[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. II. THE INFLUENCE OF MERCURIC MERCURY UPON BROMIC ACID REACTIONS

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In a former article[1] the stability of bromic acid in boiling solutions containing various concentrations of mineral acids was demonstrated and the application of this stability to several proposed volumetric procedures suggested. Free bromine and ferric iron in considerable amount as well as small amounts of chloride were found to be without influence on the stability of bromic acid.

Since oxidation reactions with bromic acid in excess result in the formation of free bromine,[2] this must be removed before the usual iodimetric determination of the excess of bromic acid can be made. It would obviously be a distinct advantage in many cases if the bromate reactions could be carried either to the formation of a bromide or free bromine as occasion demanded. The object of the present paper is to demonstrate the use of mercuric mercury in accomplishing this result.

Mercuric Mercury as a Preventive of the Reaction of Bromate upon Bromide in Acid Solution

The reaction of mercuric mercury with soluble thiocyanates in acid solution to form undissociated mercuric thiocyanate has long been known and is the basis of a volumetric procedure for the determination of mercury.[3] Solutions of mercuric chloride and bromide are likewise known to be but very slightly dissociated, and procedures in quantitative analysis have been based upon this fact.[4] The formation of undissociated mercuric bromide as a means of preventing the reaction of bromates upon bromides in acid solutions is, however, new. This preventive action of mercuric mercury would be of broader application if it were effective in boiling acid solutions containing bromate and bromide. Reactions of bromic acid ordinarily resulting in the formation of free bromine instead of a bromide would be better adapted to volumetric processes if the reactions could be extended, when desirable, to the formation of bromide rather than bromine. These points were considered in the experiments subsequently described.

The choice of mercuric compound for these reactions is of importance. Because a compound highly dissociated in solution is required, only

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[1] THIS JOURNAL, **45**, 1115 (1923).

[2] The reaction of Koppeschaar's solution, *Z. anal. Chem.*, **15**, 233 (1876).

[3] Rupp and Kraus, *Ber.*, **35**, 2015 (1902).

[4] Kolthoff, *Z. anal. Chem.*, **61**, 332 (1922).

salts of mercury with oxygen acids are available. Mercuric nitrate, sulfate and perchlorate were considered. Some difficulty is frequently encountered in obtaining the sulfate free from mercurous mercury, and in the case of both the nitrate and sulfate appreciable concentration of acid must be maintained to prevent hydrolysis and precipitation of insoluble mercury compounds. Neither of these objections is applicable to mercuric perchlorate, which was therefore selected.

Mercuric perchlorate was readily prepared from mercuric nitrate and perchloric acid. A weighed amount of stock nitrate was treated with a small excess of 70% perchloric acid and the product heated to drive off the nitric acid formed. The solution thus obtained was rapidly boiled until copious white fumes of perchloric acid appeared. The mercuric perchlorate solution containing a small excess of perchloric acid was allowed to cool until the crystal mass became pasty, after which the crystals were centrifuged. The product thus obtained was found to contain approximately 44% of mercury. Dilute, clear solutions of this product extremely dilute in free acid content were made by adding the mercuric perchlorate to a small volume of water slightly acidified with perchloric acid, followed by dilution to any desired strength.

The method of testing the stability of bromates in acid bromide solutions in the presence of mercuric mercury was carried out as described in a former paper.[1] Results tabulated in Table I were thus obtained. The iodimetric determination of bromate is unaffected by the presence of mercuric mercury except that more potassium iodide is needed, mercuric potassium iodide being first formed.

Table I

The Effect of Mercuric Perchlorate in Preventing the Oxidation of Bromide by Bromate in Acid Solution at the Boiling Temperature

25.00 cc. of 0.09906 N $Ba(BrO_3)_2$ used, equivalent to 26.04 cc. of 0.09511 N $Na_2S_2O_3$. Time of boiling, 5 minutes. Dilution to 100 cc.

0.01 N KBr added Cc.	0.1 N $Hg(ClO_4)_2$ in 0.2 N $HClO_4$ added Cc.	HNO_3 N	Iodine value of boiled samples Cc. of $Na_2S_2O_3$	Difference Cc. of $Na_2S_2O_3$
10.0	1.0	1.0	26.03	—0.01
20.0	2.0	1.0	26.03	—0.01
30.0	3.0	1.0	25.99	—0.05
30.0	3.0	0.8	26.00	—0.04
30.0	3.0	0.5	26.02	—0.02
50.0	5.0	0.4	26.05	+0.01
100.0	10.0	0.3	26.01	—0.03
100.0[a]	10.0	0.5	25.94	—0.10

[a] Heated on the steam-bath (app. 70°) during 4½ hours.

Each cubic centimeter of equivalent N bromate solution, upon reduction to bromide, equals 1 cc. of 0.1667 N bromide solution. Thus 100 cc. of 0.01 N potassium bromide solution corresponds to 60 cc. of 0.1 N bromate solution, an amount in excess of that ordinarily required for analytical procedures. In 0.3 N nitric acid solution many oxidation reactions involving bromate would be rapidly accomplished, especially in boiling solution. Duplicate tests using potassium bromate and perchloric acid were made and the results listed in Table II.

TABLE II

THE EFFECT OF MERCURIC PERCHLORATE IN PREVENTING THE OXIDATION OF BROMIDE BY BROMATE IN ACID SOLUTION AT THE BOILING TEMPERATURE

25.00 cc. of 0.09972 *N* $KBrO_3$ used, equivalent to 25.75 cc. of 0.09682 *N* $Na_2S_2O_3$. Time of boiling, 5 minutes. Dilution to 100 cc.

0.01 *N* KBr added Cc.	0.1 *N* $Hg(ClO_4)_2$ added Cc.	$HClO_4$ *N*	Iodine value of boiled samples Cc. of $Na_2S_2O_3$	Difference Cc. of $Na_2S_2O_3$
10.0	1.0	1.0	25.50	−0.25
10.0	1.0	0.5	25.70	−0.05
10.0	1.0	0.3	25.75	±0.00
30.0	3.0	0.3	25.73	−0.02
50.0	5.0	0.3	25.70	−0.05
50.0	5.0	0.3	25.66	−0.09
50.0	10.0	0.3	25.69	−0.06
50.0	5.0	0.15	25.73	−0.02
70.0	7.0	0.10	25.76	+0.01
100.0[a]	10.0	0.20	25.72	−0.03

[a] Heated on the steam-bath (app. 70°) during 75 minutes.

The results recorded in Table II show that perchloric acid can be used in place of nitric acid, but for equally favorable results an acid concentration roughly half as great must be maintained. The seventh experiment shows that more mercury than that equivalent to the bromide present is of inappreciable effect.

The Extension of the Process to Include Chlorides and Iodides.—The protective action of mercuric mercury for bromides in contact with bro-

TABLE III

THE EFFECT OF MERCURIC PERCHLORATE UPON THE STABILITY OF POTASSIUM BROMATE IN BOILING ACID SOLUTION IN THE PRESENCE OF CHLORIDES

25.00 cc. of approximately 0.1*N* $KBrO_3$ taken. Dilution to 100 cc. Mercury added as 0.5 *N* $Hg(ClO_4)_2$ solution 0.2 *N* in $HClO_4$. Time of boiling, 5 minutes.

NaCl taken G.	Mercury solution added Cc.	Acid *N*	Iodine value of untreated $KBrO_3$ solution Cc. of $Na_2S_2O_3$	Iodine value of boiled solution Cc. of $Na_2S_2O_3$	Difference Cc. of $Na_2S_2O_3$
		HNO_3			
0.100	5.0	1.0	26.20	26.21	+0.01
0.200	10.0	1.0	26.20	26.19	−0.01
0.234	10.0	1.0	26.20	26.17	−0.03
0.300	15.0	1.0	26.20	21.86	−5.34
0.400	15.0	0.5	26.20	26.16	−0.04
0.400	15.0	0.5	26.18	26.19	+0.01
0.468	20.0	0.5	26.20	26.10	−0.10
0.500[a]	20.0	0.5	26.18	26.00	−0.18
0.500	20.0	0.5	26.20	22.35	−3.85
0.600	25.0	0.25	26.20	26.14	−0.06

TABLE III (*Continued*)

NaCl taken G.	Mercury *solution* added Cc.	Acid *N*	Iodine value of untreated *KBrO$_3$ solution* Cc. of $Na_2S_2O_3$	Iodine value of boiled *solution* Cc. of $Na_2S_2O_3$	*Difference* Cc. of $Na_2S_2O_3$
		$HClO_4$			
0.0585	5.0	0.3	26.21	26.17	—0.04
0.1169	10.0	0.15	26.20	26.18	—0.02
0.200	10.0	0.15	26.20	26.15	—0.05
0.1169	10.0	0.3	26.20	26.15	—0.05
0.500[a]	20.0	0.1	26.18	26.15	—0.03

[a] Heated on the steam-bath during 70 minutes.

mates in acid solution naturally suggests the study of a similar effect with chlorides and iodides. Tests duplicating those included in Table I and Table II were carried out with the substitution of sodium chloride for potassium bromide, with the results listed in Table III.

Duplicate tests substituting potassium iodide for sodium chloride were carried out and the results recorded in Table IV.

TABLE IV

THE EFFECT OF MERCURIC PERCHLORATE UPON THE STABILITY OF POTASSIUM BROMATE IN BOILING ACID SOLUTION IN THE PRESENCE OF IODIDES

25.00 cc. of approximately 0.1 *N* $KBrO_3$ used, equivalent to 26.16 cc. of approximately 0.1 *N* $Na_2S_2O_3$. Mercury added as 0.5 *N* Hg $(ClO_4)_2$ solution in 0.2 *N* $HClO_4$. Time of boiling, 5 minutes. Dilution to 100 cc.

0.0954 *N* KI added Cc.	Mercury solution added Cc.	Nitric acid *N*	Iodine value of boiled solution Cc. of $Na_2S_2O_3$	Difference Cc. of $Na_2S_2O_3$
10.0	10.0	−0.25	26.17	±0.01
11.0	10.0	−0.50	26.16	±0.00
10.0	10.0	−1.0	26.17	+0.01
16.0	16.0	−1.0	26.15	—0.01
16.0	16.0	−1.0[a]	26.13	—0.03

[a] $HClO_4$ used.

It was found that excess of mercuric mercury was advantageous in the case of the iodide protective effect. The precipitate of mercuric iodide obtained upon the first addition of mercuric perchlorate is readily soluble in the excess of the salt. A white precipitate, probably mercuric bromate, was obtained upon boiling each of the above solutions. This precipitate was readily soluble in excess of potassium iodide and hence did not interfere with the determination of bromate iodimetrically.

The Effect of Mercuric Mercury upon Other Reactions of Bromic Acid

Some of the important reactions of bromate in acid solution as they take place in the presence of sufficient mercuric salt to form undissociated mercuric bromide are the following.

I $3Mn(NO_3)_2 + KBrO_3 + 3H_2O \longrightarrow 3MnO_2 + KBr + 6HNO_3$

II $2Cr(NO_3)_3 + KBrO_3 + 5H_2O \longrightarrow 2H_2CrO_4 + KBr + 6HNO_3$

III $3HNO_2 + KBrO_3 \longrightarrow 3HNO_3 + KBr$

IV $3H_2C_2O_4 + KBrO_3 \longrightarrow 6CO_2 + 6H_2O + KBr$

In the absence of mercury the reactions given above both with and without excess of bromic acid yield bromine rather than potassium bromide.

The effect of mercuric mercury in preventing the oxidation of halides is not limited to bromic acid reactions. Bromides in the presence of sufficient mercuric mercury are not decomposed by potassium permanganate in hot sulfuric acid solution. As will be shown in a subsequent paper, Reaction IV involving the use of excess of sodium oxalate in hot sulfuric acid solutions of potassium bromate can be used in the determination of bromates, the excess oxalate being estimated with potassium permanganate in the ordinary way. Excess of standard ferrous sulfate in cold sulfuric acid solutions shows promise of usefulness in the same determination. Using mercuric salt as preventive, unpurified samples of bromate containing otherwise excessive amounts of bromide can be used in volumetric processes. The objection to the use of sodium bromate in place of potassium bromate is thus minimized.

Mercuric perchlorate can be used as preventive in other reactions involving halides and their oxygen acids; for example, the liberation of iodine from potassium iodide by hydrogen peroxide may be thus prevented. Mercuric mercury may be found to be a preventive of reactions with which quite contrary results would be expected. Thus the oxidation of sodium oxalate in hot sulfuric acid solution by potassium iodate according to the reaction,[5] $2KIO_3 + 5Na_2C_2O_4 + 6H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 5Na_2SO_4 + 10CO_2 + 6H_2O$, is entirely prevented by the presence of sufficient mercuric perchlorate. Reactions involving mercury are thus seen to be available for increasing the flexibility of many analytical processes.

The Mechanism of the Preventive Effect of Mercuric Mercury

The slight extent to which solutions of the mercuric halides are dissociated may be demonstrated by the following experiments: 10 cc. of 0.1 *N* potassium iodide solution is added to 20 cc. of 0.5 *N* mercuric perchlorate slightly acidified with nitric or perchloric acid. Upon adding 10 cc. of 0.1 *N* silver nitrate solution no precipitate of silver iodide is obtained. The same is true when mercuric sulfate is used except that more of this reagent is required. Silver iodide may be precipitated from this solution when considerable excess of silver nitrate is added but the precipitate is redissolved when more mercuric salt is added.

The facts are explained by the assumption that mercuric iodide which is formed is so completely undissociated in the presence of excess mercuric ion that the solubility product of silver iodide is not exceeded. With excess of silver nitrate this solubility product can be exceeded with precipitation of silver iodide. The addition of more mercuric ion again

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[5] Rosenthaler, *Z. anal. Chem.*, **61**, 219 (1922).

reverses the reaction. Since mercuric perchlorate is dissociated to a greater extent than mercuric sulfate a smaller excess of the former would be required to account for the observed phenomena.

Because of the great dissociation of mercuric bromide and chloride, potassium bromide and chloride cannot be substituted for potassium iodide in the above experiments without precipitating silver bromide and chloride. That the mechanism of the preventive action of mercuric mercury is the same for bromides as with iodides is to be inferred and may be demonstrated as follows.

If mercuric bromide is highly undissociated, its formation in solution is practically equivalent to the formation of precipitated silver bromide. Therefore, since mercuric mercury can be determined by its reaction with ammonium thiocyanate,[3] the silver of the familar Volhard chlorine determination should be replaceable by mercuric perchlorate or sulfate with fairly comparable results. The reaction using pure potassium bromide and mercuric perchlorate with ferric alum as indicator was tested as follows: to 0.1025 g. of potassium bromide was added 25.00 cc. of 0.1034 *N* mercuric perchlorate solution; this required 16.89 cc. of 0.0178 *N* potassium thiocyanate solution, equivalent to 0.1030 g. of potassium bromide "found;" a duplicate determination gave 0.1211 g. of potassium bromide for 0.1204 g. taken.

Because of the appreciable stability of chlorides in the presence of oxidizing agents such as bromate, permanganate, etc., an extremely slight dissociation of mercuric chloride is not necessary for considerable preventive effects.

Summary

1. The action of mercuric mercury as a preventive of the reaction of strong oxidizing agents such as bromate and permanganate upon chlorides, bromides and iodides was demonstrated and some advantages thus attained in volumetric bromate processes pointed out.

2. The effect of mercuric perchlorate in extending some reactions of bromic acid, ordinarily resulting in the formation of free bromine to the formation of a bromide instead, was noted and the reaction given.

3. The preparation of mercuric perchlorate from mercuric nitrate and 70% perchloric acid was described and its advantages over mercuric sulfate and nitrate were stated.

4. The explanation of the preventive effect of mercuric mercury for the reactions studied was shown experimentally to be due tc the formation of slightly dissociated mercuric halides.

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