3.14 ± 0.02 Å as the Cl–Cl distance in the bichloride ion in this compound.

In $CsBr \cdot {}^1/_3H_3OHBr_2$ the geometry around oxygen has O–Br distances of 3.04 ± 0.02 Å and a Br–O–Br angle of 111°. Again our evidence for the bibromide ion stems from the composition and Br–Br contacts. All Br–Br contacts are 4.2 Å or greater with the exception of the Br_2–Br_2 contacts. They are either 3.73 or 3.35 Å while the sum of usual van der Waals radii for bromide is 3.90 Å. The closest approach of two nonbonded bromines has been reported as 3.70 Å.[16–18] This leaves one with the Br_2 contact of 3.35 Å which is shorter than any reported nonbonded contact.

The nonbonded distance of 3.73 Å could be accounted for by a static disorder of the bibromide ions in the following manner. Some of the bibromide ions could be directly opposite to each other instead of alternating as in Figure 1. The Br_2–Br_2 distances 3.73 and 3.35 Å would both be weighted averages of the normal van der Waals and the Br–Br distance in the bibromide ion. Consequently, the scattering density due to bromine would be smeared over a region 0.38 Å in the vertical direction. Thus the root-mean-square amplitude of vibration parallel to the strings should be greater than that perpendicular to the strings. However, the root-mean-square amplitude of vibration parallel to the strings is 0.163 ± 0.011; the corresponding value perpendicular to the strings is 0.188 ± 0.006 Å. Therefore, we conclude that the strings of bibromide ions are ordered and that 3.35 ± 0.02 Å[19] is the Br–Br distance in the bibromide ion.

The model of thermal motion obtained in this study (see Figure 1) suggests that the ion is vibrating more in a bending mode than in a stretching mode. This seems physically reasonable considering that the bibromide ions are packed tightly end to end. The distance between the nonbonded bromines is only 3.73 Å.

The infrared spectrum of $CsCl \cdot {}^1/_3H_3OHCl_2$ gave some indications of band positions corresponding to those expected for the hydronium ion, but the results were largely inclusive owing to rapid decomposition of the material in Nujol or perfluorocarbon mulls.

The bibromide ion is 0.20 Å longer than the bichloride as expected. If we compare the radius sum with the observed X–X distance for the bihalide ions we see that the difference is about 0.47 Å for all three.[20]

TABLE VI

COMPARISON OF H BONDED AND VAN DER WAALS DISTANCES[20]

X–H–X	Radius sum, Å	X–X_{obsd}, Å	Difference, Å
HF_2^-	2.73	2.26	0.47
HCl_2^-	3.62	3.14	0.48
HBr_2^-	3.81[a]	3.35	0.46

[a] This value represents the average of distances reported for the closest approach of two bromines not bonded to each other.

This comparison may be somewhat artificial because of the uncertainty in the value for the closest approach of two nonbonded bromines. Nevertheless, the contraction that occurs in the X–X distance when a bihalide ion is formed is larger than in the corresponding O–H–O bonds.[21] This indicates a very strong hydrogen bond, in agreement with thermodynamic measurements.[7]

We are attempting to make a corresponding iodine compound in hopes of studying HI_2^-.

Acknowledgment.—This work has been generously supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center.

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Bromine Monofluorosulfate

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The preparation and properties of bromine monofluorosulfate $BrOSO_2F$ have been reinvestigated. The electrical conductivity of $BrOSO_2F$ is compared with the conductivities of the other bromine and iodine fluorosulfates which have also been measured over a temperature range. There is no evidence for the formation of either Br^+ or Br_2^+ in solutions of $BrOSO_2F$ in fluorosulfuric acid.

Introduction

It has been shown that peroxydisulfuryl difluoride, $S_2O_6F_2$, reacts directly with bromine to yield bromine(I) fluorosulfate, $BrOSO_2F$, when Br_2 is in excess, and bromine(III) fluorosulfate, $Br(OSO_2F)_3$, when $S_2O_6F_2$ is in excess.[1] Both compounds are also formed when $S_2O_6F_2$ is allowed to react with CF_3Br.[2] Bromine(I) fluorosulfate has been described as a red-black liquid of

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

(2) C. T. Ratcliffe and J. M. Shreeve, *Inorg. Chem.*, **3**, 631 (1964).

relatively high thermal stability, which does not have a definite melting point but solidifies to a glassy material on cooling.[1] It seemed important to study the properties of bromine(I) fluorosulfate in more detail as all other inorganic unipositive bromine compounds that have been studied are either thermally unstable, *e.g.*, $BrONO_2$[3] and BrCl,[4] or are extensively disproportionated at room temperature, *e.g.*, BrF.[5] Moreover, iodine monofluorosulfate when dissolved in fluorosulfuric acid gives a cationic paramagnetic iodine species[6] that has now been identified[7] as I_2^+, and it was of interest to search for analogous bromine cations.

Preliminary attempts to prepare $BrOSO_2F$, by direct reaction of Br_2 in slight excess and $S_2O_6F_2$, always appeared to give a mixture of $BrOSO_2F$ and bromine which could not be separated by distillation. As bromine(III) fluorosulfate has a negligible vapor pressure at room temperature,[1] it appeared that it would be possible to prepare pure bromine(I) fluorosulfate, free from bromine, by allowing bromine to react with a small excess of $S_2O_6F_2$ and then separating the monofluorosulfate from the small amount of the involatile trifluorosulfate by distillation.

Experimental Section

Preparation of Bromine(I) Fluorosulfate.—Peroxydisulfuryl difluoride was prepared and purified by the method of Cady and Shreeve[8] followed by extraction of traces of sulfur trioxide with 100% sulfuric acid and a final vacuum distillation. The purity was checked by infrared, nmr, and vapor density measurements. Reagent grade bromine was purified by literature methods[9] and freshly distilled from KBr and P_2O_5 before each experiment. The apparatus used for the controlled addition of the reactants and the reaction vessel were similar in design to those used by Aubke and Cady for the preparation of iodine monofluorosulfate.[6]

In a typical run 13.946 g of purified Br_2 was distilled into the reactor, and 17.595 g of $S_2O_6F_2$ was added; the reactor was then flame sealed and removed from the vacuum line. The mole ratio of $S_2O_6F_2$ to Br_2 was 1.018. The reaction mixture was allowed to warm slowly by leaving it overnight in a trichloroethylene bath initially at a temperature of approximately −75°. When the mixture had warmed to +10°, the reactor was heated in a water bath for 30 min at approximately +50°. To make sure that no unreacted $S_2O_6F_2$ remained in the vapor phase, the reactor was cooled to liquid air temperature and warmed to +50° several times until no unreacted $S_2O_6F_2$ condensed out in the upper portion of the reactor. The product had a red-brown color, somewhat paler than pure bromine. Upon cooling, the whole solidified to a yellow solid, but when the $S_2O_6F_2$ to Br_2 ratio was greater than 1.15, only a brown glass-like material was obtained. The reactor was then again attached to a high-vacuum all-Pyrex manifold and bromine monofluorosulfate was distilled off and collected in break-seal storage traps. Small amounts of a yellow solid were left behind, having the melting point reported for bromine(III) fluorosulfate.[1] It was convenient to store $BrOSO_2F$ over $Br(OSO_2F)_3$ to remove any bromine formed by slight hydrolysis or reaction with Kel-F grease. Pure bromine monofluorosulfate could then be obtained by vacuum distillation in an all-Pyrex system with break-seals. A typical analysis gave the following results. *Anal.* Calcd for $BrOSO_2F$: Br, 44.7; oxidation value, 1.00; F, 10.62. Found: Br (gravimetrically), 44.6; oxidation value (iodimetrically), 1.02; F ($Th(NO_3)_4$ titration), 10.8.

Preparation of Iodine(I) Fluorosulfate, Iodine(III) Fluorosulfate, and Bromine(III) Fluorosulfate.—These compounds were prepared in order to compare their electrical conductivities with those of bromine(I) fluorosulfate. The iodine fluorosulfates were prepared from the stoichiometric amounts of iodine and purified $S_2O_6F_2$ by the method of Aubke and Cady.[6] Bromine(III) fluorosulfate was prepared from bromine and excess $S_2O_6F_2$.[1]

Electrical Conductivity Measurements.—Conductivity cells of Pyrex glass with sealed-in platinum electrodes were used. The electrodes were coated with platinum black. The volume was approximately 1–2 ml and the cell constants were ~1.0 cm^{-1}. The cell constant was determined by using standard potassium chloride solutions.[10] As $IOSO_2F$, $I(OSO_2F)_3$, and $Br(OSO_2F)_3$ are solid at room temperature, they were added to the conductivity cell in a drybox. The cell for the $BrOSO_2F$ measurements was incorporated into an all-Pyrex vacuum system and flame-sealed after filling with dry N_2. An Industrial Instruments Inc. conductivity bridge, Model RC-18, was used. Measurements in the temperature range 5–95° were carried out by immersing the cell in an oil thermostat; the temperature was measured with a platinum resistance thermometer. For higher temperatures an oil bath was used and the temperature was measured with a calibrated Hg thermometer. Low-temperature measurements were carried out in a dewar flask with trichloroethylene–Dry Ice mixtures and the temperature was measured with a pentane thermometer. To detect electrode reactions or irreversible decomposition at elevated temperatures, the samples were remeasured after each experiment at a constant lower temperature in a second oil bath. The measurements on solids were made on solidified melts.

The results for $BrOSO_2F$, $IOSO_2F$, and $I(OSO_2F)_3$ are given in Table I. $Br(OSO_2F)_3$ was measured at approximately 60°. The conductivity changed rapidly, and colorless gases were slowly produced on both electrodes, indicating decomposition and/or electrode reactions. Two different preparations gave the following results: $\kappa = 1.72 \times 10^{-3}$ ohm^{-1} cm^{-1} (61.3°); 1.48×10^{-3} ohm^{-1} cm^{-1} (60.0°).

Properties of Bromine(I) Fluorosulfate.—Bromine(I) fluorosulfate is a red-brown liquid, stable in a sealed Pyrex tube up to 150°. It is extremely sensitive to moisture and grease which cause it to darken to a deep red-brown color. It tends to supercool before solidifying to a yellow crystalline material, mp −31.5°.

Vapor pressures were measured in an apparatus similar to that described by Kellog and Cady.[11] The accuracy of the apparatus was checked with analytical reagent grade benzene. There was good agreement between sets of results obtained while both raising and lowering the temperature. The results are given in Table II. The dependence of the vapor pressure on temperature may be described by the expression

$$\log p = 8.544 - \frac{2.195 \times 10^3}{T}$$

from which we find that the extrapolated boiling point is 117.3° (760 mm), $\Delta H = 10.05$ kcal $mole^{-1}$, and the Trouton constant = 25.75.

The vapor density was measured by Regnault's method using a manometer filled with Flurolube oil. This gave a molecular weight of 180.5 (calcd 179.0).

The density was measured with a dilatometer which was incorporated in the vacuum system, filled by distillation, and then sealed off. The density was found to be 2.251 g/ml at 20° and 2.238 g/ml at 25°.

The viscosity was measured with an Ostwald viscometer and found to be 2.65 cP at 25.0°.

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TABLE I

ELECTRICAL CONDUCTIVITIES

Temp, °C	$10^3\kappa$, ohm^{-1} cm^{-1}	Temp, °C	$10^3\kappa$, ohm^{-1} cm^{-1}	Temp, °C	$10^3\kappa$, ohm^{-1} cm^{-1}
		$BrOSO_2F$			
−45.0[a]	0.276	−9.0	0.580	35.0	0.727
−39.6[a]	0.328	0.0	0.640	40.0	0.726
−35.0[a]	0.373	+5.05	0.664	44.9	0.720
−30.0	0.422	9.85	0.684	50.0	0.712
−25.0	0.465	20.0	0.707	57.4	0.693
−22.9	0.481	25.0	0.721	65.2	0.663
−15.0	0.538	30.0	0.726	93.0	0.488
		$IOSO_2F$			
+40.0[a]	0.384	73.2	1.87	115.4	6.44
+44.9[a]	0.505	77.6	2.17	120.0	7.20
+50.0[a]	0.671	77.8	2.19	125.0	8.00
+51.1[a]	0.712	88.6	3.10	130.0	8.78
+54.9	0.855	93.3	3.62	135.0	9.98
+59.6	1.066	99.0	4.33	140.0	11.04
+64.8	1.34	104.0	4.70	141.0	11.20
+68.1	1.53	110.0	5.76		
		$I(OSO_2F)_3$			
+25.0[a]	0.367	35.0	0.680	65.2	2.59
+30.0[a]	0.501	44.7	1.13	75.96	3.66
+34.0	0.641	54.7	1.75		

[a] Supercooled liquid.

TABLE II

VAPOR PRESSURES OF $BrOSO_2F$

p, mm	Temp, °K	p, mm	Temp, °K	p, mm	Temp, °K
45.0	321.6	156.6	348.0	450.3	375.1
49.1	323.4	192.0	352.8	482.7	377.1
60.0	326.9	204.0	354.2	506.0	378.5
69.1	330.0	231.4	357.4	514.9	378.9
74.6	331.4	261.5	360.5	551.4	381.0
100.5	337.8	285.4	362.7	574.3	382.1
102.4	338.3	341.5	367.5	616.0	384.2
119.0	341.6	358.6	368.8	649.7	385.6
143.6	345.8	406.3	372.2	664.1	386.4
144.6	346.0			733.6	389.4

The mass spectrum was recorded using a Consolidated Engineering Corp. Type 21-103 mass spectrometer. At an ionization potential of 70 V, peaks were found which could be attributed to SO_2F^+, SO_2^+, SO_3^+, Br^+, Br_2^+, SOF^+, $BrSO_2F^+$, and SF^+; small peaks due to SiF_3^+, CO_2^+, HCl^+, and $S_2O_5F^+$ were also present indicating some reaction of the compound with water, grease, and glass. No peak could be found for the parent compound.

Because of the great reactivity of $BrOSO_2F$ no satisfactory infrared spectra could be obtained either in the gas phase or the solid state. In the uv–visible region a gaseous sample showed a maximum absorption at 378 mμ.

The ^{19}F nmr spectrum of $BrOSO_2F$ is a single line. Using $S_2O_5F_2$ as an internal standard the chemical shift with respect to CCl_3F was found to be −35.0 ppm and using Freon 11 as an external standard it was found to be −34.6 ppm. These values do not agree with the previously reported value of −41.3 ppm.[12]

Solutions of Bromine(I) Fluorosulfate.—From similar observations on iodine(I) fluorosulfate[6] it was expected that bromine(I) fluorosulfate would react readily with conventional nonpolar solvents. This was confirmed by studying a solution in CCl_4. The uv absorption of this solution was identical with that assigned to the equilibrium mixture[13,14] $2BrCl \rightleftharpoons Br_2 + Cl_2$. In more concentrated solutions than those used for the uv spectroscopy disulfuryl difluoride and phosgene were detected by their infrared spectrum indicating the reaction

$$2BrOSO_2F + CCl_4 \longrightarrow COCl_2 + 2BrCl + S_2O_5F_2$$

Stable solutions were obtained in disulfuryl difluoride, $S_2O_5F_2$, and trisulfuryl difluoride, $S_3O_8F_2$. The ^{19}F nmr spectra showed that there was no fluorine exchange in either solution. The visible spectrum showed a single absorption with λ_{max} 408 mμ and ϵ_{max} 32.6. Bromine(I) fluorosulfate dissolves readily in fluorosulfuric acid to give stable brown solutions. The electrical conductivities of these solutions are given in Table III. They were measured using techniques that have been described elsewhere.[15] All solutions were prepared and handled in a drybox. These solutions had a strong uv absorption at ~250 mμ and another peak at 325 mμ which had ϵ_{max} 477. The ^{19}F nmr spectrum showed only a single line.

TABLE III

Electrical Conductivities of $BrOSO_2F$ Solutions in HSO_3F at 25°

$10^2[BrOSO_2F]$, m	$10^4\kappa$, ohm^{-1} cm^{-1}	$10^2[BrOSO_2F]$, m	$10^4\kappa$, ohm^{-1} cm^{-1}
0.00	1.41	0.00	1.315
0.387	1.56	1.134	4.12
0.746	3.405	2.390	6.32
1.240	5.37	3.32	7.634
1.794	6.42	4.17	8.452
2.300	7.26	5.39	9.142
		6.55	9.662
		7.645	10.104
		8.565	10.44

Electrical Conductivities of $BrOSO_2F$–KSO_3F Solutions at 25°

$10^2[BrOSO_2F]$, m	$10^2[KSO_3F]$, m	$10^4\kappa$, ohm^{-1} cm^{-1}
0.00	0.00	1.41
2.30	0.00	7.26
2.30	0.391	16.13
2.30	0.868	27.08
2.30	1.279	37.21
2.30	1.940	53.66
2.30	2.729	70.44

Discussion

It seems probable that the material previously described as bromine monofluorosulfate[1] contained bromine as an impurity. This would, at least partly, account for the high density of 2.60, the low Trouton constant of 22.05, the deep red-black color, and the indefinite melting point.

Our value of the Trouton constant of 25.75 is comparable to the values for the interhalogen compounds which are generally supposed to be associated in the liquid phase, *e.g.*, BrF_3, $T_c = 25.7$;[16] IF_5, $T_c = 26.3$;[17] and ICl, $T_c = 26.7$.[18]

The observed melting point and boiling point of bromine monofluorosulfate given in Table IV are in line with those of the other halogen monofluorosulfates. There is a steady increase in both the melting point and the boiling point in the series $FOSO_2F$, $ClOSO_2F$, $BrOSO_2F$, and $IOSO_2F$. A similar trend is shown by the boiling points and melting points of the halogen nitrates. It is noteworthy that although fluorine and chlorine fluorosulfates strongly resemble fluorine and chlorine nitrates in melting point, boiling point, color, and thermal stability, bromine and iodine fluorosulfates have

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TABLE IV

MELTING POINTS AND BOILING POINTS OF HALOGEN FLUOROSULFATES AND HALOGEN NITRATES

	Mp, °C	Bp, °C		Mp, °C	Bp, °C
$FOSO_2F$[a]	−158.5	−31.3	$FONO_2$[e]	−175	−45.9
$ClOSO_2F$[b]	−84.3	45.1	$ClONO_2$[f]	−107	18
$BrOSO_2F$[c]	−31.5	117.3	$BrONO_2$[f]	−42.0	Dec pt 0°
$IOSO_2F$[d]	51.5	>200	$IONO_2$[f]	Dec pt 0°	

[a] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78,** 290 (1956). [b] W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2,** 496 (1963). [c] This work. [d] Reference 6. [e] O. Ruff and W. Kwasnik, *Angew. Chem.*, **48,** 238 (1935). [f] M. Schmeisser and K. Brändle, *ibid.*, **73,** 388 (1961).

considerably higher melting points and boiling points than the corresponding nitrates and they are also more stable and more highly colored.

The physical properties of bromine(I) fluorosulfate are summarized in Table V and it may be seen that they are quite similar to those of bromine trifluoride. It is possible that bromine(I) fluorosulfate might have some application as a nonaqueous solvent system. The specific conductances of $BrOSO_2F$, $IOSO_2F$, and $I(OSO_2F)_3$, are compared in Table VI. These values are quite similar to values obtained previously for some interhalogen compounds such as bromine trifluoride, iodine pentafluoride, and iodine mono- and trichloride (Table VII). The specific conductivity *vs.* temperature plot for $BrOSO_2F$ shows first a slow increase and, after a maximum at 35°, a slow decrease. Similar behavior has been reported for the iodine chlorides.[19]

TABLE V

PHYSICAL PROPERTIES OF BROMINE TRIFLUORIDE AND BROMINE MONOFLUOROSULFATE

Properties	BrF_3[22]	$BrOSO_2F$
Density (25°), g/cm	2.803	2.238
Freezing point, °C	+8.7	−31.5
Boiling point, °C	+125.6	+117.3 (extrapolated)
Heat of vaporization, kcal mol^{-1}	10.200	9.940
Trouton constant	25.7	25.5
Spec conductivity (25°), ohm^{-1} cm^{-1}	8.0×10^{-3}	7.21×10^{-4}
Viscosity (25°), cP	2.22	2.65

TABLE VI

COMPARISON OF THE ELECTRICAL CONDUCTIVITIES OF THE HALOGEN FLUOROSULFATES

Temp, °C	$10^3\kappa$, ohm^{-1} cm^{-1}		
	$BrOSO_2F$	$IOSO_2F$	$I(OSO_2F)_3$
0.0	0.64	...	...
10.0	0.69	...	...
20.0	0.71	...	...
30.0	0.72	...	0.50
40.0	0.73	0.38	0.82
50.0	0.71	0.67	1.40
60.0	0.68	1.10	2.20
70.0	0.64	1.60	3.15
80.0	0.58	2.30	4.10
90.0	0.51	3.20	...
100.0	0.43	4.40	...

The electrical conductivities of the interhalogens have been attributed to ionic self-dissociation in the liquid state, *e.g.*, for bromine trifluoride the generally accepted dissociation is

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

The tetrafluorobromate(III) anion has been found in compounds such as $KBrF_4$, and the 1:1 addition compounds of BrF_3 with strong Lewis acids such as SbF_5 and AsF_5 are presumed to contain BrF_2^+ cations.[20] Similar self-dissociation equilibria have been postulated for the other interhalogens. It should be pointed out, however, that definite proof for the cations has only been obtained for a single species, the ICl_2^+ cation,[21] by means of X-ray diffraction. Similar self-dissociation equilibria may be postulated for the halogen fluorosulfates, *e.g.*

$$2Br(OSO_2F)_3 \rightleftharpoons Br(OSO_2F)_2^+ + Br(OSO_2F)_4^-$$

Compounds of the type $K[Hal(OSO_2F)_4]$ have been reported by Lustig and Cady[22] where Hal is Br and I, and evidence for $I(OSO_2F)_4^-$ has been obtained from studies of solutions of $I(OSO_2F)_3$ in fluorosulfuric acid.[23]

The most likely self-dissociation for ICl would appear to be

$$3ICl \rightleftharpoons I_2Cl^+ + ICl_2^-$$

as evidence for the existence of I_2Cl^+ has been obtained from cryoscopic and conductometric studies in sulfuric acid[24] and the ICl_2^- ion is well established.[25] The corresponding dissociation for bromine monofluorosulfate would be

$$3BrOSO_2F = Br_2OSO_2F^+ + Br(OSO_2F)_2^-$$

The compound $CsBr(OSO_2F)_2$ has been reported by Cady[26] but there is at present no evidence for the cation.

An alternative possibility for the self-dissociation of $BrOSO_2F$ is

$$BrOSO_2F \rightleftharpoons Br^+ + OSO_2F^-$$

or

$$2BrOSO_2F \rightleftharpoons Br^+ + Br(OSO_2F)_2^-$$

but in fact Br^+ is unlikely to be a product as no other evidence for this ion has been obtained and the species that was formerly believed to be I^+ has been shown to be I_2^+.[7]

The decrease in specific conductivity for $BrOSO_2F$ at temperatures above +35° must be attributed to a decrease in the extent of ionization with increasing temperature as has also been postulated previously in the cases of BrF_3[27] and ICl.[19]

Like the halogen fluorides, the fluorosulfates also show electrical conductivity in the solid state. The

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TABLE VII

COMPARISON OF THE TEMPERATURE COEFFICIENT OF SPECIFIC CONDUCTANCE FOR THE HALOGEN FLUORIDES AND HALOGEN FLUOROSULFATES

Compound	Temp range, °C	κ, ohm^{-1} cm^{-1}	Temp coeff	Ref
Br_2	0–30.0	6.32–12.63 × 10^{-10}	+	*a*
I_2	113.0–155.0	5.35–3.95 × 10^{-5}	−	*b*
ClF_3	0 and 25.0	3.0 and 4.9 × 10^{-9}	+	*c, d*
BrF_3	10.0–60.0	8.14–6.75 × 10^{-3}	−	21
BrF_5	−60.0–25.0	7.8–9.9 × 10^{-8}	+	*e*
IF_5	13.0–25.0	4.19–5.72 × 10^{-6}	+	*f*
ICl	27.0–122.0	4.403–1.817 × 10^{-3}	max = 4.637 × 10^{-3} at 39.9°	18
I_2Cl_6	102.0–146.5	8.60–0.36 × 10^{-3}	max = 9.55 × 10^{-3} at 109.3°	18
IBr	45.0 and 55.0	6.4 and 10.4 × 10^{-4}	+	*g*
$BrOSO_2F$	−45.0–93.0	2.76–4.88 × 10^{-4}	max = 7.27 × 10^{-4} at +35.0°	This work
$Br(OSO_2F)_3$	60	1.5	...	This work
$IOSO_2F$	40.0–141.0	0.38–11.20 × 10^{-3}	+	This work
$I(OSO_2F)_3$	25.0–75.96	0.367–3.66 × 10^{-3}	+	This work

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conductivities are generally lower by a factor of ~100 than the values for the liquids, and the temperature coefficients are positive as found for the interhalogens, but the problem of electrode contact of solids during the measurements makes the values obtained rather uncertain.

The fluorides of bromine and iodine become more stable with increasing oxidation state of the halogen, and the univalent fluorides readily disproportionate to the halogen and a higher fluoride. In contrast, however, bromine(I) and iodine(I) fluorosulfate are more stable than the trifluorosulfates and indeed they are formed by thermal decomposition of the trifluorosulfates. Moreover the monofluorosulfates do not show any tendency to disproportionate. The fluorosulfates also resemble the corresponding chlorides and bromides in having absorption spectra shifted to shorter wavelengths from the parent halogen by approximately the same amount (Table VIII).

The fact that bromine and bromine(I) fluorosulfate cannot be separated by distillation and the color change to black-red when small amounts of bromine are added to $BrOSO_2F$ can be accounted for by the assumption that Br_3OSO_2F is formed. A similar iodine compound I_3OSO_2F is known.[6] Vapor pressure measurements on $BrOSO_2F$–Br_2 mixtures, however, indicated almost complete dissociation of Br_3OSO_2F at elevated temperatures.

TABLE VIII

ABSORPTION MAXIMA

Compound	Solvent	λ_{max}, mμ	ε
I_2	CCl_4	520	985
IBr	CCl_4	490	420
ICl	CCl_4	460	450
$IOSO_2F$	$S_3O_8F_2$	456	227
Br_2	CCl_4	417	208
BrCl	CCl_4	380	97
$BrOSO_2F$	$S_3O_8F_2$	408	32.6
$BrOSO_2F$ (gas)		378	...

Addition of bromine(I) fluorosulfate to fluorosulfuric acid causes only a very slight increase in the conductivity showing that it behaves as a very weak electrolyte. Addition of potassium fluorosulfate to a solution of bromine fluorosulfate gave an increase in conductivity essentially the same as would have been produced in the absence of bromine trifluorosulfate. This probably rules out acid behavior to give $H_2SO_3F^+$ + $Br(OSO_2F)_2^-$, but no certain conclusions can be reached concerning the nature of the ionization and the possible formation of Br^+ or Br_2^+. Measurement of the magnetic susceptibility by the Gouy method gave no evidence for the formation of a paramagnetic species in solutions of $BrOSO_2F$ in fluorosulfuric acid. The marked shift in the maximum in the absorption spectrum on dissolving bromine(I) fluorosulfate in fluorosulfuric acid can probably be best explained as a solvation effect.

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