[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Photo-oxidation of Hydrogen and Deuterium Iodides[1]

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Many investigations[2] have been made of the reaction of hydrogen atoms with oxygen molecules. One such study was that of Bates and Lavin,[3] who obtained the hydrogen atoms for the reaction by the photo-dissociation of hydrogen iodide. It was pointed out by Bodenstein and Schenk[4] that the results of Bates and Lavin might be equally well explained on the assumption that the reaction $H+O_2$ occurred as either a two-body or a three-body process. The present work represents an attempt to differentiate between these two alternatives by studying the same reaction with improved experimental accuracy and under much more widely varied conditions. The problem is of theoretical importance in connection with the interpretation of a number of different reactions[2] such as the explosion limits of hydrogen and oxygen,[5] the effect of oxygen on the photochemical hydrogen–chlorine reaction,[4] etc. The general theoretical implications of the problem have been discussed by Kassel.[6]

A similar study was also made on the reaction of deuterium iodide with oxygen. A comparison of the results for hydrogen and deuterium iodides is of interest in connection with the effect of mass and zero point energy on chemical reactions.[7]

Method and Apparatus

The method used was similar to that of Bates and Lavin.[3] A mixture of hydrogen (or deuterium) iodide with oxygen (and also in a few cases with nitrogen) in a quartz reaction vessel of 277.1 cc. effective volume, was illuminated, the pressure change was noted and the products analyzed for hydrogen and iodine. The reaction vessel was kept at 0° except in two 20° runs. The source of light was a low-voltage mercury–argon quartz lamp designed by Duffendack and Owens.[8] It used a nickel cathode activated by a coating of barium and strontium oxides.

The hydrogen iodide was synthesized by passing a mixture of hydrogen and iodine vapor through a tube containing two glowing platinum spirals, the first spiral being kept hotter than the second. Deuterium iodide was made in a similar way, using deuterium obtained by electrolysis of 99.9% D_2O.

No stopcocks were employed in connection with the reaction vessel or the storage tube for hydrogen iodide; instead, two greaseless valves were employed. These made use of a glass bellows similar to that of Bodenstein,[9] but substituting for his glass-in-glass seat a fused silver chloride seat as described by Ramsperger.[10]

The hydrogen was analyzed by a method suggested by Professor H. N. Alyea of Princeton. It made use of a sensitive slanting mercury manometer, calibrated for the purpose, to measure the decrease in both pressure and volume resulting from the combustion of hydrogen in a sample of known volume.

The rest of the apparatus was essentially the same as that described by Bates and Lavin.[3]

Experimental Results

Results of the runs are incorporated in the tables.

TABLE I

RUNS MADE WITH HYDROGEN IODIDE AND OXYGEN

HI_0	Initial oxygen	HI decomposed	H_2 formed	k_2/k_1[a]	$k_5/k_1 \times 10^4$
200.6	506.4	36.57	14.84	0.084	1.20
200.5	449.9	37.15	15.20	.090	1.53
199.9	400.7	41.92	17.39	.092	1.56
150.8	551.1	41.56	15.22	.086	1.25
150.6	550.0	44.44	16.99	.072	1.05
151.3	449.2	32.38	13.57	.058	0.98
150.2	450.0	35.19	13.88	.079	1.34
151.4	350.6	35.23	14.89	.070	1.42
150.9	352.5	32.96	14.15	.063	1.27
100.6	601.3	35.41	11.64	.072	1.04
99.9	608.8	40.48	13.19	.069	1.00
99.3	499.5	27.86	9.64	.076	1.28
101.0	451.1	37.95	14.40	.057	1.06
50.0	699.4	41.07	7.07	.077	1.05
49.8	700.7	34.34	6.19	.081	1.10
50.2	600.3	30.01	6.83	.068	1.07
50.0	602.1	30.42	6.94	.067	1.06
50.2	499.7	30.24	7.47	.070	1.31
50.1	500.3	32.82	7.89	.070	1.32
50.0	398.6	25.38	6.89	.077	1.76
50.2	400.0	37.77	10.36	.060	1.39
38.5	362.1	10.82	3.39	.054	1.37
25.5	702.4	21.44	2.75	.059	0.82
25.7	507.1	20.55	3.21	.063	1.22
24.8	499.9	21.95	3.24	.062	1.20
25.1	300.3	20.57	5.32	.042	1.32
26.1	300.3	21.95	5.37	.048	1.51

[a] Assuming that $k_4/k_3 = 0$.

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[1] (a) The material in this paper comprises a portion of a thesis presented by Gerhard Albert Cook to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1935. (b) Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 22–26, 1935.

[2] (a) For references see Bates, *J. Chem. Phys.*, **1**, 457 (1933); (b) Farkas and Sachsse, *Z. physik. Chem.*, **B27**, 111 (1934).

[3] Bates and Lavin, THIS JOURNAL, **55**, 81 (1933).

[4] Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

[5] Kassel and Storch, paper presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 22–26, 1935.

[6] Kassel, in "Annual Survey of American Chemistry," Chemical Catalog Company, New York, 1934, Vol. VIII, pp. 27–30.

[7] Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[8] Unpublished paper.

[9] Bodenstein, *Z. physik. Chem.*, **B7**, 387 (1930).

[10] Ramsperger, *Rev. Sci. Instruments*, **2**, 738 (1931).

TABLE II

RUNS MADE WITH DEUTERIUM IODIDE AND OXYGEN

DI_0	Initial O_2	DI_0-HI_F	D_2 formed	k_2/k_1[b]	$k_5/k_1 \times 10^4$
198.7	516.6	51.59	17.22	0.166	2.39
200.8	513.5	29.91	10.19	.169	2.39
201.4	301.0	29.20	11.62	.158	3.21
151.2	543.0	33.95	10.65	.147	2.16
150.0	399.7	44.26	15.44	.138	2.58
150.3	297.6	28.31	10.70	.148	3.38
99.3	605.0	53.37	11.73	.152	2.24
100.4	599.0	28.31	7.45	.129	1.88
100.6	499.9	25.64	7.67	.118	1.99
100.1	397.7	26.31	8.96	.102	2.09
50.7	649.3	25.55	4.98	.090	1.31
52.2	300.8	26.62	7.59	.096	2.83
26.1	688.1	20.35	1.68	.115	1.64
25.1	297.3	18.35	3.45	.085	2.73
101.3[a]	497.6	47.64	13.18	.124	2.15
100.5[a]	498.5	26.95	8.31	.108	1.85

[a] 20.0°, all other runs at 0°. [b] Assuming that $k_4/k_3 = 0$.

TABLE III

SPECIAL PAIRS OF RUNS MADE WITH AND WITHOUT NITROGEN

HI_0	Initial O_2	Initial N_2	$HI_0 - HI_F$	H_2 formed	k_2/k_1[a]	$k_5/k_1 \times 10^4$
50.3	299.0	...	23.51	8.99	0.039	1.14
51.3	301.7	388.4	24.26	6.75	.102	1.39
50.9	198.4	...	30.93	12.73	.036	1.52
50.5	205.1	474.2	34.66	10.65	.096	1.34
25.6	150.3	...	18.97	7.58	.024	1.43
24.7	150.2	473.7	21.11	5.02	.094	1.46
DI_0				D_2		
50.5	101.7	...	19.69	8.77	0.048	3.31
51.8	104.2	391.8	16.35	5.99	.149	2.75
24.3	100.4	...	14.75	6.15	.032	2.67
24.5	98.2	369.3	17.69	4.42	.152	3.14

[a] Assuming that $k_4/k_3 = 0$.

In general these data confirm the experimental results of Bates and Lavin, and in addition it is immediately evident that the following qualitative statements are true: (1) in any two runs, if all conditions are the same except that hydrogen iodide is used in one and deuterium iodide in the other, more of the deuterium is always oxidized than of the hydrogen; and (2) in any two runs, if all conditions are the same except that nitrogen is added in one case and not in the other, a great deal more of the hydrogen is oxidized when the nitrogen is added than when it is absent. In other words, the presence of an inert gas greatly speeds up the reaction of hydrogen atoms with oxygen molecules. This is true whether hydrogen or deuterium is used.

Products of the Oxidation

No experimental test was made for hydrogen peroxide in the presence of the hydrogen iodide; instead, the pressure of hydrogen that should have been formed was calculated from the observed decrease in pressure[3] (page 86) under two assumptions: (1) that only hydrogen peroxide formed; (2) that only water formed. These calculated results were then compared with the actual pressure of hydrogen formed as determined by the gas analysis. Results showed that assumption (1) gave about twice as good results as (2), the two hydrogen pressures always lying between the values calculated on each of the two assumptions. Thus apparently about one-third of the hydrogen peroxide formed[11] decomposed to water during the run. Most of the runs lasted ten minutes; a few of them fifteen minutes.

Theoretical Discussion

The two mechanisms to be compared were as follows.

MECHANISM I

(A)	$HI + E \longrightarrow H + I$	A
(1)	$H + HI \longrightarrow H_2 + I$	k_1
(2)	$H + O_2 \longrightarrow HO_2$	k_2
(3)	$HO_2 + HI \longrightarrow H_2O_2 + I$	k_3
(4)	$HO_2 \longrightarrow H + O_2$	k_4

leading to the integrated expression

$$[H_2] = -\frac{1}{2}\Big[HI_F - HI_0 + ([O_2]k_2/k_1) \ln \frac{HI_0 + [O_2]k_2/k_1 + k_4/k_3}{HI_F + [O_2]k_2/k_1 + k_4/k_2}\Big] \qquad (I)$$

in which $[H_2]$ = the pressure of hydrogen formed during the reaction; HI_0 = the initial pressure of hydrogen iodide; HI_F = the final pressure of hydrogen iodide; $[O_2]$ = the average pressure of oxygen; all pressures being measured in millimeters.

MECHANISM II

(A)	$HI + E \longrightarrow H + I$	A
(1)	$H + HI \longrightarrow H_2 + I$	k_1
(5)	$H + O_2 + M \longrightarrow HO_2 + M'$	k_5
(3)	$HO_2 + HI \longrightarrow H_2O_2 + I$	k_3

leading to the integrated expression

$$[H_2] = -\frac{1}{2}\Big[HI_F - HI_0 + ([O_2][M]\,k_5/k_1) \ln \frac{HI_0 + [O_2]\,[M]\,k_5/k_1}{HI_F + [O_2]\,[M]\,k_5/k_1}\Big] \qquad (II)$$

in which $[M]$ = the average total pressure.

From equation (I) values of k_2/k_1 may be calculated for any assumed value of k_4/k_3. From equation II values of k_5/k_1 may be calculated directly. Results of these calculations are given in Tables I, II and III.

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(11) Bates and Salley, THIS JOURNAL, **55**, 110 (1933).

It is seen that for pairs of runs in which the only difference is the presence or absence of nitrogen (Table III) the value of k_5/k_1 remains fairly constant, whereas the value of k_2/k_1 (assuming $k_4 = 0$) is not constant. k_2/k_1 values were calculated also for values of k_4/k_3 up to 10^6, but the values of k_2/k_1 did not stay constant under any conditions. The evidence seems to show, therefore, that Mechanism II is much to be preferred to Mechanism I, and hence that the action of hydrogen atoms on oxygen molecules is a trimolecular process.

The values of k_5/k_1 show a slight variation with the O_2:HI ratio employed. This particular variation can be eliminated by using a more complicated mechanism, replacing the step H + O_2 + M with the steps:

$$\begin{array}{lll} (6) & H + O_2 + O_2 \longrightarrow HO_2 + O_2' & k_6 \\ (7) & H + O_2 + N_2 \longrightarrow HO_2 + N_2' & k_7 \\ (8) & H + O_2 + HI \longrightarrow H_2O_2 + I & k_8 \end{array}$$

For this the integrated expression is found to be

$$\frac{1}{K} = \frac{1}{(HI_0 - HI_F - 2[H_2])\,(1 + [O_2]k_8/k_1)} \ln \frac{HI_0 + K}{HI_F + K}$$

$$\text{Where } K = \frac{[O_2]\,k_6/k_1 + [O_2]\,[N_2]\,k_7/k_1}{1 + [O_2]\,k_8/k_1}$$

To simplify the calculations, it was assumed that $k_6 = k_7$. Various values of k_6/k_1 were assumed and the corresponding values of k_8/k_1 calculated. For both hydrogen and deuterium it was found that $k_8/k_1 \cong 2k_6/k_1$; hence $k_8 \cong 2k_6$.

The mean values found experimentally were as follows, the errors indicated being mean deviations.

(1) From Table I, hydrogen iodide plus oxygen
$k_5/k_1 = (1.24 \pm 0.17) \times 10^{-4}$ mm.$^{-1}$ = $(2.11 \pm 0.29) \times 10^3$ cc. mol.$^{-1}$

(2) From Table II, deuterium iodide plus oxygen,
$k_5/k_1 = (2.34 \pm 0.44) \times 10^{-4}$ mm.$^{-1}$ = $(3.98 \pm 0.75) \times 10^3$ cc. mol.$^{-1}$

The rate k_5 of the reaction H + O_2 + M varies somewhat with the nature of the third body.[12] In the present work, the third body was chiefly either oxygen or hydrogen iodide.

Moreover, the value to be assigned to k_5 depends on the value assumed for k_1, since experiment gave only the ratio of k_5 to k_1. It is known from the work of Bonhoeffer and Farkas[13] that $(k_{H + I_2})/(k_{H + HI}) \cong 100$. The reaction H + I_2 should go on every collision since the reaction has zero activation energy and there is no reason to ascribe to it a steric factor which would materially differ from unity.[14] However, the value 100 is only approximate and can be trusted only to an order of magnitude.

The constant $k_{H + HI}$ may be calculated, using the usual equation given for the number of collisions per cubic centimeter per second between the molecules of two different gases. The result is $k_{H + I_2} = 2.699 \times 10^{14}$ cc.^{2} moles^{-1} sec.$^{-1}$. Then $k_{H + HI} = 2.699 \times 10^{12}$, and $k_{H + O_2 + M} = 5.7 \times 10^{15}$. That k_5 is probably smaller than this value may be seen from the following considerations.

It was shown above that $k_{H + O_2 + HI} \cong 2k_{H + O_2 + O_2}$. If the reaction H + O_2 + HI goes on every collision, then its specific reaction rate as calculated by the method outlined by Bates[2a] (p. 460) using $\bar{\nu} = 3804$ cm.$^{-1}$, is $k_8 = 2.4 \times 10^{14}$ cc.^{3} moles^{-2} sec.$^{-1}$. This would give $k_6 \cong k_8/2 \cong 1.2 \times 10^{14}$. There are two other reasons for choosing this value rather than the maximum value of 5.7×10^{15} calculated above for H + O_2 + M.

(1) Calculation shows that if the reaction H + O_2 + O goes on every trimolecular collision, k_6 would be only 3.0×10^{14}. This makes the high value of 5.7×10^{15} seem improbable.

(2) In a study of the rate of recombination of hydrogen atoms and of the reaction H + O_2, Farkas and Sachsse[2b] found that $k_{H + H + H_2} \cong 3.4 \times 10^{16}$ cc.^{3} moles^{-2} sec.$^{-1}$, and that $k_{H + H + H_2}/k_{H + O_2 + H_2} \cong 500$. If their value for $k_{H + H + H_2}$ is used together with the value of 1.2×10^{14} for $k_{H + O_2 + O_2}$, it is seen that $k_{H + H + H_2}/k_{H + O_2 + O_2} = 283$, which is in remarkably good agreement with their ratio of 500 mentioned above. If Steiner's best value[15] for $k_{H + H + H_2} = 1.1 \times 10^{16}$ is used, $1.1 \times 10^{16}/1.2 \times 10^{14} = 91$, which is still in fair agreement with the ratio found by Farkas and Sachsse. But if Smallwood's value[16] of $k_{H + H + H_2} = 3.4 \times 10^{14}$ is used, the ratio is 3, in disagreement by a factor of over 150 with the findings of Farkas and Sachsse. Extremely poor agreement is found if the maximum value of 5.7×10^{15} for $k_{H + O_2 + M}$ is used, the ratios with the same three values of $k_{H + H + H_2}$ mentioned above being 6, 2 and 0.06, respectively.

If the value of $k_{H + O_2 + O_2}$ is taken, therefore, as 1.2×10^{14}, and compared with the calculated value for the same reaction if it went on every collision, namely, 3.0×10^{14}, it is seen that the reaction goes on at least one out of every two or

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[12] Senftleben and Hein, *Ann. Physik*, **22**, 1 (1935).

[13] Bonhoeffer and Farkas, *Z. physik. Chem.*, **132**, 235 (1928).

[14] Bates, *ibid.*, **B22**, 469 (1933).

[15] Steiner, *Trans. Faraday Soc.*, **31**, 623 (1935).

[16] Smallwood, THIS JOURNAL, **56**, 1542 (1934).

three trimolecular collisions, a result that is not at all in bad agreement with the conclusion of Bodenstein and Schenk[4] that $H + O_2 + M$ goes on every trimolecular collision. Their third body was in part oxygen, but also largely hydrogen and chlorine.

The results of the present study together with that of Farkas and Sachsse[2b] may be taken as evidence that Steiner's value[15] for the rate of recombination of hydrogen atoms is much to be preferred to Smallwood's latest value.[16] In this connection it is interesting to note that Senftleben in his most recent work[12] completely reverses his previous stand[17] with regard to the relative efficiencies of hydrogen atoms and molecules as the third body in the recombination of hydrogen atoms, bringing his latest findings in this regard into line with those of Steiner[15] and Farkas and Sachsse.[2b] This is doubly confusing in that Smallwood's method, of all those used, seems to offer the least possibility of experimental difficulty. In addition, Amdur[18] in a recent publication claims to have as yet unpublished data which confirm the results of Smallwood.

It may also be shown in this connection that if the trimolecular recombination of hydrogen atoms takes place almost wholly with hydrogen *atoms* as third body, as Smallwood[16] believes, the thermal decomposition of the molecules must proceed through activation by collision with atoms: $H + H_2 \longrightarrow 3H$. This would mean that activation by an atomic collision must be about 100 times more effective than a similar collision involving molecules. Why this should be is not at present immediately evident.

There are several reasons why an exact agreement between the values of $k_{H + O_2 + M}$ as determined by Farkas and Sachsse and ourselves should not be obtained. The third bodies (M) are different, and in addition, the re-formation of hydrogen atoms by the reaction $HO_2 + H_2$ might take place to a large extent at low oxygen pressures[2a] (p. 461). It is apparent that for a better comparison between our work and that of Farkas and Sachsse the large discrepancy between the results of Smallwood and Steiner's work on the rate of recombination of hydrogen atoms should be cleared up, and an investigation of the inhibiting effect of iodine on the reaction $H + HI$ should be included in our program of photoreaction studies.

Deuterium Atoms

The experimental results yield the relationship $\frac{k_{D + O_2 + M}}{k_{H + O_2 + M}} \times \frac{k_{H + HI}}{k_{D + DI}} = 1.89$. Kinetic theory leads to the conclusion that the rates of the two trimolecular reactions should not be a function of the masses of the hydrogen and deuterium atoms, since the increased number of collisions between the H and O_2 would be just compensated by the smaller lifetime of HO_2. On the other hand, if the full zero point energy difference (936 calories) were operative, the reaction $H + HI$ should be 7.8 times as fast as the reaction $D + DI$. Thus we are led to the belief that the zero point energies of the respective activated complexes[7] are of the same magnitude as those of the halide molecules. If this is so, the frequencies of the complex must be fairly high, calling for a dependence of the reaction rates upon mass lying between $(\mu_1/\mu_2)^{1/2}$ and $(\mu_1/\mu_2)^{3/2}$, where the μ's are reduced masses. This is in agreement with the results found.

Summary

1. Definite evidence has been given to show that the reaction between hydrogen atoms and oxygen molecules is a three-body process.

2. The experimental data yielded the following mean values (with mean errors). $k_{H + O_2 + M}/k_{H + HI} = (2.11 \pm 0.29) \times 10^3$ cc. $\times$ mole^{-1}, and $k_{D + O_2 + M}/k_{D + DI} = (3.98 \pm 0.75) \times 10^3$ cc. $\times$ mole^{-1}.

3. Evidence has been given to show that Steiner's value[15] for $k_{H + H + H_2}$ is to be preferred to the very different one given by Smallwood.[16]

4. Calculation shows that $k_{H + O_2 + O_2} \cong k_{D + O_2 + O_2} \cong 1.2 \times 10^{14}$ cm.^{2} moles^{-2} sec.$^{-1}$.

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[17] Senftleben and Riechemeier, *Physik. Z.*, **30**, 745 (1929).

[18] Amdur, This Journal, **57**, 856 (1935).