746. *A Potentiometric Study of the Reduction by Potassium Iodide of Potassium Bromate in Sulphuric and Hydrochloric Acid Solutions.*

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Bromic acid can be accurately titrated potentiometrically with potassium iodide in sulphuric acid solutions over a wide range of concentration, but in hydrochloric acid solutions only when the acid concentration is not greater than 0·2N. In neither of these solutions is the mechanism of the reduction process given by the equation $BrO_3' + 6I' + 6H^{\cdot} \longrightarrow 3I_2 + 3H_2O + Br'$. Examination of the curves obtained leads to the two reaction sequences shown on p. 3892.

THIS work was undertaken to ascertain whether bromates in acid solution could be determined by potentiometric titration with potassium iodide. The first titrations, made on potassium bromate in dilute hydrochloric acid solution, revealed that, although apparently satisfactory redox titration curves could be obtained, their final inflections did not correspond with the theoretical equation $KBrO_3 + 6KI + 6HCl \longrightarrow 6KCl + 3I_2 + KBr + 3H_2O$, for not only were less than 6 mols. of potassium iodide needed, but the results were never reproducible. A systematic study was therefore made of the effects of the concentration of hydrochloric and sulphuric acid on the mode of the reduction of bromic acid with hydriodic acid in order (i) to find whether the potentiometric titration of bromates is possible and (ii) to gain some insight into the nature of individual reactions that occur.

It seemed probable that the premature variable inflections in the curves might have been caused by the slowness of the reaction between bromic and hydriodic acids (see, *inter alii*, Ostwald, *Z. physikal. Chem.*, 1888, **2**, 127; Meyerhoffer, *ibid.*, p. 585; Noyes, *ibid.*, 1895, **18**, 118; 1896, **19**, 599).

EXPERIMENTAL

Potentiometric Titration of Potassium Bromate by Potassium Iodide.—(1) *In sulphuric acid solution.* Fig. 1 gives typical curves showing the effect on the redox potentials, set up at bright platinum electrodes, of an increasing concentration of sulphuric acid. They refer to the titration at 20° of 100 c.c. of 0·005M-potassium bromate containing severally 2, 5, 10, and 20 c.c. of concentrated sulphuric acid (as indicated by numerals on the curve); for the first three titrations, N-potassium iodide was the titrant, and for the last 0·1N-iodide. The abscissæ give the number of mols. of iodide added per mol. of bromate.

The first addition of iodide immediately gave the solution an orange tinge which on stirring changed to a pale yellow. This colour persisted until the first inflections were reached, after which one drop of the iodide caused the colour to change suddenly to that of iodine, which soon began to be precipitated. To ensure the reproducibility of the observed E.M.F.s (within 1 mv) two bright platinum electrodes (1 cm. × 1 cm.) were used and the solution undergoing titration was connected through a " salt bridge " of saturated potassium chloride solution to a normal calomel electrode.

The theoretical end-point, *i.e.*, 6 mols. of iodide per 1 mol. of bromate, is indicated in the first three titrations by well-defined inflections, but in the fourth curve the high concentration of sulphuric acid (*ca.* 8N) causes a premature inflection at 5·8 mols. of iodide. In each of the first three curves, inflections also appear with 1·67 mols. and in the last with 0·9 mol. In the third curve, too, a small inflection is discernible with 0·9 mol.

Fig. 1.

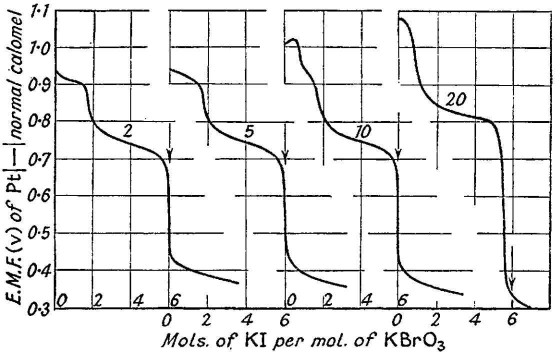
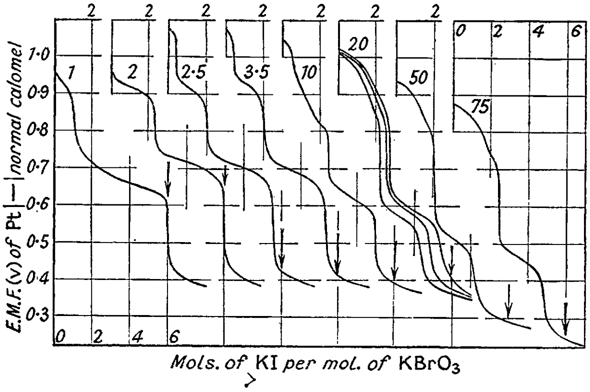


Fig. 2.



(2) *In hydrochloric acid solution.* In Fig. 2 are given similar curves for the titration by N-potassium iodide of a similar solution containing the volumes (c.c.) of concentrated hydrochloric acid denoted by the numerals. The three curves marked " 20 " show the effect of allowing greater time, after each addition of reductant, for the reaction to proceed before observing the E.M.F.s, those from left to right corresponding to readings after 1, 2, and 5 minutes' vigorous stirring after each addition. The other E.M.F.s were observed after 2 minutes' stirring after each addition, except that in the " 50 " curve potentials were recorded after 1 minute.

The colour changes resembled those in the presence of sulphuric acid, but it was only in the " 1 " and " 2 " titrations that iodine was precipitated. These two titrations were exceptional also in that the final inflections occurred when the stoicheiometric quantity of potassium iodide, 6 mols., had been added; in the more acid solutions they appeared prematurely, as shown in Table 1.

TABLE 1.

	First section :	Final section :				First section :	Final section :		
	Mols. of KI at					Mols. of KI at			
Curve	Prel. infln.	1st Infln.	2nd Infln.†	*f* *	Curve	Prel. infln.	1st Infln.	2nd Infln.†	*f* *
1	—	1·00	6·00	—	20 (i)	—	2·15	4·32 (4·30)	0·72
2	—	2·40	6·00	—	20 (ii)	—	2·45	4·90 (4·90)	0·82
2·5	0·22	2·10	5·60	—	20 (iii)	—	2·67	5·40 (5·34)	0·89
3·5	0·40	2·16	5·36	—	50	—	2·08	5·20 (4·16)	0·69
10	0·55	2·46	4·90 (4·92)	0·82	75	—	2·48	4·92 (4·96)	0·83

* See p. 3891. † The values in parentheses are double those at the first inflection.

(3) *Effect of Time on the Reactions occurring during Potentiometric Titration by Potassium Iodide of Potassium Bromate in Hydrochloric Acid Solution.*—The redox curves depicted in Fig. 3 show a reproduction of curve " 50 " from Fig. 2 (heavy line) together with curves corresponding to titrations of identical solutions to which had been added the amounts of potassium iodide shown in Table 2. Titrations were completed after the solutions had been kept in stoppered bottles for the times stated, with intermittent shaking. In this way it was hoped to ascertain in which stage of the titration the slow reaction occurs. The solutions were pale yellow during the first section and red during the second.

TABLE 2.

	KI,		Time	KI, mols.				KI,		Time	KI, mols.		
Curve	c.c.	mols.	(hr.)	1st Infln.	2nd Infln.	*f*	Curve	c.c.	mols.	(hr.)	1st Infln.	2nd Infln.	
" 50 "	0	0	0	2·08	4·20	0·69	*F*	1·50	3·00	24	3·00 (?)	5·96	1·00
A	0·50	1·00	26	2·64	5·28	0·88	*G*	1·80	3·60	44	—	5·94	—
B	0·80	1·60	27	2·84	5·66	0·95	*H*	2·00	4·00	28	—	5·96	—
C	1·00	2·00	24	2·86	5·74	0·95	*I*	2·25	4·50	40	—	5·92	—
D	1·10	2·20	4	2·76	5·56	0·92	*J*	3·00	6·00	48	—	—	—
E	1·45	2·90	5	2·90	5·80	0·97							

DISCUSSION

Fig. 1 shows that, provided the concentration of sulphuric acid is not too high, it is possible to titrate potassium bromide with potassium iodide potentiometrically. Accurate results were obtained when the normality of the sulphuric acid was as high as 4, but in the presence of *ca.* 8N-acid the end-point inflection appeared prematurely, probably owing to some decomposition of the hydriodic acid by the sulphuric acid. In hydrochloric acid, however, as the first two curves in Fig. 2 show, it is only when its concentration is exceedingly low, *viz.*, 0·1—0·2N, that the final inflections appear at the theoretical point. With greater concentrations of hydrochloric acid the final inflections are produced with less than 6 mols. of potassium iodide, the amounts depending on the time taken to perform the titration, but as demonstrated by Fig. 3, the final inflection is very near the theoretical titre if a long time is allowed for completion of the reaction.

Earlier inflections occur in all the curves of Figs. 1 and 2 at points which correspond with an abrupt change in colour from a pale yellow to the orange-red imparted by free iodine. It is obvious that more than one reaction took place, so in those titrations in which accurate end-point inflections were obtained the theoretical equation can only be true in a composite sense in that it gives no information regarding the mechanism of the reduction.

It would be inferred from the standard redox potentials of the two systems :

$$BrO_3' + 6H^{\bullet} \longrightarrow 3H_2O + \tfrac{1}{2}Br_2 + 5\text{F}, \ \varepsilon_0 = 1{\cdot}52 \text{ volt}$$

and

$$BrO_3' + 6H^{\bullet} \longrightarrow 3H_2O + Br' + 6\text{F}, \ \varepsilon_0 = 1{\cdot}44 \text{ volt}$$

that the first stage in the reduction of the bromate ion would be to bromine itself, although the relative closeness of the two standard potentials might cause some reduction to bromide ions. Furthermore, the standard redox potential of the system $IO_3' + 6H^{\bullet} \longrightarrow 3H_2O + I' + 6\text{F}$ is 1·085 V, whence it appears that as a result of the oxidation of iodide to iodate by bromate, reduction of the bromate to bromine or bromide ions should be possible. If in acid solution the bromate is reduced to (*a*) bromine, then the reaction would be

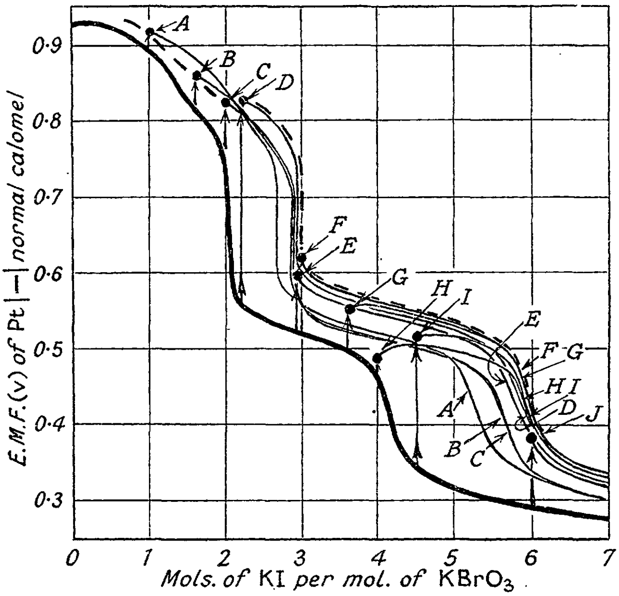
$$\mathrm{BrO_3' + H^{\bullet} + \tfrac{5}{6}I' \longrightarrow \tfrac{5}{6}IO_3' + \tfrac{1}{2}Br_2 + \tfrac{1}{2}H_2O} \quad . \; . \; . \quad (1)$$

requiring $\frac{5}{6}$ mol. of iodide per mol. of bromate, whereas if to (*b*) bromide ions it would be

$$\mathrm{BrO_3' + I' \longrightarrow Br' + IO_3'} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

requiring 1 mol. of iodide. In curve " 1 " in Fig. 2 the first inflection occurs with 1 mol. apparently indicating that reaction (2) must have been the first to take place. On the other hand, the preliminary inflection of curve " 10 " and the first inflection of curve " 20 " (Fig. 1) correspond with *ca.* 0·9 mol., which is of the order required by equation (1). The preliminary inflections of the " 2·5," " 3·5," and " 10 " curves in Fig. 2 are respectively at 0·22, 0·40, and 0·55 mol. of iodide, probably owing to reactions (1) or (2) or both having taken place incompletely.

FIG. 3.



If the first reaction were that represented by equation (1), the bromine liberated would be expected to oxidise more iodide to iodate :

$$\mathrm{\tfrac{1}{2}Br_2 + \tfrac{1}{6}I' + \tfrac{1}{2}H_2O \longrightarrow Br' + \tfrac{1}{6}IO_3' + H^{\bullet}} \quad . \; . \; . \; . \quad (3)$$

If both reactions (1) and (2) occurred simultaneously, the redox system $\mathrm{Br_2 \rightleftharpoons 2Br'}$ would be established, for which $\varepsilon_0 = 1{\cdot}087$ v. Hence, whichever preliminary reactions may have taken place, the products of the reaction formed when 1 mol. of iodide has reacted completely should be in accord with equation (2).

The authors (preceding paper) have shown that reaction (3) is extremely slow, and should this reaction participate in the initial stage of the reduction of bromate ions with those of iodide it is highly probable that the reduction as a whole will be incomplete and the final inflections will appear before the stoicheiometric amount of potassium has been added (cf. curves " 2 " to " 75 " in Fig. 2).

It is significant in the " 2," " 5," and " 10 " curves in Fig. 1 that the first inflection should correspond with the addition of 1·67 mols. of iodide. If in each of these titrations, carried out in the presence of sulphuric acid, the slow reaction was eliminated and the first mol. of potassium iodide had reacted solely in accordance with equation (2) and the iodic acid thereby formed had subsequently been reduced to iodine monobromide with more potassium iodide thus :

$$IO_3' + 6H^{\cdot} + 3Br' + 2I' \longrightarrow 3IBr + 3H_2O \quad . \quad . \quad . \quad . \quad (4)$$

then equation (2) reveals that only 1 mol. of the 3 mols. of bromide demanded by (4) existed in the solution. Hence only 1 mol. of iodine bromide could be formed, which involved $\frac{1}{3}$ mol. of iodate and $\frac{2}{3}$ mol. of iodide, and therefore for the completion of reaction (2) and the subsequent formation of 1 mol. of iodine bromide (4), a total of $1\frac{2}{3}$ mol. of iodide were required to bring each of the curves " 2," " 5," and " 10 " in Fig. 1 to their first inflection. Two reactions must consequently have occurred during the second sections of the " 2," " 5," and " 10 " sulphuric acid–bromate titrations, *viz.*, (4) and

$$\tfrac{2}{3}IO_3' + 4H^{\cdot} + \tfrac{10}{3}I' \longrightarrow 2I_2 + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad (5)$$

thereby indicating the need of $4\frac{1}{3}$ mols. of iodide for the second section, making a total of 6 mols.

Table 1 and Fig. 2 show that in the presence of hydrochloric acid at concentrations equal to, or greater than, 0·2N, the first sections of the titration curves terminate at amounts of iodide which lie between 2 and 3 mols., whereas Table 2 and Fig. 3 reveal that when adequate time is allowed the first inflection is postponed until precisely 3 mols. of iodide have been added. The final inflection then appeared with 5·96 mols.

Another important observation is that the amounts of potassium iodide required to bring the curves " 10 " to " 75 " to their first inflection were one-half of that required to bring them to the respective final inflections (see Table 1). This relationship is again seen to exist in Table 2.

If it can be assumed that, had sufficient time been allowed after addition of 1 mol. of potassium iodide for the reaction, or reactions, shown by equation (2) to become complete, then the remaining reactions would be :

With 2 mols. of iodide (*i.e.*, a total of 3 mols.)

$$IO_3' + 2I' + 3Cl' + 6H^{\cdot} \longrightarrow 3ICl + 3H_2O \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and with another 3 mols. of iodide (*i.e.*, a total of 6 mols.)

$$3ICl + 3I' \longrightarrow 3I_2 + 3Cl' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus there is reason to believe that reactions (6) and (7) take place spontaneously.

It has been suggested that the initial oxidation of iodide to iodate ions might take place according to either equations (1) or (2) or else first according to equation (1) and then, by the bromine thus set free, according to equation (3); in the latter case equation (2) becomes composite in that it incorporates both reactions by which 0·833 mol. of iodic acid would be produced according to equation (1) and the remaining 0·167 mol. by the slow reaction (3). The following is an attempt to explain why the two sections of almost every hydrochloric acid–bromate curve in Figs. 2 and 3 require equal amounts of potassium iodide. Owing to the slowness of one or both of the reactions included in the composite equation (2), we assume that in the time allowed a fraction, f, of a mol. of iodide is able so to react. Then in the presence of ample hydrochloric acid $2f$ mols. of iodide will be needed to reduce the f mol. of iodic acid to $3f$ mols. of iodine chloride (equation 6), which in turn will require another $3f$ mols. of iodide to liberate $3f$ mols. of iodine (equation 7). If it can be assumed that the oxidant, either bromine or perhaps potassium bromate, did not react with the potassium iodide until $6f$ mols. of iodide had been added, then $3f$ mols. of iodide would be required for the first section consisting of reactions (2) and (6) and another $3f$ mols. for the second section consisting of reaction (7) only. Hence,

$$f = \tfrac{1}{3}\text{ (number of mols. of KI required by 1st section)}$$
$$= \tfrac{1}{6}\text{ (total number of mols. of KI indicated by final inflection)}$$

Values of f so obtained are given in Tables 1 and 2. In Table 1, which refers to titrations carried out fairly rapidly, f varies from 0·69 to 0·89, although it is perhaps significant that of the six values recorded two should be 0·82 and one 0·83. Equation (1) requires $\frac{5}{6}$ mol.

(0·83) of iodide, whence it seems to follow that if the titration in hydrochloric acid is carried out moderately quickly the iodic acid produced results entirely from reaction (1). The allowance of too little time leads to values of *f* which are somewhat less than 0·83. Greater time enables *f* ultimately to become 1 as shown in Table 2.

Conclusion.—Our conclusions from the foregoing discussion are summarised herewith:

(i) In sulphuric acid solution the following reactions occur, the last two being simultaneous:

$$BrO_3' + I' \longrightarrow IO_3' + Br'$$

$$\tfrac{1}{3}IO_3' + Br' + 2H^{\bullet} + \tfrac{2}{3}I' \longrightarrow IBr + H_2O$$

$$\tfrac{2}{3}IO_3' + 4H^{\bullet} + \tfrac{10}{3}I' \longrightarrow 2I_2 + 2H_2O$$

$$IBr + I' \longrightarrow I_2 + Br'$$

(ii) In hydrochloric acid solutions of concentration >0·2N, instead of the first reaction above there occur:

$$BrO_3' + \tfrac{5}{6}I' + H^{\bullet} \longrightarrow \tfrac{5}{6}IO_3' + \tfrac{1}{2}Br_2 + \tfrac{1}{2}H_2O$$

$$\tfrac{1}{2}Br_2 + \tfrac{1}{6}I' + \tfrac{1}{2}H_2O \longrightarrow \tfrac{1}{6}IO_3' + HBr$$

of which the latter is very slow. If adequate time is allowed for completion of the reaction, then follow successively:

$$IO_3' + 2I' + 3Cl' + 6H^{\bullet} \longrightarrow 3ICl + 3H_2O$$

$$3ICl + 3I' \longrightarrow 3I_2 + 3Cl'$$

Otherwise, only the iodate ions initially formed will undergo reduction according to the last two equations, and any bromine which failed to react according to the second equation will thereafter slowly react with iodide ions.

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