

proposed that  $\nu_{\text{asym}} > \nu_{\text{sym}}$ . This fact has been confirmed by recent Raman polarization studies<sup>17</sup> and normal-coordinate analysis.<sup>14</sup> For coordinated nitrito groups  $\nu_{\text{asym}} > \nu_{\text{sym}}$ .<sup>8,18</sup> Generally  $\nu_{\text{sym}}(\text{ONO}) < \nu_{\text{sym}}(\text{NO}_2)$  and  $\nu_{\text{asym}}(\text{ONO}) > \nu_{\text{asym}}(\text{NO}_2)$ .<sup>8,17</sup> It should be noted that the converse applies to the free  $\text{NO}_2^-$  ion where  $\nu_{\text{sym}} > \nu_{\text{asym}}$ ,<sup>1,19</sup> a fact that has often been misquoted.<sup>8,20</sup> The assignments given in Table I are consistent with normal-coordinate analysis<sup>14</sup> al-

though that computation does not predict two intense bands at *ca.* 813 and 837  $\text{cm}^{-1}$ .

It should be possible to use variations of the  $\text{NO}_3^-$  analysis to determine the purity of a wide variety of nitrite complexes. One may then assign bands to  $\text{NO}_3^-$  impurity if it occurs in nitrite complexes for  $\text{NO}_3^-:\text{NO}_2^- > 0.002$ . High-quality infrared spectra of inorganic compounds can be obtained by MATR techniques for which the inherent weaknesses of alkali halide pellets and organic mulls are not a problem.

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## Perbromic Acid and Perbromates: Synthesis and Some Properties<sup>1</sup>

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A new and more convenient synthesis of perbromates has been developed, consisting of oxidation of bromate with fluorine in alkaline solution. Perbromic acid is a strong monobasic acid. Its aqueous solutions are stable up to about 6 *M* (55%  $\text{HBrO}_4$ ) but decompose at higher concentration. It is a sluggish oxidant, intermediate in apparent oxidizing power between perchlorate and periodate. Potassium perbromate analyzes as  $\text{KBrO}_4$ . It decomposes at 280° to the bromate. Spectral evidence indicates that the tetrahedral  $\text{BrO}_4^-$  ion is the principal perbromate species in solid  $\text{KBrO}_4$  and in neutral and acid perbromate solutions. There is no rapid oxygen exchange between  $\text{BrO}_4^-$  and water.

### Introduction

In a recent communication<sup>2</sup> this author has reported the synthesis of ponderable amounts of perbromates by oxidation of bromate either electrolytically or with xenon difluoride. Neither method lends itself readily to large-scale preparations, and we have now found a much more convenient synthesis to be the oxidation of bromate in alkaline solution by molecular fluorine. By means of this method we have prepared a solution containing 24 g of  $\text{HBrO}_4$ , which we have used to begin the investigation of perbromate chemistry.

### Experimental Section

**Synthesis of Perbromic Acid and Perbromates.**—A 0.5-lb fluorine cylinder was equipped with a Monel pressure-reducing regulator incorporating a Kel-F diaphragm (Matheson Co.). A Teflon-packed Monel needle valve was attached to the regulator, and a length of copper tubing was connected to the needle valve. A length of platinum tubing was silver-soldered to the end of the copper tube, and a short piece of Teflon tubing was fitted over the platinum tube. The Teflon extended about 1 in. below the end of the platinum.<sup>3</sup> This Teflon-tipped platinum

tube was placed in a Teflon bottle containing about 1200 ml of a solution *ca.* 5 *M* in  $\text{NaOH}$  and *ca.* 1 *M* in  $\text{NaBrO}_3$ .<sup>4</sup> The bottle was cooled in an ice bath, and fluorine was bubbled in slowly until the solution became acid.<sup>5</sup> The resulting solution was *ca.* 0.2 *M* in perbromate.

In the following purification procedure, all solutions containing substantial amounts of fluoride and/or alkali were handled in Teflon or polypropylene vessels.

The solution was concentrated by evaporation in a Teflon beaker under a heat lamp and was then chilled. The precipitated sodium fluoride and bromate were removed by centrifugation.

(3) The Teflon tip prevents clogging. It should have at least a  $\frac{3}{16}$ -in. i.d. More recent experiments indicate that platinum inhibits the formation of perbromate, and 50–100% higher yields may be obtained if only Teflon is in contact with the solution. A disadvantage of Teflon is that it sometimes catches fire in fluorine. Although the combustion stops at once when the fluorine supply is turned off, the Teflon may require replacement. TFE Teflon is preferable to the FEP type.

(4) The solution is made by adding 1 part of 50%  $\text{NaOH}$  solution to 3 parts of *ca.* 1.3 *M*  $\text{NaBrO}_3$ . It is supersaturated in sodium bromate, which slowly crystallizes out. The presence of solid sodium bromate in the reaction mixture improves the yield of perbromate with respect to fluorine consumed, probably by maintaining saturation as the reaction proceeds.

(5) Although most of the fluorine is absorbed by the base, enough escapes to make it imperative that the reaction be carried out in a well-ventilated fume hood. The reaction is not smooth, and small explosions may take place in the vapor above the solution. Under no circumstances should the apparatus be left to run unattended. Introduction of more fluorine after the base has been neutralized turns the solution yellow but does not appreciably increase the yield of perbromate.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).

An excess of silver fluoride was added to precipitate the remaining bromate as  $\text{AgBrO}_3$ , which was also removed by centrifuging the chilled mixture. The supernatant solution was stirred overnight with an excess of calcium hydroxide to precipitate the remaining silver as  $\text{Ag}_2\text{O}$  and the fluoride as  $\text{CaF}_2$ . The precipitate was once more removed by centrifugation. The supernatant solution was stirred with just enough acid-form cation-exchange resin (Bio-Rad AG50X8, 50–100 mesh) to neutralize the alkali present. It was then passed through a column of 36-mm i.d. and 500-mm length filled with more resin of the same type. The effluent was mixed with diatomaceous earth filter aid and passed through a fine sintered-glass filter. The filtrate was concentrated under a heat lamp to give a stock solution consisting of about 55 ml of 3 *M*  $\text{HBrO}_4$ . The solution was very faintly yellow.

Alkali perbromates were prepared by neutralizing the acid potentiometrically with a solution of the appropriate hydroxide. Sodium perbromate was obtained as a solution, while the much less soluble potassium salt usually precipitated out. (Its solubility is only about 0.2 *M* at room temperature.)

Potassium perbromate was isolated by chilling the neutralized solution in an ice bath, filtering quickly, washing the precipitate with a little ice-cold water, and then drying it either in a vacuum desiccator at room temperature or in an oven at 110°. The salt was recrystallized by dissolving it in a minimal volume of hot water, allowing the solution to cool gradually, and then finally chilling it and filtering out the precipitate as before. The salt is colorless.

**Other Chemicals.**—To make silver fluoride solution, a solution of silver perchlorate (G. F. Smith Chemical Co.) was neutralized with sodium hydroxide. The  $\text{Ag}_2\text{O}$  precipitate was washed and then stirred in a Teflon beaker with slightly less than the stoichiometric amount of HF solution. Filtration yielded a solution of AgF.

Saturated aqueous HBr was made from commercial hydrogen bromide. Distilled water was redistilled through cupric oxide at 800° before use. "Ultra-high-purity" argon was used as an inert flushing gas. All other chemicals were commercial products of reagent grade.

**Perbromate Determination.**—Perbromate was reduced to  $\text{Br}_3^-$  by 12 *M* HBr. The  $\text{Br}_3^-$  was reduced with iodide, and the the  $\text{I}_3^-$  formed was titrated with thiosulfate in an  $\text{H}_3\text{PO}_4$ – $\text{H}_2\text{PO}_4^-$  buffer. The sample was diluted with at least five times its volume of saturated HBr and was allowed to stand for 10 min in a stoppered vessel.<sup>6</sup> It was then transferred to at least ten times its volume of a 2% NaI solution containing slightly more than enough  $\text{NaH}_2\text{PO}_4$  to neutralize the acid present. The solution was titrated at once with a thiosulfate solution that had been standardized against primary standard grade  $\text{KIO}_3$ .

If the perbromate solution contained large amounts of lower bromine oxidation states, these were first reduced by dilute HBr, and the bromine formed was removed by bubbling argon through the solution. The concentration of reducible lower states was kept below 1 *N*, and the HBr concentration after the reduction was between 0.5 and 1 *M*. Under these conditions reduction of perbromate is extremely slow.

**Other Analyses.**—Bromate, bromine, and hypobromite were determined by reaction with 2% iodide followed by titration with standard thiosulfate. The bromate reaction was carried out in 0.1 *M* acid with molybdate catalyst. The bromine and hypobromite reactions were carried out in 0.01 *M* acid with no catalyst. In mixtures, the bromate titer was the difference between the high and low acid titers.

If bromine and hypobromite were both present, argon was bubbled through an aliquot of the solution before reaction with iodide in 0.01 *M* acid. The residual titer was taken to be that of the hypobromite, and the bromine titer was taken to be the difference from the titer without argon bubbling.

If bromate, bromine, and hypobromite were present as traces in a perbromate solution, the foregoing procedures were un-

satisfactory, because of slow reduction of the perbromate, and spectrophotometric methods were used. Bromine was determined separately from its absorption peak at 395 nm ( $\epsilon$  160). The other species were determined as  $\text{Br}_3^-$  at 275 nm. At this wavelength, the tribromide extinction coefficient is about  $3.5 \times 10^4$ , while that of  $\text{BrO}_4^-$  is only 5.8.

The bromate determination was made in 0.5 *M* HBr. Optical density readings were taken as a function of time, and the slow drift was extrapolated to time zero to correct for the slight reduction of perbromate. Hypobromite and bromine were determined in 0.5 *M* NaBr that was 0.001–0.005 *M* in acid. Again, in mixtures, the bromate was calculated from the difference between the two results.

The acidities of perbromic acid solutions were determined by titration with 1 *M* NaOH standardized against potassium acid phthalate. A 1:1 phenolphthalein–thymolphthalein mixed indicator was used.

To determine the bromine content of  $\text{KBrO}_4$ , the sample was ignited to KBr at *ca.* 480° in a covered porcelain crucible. The residue was dissolved in water and titrated with standard  $\text{AgNO}_3$  solution using dichlorofluorescein as an indicator. The weight loss during ignition was taken as a measure of the oxygen content of the salt.

To determine the potassium content of  $\text{KBrO}_4$ , 0.25-mmol samples were decomposed with saturated HBr, and the HBr and bromine were removed by evaporation to dryness. The potassium was then determined gravimetrically as potassium tetraphenylboron.<sup>7</sup> Similar treatment was given to 0.25-mmol samples of standard KCl, and a 99.25% recovery of the potassium was obtained. This was used as an empirical correction factor.

Fluoride ion was determined potentiometrically, using a fluoride-sensitive electrode (Orion Research Inc.), a calomel reference electrode, and a Beckman Research pH meter. Acidic solutions were first neutralized potentiometrically with NaOH.

Trace metallic impurities were determined by optical emission spectrography.

**Dehydration of Perbromic Acid.**—Very dehydrated perbromic acid solutions were prepared either on a high-vacuum line or in a vacuum desiccator over calcium chloride. No heat was used. Several samples were dehydrated on the line until they decomposed, and the products were collected in a U tube cooled with liquid nitrogen. No joints or stopcocks were in the system between the sample and the U tube. After decomposition, the contents of the U tube were washed out with 0.1 *M* NaOH and were analyzed.

To determine at what perbromic acid concentration decomposition took place, a sample of 6 *M*  $\text{HBrO}_4$  was placed in an alumina crucible in a recording thermogravimetric balance (Mettler Thermoanalyzer Model 03). It was dehydrated without heating by pumping with a mechanical vacuum pump.

**Decomposition of  $\text{KBrO}_4$ .**—The thermal decomposition of  $\text{KBrO}_4$  was followed on the recording thermogravimetric balance, using a covered alumina crucible in a flowing argon atmosphere. The heating rate was 2°/min.

**Spectral Measurements.**—Ultraviolet spectra of solutions were determined in quartz cells on a Cary 14 recording spectrophotometer. Infrared spectra were measured between 200 and 4000  $\text{cm}^{-1}$  with a Beckman IR-12 spectrophotometer. Samples were powders milled with Nujol on polyethylene or KBr disks. Raman spectra were measured on a Cary 81 spectrophotometer equipped with a laser source. Solid samples were measured as powders in glass vials. Solutions were measured in a quartz capillary cell.

**Potentiometric Titrations.**—These were carried out with a glass–calomel combination electrode made with "low alkali error" glass, using a Beckman Research pH meter.

**Oxygen Exchange.**—The exchange of oxygen between perbromate and water was studied in water that was 11.2% en-

(6) If the reaction is to be complete in 10 min, the excess HBr concentration must be at least 11.5 *M*. In 10.4 *M* HBr, 40 min is required.

(7) H. J. Cluley, *Analyst*, **80**, 354 (1955).

riched in  $O^{18}$  (Yeda Research and Development Co., Inc., Rehovoth, Israel). In one experiment 3 *M*  $HBrO_4$  in normal water was diluted with the enriched water. An excess of  $KOH$  was added to make the solution basic, and it was then neutralized potentiometrically with a little more 3 *M*  $HBrO_4$ . In another experiment, enriched water was saturated with solid  $KBrO_4$  of normal oxygen content. After each experiment, a portion of the solution was placed in a glass tube closed at one end with a break-seal, and the water and air were removed by pumping on a high-vacuum line. The tube was sealed and ignited at  $480^\circ$  to decompose the perbromate, and the oxygen was analyzed mass spectrometrically.

### Results

**Perbromic Acid.**—The 3 *M* perbromic acid stock was found to contain 0.2 mol % fluoride, 0.16 mol % hypobromite, 0.1 mol % bromate, 0.02 mol % sodium, and less than 0.003 mol %  $Br_2$ . Its ratio of oxidizing power to acidity was 7.94. For pure  $HBrO_4$ , the calculated value is 8.00, but allowance for the known impurities brings this down to 7.975.

Potentiometric titration of 0.6 *M* perbromic acid with 3.6 *M*  $NaOH$  gave a titration curve substantially the same as that obtained with perchloric acid under similar conditions. No significant buffering was observed on either side of the end point.

Perbromic acid may be concentrated under a heat lamp to about 6 *M* (55%  $HBrO_4$ ) without noticeable decomposition, but at slightly higher concentrations marked yellowing generally occurs. The 6 *M* acid is stable indefinitely at room temperature. When it is heated for 1 hr in a boiling water bath, a slight yellowing is sometimes seen, but there is less than 1% loss of oxidizing power. The yellow color appears to be bromine, as it can be removed readily by bubbling argon through the solution.

By vacuum distilling away the water at room temperature, perbromic acid can sometimes be concentrated to about 83% before it decomposes. However, much above 6 *M* the acid does not seem to be stable in air. After a few minutes, an autocatalytic decomposition takes place, which goes to completion if the concentration is near 80%. At lower concentrations, the decomposition stops after substantial dilution of the acid has occurred.

If the removal of water from a perbromic acid solution is carried out very rapidly, crystallization takes place just before decomposition. When exposed to air at the moment of crystallization, the material liquefies at once, and analysis indicates a composition of  $78 \pm 1\%$   $HBrO_4$  (12 *M*). The crystals may be  $HBrO_4 \cdot 2H_2O$  (80.1%  $HBrO_4$ ).

Attempts to vacuum distil perbromic acid showed little or no oxidizing material distilling before the decomposition point. An 0.293-mmol sample of 3 *M*  $HBrO_4$  was dehydrated on the vacuum line until it decomposed, and the distillation products were dissolved in  $NaOH$ . After the solution was acidified, it was found to contain 0.0274 mmol of perbromate, 0.00825 mmol of bromate, 0.171 mmol of hypobromite, and 0.043 mmol of  $Br_2$ .

Perbromic acid is a sluggish oxidant at room tem-

perature. Dilute solutions oxidize iodide and bromide rather slowly and chloride not at all. The 12 *M* acid, however, rapidly oxidizes chloride. It also reacts explosively with laboratory tissue paper. The 3 *M* acid readily oxidizes stainless steel.

At  $100^\circ$ , 6 *M*  $HBrO_4$  fairly rapidly oxidizes  $Mn(II)$  to  $MnO_2$ ,  $Cr(III)$  to dichromate, and cerous nitrate to  $Ce(IV)$ . In the case of cerous perchlorate, no  $Ce(IV)$  is observed, but catalytic decomposition of the perbromate takes place. This is probably due to the instability of uncomplexed  $Ce(IV)$  at  $100^\circ$ . In a similar fashion, silver ion catalyzes the decomposition of 6 *M* perbromic acid at  $100^\circ$ .

$Mn(II)$ ,  $Cr(III)$ , and  $Ce(IV)$  nitrate or perchlorate can be oxidized by perbromic acid at room temperature if solutions of these materials in the acid are dehydrated by evaporation under vacuum.

**Potassium Perbromate.**—A sample prepared from perbromic acid gave the following analysis. *Anal.* Calcd for  $KBrO_4$ : K, 21.36; Br, 43.67; O, 34.97. Found: K, 21.33; Br, 43.56; O, 35.04 (by oxidizing power), 35.0 (by weight loss at  $480^\circ$ ). This sample had approximately 0.1 mol % bromate impurity, which was reduced to 0.003 mol % by recrystallization.

Thermogravimetric measurements showed an exothermic decomposition at  $275$ – $280^\circ$  to potassium bromate, which did not decompose to  $KBr$  until around  $390$ – $395^\circ$ . A recrystallized  $KBrO_4$  sample lost 8.78% of its weight at the lower temperature and another 26.16% at the higher. The calculated values are 8.74 and 26.23%.

The sharpness of the decomposition to bromate appears strongly dependent on the purity of the material. A sample of the original preparation showed some decomposition at  $150^\circ$ . After recrystallization, there was virtually no decomposition below  $260^\circ$ .

**Spectral Characteristics.**—The ultraviolet absorption spectra of solutions of twice-recrystallized  $KBrO_4$  appear in Figures 1 and 2. The spectra of  $HBrO_4$  solutions are identical to within a few per cent. All the solutions obey Beer's law.

Figure 3 shows the infrared absorption spectrum of

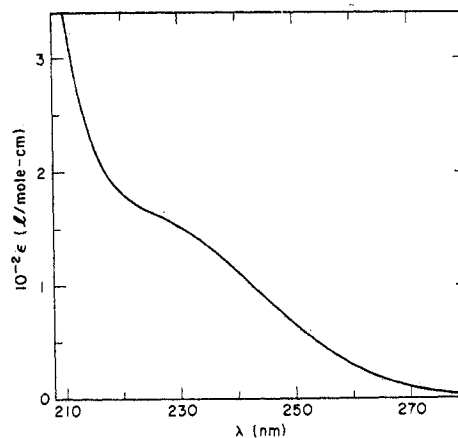
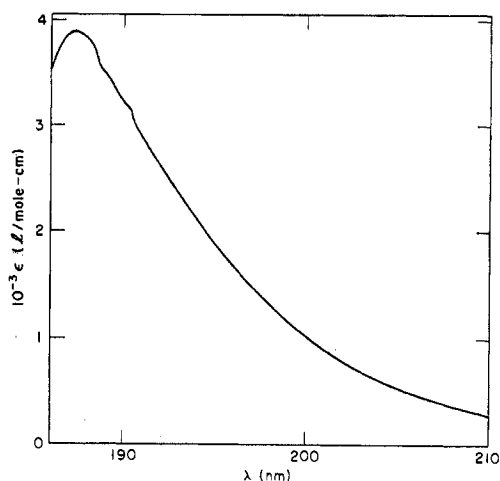
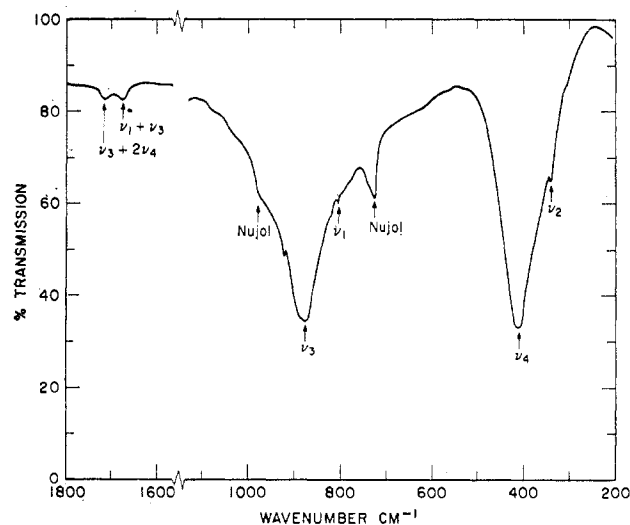


Figure 1.—Ultraviolet absorption spectrum of aqueous  $KBrO_4$ .

Figure 2.—Far-ultraviolet absorption spectrum of aqueous  $\text{KBrO}_4$ .Figure 3.—Infrared absorption spectrum of solid  $\text{KBrO}_4$ .

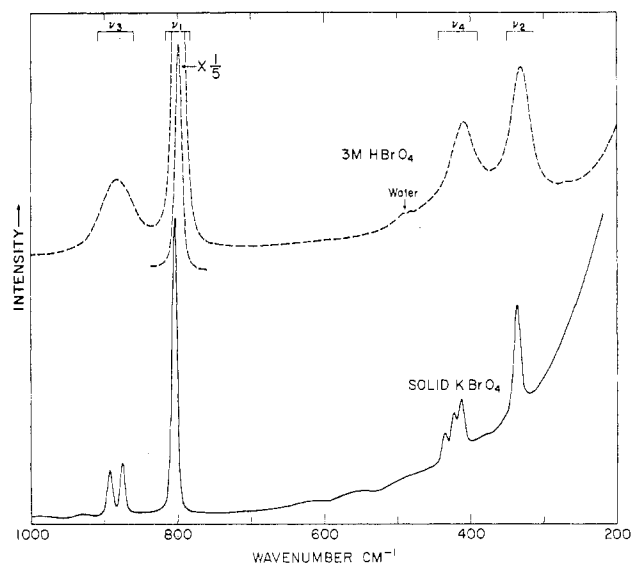
twice-recrystallized  $\text{KBrO}_4$  and gives probable assignments to the bands. The identifications of the weak bands, and especially of the combination bands around  $1700\text{ cm}^{-1}$ , are open to question. The weak band at  $920\text{ cm}^{-1}$  may be a combination of  $\nu_3$  with a lattice vibration.

Figure 4 shows the Raman spectra of aqueous  $3\text{ M HBrO}_4$  and twice-recrystallized solid  $\text{KBrO}_4$ , with the appropriate band assignments. An aqueous solution of  $\text{NaBrO}_4$  has a Raman spectrum nearly the same as that of the perbromic acid solution with respect both to peak positions and to relative peak heights.

**Oxygen Exchange.**—The exchange experiments showed that in 5–10 min at room temperature, less than 1% exchange of oxygen took place between water and  $0.2\text{--}0.3\text{ M}$  perbromate in neutral solution, in  $0.3\text{ M}$  acid, or in *ca.*  $0.06\text{ M}$  base.

### Discussion

The titrimetric results show that perbromic acid is a strong acid with one proton per heptavalent bromine,

Figure 4.—Raman spectra of solid  $\text{KBrO}_4$  and aqueous  $\text{HBrO}_4$ .

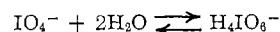
like perchloric acid, but unlike periodic acid.<sup>8</sup>

The ultraviolet spectrum of perbromate may be considered intermediate between that of perchlorate, which does not absorb appreciably above  $185\text{ nm}$ , and that of periodate, which has an absorption maximum at  $222.5\text{ nm}$ .<sup>9</sup>

The fact that perbromic acid and alkali perbromate solutions have the same ultraviolet and Raman spectra indicates that the same ionic species is present in both, while the similarity of the Raman spectrum of solid  $\text{KBrO}_4$  to the spectra of the solutions indicates that the same species is also present in the solid. Intercomparison of the Raman and infrared spectra shows that two of the four Raman bands are strongly active in the infrared spectrum, which is the relationship expected for a tetrahedral molecule.<sup>1</sup> We may therefore conclude that the perbromate species is indeed a tetrahedral  $\text{BrO}_4^-$  ion in solid  $\text{KBrO}_4$  and in acid and neutral aqueous solutions. Table I compares the fundamental vibrational frequencies of  $\text{BrO}_4^-$  with those of the other perchalates.

	$\text{ClO}_4^-$ <sup>10</sup>	$\text{BrO}_4^-$	$\text{IO}_4^-$ <sup>10</sup>
$\nu_1$	935	798	791
$\nu_2$	460	331	256
$\nu_3$	1050–1170	883	853
$\nu_4$	630	410	325

The lack of rapid oxygen exchange between  $\text{BrO}_4^-$  and water indicates the absence of any fast hydration equilibrium such as that found in periodates<sup>8</sup>



(8) C. E. Crouthamel, A. M. Hayes, and D. S. Martin, *J. Am. Chem. Soc.*, **73**, 82 (1951).

(9) C. E. Crouthamel, H. V. Meek, D. S. Martin, and C. V. Banks, *ibid.*, **71**, 3031 (1949).

(10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 103–110.

As an oxidant, perbromate exhibits properties intermediate between those of perchlorate and those of periodate. However, because of their slowness, the reactions shed little or no light on the thermodynamic stability and oxidizing power of perbromate.

The instability of concentrated perbromic acid warrants detailed study to elucidate the mechanism of decomposition. It is interesting to note that some perbromic acid can be distilled in spite of this decomposition, confirming the early observation of vapor-phase  $\text{HBrO}_4$  in the mass spectrometer.<sup>11</sup>

The properties found for the perbromates do not explain why these compounds have been so hard to prepare. Although the thermal decomposition studies

(11) M. H. Studier, *J. Am. Chem. Soc.*, **90**, 1901 (1968).

show that efforts to make perbromates by disproportionation of bromates are most likely doomed to failure, it is not at all clear why electrolytic synthesis is so unsatisfactory.<sup>2</sup> It may be that the stumbling block is a prohibitively high activation energy caused by an extremely unstable Br(VI) intermediate through which the synthesis must proceed.

**Acknowledgment**—The author is indebted to Mr. Frank Gallagher and Mr. William Johnson for the thermogravimetric measurements, to Mr. Kenneth Jensen for the potassium analyses, to Mrs. Donald Engelkemeir for measurement of oxygen isotope ratios, and to Mr. Jerome Lech for the analyses by emission spectrography.

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## The Lower Halides of Hafnium. A Nonstoichiometric Hafnium Triiodide Phase<sup>1</sup>

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A hafnium iodide phase of the composition  $\text{HfI}_{3.2-3.3}$  which is free of unreacted metal is obtained by the reaction of liquid  $\text{HfI}_4$  with metal foil (600 ppm of Zr) in a sealed tantalum container at 500–550°. The lower composition limit established from equilibration with separate metal powder is  $\text{HfI}_{3.0}$  at 425–575°; the phase in equilibrium with  $\text{HfI}_4(1)$  varies from  $\text{HfI}_{3.46}$  at 475° to  $\text{HfI}_{3.20}$  at 550°. Neither equilibration of  $\text{HfI}_4$  or  $\text{HfI}_3$  with metal at up to 1000° nor disproportionation of  $\text{HfI}_3$  under high vacuum gives any indication of the existence of still lower iodide, specifically  $\text{HfI}_2$ . X-Ray powder data indicate that the *a* and *c* dimensions of the previously suggested hexagonal unit cell<sup>2</sup> should probably be doubled and quadrupled, respectively. The composition  $\text{HfI}_{3.3}$  shows a small temperature-independent paramagnetism corresponding to a  $\mu_{\text{eff}}$  value of 0.68 at 300°K; the susceptibilities are considerably smaller than reported earlier<sup>3</sup> for impure samples.

### Introduction

The lower halides of hafnium have been only partially characterized, principally because reductions of the tetrahalides under diverse conditions are characteristically slow and incomplete. To some extent the interpretation of what is known has been based on the assumption that there should be a close parallel with the better known lower halides of zirconium as there is in many ways in the chemistries of the tetravalent states. The latter, of course, arises from the well-known effect of the lanthanide contraction, at least as it affects properties largely determined by radii of the tetrapositive state, but it is less clear how the interjection of the 4f elements should influence the stabilities of lower oxidation states.

The direct reduction of hafnium(IV) to hafnium(III) halides (except fluoride) by hafnium metal itself has been brought to completion best by Larsen and Leddy.<sup>4</sup>

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 8–13, 1968.

(2) L. F. Dahl, T. Chiang, P. W. Seabaugh, and E. M. Larsen, *Inorg. Chem.*, **3**, 1236 (1964).

(3) W. A. Baker, Jr., and A. R. Janus, *J. Inorg. Nucl. Chem.*, **26**, 2087 (1964).

(4) E. M. Larsen and J. J. Leddy, *J. Am. Chem. Soc.*, **78**, 5983 (1956).

Stoichiometric amounts of tetrahalide and metal powder sealed in glass ampoules were heated up to 700° using a bomb to counteract the internal pressures. This procedure gave up to 80–85% conversion to the tribromides and triiodides of both hafnium and zirconium but only about 40% for the chlorides. The unreacted tetrahalide sublimed off during the quenching process, and solutions of the residues in water gave appropriate analyses for the trihalides after a precipitate of unreacted metal was filtered off. Trihalides of greater than 99% purity were obtained when the initial products were re-ground and reheated with large excesses of the appropriate tetrahalide, although analytical data were not reported. In later work such an  $\text{HfI}_3$  product was found to contain a residue of 6.4% metal, with larger amounts in the chloride and bromide.<sup>2</sup> The hafnium (and zirconium) trihalides all appeared to disproportionate incompletely into gaseous tetrahalide and a presumed dihalide when heated above 450° in sealed, evacuated tubes, and the reaction was followed either by tetrahalide loss or in a high-temperature X-ray camera.<sup>4</sup> The same synthesis reactions at 37–60 atm and ca. 500° gave  $\geq 99\%$  conversion to the zirconium(III) chloride and bromide<sup>5,6</sup> but unreproducible compositions with