and the  $\Gamma$  effect for CH<sub>3</sub>D and other deuterium containing molecules.

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# The Mercury Photo-Sensitized Reaction Between Hydrogen and Oxygen<sup>1</sup>

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The mercury sensitized reaction between hydrogen and oxygen in a flowing system was studied. The quantum vield of the reaction was found to be less than unity, and no evidence of a chain reaction at 40° was found. Hydrogen peroxide was the principal product, and yields of peroxide above 90 percent were found for many of the experiments. It was shown that in the gas phase reaction between ozone and hydrogen peroxide, water was rapidly formed. The yield of product was found to increase with increasing oxygen flow rate, with increasing total flow rate for a fixed hydrogen to oxygen ratio, and to increase and then decrease with increasing hydrogen to oxygen ratio. The reaction scheme proposed is

#### $Hg + h\nu \rightarrow Hg^*$ ,

#### INTRODUCTION

T has been shown by Coehn and Grote<sup>2</sup> that hydrogen peroxide could be detected among the reaction products if a mixture of hydrogen and oxygen was passed rapidly through an irradiated quartz vessel. In a static experiment or

$$\begin{array}{c} Hg^{*}+H_{2} \rightarrow H+H+Hg, \\ Hg^{*}+O_{2} \rightarrow O_{2}+Hg, \\ H+O_{2} \rightarrow HO_{2}, \\ H+M \rightarrow HM, \\ HM+HM \rightarrow H_{2}+M, \\ HO_{2}+HO_{2} \rightarrow H_{2}O_{2}+O_{2}. \end{array}$$

This leads to the rate equation.

$$\frac{d(H_2O_2)}{dt} = \frac{k_3/k_4''(O_2)}{k_3/k_4''(O_2)+1} \frac{I_a k_1/k_2(H_2)}{k_1/k_2(H_2)+(O_2)},$$

using the flow rates of hydrogen and oxygen.  $k_1/k_2$  is the ratio of quenching efficiencies of hydrogen and oxygen for activated mercury or 1.62.  $k_3/k_4''$  is taken equal to  $1.2 \times 10^{-3}$ .

when using low rates of flow no peroxide was detected. That hydrogen and oxygen can react in the presence of photo-activated mercury atoms at room temperature was first established by Dickinson.<sup>3</sup> Later it was demonstrated by Marshall<sup>4</sup> that, in a flowing system, hydrogen peroxide was formed and that the quantum yield of the reaction was about 6.6. This value was later corrected to about 2.5.5 Bates and

<sup>&</sup>lt;sup>1</sup> The experimental work reported herein was carried out at the University of Illinois, and this report is based on work performed for the O.S.R.D. under Contract No. OEM-sr-1452.

<sup>&</sup>lt;sup>2</sup>G. K. Rollefson and M. Burton, Photochemistry and the Mechanism of Chemical Reactions (Prentice-Hall, Inc., New York, 1939), p. 173.

 <sup>&</sup>lt;sup>3</sup> R. G. Dickinson, Proc. Nat. Acad. Sci. 10, 409 (1924).
 <sup>4</sup> A. L. Marshall, J. Phys. Chem. 30, 1078 (1926).
 <sup>5</sup> A. L. Marshall, J. Am. Chem. Soc. 54, 4460 (1932).



FIG. 1. Gas flow system.

Taylor<sup>6</sup> and Bates and Salley<sup>7</sup> demonstrated that under suitable flow conditions, and with a proper ratio of hydrogen and oxygen, hydrogen peroxide was the principal reaction product. Frankenburger and Klinkhardt<sup>8</sup> report results at variance with those of Marshall and Bates and co-workers in that they found a quantum yield of only about unity and considerable water in the reaction products.

The data existing in 1933 were considered critically by Bates<sup>9</sup> who advanced the following reaction scheme:

$$Hg + h\nu \rightarrow Hg^*$$
  $I_a$  (1)

$$Hg^* + H_2 \rightarrow H + H + Hg \qquad k_1 \qquad (2)$$

$$Hg^* + O_2 \rightarrow O_2 + Hg \qquad k_2 \qquad (3)$$

$$H + O_2 \rightarrow HO_2$$
  $k_3$  (4)

$$HO_2 + H_2 \rightarrow H_2O_2 + H \qquad k_4 \qquad (5)$$

$$\mathrm{HO}_{2} + \mathrm{HO}_{2} \rightarrow \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{O}_{2}. \qquad k_{5} \qquad (6)$$

This chain mechanism allows quantum yields of greater than unity and predicts that hydrogen peroxide is the sole product. The mechanism is based on assumptions in regard to the incident intensity in the experiments of the earlier investigations, and explains the difference in the <sup>6</sup> J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. 49, 2438 (1927). <sup>7</sup> J. R. Bates and D. J. Salley, J. Am. Chem. Soc. 55,

quantum yields reported by Frankenburger and Klinkhardt, and by Marshall quantitatively by use of the differences in incident intensity. The quantum yield given by Frankenburger and Klinkhardt is based on the use of monochloroacetic acid as an actinometer and the values of the quantum yield for the photo-hydrolysis reaction given by Rudberg.<sup>10</sup> However, more recent work<sup>11</sup> has established a value somewhat less than that reported by Rudberg. These newer data indicate that the values given by Frankenburger and Klinkhardt should be lowered, probably well below unity. These considerations, especially the uncertainties in quantum yield, throw some question on the necessity for postulating a chain mechanism. In this paper a re-investigation of some of the experimental work and a revised interpretation of the reaction mechanism are presented.

#### EXPERIMENTAL

### Apparatus

The apparatus used to study the photochemical reaction is shown diagrammatically in Fig. 1. Tank oxygen and hydrogen were measured by calibrated flowmeters,  $F_1$  and  $F_2$ . The hydrogen was made oxygen free by prior passage over heated copper. Constant flow was maintained by allowing a small amount of gas to escape through the constant head stabilizers,  $S_1$ and  $S_2$ . The gases were mixed and dried in D over magnesium perchlorate. The mixture of gases then passed through the mercury saturator M-C. From here they were brought to 20° in the water bath, C, and then passed through the quartz reaction tube R at 40°. The reaction tube was enclosed by a mercury resonance lamp of the rare gas-mercury discharge type which was in the form of a helix 25 mm in diameter and 200 mm long, L. Condensable product was collected in the liquid air trap N.

To insure a constant pressure of mercury vapor it was decided to saturate the gas stream at some temperature below the reaction temperature so that there would be no condensation of mercury vapor in the reaction tube. Mercury is held in cuplike depressions, b. The electrical

<sup>110 (1933).</sup> <sup>8</sup> W. Frankenburger and H. Klinkhardt, Zeits. f. physik.

Chemie **B15**, 421 (1932). <sup>9</sup> J. R. Bates, J. Chem. Phys. **1**, 457 (1933).

<sup>&</sup>lt;sup>10</sup> E. Rudberg, Leitz. f. Physik **24**, 247 (1924). <sup>11</sup> R. N. Smith, P. A. Leighton, and W. G. Leighton, J. Am. Chem. Soc. **61**, 2299 (1939).

heater, c, and the water-jacketed condenser, a, maintain boiling water in the space surrounding the cups. The gas stream is very likely only partially saturated at 100° in passing over the mercury containers. However, reducing the temperature to 20° in C insures saturation at this temperature, and a constant pressure of mercury vapor is obtained.

It is difficult to trap out a small quantity of condensable gas from a large quantity of noncondensable gas at atmospheric pressure. Using liquid air or dry ice as the refrigerant, fogs are readily formed and are carried through the trap. In the case where water is the condensable gas, a characteristic snow may sometimes be seen in the effluent gas stream. Bates and Salley<sup>7</sup> in experiments similar to ours found that it was necessary to use several U type or bubbler type traps in series in order to insure capturing almost all of the condensable fraction. In our experiments it was found that it was not possible to collect all of the product in an ordinary bubbler type trap, and a trap of rather unique design was constructed. A stream of room temperature air enters the well as shown. This sets up a large temperature gradient in the annular space through which the gases are forced to pass. The space is only about 1 mm thick. The arrangement is effective in preventing or dissipating water or hydrogen fogs, and the entire condensable product is collected on the cold surface of the outer glass cylinder.

### **Analytical Procedure**

Although considerable work has been carried out to establish the fact that hydrogen peroxide could be produced in yields in the neighborhood of 85 percent or even higher, the evidence did not appear to be conclusive. Bates and Salley have described their technique in considerable detail. At the end of an experiment, the trap was allowed to come to room temperature, weighed, and then titrated. Since the gas mixture was usually about 10 volumes of hydrogen to 1 of oxygen, the difference between the weight of this gas mixture and the weight of an equal volume of air would be an important factor. In this study it was found that diffusion was too slow to allow for replacement of the gas mixture by air. However, dry air could be used to flush out the trap while the trap was still very cold so that none of the condensed product was lost. The most satisfactory technique was to turn off the hydrogen gas at the end of an experiment and then continue the flow of oxygen until all of the hydrogen was replaced. A relatively small correction for the difference in density of oxygen and air could then be made. This procedure served a dual role in that it eliminated the danger of leaving an explosive mixture in the reaction system. The peroxide content was then determined by titration with potassium permanganate.

### **Reaction with Mercury**

In many of the experiments, an oxide deposit was observable in the region just past the illumination zone. In all experiments, however, the major part of the mercury was collected in the trap along with the condensable products. This mercury appeared black until the trap was allowed to warm up, when it assumed an appearance characteristic of mercuric oxide. Bates and Salley have observed similar effects. It was important to know whether the reaction resulted in catalytic decomposition of the peroxide.

In experiments in which solutions of 30 percent hydrogen peroxide were mixed with mercury, mercuric oxide was forned and only stoichiometric amounts of peroxide were used up; oxygen gas is liberated in the reaction. Hydrogen peroxide was found to decompose only very slightly more rapidly over mercuric oxide than it does ordinarily in Pyrex vessels. These results are similar to those obtained by Elder and Rideal<sup>12</sup> for the reaction between hydrogen peroxide gas and liquid mercury.

It was still necessary to investigate the possibility of catalytic decomposition of hydrogen peroxide when high percentage liquid peroxide

 TABLE I. Effect of warming the trap on hydrogen peroxide yield.

Expt. No.	Trap condition when rinsed	Product wt., mg	H2O2 wt., mg	H2O2 percent
74 75	Room temp. Cold	100	79.7 81.6	79.7
76 77	Room temp. Cold	98	80.3 79.9	82.0

<sup>12</sup> J. W. Elder, Jr. and E. F. Rideal, Trans. Faraday Soc. 23, 545 (1927).



FIG. 2. Yield of product versus oxygen flow rate. Hydrogen flow fixed at 3000 ml/min.

is in contact with liquid mercury. This could account for appreciable peroxide loss on warming the trap prior to weighing the final product. If the reaction results only in a stoichiometric loss of hydrogen peroxide caused by the reaction with the small quantity of mercury present, the amount decomposed should be negligible. Any decomposition loss should be avoided by rinsing out the trap immediately after removing from

TABLE II. Variation of O<sub>2</sub> flow rate at constant H<sub>2</sub> flow of 3000 ml/min.

Expt. No.	O2 flow ml/ min	Prod- uct mg	H2O2 %	H2O2 moles/ hr	H2O moles/ hr	Moles/ hr total	ΦH2O2	$\Phi_T$
115	300	68	94.8	0.0114	0.0012	0.0126	0.27	0.29
118	300	60	91.2	.0097	.0017	.0114	.23	,27
121	300	64	85.6	.0097	.0030	.0127	.23	.30
125	300	73	82.0	.0106	.0043	.0149	.25	.35
130	300	72	79.7	.0101	.0050	.0151	.23	.35
123	600	96	84.0	.0143	.0050	.0193	.33	.45
126	600	82	80.8	.0117	.0053	.0170	.27	.40
134	600	76	79.6	.0107	.0053	.0160	.25	.37
117	1000	75	81.5	.0118	.0047	.0165	.28	.39
120	1000	73	81.5	.0105	.0043	.0148	.25	.35
131	1000	80	79.0	.0111	.0057	.0167	.26	.39
122	1500	101	81.5	.0146	.0063	.0209	.34	.49
127	1500	88	76.7	.0119	.0067	.0186	.28	.43
129	1500	91	63.7	.0102	.011	.0213	.24	.50
132	1500	97	70.5	.0120	.0097	.0217	.28	.51
116	2000	91	81.5	.0131	.0057	.0188	.31	.44
119	2000	93	82.8	.0136	.0053	.0189	.32	.44
124	2000	96	76.2	.0129	.0077	.0206	.30	.48
128	2000	104	70.0	.0129	.010	.0229	.30	.54



FIG. 3. Yield of product versus total flow rate. Hydrogen to oxygen ratio fixed at 3 to 2.

the liquid air and titrating the hydrogen peroxide. Since the trap cannot be weighed, it is not possible to determine the percent of peroxide in the reaction products when analysis is made in this manner. It may be seen from Table I that there is no observable loss caused by the interaction between mercury and hydrogen peroxide in the trap.

# The Quantum Yield

A determination of the incident quanta was made using uranyl oxalate as an actinometer.<sup>13</sup> The reaction vessel was filled with a solution

TABLE III. Variation of total flow rate at fixed  $H_2:O_2$  ratio. Ratio of  $H_2:O_2=3:2$ .

Expt. No.	Total flow ml/min	Prod- uct mg	H2O2 %	H2O2 moles/hr	H₂O moles/hr	Moles/hr total
139	1000	31	56.5	0.00308	0.0043	0.00738
138	2000	39	65.5	.00450	.0043	.00880
148	2000	36	68.3	.00433	.0037	.00803
136	3300	54	70.9	.00675	.0053	.01205
149	3300	55	67.8	.00657	.0060	.01257
143	5000	68	73.8	.00893	.0060	.01493
146	5000	87	80.3	.0123	.0057	.0180
150	500	83	64.7	.00945	.0097	.01915

<sup>13</sup> W. G. Leighton and G. S. Forbes, J. Am. Chem. Soc. **52**, 3139 (1930).

containing 0.01 mole per liter uranyl oxalate and 0.05 mole per liter oxalic acid. After a known period of irradiation, an aliquot of the solution was titrated with standard 0.1 N potassium permanganate. The intensity of light entering the reaction cell was found to be  $7.1 \times 10^{-4}$  Einstein per minute. The quantum yields subsequently given are based on this value.

# The Hydrogen-Oxygen Reaction

For experiments in which the flow rate of hydrogen was kept constant and the oxygen flow rate was varied, results are shown in Table II and Fig. 2.

The yield of product at varying total flow rate for a constant ratio of  $H_2O_2$  was followed. The period of irradiation again was 10 minutes. Results are shown in Table III and Fig. 3.

Table IV and Fig. 4 show results obtained for a variation of H<sub>2</sub>:O<sub>2</sub> ratio at a constant total flow rate of 3300 ml/min. The exposure time for these runs was also 10.0 minutes.

# **Reaction Between Ozone and** Hydrogen Peroxide

Ozone may be formed by the photo-sensitized reaction of oxygen with mercury.<sup>14</sup> The reaction between ozone and hydrogen peroxide has been studied in aqueous solution by several investigators. The most extensive study was made by Taube and Bray,<sup>15</sup> and the following mechanism was advanced:

$$H_2O_2 + O_3 \rightarrow HO + HO_2 + O_2, \tag{7}$$

$$HO_2 + O_3 \rightarrow HO + 2O_2,$$
 (8)

$$HO + O_3 \rightarrow HO_2 + O_2,$$
 (9)

$$HO + H_2O_2 \rightarrow HO_2 + H_2O. \tag{10}$$

TABLE IV.

Expt. No.	H2O2 ratio	Product mg	H2O2 %	H2O2 moles/hr	H2O moles/hr	Moles/hr total
142	10	46	74.0	0.00600	0.0043	0.00103
137	3	55	73.3	.00713	.0050	.01213
136	1.5	54	70.9	.00675	.0053	.01205
149	1.5	55	67.8	.00657	.0060	.01257
140	0.67	52	57.8	.00532	.0073	.01262
141	0.33	40	25.9	.00184	.0100	.0118
		-				

14 R. G. Dickinson and M. S. Sherill, Proc. Nat. Acad. Sci. 12, 175 (1926). <sup>15</sup> H. Taube and W. C. Bray, J. Am. Chem. Soc. 62,

3357 (1940).

Reaction (7) is the chain initiating step. (8)and (9) result in chain decomposition of ozone. (8) and (10) constitute a chain for the reaction between ozone and peroxide.

Since it was likely that ozone was being formed in our experiments, we were interested in determining whether the reaction occurred in the vapor phase and whether it could occur between a condensed phase of peroxide and ozone gas at low temperatures. Ozone was prepared by passing a measured amount of oxygen gas through a quartz tube under irradiation of a strong mercury discharge. Hydrogen peroxide was prepared by the mercury sensitized hydrogen-oxygen reaction. The streams containing ozone and peroxide were brought together in a mixing chamber, and the resulting product was condensed in a dry ice-alcohol trap. The results are given in Table V. Experiment M-1 shows the rate of ozone formation in the apparatus, and experiments M-3 and M-5 show the rate of product yield when no ozone is added. M-4 and M-6 show the effect of adding ozone. M-7 shows the effect of passing ozone over hydrogen peroxide previously trapped out.

It may be seen that ozone and  $H_2O_2$  are present at the time of mixing in almost equal molal quantities. The reaction between ozone and  $H_2O_2$  results in almost complete removal of  $H_2O_2$  when the two are brought together in the gas phase. Passing ozone over H<sub>2</sub>O<sub>2</sub> at dry ice temperature has no appreciable effect.



FIG. 4. Yield of product versus hydrogen to oxygen ratio. Total flow fixed at 3300 ml/min.

A very interesting observation is the fact that there seems to be a loss of hydrogen in the reaction products when hydrogen peroxide and ozone are mixed in the gas phase. A comparison of M-3, 5, 7 with M-4, 6 shows this to be the case. A discrepancy between the total moles of peroxide plus water for the experiments with and without adding ozone seems greater than can be accounted for by experimental error. This implies that the reactions involving the free radicals formed in the ozone-peroxide reactions produce gaseous hydrogen.

## MECHANISM OF THE MERCURY SENSITIZED HYDROGEN-OXYGEN REACTION

The reaction scheme proposed by Bates<sup>9</sup> leads to the kinetic equation,

$$\frac{d(\mathrm{H}_{2}\mathrm{O}_{2})}{dt} = \frac{k_{4}(\mathrm{H}_{2})}{k_{5}^{\frac{1}{2}}} \left(\frac{k_{1}l_{a}(\mathrm{H}_{2})}{k_{1}(\mathrm{H}_{2}) + k_{2}(\mathrm{O}_{2})}\right)^{\frac{1}{2}} + \frac{k_{1}I_{a}(\mathrm{H}_{2})}{k_{1}(\mathrm{H}_{2}) + k_{2}(\mathrm{O}_{2})}.$$
 (a)

This mechanism purports to explain the rate variation with the concentration of hydrogen and oxygen and the variation of quantum yield with intensity of light. Objections to this correlation have already been formulated in the introduction to this paper. The quantum yields reported herein are also well below unity which, although not proof of a non-chain mechanism, allows the formulation of a non-chain mechanism at the temperature used.

Bonhoeffer and Haber<sup>16</sup> and Frankenburger and Klinkhardt<sup>8</sup> arrive at a mechanism which substitutes, for reactions (5) and (6) above, the

TABLE V. The ozone-hydrogen peroxide reaction.

Expt. No.	M	oles per	hour 🗙 1		
	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	O3	Total	Remarks
M-1 M-3 M-4	0 1.64 0.19	0 2.4 2.8	1.59	1.6 4.0 3.0	Only ozonizer operating Ozonizer dark
M-5 M-6	1.44 0.13	2.0 3.0		3.4 3.1	Ozonizer dark
M-7	1.39	2.1		3.5	Ozonizer operating only after H <sub>2</sub> O <sub>2</sub> synthesis stopped.

<sup>16</sup> K. F. Bonhoeffer and F. Haber, Zeits. f. physik. Chemie **137A**, 363 (1928). reactions

$$HO_2 + H_2 \rightarrow H_2O + OH,$$
 (11)

$$OH + OH \rightarrow H_2O_2, \tag{12}$$

and to explain quantum yields slightly above unity,

$$HO_2 + H_2O \rightarrow H_2O_2 + OH. \tag{13}$$

Much of the scheme is derived from the high yields of water found in their experiments. Bates and Salley<sup>7</sup> have shown that this formulation requires at least 51.4 percent water in the products. The high percentage yields of peroxide found in this and the earlier investigations are a refutation of this mechanism.

Surface effects, the complexity of exact kinetics in a flowing system, and the obscureness of the role played by activation entering the oxygen molecule make it difficult to establish the mechanism of the reaction. However, it is possible, on the basis of some reasonable assumptions, to arrive at a rate equation which seems to have some validity.

The results of Tables II and III indicate that the total moles of product depend upon both the flow rate and the composition of the gases. The fact that the total number of moles of product for a fixed hydrogen to oxygen ratio depends on the flow rate shows that hydrogen is being reformed by interaction between free radicals or H atoms.

Since it is possible to achieve yields of hydrogen peroxide upwards of 90 percent, we may assume that all water found is formed from hydrogen peroxide. This water may come from peroxide decomposing by an over-all equation,

$$2H_2O_2 \rightarrow 2H_2O + O_2, \qquad (14)$$

or water may come from the reaction between hydrogen peroxide and ozone, to which reference has already been made. If we assume that these water forming reactions are independent ones, then we can use the number of moles of product, water plus peroxide, as the number of moles of hydrogen peroxide formed in the reaction.

The adsorption of H atoms on quartz or Pyrex is strong, and it may be concluded that H atoms reaching the wall remain and eventually recombine to give hydrogen. We may then substitute for Eq. (5) the reactions,

$$H+M\rightarrow HM, k_4'$$
 (15)

the adsorption of H atoms on the walls, and

$$HM + HM \rightarrow H_2 + M, \qquad (16)$$

the adsorption of H atoms on the walls, and

$$HM + HM \rightarrow H_2 + M, \qquad (16)$$

the formation of hydrogen on the walls. This formulation eliminates the chain character of the mechanism of Bates and, using the steady-state method, leads to the kinetic equation,

$$\frac{d(H_2O_2)}{dt} = \frac{k_3(O_2)}{k_3(O_2) + k_4'M} \frac{I_a k_1(H_2)}{k_1(H_2) + k_2(O_2)}.$$
 (b)

Since the number of collisions of H atoms with the walls will be governed by the flow rate, the effective wall may then be considered as inversely proportional to the flow rate. For  $k_4$ ' M, the expression  $k_4'' \ 1/F$ , where F is the total flow rate, may be substituted. Expressed in terms of flow rates, the concentration of each species becomes the flow rate at which it is introduced into the system divided by the total flow rate. In terms of flow rates, the kinetic equation becomes,

$$\frac{d(\mathrm{H}_{2}\mathrm{O}_{2})}{dt} = \frac{k_{3}/k_{4}''(\mathrm{O}_{2})}{k_{3}k_{4}''(\mathrm{O}_{2})+1} \frac{I_{a}k_{1}/k_{2}(\mathrm{H}_{2})}{k_{1}/k_{2}(\mathrm{H}_{2})+(\mathrm{O}_{2})}.$$
 (c)

 $k_1$  and  $k_2$  are the bimolecular rate constants for the quenching of activated mercury by hydrogen and oxygen. Zemansky<sup>17</sup> has shown that the relative quenching efficiencies of hydrogen and oxygen are 1.1 and 0.68, respectively.  $k_1k_2$  in the rate expression then is equal to 1.1/0.68 or 1.62.  $I_a$  has been shown to be equal to 0.043 Einstein per hour.

It is hardly to be expected that experimental data would be closely fitted by the above expression, since variability of walls would be such an important factor. However, for data obtained

<sup>17</sup> M. W. Zemansky, Phys. Rev. 36, 919 (1930).



FIG. 5. Comparison of experimental values, circles, with calculated values, curve. Variation of oxygen flow rate for a fixed hydrogen flow of 3000 ml/min.

over a small time interval and with consistent technique, some success might be expected. Using a ratio of  $k_3/k_4'' = 1.2 \times 10^{-3}$ , the rates for the condition represented in Table II have been calculated. Figure 5 shows a comparison of calculated rates, the curve, and the experimental values, circles. The  $k_3/k_4''$  ratio indicates that reaction (15) occurs much more readily than reaction (3). This is a reasonable result since it would be expected that some means of dissipation of excess energy is necessary to stabilize HO<sub>2</sub> formed from H and O<sub>2</sub>, while adsorption of H atoms on the wall should occur on almost every collision.

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