nadium(0) hexacarbonyl[35] and 9.3 g (0.1 mol) of freshly distilled cycloheptatriene in 100 ml of hexane.[36] Air (1 ml) was then injected into the reaction flask through a serum stopper by syringe,[37] and the solution was heated at reflux for 1 hr. The reaction mixture was cooled, transferred by cannula to a 250-ml centrifuge bottle, and centrifuged. Portions of the resulting dark green solution ($\sim$30 ml) were successively transferred into a 40-ml centrifuge tube capped with a serum stopper, and hexane and excess cycloheptatriene were removed at room temperature under vacuum until the entire solution was concentrated to $\sim$5 ml. The residual oil was diluted with 10 ml of pentane and centrifuged and the supernatant solution again transferred to another stoppered centrifuge tube. Cooling this solution to $-78°$ for 8–36 hr resulted in crystallization of **1** as green-black plates. The mother liquor was removed by cannula from these crystals at $-78°$ and the resulting **1** dried in a slow stream of nitrogen at room temperature. Final purification of **1** before preparing nmr samples was effected by sublimation (42°, 0.05 Torr). The total yield of **1** is $\sim$15%. Solid **1** reacts slowly with air; solutions of **1** oxidize very rapidly.

Sample Preparation. The preparation of samples in solvents of low viscosity was carried out with careful exclusion of oxygen and water, using unexceptional procedures. The preparation of solutions of **1** in solvents more viscous than cyclooctane required a special procedure, since the rate of solution in these solvents was very slow. *Ca.* 40 mg. of freshly sublimed **1** was transferred in a nitrogen-filled glove bag to a 5-ml round-bottomed flask, 10 μl of deoxygenated benzene was added, and the mixture was ground into an oil. Then 0.25 ml of the desired solvent, previously degassed under vacuum by three freeze–thaw cycles (liquid nitrogen), was added with further stirring, a serum stopper placed on the flask, and the solution forced into a syringe using a positive pressure of nitrogen. The solution was transferred into an oxygen-free nmr tube through a serum stopper and the tube sealed under nitrogen. The presence of these small amounts of benzene in the sample had no significant effect on the spectral line shapes. Samples in toluene and cyclooctane were $\sim$2.5–3.5 mol % **1**; samples in Nujol were $\sim$1.5–3.0 wt % **1**. The viscosities of all solutions of **1** were assumed to be the same as the viscosities of the solvents themselves. Considering the low concentration of **1** in these samples, this assumption seems reasonable.

Values of T_{1V} were obtained by comparison of the shapes and half-height line widths of calculated (Figure 2) and observed spectra. The peak widths of **1** were corrected for viscous broadening unrelated to the vanadium quadrupole relaxation by the use of benzene as an internal line width standard in the hydrocarbon solvents and TMS in the toluene-d_8 sample. All of the data in Figure 4 have been so corrected.

Acknowledgments. We are indebted to Professor E. W. Merrill of the Department of Chemical Engineering for the use of the Brookfield viscometer used in these studies, to Professor Alan Davison of this department for helpful suggestions concerning the preparation of **1**, and to John Lisle for extensive assistance with the computer calculations.

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(35) R. Ercoli, F. Calderazzo, and A. Alberola, *J. Amer. Chem. Soc.*, **82**, 2966 (1960); R. P. M. Werner and H. E. Podall, *Chem. Ind.* (London), 144 (1961); R. B. King, "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, p 82.

(36) Oxygen and olefins were carefully removed from the hexane before use by stirring with 96% H_2SO_4, followed by distillation from a suspension of sodium benzophenone ketyl under nitrogen.

(37) If this reaction is carried out with *strict* exclusion of oxygen, no **1** is formed. Presumably, traces of vanadium in higher oxidation states than V(0) or V($-$I) are required as catalysts for the formation of **1**.

Production of Bromite and Perbromate Ions in Crystalline $CsBrO_3$ Irradiated with Cobalt-60 γ Rays and the Vibrational Spectrum of the BrO_4^- Ion[1]

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Contribution from the Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830. *Received December 16, 1968*

Abstract: The formation at *ca.* 30° by ^{60}Co γ rays of perbromate and bromite ions in $CsBrO_3$ was demonstrated by infrared absorption measurements on irradiated crystals and by ion-exchange column chromatographic separations on aqueous solutions of the radiolyzed solid. Vibrational spectra (infrared and laser-excited Raman measurements) were obtained for BrO_4^- ion in solution and in crystalline $RbBrO_4$ and $(C_6H_5)_4AsBrO_4$. The frequency assignments are ν_1 801, ν_2 331, ν_3 878, and ν_4 410 cm^{-1}. Force constants derived from these frequencies suggest that there is a close similarity in bonding between BrO_4^- and IO_4^- and that a significant decrease in the nonbonding interactions occurs in the series ClO_4^-, BrO_4^-, IO_4^- as the size of the central atom increases and the oxygens become less crowded. An unsuccessful search was made for $^{82}BrO_4^-$ ion formed in $^7LiBrO_3$ by thermal neutron capture. The yield of $^{82}BrO_4^-$ ion, if formed, was less than 0.05%.

A continuing objective in our researches on the decomposition of bromate ion in crystalline alkali-metal and alkaline-earth bromates[2] by energetic ionizing radiations has been to relate the species observed in an aqueous solution of the irradiated salt to those trapped in the crystal. It is by no means certain that these are always the same species; in at least one instance[3a] there is evidence that they were quite different. On the other hand, recent studies[3b] with crystalline $KClO_3$ irradiated with ^{60}Co γ rays have shown that within experimental error all the perchlorate ion found in aqueous solution was originally present as ClO_4^- in the crystal lattice. Evidence for stable products in radiolyzed $CsBrO_3$ crystals also has been obtained: cesium bromide in the lattice has been indicated by X-ray diffraction techniques,[2] and reflectance spectra[2] of solid samples show an absorption band in

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) For a review see J. W. Chase and G. E. Boyd, "The Radiolytic Decomposition of Crystalline Alkali-metal and Alkaline-earth Bromates," ASTM Special Publication No. 400, 1966, p 17 ff.

(3) (a) L. J. Sharman and K. J. McCallum, *J. Am. Chem. Soc.*, **77**, 2989 (1955); (b) L. C. Brown and G. E. Boyd, *J. Phys. Chem.*, **73**, 396 (1969).

the ultraviolet (peak at *ca.* 3300 Å) which may be assigned[4] to BrO^-.

Oxygen gas is evolved on dissolving irradiated alkali-metal and alkaline-earth bromates in water, and Br^-, BrO^-, and BrO_2^- ions are found in solution.[2,5,6] The presence of bromite ion in the crystal lattice, however, has not been demonstrated. The amount of oxygen gas was found to increase linearly with the absorbed dose for low and intermediate extents of radiolysis, but for large doses its concentration increased less rapidly than linearly. This result and other considerations led to the suggestion[5,6] that oxygen may be reacting with bromate to give perbromate ion, BrO_4^-, analogous to the formation of ClO_4^- ion in the radiolysis of the alkali-metal chlorates. Perbromate ion until recently, however, has been unknown, despite many attempts to prepare it. The report[7] that it can be prepared by oxidation of bromate ion in aqueous solution by XeF_2 and that crystalline $RbBrO_4$ is stable at room temperature prompted us to renew our search for the species in crystalline $CsBrO_3$ radiolyzed by ^{60}Co γ rays. Rubidium perbromate and tetraphenylarsonium perbromate, $(C_6H_5)_4AsBrO_4$, were prepared, and the vibrational spectrum of BrO_4^- ion has been observed with infrared and laser-excited Raman techniques. The ir "fingerprint" of perbromate ion was used to show that BrO_4^- was formed by γ rays in crystalline $CsBrO_3$. Further demonstration of the production of perbromate ion was obtained with ion-exchange column chromatography.

Experimental Section

Materials. The preparation and analysis of anhydrous $^7LiBrO_3$[8] and $CsBrO_3$[5] have been described. Xenon difluoride (purchased from Peninsular Chemresearch, Inc., Gainesville, Fla. 32601) was used "as received" without further purification. Other chemicals were reagent grade and were used without further purification.

Ir and Raman Spectral Measurements. The infrared spectrum of BrO_4^- ion, to be used for the identification of BrO_4^- in ^{60}Co γ-ray irradiated $CsBrO_3$, was determined with two salts, $RbBrO_4$ and tetraphenylarsonium perbromate, $(C_6H_5)_4AsBrO_4$. Laser-excited Raman spectra of the solids and of aqueous solutions of BrO_4^- ion also were obtained to provide additional structural data on this long-sought species.

Centigram quantities of $RbBrO_4$ were prepared by oxidizing aliquots of aqueous 0.4 *M* $NaBrO_3$ solutions with decigram amounts of XeF_2 as described by Appelman.[7] Crystalline $RbBrO_4$, free of BrO_3^- ion, was obtained by dissolving the initial impure product in 1.5 *M* HBr, sparging the solution with N_2 to remove Br_2 formed by reduction of the BrO_3^-, and finally recrystallizing the slightly soluble compound. The infrared spectrum of the purified salt (Figure 1) did not show any absorptions at *ca.* 365 and 800 cm^{-1} which were observed in the initial salt and are attributable to BrO_3^- ion. Tetraphenylarsonium perbromate was precipitated in centigram quantities by addition of excess tetraphenylarsonium chloride to XeF_2-oxidized $NaBrO_3$ solutions. The salt was filtered and washed with water to remove traces of BrO_3^- ion. The final product was recrystallized from 50% ethyl alcohol–water solution and vacuum dried at room temperature. The infrared spectrum of the final product showed no BrO_3^- ion absorbancies.

Infrared spectra of the solids were obtained with KBr pressed pellet techniques and a Beckman IR-12 grating infrared spectrophotometer operated in the double-beam mode with dry air in the reference beam. Raman spectra were recorded on a modified Cary Model 81 spectrophotometer equipped with a Spectra-Physics 125 helium–neon laser emitting *ca.* 65 mW of radiation at 6328 Å. Polarization measurements were made with a half-wave, retardation-plate polarizer mounted in the laser beam.

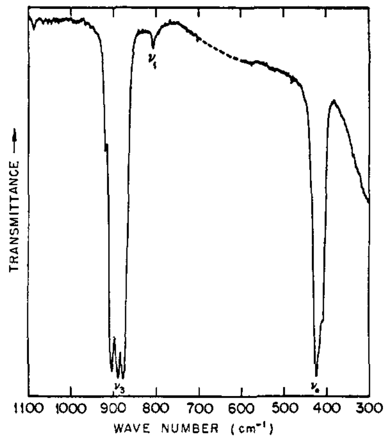

Figure 1. Infrared spectrum of cyrstalline $RbBrO_4$ (KBr pellet; grating change indicated by dashed line).

Anion-Exchange Column Chromatography. An extension of the anion-exchange chromatographic separation technique employed previously[9] to separate anionic radiobromine species in alkaline solutions was used to separate and identify BrO_4^- ion. It had been shown that BrO_2^-, BrO_3^-, and Br^- ions can be eluted quantitatively from Dowex-1 anion exchanger with aqueous 0.5 *M* HCO_3^-, 1.0 *M* HCO_3^-, and 1.0 *M* NO_3^- solutions, respectively, and that BrO^- ion reacts and remains irreversibly bound at the top of the exchanger bed.

Preliminary experiments to determine the chromatographic behavior of BrO_4^- on Dowex-1 resin were performed with 0.25-ml aliquots of 0.5 *M* solutions of ^{82}Br tagged bromate ion which had been oxidized with 200-mg portions of XeF_2. Bromine-82 labeled BrO_3^- was prepared by neutron irradiation of $^7LiBrO_3$ followed by a waiting period of *ca.* 48 hr to allow for the decay of the short-lived bromine isotopes, *i.e.*, ^{80m}Br ($t_{1/2}$ = 4.38 hr), ^{80}Br ($t_{1/2}$ = 17.6 min), and ^{82m}Br ($t_{1/2}$ = 6.1 min). The XeF_2-oxidized $^{82}BrO_3^-$ solutions were neutralized with $NaHCO_3$, an aliquot was transferred to the top of a cylindrical bed of 200–400 mesh Dowex 1-X10 anion-exchange resin (HCO_3^- form), and the elution sequence described above was followed. After sufficient 1 *M* NO_3^- solution had been passed to reduce the activity of the effluent from the column to the background level, thereby ensuring complete removal of Br^- ion, the eluting agent was changed to freshly prepared 1.0 *M* $NaBF_4$ solution and radioperbromate ion was desorbed. The elution of BrO^- from the top of a resin column by 1.0 *M* $NaBF_4$ was negligible. Chromatograms of XeF_2-oxidized, neutron-irradiated $^7LiBrO_3$ (A) and of irradiated $^7LiBrO_3$ dissolved in 0.1 *M* $NaHCO_3$ (B) are shown in Figure 2.

The ion-exchange column separations were complemented by coprecipitation experiments designed to determine quantitatively the oxidation state of the ^{82}Br species in the XeF_2-oxidized $^7LiBrO_3$ solutions. Bromate ion was separated from solution by precipitation of slightly soluble $AgBrO_3$ at 0°, and the procedure was repeated until an inactive precipitate was obtained. Perbromate ion in the supernatant liquid was determined either by precipitation of $(C_6H_5)_4AsBrO_4$ or by direct counting of an aliquot. Initially ClO_4^- ion was added as a "stand-in" carrier for BrO_4^- before the first $AgBrO_3$ precipitation. After the BrO_3^- ion had been precipitated, $(C_6H_5)_4AsCl$ was added and BrO_4^- ion was coprecipitated with tetraphenylarsonium perchlorate. The direct counting method appeared to be feasible after it had been shown by the chromatographic separations that only BrO_3^- and BrO_4^- ions remained after the XeF_2 oxidation (*cf.* Figure 2). Once bromate ion had been removed by precipitation, an aliquot of the supernatant solution was counted and the amount of perbromate ion was calculated.

Bromine-82 radioactivity was determined by γ counting with a 3 in. × 3 in. NaI (Tl activated) well crystal connected with a single-channel analyzer and scaling system. Empirically determined coincidence corrections were applied when the counting loss exceeded 1%.

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[4] C. Ramasastry and Y. V. G. S. Murti, *Indian J. Pure Appl. Phys.*, **2**, 35 (1964).

[5] G. E. Boyd and Q. V. Larson, *J. Phys. Chem.*, **68**, 2627 (1964).

[6] G. E. Boyd and Q. V. Larson, *ibid.*, **69**, 1413 (1965).

[7] E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).

[8] G. E. Boyd and T. G. Ward, Jr., *J. Phys. Chem.*, **68**, 3809 (1964).

[9] G. E. Boyd and Q. V. Larson, *J. Am. Chem. Soc.*, **90**, 254 (1968).

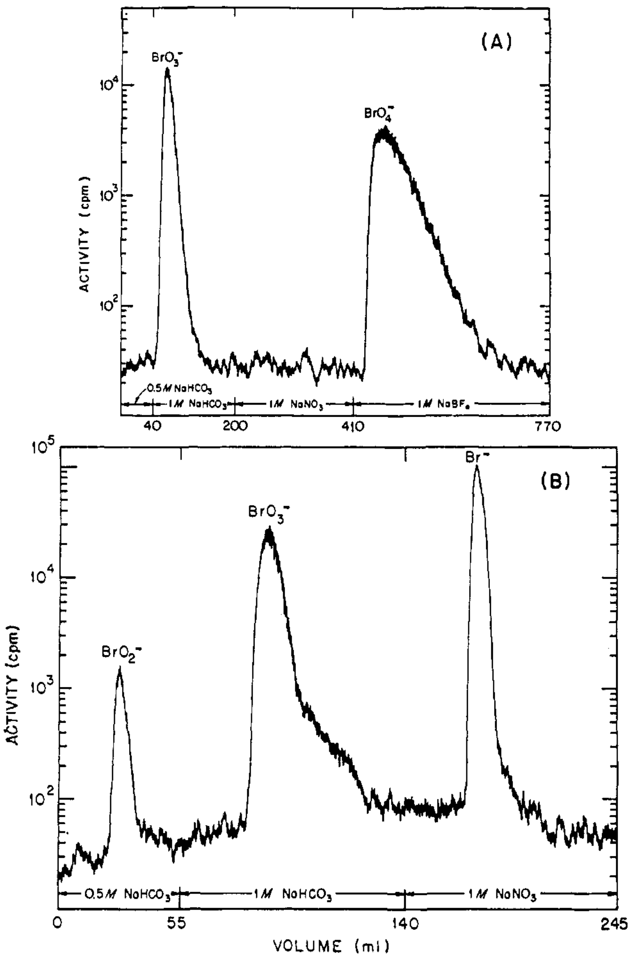

Figure 2. Anion-exchange chromatographic separation of radioperbromate ion in neutron-irradiated $^7LiBrO_3$: (A) irradiated crystals dissolved in H_2O and oxidized with XeF_2; (B) irradiated crystals dissolved in 0.1 *M* $KHCO_3$.

Radiolysis of Crystalline $CsBrO_3$. Cesium bromate appeared to be the best compound for detecting radiolytically produced BrO_4^- ion as it is the most easily radiolyzed of all the alkali-metal bromates, and therefore the highest concentration of radiolytic products would be produced. Infrared spectra of ^{60}Co γ-ray irradiated $CsBrO_3$ were obtained with crystals irradiated in a constant geometry ^{60}Co source (equilibrium temperature *ca.* 30°) where the dose rate was 1.89×10^{20} eV min^{-1} (mole of $CsBrO_3)^{-1}$. A sample exposed to a dose of 2.9×10^{24} eV (mole of $CsBrO_3)^{-1}$ was examined. Potassium bromide disks containing *ca.* 2.4% by weight of unirradiated or of irradiated salt were prepared, and infrared spectra were recorded from 300 to 1100 cm^{-1}. A portion of the irradiated salt was heated for 1 hr at 250° before infrared analysis. The spectra of the thermally annealed radiolyzed $CsBrO_3$ and of the unirradiated salt were identical.

The chromatographic detection of BrO_4^- ion in ^{60}Co γ-ray irradiated $CsBrO_3$ was accomplished with ^{82}Br-tagged $CsBrO_3$ samples. Labeled $CsBrO_3$ was prepared from a 25-mg sample of $^7LiBrO_3$ neutron-irradiated as described above. The radioactive $^7LiBrO_3$ was heated at 255° for 1 hr to convert >98% of the bromine-82 to $^{82}BrO_3^-$ ion,[9] and then dissolved in a solution containing 500 mg of inactive $CsBrO_3$. The ^{82}Br-labeled $CsBrO_3$ was recrystallized from hot aqueous solution, air-dried under suction for 30 min, and oven-dried at 140° for 90 min. A 200-mg portion was irradiated in a high-intensity, constant-geometry ^{60}Co γ-ray source (equilibrium temperature *ca.* 30°) where the dose rate was 8.0×10^{20} eV min^{-1} (mole of $CsBrO_3)^{-1}$. A 90-mg portion of the irradiated salt was dissolved in 0.1 *N* arsenous acid–0.1 *M* $NaHCO_3$ solution, and an ion-exchange column separation was performed. A 60-mg portion of the preparation which had not been exposed to ^{60}Co γ rays also was separated, and the oxidation state of the ^{82}Br in it was inferred from the volume at which radioactivity appeared in the eluate from the ion-exchange column.

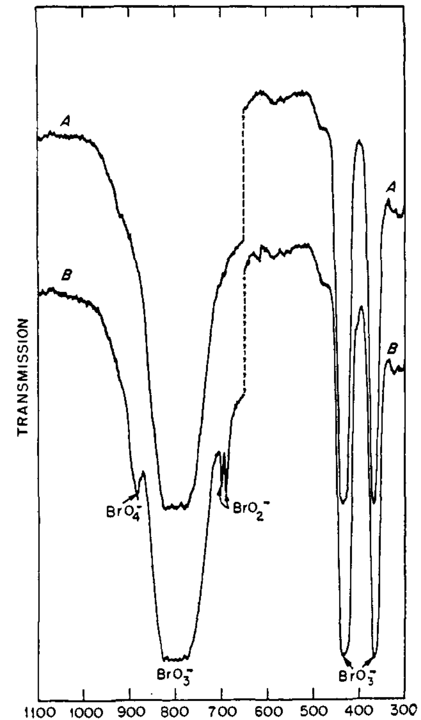

Figure 3. Infrared spectra of crystalline $CsBrO_3$: (A) unirradiated $CsBrO_3$; (B) ^{60}Co γ-ray irradiated $CsBrO_3$, dose = 2.9×10^{24} eV (mole of $CsBrO_3)^{-1}$ (KBr pellets; grating change indicated by dashed line).

Search for Perbromate Ion in Neutron-Irradiated $^7LiBrO_3$. Lithium-7 bromate was selected for neutron bombardment in a search for $^{82}BrO_4^-$ ion possibly formed *via* "hot-atom" reactions. Samples (25 mg) of highly irradiated $^7LiBrO_3$ [nvt (thermal) = 1.8 to 5.4×10^{16} neutrons/cm^2] were dissolved in 1-ml aliquots of either 0.1 *N* $NaHCO_3$ or 0.1 *N* arsenous acid–0.1 *N* $NaHCO_3$ and chromatographed as before. Dissolution in the latter medium reduced $^{82}BrO^-$ and $^{82}BrO_2^-$ ions to $^{82}Br^-$ ion and thus allowed the detection of smaller amounts of $^{82}BrO_4^-$ ion. Separate experiments indicated that the reduction of BrO_4^- ion by 0.1 *N* arsenous acid–0.1 *N* $NaHCO_3$ was negligible during the required handling time ($\leq$10 min).

Experimental Results and Discussion

Formation of Perbromate and Bromite Ions in Radiolyzed $CsBrO_3$ Crystals. The infrared spectra of unirradiated and ^{60}Co γ-ray irradiated $CsBrO_3$ [total absorbed dose = 2.9×10^{24} eV (mole of $CsBrO_3)^{-1}$] are shown in Figure 3. The peak observed at 883 cm^{-1} was attributed to the ν_3 vibration of BrO_4^- (see Figure 1 and Table I), whereas the two peaks at 688 and 698 cm^{-1} were assigned to BrO_2^-. The latter frequencies are in approximate agreement with those observed by Evans and Lo[10] for BrO_2^- in aqueous solution (709 and 680 cm^{-1}) by Raman spectroscopy.

The relative order and spacing of the $BrO_4^-:BrO_3^-:BrO_2^-$ bands in Figure 3 are consistent with those for the analogous chlorine oxyanions in ^{60}Co γ-ray irradiated $KClO_3$,[3b] and this lends additional credence to the above band identifications.

Anion-exchange column chromatograms of ^{82}Br-tagged unirradiated and ^{60}Co γ-ray irradiated $CsBrO_3$ [total absorbed dose = 3.2×10^{24} eV (mole of $CsBrO_3)^{-1}$] are shown in Figures 4A and 4B, respectively. The chromatogram for the unirradiated salt illustrates

(10) J. C. Evans and G. Y. S. Lo, *Inorg. Chem.*, **6**, 1483 (1967).

Table I. Vibrational Frequencies of BrO_4^- (cm^{-1})[a]

Compound	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
$RbBrO_4$	802 R	335 R	872, 890 R 879, 890, 904 IR	415 R 410, 420, 426 IR
$RbBrO_4$(aq)	801 R, P	331 R	874 R	411 R
$(C_6H_5)_4AsBrO_4$[b]	799 R	. . .	878 IR	410 IR

[a] R = Raman, IR = infrared, P = polarized, aq = aqueous. [b] The ν_3 and ν_4 bands of $(C_6H_5)_4AsBrO_4$ showed no splitting indicating little or no perturbation of the BrO_4^- ion's T_d symmetry in this compound.

that the initial oxidation state of the ^{82}Br activity was pentavalent, *i.e.*, >99.9% BrO_3^- ion, and that self-radiolysis of the radioactive salt produced no detectable amounts of other bromine oxidation states. The chromatographic separation and identification of BrO_4^- ion in ^{60}Co γ-ray irradiated $CsBrO_3$ are shown in Figure 4B. Analysis of the various chromatographic fractions, Br^-, BrO_3^-, and BrO_4^-, yielded a ^{82}Br activity distribution of 6.4, 92.7, and 0.86%, respectively. The Br^- ion yield, of course, contained contributions from all arsenous acid reducible species, *e.g.*, BrO^- and BrO_2^-. The following "100-eV yields" (*i.e.*, *G* values, molecules/100 eV) were calculated from these data for an exposure of 3.2×10^{24} eV (mole of $CsBrO_3$)$^{-1}$: $G(Br^- + BrO^- + BrO_2^-) = 1.21$; $G(-BrO_3^-) = 1.37$; and $G(BrO_4^-) = 0.16$.

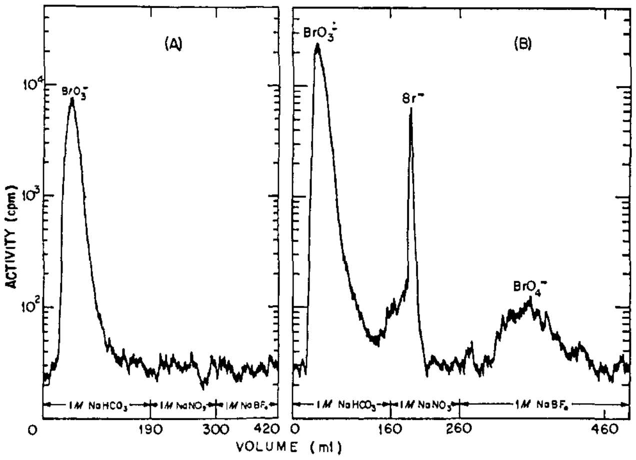

Figure 4. Anion-exchange chromatographic separation of radioperbromate ion in ^{60}Co γ-ray irradiated $CsBrO_3$ (BrO_3^- tagged with ^{82}Br): (A) unirradiated; (B) ^{60}Co γ-ray irradiated, dose = 3.2×10^{24} eV (mole of $CsBrO_3$)$^{-1}$.

Attempts to detect $^{82}BrO_4^-$ ion in neutron-irradiated $^7LiBrO_3$ samples were fruitless. A limit for the yield of radioperbromate ion of ≤0.05% was estimated from these experiments. The relative yields of bromine species for different neutron irradiation times were in good agreement with earlier work.[9]

The Vibrational Spectrum of Perbromate Ion. Raman spectra of crystalline $RbBrO_4$ (B) and of a 0.1 *M* $RbBrO_4$–0.6 *M* HBr aqueous solution (A) are shown in Figure 5. These spectra reveal the characteristic tetrahedral ion pattern analogous to that for ClO_4^- and IO_4^-. Four Raman bands were observed, two of which coincided with two infrared absorptions (*cf.* Figure 1 and Table I). Vibrational frequencies and their assignments, made by analogy with ClO_4^- and IO_4^-, are listed in Table I. The Raman polarization measurements on the aqueous solution showed the ν_1 vibration to be strongly polarized and the other lines to be highly depolarized. Crystalline $RbBrO_4$ exhibits a weak ν_1 absorption in the infrared spectrum and a splitting of the ν_3 and ν_4 degenerate frequencies in both the infrared (Figure 1) and Raman spectra (Figure 5). This splitting is attributed to a lowering of the T_d symmetry of the BrO_4^- ion in the crystal. The shoulder on the high-frequency side of ν_3 in the infrared spectrum (Figure 1) may be caused by a combination band involving a lattice vibration. Similar effects in ClO_4^- ion have been summarized by Hezel and Ross.[11]

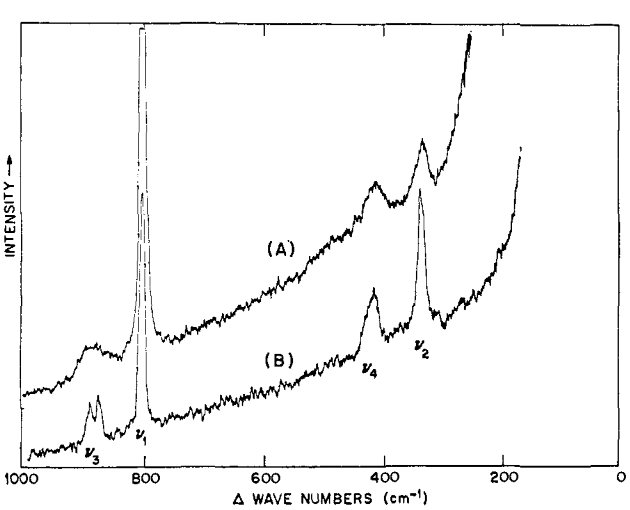

Figure 5. Raman spectra of perbromate ion: (A) 0.1 *M* $RbBrO_4$–0.6 *M* HBr aqueous solution; (B) crystalline $RbBrO_4$.

Venkateswarlu and Sundaram[12] have computed simple force constants for ClO_4^- and IO_4^- ions. Following a similar method which employs the symmetry coordinates of Meister and Cleveland,[13] valence force constants for ClO_4^-, BrO_4^-, and IO_4^- have been calculated with the Wilson *F* and *G* matrix method.[14] The following BrO_4^- ion frequencies were taken from Table I for the calculation: ν_1 801, ν_2 331, ν_3 878, and ν_4 410 cm^{-1}. These values are in good agreement with frequencies obtained recently by Appelman.[15] The Br–O bond distance was assumed to be the same as in $KBrO_3$ (1.68 Å)[15a,16] based on the systematics of the X–O bond-

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(11) A. Hezel and S. D. Ross, *Spectrochim. Acta*, 22, 1949 (1966).

(12) K. Venkateswarlu and S. Sundaram, *J. Chem. Phys.*, 23, 2365 (1955).

(13) A. G. Meister and F. F. Cleveland, *Am. J. Phys.*, 14, 13 (1946).

(14) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 61 ff.

(15) E. H. Appelman, *Inorg. Chem.*, 8, 223 (1969).

(15a) NOTE ADDED IN PROOF. The force constants reported here have been recalculated and are reported using a value of 1.61 Å for the Br–O bond distance as reported for $KBrO_4$ by S. Siegel, B. Tani, and E. Appelman, private communication; submitted for publication.

length ratios for the halate and perhalate ions, *e.g.*, ClO_3^-:ClO_4^- (1.48 Å:1.48 Å)[16] and IO_3^-:IO_4^- (1.82 Å:1.79 Å).[16] Perchlorate[11,17] and periodate[18] frequencies were selected from the literature and are listed in Table II. It is interesting to note the close similarity between the BrO_4^- ion frequencies and those of the isoelectronic SeO_4^{2-} ion. For SeO_4^{2-} in aqueous solution, the Raman values are ν_1 835, ν_2 342, ν_3 875, and ν_4 415 cm^{-1}.[19]

Table II. Vibrational Frequencies of Perhalate Ions (cm^{-1})

Ion	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
ClO_4^-	935	460	1110	630
BrO_4^-	801	331	878	410
IO_4^-	791	256	853	325

It was possible to fit the frequencies closely by various combinations of valence force constants, and one of the simplest sets is given in Table III. The nonzero force constants used were: f_d, stretching; f_α, bending; $f_{\alpha\alpha'}$, bend–bend interaction between opposite angles; $f_{d\alpha}$ and $f_{d\alpha'}$, stretch–bend interactions. The force constants clearly illustrate the close similarity in bonding between BrO_4^- and IO_4^- ions and the considerable decrease in nonbonding interactions as the central atom increases in size and the oxygens become less crowded.

Table III. Valence Force Constants for ClO_4^-, BrO_4^-, and IO_4^- Ions (mdyn/Å)

Ion	f_d	f_α/d^2	$f_{\alpha\alpha'}/d^2$	$(f_{d\alpha} - f_{d\alpha'})/d$
ClO_4^-	8.24	0.87	−0.21	0.78
BrO_4^-	6.05	0.48	−0.12	0.38
IO_4^-	5.90	0.30	−0.09	0.07

Thermal Stability and Radiolytic Formation of the Perhalates. The similarity in bonding between BrO_4^- and IO_4^- appears to be reflected in some of the properties of these ions when they are present in a crystal lattice. Thus, on heating, $KClO_4$ decomposes at its melting point of 588° [20] to give KCl and O_2(g), whereas $KBrO_4$ decomposes to $KBrO_3$ and $^1/_2O_2$(g) at 274° [20a] and KIO_4 to KIO_3 and $^1/_2O_2$(g) at 285°.[21] Crystalline $KBrO_3$ and KIO_3 do not decompose until their fusion temperatures of 396[22] and 560°,[21] respectively, are exceeded; hence, neither $KBrO_4$ nor KIO_4 would be expected as products of halate ion thermolysis. The negative findings in recent thermal decomposition studies on alkali-metal, alkaline-earth, rare earth, and other crystalline bromates[23] appear to confirm this conclusion. In contrast, ClO_4^- ion is formed during the pyrolysis of the alkali-metal chlorates.[24]

Perchlorate ion also is formed in surprisingly good yields in crystalline $NaClO_3$,[25] $KClO_3$,[3b,25] and $Ba(ClO_3)_2$[25] by ^{60}Co γ rays. The amounts of BrO_4^- and IO_4^- produced in $CsBrO_3$ and KIO_3, respectively, by γ rays are relatively much smaller than is the case for ClO_4^-. This difference may result either from the greater intrinsic radiolytic stability of BrO_3^- and IO_3^- ions or because BrO_4^- and IO_4^- are themselves much more easily radiolyzed than ClO_4^- ion. Preliminary measurements by ourselves[21] and others[26] have in fact shown that IO_3^- ion in KIO_3 is exceptionally stable, while IO_4^- ion in KIO_4 is extensively radiolyzed to KIO_3 and oxygen gas.[21] It seems possible that the balance between the rates of radiolytic formation and destruction of the perhalate ions may determine whether or not detectable amounts of them may accumulate in their respective halate crystals.

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(20a) NOTE ADDED IN PROOF. DTA and TGA of recrystallized $KBrO_4$ (original $KBrO_4$ solution obtained from E. H. Appelman, Argonne National Laboratory) indicated a gradual exothermic decomposition of BrO_4^- ion over the temperature range 274–308° (heating rate = 0.5°/min). A second, sharp exothermic decomposition, attributable to the decomposition of $KBrO_3$, was observed over the range 391–396°. The observed weight losses for these decompositions agreed well (within ±2%) with the calculated weight losses for the formation of $KBrO_3$ and KBr, respectively.

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