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Selected reactions of fluorine-fluorosulfate, $FOSO_2F$*

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Abstract

The reactions of fluorine-fluorosulfate, $FOSO_2F$, with SSF_2, SeF_4, AsF_3 and MoF_5 have been studied, and its previously reported reactions with SF_4, Br_2 and I_2 re-investigated in order to test its suitability as a synthetic reagent. All substrates reacted exothermically, and sometimes explosively, between 80–298 K. The presence of the byproducts obtained may be rationalized by the thermal decomposition of some of the $FOSO_2F$, which proceeds along two pathways, i.e. $FOSO_2F \rightarrow 1/2O_2 + SO_2F_2$ and $FOSO_2F \rightarrow 1/2F_2 + 1/2S_2O_6F_2$, during the extremely exothermic reactions via radical intermediates.

The fluorine formed gives rise to fully fluorinated products, and the $SO_3F\cdot$ radicals, initially formed, either dimerize to give $S_2O_6F_2$ or decompose to O_2 and $S_2O_5F_2$. Element fluoride-fluorosulfates, when formed at all, were obtained in low yields only when SO_2F_2 or SO_2FCl were used as suitable moderators. The complete vibrational spectra of EF_5OSO_2F (E = S, Se or Te) have been studied and assigned. The reactions of I_2, Br_2 and AsF_3 with $FOSO_2F$ yielded viscous liquids of the approximate, non-stoichiometric composition $EF_n(SO_3F)_{5-n}$ (E = As or I) and $EF_n(SO_3F)_{3-n}$ (E = Br), with n = non-integral number. All compounds were characterized by their vibrational and ^{19}F NMR spectra, and in the case of SeF_5OSO_2F by ^{77}Se NMR methods.

Introduction

Fluorine-fluorosulfate, $FOSO_2F$, is a hypofluorite [1] and, like most of its congeners, is a powerful oxidizer. It is frequently formed as a byproduct in the synthesis of bis(fluorosulfuryl) peroxide, $S_2O_6F_2$ [2]. Shortly after its discovery [3], the compound found some limited use as a synthetic reagent [4]. However, following a cautionary note, published in 1968, regarding the unpredictably hazardous and explosive nature of $FOSO_2F$ [5], its use in synthesis has largely stopped. This study addresses the questions as to whether $FOSO_2F$, when carefully purified and used in a cautious manner, is still hazardous, and whether the compound has a uniquely useful reaction chemistry.

It appears that $FOSO_2F$ may find some use in the one-step synthesis of element fluoride-fluorosulfates of the type $EF_n(OSO_2F)_m$, either by oxidative

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addition to a low-valent fluoride or fluorosulfate or by the oxidation of an element, with $FOSO_2F$ acting simultaneously as a fluorinating and fluorosulfonating agent. Previous studies provide examples for these reaction types [4], but it is unclear from the reports [4c] whether a straightforward addition occurs or a more complex reaction takes place, because the studies reported so far provide examples for both the straightforward and complex behaviour of $FOSO_2F$ [4].

For the element fluoride-fluorosulfates obtained from the reactions of $FOSO_2F$, only limited structural information is available, mainly from ^{19}F NMR spectroscopic studies. Only very fragmentary and inconclusive infrared spectra have been reported for most of the $EF_n(OSO_2F)_m$ compounds.

We have been interested in the synthesis, structure and reactivity of element fluoride-fluorosulfates for some time [6–8]. For the most part, however, different synthetic approaches have been chosen. In order to find answers to the questions raised regarding the use of $FOSO_2F$, and also to provide more complete vibrational and NMR spectra of the principal reaction products, we decided to re-investigate the previously reported reactions of $FOSO_2F$ with SF_4 [9], Br_2 [9] and I_2 [10], and to expand the scope of this study to the addition of $FOSO_2F$ to SeF_4, SSF_2, AsF_3 and MoF_5. Our previous experience with $FOSO_2F$ involves its addition to SbF_3 to give SbF_4SO_3F in a straightforward reaction [6].

In spite of the hazards involved in handling $FOSO_2F$ [5], some information on its molecular structure is available from spectroscopic studies. According to Raman [11] and IR spectra [12] taken at 298 K and 80 K, respectively, fluorine-fluorosulfate has C_s symmetry in the liquid and solid state. Of the two possible structural isomers, the *trans* form appears to be present in the solid state according to a wide-line ^{19}F NMR study [13].

Experimental

Chemicals

Selenium dioxide, cesium fluoride, trichlorofluoromethane, iodine and bromine were obtained from commercial sources, with the latter stored over phosphorus(V) oxide and KBr before use. AsF_3 (Ozark Mahoning) and SF_4 (Matheson) were also obtained commercially and purified by repeated trap-to-trap distillation. Selenium(IV) fluoride was synthesized from SeO_2 and SF_4 as reported [14] and MoF_5 was obtained by the reaction of MoF_6 with Mo metal [15]. Fluorine-fluorosulfate, $FOSO_2F$, was obtained as a byproduct during the preparation of bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, although dry ice was used to trap the crude product as recommended [5]. Purification was carried out by trap-to-trap distillation *in vacuo*, ^{19}F NMR spectroscopy was used to test for purity [3] and check for the absence of $S_2O_6F_2$. $FOSO_2F$ was sealed off in glass ampoules and stored at liquid N_2 temperature in a long-term storage Dewar (model 18-XT, Taylor–Wharton). SSF_2 was prepared by the reaction of sulfur and AgF [16], and SO_2FCl, used as a solvent on occasions, was prepared by the partial fluorination of SO_2Cl_2.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer model 598 grating infrared spectrophotometer with gaseous samples contained in a 10-cm gas cell fitted with AgBr windows (Harshaw Chemicals, USA) or IR grade silicon windows (Wacker Chemie, Burghausen, Germany). Raman spectra were obtained on a Spex Ramalog 5 instrument equipped with an argon-ion laser (Spectra Physics 164) with the liquid samples contained in 5 mm o.d. NMR tubes or 6 mm o.d. glass tubes. The 514.5 nm line was used for excitation. ^{19}F NMR spectra were obtained on a Varian XL-300 spectrometer operating at 282 MHz fitted with a 5-mm bore multinuclear switchable probe. A 5-mm bore broad-band probe with a tuneable range of 30–122 MHz was employed to obtain the ^{77}Se NMR spectra with the instrument operating at 57 MHz. For the manipulation and trap-to-trap distillation of volatile reaction products, a Pyrex vacuum line of known internal volume, fitted with a Setra pressure transducer model 280E (Setra Systems Inc., Acton, MA, USA) was employed. Vapor density measurements were used to determine the molecular weights of volatile reaction products.

Depending on the amount of reactant used, the exothermicity of the reaction with $FOSO_2F$, the anticipated total pressure of the reaction mixture during the reaction and the desired information on the reaction product, four types of reaction vessels were employed: (i) NMR tubes (5 mm o.d.), fitted with rotationally symmetrical Young valves, for exploratory studies; (ii) flame-sealed glass vials made from standard 6 mm o.d. Pyrex tubing of 250–300 mm length for exploratory, initial experiments in conjunction with a previously described 'ampoule key' [17] to permit opening and re-sealing of the vial *in vacuo*; (iii) one part Pyrex reactors made from standard or thick wall tubing or from round-bottom flasks, and fitted with Kontes Teflon stem valves with an internal volume between 10 and 100 ml. Reaction products were removed from the reactor either by distillation or, in the case of non-volatile products, by opening the reactor inside a drybox (Vacuum Corp. Dri-Lab Dri-Train model HE-493) filled with N_2; and (iv) a stainless-steel reactor of *c* 150 ml capacity fitted with a Hoke valve for violent reactions (e.g. the reaction of SF_4 and $FOSO_2F$) or those involving high pressure.

Reactions

In general, the reactants were combined in the respective reactor on the vacuum line with the mixture held at liquid N_2 temperature. The reactor was then allowed to slowly warm up to room temperature; however, in most instances, the reaction occurred immediately upon warming, and SSF_2 and $FOSO_2F$ reacted explosively at 77 K. We were unable to scale-up this reaction beyond the 20–40 mg range. It was possible to moderate the reaction sufficiently by the addition of $CFCl_3$ to obtain a reaction at -100 °C, but only fragmentation products such as SOF_2, $S_2O_5F_2$, SF_4 and a solid identified as S_8 were observed.

TABLE 1

Summary of attempted reactions of fluorine-fluorosulfate, $FOSO_2F$

Reaction No.	Substrate	Reactor type[a]	Reaction products (principle product underlined)	Comments and observations on the reaction[b]	Description of principal product
1	SSF_2	i or ii	SOF_2, $S_2O_5F_2$, SF_4 and S_8	At − 100 °C in $CFCl_3$; in pure form explosion, at − 196 °C	Only decomposition and side products are obtained
2	SF_4	iv	$\underline{SF_5OSO_2F,}$ SO_2F_2 SF_6 and O_2	CsF added, SO_2F_2 formed *in situ*, see Experimental section	Volatile, colorless liquid as previously described [9, 18, 19]
3	SeF_4	ii or iii	$\underline{SeF_5OSO_2F,}$ SeF_6 $S_2O_6F_2$ and SF_3SO_3F	Moderate reaction at 25 °C; requires shaking of reaction mixture	Volatile, colorless liquid
4	AsF_3	i, ii or iii	$\underline{AsF_n(SO_3F)_{5-n},}$ SiF_4 $S_2O_5F_2$, $S_2O_6F_2$ and O_2	Explosive, vigorous; requires slow careful addition of $FOSO_2F$	Viscous liquid of low volatility $n \sim 3.5$; similar to $AsF_3(SO_3F)_2$ [7]
5	MoF_5	ii	$\underline{MoOF_3(OSO_2F),}$ MoF_6 and $S_2O_5F_2$	Slow reaction; similar to the MoF_5–$S_2O_6F_2$ reaction	Viscous liquid, may be sublimed *in vacuo* to give low melting solid
6	SbF_3	iii	$\underline{SbF_4SO_3F}$	Slow reaction at 25 °C over 8 d	Viscous, colorless liquid [6]
7	Br_2	iii	$\underline{BrF_n(SO_3F)_{3-n},}$ SiF_4, O_2 $S_2O_5F_2$, $S_2O_6F_2$	Vigorous, occasionally explosive reaction at room temperature	Viscous, pale yellow liquid, as described before [9], $n \sim 1$
8	I_2	i or iii	$\underline{IF_n(SO_3F)_{5-n},}$ SiF_4, O_2 $S_2O_5F_2$, $S_2O_6F_2$	Vigorous; flames are visible; goes through yellow intermediate	Viscous, clear, colorless liquid distillable [10], $n \sim 3.3$

[a] See Experimental section for explanation.

[b] Details from W. W. Wilson, *Ph.D. Thesis*, University of British Columbia, 1975.

The reactions of SF_4, SeF_4 and AsF_3 with $FOSO_2F$ are described in detail. Although the reaction with SF_4 has been reported previously [9], our findings regarding the reactivity of the mixture differ.

SF_4+$FOSO_2F$

A reactor of type iv above (stainless-steel) was charged with 10 g SF_4 and *c* 15 g CsF. An equimolar amount of $FOSO_2F$ was added in portions of *c* 10 mmol (*c* 1.2 g) by condensation. On warming, the mixture reacted explosively in some instances and the O_2 formed was removed *in vacuo* with the reactor kept at liquid N_2 temperature, before another portion of $FOSO_2F$ was added and found to react explosively again. After all the $FOSO_2F$ had been added in this manner, 1.7 g of pure SF_5OSO_2F (10% yield) was obtained by trap-to-trap distillation in addition to O_2, SF_6 and SO_2F_2. SF_5OSO_2F was identified by its IR spectrum [18] and vapor pressure [19]. In subsequent attempts, it was noted that the addition of CsF was not necessary. When the reaction was carried out on a smaller scale with a four-fold excess of SO_2F_2, the formation of oxygen was not observed.

SeF_4+$FOSO_2F$

A mixture of 5 g SeF_4 (*c* 32 mmol) and 1.5 g SO_2FCl was placed in a Pyrex reactor (type iii above) of *c* 100 ml capacity. To this, an equimolar amount of $FOSO_2F$ was added in portions of about 3 mmol by condensation at liquid N_2 temperature. Upon melting, the mixture reacted sluggishly and had to be shaken repeatedly. The reaction was monitored by the vapour pressure of $FOSO_2F$ at −100 °C [3]. After the final addition, two liquid layers were observed. Trap-to-trap distillation yielded 1.6 g of pure SeF_5OSO_2F (18% yield) in addition to SeF_6, solid SeF_3OSO_2F [20] and some $S_2O_6F_2$.

AsF_3+$FOSO_2F$

Typically, 150–400 mg of AsF_3 were allowed to react in a Pyrex reactor (type iii above) with a slight excess (10–20% over the equimolar amount) of $FOSO_2F$. Warming the reaction mixture from liquid N_2 temperature to room temperature led to a violent reaction which could be moderated by cooling the mixture with liquid N_2. Repeated cooling and warming was necessary before the reaction reached completion and yielded a viscous liquid together with some volatile materials identified as SiF_4, $S_2O_5F_2$ and $S_2O_6F_2$, and some O_2. The amount of O_2 formed depended inversely on the cooling applied to the mixture.

The remaining reactions were performed in a similar manner and the results, along with some details, are summarized in Table 1.

Results and discussion

Selected reactions of $FOSO_2F$

The three reactions involving SF_4, SeF_4 or AsF_3 as reactants have been described in detail in the Experimental section. The addition of $FOSO_2F$ to

SF_4 and SeF_4 gives rise to well-defined compounds, whereas with AsF_3 a non-stoichiometric compound, $AsF_n(OSO_2F)_{5-n}$ (n between 3 and 4), was formed. These reactions, together with the others, are summarized in Table 1, with the emphasis placed on those reaction products that were identified either by IR or ^{19}F NMR spectroscopy.

Initial interest is focused on the byproducts in order to elucidate the course of these rather complex reactions, which yield a range of different products. It appears that the addition of $FOSO_2F$ is always accompanied by side or secondary reactions. All the reactions proceed vigorously, even explosively in some instances. Our observations suggest the following order of reactivity towards $FOSO_2F$ under the conditions employed here: $S_2F_2 \gg SF_4 > Br_2 > I_2 > AsF_3 \simeq MoF_5 \simeq SeF_4$. Attempts to moderate the reactions by adding a third component as a dilutant to the starting mixture have had limited success, because the additive $CFCl_3$, and eventually also SO_2FCl, reacted under the reaction conditions. SO_2F_2 contributes to a high internal pressure and can only be used safely in a metal reactor.

The *in-situ* generation of SO_2F_2 during the addition of $FOSO_2F$ to SF_4, as described in the Experimental section, is an interesting variation. Its formation, together with O_2, may be explained by the decomposition of fluorine-fluorosulfate according to

$$FOSO_2F \longrightarrow 1/2O_2 + SO_2F_2 \quad (1)$$

The kinetics of this decomposition over the temperature range 509–536 K have been studied by Dudley [21], who found that the reaction is catalyzed by the addition of fluorine. In the absence of fluorine, an alternative decomposition reportedly occurs [21] via intermediate $SO_3F\cdot$ radicals according to

$$FOSO_2F \longrightarrow 1/2S_2O_6F_2 + 1/2F_2 \quad (2)$$

This mode may explain the formation of bis(fluorosulfuryl) peroxide during the reactions of SeF_4, AsF_3, Br_2 and I_2 with a slight excess of $FOSO_2F$, if it is assumed that the F_2 formed will react further immediately. In three of the above reactions, large quantities of SiF_4 were observed, and in the reaction with SeF_4, SeF_6 was produced, presumably by fluorination of unreacted SeF_4 because this reaction proceeds rather slowly. It can be argued that $FOSO_2F$ acts primarily as a fluorinating agent in these cases; however, when Br_2 is used as a reactant, any $S_2O_6F_2$ formed is capable of oxidizing it as well, resulting in the formation of $BrF_n(OSO_2F)_{3-n}$ ($n \approx 1$).

The simultaneous formation of $S_2O_6F_2$, $S_2O_5F_2$ and O_2, together with SiF_4, suggests another probable side-reaction which has been previously observed in quartz cells above 120 °C [22], *i.e.* the decomposition of $SO_3F\cdot$ radicals to give $S_2O_5F_2$ and O_2. The reactions studied here are sufficiently exothermic and produce temperatures high enough to allow the secondary reactions suggested above to occur.

A different source of bis(fluorosulfuryl) oxide, $S_2O_5F_2$, is suggested when MoF_5 is allowed to react with a slight excess of $FOSO_2F$. Besides molybdenum hexafluoride, a molybdenum oxygen derivative, $OMoF_3OSO_2F$, is formed in a rather mild reaction. The same reaction products are formed at different mole ratios when MoF_5 is allowed to react with $S_2O_6F_2$ [23]; in both cases, the formation of $OMoF_3OSO_2F$ is puzzling and no simple, straighforward explanation can be offered.

Equally puzzling is the formation of a white solid in the reaction between SeF_4 and $FOSO_2F$, identified from its IR spectrum as SeF_3OSO_2F [20]. The reaction proceeds slowly and the oxidation of selenium to the +6 oxidation state may not occur so readily. It is possible to formulate the overall reaction as

$$3SeF_4 + 2FOSO_2F \longrightarrow SeF_5OSO_2F + SeF_3OSO_2F + SeF_6 \qquad (3)$$

which accounts for all observed products, but does not clearly explain how they form. It is also possible to explain the formation of SeF_3OSO_2F via a ligand-exchange reaction

$$SeF_5OSO_2F + SeF_4 \longrightarrow SeF_6 + SeF_3OSO_2F \qquad (4)$$

Likewise, the reaction of SSF_2 with $FOSO_2F$ at -100 °C in $CDCl_3$ can be formulated as

$$2SSF_2 + 4FOSO_2F \longrightarrow 2S_2O_5F_2 + 2SOF_2 + SF_4 + 1/8S_8 \qquad (5)$$

but a detailed reaction mechanism is again lacking.

All reactions, except the one involving SSF_2, will produce fluoride-fluorosulfate derivatives, albeit frequently in rather low yield. The materials derived from SF_4 and SeF_4 are volatile, well-defined, stoichiometric compounds of the type EF_5OSO_2F. Both compounds are easily purified, and their compositions were established by vapor density and spectroscopic measurements. The yield was around 10% in the case of SF_5OSO_2F, which is lower than the 25% reported previously, where a temperature of 70 °C and a reaction time of 3 h were claimed [9]. It appears that alternate published routes to SF_5OSO_2F [18, 19] may be more efficient and less hazardous. This conclusion, however, does not apply to the synthesis of SeF_5OSO_2F. The previously reported route, the photolysis of a mixture of $(SeF_5)_2O_2$ and $S_2O_6F_2$ [24], offers no advantage on account of the thermal and photolytic instability of $(SeF_5)_2O_2$.

There is a remarkable difference in reactivity between SF_4 and SeF_4 towards $FOSO_2F$. The yield of SeF_5OSO_2F is considerably higher (18%) and decomposition products such as O_2, SO_2F_2 or $S_2O_6F_2$ are not observed. A similar situation is noted when the reactivities of AsF_3 and SbF_3 towards $FOSO_2F$ are compared [6]. Some of the light flashes observed during the reaction of AsF_3 with $FOSO_2F$ may be due to warming AsF_3 from liquid N_2 temperature, which reportedly [25] causes greenish-yellow luminescence and acoustic emission.

The viscous materials of low volatility produced when AsF_3, Br_2 or I_2 are reacted with $FOSO_2F$ are non-stoichiometric. Their exact composition depends on the reaction conditions and the amounts of reactants used. This

TABLE 2

Vibrational spectra of the pentafluoro monofluorosulfates of sulfur, selenium and tellurium in the frequency range 1500–100 cm^{-1}

SF_5OSO_2F					SeF_5OSO_2F					TeF_5OSO_2F[a]					Approximate band description	
Infared $\bar{\nu}$ (cm^{-1})	gas int.	Raman $\Delta\nu$ (cm^{-1})	liquid int. (M)	ρ	Infared $\bar{\nu}$ (cm^{-1})	gas int.	Raman $\Delta\nu$ (cm^{-1})	liquid int. (M)	ρ	Infared $\bar{\nu}$ (cm^{-1})	gas int.	Raman $\Delta\nu$ (cm^{-1})	liquid int. (M)	ρ		
1493	s	1490	0.3	−p	1492	vs	1486	0.8	0.5p	1490	vs	1476	m		SO_2	ν_{as}
					1453	w										
1255	s	1252	5	0.02p			1249	4	0.05p	1250	vs	1242	s	p	SO_2	ν_{sym}
										1160	vw	1150	vw			
888	vs	885	0.2	<0.1p	872	vs	880	1	0.5p	895	vs	893	vw		$\mathrm{S}{<}^{\mathrm{O}}_{\mathrm{F}}$	ν_{as}
830	s	~830	0.5	<0.1p	851	vs	845	1.5	0.1p	850	vs	844	m	p	$\mathrm{S}{<}^{\mathrm{O}}_{\mathrm{F}}$	ν_{sym}
947	vs				772	vs	770	0.5	p	750	vs				EF_5O	ν_{as} B
907	m	910	0.1	<0.1p	746	s	744	0.5	p	730	vs	728	m	p	EF_5O	ν_{as} E
848	s															
776	w, sh															
730	m	733	10	~0p	675	w	676	10	~0p			681	vs	p	EF_5O	ν_{sym} A_1
							660	0.01	dp							
673	m	675	0.5	<0.1p	647	m	645	6.4	p	641	s	641	s	p	EF_5O	ν_{sym} A_1
645	w, sh	650	0.3	~1d											Uncertain,	possibly δ SP_5O
620	w, sh	632	0.5	<0.5p												
604	m															
575	ms	580	0.1	p	593	m	590	0.1	p	578	m	579	s	p	SO_2	δ_{as}
553	w, sh	555	0.1	p	541	w, sh	540	0.1	p	545	w	532	w		SO_2	δ_{sym}
503	m, w															

475	w	483	0.2	~1dp	460		460	1.0	0.3p	448	m	EF_5O	δ_{as}
418	w	420	0.7	0.3p			424	0.1	0.5p	2		SO_3	rock_{as}
					333	w	335	1.6	0.5p	315	s	unassigned deformation and torsion vibrations	
		286	0.5	~1dp			291	4	0.2p	277	s		
		266	1.5	0.2p						263	s		
							230	0.2	0.5p				
							217	2	0.2p				
		160	0.2	0.5p			140	0.2		175	m		

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[a] Ref. 24, IR spectra recorded between NaCl windows. Abbreviations: int. = estimated intensity of IR band; int. m = measured intensity, range 0.1 to 10, of Raman bands; ρ = depolarization ratio, I_{vp}/I_{II}; p = polarized, dp = depolarized, v = very, s = strong, m = medium, w = weak; $\bar{\nu}$ = wavenumber (cm^{-1}); $\Delta\nu$ = Raman shift (cm^{-1}); ν = stretch; δ = bending; sym = symmetric; as = asymmetric.

observation contradicts earlier reports on the Br_2 and I_2 reactions where compositions such as $Br_2 \cdot 3FOSO_2F$ [9] and $IF_3(OSO_2F)_2$ [10] were claimed. For the reaction with iodine, compositions ranged from $IF_{3.3}(OSO_2F)_{1.7}$ to $IF_3(SO_3F)_2$, and with bromine, the approximate composition $BrF(OSO_2F)_2$ was obtained. Here, and in the case of the reaction product formed from AsF_3 and $FOSO_2F$ [approximate composition $AsF_{3.5}(OSO_2F)_{1.5}$], the SO_3F content is higher than expected, implying that $S_2O_6F_2$, formed as a byproduct, may also be involved in the oxidation process, while some of the fluorine is converted to SiF_4 during the highly exothermic reaction. Attempts to detect either AsF_5 or any bromine(V) fluoro species by either ^{19}F NMR or vibrational spectroscopy were unsuccessful; however, both compounds may have reacted with glass under the reaction conditions.

In summary, fluorine-fluorosulfate, $FOSO_2F$, is extremely reactive leading to very exothermic and frequently explosive reactions with various substrates. The simultaneous oxidative addition of fluorine and fluorosulfate is almost always so exothermic that decomposition and side-reactions occur, thereby markedly reducing the yield of the expected products. The addition of $FOSO_2F$ to SeF_4 and, as reported previously, to SbF_3 [6] are useful synthetic reactions but in most instances, the risks in preparing, storing and handling $FOSO_2F$, and using it as a synthetic reagent far outweigh its rather limited usefulness, and the words of warning by Cady [5] have not lost their validity.

It is somewhat surprising to us that in the earlier uses of $FOSO_2F$ in synthetic chemistry, neither the explosive nature of this compound, the complex course of its reactions nor the non-stoichiometric composition of some of its reaction products have been fully recognized [4].

Spectroscopic studies on element fluoride-fluorosulfates

This section deals primarily with the vibrational and NMR spectra which have not been reported previously. The complete vibrational spectra of the monomeric, well-defined compounds of composition EF_5OSO_2F (E = S or Se) are compared with the previously reported IR and Raman spectra of TeF_5OSO_2F [26]. The data for all three compounds are listed in Table 2 together with estimated intensities, depolarization ratios for the more intense Raman bands and an approximate band description. The previous report on the IR spectrum of gaseous SF_5OSO_2F [18] lists a limited number of bands in the region from 1500–553 cm^{-1}, with band positions in good agreement with our findings.

It is apparent from the listings in Table 2 that all three EF_5OSO_2F (E = S, Se and Te) compounds have a covalent, monodentate fluorosulfate group bonded to an EF_5 moiety. As expected, the SO_3F vibrations show little variation with E, while mass differences between S, Se and Te cause a gradual shift of the EF_5 vibrations to lower frequencies. For this group, local C_{4v} symmetry is suggested and four EF_5 stretching vibrations (E, $2A$, B) are expected. The assignments previously reported for TeF_5OSO_2F [26] are retained here.

There are two general areas of ambiguity regarding the attempted group-frequency assignment in the stretching region. For the monodentate $-OSO_2F$ group, a clear distinction between ν(SF) and ν(SO) is not possible; both are observed in the narrow region of 890–840 cm^{-1} and the vibrations are expected to couple. Hence, an assignment as asymmetric and symmetric stretches of an $O-S-F$ moiety has been used. In addition, $\nu(SF_5)$ vibrations are expected to occur in this region as well, resulting in both partial band overlap as seen in the 830–840 cm^{-1} region of the Raman spectrum, and in vibrational coupling and extensive band proliferation in the $S-F$ and $S-O$ stretching region (600–950 cm^{-1}). These complexities are absent in the spectra of SeF_5OSO_2F and TeF_5OSO_2F [26].

In agreement with local C_{4v} symmetry of the EF_5O moiety, very intense polarized Raman bands are assignable to the symmetric stretching motion of this group. These bands are observed at 733 cm^{-1} for SF_5OSO_2F and at 676 cm^{-1} and 581 cm^{-1} for the Se and Te analogs. In addition, some weak and probably depolarized Raman bands are attributed to this group. In contrast, the SO_3F vibrations are polarized for all three compounds.

While symmetric stretching vibrations are observed for all three EF_5OSO_2F compounds about 20–30 cm^{-1} lower than the A_{1g} mode in the corresponding hexafluorides [27], the frequency of the highest IR-active EF_5O stretch is in about the same position as ν_3 (F_{2u}) for the EF_6 compounds. This band is not observed in the Raman spectra of TeF_5OSO_2F and SF_5OSO_2F. Additional instances of mutual exclusion of IR and Raman bands are listed in Table 2. The near-octahedral symmetry observed in the EF_5O moiety of the monofluorosulfates also explains why the EO vibrations are not clearly identifiable, but are mixed in with the EF_5 vibration.

A final comment concerns the SO_2F stretching vibrations. There is generally very good agreement between the IR band positions, obtained from gaseous molecules, and the Raman bands, found in the spectra of the liquid compounds. For TeF_5OSO_2F small discrepancies are noticeable, with the Raman bands being found at slightly lower frequencies than their infrared counterparts. Very weak intermolecular association in the liquid via fluorosulfate groups is the most plausible cause for the gas-to-liquid phase shift.

The high frequencies of the $\nu(SO_2)$ vibrations are typical for covalent, monodentate fluorosulfate groups (e.g. $FOSO_2F$ or $S_2O_6F_2$ [11]), where frequency lowering of the $E-OSO_2F$ band because of intermolecular association or increasing ionicity of the $E-OSO_2F$ bond can be ruled out. A very slight shift to lower frequencies is noted when comparing both SO_2 stretching vibrations in the EF_5OSO_2F compounds ($S < Se < Te$) and suggests increasing polarity of the $E-OSO_2F$ bond.

A different bonding situation for the fluorosulfate group is encountered for $IF_n(OSO_2F)_{5-n}$ ($n \approx 3$) and more so for $BrF_n(OSO_2F)_{3-n}$ ($n = 1$). The Raman shifts are listed in Table 3. Due to the high reactivity of the materials, infrared spectra could not be obtained.

A relatively simple Raman spectrum is obtained for $IF_n(OSO_2F)_{5-n}$. The $\nu(SO_2)$ vibrations at 1424 and 1212 cm^{-1} are at considerably lower frequencies

TABLE 3

Raman spectra of $IF_n(SO_3F)_{5-n}$, $BrF_n(SO_3F)_{3-n}$ and $Br(SO_3F)_3$

$Br(SO_3F)_3$ (s)[a] $\Delta\nu$ (cm^{-1})	int	$BrF_n(SO_3F)_{3-n}$ (l) $\Delta\nu$ (cm^{-1})	int	$IF_n(SO_3)_{5-n}$ (l) $\Delta\nu$ (cm^{-1})	int	HSO_3F[b] $\Delta\nu$ (cm^{-1})	int
1490	mw	1480	mw				
1467	w	1460	w, sh	1424	m, br	1443	m
1372	m						
1356	mw, sh	1360	m, br				
1241	s	1240	s	1212	s	1205	s
1230	mw, sh						
1168	mw	1140	w, br				
1122	m	1065	w				
1010	m	1030	m				
		920	vw	940	vw	961	w
859	m	850	m	857	ms	851	m
827	vw	830	w, sh				
801	m						
721	ms	750	s, br	706	vs		
645	vs, br	650	vs	652	vs		
612	vs	610	vs	612	vs		
583	ms	580	ms	585	ms	560	m
563	m	~550	m, sh	555	m	552	m
551	vw						
540	w						
455	s	455	s	460	m	490	m
430	w			435	ms	405	w
408	mw	408	mw				
384	mw			395	m	393	m
303	vs	305 300	s	280	s		
276	vs	260	ms				
225	ms	220	m	257	vs		
206	ms						
		150	w, sh	160	w		

[a] Ref. 25.

[b] Ref. 11, bands due to the OH group such as OH stretching (2940 cm^{-1}), OH bending (1179 cm^{-1}) and OH torsion (686 cm^{-1}) are omitted.

than those observed for EF_5OSO_2F. A slightly polar monodentate fluorosulfate group is suggested, consistent with ν(SO) and ν(SF) at 940 and 857 cm^{-1}, with weak intermolecular association, probably causing a lowering of the SO_2 stretching frequencies. A very similar Raman spectrum is obtained from the fluorosulfate group in HSO_3F [11] (included for comparison in Table 3). The good correspondence in the band positions also extends into the region of the deformation modes.

Very prominent and intense Raman bands are observed at 706, 652 and 612 cm^{-1}; these are not assignable to the fluorosulfate group. Comparison with the Raman spectrum of IF_5 [27], which displays strong bands at 710, 693 and 605 cm^{-1}, might suggest an assignment as I–F stretching vibrations. However this assignment is ambiguous for the bands at 652 and 612 cm^{-1}, because for $I(SO_3F)_3$ and the salts $M[I(SO_3F)_4]$ (M = Na or K) very strong Raman bands are observed between 640 and 612 cm^{-1} [28], which may involve iodine–oxygen stretching motions.

A very similar situation is encountered for $BrF_n(OSO_2F)_{3-n}$ ($n = 1$), where very intense Raman bands in the same region (650 and 610 cm^{-1}) are also found for $Br(SO_3F)_3$ [28] (included for comparison in Table 3). A single Br—F stretch is expected for a material having the composition $BrF(OSO_2F)_2$, and an assignment of ν(Br—F) is suggested for the broad band found at 750 cm^{-1}.

The similarity between the Raman spectra of $BrF(OSO_2F)_2$ and $Br(SO_3F)_3$ extends over the entire spectral range. It is not unexpected to see a greater degree of band splitting in the case of $Br(SO_3F)_3$, which is a crystalline solid. It is hence reasonable to suggest oligomeric structures which imply the presence of bridging, bidentate and terminal monodentate fluorosulfate groups for both $BrF(OSO_2F)_2$ and $Br(SO_3F)_3$. Formulation as $BrF(OSO_2F)_2$ is preferred because no single, bond type is likely here, in contrast to EF_5OSO_2F (E = S, Se or Te).

It is also noted that this spectral similarity extends to the Raman spectra of $I(SO_3F)_3$ [28] and $Au(SO_3F)_3$ [29] where, in all instances, a nearly square-planar coordination environment for the central atom is suggested. In the case of $[Au(SO_3F)_3]_2$, this assumption has been confirmed by an X-ray diffraction study [30]. Intense Raman bands at 650, 450 and 280 cm^{-1} are observed for $BrF(OSO_2F)_2$ as well as for the tris(fluorosulfates) of bromine, iodine and gold. These vibrations involve, in part, EO_4 skeletal vibrations (E = Br, I [28] or Au [29]) or in this case BrO_3F vibrations. Hence, as in the case of the nearly octahedral EF_5O environment in EF_5OSO_2F (E = S, Se or Te) relative to EF_6 as discussed above, substitution of a single F by O or, as in the case O by F, involving atoms of similar mass and bonding characteristics, does not alter appreciably the vibrational spectrum of the still fairly symmetrical coordination environment around the central atom.

Little needs to be said at this point about the vibrational spectra of the remaining fluoro-fluorosulfate species discussed in this study. The Raman and IR spectra of SbF_4OSO_2F have been reported and discussed in terms of a bidentate, presumably bridging fluorosulfate group [6], and those of $OMoF_3(OSO_2F)$ will be included in an extensive study of molybdenum oxo-fluoride-fluorosulfato derivatives [23].

The Raman spectrum of $AsF_n(OSO_2F)_{5-n}$ ($n = 3.5$) is largely identical to the one observed previously for $AsF_3(OSO_2F)_2$ [7]; in the As—F–As—O stretching region, a new band is observed at 684 cm^{-1}, in addition to previously reported bands which are shifted very slightly relative to those reported for $AsF_3(OSO_2F)_2$ and which are quoted in squared brackets 754 (s) [750 (s)], 669 (vs) [670 (vs)], 645 (s, sh) [652 (vs, sh)] and 610 (vw) [610 (vw)]. It is tentatively suggested that the product obtained from the reaction of AsF_3 and $FOSO_2F$ is a mixture of $AsF_3(OSO_2F)_2$ formed when

$S_2O_6F_2$ reacts with AsF_3 [7] and AsF_4OSO_2F, consistent with its non-stoichiometric composition.

Similar to the vibrational spectra of the five compounds discussed here, the ^{19}F NMR spectra fall into two groups: (i) SeF_5OSO_2F and SF_5OSO_2F, reported previously [18, 24, 31], give reproducable AM_4X-type spectra; (ii) the non-stoichiometric, low-boiling or non-volatile products of the reactions of $FOSO_2F$ with AsF_3, I_2 and Br_2, give spectra that differ slightly, depending on the experimental conditions, from one preparation to the next in chemical shifts, number of peaks, peak shape and peak integration ratio.

The pertinent data are summarized in Table 4. The ^{19}F NMR spectra of SF_5OSO_2F and SeF_5OSO_2F have been reported previously [18, 24] and are in good agreement with this work. The strong similarity between the ^{19}F NMR spectra of SF_5OSO_2F and its selenium analog is expected. In addition, satellite resonances due to coupling of ^{19}F to ^{77}Se nuclei are observed. The

TABLE 4

Characterization of the fluoride-fluorosulfates of sulfur, selenium, arsenic, bromine and iodine by NMR spectroscopy

Compound		δ (ppm)[a]	I	Assignment
SF_5SO_3F		72.8 d	4	F_{eq}
		56.8 q	1	F_{ax} $J(F_{ax}-F_{eq})=155$ Hz
		46.3 s	1	$F_{(SO_3F)}$
SeF_5SO_3F		74.9 d	4	F_{eq}
		58.3 q	1	F_{ax} $J(F_{ax}-F_{eq})=217$ Hz
		46.9 s	1	$F_{(SO_3F)}$
		$\delta^{77}Se=-675$ ppm rel. SeO_2 in H_2O/D_2O $J(^{77}Se-F_{ax})\sim J(^{77}Se-F_{eq})\sim 1430$ Hz		
$AsF_n(SO_3F)_{5-n}$	(I)	−25.6	1	As–F
		−37.8	2.5	As–F
		43.8		$F_{(SO_3F)}$
	(II)	−41.4 broad		As–F
		42.5		$F_{(SO_3F)}$
$BrF_n(SO_3F)_{3-n}$[b]		−46.2 to −48.8		Br–F
$n\sim 0.84$ to 1.13		45.8 to 47.9		$F_{(SO_3F)}$
$IF_n(SO_3F)_{5-n}$	(I)	−14.3 and −18.3		I–F
$n=2.89$		45.7		$F_{(SO_3F)}$
$n=2.65$	(II)	−15.4 and −19.6		I–F
		47.3		$F_{(SO_3F)}$
$n=3.32–3.17$	(III)	−18.2 and −2.09		I–F
		48.7		$F_{(SO_3F)}$
$n=1.63$	(IV)	−29.6		I–F
		51.1		$F_{(SO_3F)}$

[a] Relative to $CFCl_3$.

[b] Values from three different samples.

^{77}Se NMR spectrum shows a six-line pattern of relative intensity ratio 1:4:6:6:4:1, which implies that $J(^{77}\text{Se}–^{19}\text{F}_{\text{ax}}) \approx J(^{77}\text{Se}–^{19}\text{F}_{\text{eq}})$. A slight splitting of the individual lines suggest a difference of about 20 Hz in the coupling constants.

For $AsF_{3n}(OSO_2F)_{5-n}$, two broad resonances are observed for one sample. One of the resonances has an almost identical chemical shift of −37.8 ppm compared to the reported value of −37.2 ppm for $AsF_3(OSO_2F)_2$, [7], which suggests two different arsenic–fluorine regions in the non-stoichiometric mixtures with one of these being $AsF_3(OSO_2F)_2$. As in $AsF_3(OSO_2F)_2$ [7], only a single resonance in the fluorine–sulfur region is observed with $\delta = 43.8$ ppm compared to the reported value of 45.6 ppm for $AsF_3(OSO_2F)_2$ [7]. In another preparation, only a single broad As−F resonance was observed at −41.4 ppm.

Single resonances are found for $BrF_n(OSO_2F)_{3-n}$ in agreement with the observations of Gilbreath and Cady [9], who used mixtures of BrF_3 and $Br(SO_3F)_3$ to study the entire composition range and who have reached similar conclusions regarding the non-stoichiometric nature of these mixtures [9]. Only a slight discrepancy concerns the chemical shift range for the single fluorine on sulfur resonance: our observed values of between 45.8 and 47.9 ppm are higher than the range of 39–41 ppm reported [9].

^{19}F NMR spectra for $IF_n(OSO_2F)_{5-n}$ show the greatest variation. Either one or two broad resonances are found in the O−F region, and peak positions vary with composition. Previous reports [9, 10, 32] differed on the number of resonances in the I−F region and on the peak integration ratios. It now seems that the previous studies, which used different synthetic routes, may have produced materials of varying composition rather than well-defined stoichiometric compounds as claimed.

Considering the different shapes of the resonances, with broad peaks found in particular for the IF_n and AsF_n species, peak integration is of limited use and compositions determined in this manner are very approximate. Frequently repeated measurements on the same sample as, for example, $IF_n(OSO_2F)_{5-n}$ [Table 4 (III)] give different values for n.

Unresolved ^{19}F–^{19}F splitting or coupling to the quadrupolar nuclei I ($I = 5/2$) or As ($I = 3/2$), both in 100% natural abundance, are a likely cause for the broad resonances. It is unclear whether the two broad resonances observed frequently for both materials implies the presence of different species, for example AsF_3- or AsF_4-fluorosulfates, as suggested by the Raman spectrum of $AsF_n(OSO_2F)_{5-n}$, or are due to a different fluorine in the same molecule, e.g. F in an equatorial or axial site of an approximately square-pyramidal iodine(V) in $IF_n(OSO_2F)_{5-n}$.

A common feature of all three non-stoichiometric fluoro-fluorosulfates is the observation of a single ^{19}F resonance for the fluorosulfate group. For $BrF_n(OSO_2F)_{3-n}$, rapid exchange has been suggested [9] to account for this feature, and various ionic fragments formed by dissociation of an oligomeric substance have been proposed [9]. A similar argument can be made for $IF_n(OSO_2F)_{5-n}$ or $AsF_n(OSO_2F)_{5-n}$.

In summary, vibrational and, more so, ^{19}F NMR spectra support the contention that the reaction of AsF_3I_2 or Br_2 with $FOSO_2F$ produce non-stoichiometric oligomeric mixtures of variable composition, depending on the mole ratios of reactants used and the reaction conditions.

Conclusions

The results of this study strongly support previous [5] comments regarding the hazardous nature of fluorine-fluorosulfate, $FOSO_2F$. Its reaction with the representative reactants chosen are, for the most part, highly exothermic and will result in the thermal decomposition of excess $FOSO_2F$ or the $SO_3F\cdot$ radical formed during the reactions in addition to reactions with the glass vessel.

While some useful and interesting information on the element fluoride-fluorosulfates has been obtained, the use of fluorine-fluorosulfates in their synthesis is questionable and preferably avoided. Alternative routes to these compounds involving bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, are therefore preferred, and when ligand exchange is observed this can be exploited very well as demonstrated recently [33] by the facile one-step synthesis of the fluoride-fluorosulfates of niobium and tantalum of the general formula $MF_n(OSO_2F)_{5-n}$ according to

$$(5-n)M+nMF_5+2.5(5-n)S_2O_6F_2 \longrightarrow 5MF_n(OSO_2F)_{5-n}$$

($M=Nb$ or Ta, $n=0$, 1, 2, 3 or 4), where the syntheses proceed smoothly without side-reactions and where the composition of the resulting product is determined by the ratio of M to MF_5.

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