173. *Reaction Mechanism of the Oxidation of Hydrogen Bromide.*

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Experiments have been made to elucidate the mechanism of hydrogen bromide oxidation in the temperature range 490—635°. The velocity constants depend on the total pressure. Corresponding to this fact a reaction scheme is suggested, the accuracy of which is shown by the constancy of the computed velocity constants. The activation energy and the steric factor proved to be plausible values. With the aid of these quantities the calculated velocity constants agree quite satisfactorily with the empirical ones.

HITHERTO the only publications relating to this reaction have been mainly of a qualitative nature (Ballard, *Ann. Chim. Phys.*, 1826, **32**, 349; *Pogg. Ann.*, 1826, **8**, 321; Richardson, *J.*, 1887, **51**, 804), the work of Berthelot (*Compt. rend.*, 1878, **87**, 670; *Ann. Chim. Phys.*, 1879, **16**, 446) and Abel (Abegg's "Handbuch," Bd. IV, 2, 5, 276) not being of sufficient accuracy. In Harteck and Kopsch's experiments (*Z. Elektrochem.*, 1930, **36**, 715) the oxidation was effected by oxygen *atoms*, so was not relevant to our work. We therefore investigated the reaction by a modern technique.

EXPERIMENTAL.

Apparatus.—The reactants were mixed in a vessel of resistance glass, and the pressure change of the reaction $4HBr + O_2 = 2H_2O + 2Br_2$ was measured by a Bodenstein quartz spiral manometer, used as a null instrument. The reaction vessel was separated from the other parts of the apparatus by a Bodenstein glass valve. The connexion between the resistance glass, the normal glass, and the quartz tube was made by a ground-glass joint, which was also secured by sealing wax. The vessel was heated in an electric furnace of high heat capacity, and temperature was regulated by rheostats and checked by an electric pyrometer. The gases were kept in stock vessels, which led into the common pipe of the glass valve. The apparatus was exhausted by a mercury-diffusion pump.

Preparation of Gases.—The hydrogen bromide was prepared by Fileti's method (*Gazzetta*, 1891, **21**, 64). The evolved hydrogen bromide was scrubbed on glass beads covered with red phosphorus, suspended in a concentrated solution of hydrogen bromide, then conducted through six freezing-out tubes, the temperatures of which were arranged at intervals from −20° to −80°, so as to free it from the last traces of water. The pure gas condensed in the final tube was distilled into the stock vessel, the first and the last fraction being rejected.

The oxygen, from a cylinder, was purified by Stock and Ritter's method (*Z. physikal. Chem.*, 1926, **124**, 210). The gas was conducted through concentrated alkali, then over granulated calcium chloride and phosphoric oxide. The nitrogen was led over heated copper and through concentrated potassium hydroxide, then over calcium chloride and phosphoric oxide to free it from traces of water.

In an experiment the order of introduction of the gases was hydrogen bromide, nitrogen, and oxygen.

Results.—At 166° no reaction was detectable, and between 345° and 435° it was very slow, so we conducted experiments at 490°, 520°, 550°, 560°, 575°, 605°, and 635°.

As the simplest mechanism of the oxidation we assumed the following sequence (k_1, k_2, and k_3 being the velocity constants):

$$HBr + O_2 = HOOBr \quad \ldots\ldots\ldots\ldots \quad k_1$$

$$HOOBr + HBr = 2HOBr \quad \ldots\ldots\ldots\ldots \quad k_2$$

$$HOBr + HBr = H_2O + Br_2 \quad \ldots\ldots\ldots\ldots \quad k_3$$

From Bodenstein's principle of the stationary concentration of intermediate products, this leads to

$$-d[HBr]/dt = 3k_1[HBr][O_2] \quad \ldots\ldots\ldots\ldots \quad (1)$$

The velocity constant was calculated from the equation $dx/dt = k(a - x_1)(b - x_2)$ from point to point. The measured constant, k, would therefore be equal to $3k_1$.

The course of some typical experiments is shown in Table I. The velocity constants thus obtained were reasonably constant for any one experiment (although decreasing slightly) but they rose rapidly with decreasing initial pressure, as shown in col. 4 of Table II. This inhibitory influence of total pressure could be interpreted by insertion of another stage involving a slackening by any gas molecule M:

$$HOOBr + M = HBr + O_2 + M \quad . \; . \; . \quad \text{velocity constant } k_1'.$$

This leads to the equation

$$-\frac{d[HBr]}{dt} = \frac{3k_1[HBr][O_2]}{1 + k_1'[M]/k_2[HBr]} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Calculation from this formula is complicated because k_1'/k_2 occurs in the denominator, but by trial, a value of 6 for this ratio was found to lead to satisfactory constancy (see col. 5, Table II). However, this value was independent of temperature, and a similar phenomenon is to be found in the combination of hydrogen and bromine.

TABLE I.

Experiments at 575°.

Time. mins.	Press., mm.	Δp.	$\Delta p/\Delta t$.	$3k_1\times 10^4$. from (1).	$3k_1\times 10^3$. from (2).	Time, mins.	Press., mm.	Δp.	$\Delta p/\Delta t$.	$3k_1\times 10^4$. from (1).	$3k_1\times 10^3$. from (2).
No. 50. $[O_2]$ = 40·0 mm.; [HBr] = 213·0 mm.											
0	253	—	—	—	—	21	233	20	0·50	1·9	2·2
3	247	6	2·0	3·1	2·75	37	228	25	0·31	1·8	2·4
6	243	10	1·3	2·6	2·5	45	226	27	0·25	1·8	2·5
10	239	14	1·0	2·45	2·5	55	224	29	0·20	1·9	2·8
15	236	17	0·6	1·8	1·9	72	221	32	0·176	2·6	(4·3)
No. 52. $[O_2]$ = 203·0 mm.; [HBr] = 104·0 mm.											
0	307	—	—	—	—	25	289·5	17·5	0·214	0·34	1·8
3	299	8	2·67	1·9	4·9	35	288	19	0·150	0·29	1·8
6	296·5	10·5	0·83	0·70	2·1	45	286·5	20·5	0·150	0·37	3·0
10	293	14	0·87	0·97	3·6	55	286	21	0·10	0·31	2·9
18	291	16	0·25	0·33	1·5	65	284	23	0·15	0·09	(9·9)
No. 55. $[O_2]$ = 40·0 mm.; [HBr] = 122·3 mm.											
0	162·3	—	—	—	—	20	148·8	13·5	0·283	1·6	2·2
3	155·3	7·0	2·3	7·5	(8·1)	32	146·3	16·0	0·208	1·5	2·4
5	153·7	8·6	0·8	2·9	3·3	43	144·3	18·0	0·181	1·6	3·0
8	152·5	9·8	0·4	1·6	1·9	55	142·7	19·6	0·133	1·5	3·0
14	150·5	11·8	0·33	1·6	2·0	71	140·8	21·5	0·118	1·5	(3·7)
No. 175. $[O_2]$ = 122·9 mm.; [HBr] = 128·8 mm.											
0	251·7	—	—	—	—	20	229·5	22·2	0·340	0·84	3·0
2	242·2	9·5	4·75	4·6	(7·8)	28	227·3	24·4	0·275	0·89	4·0
5·5	236·8	14·9	1·54	2·1	(4·4)	40	225·9	25·8	0·117	0·47	2·5
8	235·0	16·7	0·72	1·1	2·6	51	225·1	26·6	0·073	0·34	2·1
11	233·1	18·6	0·63	1·1	3·0	70	223·5	28·2	0·084	0·56	(4·7)
15	231·2	20·5	0·47	1·0	3·0						
No. 63. O_2 = 80·5 mm.; HBr = 81·6 mm.; N_2 = 160·7 mm.											
0	322·8	—	—	—	—	25	311·6	11·2	0·186	0·73	3·8
3	319·0	3·8	1·27	2·5	(7·4)	33	310·7	12·1	0·113	0·50	2·8
7	316·2	6·6	0·70	1·7	(6·1)	45	309·8	13·0	0·075	0·38	2·4
12	314·3	8·5	0·38	1·1	(4·5)	60	308·7	14·1	0·073	0·44	3·25
18	312·9	9·9	0·23	0·79	3·6	110	307·4	15·4	0·026	0·20	1·9
No. 66. O_2 = 29·6 mm.; HBr = 150·0 mm.; N_2 = 119·4 mm.											
0	299·0	—	—	—	—	32	285·5	13·5	0·200	1·3	2·4
3	295·2	3·8	1·27	3·6	(5·1)	45	283·7	15·3	0·138	1·1	2·2
7	293·8	5·2	0·35	1·1	1·6	60	282·1	16·9	0·106	1·0	2·2
11	291·2	7·8	0·65	2·5	3·9	75	280·0	19·0	0·140	1·8	4·2
16	289·0	10·0	0·44	2·0	3·4	100	278·0	21·0	0·080	1·4	3·7
22	287·5	11·5	0·25	1·3	2·3	140	276·6	22·4	0·035	0·80	2·3

Note to Table.—The first, and sometimes the second, value of the velocity constants was higher than the later ones. We could not find any reason for this. Later, the process became stabilized and the velocity constants became suitably constant for one experiment. For the calculation of the mean values of the velocity constant only these stabilized values were taken. In Tables II and III the relation between the corresponding partial pressures and the mean velocity constants cannot be examined exactly, because the partial pressures given are initial values. The velocity constants in the tables were only calculated after the second or third readings, when the partial pressures, especially in the case of HBr, differ already considerably from the initial values. The strict validity of formula (2), as is shown by the experiments cited, refers only to this stabilized zone.

TABLE II.

Experiments at 575° (*concentrations in mm. of* Hg).

p_{O_2}.	p_{HBr}.	Total press.	$3k_1 \times 10^4$ from (1).	$3k_1 \times 10^3$ from (2).	p_{O_2}.	p_{HBr}.	Total press.	$3k_1 \times 10^4$ from (1).	$3k_1 \times 10^3$ from (2).
258·6	60·0	318·6	0·18	2·8	40·0	122·3	162·3	1·55	2·6
203·0	104·0	307·0	0·33	2·4	142·5	75·1	217·6	0·58	2·2
122·9	128·8	251·7	0·79	2·9	40·0	213·0	253·0	1·85	2·4
121·0	118·0	239·0	0·89	2·7	41·8	157·3	199·1	1·93	2·4
100·1	106·4	206·5	1·1	3·3	118·7	293·7	412·4	1·55	3·3
102·0	97·0	199·0	1·2	3·2	34·2	115·0	149·2	1·62	2·25
56·7	112·5	169·2	1·4	2·9					

TABLE III.

Experiments at 575° (*concentrations in mm. of* Hg).

p_{O_2}.	p_{HBr}.	p_{N_2}.	Total press.	$3k_1 \times 10^4$ from (1).	$3k_1 \times 10^3$ from (2).	p_{O_2}.	p_{HBr}.	p_{N_2}.	Total press.	$3k_1 \times 10^4$ from (1).	$3k_1 \times 10^3$ from (2).
46·6	65·3	264·1	376·0	0·39	2·5	29·6	150·0	119·4	299·0	1·51	2·8
80·5	81·6	160·7	322·8	0·69	2·9	50·0	202·5	98·4	350·9	1·03	2·2
122·0	62·6	119·7	304·3	0·65	3·5	42·1	158·9	315·2	516·2	0·91	3·7
56·0	99·6	99·6	255·2	0·95	2·6	50·2	200·3	99·1	349·6	1·56	3·4
59·4	119·8	59·7	238·9	1·62	2·9						

TABLE IV.

Experiments at 635° (*concentrations in mm. of* Hg).

p_{O_2}.	p_{HBr}.	p_{N_2}.	Total press.	$3k_1 \times 10^3$ from (2).	p_{O_2}.	p_{HBr}.	p_{N_2}.	Total press.	$3k_1 \times 10^3$ from (2).
51·4	143·5	—	194·9	11·0	57·1	193·0	94·8	344·9	4·5
38·9	91·2	109·9	240·0	12·7	61·7	54·0	291·8	406·5	38·1
260·4	187·6	—	248·0	7·7	60·9	183·2	—	244·1	8·7
200·8	106·4	—	307·2	13·7	177·4	88·6	—	266·0	12·1
104·2	102·3	98·6	324·9	9·51	101·8	103·0	—	204·8	11·8

As M stands for any molecule, an inert gas also accelerates the decomposition of the complex HOOBr, by which the reaction has been inhibited. In many experiments we have diluted the concentration of the reactants with nitrogen, thus increasing the total pressure. The results are summarised in Table III.

The experiments at 490°, 520°, 550°, 560°, and 605° led to the same result. The velocity constant depends in just the same way upon the total pressure, as the added neutral gas slackens the reaction according to equation (2).

The mean values of all experiments are summarised in the Table V.

Experiments at 635° did not give reproducible constants (see Table IV), especially with vessels that had undergone long heating at this temperature, and we attribute this to a change in the structure of the wall of the vessel. That this lack of constancy is not due to impurities in the gas follows from control experiments at 575°, which were satisfactory.

Homogeneity of the Reaction.—As a further test of the homogenity of the reaction, we increased the ratio of surface to volume about 70-fold by filling the vessel with capillary rings of the same glass, and although the constants were slightly different from those obtained before (being higher at low temperatures and *vice versa*), the deviation was of a smaller order of magnitude than the above ratio, and we deduce that the glass wall is only responsible for less than 5% of the total reaction.

Discussion.—It is first necessary to convert k from the units mm./min. to mols. l.$^{-1}$ sec.$^{-1}$, and the values of log k_c thus obtained are in line 2 of Table V. From the data at 833° and 878° K., and with log k_1 = 0·353 and 0·150, respectively, we obtain the activation energy $Q = 37{\cdot}3$ kcals. From this we determine the theoretical values of k_c by the formula

TABLE V.

t° C.	490	520	550	560	575	605
T°, K.	763	793	823	833	848	878
$k_p \times 10^3$, exp.	0·3878	1·39	2·028	2·308	3·003	7·941
log k_c, exp.	−0·979	−0·494	−0·228	−0·150	−0·045	0·353
log k_c, calc.	−1·034	−0·616	−0·236	−0·117	0·062	0·398

$$\log k_c = -Q/4{,}571T + \tfrac{1}{2}\log T + \log Z_0 + \log f \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where Z_0 is the collision number at 1° K. and f is the steric factor. For the calculation of Z from the formula

$$Z = 5{\cdot}64 \times 10^{28}\, s_1\, s_2 \sqrt{T}\,\sqrt{(M_1 + M_2)/M_1M_2}$$

we have M_1 (for HBr) = 82·294; M_2 (for O_2) = 32·000; s_1 (for HBr) = 3·06 A.; s_2 (for O_2) = 3·2 A.; whence we find log Z_0 = 10·061 mols. l.$^{-1}$ sec.$^{-1}$ at 1° K. Insertion of this value into (3) with one value of k_c gives $\log f = -1{\cdot}826$ or $f = 0{\cdot}015$, a value often found in similar reactions. Substitution of this value in the equation giving k_c leads to the values in line 3 of Table V. The agreement between the experimental and the calculated values, coupled with the plausible values for Q and f, affords strong support for the mechanism outlined.

No information can be obtained as to the individual values of k_1' and k_2, their ratio having been found by trial and error. If k_1'/k_2 is made larger than 10 or smaller than 0·1, k_c becomes markedly dependent upon pressure. Moreover, the ratio 1 leads to an improbably small value of f, whereas if $k_1'/k_2 = 10$, $\log f = -1{\cdot}355$, the probable upper limit.

Hence, the oxidation of hydrogen bromide is a catalysed reaction type. The added inert gas inhibits the process. The inhibitory effect is manifested by the decomposition of the intermediate complex. The oxidation of hydrogen bromide is therefore, in our opinion, unique as a case of a negative catalysis through deactivation in a thermal reaction, no examples of this kind of catalysis having yet been reported (see Schwab, Taylor, and Spence, "Catalysis," New York, 1937).

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