thalpy for reactions between rings and chains (see eq 1). However, we have calculated such overall equilibrium constants, K_1 and K_2, from the data of Tables II and IV and the results are shown in Tables V and VI, in which the constants are defined. For the sodium metaphosphates, the equilibrium constants, K_1 and K_2, seem to be much smaller than the values obtained in Tables VI and V for the tri-*n*-butylammonium system. From tabulated thermodynamic data,[29] we estimate that for the sodium phosphates, $K_1 = ca.\ 10^{-10}$ and $10^{-14} < K_2 < 10^{-10}$. Reported molecular distribution data[25] from rapid quenching of mixed alkali metal phosphate melts near the tripolyphosphate composition to give glasses indicate that $K_1 = 10^{-3}$ for these systems.

If the scrambling of the bridging and nonbridging oxygens of the phosphoryl groups making up the condensed-phosphate molecular assemblages were completely random ($\rho = 0$), K_1 and K_2 would be equal to 0.25. The fact that the values shown for these constants in Tables V and VI are considerably closer to the random values than those estimated for the alkali metal phosphates may indicate that in tetramethylurea the trialkylammonium cations effectively shield and hence neutralize the ionic charges on the phosphate anions more than do the alkali metal cations in a neat melt. In other words, it seems that the alkylammonium phosphates serve as a more inert "solvent" for their anions than do the alkali metal phosphates.

Table VI. Calculation[a] of $K_1 = [\mathrm{o}][\mathrm{m}]/[\mathrm{e}]^2$ from the Data of Table IV

	% of total p as			
D_{obsd}	o	e	m	K_1
1.89	5.00	1.20	93.80	325
1.82	6.99	3.76	89.25	44.1
1.77	8.80	5.05	86.15	29.7
1.73	9.70	7.27	83.03	15.2
1.67	12.10	8.82	79.08	12.3
1.58	14.50	12.64	73.86	6.61
1.48	18.71	14.55	66.74	5.90
1.37	22.89	16.86	66.25	4.85

[a] The use of this equilibrium constant involving building units is applicable only when the reorganizational heat order[1] is zero or unity, a situation which is not found to be true for the condensed sodium phosphates but is a reasonable approximation for the condensed phosphoric acids.

Acknowledgment. This work was supported in part by Grants USPHS-11702 and NSF-GP-28698X2, as well as by the General Research Support Grant awarded to the University of Illinois, College of Medicine, and a grant from the Research Board of the Graduate College, University of Illinois at the Medical Center.

Registry No. $H_8P_6O_{19}\cdot 8Bu_3N$, 50859-04-6; $H_9P_7O_{22}\cdot 9Bu_3N$, 50859-06-8; $H_3P_3O_9\cdot 3Bu_3N$, 50859-07-9; $H_4P_4O_{12}\cdot 4Bu_3N$, 50859-08-0; $H_5P_5O_{15}\cdot 5Bu_3N$, 50859-10-4; $H_6P_6O_{18}\cdot 6Bu_3N$, 50859-11-5; $H_7P_7O_{21}\cdot 7Bu_3N$, 50859-13-7; $H_8P_8O_{24}\cdot 8Bu_3N$, 50859-15-9; $H_2P_3O_9\cdot PO_3H_2\cdot 4Bu_3N$, 50859-17-1; $H_2P_4O_{11}\cdot 2Bu_3N$, 50978-08-0; $H_3PO_4\cdot xBu_3N$, 29306-76-1; $H_4P_2O_7\cdot xBu_3N$, 50859-18-2; $H_5P_3O_{10}\cdot xBu_3N$, 50859-19-3; $H_6P_4O_{13}\cdot xBu_3N$, 35249-67-3; $H_8P_6O_{19}\cdot xBu_3N$, 50859-20-6; $H_3P_3O_9\cdot xBu_3N$, 50859-21-7; $H_4P_4O_{12}\cdot xBu_3N$, 50932-74-6; $H_5P_5O_{15}\cdot xBu_3N$, 50859-22-8; $H_6P_6O_{18}\cdot xBu_3N$, 50859-23-9; $H_2P_3O_9\cdot PO_3H_2\cdot xBu_3N$, 50859-24-0; $H_2P_4O_{11}\cdot xBu_3N$, 50859-26-2; $Me_2NCONMe_2$, 632-22-4; Bu_3N, 102-82-9; ^{31}P, 7723-14-0.

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The Hexafluorobromine(VII) Cation, BrF_6^+. Preparation of $BrF_6^+AsF_6^-$ and $BrF_6^+Sb_2F_{11}^-$ and Characterization by Fluorine-19 Nuclear Magnetic Resonance and Raman Spectroscopy[1]

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The BrF_6^+ ion has been synthesized for the first time by oxidation of BrF_5 using $Kr_2F_3^+$ or KrF^+ as the oxidant and isolated as the solid compounds $BrF_6^+AsF_6^-$ and $BrF_6^+Sb_2F_{11}^-$, the latter as a mixture with $BrF_4^+Sb_2F_{11}^-$. Fluorine-19 nmr and Raman spectroscopy show that BrF_6^+, like the chlorine and iodine analogs, has O_h symmetry both in the solid state and in HF solution. Both $^{79}Br-^{19}F$ and $^{81}Br-^{19}F$ spin-spin couplings have been observed for the first time. The BrF_6^+ cation is a powerful oxidant and readily oxidizes oxygen and xenon to the cations O_2^+ and XeF^+, respectively, under ambient conditions.

Introduction

The first successful synthesis of perbromates in 1968[2] was followed shortly thereafter by the preparation of BrO_3F.[3] In a recent preliminary communication on the preparation of $Kr_2F_3^+$ we briefly mentioned its ability to oxidize BrF_5 to BrF_6^+ [4] and in the present paper we describe in detail the preparation of this new cation which completes the interesting series of halogen hexafluoride cations ClF_6^+, BrF_6^+, and IF_6^+.[5-8] Earlier attempts in our laboratory to prepare the BrF_6^+ cation by high pressure–high temperature techniques failed. Other attempts to prepare BrF_6^+ by the photolysis of PtF_6 in the presence of BrF_5, a method analogous to that used to prepare ClF_6^+, have also been unsuccessful.[9] We have now shown that the oxidation of BrF_5 to BrF_6^+ can be carried out

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(1) Presented in part at the XXIVth International Congress of Pure and Applied Chemistry, Hamburg, Germany, Sept 3-8, 1973.

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Table I. ^{19}F Nmr Parameters for the BrF_6^+ and BrF_4^+ Ions[a]

Solutes (molality)	Solvent	Species	Chem shift, ppm	Line width, Hz	$J_{^{79}Br-^{19}F}$, Hz	$J_{^{81}Br-^{19}F}$, Hz
$BrF_6^+Sb_2F_{11}^-$ $BrF_4^+Sb_2F_{11}^-$ [b,c]	HF	BrF_6^+	−339.4	35	1575	1697
		F on Sb	121	1800		
		$HF-BrF_4^+$	172	450		
$BrF_6^+AsF_6^-$ [d] (~0.5)	HF	BrF_6^+	−337.4	49	1587	1709
		$HF-AsF_6^-$	173.9	280		
$BrF_4^+Sb_2F_{11}^-$ [c] (1.48)	HF	F on Sb	125	2300		
		$HF-BrF_4^+$	160	590		
BrF_5 (0.43)	SbF_5	BrF_4^+	−180.4	30		
		F on Sb	112	440		

[a] Spectra recorded at 26° and referenced with respect to external $CFCl_3$. [b] Composition with respect to BrF_6^+ and BrF_4^+ unknown; *ca.* 1 *m* in total SbF_5. [c] A separate BrF_4^+ peak could not be observed owing to rapid exchange of fluorine on bromine(V) with fluorine on antimony and/or HF. [d] A separate AsF_6^- peak could not be observed due to rapid fluorine exchange between AsF_6^- and HF.

using the recently characterized $Kr_2F_3^+$ and KrF^+ cations as oxidants.

Results and Discussion

^{19}F Nmr Spectroscopy. Bromine pentafluoride solutions of $Kr_2F_3^+SbF_6^-$ and $Kr_2F_3^+AsF_6^-$ at low temperatures initially gave the nmr spectrum of $Kr_2F_3^+$.[4] On warming these solutions or a solution of $KrF^+AsF_6^-$ in BrF_5 we found that they were not stable and that BrF_5 was rapidly oxidized to BrF_6^+ according to eq 1 and 2. After gas evolution had ceased,

$$BrF_5 + Kr_2F_3^+ \rightarrow BrF_6^+ + KrF_2 + Kr \tag{1}$$

$$BrF_5 + KrF^+ \rightarrow BrF_6^+ + Kr \tag{2}$$

excess BrF_5 and KrF_2 were removed under vacuum, leaving behind white solids. The Raman spectra of the solids are reported below and they are shown to consist of a $BrF_4^+Sb_2F_{11}^-$-$BrF_6^+Sb_2F_{11}^-$ mixture and $BrF_6^+AsF_6^-$, respectively.

The ^{19}F nmr spectra of the solids dissolved in anhydrous HF were recorded and the nmr parameters obtained from their spectra are given in Table I. The room-temperature spectrum of a mixture of $BrF_4^+Sb_2F_{11}^-$ and $BrF_6^+Sb_2F_{11}^-$ consists of the HF solvent line, a broad line arising from fluorine on antimony, and two overlapping 1:1:1:1 quartets at very low field (Figure 1). A similar spectrum was obtained for $BrF_6^+AsF_6^-$ except that a separate line due to AsF_6^-, which was presumably undergoing rapid exchange with HF solvent, could not be observed. The two quartets are assigned to $^{79}BrF_6^+$ and $^{81}BrF_6^+$. They arise from spin-spin coupling of six equivalent fluorines with ^{79}Br and ^{81}Br, both with $I = 3/2$, and represent the first reported case of a Br-F coupling. The equal intensities of the two quartets are in agreement with the natural abundances of the two bromine isotopes (^{79}Br, 50.57%; ^{81}Br, 49.43%). The ratio $J_{^{19}F-^{81}Br}/J_{^{19}F-^{79}Br} = 1.078$ is in excellent agreement with the ratio of the gyromagnetic ratios, $\gamma_{^{81}Br}/\gamma_{^{79}Br} = 1.0779$. Bromine-fluorine spin-spin coupling is not observed for bromine fluorides due to rapid relaxation caused by the interaction of the bromine quadrupole moment with the asymmetric electric field gradient. The observation of well-resolved Br-F spin-spin couplings for BrF_6^+ indicates a spherically symmetric electric field about the bromine nucleus. This confirms the expected O_h symmetry for the BrF_6^+ ion in solution.

A separate peak due to BrF_4^+ was not observed in the nmr spectrum of the BrF_4^+-BrF_6^+ mixture in HF solvent. This peak was also not observed in the spectrum of a solution of pure $BrF_4^+Sb_2F_{11}^-$ in HF at room temperature (Table I). In both solutions the BrF_4^+ cation apparently undergoes rapid fluorine exchange with HF and/or F on Sb at room temperature.[10,11] We were, however, able to obtain the chemical shift of the BrF_4^+ cation in SbF_5 solvent (Table I). In addition to the broad fluorine-on-antimony line, a sharp signal at low field was observed which can be assigned to the BrF_4^+ ion. The low-field shift of BrF_6^+ (−339.4 ppm) with respect to that of BrF_4^+ (−180.4 ppm) is in line with the anticipated deshielding of the fluorines with an increase in the formal oxidation state of bromine. The resonance of the BrF_6^+ cation also occurs at much lower field than that of IF_6^+ (−70.5 ppm)[12] and at slightly higher field than that of ClF_6^+ (−391 ppm).[7,13] This is in accord with the expected deshielding of the fluorines with increasing electronegativity of the central halogen. The resonance of ClF_6^+, however, does seem to occur to anomalously high field. This may be a consequence of crowding in the valence shell of chlorine, which presumably can barely accommodate six electron pairs, thus giving Cl-F bonds that are rather longer than might be expected for a chlorine(VII) fluoride.[14]

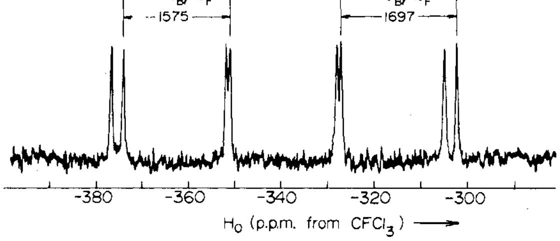

Figure 1. The ^{19}F nmr spectrum (58.3 MHz, 26°) of the BrF_6^+ cation in HF solution.

An empirical relation, the parallelogram rule, which correlates the square root of the reduced coupling constant with the atomic number for an isoelectronic series of hexafluorides, has been proposed for groups IV-VI.[15,16] Figure 2 illustrates this rule using the latest available data[7,12,13,16-21] and it can

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(10) Subsequent to the completion of our work we have learned that Christe and Sawodny[11] have been able to observe a separate peak at −197 ppm for BrF_4^+ in HF solutions of $BrF_4^+Sb_2F_{11}^-$ in the temperature range −80 to +20°. Our inability to observe a separate peak for BrF_4^+ was presumably due to a concentration effect.

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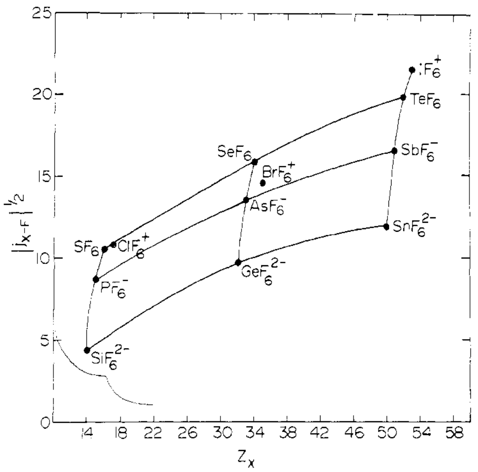

Figure 2. Reduced coupling constants, $|j_{X-F}|^{1/2}$, for XF_6 species of groups IV-VII as a function of the atomic number, Z_X.

be seen that the hexafluoro cations of group VII do not, however, follow the rule. In particular, the reduced coupling constants for bromine and chlorine appear to be smaller than expected. The reason for this is not clear, but one factor could be the crowding of the electron pairs in these small valence shells, giving rise to Cl-F and Br-F bonds that are somewhat longer than expected for the +VII oxidation state and halogen-fluorine reduced coupling constants that are correspondingly smaller than expected. On the basis of this parallelogram relationship it can, nevertheless, be concluded that the signs of the Br-F reduced coupling constants are both negative.[16]

In addition, the center of the $^{79}BrF_6^+$ resonance is shifted 0.14 ± 0.02 ppm to low field of $^{81}BrF_6^+$. This shift may be explained by the difference in the vibrational amplitudes of the two bromine isotopes. The heavier isotope has a smaller vibrational amplitude causing the electrons of the fluorine atom to be less polarized, resulting in increased shielding of the fluorines. The isotopic shift per unit mass difference for BrF_6^+ (0.07 ± 0.01) is considerably greater than has been observed for the isoelectronic SeF_6 molecule (0.007 ± 0.001)[20] and parallels the large change that has been observed within the series SiF_6^{2-} (0.004 ± 0.001),[17] SF_6 (0.026 ± 0.0002),[18] and ClF_6^+ (0.08 ± 0.01).[7,13] The original suggestion by Tiers[22] that there is a strong inverse dependence of the isotopic shift on the bond lengths, which are expected to decrease with increasing atomic number in each series of isoelectronic species, therefore appears to be valid.

Raman Spectroscopy. Three Raman-active modes are expected for a BrF_6^+ ion with O_h symmetry. The spectrum of the white solid obtained in the reaction of $Kr_2F_3^+SbF_6^-$ with BrF_5 is complex and arises from a mixture of $BrF_6^+Sb_2F_{11}^-$ and $BrF_4^+Sb_2F_{11}^-$ (Figure 3a and Table II). The spectrum of the pure $BrF_4^+Sb_2F_{11}^-$ salt was also recorded and is given in Figure 3b and Table II for comparison. The low-temperature spectra of $BrF_4^+Sb_2F_{11}^-$ obtained in the present work, though considerably better resolved, are in excellent agreement with the room-temperature spectrum recently reported by Surles, *et al.*,[23] and by Christe and Sawodny.[11]

Since a 1:2 SbF_5:KrF_2 mole ratio was used in the preparation, it might have been expected that the product of reaction 1 would have been $BrF_6^+SbF_6^-$ and it is not entirely clear why the $Sb_2F_{11}^-$ salt was obtained. Moreover, the origin of the $BrF_4^+Sb_2F_{11}^-$ salt is also somewhat obscure. As a part of our study of Kr(II) cations,[4] we have observed that solutions of $KrF^+SbF_6^-$ rapidly evolve krypton and fluorine gas at room temperature. Particularly noteworthy is the reaction of $KrF^+SbF_6^-$ in either HF or SbF_5 solution, which does not result in oxidation of either solvent but which corresponds to the redox decomposition

$$KrF^+Sb_nF_{5n+1}^- \xrightarrow{\text{HF or SbF}_5} Kr + F_2 + nSbF_5 \tag{3}$$

It appears that KrF^+ and $Kr_2F_3^+$ compounds undergo related decompositions at room temperature in BrF_5 in addition to the oxidations described in eq 1 and 2 to give excess MF_5 (M = As, Sb).

$$Kr_2F_3^+MF_6^- \xrightarrow{\text{HF or SbF}_5} KrF^+MF_6^- + Kr + F_2 \tag{4}$$

$$KrF^+MF_6^- \rightarrow MF_5 + Kr + F_2 \tag{5}$$

Since the $As_2F_{11}^-$ ion is not stable at room temperature[24,25] and AsF_5 does not form a stable adduct with BrF_5 at room temperature,[11,23] the problems of polyanion formation and adduct formation with the solvent were overcome by allowing $Kr_2F_3^+AsF_6^-$ or $KrF^+AsF_6^-$ to react with excess BrF_5 at room temperature. After pumping off excess BrF_5 and KrF_2, the Raman spectra of the remaining white solids were recorded (Table II and Figure 4). In addition to the known bands of the AsF_6^- anion, three bands were observed which can be assigned to BrF_6^+. The same three bands with the same relative intensities were observed for the $BrF_4^+Sb_2F_{11}^-$-$BrF_6^+Sb_2F_{11}^-$ mixture (Table II and Figure 3a). Lines attributable to KrF^+ and $Kr_2F_3^+$ salts were not observed in either case.[4]

Octahedral BrF_6^+ is isoelectronic with AsF_6^- and should exhibit the same spectrum as AsF_6^- except for slight frequency shifts. This is in fact the case except that $\nu_2(e_g)$ for BrF_6^+ occurs at a slightly higher frequency than $\nu_1(a_{1g})$.

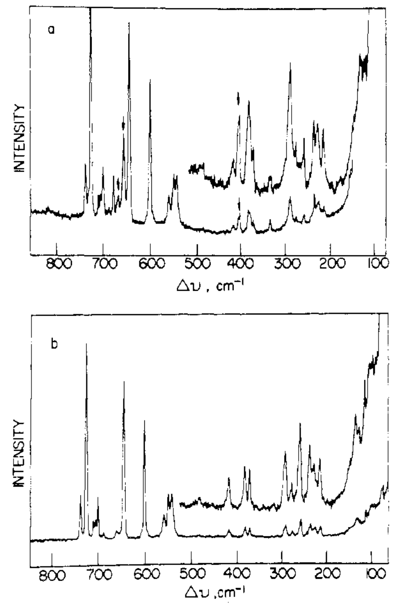

Figure 3. Raman spectra (−90°): (a) a mixture of solid BrF_6^+-$Sb_2F_{11}^-$ and $BrF_4^+Sb_2F_{11}^-$; arrows denote lines arising from the BrF_6^+ cation; (b) solid $BrF_4^+Sb_2F_{11}^-$; the spectrum was recorded in a glass sample tube.

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Table II. Raman Spectra of $BrF_6^+Sb_2F_{11}^-$, $BrF_6^+AsF_6^-$, and $BrF_4^+Sb_2F_{11}^-$ and Their Assignments[a]

Obsd freq, cm^{-1}				Assignments		
$BrF_6^+Sb_2F_{11}^-$-$BrF_4^+Sb_2F_{11}^-$ mixture[b]	$BrF_4^+Sb_2F_{11}^-$ [c]	$BrF_6^+AsF_6^-$ [d] Solid	$BrF_6^+AsF_6^-$ [d] HF soln	$BrF_6^+Sb_2F_{11}^-$-$BrF_4^+Sb_2F_{11}^-$ mixture	$BrF_4^+Sb_2F_{11}^-$ [c]	$BrF_6^+AsF_6^-$
737 (22)	738 (22)			$Sb_2F_{11}^-$	$Sb_2F_{11}^-$	
725 (100)	725 (100)			$\nu_1(a_1)$, BrF_4^+	$\nu_1(a_1)$, BrF_4^+	
709 (9)	710 (10)					
703 (10)	705 (11)			$\nu_6(b_1)$, BrF_4^+, $Sb_2F_{11}^-$ (?)	$\nu_6(b_1)$, BrF_4^+	
699 (23)	700 (21)					
686 (7)	688 (4)					
679 (20)				$Sb_2F_{11}^-$	$Sb_2F_{11}^-$	
		679 (41)	684 (25) p			$\nu_1(a_{1g})$, AsF_6^-
666 (9)		668 (28)	671 sh, dp	$\nu_2(e_g)$, BrF_6^+		$\nu_2(e_g)$, BrF_6^+
	659 (4)				$Sb_2F_{11}^-$	
656 (37)		658 (100)	661 (100) p	$\nu_1(a_{1g})$, BrF_6^+		$\nu_1(a_{1g})$, BrF_6^+
645 (81)	646 (80)			$Sb_2F_{11}^-$	$Sb_2F_{11}^-$	
600 (57)	601 (61)			$\nu_2(a_1)$, BrF_4^+	$\nu_2(a_1)$, BrF_4^+	
		575 (4)[e]	575 (3) dp			$\nu_2(e_g)$, AsF_6^-
559 (12)	560 (14)					
550 (20)	550 (22)			$Sb_2F_{11}^-$	$Sb_2F_{11}^-$	
542 (20)	542 (22)					
483 (1)	485 (1)			ν(Sb–F)	ν(Sb–F)	
416 (3)	418 (4)			$\nu_7(a_1)$, BrF_4^+	$\nu_7(a_1)$, BrF_4^+	
404 (7)		405 (34)	405 (16) dp	$\nu_5(t_{2g})$, BrF_6^+		$\nu_5(t_{2g})$, BrF_6^+
382 (9)	382 (5)			$\nu_3(b_1)$, BrF_4^+	$\nu_3(b_1)$, BrF_4^+	
372 (4)	371 (5)			$\nu_9(b_2)$, BrF_4^+	$\nu_9(b_2)$, BrF_4^+	
		367 (6)	358 (7) dp			$\nu_5(t_{2g})$, AsF_6^+
335 (1)						
291 (13)	293 (7)					
277 (5)	278 (3)					
260 (6)	260 (10)			$Sb_2F_{11}^-$	$Sb_2F_{11}^-$	
236 (7)	236 (8)					
227 (7)	227 (5)					
216 (7)	214 (6)			$\nu_4(a_1)$, BrF_4^+	$\nu_4(a_1)$, BrF_4^+	
131 (5)	132 (6)			Lattice mode	Lattice mode	

[a] Solid-state spectra were obtained at −90°; the HF solution spectrum was obtained at room temperature. [b] Lines due to the FEP sample tube were too weak to be observed. [c] Spectrum recorded in a glass sample tube. Assignments are based on those given in ref 11 for the room-temperature spectrum of $BrF_4^+Sb_2F_{11}^-$. [d] Lines due to the FEP sample tube have been deleted. [e] Coincident with an FEP line; the intensity given is the corrected intensity.

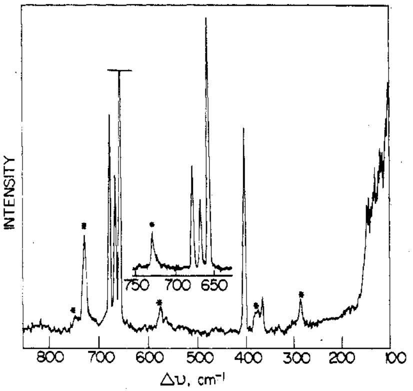

Figure 4. The Raman spectrum of solid $BrF_6^+AsF_6^-$ recorded at −90°; asterisks denote FEP lines arising from the sample tube.

This feature is unusual and up to the present has only been observed for one other octahedral XF_6 molecule, namely, IF_6^+ (Table III).[5,26] The relative intensities of ν_1 and ν_2 support our assignments and further support is given by comparison with the spectra of the electronically related series SF_6-SeF_6-TeF_6 and ClF_6^+-BrF_6^+-IF_6^+ (Table III). Within each series the difference $\nu_1 - \nu_2$ decreases markedly with increasing atomic number. This change is presumed to arise from a decrease in the nonbonded fluorine interactions with an increase in the size of the central atom.[5,27]

Our assignment of the solid-state spectrum was confirmed by recording the Raman spectrum of $BrF_6^+AsF_6^-$ in HF solution (Table II). All the lines broadened somewhat, but in particular those assigned to $\nu_1(a_{1g})$ and $\nu_2(e_g)$ of AsF_6^- were most affected. This behavior is similar to that of other complex fluoro ions in HF solution.[26,28] The lines at 661 and 679 cm^{-1} were found to be strongly polarized, confirming their assignment as $\nu_1(a_{1g})$ of BrF_6^+ and AsF_6^-, respectively. The lines at 575, 405, and 358 cm^{-1} were depolarized which confirms their assignment to $\nu_2(e_g)$ of AsF_6^-, $\nu_5(t_{2g})$ of BrF_6^+ and $\nu_5(t_{2g})$ of AsF_6^-, respectively. The broad intense band due to $\nu_1(a_{1g})$ of AsF_6^- overlapped rather severely with $\nu_2(e_g)$ of BrF_6^+ and thus the latter band was discernible only as a shoulder on $\nu_1(a_{1g})$ of AsF_6^-; nevertheless, polarization measurements gave some useful information. In the polarized spectrum the low-frequency shoulder on $\nu_1(a_{1g})$ of AsF_6^- be-

Table III. Vibrational Frequencies and Assignments of the BrF_6^+ Cation and Some Related Species

Assignment	Obsd freq, cm^{-1} ClF_6^+ [a]	BrF_6^+ [b]	IF_6^+ [c]	SF_6 [d]	SeF_6 [d]	TeF_6 [d]
$\nu_1(a_{1g})$	679	658	708	769	708	701
$\nu_2(e_g)$	630	668	732	640	662	674
$\nu_3(t_{1u})$	890		797, 790	948	780	752
$\nu_4(t_{1u})$	582		404	614	437	325
$\nu_5(t_{2g})$	513	405	340	522	405	313

[a] References 7 and 8. [b] This work. [c] Reference 5. [d] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 119.

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came the more intense peak centered at 671 cm^{-1} and the former main peak at 679 cm^{-1} was also well resolved and appeared as the weaker of the two peaks. It is apparent that the low-frequency peak is depolarized and that its depolarization supports our assignment of this peak to $\nu_2(e_g)$ of BrF_6^+.

The BrF_6^+ bands in the Raman spectrum are relatively more intense than those of AsF_6^-. This is somewhat surprising since one would expect that AsF_6^- would have a higher polarizability than BrF_6^+ owing to the anticipated larger size of the AsF_6^- ion.

In summary, all three Raman-active fundamental vibrations expected for both BrF_6^+ and AsF_6^- were observed. Thus, the Raman spectrum is consistent with the ionic formulation of the adduct $BrF_6^+AsF_6^-$. The BrF_6^+ spectrum of the product obtained from the $Kr_2F_3^+SbF_6^-$ reaction is readily assigned by comparison with the spectra of the $BrF_6^+AsF_6^-$ and $BrF_4^+Sb_2F_{11}^-$ salts.

Reaction of BrF_6^+ with Oxygen and Xenon. The BrF_6^+ cation is an extremely powerful oxidant and reacts rapidly with xenon and oxygen gas at room temperature according to eq 6 and 7. In both cases, lines attributable to BrF_6^+ in

$$BrF_6^+AsF_6^- + Xe \rightarrow BrF_5 + XeF^+AsF_6^- \tag{6}$$

$$BrF_6^+AsF_6^- + O_2 \rightarrow BrF_5 + O_2^+AsF_6^- + {}^1/_2F_2 \tag{7}$$

the low-temperature Raman spectrum disappeared and the original AsF_6^- lines were replaced with a new set of AsF_6^- lines slightly shifted in frequency. In addition, single intense bands appeared at 1857 cm^{-1} (reaction with O_2) and 609 cm^{-1} (reaction with Xe) which can only be assigned to the O_2^+ [29] and XeF^+ [30] vibrations, respectively, together with other bands which are readily assignable to solid BrF_5. Upon warming to room temperature and pumping off the BrF_5, the low-temperature spectra of the respective solids were reexamined and found to be identical with the spectra of $O_2^+AsF_6^-$ or $XeF^+AsF_6^-$.

Attempted Synthesis of BrF_7. Fogle and Rewick[31] have reported the preparation of very small quantities of BrF_7 according to eq 8. They reported that their product, which

$$BrF_5 + F_2 \xrightarrow[110-340^\circ]{CsF} BrF_7 \tag{8}$$

they obtained pure in only milligram amounts, was at least partially stable up to temperatures as high as 250°. In view of the stability of the BrF_6^+ ion and the reported stability of BrF_7, a displacement reaction between $BrF_6^+AsF_6^-$ and NOF was carried out under conditions similar to those which had successfully been used for the synthesis of ClO_2F_3 from $ClO_2F_2^+PtF_6^-$ and NOF.[32] The reaction was found to proceed according to the equation

$$BrF_6^+AsF_6^- + 2NOF \xrightarrow{-78^\circ} NO^+AsF_6^- + NO^+BrF_6^- + F_2 \tag{9}$$

A similar displacement reaction has been carried out using $ClF_6^+PtF_6^-$ and NOF. Under the reaction conditions employed (temperatures as low as −78°) ClF_7 was also found to be unstable toward decomposition to the +V oxidation state and F_2.[7,8] This indicates that although BrF_7 should be sterically more favored than ClF_7 neither of the heptafluorides is stable under the given reaction conditions and Fogle and Rewick's claim to have prepared BrF_7 must for the present be regarded with some skepticism.

Conclusions

In spite of the apparent nonexistence of BrF_7, the heptavalent BrF_6^+ cation has been successfully synthesized and characterized. The BrF_6^+ cation readily oxidizes oxygen gas and xenon gas under ambient conditions, whereas fluorine does not. The BrF_6^+ cation is, therefore, a more powerful oxidant than fluorine gas under ambient conditions. Although ClF_6^+ can be prepared from ClF_5 using PtF_6 as the oxidative fluorinating agent,[6-8] PtF_6 does not oxidize BrF_5 to BrF_6^+, even when exposed to unfiltered ultraviolet radiation[9] and an even stronger oxidizer, $Kr_2F_3^+$ or KrF^+, is required for the synthesis of BrF_6^+.

The present work demonstrates the potential utility of Kr(II) cations as oxidative reagents and could well provide a method of preparing compounds of other elements in unusual high oxidation states. It is interesting to note that it has already been shown that IF_5 is readily oxidized to IF_6^+ by $KrF^+Sb_2F_{11}^-$ [33] and we have now shown that KrF^+ and $Kr_2F_3^+$ salts also oxidize BrF_5 to BrF_6^+, O_2 to O_2^+,[34] and Xe to XeF^+.[34]

Experimental Section

Apparatus and Materials. All vacuum manipulations were carried out on an all-Monel vacuum line previously passivated with fluorine. Bromine pentafluoride, krypton difluoride, anhydrous hydrogen fluoride, and arsenic pentafluoride were transferred under vacuum through all-Teflon connections previously passivated with fluorine. Antimony pentafluoride was syringed into reaction vessels in a drybox. Preparative work was carried out in 3.91-mm o.d. (0.31-mm wall) lengths of Teflon FEP spaghetti tubing heat sealed at one end and connected through a 45° SAE flare to a Teflon adaptor. The reaction tubes were attached to Teflon valves using standard $^1/_4$-in. Teflon Swagelok nuts and ferrules, washed several times with anhydrous HF, and passivated with F_2. Fluorine-19 nmr and Raman spectra were recorded using the reaction vessel as the sample container.

Krypton difluoride was prepared from krypton (Matheson), 99.995%, and fluorine (Matheson) using a glow discharge technique similar to that described by Schreiner, *et al.*[35] The details of the preparation of KrF_2 and the AsF_6^- and SbF_6^- salts of KrF^+ and $Kr_2F_3^+$ from KrF_2 and their respective pentafluorides will be described in a subsequent paper.[34]

Antimony pentafluoride (Ozark-Mahoning) was purified by double distillation in an atmosphere of dry nitrogen using an all-glass apparatus and stored in glass vessels in a drybox.

Bromine pentafluoride (Matheson) was distilled into a Kel-F trap fitted with Teflon valves and purified by passing fluorine at atmospheric pressure through the liquid until all the Br_2 and BrF_3 had reacted. After degassing several times, the BrF_5 was vacuum distilled and stored over dry sodium fluoride in a Kel-F storage vessel.

Anhydrous hydrogen fluoride (Harshaw) was distilled directly from the cylinder into a Kel-F storage vessel from which it was used without further purification.

Arsenic pentafluoride (Ozark-Mahoning), oxygen, <10 ppm of H_2O (Canadian Liquid Air), and argon, 99.998% (Matheson), were used without further drying or other purification.

Nitrosyl fluoride (Ozark-Mahoning) was treated with fluorine by transferring 100 g of the commercial material into a previously passivated 250-ml Monel can and distilling in sufficient F_2 at −196° to give a partial pressure of F_2 gas of 25 atm at room temperature. After standing for several hours at room temperature, the remaining F_2 gas was removed under vacuum at −196° and the NOF with small quantities of NO_2F impurity (<1%) was used directly from the can.

Instrumentation. Fluorine-19 nmr spectra were measured with a Varian DA-60IL spectrometer operating at 58.3 MHz and modified as described previously[36] to record spectra from the first upper side

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band in field sweep unlock mode. The spectra were calibrated by the usual audio-side-band method and referenced relative to external $CFCl_3$ by sample interchange. Chemical shifts are estimated to be accurate to ±0.5 ppm.

Raman spectra were obtained with a Spex Industries Model 1400 spectrometer using the 5145-Å radiation from a Spectra Physics Model 164 argon ion laser. Spectra were recorded at −90° by placing the sample tube inside a glass tube surrounded by an evacuated jacket, silvered except at the center. Liquid nitrogen was boiled off from a dewar and passed through the tube. The temperature was monitored with a copper–constantan thermocouple positioned in the stream just ahead of the sample region. The Raman shifts are estimated to be accurate to ±2 cm^{-1}.

Preparation of BrF_6^+ Salts. Solutions of $Kr_2F_3^+SbF_6^-$, $Kr_2F_3^+AsF_6^-$, and $KrF^+AsF_6^-$ were prepared by dissolving approximately 0.2–0.5 mmol of $Kr_2F_3^+$ or KrF^+ salt in approximately 0.25 g of BrF_5 at 0°. The nmr spectra of solutions of the $Kr_2F_3^+$ salts were recorded at −60° and were found to consist of lines readily assignable to $Kr_2F_3^+$, MF_6^-, and BrF_5.[4] Solutions were allowed to warm up rapidly to room temperature at which point vigorous evolution of krypton and fluorine ensued. To avoid excessive pressures within the reaction tube, the reaction was periodically quenched by rapid cooling to −196° and the volatiles were removed under vacuum. After gas evolution had ceased, the solutions were maintained at room temperature for an additional $^1/_2$ hr to ensure that the oxidation was complete. The remaining BrF_5 was removed under vacuum at room temperature. Yields of BrF_6^+ salts were in general low. Owing to inherent experimental difficulties, no effort was made to obtain precise values for the yields, but it is estimated that based on the initial amounts of $Kr_2F_3^+MF_6^-$ and $KrF^+AsF_6^-$ the yields did not exceed 20%. Although the resulting white solids were stable at room temperature for periods up to several days, samples were routinely stored at −78° under a positive pressure of high-purity argon until their Raman or nmr spectra could be recorded.

Attempted Synthesis of $BrF_6^+AsF_6^-$ by Other Means. Mixtures of BrF_5, F_2, and AsF_5 in different mole ratios were heated in a Monel reactor for 3 days at 200–250° under autogenous pressures of 125–200 atm. Only the unreacted starting materials and very small quantities of $O_2^+AsF_6^-$ and metal AsF_6^- salts were recovered.

Displacement Reaction between NOF and $BrF_6^+AsF_6^-$. Nitrosyl fluoride (6.9 mmol) was condensed onto 0.20 g (0.52 mmol) of $BrF_6^+AsF_6^-$ at −196° in a passivated Teflon tube equipped with a Teflon valve. The reaction vessel and contents were warmed to −78° and kept at this temperature for $^1/_2$ hr. The reaction vessel was then cooled to −196° and the F_2 generated at −78° according to eq 9 was removed under vacuum. The vessel was warmed to −63° for an additional $^1/_2$ hr and since upon cooling to −196° no further F_2 gas was pumped off, the reaction was assumed to be complete. The reaction vessel was slowly warmed to 0° while its volatile contents were transferred by static vacuum distillation through all-Teflon and FEP connections to an FEP Raman sample tube equipped with a Teflon valve. At −90°, two phases were present in the FEP sample tube, a colorless volatile liquid phase that was identified from its Raman spectrum as NOF and a white crystalline solid. The Raman spectrum of the white solid was recorded at −90° both in the presence of excess NOF and after the NOF had been removed under vacuum at −78°. Based on a comparison with the known spectra of $Cs^+BrF_6^-$ [37] and $NO^+BrF_6^-$,[38] the white solid was unambiguously identified as $NO^+BrF_6^-$. A less volatile white solid, which remained in the Teflon reaction vessel at 0° and which was rapidly pumped off under dynamic vacuum at room temperature, was identified as $NO^+AsF_6^-$ from its Raman spectrum.[39]

Preparation of $BrF_4^+Sb_2F_{11}^-$ and BrF_4^+ Solutions. The adduct was prepared according to the method of Surles, *et al.*[23] The solid sample was prepared in a 5-mm o.d. glass nmr tube attached to a Teflon valve which also served as the Raman sample tube. After recording the Raman spectrum, 0.108 g (0.177 mmol) of $BrF_4^+Sb_2F_{11}^-$ was transferred in a drybox to an FEP sample tube equipped with a Teflon valve and dissolved in 0.120 g (6.0 mmol) of anhydrous HF. A solution of BrF_4^+ in SbF_5 was prepared in a 5-mm o.d. glass nmr tube by dissolving 0.146 g (0.83 mmol) of BrF_5 in 1.93 g (8.9 mmol) of SbF_5. The nmr spectra of both solutions were recorded at 26°.

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Registry No. $Kr_2F_3^+SbF_6^-$, 50921-18-1; $Kr_2F_3^+AsF_6^-$, 50921-17-0; $KrF^+AsF_6^-$, 50859-36-4; BrF_5, 7789-30-2; NOF, 7789-25-5; Xe, 7440-63-3; O_2, 7782-44-7; $BrF_6^+Sb_2F_{11}^-$, 51063-28-6; BrF_4^+-$Sb_2F_{11}^-$, 36445-03-1; $BrF_6^+AsF_6$, 51063-29-7; $NO^+BrF_6^-$, 50859-39-7; ^{79}Br, 14336-94-8; ^{81}Br, 14380-59-7.

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Spectral Studies of Oxouranium(V) Species

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Electronic spectral studies and semiempirical theoretical calculations of energy levels of UOF_5^{2-} and $UOBr_5^{2-}$ have been made in order to locate and assign all of the six electronic transitions in these $5f^1$ species. The data are compared with previous results for $UOCl_5^{2-}$ and reveal that each of the six electronic transitions is shifted to higher energy in the expected order: $Br^- < Cl^- < F^-$. The best-fit spin–orbit coupling constants also increase in this same order: 1750, 1770, and 1850 cm^{-1}, respectively. Electron paramagnetic resonance spectra have been obtained for polycrystalline solids at ambient temperature for all species UX_6^- and UOX_5^{2-} ($X^- = F^-, Cl^-, Br^-$) except for UF_6^-. The significance of these epr results is discussed.

In an earlier paper[1] we elaborated a theoretical treatment of a tetragonally distorted hexacoordinated U^{5+} species, making calculations specifically for the $UOCl_5^{2-}$ anion and utilizing the theory to make assignments of the observed electronic spectral bands for this complex. We have now extended both the theory and the experimental data to encompass the other two known oxohalo species, UOF_5^{2-} and $UOBr_5^{2-}$. These new results are presented in this paper along with an analysis of the data for all three oxohalo complexes.

Experimental Section

A. Preparation of Compounds. Since most compounds of uranium(V) are sensitive to both oxygen and moisture, compounds were prepared and handled in an inert atmosphere. Both a steel drybox

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