Acknowledgment is made of a grant from the Rumford Fund of the American Academy of Arts and Sciences, with which some of the instruments used in this investigation were purchased.

Summary

1. Distinct irregularities occur in the temperature–specific heat curves of benzene, ethyl benzene and carbon tetrachloride, which indicate molecular changes in the liquid.
2. Measurements of vapor pressure and density fail to show corresponding irregularities.
3. Water catalyzes the change from one molecular species to the other in the case of benzene and ethyl benzene.
4. Differential specific heat measurements of liquids offer an excellent method for the study of association.

MADISON, WISCONSIN

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

THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. IV. THE PREPARATION AND PROPERTIES OF NORMAL AND BASIC MERCURIC BROMATE[1a]

BY G. FREDERICK SMITH

RECEIVED MARCH 21, 1924 PUBLISHED JULY 7, 1924

In former papers of this series[1b] it has been demonstrated that the presence of the mercuric ion advantageously alters the usual course of oxidation reactions involving bromate. The oxidation value of bromates in certain reactions was shown to be increased from five equivalents to six, new reactions were indicated, and a general increase in flexibility was obtained.

For these reactions the mercuric ion must be present in amount equivalent to the bromide ion resulting from the reduction of the bromate. This condition would be automatically adjusted in the reduction of the mercuric bromates. If their preparation and properties were satisfactory their value for use as oxidation reagents would be proved.

The following paper describes the preparation of normal and basic mercuric bromates, their stability, solubilities and general theoretical relationships.

Previous Studies

The preparation and properties of normal and basic mercuric bromate are described in Gmelin-Kraut.[2] Groth[3] describes the preparation of hydroxy-mercuric bromate from freshly precipitated mercuric oxide and excess of bromic acid and gives crystal

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[1a] Read before the Division of Physical and Inorganic Chemistry, 67th Meeting of the American Chemical Society, Washington, D. C.

[1b] Smith, THIS JOURNAL, **45,** 1115, 1417, 1666 (1923).

[2] Gmelin-Kraut, **5**, part 2, p. 752 (1914).

[3] Groth, "Chem. Kryst.," **1908** [II] p. 126.

measurements and density determination. Topsöe[4] describes its preparation from mercuric nitrate and potassium bromate and states that cold water slowly decomposes it, hot water more rapidly.

Less is known concerning normal mercuric bromate. The dihydrate, slightly soluble in bromic acid, can be prepared from freshly precipitated mercuric oxide and bromic acid or by the evaporation of the mother liquor from the preparation of basic mercuric bromate.[3] Mercuric bromate is described as stable up to 130–140° and its solubilities in cold and hot water have been reported.[5]

No more recent data are available on these materials.

Preparation of Hydroxy-mercuric Bromate

Because of high solubility, hydroxy-mercuric bromate cannot be prepared with good yields in the presence of nitric acid, which excludes the use of mercuric nitrate in nitric acid solution. Sulfuric acid solutions would be more favorable, but the insolubility of mercuric sulfate in sulfuric acid renders it undesirable. Mercuric chloride is obviously even less suitable. Mercuric perchlorate can be easily prepared from mercuric nitrate and perchloric acid. It does not hydrolyze forming insoluble salts in practically neutral solution, it is extremely soluble, and its properties are well suited to the preparation of hydroxy-mercuric bromate by reaction with sodium bromate in the absence of acids.

Mercuric perchlorate can be easily prepared as described in the second paper of this series.[1] By this means a salt containing 42–44% of mercury is obtained. This product is dissolved in a small volume of water and added slowly with constant stirring to a hot, half saturated solution of sodium bromate. Proportions calculated from the following reaction should be taken, preferably with a slight excess of sodium bromate: $Hg(ClO_4)_2 + NaBrO_3 + H_2O \longrightarrow Hg(OH)BrO_3 + NaClO_4 + HClO_4$.

Precipitation occurs upon the first addition of mercuric perchlorate and even with concentrated solutions there is little or no tendency for contamination with other substances. The solution and crystals are cooled to room temperature, decanted and the crystals filtered and washed with water using centrifugal drainage. The basic bromate thus prepared is anhydrous and can be dried indefinitely at 130–140° without decomposition. By this process a practically quantitative yield is obtained. The product was found to be completely volatile when heated with a very mild deflagration at 190–200°.

The bromates and bromate solutions dealt with in this paper were analyzed for bromate and mercury. The bromate was determined by adding nitric or perchloric acid, excess of potassium iodide, and the iodine liberated was titrated using sodium thiosulfate with starch as indicator. The volumetric method of Rupp[6] based upon titration with potassium

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[4] Topsöe, *Akad. Wiss. Wien*, **66**, [II] 38 (1872).

[5] Rammelsberg, *Pogg. Ann.*, **55**, 79 (1842).

[6] Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).

thiocyanate using ferric alum as indicator was found satisfactory for the determination of mercury. High results might be expected in the application of this method to mercuric bromate because of some oxidation of the thiocyanate by the bromic acid liberated during the reaction. The end-point was, however, permanent, and results showed a tendency to be low rather than high. The method was therefore selected because of its rapidity and simplicity.

The hydroxy-mercuric bromate prepared as described gave upon analysis 22.95% of bromine and 56.78% of mercury; the calculated percentages are 23.13% and 58.06%, respectively. It was recrystallized from 3 *N* perchloric acid with the intention of converting to the normal bromate. Instead, the salt was recovered unchanged except for an appreciable purification as shown by analysis in which 23.11% of bromine and 57.12% of mercury were found. Crystallization from 5 *N* perchloric acid did not alter this result. The stability of this basic compound in acid solution is thus one of its unusual characteristics, for purification of the basic bromate crystallization from hot *N* perchloric acid solution gives a 65% yield. The temperature coefficient of solubility is high and cooling to ice-bath temperatures to increase the yield is recommended.

The Relation of Basic Mercuric Bromate to Known Mercuric Salts with Complex Cations

Borelli[7] has made a study of the preparation of numerous mercuric salts with complex cations. Such compounds as bromomercuric perchlorate ($HgBrClO_4$), cyanomercuric perchlorate ($HgCNClO_4$) and thiocyanomercuric perchlorate ($HgCNSClO_4$) were prepared by the addition of mercuric bromide, mercuric cyanide and mercuric thiocyanate, respectively, to cold saturated water solutions of mercuric perchlorate. In the case of these compounds the complex cations $(HgBr)^-$, $(HgCN)^-$ and $Hg(CNS)^-$ were shown to exist in stable form by a study of the transference relationships. Fairly concentrated solutions of mercuric perchlorate were shown by cryoscopic methods to exhibit abnormalities not explained on the basis of hydrolysis alone. Ley,[8] and Ley and Kissell[9] had previously shown by conductivity studies that mercuric perchlorate possesses abnormal dissociation values. It is probable, therefore, as indicated by the preparation of hydroxymercuric bromate as described, that mercuric perchlorate in water solution reacts thus: $Hg(ClO_4)_2 + HOH \longrightarrow (HgOH)ClO_4 + HClO_4$. The complex hydroxy-mercuric ion would appear to be of the same nature as the complex mercuric cations studied by Borelli. The stability of hydroxy-mercuric bromate as shown by its property of crystallizing unchanged from 5 *N* perchloric

[7] Borelli, *Gazz. chim. ital.*, **38,** 421 (1908); *Chem. centr.*, **1908** [IV] 1987.

[8] Ley, *Z. physik. Chem.*, **30,** 248 (1899).

[9] Ley and Kissell, *Ber.*, **32,** 1024, 1362 (1899).

acid would thus be dependent upon the practically total absence of dissociation of this complex cation. That the hydrolysis of mercuric perchlorate indicated above is not appreciably reversed in the presence of a considerable excess of perchloric acid will be shown in connection with the preparation of normal mercuric bromate.

Preparation of Normal Mercuric Bromate

Normal mercuric bromate, like basic mercuric bromate, was prepared by precipitation of sodium bromate with mercuric perchlorate, the reaction taking place in fairly high concentrations of perchloric acid. At 3 *N* acid concentrations cold sodium bromate solutions decompose slightly, more pronouncedly in hot solutions. A hot, 3 *N* perchloric acid solution nearly saturated with sodium bromate was treated with an equivalent amount of mercuric perchlorate dissolved in 3 *N* perchloric acid; the crystals thus obtained after cooling the reaction mixture to 0° were filtered off and washed with several portions of water, using centrifugal drainage.

Sixty g. of sodium bromate precipitated in 150 cc. of solution gave 83 g. of product. A portion of this material was dried between filter paper sheets and analyzed for mercury giving 40.66% as the average of closely agreeing duplicates. The calculated percentage for mercuric bromate dihydrate is 40.73%. A yield of 85% was therefore obtained. Mercuric bromate dihydrate can be dehydrated by storage over anhydrous calcium chloride at room temperature. Samples dried over phosphorus pentoxide at 90° were analyzed for mercury, giving as the average of duplicate analyses 43.82% of mercury, while the calculated percentage for anhydrous mercuric bromate is 43.95. Mercuric bromate was found to be slightly decomposed at 130–140° and to deflagrate at 155–160°, forming mercuric bromide as the major decomposition product.

Mercuric bromate is obtained by following the procedure as given in approximately 2 *N* perchloric acid solution with slightly decreased yield. At approximately *N* acid concentration a mixture of the basic and normal bromate is obtained. An increase in the hydrolysis of mercuric perchlorate at an acid concentration between *N* and 2 *N* is thus indicated. For calculating acid concentrations attention is called to the volume relations resulting upon solution of mercuric perchlorate in water; 170 g. of the salt when dissolved in 25 cc. of water had a volume of 83 cc.

Mercuric bromate may be prepared by the reaction of mercuric nitrate with potassium bromate in the presence of nitric acid. The solubility of potassium bromate is less than that of sodium and from a volume of 150 cc. 3 *N* with nitric acid, 35 g. of potassium bromate yielded 12 g. of product or 50% of the calculated yield. The disadvantage in the cost of perchloric acid as compared with nitric acid is offset by the possibility of recovering perchloric acid from the filtrates. The filtrates containing perchloric acid and sodium perchlorate together with the small amount of sodium bromate used in excess and the mercuric bromates unprecipitated, are concentrated, accompanied by decomposition of the bromates at increased acid concentration, sodium hydroxide is added to neutralize most of the perchloric acid and the solution finally heated until fumes of perchloric acid are evolved. The sodium perchlorate is then separated from the resulting solution after it has been cooled to 0° and is treated for the recovery of perchloric acid and mercuric perchlorate by the method of Kreider,[10] based upon the precipitation of sodium chloride from sodium perchlorate by the addition of concd. hydrochloric acid. The sodium chloride is separated from the perchloric acid and the excess of hydrochloric acid and the latter removed by again concentrating the solution until fumes of perchloric acid are evolved.

The Preparation of Bromic Acid from Mercuric Bromate

The preparation of mixed hydroxymercuric bromate and normal mercuric bromate from approximately *N* perchloric acid solutions suggests the hydrolysis of normal mercuric bromate to form the basic salt even in fairly concentrated acid solution according to the reaction, $Hg(BrO_3)_2 + HOH \longrightarrow HgOHBrO_3 + HBrO_3$. The reaction was therefore tested as follows.

Approximately 15 g. of mercuric bromate was treated with 25 cc. of water and the mixture rotated in a sealed tube during 36 hours at 25°. After settling, two 10cc. portions were withdrawn from the supernatant liquid and analyzed.

One 10cc. portion was diluted to 500 cc. and 25 cc. of this solution tested for iodine value with an excess of standard potassium iodide solution followed by titration with sodium thiosulfate solution. That the solutions were acid as taken from the reaction tube was shown by the liberation of iodine upon the addition of potassium iodide; 5930 cc. of *N* sodium thiosulfate was calculated to be equivalent to 1000 cc. of the original solution.

The second 10cc. portion was evaporated to dryness on the steam-bath, the residue dissolved in dil. acid and the mercury determined with potassium thiocyanate. It contained mercury equivalent to 16.9 g. per 1000 cc. of the original solution and to 504 cc. of *N* sodium thiosulfate solution when calculated as basic mercuric bromate. The bromic acid present therefore required 5426 cc. of *N* sodium thiosulfate solution and was accordingly a little stronger than 0.9 *N* with bromic acid.

The solid phase of the reaction mixture was centrifuged and dried, and upon analysis proved to be hydroxymercuric bromate containing 23.21% of bromine as called for by the reaction as given. The values in the literature for the solubility of normal mercuric bromate are thus seen to be based upon a misconception.

The Solubilities of Basic and Normal Mercuric Bromate in Nitric and Perchloric Acids

To obtain data useful in the preparation and purification of these salts and their application to analytical operations, their solubilities in various concentrations of perchloric and nitric acids were determined.

An excess of solute was added to 15cc. portions of the various acid solutions which were then sealed in solubility tubes and rotated end over end during 6 to 15 hours at 25° to attain equilibrium. The solutions

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[10] Kreider, *Z. anorg. Chem.*, **9**, 343 (1895); *Am. J. Sci.*, [3] **49**, 443 (1895).

TABLE I

THE SOLUBILITIES OF NORMAL AND BASIC MERCURIC BROMATE IN NITRIC AND PERCHLORIC ACID SOLUTIONS AT 25° ± 0.1°

Approx. normality $HClO_4$	Solubility G. per 100 cc.	Approx. normality HNO_3	Solubility G. for 100 cc.
	SOLUTE $HgOHBrO_3$		
None	0.081	...	...
1.0	4.34	1.0	12.52
2.0	5.94	2.0	21.30
2.5	6.06	...	...
3.0	6.06	...	...
	SOLUTE $Hg(BrO_3)_2$		
2.0	6.58	2.0	14.66
2.5	5.22	...	...
3.0	4.13	3.0	15.00
3.5	3.40	...	...
4.0	2.58	4.0	14.99
5.0	1.55	5.0	14.75

thus obtained were allowed to settle and from the clear supernatant liquid 10cc. portions were withdrawn, diluted to 500 cc. and an appropriate aliquot of each was taken for analysis. The bromate content was then determined as previously described. The results of these analyses are listed

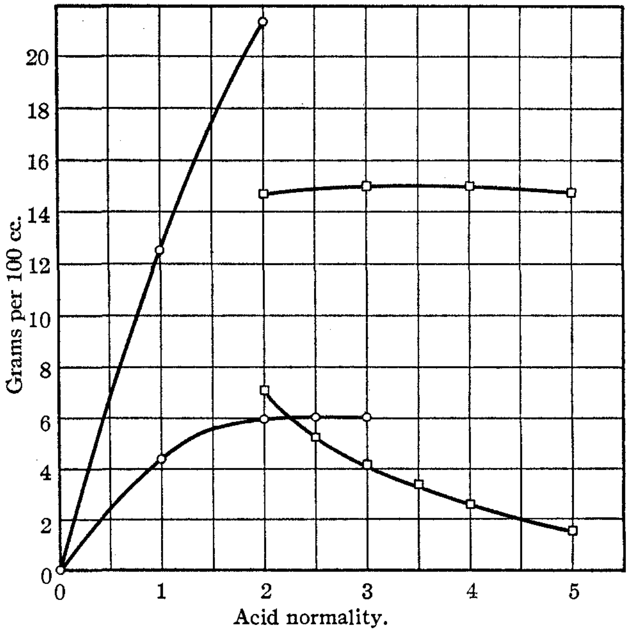

Fig. 1.—Solubility of $HgOHBrO_3$ and $Hg(BrO_3)_2$ in $HClO_4$ and HNO_3 at 25° ± 0.1°.

in Table I and plotted for the purpose of ready comparison in Fig. 1. All determinations were carried out in duplicate and are the mean of closely concordant results. Anhydrous solutes were used for all solubility determinations with calculation of the solubility on the same basis.

The two upper curves of Fig. 1 represent solubility in nitric acid. The two lower curves represent solubility in perchloric acid. The points marked with squares represent solubility of normal mercuric bromate, those with circles basic mercuric bromate.

It will be seen from an examination of Fig. 1 that the preparation of the two mercuric bromates can be accomplished with best yields by use of perchloric acid solutions with mercuric perchlorate as precipitant. The decrease in solubility of normal mercuric bromate with increase in concentration of perchloric acid is pronounced, indicating that best yields are obtained using strong acid solutions for the preparation of the normal salt.

5 *N* Nitric and perchloric acid solutions of the bromates were perfectly stable at 25°, remaining odorless and colorless; 4 *N* perchloric acid solution of the basic salt gave no odor of bromine at the boiling point, thus showing a much greater stability than for ordinary bromates under the same conditions. Pure basic mercuric bromate is stable in contact with cold water indefinitely. Decomposition of this material in contact with boiling water with the formation of a yellow, insoluble decomposition product results, but the solution thus obtained is not acid. Both of the last two observations are in contradiction of published data.

Basic mercuric bromate is to be preferred as a reagent in volumetric reactions because of its stability in 2 *N* nitric and perchloric acids and the ease with which it can be prepared.

Summary

1. The preparation of normal and basic mercuric bromates by the interaction of mercuric perchlorate and sodium bromate in acid and practically neutral solutions has been described.

2. The relation of hydroxymercuric bromate to known mercuric salts with complex cations was pointed out.

3. The solubilities of the two bromates in various concentrations of nitric and perchloric acids at 25° have been determined.

4. The hydrolysis of normal mercuric bromate with the formation of basic mercuric bromate and free bromic acid in considerable concentration has been demonstrated.

5. Basic mercuric bromate has been shown to be preferable as a reagent for volumetric bromate reactions.

URBANA, ILLINOIS