

CCCCXXVII.—*The Thermal Reactivity of Ozone in Presence of Hydrogen.*

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IN a previous communication (Griffith and McKeown, J., 1925, 127, 2087) it was noted that helium, argon, nitrogen, and carbon dioxide exert a definite positive catalytic effect on the rate of thermal decomposition of ozone at 100°, whilst oxygen retards the deozonisation. We have now extended the measurements to include the effect of hydrogen on the same reaction. The interpretation of the results is in this case complicated by the simultaneous formation of water by reaction between hydrogen and ozone; the only publication relating to this thermal reaction, so far as we are aware, is that of Pickel (*Z. anorg. Chem.*, 1904, 38, 307), who established qualitatively its occurrence at temperatures between 80° and 226°. Data of a more quantitative character have been obtained for the corresponding photochemical reaction—in ultra-violet light by Weigert and Böhm (*Z. physikal. Chem.*, 1915, 90, 194) and in the visible region by Griffith and Shutt (J., 1923, 123, 2752). In both cases, hydrogen, in addition to reacting with part of the ozone to give water, produces a marked accelerating effect on the deozonisation process itself. For example, in the experiments of Griffith and Shutt a mixture of hydrogen, oxygen, and ozone at ordinary pressure and containing 20% of hydrogen had an intrinsic rate of deozonisation about four times that obtained in the absence of hydrogen. This increase is considerably greater than that found with corresponding amounts of any of the gases helium, argon, nitrogen, and carbon dioxide for both the thermal and the photochemical mode of decomposition, but is of the same order of magnitude as the positive catalytic effect of hydrogen now obtained for the thermal decomposition.

## EXPERIMENTAL.

The apparatus and the experimental method were essentially those employed by Griffith and McKeown (*loc. cit.*). Ozonised

oxygen was generated by the method of Fischer and Massenez, which with suitable anode cooling gave a yield of ozone up to 10—11% by volume. Hydrogen was prepared by the electrolysis of a sodium hydroxide or baryta solution. The gases, collected in approximately the required proportions, were mixed and dried over-night above concentrated sulphuric acid. The exact composition of the system before reaction was obtained as follows: The ozone content of a known volume was determined iodometrically, and the hydrogen content by collecting a sample of the mixture over potassium iodide solution and sparking over water.

The glass reaction tube (Tube D of the previous communication; *loc. cit.*, p. 2088) always contained 3—5 c.c. of concentrated sulphuric acid spread along its whole length and covering about one-eighth of its inner surface. Since no part of the gaseous phase was more than 2 cm. distant from the acid surface, this disposition was considered efficient for the immediate removal of water vapour from the gaseous phase. Observations were made at two temperatures, approximately 78° and 100°, by using alcohol vapour or steam for jacketing the reaction- and compensator-tubes. The total pressure of the system (measured at 100°) ranged between 400 and 1000 mm. Hg; the content of hydrogen was varied between 2 and 50%, and the ratio of oxygen to ozone in the gas was usually about 11.

The course of the reaction was followed by time readings of the pressure increase or decrease of the system as registered by a sulphuric acid manometer. The pressure change is the sum of two opposite effects, the process of deozonisation being attended by an increase of pressure, whilst the reaction between hydrogen and ozone, with absorption of the resultant water, is accompanied by a decrease. Of special significance for purposes of calculation are (1) the maximum pressure usually attained at some time during the course of a run, and (2) the final pressure reached when all the ozone has reacted. Actually a maximum pressure was obtained only when the initial hydrogen concentration was within certain limits relative to the ozone concentration. With very low hydrogen concentrations, the pressure increased progressively and the theoretical maximum was not reached in the time of observation—usually 3—5 hours. With high hydrogen concentrations, the pressure decreased from the beginning, and either a maximum was not theoretically possible, or it occurred so near the start that it escaped detection. (On raising the temperature of the system, before significant readings could be taken, a few minutes were always necessary to allow the reaction- and compensator-tubes to attain a uniform temperature.) At 78°, where the rate of reaction is

much slower, the upper limit of hydrogen concentration, for which a pressure maximum could be recorded, was higher than at 100°.

*Interpretation of Experimental Data.*—In certain cases, a check on the manometric readings was attempted by direct analysis of the system for ozone and hydrogen after the reaction had proceeded to a considerable extent. The results of the six experiments for which this was done are in Table I, in which  $p$  is the observed pressure change (in mm. of sulphuric acid),  $a$  and  $a'$  the initial and the final concentration of ozone (g.-mol. per litre), and  $b$  and  $b'$  the initial and the final concentration of hydrogen. All except the last of these experiments were carried out at 100°.

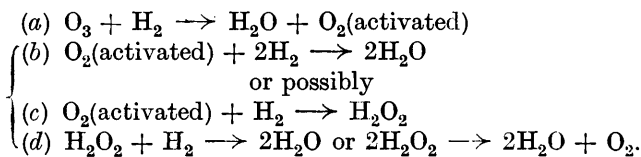
TABLE I.

$p$ .	$a$ .	$a'$ .	$b$ .	$b'$ .	$b'$ (calc.).
+20.0	0.001757	0.000042	0.004948	0.004419	0.004454
+49.5	0.003102	0.000016	0.006726	0.005879	0.005889
-16.8	0.001753	0.000055	0.007232	0.006560	0.006601
- 7.1	0.001551	0.000115	0.006472	0.005890	0.005964
+ 4.1	0.002140	0.000021	0.006570	0.005812	0.005879
-35.5	0.001670	0.000155	0.01048	0.009738	0.009837

The table shows that, whilst an appreciable amount of hydrogen reacts, the change in the concentration of hydrogen is always less than that of ozone. The figures in the last column were calculated in the following manner. In addition to the reaction (2)  $2\text{O}_3 \rightarrow 3\text{O}_2$ , there takes place a water-forming reaction which may be either (1)  $\text{H}_2 + \text{O}_3 \rightarrow \text{H}_2\text{O} + \text{O}_2$ , or (1')  $3\text{H}_2 + \text{O}_3 \rightarrow 3\text{H}_2\text{O}$ . Assuming that (1) is the reaction which occurs, then the disappearance of  $(b-b')$  mols. of hydrogen involves a pressure decrease (the water formed being absorbed by sulphuric acid) of  $A(b-b')$ , where  $A$  is a calculable constant. The total ozone reacting is  $(a-a')$  mols., of which  $\{a-a'-(b-b')\}$  mols. react according to (2), involving a pressure increase of  $A\{a-a'-(b-b')\}/2$ . The net pressure change is thus  $A\{a-a'-(b-b')\}/2 - A(b-b')$ , i.e.,  $A\{a-a'-3(b-b')\}/2$ . Equating this to the observed pressure change  $p$ , and substituting the values of  $a$ ,  $a'$ , and  $b$ , the value of  $b'$ , that is the final concentration of hydrogen, can be calculated.

There is a systematic discrepancy of about 1% between the calculated and the observed values of  $b'$ . In all probability this error is inherent in the experimental measurement of the final concentration of hydrogen, since the sample for analysis could be taken conveniently only from the reaction-tube maintained at 100° (or 78°), and containing the reacting system at a pressure greater than atmospheric. The hydrogen content obtained would tend to be too low owing to failure to obtain a representative sample of the gas mixture. An alternative cause of the discrepancy would

be the partial formation of hydrogen peroxide, but the necessary assumption that the peroxide should remain undecomposed in the gaseous phase in the presence of ozone is untenable. Unfortunately, the other stoichiometric possibility (1'), taken in conjunction with (2), leads to exactly the same calculated values of  $b'$  as in the table above, so that analytically it is impossible to differentiate between the mechanisms (1) and (1') for the disappearance of hydrogen. Thus, assuming reactions (2) and (1') to occur, the pressure decrease associated with the disappearance of  $(b-b')$  mols. of hydrogen is now  $4A(b-b')/3$ , and the pressure increase due to the deoxygenation of the remaining  $\{a-a' - \frac{1}{3}(b-b')\}$  mols. of ozone is  $A\{a-a' - \frac{1}{3}(b-b')\}/2$ . The net pressure change is thus  $A\{a-a' - 3(b-b')\}/2$  as before. From the kinetic point of view, however, reaction (1) is much more probable than (1'). If reaction (1') does occur, it will be a two-stage reaction of the type:



Another conceivable alternative for (d) would be (e)  $\text{H}_2\text{O}_2 + \text{O}_3 \rightarrow \text{H}_2\text{O} + 2\text{O}_2$ , which, in conjunction with (a) and (c), is equivalent to (1). In view of these complications, all of which it would be impossible to take into account in the kinetic treatment, we have deemed it best to base our calculations on the assumption that only reactions (1) and (2) occur. If any of the reactions (b), (c), and (d) do take place, a certain error will be introduced into the values calculated below for the intrinsic rates of reaction (2) and the reaction forming water. The error for the former cannot be very serious in the experiments with not too high partial pressures of hydrogen, and it will be in such a direction as to give too small values for the velocity coefficient  $k_2$  of the deoxygenation reaction (2). On the other hand, our calculated values of  $k_1$ , the velocity coefficient for reaction (1), will be too high if reactions (b), (c), and (d) occur; here the error will be greater, up to a maximum of three times the calculated velocity coefficient.

We assume that the two simultaneous reactions (1) and (2) conform to the bimolecular law. This is at least approximately true for the latter process in the absence of hydrogen and in tubes free from catalysing action, although the absolute value for the velocity coefficient depends upon the concentrations of oxygen and other non-reactive gases present. If the presence of hydrogen also affects the velocity of (2), this effect will probably be manifested in

the variation of the velocity coefficient with varying initial concentration of hydrogen, but the small change in the concentration of hydrogen throughout any particular run can produce very little trend in the coefficients obtaining for that run.

Accordingly, if  $x$  and  $y$  represent the amounts of ozone which have reacted after a time  $t$  according to (1) and (2), respectively, then

$$dx/dt = k_1(a - x - y)(b - x) \quad \dots \quad (3)$$

$$dy/dt = k_2(a - x - y)^2 \quad \dots \quad (4)$$

and 
$$p_t = A(\frac{1}{2}y - x) \quad \dots \quad (5)$$

where  $p_t$  is the change in pressure of the system (at constant volume) and  $A$ ,  $a$ ,  $b$ ,  $k_1$ , and  $k_2$  are as already specified. Since we do not know  $x$  and  $y$  separately at various times during a run, the evaluation of  $k_1$  and  $k_2$  can be effected only by an indirect process which is both involved and laborious. From (3) and (4) we obtain

$$dy/dx = k_2(a - x - y)/k_1(b - x) \quad \dots \quad (6)$$

the solution of which (with initial conditions  $x = 0, y = 0$ ) is

$$y = a - x + \frac{b - x}{K - 1} - \left\{ \frac{(K - 1)a + b}{K - 1} \right\} \left( \frac{b - x}{b} \right)^K \quad (7)$$

where  $K$  is written for the ratio  $k_2/k_1$ . It is now possible to evaluate  $K$ , either from the conditions obtaining at the maximum of pressure ( $p_m$ ) or from the final conditions when all the ozone has disappeared.

In the first case, at the moment when the pressure has attained a maximum value, the rate of disappearance of ozone according to reaction (2) must be just double its rate of disappearance according to (1), so that

$$2 = K_m(a - x_m - y_m)/(b - x_m) \quad \dots \quad (8)$$

where the suffix  $m$  refers to conditions at the maximum. This equation, combined with

$$p_m = A(\frac{1}{2}y_m - x_m) \quad \dots \quad (5')$$

and

$$y_m = a - x_m + \frac{b - x_m}{K_m - 1} - \left\{ \frac{(K_m - 1)a + b}{K_m - 1} \right\} \left( \frac{b - x_m}{b} \right)^{K_m} \quad (7')$$

leads to

$$\{(3b - a_1)K_m/b(3K_m - 2)\}^{K_m} = (3b - a_1)/\{(K_m - 1)a + b\} \quad (9)$$

in which  $a_1 = a - 2p_m/A$ , from which the value of  $K_m$  can be obtained by trial.

At the end, when the pressure has become constant and all the ozone has reacted (suffix  $\infty$ ), we have

$$x_\infty + y_\infty = a \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$p_\infty = A\left\{\frac{1}{2}y_\infty - x_\infty\right\} \quad . \quad . \quad . \quad . \quad . \quad (5'')$$

from which  $x_\infty$  and  $y_\infty$  separately can be calculated. By substitution of the value of  $x_\infty$  in the equation

$$b = \{(K_\infty - 1)a + b\} \left(\frac{b - x_\infty}{b}\right)^{K_\infty - 1} \quad . \quad . \quad . \quad (11)$$

which results from (10) and (7''), *i.e.*, the form assumed by (7') for  $t = \infty$ , the value of  $K_\infty$  also can be obtained by the method of trial and error.

The possibility of a preliminary test of the kinetic equations (1) and (2) is now available, since the values of  $K_m$  and  $K_\infty$  calculated as above for any particular experiment should be equal. The last two columns of Table II show that a fair agreement exists in every case between these ratios of velocity coefficients, referring as they do to two very different epochs in the history of the reacting system. The value of  $K_\infty$  is in nearly every case slightly less than the corresponding value of  $K_m$ . The latter is likely to be the more accurate, since  $K$  depends ultimately upon the relevant pressure reading (an error of about 1 mm. in this affects the value of  $K$  by nearly half a unit in most cases), and usually the final pressure difference had to be extrapolated from a knowledge of the last pressure difference read and the slight residual concentration of ozone in the reaction tube when reaction was stopped.

However, the agreement between  $K_m$  and  $K_\infty$  does not necessarily imply that (3) and (4) constitute a correct mathematical statement of the kinetic laws, since neither equation separately, but only their combination in (5), is used for the derivation of equations (9) and (11). Any alternatives to (3) and (4) which would also lead to (5) would be equally well supported by this agreement. It is necessary to calculate the separate velocity coefficients,  $k_1$  and  $k_2$ , and to find whether these, as well as their ratio, remain constant throughout the course of the two simultaneous reactions. An analytical solution of the differential equations to give, say,  $k_1$ , as a function of the variables  $p$  and  $t$  is not possible. We have therefore resorted to the following indirect method. Knowing  $K$  from the final, or preferably the maximum, conditions, the values of  $y$  and  $p$  corresponding to a series of values of  $x$  are calculated from (7) and (5), respectively. These are plotted against  $x$  and from the graphs the values of  $x$  and  $y$  corresponding to any observed pressures  $p$  at a known time  $t$  are read off. From the series of  $(x, y, t)$  data thus obtained, equations (3) and (4) can now be solved

approximately for  $k_1$  and  $k_2$  by the method of finite differences. The values thus obtained are given below.

In the tables,  $P$  represents the total pressure of the system,  $p_{O_2}$  and  $p_{H_2}$  the partial pressures of oxygen plus ozone and of hydrogen respectively (all calculated for  $100^\circ$  in mm. Hg) at the start of an experiment, and  $c$  the initial concentration of oxygen in g.-mols. per litre. The coefficients  $k_1$  and  $k_2$  are in absolute units (litres/mols.-minutes) and have been corrected from the temperature of experiment (lying for the two series of data within the limits  $99.3$ — $100.3^\circ$  and  $77.7$ — $78.2^\circ$ ) to the common temperature of  $100^\circ$  or  $78^\circ$ —this correction amounts in no case to more than a few units per cent. In general, the velocity coefficients calculated throughout a run vary irregularly by not more than 15% from the mean value tabulated. However, with concentrations of hydrogen higher than that corresponding to a partial pressure of about 200 mm., there is always a definite decrease of both  $k_1$  and  $k_2$  as the reaction proceeds; this tendency is indicated by tabulating the limits of such falling coefficients.

TABLE II.

*Hydrogen-Oxygen-Ozone Mixtures at  $100^\circ$ .*

Expt. No.	$P$ .	$p_{O_2}$ .	$p_{H_2}$ .	$a \cdot 10^6$ .	$b \cdot 10^6$ .	$c \cdot 10^5$ .	$k_1$ .	$k_2$ .	$K_m$ .	$K_\infty$ .
46	759.6	743.6	16.0	2007	689	2995	0.83	18.4	(22)	—
47	758.0	725.4	32.6	2479	1402	2870	1.14	23.0	20.22	—
43	767.8	722.3	45.5	3052	1955	2754	1.15	26.0	22.5	22.5
25	766	720.4	45.6	2597	1962	2811	1.60	28.6	17.83	15.7(?)
44	764.3	714.5	49.8	2952	2142	2776	1.17	26.5	22.5	—
48	757.4	706.7	50.7	2224	2181	2815	1.35	27.9	21.3	—
49	759.3	687.2	72.1	2069	3100	2746	1.93	36.8	19.2	—
36	768.6	691.7	76.9	2627	3332	2705	1.81	36.3	20.5	20.9
26	757.5	680.1	77.4	2701	3327	2655	2.02	37.0	18.46	17.75
27	996.6	918.6	78.0	3778	3354	3572	1.72	32.6	18.85	18.0
28	498.5	420.4	78.1	1556	3360	1652	2.60	51.9	20.0	—
29	494.3	415.7	78.6	1503	3376	1637	2.57	49.6	19.3	—
30	493.3	414.1	79.0	1625	3424	1615	2.67	53.1	20.23	18.6
31	988.3	895.4	92.9	3457	3999	3505	2.15	37.2	17.4	17.2
37	501.9	404.8	97.1	1473	4170	1591	2.78	60.4	21.5	21.0
50	841.8	728.2	113.6	2211	4884	2908	2.45	46.0	18.7	—
32	760	636.8	123.2	2032	5295	2532	2.61	47.8	18.2	17.25
38	1014	878	136.0	2917	5858	3480	2.60	53.3	20.55	19.6
52	977.0	824.1	152.9	2140	6570	3329	3.27	55.2	17.25	16.9
33	985.8	829.4	156.4	3102	6727	3256	3.19	54.8	17.15	16.5
39	786.0	629.5	156.5	2261	6515	2498	3.29	60.5	18.3	18.5
40	1029	868.2	160.8	3212	6908	3406	2.93	54.4	18.6	—
53	975.0	806.8	168.2	1753	7232	3292	3.37	56.9	17.2	16.9
41	1018	883	185.0	3075	7965	3270	3.47	62.9	18.1	—
34	753.5	459.5	294	1595	12650	1818	{ 5.7- } { 4.0 }	{ 104- } { 73 }	(18.25)	18.25
45	757.9	392.7	365.2	1374	15690	1551	{ 11.5- } { 4.6 }	{ 200- } { 80 }	(17.36)	17.36
*35	998.6	421.0	69.6	1645	2997	1645	3.17	60.7	19.06	18.2

\* In this experiment argon also was present, its concentration being  $2183 \times 10^{-5}$  g.-mol./litre.

TABLE III.

*Hydrogen-Oxygen-Ozone Mixtures at 78°.*

Expt. No.	P.	$p_{O_2}$ .	$p_{H_2}$ .	$a \cdot 10^6$ .	$b \cdot 10^6$ .	$c \cdot 10^5$ .	$k_1$ .	$k_2$ .	$K_m$ .*
10	761.2	743.7	17.5	2645	752.5	2932	0.074	1.69	(22.5)
11	329.5	311.8	17.7	1049	761.9	1236	0.135	3.06	(22.5)
12	759.6	727.8	31.77	2549	1366	2873	0.109	2.39	(22.0)
13	754.2	707.7	46.53	2390	2000	2803	0.150	3.31	(22.0)
14	758.6	706.2	52.4	2307	2253	2804	0.158	3.47	22.0
15	760.6	686.0	74.6	2228	3208	2725	0.227	4.65	20.4
16	500.2	421.8	78.44	1152	3372	1698	0.237	6.36	22.1
18	799.9	718.5	78.6	2279	3381	2872	0.256	5.41	21.1
17	501.1	420.8	80.26	1368	3450	1672	0.300	6.66	22.3
19	998	916.5	81.45	3190	3501	3620	0.216	4.56	21.22
20	830.4	720.7	109.7	2291	4716	2869	0.323	6.64	20.42
21	870.4	722.5	147.9	1883	6353	2917	0.461	8.86	19.3
22	918.8	718.5	200.3	1944	8610	2895	{ 0.68- 0.4 }	{ 12- 7 }	17.9
23	971.4	726.4	245	1963	10530	2927	{ 0.86- 0.4 }	{ 15- 7 }	17.9
24	1001	726.4	274.6	1897	11810	2931	{ 1.1- 0.4 }	{ 20- 6 }	17.6
54	978	734.3	243.7	1670	10480	2989	{ 0.62- 0.38 }	{ 10.6- 6.4 }	16.9

\* Values of  $K_m$  in parentheses have been assumed for the purpose of calculating  $k_1$  and  $k_2$ .

*Discussion of Results.*

*The Ratio  $k_2/k_1$ .*—Whilst the two values of this ratio, *viz.*,  $K_m$  and  $K_\infty$ , which can be directly calculated for each experiment are equal within the limits of our accuracy, the same agreement does not hold between the values of  $K$  referring to widely different reacting systems. Since, for any one reacting system the hydrogen and oxygen concentrations remain approximately constant, whilst the ozone concentration varies, we may conclude that  $K$  is independent of ozone but not of hydrogen or oxygen concentrations. With increasing concentration of hydrogen there is a decrease in the value of  $K$  from about 22 to 17. It is impossible to say whether or not it depends also upon the concentration of oxygen present. Again, for the same system there is no definite difference between the values of  $K$  at the two temperatures 100° and 78°, so that the temperature coefficients of the two reactions (1) and (2) are approximately identical.

*The Velocity Coefficients.*—The fact that  $K$  is not a constant independent of the composition of the reacting mixture implies that the two kinetic equations (3) and (4) are not sufficiently comprehensive in respect of the dependence of the speeds of reaction on the concentration of hydrogen and possibly also on that of oxygen; this is also evident from the marked dependence of  $k_1$  and  $k_2$  on the composition of the reaction mixture. With a constant partial pressure of oxygen of about 700 mm., the coefficient



$k_2$  of the deoxygenation process increases from its normal value of 10.4 in the absence of hydrogen to about 60 for a partial pressure of hydrogen of 150 mm., and  $k_1$  increases simultaneously, although not quite so rapidly. On the other hand, with constant partial pressure of hydrogen, the velocity coefficients definitely decrease with increasing concentration of oxygen. In Tables IV and V are summarised a few data which serve to illustrate these effects.

TABLE IV.

 Variation of  $k_1$  and  $k_2$  with  $p_{H_2}$ .

 $t = 100^\circ$ .  $p_{O_2} = 680\text{--}730$  mm.

Expt. No.	$p_{O_2}$	$p_{H_2}$	$k_1$	$k_2$
—	705	—	—	10.4
47	725	32.6	1.14	23.0
43	722	45.5	1.15	26.0
44, 48	711	50.3	1.26	27.2
26, 36, 49	686	75.5	1.92	36.7
50	728	113.6	2.45	46.0

 $t = 100^\circ$ .  $p_{O_2} = 860\text{--}920$  mm.

—	890	—	—	8.6
27	919	78.0	1.72	32.6
31	895	92.9	2.15	37.2
38	878	136.0	2.60	53.3
40	868	160.8	2.93	54.4
41	883	185.0	3.47	62.9

 $t = 78^\circ$ .  $p_{O_2} = 700\text{--}740$  mm.

—	720	—	—	1.02
10	744	17.5	0.074	1.69
12	728	31.8	0.109	2.39
13	708	46.5	0.150	3.31
14	706	52.4	0.158	3.47
18	719	78.6	0.256	5.41
20	721	109.7	0.323	6.64
21	723	147.9	0.461	8.86

TABLE V.

 Variation of  $k_1$  and  $k_2$  with  $p_{O_2}$ .

 $t = 100^\circ$ .  $p_{H_2} \approx 78$  mm.

Expt. No.	$p_{H_2}$	$p_{O_2}$	$k_1$	$k_2$
28, 29, 30	78.6	417	2.65	51.5
26, 36	77.2	686	1.92	36.7
27	78.0	919	1.72	32.6

 $t = 100^\circ$ .  $p_{H_2} \approx 156.5$  mm.

39	156.5	630	3.29	60.5
33	156.4	829	3.19	54.8

 $t = 78^\circ$ .  $p_{H_2} \approx 17.6$  mm.

11	17.7	312	0.135	3.06
10	17.5	744	0.074	1.69

 $t = 78^\circ$ .  $p_{H_2} \approx 80$  mm.

16, 17	79.4	421	0.294	6.51
18	78.6	719	0.256	5.41
19	81.5	917	0.216	4.56

One of the most striking results of this work is the very strong catalytic effect of hydrogen on the reaction  $2O_3 \rightarrow 3O_2$ , compared with that of the inert gases helium and argon. Thus at  $100^\circ$ , the value of  $k_2$  in a mixture of ozonised oxygen with helium ( $p_{O_2} = 400$  mm.,  $p_{He} = 600$  mm.) is about 17, in a mixture with argon ( $p_{O_2} = 400$  mm.,  $p_A = 600$  mm.) about 22, whilst in a mixture with the same partial pressure of oxygen but with a partial pressure of hydrogen of only 78 mm., the value of  $k_2$  is 51. This very much greater catalytic effect of hydrogen has also been observed for the photochemical reaction in visible light. The values given in the tables for  $k_2$  are minimum values, for, if the stoichiometric process (1') occurs to any extent our calculated values become too small. Moreover, the establishing of the large increase in  $k_2$  caused by the

presence of hydrogen is not dependent on the special assumptions made in the interpretation of our experimental data: confirmation may be obtained from the initial pressure readings in experiments with small partial pressures of hydrogen. Under such conditions, the reaction  $2\text{O}_3 \rightarrow 3\text{O}_2$  takes place with an initial velocity considerably greater than that of the formation of water; we may thus, with small error, neglect any pressure decrease due to the latter and equate the observed increase of pressure to that caused by the deoxygenation reaction. Values of  $k_2$  have been obtained in this way for Expts. 10—14: they agree very well with those given in Table III; naturally, owing to neglect of the water-forming reaction, they are in all cases slightly lower—usually about 10%. Confirmation of the catalytic effect of hydrogen was also obtained from the results of an experiment in which sulphuric acid was omitted from the reaction tube and the water remained as vapour. The partial pressure of hydrogen was 150 mm., that of oxygen 610 mm., and the temperature  $100^\circ$ . The increase in pressure at the start is a measure of the extent of the reaction  $2\text{O}_3 \rightarrow 3\text{O}_2$ , since the reaction  $\text{O}_3 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  is now unattended by any pressure change.\* The initial value thus obtained for  $k_2$  was 86, which is somewhat greater than the value 60.5 given in Table II for Expt. 39 in which the initial partial pressures of hydrogen and oxygen were comparable with those in the present instance. This greater value is probably due to the known fact that water vapour catalyses the decomposition of ozone.

The data of any one section of Table IV give a straight line when  $k_2$  is plotted against  $p_{\text{H}_2}$ , within the limits of the rather large experimental error; thus  $k_2 = k_2^\circ + B \cdot p_{\text{H}_2}$ , where  $k_2^\circ$  is the velocity coefficient in absence of hydrogen and  $B$  is a constant. Both  $k_2^\circ$  and  $B$ , however, are functions of the partial pressure of oxygen. An empirical expression for the dependence of  $k_2^\circ$  on  $p_{\text{O}_2}$  has already been given (Griffith and McKeown, *loc. cit.*, p. 2092). The coefficient  $B$  certainly decreases with increasing partial pressure of oxygen, possibly in a manner similar to  $k_2^\circ$ , but our results are not sufficiently accurate to enable us to deal quantitatively with this point.

Table II includes the results of Expt. 35 in which argon was also present; the velocity coefficient  $k_2$  in this case is certainly greater than the value which would have been obtained in the same system in the absence of argon, but the relative smallness of the effect would suggest either that argon affects the term  $k_2^\circ$  only, or that its effect on the coefficient  $B$  is slight.

In view of the doubt as to whether the stoichiometric process

\* If the reaction  $\text{O}_3 + 3\text{H}_2 \rightarrow 3\text{H}_2\text{O}$  takes place, it would cause the calculated value of  $k_2$  to be too low.

(1') actually occurs or not, the values tabulated for  $k_1$  are subject to a much greater possible error than those of  $k_2$ . There is no doubt, however, that the value of  $k_1$  is considerably smaller than that of  $k_2$ , and also that the conditions which favour an increase in  $k_2$  have a similar effect on  $k_1$ , so that the two reactions, the deoxygenation process and the formation of water, are coupled in some way.

*Temperature Coefficients and Reaction Mechanism.*

The temperature coefficient of  $k_2$  in the absence of hydrogen was determined (for three different partial pressures of oxygen) by following the pressure change of the same system for some time at 78° and then at 100°. The results are given in Table VI.

TABLE VI.

$p_{O_2}$ .	$k_2$ ( $t = 100^\circ$ ).	$k_2$ ( $t = 78.1^\circ$ ).	$E$ .
332	17.8	1.70	27,960
743	9.5	0.925	27,750
1010	7.72	0.76	27,600

The values calculated for  $E$  are derived from the Arrhenius equation  $d \log k_2/dT = E/RT^2$ ; they correspond to a temperature coefficient  $k_{t+10}/k_t$  of 2.9. The mean value of  $E$  is 27,770 cal., as compared with 26,740 (Warburg, *Ann. Physik*, 1902, **9**, 1286) and 26,130 (Clement, *ibid.*, 1904, **14**, 342). The temperature coefficient of  $k_2$  (and also that of  $k_1$ ) decreases with increasing partial pressure of hydrogen. Thus, with  $p_{H_2} = 78$  mm. and  $p_{O_2} = 710$  mm. the value of  $E$  is 23,700 cal., corresponding to a temperature coefficient of 2.48. Values of the latter intermediate between 2.9 and 2.48 are obtained with lower partial pressures of hydrogen. The temperature coefficients of  $k_2$  and  $B$  (see p. 3162), as deduced from the data at 78° and 100°, are 2.9 and 2.4 respectively, and thus the temperature coefficient of  $k_2$  for any reaction mixture containing hydrogen will lie between these limits, becoming 2.4 in presence of a large excess of hydrogen. The temperature coefficient of  $k_1$  varies similarly.

The temperature coefficient 2.9 for the deoxygenation reaction in absence of hydrogen is much higher than what would be expected for a homogeneous bimolecular reaction taking place with measurable speed at 100°. Using the well-known kinetic expression for the velocity coefficient of such a reaction,

$$k_2 = 2\sigma^2 \sqrt{\frac{4\pi RT}{M}} \cdot \frac{N_0}{1000} \cdot e^{-E/RT} \quad . \quad . \quad (12)$$

[in which  $\sigma$  = the diameter of the ozone molecule (taken as  $2.10 \times 10^{-8}$  cm.),  $N_0 = 6.06 \times 10^{23}$ , and  $E = 27,770$ ],  $k_2$  is found

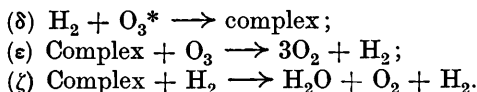
to be of the order  $10^{-4}$  (in the units used) at  $100^\circ$ , whereas the experimental values of  $k_2$  are about 100,000 times greater. To account for our observed velocity coefficients on the basis of the above equation, we should have to employ a value  $E = 19,000$  cal. (approx.). This discrepancy appears to be much greater than any possible experimental error. It may be suggested that in these experiments it is not a homogeneous change but mainly a "wall" reaction which is being measured; but, if this were so, the true value of  $E$  (for the homogeneous change) would be still greater than 27,700 cal. and no detectable decomposition of ozone at  $100^\circ$  by a homogeneous change should be possible. Chapman and Clarke (J., 1908, 93, 1638), however, found an easily measurable rate of decomposition at this temperature, the rate being independent of the ratio area/volume of the reaction vessel, so that the measured reaction was predominantly homogeneous. Moreover, our velocity coefficients at  $100^\circ$  are nearly equal to those calculated from the data of Chapman and Clarke (*loc. cit.*) and of Chapman and Jones (J., 1910, 97, 2463). The above suggestion is therefore not valid.

Granted that the change is homogeneous, a solution of the difficulty might perhaps be obtained by the following considerations. The equation (12) for the velocity coefficient is based on the assumption that all the energy increment of 27,700 cal. necessary for reaction is associated, before collision, with a single degree of freedom of one of the reacting molecules; a velocity coefficient of essentially the same magnitude also follows from the assumption that the total energy of activation is derived from the translatory energy of the colliding molecules. A very much greater value of  $k_2$  can, however, be obtained if it be assumed that the total energy of activation is shared, before collision, between a number of degrees of freedom (external and internal) of the reacting molecules. For example, limiting ourselves to the internal degrees of freedom, if these be  $n$  in number for each of the colliding ozone molecules, the expression (12) would be multiplied by  $(E/RT)^{n+1}/(n+1)$  (compare Rideal and Lewis, *J. Amer. Chem. Soc.*, 1926, 48, 2559). Since  $E/RT$  in the present case lies between 37 and 40, it would only be necessary to assume  $n = 3$ , thus making this multiplying factor of the order of  $10^5$ , to account for the discrepancy; this could be interpreted in the sense that the energy of activation is resident in the six degrees of freedom either of rotation or of vibration of the two colliding ozone molecules.

An alternative possibility is that the deozone process involves a "chain" mechanism in somewhat the same sense as postulated by Christiansen and Kramers (*Z. physikal. Chem.*, 1923, 104, 451) for the case of unimolecular reactions. The decomposition

of ozone is certainly sufficiently exothermic to permit of the resultants having an excess energy greater than that necessary for the activation of fresh reactants. But whilst the possibility of short reaction-chains cannot be ignored, the moderate quantum yields obtained in the corresponding photochemical process (where the resultant oxygen molecule would possess excess energy in even greater amounts) make it highly improbable that in the thermal process the reaction-chains could be of the enormous length required to account for the discrepancy.

In a previous paper (Griffith and McKeown, *loc. cit.*), a formal mechanism for the thermal decomposition of ozone was suggested involving the reaction stages ( $\alpha$ )  $O_3 \rightarrow O_3^*$ ; ( $\beta$ )  $O_3^* + O_3 \rightarrow$  complex; ( $\gamma$ ) complex  $\rightarrow 3O_2$ , together with the assumption that ( $\gamma$ ) and the reversal of ( $\beta$ ) could take place either spontaneously or by collision of the complex with other molecules, the nature of which decided the relative probabilities of these changes. The addition to the system of hydrogen, which has an accelerating effect much greater than that of helium, argon, or nitrogen, introduces a complication, *viz.*, the simultaneous occurrence of the reaction  $H_2 + O_3 \rightarrow H_2O + O_2$ . The fact that this process is coupled in some way with the deozoneisation reaction would suggest, as a possible explanation of the catalytic effect of hydrogen, the formation of an intermediate compound ( $H_2O_3$ ) which could decompose in two ways ( $\epsilon$  and  $\zeta$ ), either to form water or to yield oxygen. Thus, in the presence of hydrogen, in addition to reactions ( $\alpha$ ), ( $\beta$ ), and ( $\gamma$ ), the following would also occur :



In order to obtain a qualitative agreement with our experimental data, it is further necessary that the complex ( $H_2O_3$ ) should decompose to yield water only on collision with a hydrogen molecule. The complete scheme entails deozoneisation by reactions ( $\gamma$ ) and ( $\epsilon$ ).

However, the effect of hydrogen upon the complex ( $O_6$ ) molecule resulting from stage ( $\beta$ ) must also be considered. By analogy with the cases of argon, helium, and nitrogen it is probable that the stage ( $\gamma$ ) will be catalysed to some degree by collision of the complex with hydrogen molecules; but there is also the possibility that such collisions will occasionally lead to water formation:  $H_2 + (O_6) \rightarrow H_2O + O_2 + O_3$ . The occurrence of this last process to any extent would enhance the coupling between the net deozoneisation and the net water-formation, and make the ratio of the coefficients

$k_2/k_1$  much less dependent on the partial pressure of hydrogen than would otherwise be the case.

On the basis of these considerations, the observed variation of the temperature coefficient of  $k_2$  (and also of  $k_1$ ) with the hydrogen content implies a difference in the temperature coefficients of the primary reactions which yield the two complexes ( $O_6$ ) and ( $H_2O_3$ ). The temperature coefficient for the first is 2.9, that for the second is 2.4 (the value obtained with a large excess of hydrogen), and if deoxygenation takes place through the medium of both the complexes, the observed temperature coefficient in any mixture will lie between these limits. The same conclusion applies to the observed temperature coefficient of the water-forming reaction, provided that this also involves collision of the ( $O_6$ ) complex with hydrogen.

*Summary.*

Reaction-velocity measurements have been made in mixtures of ozone, oxygen, and hydrogen at 78° and 100°. Two reactions occur—the deoxygenation process  $2O_3 \rightarrow 3O_2$ , and a water-forming reaction which is most probably  $H_2 + O_3 \rightarrow H_2O + O_2$ .

The values of  $k_2$  and  $k_1$ , the respective bimolecular velocity coefficients, both increase markedly with increasing partial pressure of hydrogen, but decrease with increasing partial pressure of oxygen. The ratio  $k_2/k_1$  varies relatively slightly with the composition of the gas mixture, lying between 22 and 17 at both temperatures.

The temperature coefficient of  $k_2$  in the absence of hydrogen is 2.9; in the presence of excess of hydrogen it is reduced to 2.4.

A discussion of these results and a possible explanation of the coupling of the two reactions are given.

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