

To make a relatively large quantity of perbromate, several hundred milligrams of XeF_2 was stirred with 4 ml of 0.4 M NaBrO_3 until the XeF_2 had all reacted. The resulting solution was 0.07 M in perbromate. Bromate was removed from this solution by precipitation with excess AgF at 0° . Then the ice-cold supernatant solution was made 0.5 M in RbF , and the rubidium perbromate precipitate was isolated, washed with a little ice water, and dissolved to make 5 ml of solution.

Aliquots of this solution were analyzed for bromate by reduction with iodide in 0.1 M acid in the presence of molybdate, followed by titration with thiosulfate.¹⁶ Other aliquots were analyzed for perbromate by the HBr method. Still other aliquots were made 6 M in HCl and 0.04 M in Mo(VI) . Excess SnCl_2 was added to these aliquots, and they were heated for 30 min in boiling water to reduce the perbromate to bromide. The bromide was then determined by oxidation to BrCN with chlorine in neutral cyanide solution, reduction of the BrCN by acid iodide, and titration with thiosulfate.¹⁷ In this way the solution was found to be $< 2 \times 10^{-4}$ M in bromate, 0.0302 ± 0.0005 M in total bromine, and 0.242 ± 0.001 N in total oxidizing power. The ratio of oxidizing power to total bromine agrees well with the value of 8.00 expected for heptavalent bromine, and there can be no doubt that the precipitate contained rubidium perbromate.

A detailed investigation of the properties of perbromates is now being undertaken.

Acknowledgment. The author is grateful to Dr. Martin H. Studier for continued encouragement and many helpful discussions during the course of this investigation. Of particular importance was his persistent suggestion that redoubled effort to synthesize perbromates on a macro scale with tagged bromine might pay off.

(16) I. M. Kolthoff, *et al.*, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, pp 269-270.

(17) E. Schulek, *Anal. Chim. Acta*, **2**, 74 (1948).

Evan H. Appelman

Argonne National Laboratory
Argonne, Illinois 60439

Received February 2, 1968

Perbromic Acid. Mass Spectrum¹

Sir:

Perbromic acid has been shown to be a stable compound and its mass spectrum has been determined.

Solutions containing alkali perbromates² were acidified with dilute sulfuric acid and evaporated on platinum filaments at room temperature. These were placed into the source of a modified^{3,4} time-of-flight mass spectrometer (Bendix Corp.) which was then evacuated. When the filaments were heated, mass spectra of HBrO_4 were observed. Figure 1 is a photograph of an oscilloscope display of a spectrum showing the parent ion, HBrO_4^+ , and its principal fragment ions. The ions Br_2^+ , Br^+ , HBr^+ , BrO^+ , and HBrO^+ were observed

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

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

(3) M. H. Studier, *Rev. Sci. Instr.*, **34**, 1367 (1963).

(4) J. R. Haumann and M. H. Studier, *ibid.*, in press.

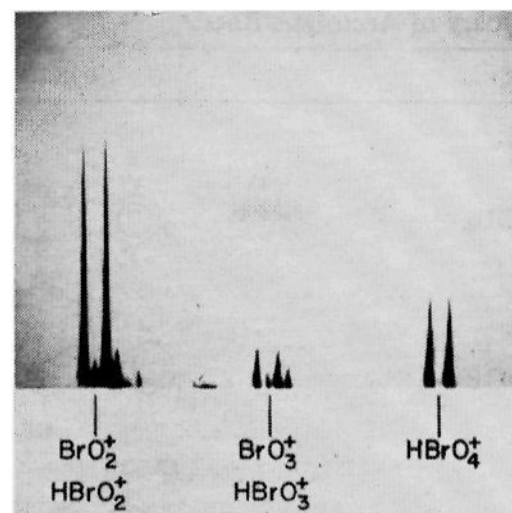


Figure 1. Mass spectrum of perbromic acid (70-V electrons). Each species is represented by two peaks from the nearly equiabundant isotopes Br^{79} and Br^{81} .

also, to a large extent from the independent species, Br_2 , HBr , and HBrO . After exhaustion of HBrO_4 from the filament, BrO_2 was observed as an independent species. On occasion, Br_2O^+ was observed.

For comparison, samples of perchloric acid were run in a similar fashion. The principal ions observed were HClO_4^+ , ClO_3^+ , and ClO_2^+ . The relative intensity of HBrO_3^+ and HBrO_2^+ puts perbromic acid in a position intermediate between periodic acid,⁵ from which HIO_3^+ and HIO_2^+ are prominent ions, and perchloric acid, from which HClO_3^+ and HClO_2^+ are not readily detected.

Perbromic acid seems to be a fairly stable compound. Spectra from a heated sample persisted for an hour. When a filament was cooled, HBrO_4 was observed to remain in the source region of the spectrometer for several minutes.

As expected, the volatility of perbromic acid is less than that of perchloric acid. The spectrum of perchloric acid was observed at room temperature as soon as the spectrometer was sufficiently evacuated to operate, whereas the spectrum of perbromic acid was not observed until the filament was heated to about 100° .

(5) M. H. Studier and J. L. Huston, *J. Phys. Chem.*, **71**, 457 (1967).

Martin H. Studier

Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

Received February 2, 1968

Methoxy Substituent Effects and Anchimeric Assistance in Solvolyses of 2-Benzonorbornenyl Bromobenzenesulfonates¹

Sir:

Reactivities and stereochemistry in acetolyses of *exo*- and *endo*-2-benzonorbornenyl bromobenzenesulfonates (*exo*-I-OBs and *endo*-I-OBs) are best interpreted with anchimerically assisted ionization (k_A) of the *exo*-I-OBs due to carbon participation and anchimerically unassisted ionization (k_S) of the epimeric *endo*-I-OBs.^{2a,b} However, as an indirect criterion for anchimeric assistance due to carbon participation in solvolysis of *exo*-I-

(1) Supported in part by the National Science Foundation.

(2) (a) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967), ref 27.