

Further, an experiment parallel to the azulene studies<sup>2</sup> using, instead, 9,10-dimethylantracene<sup>7</sup> as quencher (sensitizer, Michler's ketone; solvent, benzene) gave a rate constant ratio, equivalent to  $k_7/k_6$ , of  $115 \pm 5$  l./mole, which is the same within experimental error as that obtained in the azulene experiments.<sup>2</sup>

The extent of intimately associated molecular-pair quenching, as reflected in  $b$ , is surprisingly low, particularly in view of the notion that triplet-triplet energy transfer (eq 1 or 2) in solution involves actual contact of the donor-acceptor pair, leading to the impression that the efficiency of quenching step 3 should be close to unity.<sup>8</sup> Our results shed doubt on such a notion. If reactions 1 and 2 may take place with the donor-acceptor pair separated by at least one solvent molecule, the relatively small observed "cage" factors,  $b$ , become understandable. Our concept gains support when one considers that in glassy solution, such exchange interaction takes place with an average separation of 12–13 Å, a distance larger than the "average" separation between a neighboring donor-acceptor molecular pair.<sup>9,9a</sup>

(6) The same decay ratio as in benzene was used in the calculation because the pss composition with benzophenone in either solvent was found the same.

(7) 9,10-Dimethylantracene is chosen because of its low inter-system-crossing efficiency (<10%).

(8) The number of collisions of a set in a solvent cage is of the order  $10^{-10}$ ; see J. E. Leffer and E. Grunwald in "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 59.

(9) For a detailed discussion, see R. G. Bennett and R. E. Kellogg, *Prog. Reaction Kinetics*, **4**, 215 (1967).

(9a) NOTE ADDED IN PROOF. Professor Jack Saltiel pointed out to us an error in the published azulene rate constant ratios (p 3207 of ref 2). Thus, a factor of 1.4, the decay ratio, must be multiplied for meaningful comparison with our values.

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## The Synthesis of Perbromates<sup>1</sup>

Sir:

Past attempts to prepare perbromates, salts of heptavalent bromine, have been generally unsuccessful.<sup>2–6</sup> Very early reports of such compounds<sup>7</sup> could not be confirmed,<sup>8–11</sup> and several authors have discussed the reasons for their nonexistence.<sup>12–15</sup> In this communi-

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

(2) E. H. Cook, *J. Chem. Soc.*, **65**, 811 (1894).

(3) A. Michael and W. T. Conn, *Am. Chem. J.*, **23**, 89 (1901).

(4) P. W. Robertson, *Chem. News*, **106**, 50 (1912).

(5) W. F. DeCoursey, "Preparation of Perbromates," Doctoral Thesis, Iowa State College, 1953.

(6) G. M. Bancroft and H. D. Gesser, *J. Inorg. Nucl. Chem.*, **27**, (7) 1545 (1965).

(7) H. Kämmerer, *J. Prakt. Chem.*, **90**, 190 (1863).

(8) E. MacIvor, *Chem. News*, **33**, 35 (1876).

(9) E. MacIvor, *ibid.*, **55**, 203 (1887).

(10) M. M. P. Muir, *J. Chem. Soc.*, **30**, 469 (1876).

(11) G. Wolfram, *Ann.*, **198**, 95 (1879).

(12) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

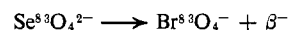
(13) R. Ferreira, *Bull. Soc. Chim. France*, 131 (1950).

(14) Z. Z. Hugus, Jr., *J. Am. Chem. Soc.*, **74**, 1076 (1952).

(15) D. S. Urch, *J. Inorg. Nucl. Chem.*, **25**, 77 (1963).

cation we describe the successful synthesis of perbromates and the isolation of the rubidium salt.

We initially synthesized perbromate by a hot-atom process—the  $\beta$  decay of radioactive  $\text{Se}^{83}$  incorporated into a selenate. The process may be written



Enriched  $\text{Se}^{82}$  (90%) was irradiated with thermal neutrons, dissolved in nitric acid, and oxidized to selenate by ozone in alkaline solution. After the 25-min  $\text{Se}^{83}$  activity had decayed, sodium perchlorate and bromate were added, and rubidium perchlorate was precipitated at 0° under conditions such that only about 1% of the bromate was coprecipitated. Approximately 14% of the 2.4-hr  $\text{Br}^{83}$  activity was found in the precipitate. This fraction was unchanged after extraction with  $\text{Br}_2$  in  $\text{CCl}_4$  or after treatment with iodide in 0.6  $M$   $\text{HCl}$ . However, after treatment with iodide in 6  $M$   $\text{HCl}$ , only 1% of the  $\text{Br}^{83}$  activity coprecipitated with rubidium perchlorate.

These results indicated the formation of a relatively unreactive perbromate ion and suggested that a determined effort might lead to the preparation of macro amounts of perbromates. We therefore attempted both chemical and electrolytic oxidation of bromate.

An electrolytic cell was set up with a platinum cathode immersed in 3 ml of 2.8  $M$   $\text{HClO}_4$  in a porous porcelain cup. The anode was a rotating platinum microelectrode in a similar cup immersed in a slurry of  $\text{Li}_2\text{CO}_3$  in 3 ml of 2.8  $M$   $\text{LiBrO}_3$  tagged with 36-hr  $\text{Br}^{82}$ . The two cups were placed in a container of 2.8  $M$   $\text{LiClO}_4$ , which in turn was immersed in a cooling bath at  $-15^\circ$ . The cell was run for about 1 A hr at an anodic current density of about 10  $\text{A}/\text{cm}^2$ . Successive portions of  $\text{Li}_2\text{CO}_3$  were added to the anolyte to maintain its neutrality, while the catholyte was periodically replaced to maintain its acidity.

At the end of the electrolysis about 2% of the bromine activity coprecipitated with  $\text{RbClO}_4$  but did not coprecipitate with  $\text{Ba}(\text{BrO}_3)_2$ . When an electrolysis was carried out at a similar current density, but in an unpartitioned cell, with dichromate used to inhibit cathodic reduction, essentially all of the bromine activity could be coprecipitated with  $\text{Ba}(\text{BrO}_3)_2$ .

The following technique was developed to analyze for perbromate in the presence of bromate. The solution, no more than 0.15  $M$  in bromate, was made 1.5  $M$  in  $\text{HBr}$  to reduce the bromate. Argon was bubbled through until the bromine color disappeared and did not return upon standing. The solution was then diluted with four times its volume of saturated  $\text{HBr}$ . After 5 min it was diluted tenfold with 2%  $\text{NaI}$  and titrated with thiosulfate. The titer of the electrolyzed solution treated in this manner agreed with the tracer results, if we assume that each mole of perbromate consumed 8 equiv of thiosulfate.

Aqueous bromate is not appreciably oxidized by sodium perxenate or by persulfate at 100°, with or without silver catalyst. Aqueous xenon difluoride, however, does oxidize bromate to perbromate. After a solution 0.14  $M$  in  $\text{XeF}_2$  and 0.24  $M$  in  $\text{NaBrO}_3$  had stood until the  $\text{XeF}_2$  had all reacted with water, analysis with  $\text{HBr}$  indicated the presence of 0.01  $M$  perbromate. A solution 0.14  $M$  in  $\text{XeF}_2$  and 1.5  $M$  in  $\text{LiBrO}_3$  yielded 0.018  $M$  perbromate.

To make a relatively large quantity of perbromate, several hundred milligrams of  $\text{XeF}_2$  was stirred with 4 ml of 0.4 *M*  $\text{NaBrO}_3$  until the  $\text{XeF}_2$  had all reacted. The resulting solution was 0.07 *M* in perbromate. Bromate was removed from this solution by precipitation with excess  $\text{AgF}$  at 0°. Then the ice-cold supernatant solution was made 0.5 *M* in  $\text{RbF}$ , 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.<sup>16</sup> Other aliquots were analyzed for perbromate by the  $\text{HBr}$  method. Still other aliquots were made 6 *M* in  $\text{HCl}$  and 0.04 *M* in  $\text{Mo(VI)}$ . Excess  $\text{SnCl}_2$  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  $\text{BrCN}$  with chlorine in neutral cyanide solution, reduction of the  $\text{BrCN}$  by acid iodide, and titration with thiosulfate.<sup>17</sup> In this way the solution was found to be  $< 2 \times 10^{-4}$  *M* in bromate,  $0.0302 \pm 0.0005$  *M* in total bromine, and  $0.242 \pm 0.001$  *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.

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(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).

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### Perbromic Acid. Mass Spectrum<sup>1</sup>

Sir:

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

Solutions containing alkali perbromates<sup>2</sup> were acidified with dilute sulfuric acid and evaporated on platinum filaments at room temperature. These were placed into the source of a modified<sup>3,4</sup> time-of-flight mass spectrometer (Bendix Corp.) which was then evacuated. When the filaments were heated, mass spectra of  $\text{HBrO}_4$  were observed. Figure 1 is a photograph of an oscilloscope display of a spectrum showing the parent ion,  $\text{HBrO}_4^+$ , and its principal fragment ions. The ions  $\text{Br}_2^+$ ,  $\text{Br}^+$ ,  $\text{HBr}^+$ ,  $\text{BrO}^+$ , and  $\text{HBrO}^+$  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.

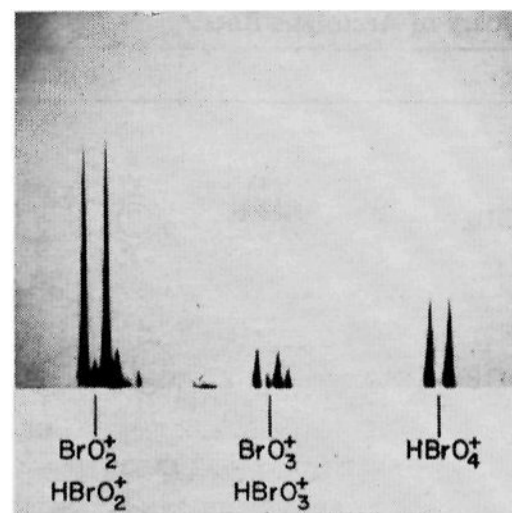


Figure 1. Mass spectrum of perbromic acid (70-V electrons). Each species is represented by two peaks from the nearly equiabundant isotopes  $\text{Br}^{79}$  and  $\text{Br}^{81}$ .

also, to a large extent from the independent species,  $\text{Br}_2$ ,  $\text{HBr}$ , and  $\text{HBrO}$ . After exhaustion of  $\text{HBrO}_4$  from the filament,  $\text{BrO}_2$  was observed as an independent species. On occasion,  $\text{Br}_2\text{O}^+$  was observed.

For comparison, samples of perchloric acid were run in a similar fashion. The principal ions observed were  $\text{HClO}_4^+$ ,  $\text{ClO}_3^+$ , and  $\text{ClO}_2^+$ . The relative intensity of  $\text{HBrO}_3^+$  and  $\text{HBrO}_2^+$  puts perbromic acid in a position intermediate between periodic acid,<sup>5</sup> from which  $\text{HIO}_3^+$  and  $\text{HIO}_2^+$  are prominent ions, and perchloric acid, from which  $\text{HClO}_3^+$  and  $\text{HClO}_2^+$  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,  $\text{HBrO}_4$  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).

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### Methoxy Substituent Effects and Anchimeric Assistance in Solvolyses of 2-Benzonorbornenyl Bromobenzenesulfonates<sup>1</sup>

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.<sup>2a,b</sup> 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.