TABLE V

COMPUTED THERMODYNAMIC PROPERTIES OF SeF_5Cl^a

T, °K	$C_p°$	$H° - H°_0$	$-(F° - H°_0)/T$	$S°$
0	0	0	0	0
100	12.035	0.895	51.149	60.103
200	21.720	2.604	58.534	71.554
298.15	27.800	5.062	64.494	81.472
300	27.885	5.113	64.600	81.644
400	31.338	8.091	69.959	90.186
500	33.331	11.333	74.746	97.412
600	34.548	14.732	79.053	103.605
700	35.336	18.228	82.954	108.994
800	35.870	21.790	86.512	113.750
900	36.248	25.397	89.778	117.998
1000	36.524	29.037	92.795	121.832
1100	36.731	32.700	95.596	125.323
1200	36.891	36.381	98.208	128.526
1300	37.016	40.077	100.656	131.484
1400	37.116	43.784	102.957	134.231
1500	37.197	47.499	105.128	136.795
1600	37.264	51.223	107.183	139.198
1700	37.320	54.952	109.134	141.458
1800	37.367	58.686	110.989	143.593
1900	37.406	62.425	112.759	145.614
2000	37.440	66.167	114.450	147.534

[a] Units for $C_p°$, $S°$, and $F°$ are calories, moles, and degrees Kelvin; for $H°$ units are kilocalories and moles.

Coriolis coupling coefficients were computed for SeF_5Cl in the belief that the e-block band contours could support the assignment. The computed values using the above given force constants were $\zeta_8 = 0.5$, $\zeta_9 = 0.5$, $\zeta_{10} = -0.4$, and $\zeta_{11} = 0.7$. However, the values of the moments of inertia are such that these values for ζ do not result in very distinctive band shapes.[8] The band shapes are further complicated by the natural chlorine and selenium isotopes and by hot bands. Although the observed band shapes are not inconsistent with those predicted, the contours could not be used to verify the computed ζ's.

The potential energy distribution was computed using the above force constants and is shown in Table IV. The assignment listed in Table I is supported by these values. The mixing of ν_3 and ν_4 is large, so that, strictly, one is not a stretching and one a deformational mode, but rather a symmetric and antisymmetric combination of the two motions.

Thermodynamic Properties.—The thermodynamic properties were computed for this molecule using the rigid-rotor, harmonic-oscillator[16] approximation. The results are given in Table V. The frequencies used were those of Table II, assuming a computed value of 336 cm^{-1} for ν_6. The moments of inertia used were $I_x = I_y = 312$ and $I_z = 214$ amu Å^2 computed from the geometry assumed above, with a symmetry factor of 4.

Acknowledgment.—We are indebted to Dr. D. Pilipovich for continuous encouragement and to Dr. J. Cape for the use of the Raman spectrometer. This work was supported by the Office of Naval Research, Power Branch.

(16) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940.

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The Formation of Br_2^+, Br_3^+, $BrOSO_2F$, and $Br(OSO_2F)_3$ by the Oxidation of Bromine with Peroxydisulfuryl Difluoride in Solution in Fluorosulfuric Acid and the Superacid System SbF_5–$3SO_3$–HSO_3F

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The oxidation of bromine with peroxydisulfuryl difluoride, $S_2O_6F_2$, in solution in fluorosulfuric acid and in the superacid system SbF_5–$3SO_3$–HSO_3F has been studied by electrical conductivity and magnetic susceptibility measurements and by Raman spectroscopy. It is shown that in fluorosulfuric acid solution Br_3^+, $BrOSO_2F$, and $Br(OSO_2F)_3$ are stable species although $BrOSO_2F$ is disproportionated to some extent into Br_3^+ and $Br(OSO_2F)_3$. In the superacid system SbF_5–$3SO_3$–HSO_3F the Br_2^+ cation can also be obtained, but it is not very stable and is in equilibrium with the disproportionation products Br_3^+ and $BrOSO_2F$. The Raman spectra of the bromine cations Br_2^+ and Br_3^+ and the bromine fluorosulfates $BrOSO_2F$ and $Br(OSO_2F)_3$ have been obtained and the resonance Raman spectrum of the Br_2^+ cation is described.

The I_2^+ and I_3^+ cations of iodine are well established[1,2] but at the time the present investigation was commenced there was no evidence for the existence of the corresponding bromine cations Br_2^+ and Br_3^+. Although the I_3^+ cation is stabilized by the very weak basicity of sulfuric acid, the I_2^+ cation is almost completely disproportionated in this solvent and it needs the still weaker basicity of fluorosulfuric acid to enable it to exist in sufficient concentration for identification by its intense blue color (λ_{max} 640 nm). Nevertheless, the very small concentration of I_2^+ in 100% sulfuric acid can be detected by its strong-resonance Raman spectrum.[3] It is to be expected that the corresponding bromine cations would be stronger Lewis acids than the iodine cations and that they would only be stable in still less basic media than can be used to stabilize the iodine cations. Thus although Br_3^+ might be obtained in solution in fluorosulfuric acid it was anticipated that it would probably need the acidity of the superacid system SbF_5–$3SO_3$–HSO_3F[4] to stabilize the Br_2^+ cation.

(1) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1577 (1966).

(2) R. A. Garrett, R. J. Gillespie, and J. B. Senior, *ibid.*, **4**, 563 (1965).

(3) R. J. Gillespie and M. J. Morton, *J. Mol. Spectrosc.*, **30**, 178 (1969).

(4) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).

By analogy with I_2^+ a strong visible absorption was expected for Br_2^+ shifted to longer wavelengths from that of bromine (λ_{max} 410 nm). It was also anticipated that Br_2^+ might exhibit a strong-resonance Raman effect like I_2^+ and therefore be detectable at rather low concentrations. In order to search for bromine cations, systems prepared from bromine and bromine(I) fluorosulfate dissolved in fluorosulfuric acid and in the superacid SbF_5–$3SO_3$–HSO_3F and from bromine and $S_2O_6F_2$ in the same solvent were investigated. The reaction of Br_2 and $S_2O_6F_2$ in the absence of any solvent has previously been shown to lead to the formation of bromine(I) fluorosulfate $BrOSO_2F$ and bromine(III) fluorosulfate $Br(OSO_2F)_3$[5,6] which are, respectively, a red-brown liquid and a yellow solid at room temperature. Some of our evidence for the bromine cations Br_2^+ and Br_3^+ was briefly summarized in a preliminary communication[7] which was published almost simultaneously with a preliminary report by Edwards, Jones, and Sills[8] of the crystal structure of a red compound prepared by the reaction of bromine, bromine pentafluoride, and antimony pentafluoride which they clearly established to be $Br_2^+Sb_3F_{16}^-$. Subsequently Br_3^+-AsF_6^- has been prepared by the reaction of $O_2^+AsF_6^-$ with bromine[9]

$$O_2^+AsF_6^- + {}^3/_2Br_2 \longrightarrow Br_3^+AsF_6^- + O_2$$

and by the reaction of BrF_3 or BrF_5 with bromine and AsF_5.[9]

Results and Discussion

When bromine monofluorosulfate was distilled into cold SbF_5–$3SO_3$–HSO_3F superacid, it dissolved on warming gently to give an intense cherry red solution with an absorption maximum at 510 nm (Figure 1). Similar solutions were obtained by oxidizing Br_2 in the same solvent with $S_2O_6F_2$ in the 1:1 mole ratio.

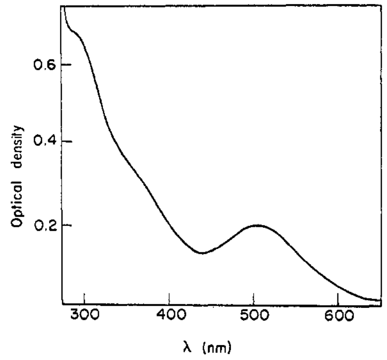

Figure 1.—Uv and visible spectrum of 0.069 *m* $BrSO_3F$ in 0.176 *m* SbF_5–$3SO_3$–HSO_3F; path length 0.144 mm.

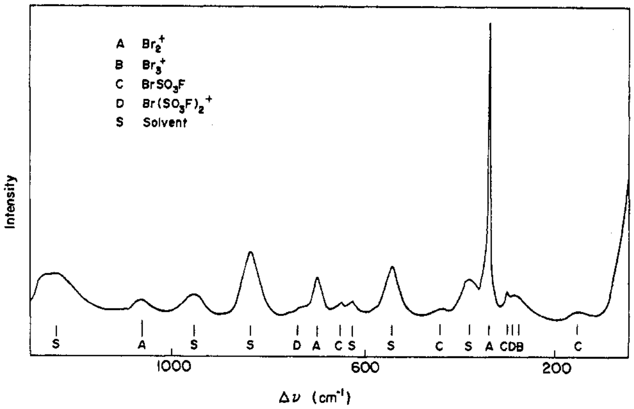

Figure 2.—Raman spectrum of 0.399 *m* $BrSO_3F$ in 0.176 *m* SbF_5–$3SO_3$–HSO_3F.

TABLE I

RAMAN SPECTRA OF Br_2^+, Br_3^+, $BrOSO_2F$, $Br(OSO_2F)_3$, AND $S_2O_6F_2$ (CM^{-1})

$S_2O_6F_2$	$BrSO_3F$	$Br(SO_3F)_3$ in HSO_3F
190 m	177 m	178 m
209 m	280 sh	294 sh
307 ms	318 s	318 s
389 w	400 w	464 m
483 w	466 m	659 ms
528 w	540 w	737 m
598 w	573 w	1267 m
798 s	613 w	
824 ms	658 s	$Br(SO_3F)_2^+$ in superacid
881 m	832 w	
1249 s	890 w	308 s
1496 w	1206 m	462 m
		1242 m
Br_2^+ in superacid	Br_2 in HSO_3F	Br_3^+ in superacid
360	320	290
710		
1070		

Raman Spectra.—The Raman spectrum of a 0.4 *m* $BrSO_3F$ solution in 0.176 *m* superacid using 6328-Å excitation is shown in Figure 2. A very intense sharp peak appears at 360 cm^{-1} and, among the other lines in the spectrum due to the solvent, etc., weaker and broader lines that are apparently overtones of the 360-cm^{-1} fundamental may be seen at 710 and 1070 cm^{-1}. The lines due to other species were identified in separate experiments and are listed in Table I. By comparison with the known vibrational frequencies of Br_2 of 320 cm^{-1}, I_2 of 215 cm^{-1}, and I_2^+ of 238 cm^{-1} it is not unreasonable to attribute the 360-cm^{-1} line to the Br_2^+ cation. Moreover, in view of the intensities of the overtones it appears that this is a resonance Raman spectrum similar to that previously observed[3] for the I_2^+ cation. This was confirmed by investigating the dependence of the intensity of this line on the wavelength of the exciting radiation. The results of such experiments are shown in Figure 3 and Table II and

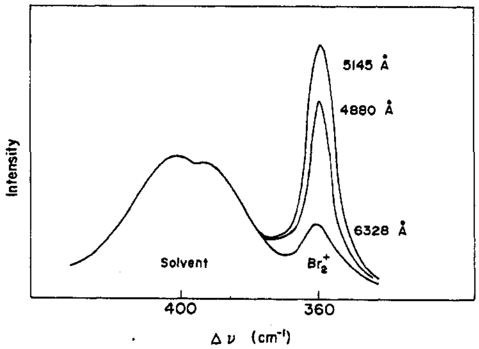

Figure 3.—Resonance Raman spectrum of the Br_2^+ cation; variation of the intensity of the 360-cm^{-1} fundamental with exciting wavelength.

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(5) J. E. Roberts and G. H. Cady, *J. Amer. Chem. Soc.*, **82**, 352 (1960).

(6) F. Aubke and R. J. Gillespie, *Inorg. Chem.*, **7**, 599 (1968).

(7) R. J. Gillespie and M. J. Morton, *Chem. Commun.*, 1565 (1968).

(8) A. J. Edwards, G. R. Jones, and R. J. C. Sills, *ibid.*, 1527 (1968).

(9) O. Glemser and A. Smalc, *Angew. Chem., Int. Ed. Eng.*, **8**, 517 (1969).

TABLE II

VARIATION OF DEPOLARIZATION RATIO AND INTENSITIES OF THE RAMAN FUNDAMENTAL AND FIRST OVERTONE OF THE Br_2^+ CATION WITH LASER WAVELENGTH

Laser wavelength, Å	Area of fundamental[a]	Rel area of overtone[b]	Depolarization ratio
6328	25	0.25	0.27
5145	100	1.0	0.30
5017	95	1.0	0.28
4965	80	1.0	0.25
4880	70	1.0	. . .
4765	65	1.0	0.20
4579	30	1.0	. . .

[a] Peak area measured relative to that of the 400-cm^{-1} solvent band. [b] Areas measured relative to that of fundamental at 5145-Å excitation.

confirm that the intensity of the Raman spectrum is a maximum at the maximum of the absorption curve as expected for a resonance Raman spectrum.[3,10] It is of interest that whereas the depolarization ratio and relative intensity of the fundamental reach a maximum with 5145-Å excitation and then decrease with shorter wavelengths, no decrease in the relative areas of the overtones to the fundamental was observed with "post-resonance" wavelengths. It is concluded that the species giving rise to the characteristic absorption spectrum with a maximum at 510 nm is the same species that gives a resonance Raman spectrum with a vibrational frequency of 360 cm^{-1} and it may plausibly be assumed to be the Br_2^+ cation. This must arise from a disproportionation of $BrOSO_2F$ in superacid solution to Br_2^+ and an oxidation state higher than 1+ which is shown to be $Br(SO_3F)_3$: $5BrOSO_2F + 2H_2SO_3F^+ \rightarrow 2Br_2^+ + Br(OSO_2F)_3 + 4HSO_3F$

The Raman spectrum of a solution of bromine in fluorosulfuric acid had a peak at 320 cm^{-1} which is close to the stretching frequency of 317 cm^{-1} for bromine in the gas phase. It is concluded that bromine dissolves in fluorosulfuric acid unchanged and this is confirmed by the absorption spectra measurements discussed later. However the Raman spectra of 3:1 Br_2–$S_2O_6F_2$ solutions in fluorosulfuric acid gave in addition to the peaks due to fluorosulfuric acid a broad peak at 290 cm^{-1}. Since the Cl_3^+ cation has vibrational frequencies ν_1, ν_2, and ν_3 of 514, 208, and 535 cm^{-1} [11] compared with that of Cl_2 of 555 cm^{-1} and since we have shown that the Br_2^+ cation has a stretching frequency of 360 cm^{-1} and Br_2 has a stretching frequency of 320 cm^{-1}, it seems reasonable to attribute the 290-cm^{-1} band to the Br_3^+ cation formed according to the equation $3Br_2 + S_2O_6F_2 = 2Br_3^+ + 2SO_3F^-$. The 290-$cm^{-1}$ band is probably due to both ν_1 and ν_3 while ν_2 which would be expected to have a lower frequency was not observed.

Conductivities in the SbF_5–$3SO_3$–HSO_3F Superacid System.—Table III and Figure 4 show the results of the measurements of the conductivity of 0.176 *m* superacid to which bromine was added and then oxidized with successive amounts of $S_2O_6F_2$.

The superacid medium may be regarded as a solution of the strong acid $HSbF_2(SO_3F)_4$ in fluorosulfuric acid

$$HSbF_2(SO_3F)_4 + HSO_3F = H_2SO_3F^+ + SbF_2(SO_3F)_4^-$$

TABLE III

CONDUCTIVITIES OF SOLUTIONS OF Br_2–$S_2O_6F_6$ IN 0.176 *m* SUPERACID

$10^2 m_{Br_2}$	Mole ratio $Br_2:S_2O_6F_2$	$10^4\kappa$, ohm^{-1} cm^{-1}	γ	$10^2 m_{Br_2}$	Mole ratio $Br_2:S_2O_6F_2$	$10^4\kappa$, ohm^{-1} cm^{-1}	γ
7.84	1:0.43	258	0.56	6.34	1:1.64	255	0.71
7.46	1:0.67	273	0.50	5.97	1:1.99	234	0.92
7.33	1:0.87	282.5	0.45	5.66	1:2.35	217	1.10
7.00	1:1.10	283.5	0.46	5.32	1:2.78	193	1.39
6.77	1:1.30	274.5	0.54	5.09	1:3.10	186.5	1.51

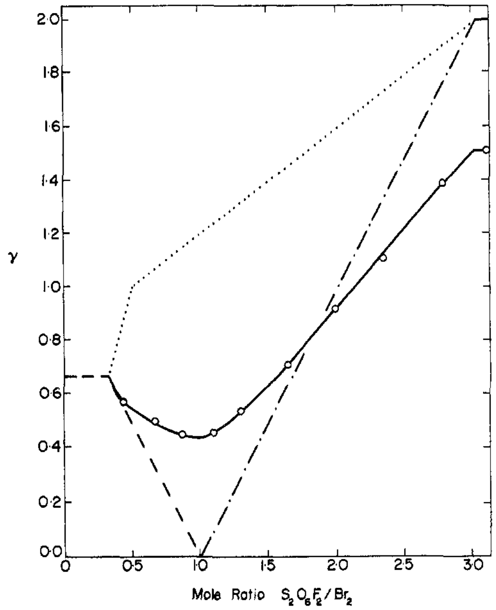

Figure 4.—Conductivities at 25°; variation of γ value on oxidation of bromine with $S_2O_6F_2$ in 0.176 *m* SbF_5–$3SO_3$–HSO_3F: O, experimental values; – – –, Br_3^+ and $BrOSOF_2$ only; —·—·—, $BrOSO_2F$ and $Br(OSO_2F)_2^+$ only; ...., Br_3^+, Br_2^+, and $Br(OSO_2F)_2^+$ only.

On addition of Br_2–$S_2O_6F_2$ the conductivity decreases because of the titration of the highly conducting $H_2SO_3F^+$ ion by SO_3F^- formed from the reaction of bromine and $S_2O_6F_2$. The results are conveniently expressed in terms of γ which is defined as the number of moles of SO_3F^- ions produced in solution per mole of electrolyte, which in this case is clearly equal to the number of moles of $H_2SO_3F^+$ ions removed. For each point the value of γ per mole of bromine was calculated and the values are shown in Figure 4 and compared with the expected values for the successive formation of Br_3^+, Br_2^+, $BrOSO_2F$, and $Br(OSO_2F)_3$ according to the equations

$$3Br_2 + S_2O_6F_2 + 2H_2SO_3F^+ = 2Br_3^+ + 4HSO_3F \quad \gamma = {}^2/_3 \quad (1)$$

$$2Br_2 + S_2O_6F_2 + 2H_2SO_3F^+ = 2Br_2^+ + 4HSO_3F \quad \gamma = 1 \quad (2)$$

$$Br_2 + S_2O_6F_2 = 2BrOSO_2F \quad \gamma = 0 \quad (3)$$

$$Br_2 + 3S_2O_6F_2 = 2Br(OSO_2F)_3 \quad \gamma = 0 \quad (4)$$

assuming, for the moment, that both $Br(OSO_2F)$ and $Br(OSO_2F)_3$ behave as nonelectrolytes.

The γ values given in Table III were obtained by comparing the decrease in conductivity produced by Br_2–$S_2O_6F_2$ with that produced by potassium fluorosulfate in the same acid medium. The results are consistent with the formation of the Br_3^+ cation according to eq 1 at the $Br_2:S_2O_6F_2$ ratio of 3:1.

The γ value then decreases somewhat with the addi-

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(10) J. Behringer in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967.

(11) R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, **9**, 811 (1970).

tion of $S_2O_6F_2$ reaching a minimum at the 1:1 ratio before rising again to a value of 1.51 at the 1:3 ratio. This latter value shows that bromine trifluorosulfate is not a nonelectrolyte in the superacid medium but acts as a base as in the equation

$$Br(SO_3F)_3 + H_2SO_3F^+ = Br(SO_3F)_2^+ + 2HSO_3F \qquad (5)$$

Complete ionization, however, would remove 2 mol of acidium cation per mole of Br_2, giving a γ value of 2.0. Therefore the observed value of 1.51 indicates that bromine trifluorosulfate under these conditions is some 75% ionized. The equilibrium constant for eq 5 can be calculated by first calculating the acidium ion concentration from the conductance of the solution and the equivalent conductivities given by Gillespie, *et al.*[12] This gives

$$K_b = \frac{[Br(SO_3F)_2^+]}{[Br(SO_3F)_3][H_2SO_3F^+]} = 60 \pm 10 \text{ mol}^{-1}\text{ kg} \qquad (6)$$

We note that formation of Br_2^+ is far from complete at the mole ratio $S_2O_6F_2:Br_2 = 0.5$ because γ decreases to $\sim$0.5 instead of increasing to 1.0. In other words Br_2^+ is extensively disproportionated to Br_3^+ and $BrOSO_2F$ even in this superacid medium. The minimum in the γ value at the 1:1 ratio may be ascribed to the formation of a maximum amount of the nonelectrolyte $BrOSO_2F$ and the γ value of 0.43 can be attributed to the disproportionation of $BrOSO_2F$ to Br_2^+, Br_3^+, and trivalent bromine, according to the equations

$$4BrOSO_2F + H_2SO_3F^+ \rightleftharpoons Br_3^+ + Br(SO_3F)_3 + 2HSO_3F \qquad (7)$$

$$5BrOSO_2F + 2H_2SO_3F^+ \rightleftharpoons 2Br_2^+ + Br(SO_3F)_3 + 4HSO_3F \qquad (8)$$

together with ionization of $Br(SO_3F)_3$ as in eq 5.

We may note from eq 7 that for every mole of Br_3^+ produced 1.0 mol of the acidium cation is consumed. Furthermore, using the value of K_b from eq 6, 80% of the $Br(SO_3F)_3$ produced is ionized at this acidium ion concentration, giving a total of 1.8 mol of acidium cation consumed per mole of Br_3^+ formed. Similarly a total of 1.4 mol of acidium cation is removed per mole of Br_2^+ formed. Hence we can put an upper limit of $\gamma/1.4 = 0.31$ on the mole ratio of bromine as Br_2^+ in solution by assuming that no Br_3^+ is formed at the 1:1 ratio. Alternatively it may be assumed that no Br_2^+ is formed in which case an upper limit of $\gamma/1.8 = 0.23$ may be placed on the mole ratio of bromine as Br_2^+ in the solution. In either case some 60% of the bromine remains as un-ionized $BrOSO_2F$.

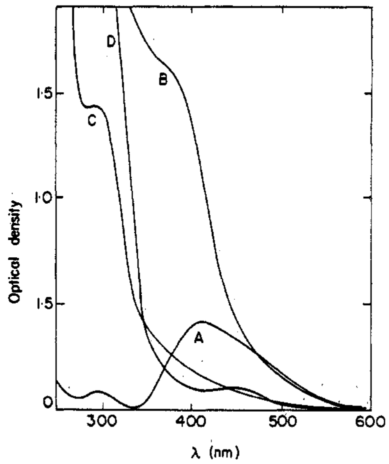

Figure 5.—Uv and visible spectra in HSO_3F. $Br_2:S_2O_6F_2$ ratio: A, 1:0; B, 1:0.33; C, 1:1; D, 1:3 and 1:5.

TABLE IV

ABSORPTION SPECTRA OF BROMINE–$S_2O_6F_2$ SOLUTIONS IN 0.176 *m* SUPERACID

Mole ratio $Br_2:S_2O_6F_2$	$10^2 m_{Br_2}$	$10^4\kappa$, $ohm^{-1}\ cm^{-1}$	Path length, mm	Molal extinction coeff (per mole of bromine)[a] 510 nm (Br_2^+)	375 nm (Br_3^+)
0.433	4.239	300.5	0.506	230	650
0.433	5.845	281	0.506	230	670
0.67	7.46	273	0.211	375	375
1.00	5.573	293	0.144	450	450
1.00	5.573	293	0.506	450	450
1.30	6.77	274.5	0.506	236	220
2.10	4.80	220	0.144	65	110
2.35	5.66	217	0.211	11	63
2.78	5.32	193	10.00	2	27

[a] Optical densities per centimeter divided by molality of bromine in solution.

Absorption Spectra.—Figure 5 shows the changes observed in the absorption spectrum of a 1.422 × 10^{-2} *m* solution of bromine in fluorosulfuric acid on oxidation with a concentrated $S_2O_6F_2$ solution to the $S_2O_6F_2:Br_2$ ratios of 0.33, 1, 3, and 5. On oxidation the extinction coefficient at 375 nm, attributed to the Br_3^+ cation increased until at the 0.33 ratio, corresponding to the formation of Br_3^+, the curve B was obtained. Above this ratio the shoulder at 375 nm decreased in intensity, but a shoulder at 310 nm increased until at the $S_2O_6F_2:Br_2$ ratio of 3, corresponding to oxidation to $Br(SO_3F)_3$, there was no further change. On repeating the experiment in 0.03 *m* SbF_5–$3SO_3$–HSO_3F the 510-nm peak attributed to Br_2^+ was observed between the ratios of 0.5 and 2. The optical density at $S_2O_6F_2:Br_2$ 0.33 in 0.03 *m* superacid gave a molal extinction coefficient of 1600 for the Br_3^+ cation at 375 nm. Table IV lists the optical densities per mole of bromine at various wavelengths of various solutions in 0.176 *m* superacid extracted from the conductivity cells with weighed Teflon-glass syringes. Although the acidium ion concentration was known from the conductivity of these solutions and the concentration of bromine and the oxidation ratio was accurately known, the absorption spectra results are not accurate to more than 10%. This is due to the very large surface to volume ratios in the short path length optical cells that had to be used and the consequent problem of adsorbed water even after very careful drying. Quantitative interpretation of the results is further complicated by the sensitivity of the disproportionation of $BrOSO_2F$ to the acidity and to the overlapping absorptions of Br_2^+, Br_3^+, and $BrSO_3F$ at 375 nm. The results listed in Table IV show however that the concentration of the Br_2^+ cation per mole of bromine in solution reaches a maximum at the 1:1 ratio. At this ratio we obtained an upper limit of 0.31 for the mole ratio of bromine as Br_2^+ from the conductivity results (see above) and this gives a lower limit of 1400 for the extinction coefficient of Br_2^+ at 510 nm using the data in Table IV. However the absorption spectra of 1:1 solutions show a weak shoulder at 375 nm and the Raman spectra of concentrated 1:1 solutions have a weak

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[12] R. J. Gillespie, J. B. Milne, and M. J. Morton, *Inorg. Chem.*, **7**, 2221 (1968).

peak at 290 cm^{-1} due to the Br_3^+ cation present at this ratio and hence some of the conductivity is due to disproportionation to the Br_3^+ cation as in eq 7. The contribution due to the Br_3^+ cation to the extinction coefficient at 375 nm in the 1:1 solutions was estimated to be at most 80, giving a value of 0.05 for the moles of Br_3^+ in solution per mole of bromine and a contribution of 0.05×1.8 to the γ value. As before, we can calculate the mole ratio of bromine as Br_2^+ in solution given by $(\gamma - 0.05 \times 1.8)/1.4$ and hence an upper limit of 1800 for the extinction coefficient of Br_2^+ at 510 nm. Hence it is concluded that the molal extinction coefficient of the Br_2^+ cation at 510 nm is 1600 ± 200.

On cooling 1:1 solutions the optical density at 510 nm decreased until at $-80°$ no shoulder at 510 nm was visible. However, as no new peaks were observed, this experiment did not provide any evidence for the formation of the Br_4^{2+} cation, which would be analogous to the I_4^{2+} cation.[12] The simplest explanation of the decrease in intensity at 510 nm would be that the degree of disproportionation of $BrSO_3F$ to bromine cations decreases with decreasing temperature.

Magnetic Measurements.—Table V gives the results of magnetic measurements on a very concentrated (1.7 *m*) solution of $BrOSO_2F$ in 1.38 *m* superacid. The solution was less diamagnetic than the solvent alone, showing that a paramagnetic species is formed. Assuming a value of 2.0 BM for the magnetic moment of the Br_2^+ cation, as observed for the I_2^+ cation, gives a concentration of 0.06 mol of Br_2^+/kg of solution. As the density of the solution was 2.0 g cm^{-3}, this gives 0.12 mol of Br_2^+/l. at 37°. The absorption spectrum of the same solution gave an optical density of 117 cm^{-1} at a path length of 0.0068 cm and using a molar extinction coefficient of 1600/1.8 where 1.8 is the density of the 0.176 *m* superacid gives a Br_2^+ concentration of 0.13 ± 0.02 *M* at 28° in good agreement with the magnetic results. On cooling, both the paramagnetism and the optical density at 510 nm decreased sharply.

TABLE V

MAGNETIC SUSCEPTIBILITIES OF A 1.7 *m* SOLUTION OF $BrSO_3F$ IN 1.38 *m* SbF_5–$3.4SO_3$–HSO_3F[a]

	Δw, μg			Optical
Temp, °C	Solvent	Sample	$\Delta(\Delta w)$, μg	density (510 nm)
+37	−660	−535	125	0.80
−20	−660	−640	20	0.41
−70	−660	−650	10	0.00

[a] Tube constant 2.08; weight of sample contents 2.62 g.

Esr and Nmr Spectra.—No esr spectra were obtained from solutions of the paramagnetic Br_2^+ cation at room temperature or any temperature down to $-100°$. The ground state of this cation should be a $^2\Pi_{3/2g}$ state in which strong spin–orbit coupling would probably broaden any esr spectrum beyond detection. The nmr spectra of solutions of the Br_2^+ cation in the superacid showed no significant broadening of the fluorosulfuric acid solvent peak. In contrast solutions of the paramagnetic I_2^+ cation cause a dramatic broadening of the ^{19}F solvent signal to a half-height width of over 50 Hz at similar concentrations. This indicates that the relaxation rate of the unpaired electron spin in the Br_2^+ cation is very short on the nmr time scale, unlike that of the I_2^+ cation. A recent study of the photoelectron spectra of the halogens in the gas phase[13] showed that the $^2\Pi_{3/2g} - {}^2\Pi_{1/2g}$ separation for the I_2^+ cation is 0.63 eV while that for gaseous Br_2^+ is only 0.39 eV. Also the smaller Br_2^+ cation would be more highly solvated than the I_2^+ cation, so that any relaxation arising from coupling of the electron spin with solvent molecules would be more effective for the Br_2^+ cation.

Conductivities in Fluorosulfuric Acid.—Table VI gives the conductivities of solutions in fluorosulfuric acid having the $S_2O_6F_2$:Br_2 ratio equal to 0.33. A γ value of 0.37 was obtained from these results. Since $\gamma = 0.67$ is expected for complete ionization according to eq 9, this indicates that approximately 50% of the bromine is ionized to the Br_3^+ cation

TABLE VI

CONDUCTIVITIES AT 25° IN HSO_3F[a]

$10^2 m_{Br_2}$	$10^4\kappa$, ohm^{-1} cm^{-1}	$10^2 m_{Br_2}$	$10^4\kappa$, ohm^{-1} cm^{-1}	$10^2 m_{Br_2}$	$10^4\kappa$, ohm^{-1} cm^{-1}
...	14.60	6.519	70.66	10.760	110.44
2.291	35.46	8.696	91.65	13.504	133.21
4.392	52.99				

[a] $S_2O_6F_2$:Br_2 = 1:3.

$$3Br_2 + S_2O_6F_2 \longrightarrow 0.5Br_2 + 2BrSO_3F \rightleftharpoons 2Br_3^+ + 2SO_3F^- \quad (9)$$

By analogy with iodine, the Br_5^+ cation could also be formed by the equilibrium

$$Br_3^+ + Br_2 \rightleftharpoons Br_5^+ \quad (10)$$

However, this is probably present only in trace quantities in fluorosulfuric acid as even at the 3:1 ratio bromine could be pumped off the concentrated solution quite readily. This shows that Br_3^+ cation is unstable according to eq 9 as is also indicated by the conductivity results and presumably the Br_5^+ cation is still less stable.

Conclusions

Oxidation of bromine with an increasing amount of $S_2O_6F_2$ in solution in HSO_3F gives rise to the successive formation of Br_3^+, $BrOSO_2F$, and $Br(OSO_2F)_3$. The cation Br_3^+ is however not completely stable in this medium and $Br_3^+SO_3F^-$ is approximately 50% disproportionated in a dilute solution according to the equation $4Br_3^+SO_3F^- = Br_2 + 4BrOSO_2F$. Oxidation of bromine with $S_2O_6F_2$ in the superacid SbF_5–$3SO_3$–HSO_3F gives rise to the successive formation of Br_3^+, Br_2^+, $BrOSO_2F$, and $Br(OSO_2F)_3$. In this medium the Br_3^+ ion appears to be stable but the Br_2^+ ion is considerably disproportionated to Br_3^+ and $BrOSO_2F$ and $Br(OSO_2F)_3$. The system is somewhat complicated by the simultaneous disproportionation of $BrOSO_2F$ to Br_3^+, Br_2^+, and $Br(OSO_2F)_3$. We may note that no evidence has been obtained for $IOSO_2F$ even in solution in HSO_3F and it appears to be completely disproportionated to I_2^+ and $I(OSO_2F)_3$.[1] It was found that, like $I(OSO_2F)_3$, bromine(III) fluorosulfate behaves as a base in the superacid medium ionizing rather extensively to $Br(OSO_2F)_2^+$. No evidence was obtained for the dimerization of Br_2^+ although it has been shown previously that I_2^+ dimerizes

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(13) D. C. Frost, C. A. McDowell, and D. A. Vroom, *J. Chem. Phys.*, **46**, 4255 (1967).

to I_4^{2+} at low temperatures.[12] The bromine cations Br_2^+ and Br_3^+ are evidently considerably less stable than the corresponding iodine cations although Br_2^+ has been obtained as a stable solid with the very weakly basic anion $Sb_3F_{16}^-$, and Br_3^+ has been obtained as the hexafluoroarsenate. It may be predicted that the corresponding chlorine cations Cl_2^+ and Cl_3^+ will be still less stable in solution than the bromine cations and this is discussed in a following paper.[14] The vibrational frequencies of the halogens and their cations are summarized in Table VII. No vibrational frequencies have yet been reported for I_3^+.

TABLE VII

VIBRATIONAL FREQUENCIES OF THE HALOGENS AND THEIR CATIONS

	Cl_2	Cl_2^+	Cl_3^+	Br_2	Br_2^+	Br_3^+	I_2	I_2^+
ν_1	555	640	514	320	360	290	215	238
ν_2	...	...	208	...	...	?	...	...
ν_3	...	...	535	...	...	290	...	...

Experimental Section

The methods used for magnetic susceptibility, uv and visible, and conductometric measurements and the calculation of γ values have been described previously.[1,4,6,12,15] Solutions were handled in a drybox using smooth glass syringes fitted with Teflon plungers and platinum needles (Hamilton Syringe Co.) as weight droppers. Materials were prepared and purified as described previously.[1,3,6,12,15]

Raman spectra were recorded using a Spex Industries Model 1400 double monochromator with dc amplification and with a spectral slit width of 3 cm^{-1}. Raman shifts were accurate to ± 2 cm^{-1}. The beam of exciting radiation from a Spectra Physics Model 125 helium-neon laser or a Spectra Physics Model 140 argon ion laser entered the sample compartment in a vertical direction and was focused on the sample sealed in a horizontally mounted 2-mm o.d. glass melting point tube. The light scattered at right angles to the incident beam and the tube axis was focused on the entrance slit of the monochromator. For resonance Raman studies in which the Raman intensities were compared using different excitation frequencies, the laser output at the sample was attenuated to 10 mW to minimize heating. The areas of the Raman peaks on the recording chart were measured using a Du Pont 310 curve analyzer and at each exciting wavelength the areas of the Br_2^+ resonance Raman peaks were compared to the areas of the solvent peaks.

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Chlorine Cations in Highly Acidic Media

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The reaction of ClF and of ClF–Cl_2 with the superacid medium HSO_3F–SbF_5–$3SO_3$ has been investigated in order to obtain further evidence on the possible formation of ClF^+ and Cl_2^+ which have been claimed to be products from the reaction of ClF with SbF_5 and HSO_3F–SbF_5. This reaction was however found to produce $ClOSO_2F$ and no evidence was obtained for Cl_2^+ or ClF^+. An esr spectrum that is obtained from many of these solutions and which was assigned previously to ClF^+ appears to be due to an oxygen-containing species which is proposed to be either $OClF^+$ or O_2ClF^+.

Iodine in the 1+ oxidation state is completely disproportionated in solution in fluorosulfuric acid to the I_2^+ ion and $I(SO_3F)_3$.[1] Recently we have shown[2] that bromine(I) fluorosulfate is disproportionated to an appreciable extent to the Br_2^+ ion and $Br(SO_3F)_3$ in solution in the superacid SbF_5–$3SO_3$–HSO_3F. It was interesting therefore to explore the possibility that chlorine in the 1+ oxidation state might disproportionate in a similar manner in a sufficiently acidic medium at least to an extent which would enable the Cl_2^+ cation to be detected by a sensitive technique, *e.g.*, the resonance Raman spectrum which has proved particularly useful for the detection of the I_2^+ and Br_2^+ cations at low concentrations.[2,3]

By oxidizing iodine or bromine with a suitable oxidizing agent, *e.g.*, $S_2O_6F_2$, the cations I_3^+ and Br_3^+ have been obtained in highly acidic solutions,[1,2] a rather lower acidity being sufficient to stabilize these ions than is necessary for the corresponding I_2^+ and Br_2^+ cations. Consequently it also seemed reasonable to search for the formation of the Cl_3^+ cation in acidic media, particularly as we have recently been able to prepare the solid compound $Cl_3^+AsF_6^-$ at low temperature and to establish its identity by means of its Raman spectrum.[4] There has been an as yet unpublished claim (cited in ref 5) that Cl_2^+ can be obtained as the salt $Cl_2^+IrF_6^-$ and Olah and Comisarow have attributed a seven-line esr spectrum which they obtained on dissolving ClF in SbF_5, HSO_3F–SbF_5, or HF–SbF_5 to the Cl_2^+ cation.[6] These authors also attributed a second more complex esr spectrum that they observed in solutions of ClF_3 or ClF_5 in these solvents to the ClF^+ radical ion[7] and they suggested that

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