Preparation and Identification of Various Chlorodifluoro-oxosulphur(VI) Salts. Evidence for Chlorotrifluorosulphur(VI) Oxide

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The salts $OSClF_2^+X^-$ ($X^- = AsF_6^-, PF_6^-, SbF_6^-$, and $Sb_2F_{11}^-$) are prepared in good yield by the reaction of thionyl fluoride with the Cl_2F^+ salt, or chlorine monofluoride and the corresponding pentafluoride under the appropriate conditions. The identity, and ionic formulation of these salts is established by comparison of their i.r. and Raman spectra with those of the corresponding anions and $OPClF_2$. The thermal stability increases in the order: $PF_6^- < AsF_6^- < SbF_6^- < Sb_2F_{11}^-$. Their mass spectra are consistent with initial dissociation into $OSClF_3$ and the corresponding pentafluoride.

THE adducts $2ClF,AsF_5$ and $2ClF,BF_3$ were shown[1] to be essentially ionic on the basis of their i.r. spectra. Gillespie and Morton[2] later demonstrated that the cation is asymmetric $[Cl–Cl–F]^+$, and suggested that it was reasonable to regard Cl_2F^+ as being derived from the co-ordination of Cl^+ with ClF. It was found that chlorine monofluoride could be displaced by the better donor chlorine to give the Cl_3^+ cation [equation (1)].

$$Cl_2F^+AsF_6^- + Cl_2 \longrightarrow Cl_3^+AsF_6^- + ClF \quad (1)$$

As part of an investigation to determine whether ClF could be displaced by other poor donors as a means of preparing salts of the type $XCl^+AsF_6^-$, $Cl_2F^+AsF_6^-$ was allowed to react with thionyl fluoride and found to give $OSClF_2^+AsF_6^-$ in good yield.

Various OSF_3^+ salts[3,4] are readily formed by fluoride ion abstraction from OSF_4; however, the unavailability of $OSClF_3$, as a stable entity, precluded the use of similar reactions as a route to $OSClF_2^+$. The isoelectronic molecule $OPClF_2$ has been known for many years.[5] A preliminary report of part of this work has been published.[6]

RESULTS AND DISCUSSION

Preparation of $OSClF_2^+$ *Salts*.—Thionyl fluoride reacts with $Cl_2F^+AsF_6^-$ at −78 °C to give $OSClF_2^+AsF_6^-$ in *ca*. 85% yield [equation (2)]. The other reaction

$$OSF_2 + Cl_2F^+AsF_6^- \longrightarrow OSClF_2^+AsF_6^- + ClF \quad (2)$$

products are OSF_4, O_2SF_2, Cl_2, and $OSF_3^+AsF_6^-$ which can be accounted for by the competing reaction of OSF_2 with liberated ClF to give thionyl tetrafluoride and chlorine. Thionyl tetrafluoride readily combines with oxide to produce sulphuryl fluoride, and with arsenic pentafluoride to give $OSF_3^+AsF_6^-$.

Thionyl fluoride reacts instantaneously, as far as can be ascertained, with a mixture of chlorine monofluoride and arsenic pentafluoride at room temperature and ambient pressures yielding similar products.

The $OSClF_2^+$ salts of PF_6^-, SbF_6^-, and $Sb_2F_{11}^-$ were also produced in good yield under the appropriate reaction conditions.

Chlorine monofluoride combines with carbonyl fluoride and thionyl tetrafluoride in the presence of some Lewis acids to yield[7] the hypochlorites $ClOCF_3$ and $ClOSF_5$. A gaseous intermediate of the type Cl–F ··· (Lewis Acid) which enhances the positive character of the chlorine atom was suggested. It is possible that $OSClF_2^+AsF_6^-$ is formed by the reaction of $Cl_2F^+AsF_6^-$ or the gaseous intermediate $ClFAsF_5$, with OSF_2, *via* the hypochlorite $ClOSF_2^+$ which may rearrange to $OSClF_2^+$.

Formation of other $OSClF_2^+$ salts may proceed by similar routes. We observed that $OSClF_2^+PF_6^-$ was prepared at −78 °C and that the reaction did not proceed at room temperature. Similarly, chlorine monofluoride and carbonyl fluoride do not yield $ClOCF_3$ in the presence[7] of PF_5 at −20 °C, which suggests that the intermediate $ClFPF_5$ was not formed in either reaction at the higher temperatures. Thionyl fluoride combines smoothly with the adduct of approximate composition ClF,SbF_5 (probably $Cl_2F^+Sb_2F_{11}^-$) over which there is no detectable chlorine monofluoride, to give a good yield of $OSClF_2^+Sb_2F_{11}^-$. Thionyl fluoride also reacts with $Cl_2F^+AsF_6^-$ at −130 °C. This suggests that the reaction does not proceed by direct combination of thionyl fluoride and free chlorine monofluoride to yield $OSClF_3$ followed by abstraction of fluoride ion, but rather the reaction proceeds *via* the hypochlorite $ClOSF_2^+$ as described above.

Thermal Stability of $OSClF_2^+$ *Salts*.—The thermal stability of $OSClF_2^+$ salts increases in the order $PF_6^- < AsF_6^- < SbF_6^- < Sb_2F_{11}^-$. $OSClF_2^+PF_6^-$ dissociates detectably at −20 °C and $OSClF_2^+AsF_6^-$ very slowly at room temperature, although bulk samples of the arsenic salt were kept several weeks without gross decomposition. The gaseous decomposition products were OSF_2, OSF_4 (trace O_2SF_2), and the corresponding pentafluoride, and probably also chlorine. The decomposition may proceed *via* initial formation of the unstable $OSClF_3$ molecule and the pentafluoride. In the case of $OSClF_2^+SbF_6^-$, presumably SbF_5 combines with unreacted salt to give the observed $Sb_2F_{11}^-$, and with OSF_4 to yield $OSF_3^+Sb_2F_{11}^-$.

Reactions of $OSClF_2^+AsF_6^-$ *with Fluoride Ion Donors*.

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[1] K. O. Christe and W. Sawodny, *Inorg. Chem.*, 1969, **8**, 212.

[2] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 1970, **9**, 811.

[3] F. Seel and O. Detmer, *Z. anorg. Chem.*, 1959, **301**, 113.

[4] M. Brownstein, P. A. W. Dean, and R. J. Gillespie, *Chem. Comm.*, 1970, 9.

[5] H. S. Booth and F. B. Dutton, *J. Amer. Chem. Soc.*, 1939, **61**, 2937.

[6] C. Lau and J. Passmore, *Chem. Comm.*, 1971, 950.

[7] D. E. Young, L. R. Anderson, and W. B. Fox, *Inorg. Chem.*, 1970, **9**, 2602.

—$OSClF_2^+AsF_6^-$ reacts with caesium fluoride in anhydrous hydrogen fluoride at −78 °C to yield OSF_2, $CsAsF_6$, OSF_4, and probably chlorine gas. Similar results were obtained from nitrosyl fluoride at −78 °C. It is possible that the reaction proceeds by initial displacement of $OSClF_3$ [equation (3)].

$$OSClF_2^+AsF_6^- + CsF \longrightarrow CsAsF_6 + OSClF_3 \quad (3)$$

$OSClF_3$ may be fluorinated, may disproportionate, or may decompose to give thionyl fluoride and tetrafluoride, possibly *via* OSF_2 and ClF, although ClF was not detected[8] in the mass spectra of $OSClF_2^+$ salts. Chlorine monofluoride and OSF_2 react slowly at pressures encountered in these experiments to give OSF_4 and Cl_2; $OSClF_3$ has been suggested as being[9] an intermediate in this reaction. This may be formed *via* the hypochlorite $ClOSF_3$ which may rearrange to $OSClF_3$. The yield of OSF_4 in the reaction of ONF and $OSClF_2^+AsF_6^-$ in the presence of fluorine was much increased, presumably because of rapid fluorination of $OSClF_3$ or one of its decomposition products (*e.g.* OSF_3). OSF_3 has been suggested as being an intermediate in the photochemical and thermal fluorination of OSF_2 on the basis of kinetic studies.[10,11]

^{19}F *N.M.R.*—The fluorine resonance spectra of solutions of $OSClF_2^+PF_6^-$, SbF_6^-, and $Sb_2F_{11}^-$ in anhydrous hydrogen fluoride were obtained at 5 °C. Sulphuryl fluoride was used as an internal standard; CCl_3F could not be added to the solution, as it reacts with $OSClF_2^+$ salts. All solutions gave a peak at 58·14 (±0·18) p.p.m. downfield from O_2SF_2, in addition to that due to the solvent. The spectrum of the $Sb_2F_{11}^-$ salt, also gave a broad peak in the fluorine on antimony(V) region. The lack of fluorine resonance attributable to AsF_6^- or SbF_6^- in similar compounds has been attributed to solvent exchange.[12] The chemical shift of the solvent varied from 223·1 ($OSClF_2^+AsF_6^-$), to 227·1 p.p.m. ($OSClF_2^+SbF_6^-$) upfield from O_2SF_2 and was less than that of pure HF ($\delta_{O_2SF_2}$ 234·1 p.p.m.), presumably due to anion exchange. The chemical shift of $OSClF_2^+$ is about that expected by comparison with related species[13,14] (Table 1). It is clear that $OSClF_2^+$ exists as a separate entity in hydrogen fluoride and does not readily exchange chlorine with fluorine atoms of the solvent. $OSClF_2^+$ salts can be recovered from their solutions in HF.

TABLE 1

Comparison of the chemical shift[a] of $OSClF_2^+$ with those of some related species

OSF_3^+	−32[b]	O_2SF_2	−33·1	OPF_3	94·8[e]
$OSClF_2^+$	−91·2[c]	O_2SClF	−99·7[d]	$OPClF_2$	48·6[e]

[a] Chemical shifts expressed in p.p.m. relative to CCl_3F. [b] See ref. 4. [c] Measured relative to O_2SF_2 as internal standard, converted to CCl_3F scale by $\delta(CCl_3F,int) = \delta(O_2SF_2,int) - 33{\cdot}1$ p.p.m. [d] See ref. 13. [e] See ref. 14.

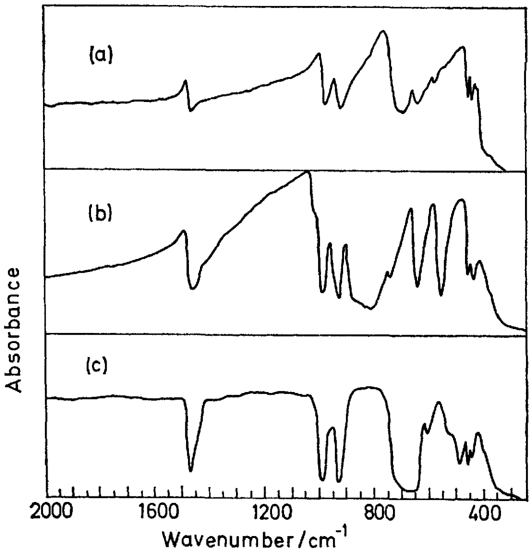

FIGURE 1 I.r. spectra of (a) powdered $OSClF_2^+AsF_6^-$ and (*b*) $OSClF_2^+PF_6^-$, and (*c*) liquid $OSClF_2^+Sb_2F_{11}^-$

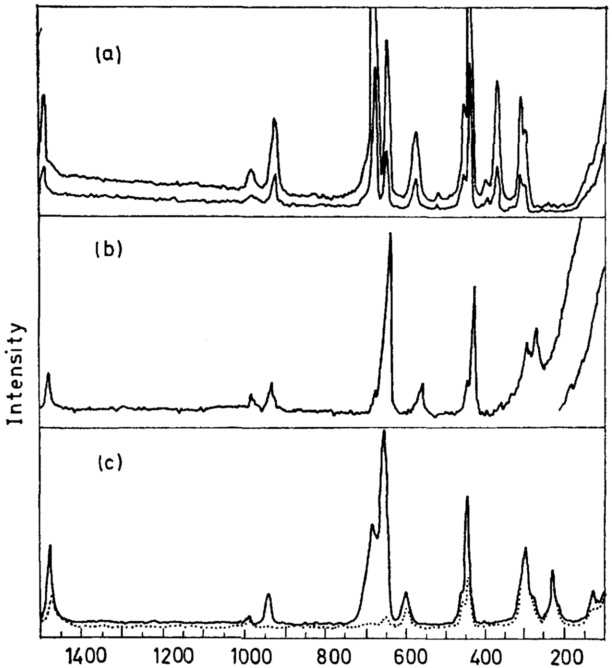

FIGURE 2 Raman spectra of (a) powdered $OSClF_2^+AsF_6^-$ and (b) $OSClF_2^+SbF_6^-$, and (c) liquid $OSClF_2^+Sb_2F_{11}^-$. Broken line indicates spectrum obtained with crossed polarizer

Vibrational Spectra of $OSClF_2^+$ *Salts.*—The i.r. spectra of $OSClF_2^+AsF_6^-$, $OSClF_2^+PF_6^-$, and liquid

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[8] S. S. Cristy and G. Mamantov, *Internat. J. Mass Spectrometry. Ion Phys.*, 1970, **5**, 309.

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[11] E. Castellano and H. J. Schumacher, *Z. phys. Chem.*, 1964, **40**, 51.

[12] M. Azeem, M. Brownstein, and R. J. Gillespie, *Canad. J. Chem.*, 1969, **47**, 4159.

[13] M. Brownstein and R. J. Gillespie, *J. Amer. Chem. Soc.*, 1970, **92**, 2718.

[14] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High-Resolution N.M.R. Spectroscopy,' vol. 2, Pergamon, London, 1966.

$OSClF_2{}^+Sb_2F_{11}{}^-$ are shown in Figure 1, and the Raman spectra of $OSClF_2{}^+AsF_6{}^-$, $OSClF_2{}^+SbF_6{}^-$, and liquid $OSClF_2{}^+Sb_2F_{11}{}^-$ in Figure 2. The i.r. spectrum of $OSClF_2{}^+SbF_6{}^-$ is not included as the quality of the spectrum is poor. Table 2 lists the vibrational spectra of the various $OSClF_2{}^+$ salts. Assignments are made by comparison with the vibrational spectra of KPF_6, $CsAsF_6$, $LiSbF_6$,[15] $VO_2Sb_2F_{11}$,[16] $N_2F_3Sb_2F_{11}$,[17] $SF_3{}^+AsF_6{}^-$,[18] and Raman spectra of $CsSb_2F_{11}$ in solution[19] and $OPClF_2$[20] (Table 3). The crystal structure[21] of $OSClF_2{}^+AsF_6{}^-$ shows $AsF_6{}^-$ as occupying a lattice site of symmetry lower than O_h. Thus various weak bands in the Raman spectra of $OSClF_2{}^+AsF_6{}^-$ and probably $OSClF_2{}^+SbF_6{}^-$ may be attributed, in part, to vibrations of non-octahedral $AsF_6{}^-$ and $SbF_6{}^-$. Similar bands were observed by Bartlett[18] *et al.* in the essentially ionic salt $SF_3{}^+AsF_6{}^-$ and attributed to 'site effects,' rather than extensive fluorine-bridging interactions. The crystal structure of $SF_3{}^+AsF_6{}^-$ also showed $AsF_6{}^-$ to be in a lattice site of less than O_h symmetry. The 660 cm^{-1} band in the Raman spectrum of $OSClF_2{}^+Sb_2F_{11}{}^-$ is made up of bands due to $OSClF_2{}^+$ and $Sb_2F_{11}{}^-$ (Figure 2). Both $Sb_2F_{11}{}^-$ and the composite bands are polarized[19] indicating that the component due to the cation is polarized also. Similarly, the $Sb_2F_{11}{}^-$ band[19] at *ca.* 300 cm^{-1} and the broad composite band are depolarized, implying that the $OSClF_2{}^+$ component is also depolarized (Figure 2).

TABLE 2

Vibrational spectra (cm^{-1}) of various $OSClF_2{}^+$ salts

$OSClF_2{}^+AsF_6{}^-$		$OSClF_2{}^+SbF_6{}^-$		$OSClF_2{}^+Sb_2F_{11}{}^-$		$OSClF_2{}^+PF_6{}^-$	
Raman	I.r.	Raman	I.r.	Raman	I.r.	I.r.	Assignment
1466	1468	1472	1460	1475p	1472	1460	ν(S–O)
983	983	988	975	988dp	988	983	ν_a(S–F)
926	928	936	918	934p	930	930	ν_s(S–F)
						820	$\nu_3(PF_6{}^-)$*
	815w						imp?
						740	$\nu_1(PF_6{}^-)$
710w							$AsF_6{}^-$
	695						$\nu_3(AsF_6{}^-)$
				683p	680		$Sb_2F_{11}{}^-$
		682vw					$SbF_6{}^-$
681							$\nu_1(AsF_6{}^-)$
			668				$\nu_3(SbF_6{}^-)$
				660p	650		ν(S–Cl), $Sb_2F_{11}{}^-$
		652					ν(S–Cl), $\nu_1(SbF_6{}^-)$
651	645		640			645	ν(S–Cl)
				604dp	600		$Sb_2F_{11}{}^-$
575	585						$\nu_2(AsF_6{}^-)$
		565					$\nu_2(SbF_6{}^-)$
						555	$\nu_4(PF_6{}^-)$
					525		$Sb_2F_{11}{}^-$
523vw			525w				imp? $AsF_6{}^-$, $SbF_6{}^-$?
					490		$Sb_2F_{11}{}^-$
456	458	456	456	460dp	455	456	$OSClF_2{}^+$ bend
442	443	442	440	445p	445	440	$OSClF_2{}^+$ bend
396w							$AsF_6{}^-$
371							$\nu_5(AsF_6{}^-)$
308		310		307dp			$OSClF_2{}^+$ bend
298		298		300dp			$OSClF_2{}^+$ bend
				286dp			$Sb_2F_{11}{}^-$
		280					$\nu_5(SbF_6{}^-)$
				230dp			$Sb_2F_{11}{}^-$
				128dp			$Sb_2F_{11}{}^-$

* Assignments for hexafluoride ions assuming O_h symmetry. p = polarized, dp = depolarized, w = weak, v = very.

TABLE 3

Comparison of the vibrational spectra (cm^{-1}) of $OSClF_2{}^+$ and $OPClF_2$

$OSClF_2{}^+$ [a]		$OPClF_2$ [b]		Assignments of $OPClF_2$ [b]	
Raman	I.r.	Raman	I.r.		
1471p	1467	1358p	1384	$\nu_1[A']$	ν[PO]
986dp	985	960dp	960	$\nu_7[A'']$	ν_{as}[PF]
932p	929	895p	900	$\nu_2[A']$	ν_s[PF]
651p	643	617p	623	$\nu_3[A']$	ν[PCl]
457dp	456	424dp?	419	$\nu_4[A']$	$\nu_5[A']$ [c]
443p	442	411p	412	$\nu_6[A']$	$\nu_8[A'']$
308dp		274dp		$\nu_9[A'']$	
298dp					

[a] Average frequencies of several $OSClF_2{}^+$ salts. [b] See ref. 20. [c] Five deformation modes.

The $OSClF_2{}^+$ vibrations are at similar frequencies in the various compounds and are very much the same in the solids and in liquid phase, suggesting an ionic formulation for the salts. The similarity of the vibrational frequencies of $OSClF_2{}^+$ and $OPClF_2$ (Table 3)

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[15] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.

[16] J. Weidlein and K. Dehnicke, *Z. anorg. Chem.*, 1966, **348**, 278.

[17] A. M. Qureshi and F. Aubke, *Canad. J. Chem.*, 1970, **48**, 3117.

[18] D. D. Gibler, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 1972, **11**, 2325.

[19] R. J. Gillespie, personal communication.

[20] A. Müller, B. Krebs, E. Niecke, and A. Ruoff, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 571.

[21] R. Dunphy, C. Lau, H. Lynton, and J. Passmore, following paper.

is convincing evidence for the identity of the chlorodifluoro-oxosulphur(VI) cation. The vibrational frequencies of $OSClF_2^+$ are, as expected, higher than those reported for $OPClF_2$. Similar trends occur in other isoelectronic series, *e.g.* OPF_3 and OSF_3^+.[4]

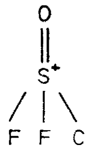
The S–Cl, S–O, and S–F stretching frequencies are the largest so far observed (using the average of the symmetric and asymmetric stretching frequencies obtained from Lehman's equation[22]) with the exception of S–O and S–F[22] in OSF_3^+. Replacement of fluorine in OSF_3^+ by less electronegative chlorine has the effect of lowering the strength of the sulphur–oxygen and sulphur–fluorine bonds (see Table 4). The high bond strengths in $OSClF_2^+$ may be accounted for by contributions of canonical structures (2)—(5), structure (1) having more importance than the rest.

TABLE 4

Comparison of the vibrational spectra (cm^{-1}) [a] of OSF_3^+ and $OSClF_2^+$

	OSF_3^+ [b]	$OSClF_2^+$
ν(SO)	1538	1466
	1529	
ν_{as}(SF)	1063	983
	1057	
ν_s(SF)	911	926
ν(SCl)		651
Bending modes	513	456
	497	442
	391	308
		298
ν(SF) [c]	1010	955

[a] Raman data for the AsF_6^- salts quoted in both cases. [b] See ref. 4. [c] Average ν_{SF} calculated by Lehman's equation, see ref. 22.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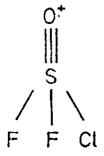
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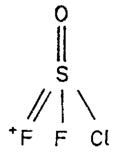
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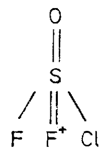
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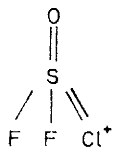
(5)

Mass Spectrum of $OSClF_2^+AsF_6^-$.—A typical mass spectrum of $OSClF_2^+AsF_6^-$ obtained by the direct-inlet method with the sample at room temperature is shown in Table 5. Ions due to hydrolysis products and obvious impurities are not included. It is not clear whether Cl_2^+ arises from hydrolysis products, trace impurities or perhaps from reactions of the species produced on initial dissociation. The identity of the ions of *m/e* >54 was confirmed by a high-resolution spectrum. The relative intensity of the peaks varied from spectrum to spectrum; however, the general pattern of intensities of ions containing sulphur and arsenic were similar in all spectra. Mass spectra of $OSClF_2^+PF_6^-$ and $OSClF_2^+SbF_6^-$ were similar to those of the arsenic salt showing peaks attributable to the same sulphur species and the corresponding pentafluorides ($PF_4^+ \cdots P^+$ and $SbF_4^+ \cdots Sb^+$). Spectra obtained at reduced voltage showed a relative increase of OSF_2^+ implying that this at least in part occurred as a molecular species.

TABLE 5

Typical mass spectrum [a] of $OSClF_2^+AsF_6^-$

m/e [b]	Ion [c]	Rel. intensity
151	AsF_4^+	100
132	AsF_3^+	73
121	$OSClF_2^+$	19
113	AsF_2^+	67
105	OSF_3^+	35
105	$SClF_2^+$	trace
102	$OSClF^+$	0·2
94	AsF^+	11
89	SF_3^+	3
86	OSF_2^+	44
75	As^+	11
70	Cl_2^+ imp?	5
70	SF_2^+	2
67	OSF^+	57
51	SF^+	8
48	SO^+	18
35	Cl^+	5

[a] Sample at room temperature, ionizing voltage 70 eV, source 200 °C. [b] *m/e* $\geqslant$ 35 included. [c] Ions attributable to isotopes ^{34}S and ^{37}Cl observed, but not included.

The mass spectrum of $OSClF_2^+AsF_6^-$ is consistent with the thermal decomposition of the salt into AsF_5 and $OSClF_3$. Ions attributable to both species, ($AsF_4^+ \cdots As^+$) and ($OSClF_2^+$, OSF_3^+, OSF_2^+, *etc.*), were observed. Molecular ions corresponding to $OSClF_3$, ClF, and OSF_4 were not detected. The strongest peak in the mass spectrum of OSF_4 is OSF_3^+,[23] whereas OSF^+ is the most intense sulphur-containing ion in the spectrum of the $OSClF_2^+$ salts. In addition, OSF_2^+ occurs, at least in part, as a molecular ion. This suggests that $OSClF_3$ partly decomposes to OSF_2 under the conditions prevailing in this experiment.

EXPERIMENTAL

Reagents.—Commercial fluorine compounds were purified by distillation when necessary. Traces of water were removed chemically from hydrogen fluoride by K_2NiF_6 in a Kel-F container.

Apparatus.—Volatile materials were manipulated in a Monel vacuum line, equipped with stainless-steel Whitey valves (1KS4) and Swagelock compression fittings. Reaction vessels were constructed from Kel-F tubing ($\frac{1}{2}$ in o.d., 5/16 in i.d.) connected to the line *via* a valve and a brass reducing Swagelock junction. High-pressure reactions were carried out in 31 cm^3 Monel vessels equipped with removable lids and Teflon gaskets. Pressures were measured on an Ashcroft stainless-steel Bourdon tube type gauge. Solids were transferred in a Vacuum Atmospheres Dri-Lab fitted with a Dri-train (HE 493). I.r. spectra of gases were obtained by use of a stainless-steel 10 cm cell equipped with silver chloride windows. Spectra of solids

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[22] W. J. Lehmann, *J. Mol. Spectroscopy*, 1961, **7**, 261.

[23] F. B. Dudley, G. H. Cady, and D. F. Eggers, jun., *J. Amer. Chem. Soc.*, 1956, **78**, 1553.

were obtained as fine powders between silver chloride plates.

Raman spectra of solids sealed in capillary tubes were obtained by use of a Spex Industries 1400 spectrometer and a Spectra Physics 140 argon-ion laser. ^{19}F N.m.r. spectra were obtained on a Varian Associates HA 60 spectrometer operating at 56·4 Mc. N.m.r. tubes were constructed from thin-walled Kel-F tubing connected to the vacuum line *via* a flair joint. Purified hydrogen fluoride was used as a solvent and sulphuryl fluoride as an internal reference. Mass spectra were obtained with a Hitachi–Perkin-Elmer RMU 6D mass spectrometer at 70 eV. Freshly prepared samples were placed in Teflon tube containers with tight-fitting caps and, on removal of the cap, quickly introduced into the spectrometer by the direct-inlet port.

Preparation of $OSClF_2^+AsF_6^-$.—In a typical reaction thionyl fluoride (5·6 mmol) was condensed into a Kel-F trap containing $Cl_2F^+AsF_6^-$ (5·6 mmol) prepared by the method of ref. 1, and was kept at −78 °C overnight. Material volatile at −130 °C was characterized as chlorine monofluoride by its i.r. spectrum and reaction with sulphur dioxide to give [9] O_2SClF. Products volatile at −78 °C were identified as OSF_4 (and trace O_2SF_2) and chlorine, which was identified by its physical properties and reaction with mercury. A small quantity of unreacted $Cl_2F^+AsF_6^-$ (dissociated to ClF and AsF_5), O_2SF_2, and solid $OSF_3^+AsF_6^-$ (*ca.* 0·3 mmol) were condensed from the reaction vessel at room temperature leaving white solid $OSClF_2^+AsF_6^-$ (4·8 mmol; *ca.* 85%). After 1 h at −78 °C yield 70%. The proportions of ClF, OSF_4, O_2SF_2, and Cl_2 varied somewhat with each reaction and with the chlorine impurity content of the chlorine monofluoride starting material. Uptake of liquid OSF_2 by solid $Cl_2F^+AsF_6^-$ proceeded at *ca.* −130 °C on contact, the reaction products being the same as before. Thionyl fluoride underwent a similar reaction with $Cl_3^+AsF_6^-$ prepared by the method of ref. 2.

The reaction between chlorine monofluoride, arsenic pentafluoride, and thionyl fluoride also occurred at room temperature. It proceeded instantaneously when carried out in the i.r. cell with all components at all times in the gas phase. In another reaction OSF_2 (2·2 mmol), AsF_5 (2·2 mmol), and ClF (4·5 mmol) were condensed into a Monel reaction vessel at −196 °C and then warmed to room temperature. The products contained OSF_4, ClF, Cl_2, O_2SF_2, $OSF_3^+AsF_6^-$ (0·28 mmol), and $OSClF_2^+AsF_6^-$ (1·81 mmol; 82%) (Found: As, 23·1; Cl, 10·6; F, 48·05; S, 10·55. Calc. for $OSClF_2^+AsF_6^-$: As, 24·15; Cl, 11·4; F, 48·95; S, 10·35%).

Preparation of $OSClF_2^+Sb_2F_{11}^-$.—In a typical experiment the chlorine monofluoride–antimony pentafluoride adduct of composition *ca.* ClF,SbF_5 ($ClF_{1\cdot2},SbF_5$) (3·6 mmol) was prepared according to the method of ref. 1. Thionyl fluoride (4·5 mmol) was condensed on this adduct and the mixture warmed and cooled between −196 °C and room temperature for 2 h, and then evacuated at room temperature for 5 h to leave a paste-like product whose weight corresponded to the formation of 3·5 mmol $OSClF_2^+Sb_2F_{11}^-$. In other cases the product was a liquid. $OSClF_2^+Sb_2F_{11}^-$ was also prepared by the reaction of $OSClF_2^+AsF_6^-$ with excess of SbF_5. $OSClF_2^+AsF_6^-$ (1·06 mmol) was warmed to 50 °C with shaking for 1/2 h with SbF_5 (4·10 mmol) in a Kel-F trap. The mixture was evacuated for 15 h until constant weight. The weight of product corresponded to formation of $OSClF_2^+Sb_2F_{11}^-$ (1·09 mmol). The salt was also prepared by the reaction of $OSClF_2^+AsF_6^-$ and excess of SbF_5 in HF (Found: Cl, 6·45; F, 42·2; S, 5·35; Sb, 42·9. Calc. for $OSClF_2^+Sb_2F_{11}^-$: Cl, 6·2; F, 43·05; S, 5·6; Sb, 42·4%).

Preparation of $OSClF_2^+SbF_6^-$.—ClF (10 mmol) was condensed in three separate aliquots on SbF_5 (4 mmol) in a Kel-F trap, and thermally cycled between −196 °C and room temperature after each addition. A yellowish orange solid was formed when the mixture was kept at −78 °C, the weight change indicating a combining ratio of SbF_5 to ClF of *ca.* 1 : 2. OSF_2 (4·0 mmol) were then added, the mixture slowly warmed to room temperature and then set aside overnight. Volatile materials were removed and the solid pumped to constant weight. Final yield *ca.* 95%. The compound was also prepared by the reaction of equimolar quantities of SbF_5 and $OSClF_2^+AsF_6^-$ in anhydrous HF (Found: Cl, 9·65; F, 42·35; S, 7·7; Sb, 34·4. Calc. for $OSClF_2^+SbF_6^-$: Cl, 9·9; F, 42·55; S, 9·0; Sb, 34·1%).

Preparation of $OSClF_2^+PF_6^-$.—In a typical experiment ClF (4·5 mmol) and PF_5 (2·25 mmol) were allowed to react in a Kel-F trap at −78 °C for *ca.* 1/2 h, giving a turbid yellow liquid which solidified at *ca.* −130 °C. OSF_2 (2·25 mmol) was added and the mixture warmed and cooled between −130 and −78 °C for 1 h. Reaction products volatile at −130 °C contained mostly ClF, and at −78 °C Cl_2, OSF_4, and a small quantity of O_2SF_2. The solid was evacuated at −78 °C for 1 h to leave $OSClF_2^+PF_6^-$ (2·1 mmol), which was stored at −78 °C. $OSClF_2^+PF_6^-$ was not formed on addition of ClF, OSF_2, and PF_5 in the gas phase at ambient temperatures and pressures.

Reaction of OSF_2 *and* $Cl_2F^+BF_4^-$.—The reaction of OSF_2 and Cl_2FBF_4 between −95 and −130 °C gave a white solid stable at −78 °C. The increase in weight of the solid was consistent with the formation of good yield of $OSClF_2^+BF_4^-$ At room temperature the solid quickly became a yellow liquid over which there developed appreciable quantities of OSF_2, OSF_4 (and O_2SF_2), and BF_3 in addition to a yellow gas which was probably chlorine. Owing to its instability, the salt was not further investigated.

Properties of $OSClF_2^+$ *Salts*.—$OSClF_2^+PF_6^-$, AsF_6^-, and SbF_6^- are white crystalline solids. Samples of $OSClF_2^+Sb_2F_{11}^-$ were sometimes paste-like and in other preparations liquid. The possibility of the presence of small amounts of SbF_5 or $OSClF_2^+SbF_6^-$ as impurities cannot be excluded.

Thermal Properties of $OSClF_2^+$ *Salts*.—In an attempt to obtain evidence for the existence of $OSClF_3$, $OSClF_2^+PF_6^-$ was placed in the isolateable side-arm of an i.r. cell and evacuated at −78 °C. I.r. spectra were taken continuously as the temperature was raised to ambient. Only bands attributable to PF_5, OSF_2, OSF_4, and O_2SF_2 were observed. The behaviour of various $OSClF_2^+$ salts is given in Table 6.

Reactions of $OSClF_2^+AsF_6^-$ *with Fluorine*.—Fluorine (0·7 mmol) was allowed to react with $OSClF_2^+AsF_6^-$ (0·48 mmol) for 1 h at room temperature. No bands were observed in the i.r. spectrum of the gas phase, and that of the solid showed only $OSClF_2^+AsF_6^-$. Quantities of $OSF_3^+AsF_6^-$, detected by its i.r. spectrum, were obtained on heating overnight at 90 °C in excess of fluorine.

Reaction of $OSClF_2^+AsF_6^-$ *with Fluoride-ion Donors*.—The i.r. cell was carefully passivated with ONF. $OSClF_2^+$-AsF_6^- (1·43 mmol) was placed in an isolateable side-arm and ONF (0·3 mmol) expanded into the main body of the cell, its purity checked, and then condensed on $OSClF_2^+$-AsF_6^- at −196 °C. The isolated side-chamber was placed

TABLE 6

Thermal decomposition of $OSClF_2^+$ salts; all reactions carried out *in vacuo* and products identified by i.r. spectroscopy

Salt	Conditions*	Time/h	Products
$OSClF_2^+PF_6^-$	(*a*)	1/2	OSF_2, PF_5, OSF_4, O_2SF_2†
	(*b*)	>1/60	OSF_2, OSF_4, PF_5, O_2SF_2
$OSClF_2^+AsF_6^-$	(*c*)	1/2	OSF_2, AsF_5†
	(*d*)	15	OSF_2, AsF_5; $OSF_3^+AsF_6^-$ and $OSClF_2^+AsF_6^-$ (0·2g)‡
$OSClF_2^+SbF_6^-$	(*b*)	48	OSF_2
	(*e*)	4	OSF_2; $OSF_3^+Sb_2F_{11}^-$ and $OSClF_2^+Sb_2F_{11}^-$ (0·1g)‡
$OSClF_2^+Sb_2F_{11}^-$	(*b*)	15	No gaseous prods.
	(*f*)	16	OSF_2, O_2SF_2; $OSF_3^+Sb_2F_{11}^-$ and $OSClF_2^+Sb_2F_{11}^-$ (0·54g)‡

*Conditions: (*a*) −22°; (*b*) room temp.; (*c*) prepared *in situ* in i.r. cell, 28 °C; (*d*) 0·4 g, 90 °C; (*e*) 0·15 g, 85 °C; (*f*) 0·59 g, 90 °C.

† Sufficient product to just enable detection by i.r. ‡ Mixture.

in a dry-ice–acetone slush-bath and the valve to the body of the i.r. cell opened. The i.r. spectrum showed the presence of OSF_2 and OSF_4 *ca.* 1 : 1, ratio determined from a comparison of the spectra of pure components in the same cell at various pressures. The experiment was repeated several times under varying conditions with similar results. $NO^+AsF_6^-$ was identified as the solid product with excess of ONF. In excess of fluorine, OSF_4 was the major gaseous product ($OSF_2 : OSF_4$ *ca.* 1 : 3).

Anhydrous hydrogen fluoride was condensed in CsF and $OSClF_2^+AsF_6^-$ (1 : 1 mol). A reaction occurred on melting of the HF. The i.r. spectrum of the gas showed the presence of OSF_2, OSF_4, and lesser amounts of O_2SF_2 ($OSF_2 : OSF_4$ *ca.* 3 : 2).

$OSClF_2^+AsF_6^-$, $OSClF_2^+Sb_2F_{11}^-$ *with* CCl_3F.—The salts were treated with an excess of CCl_3F for 5 h. The i.r. spectra of the gases in both cases revealed appreciable quantities of CCl_2F_2 and OSF_2. Small quantities of $CClF_3$ were also detected in the $Sb_2F_{11}^-$ case.

We thank the Defense Research Board of Canada and the Research Corporation for financial support of this work, Dr. R. J. Gillespie for the laser Raman Spectra, and Drs. H. L. Paige and R. Kaiser for the ^{19}F n.m.r. spectra.

[3/088 *Received, 15th January, 1973*]