Chlorodifluorosulphur(VI) Oxide Hexafluoroarsenate(V), $OSClF_2^+AsF_6^-$

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Summary Chlorodifluorosulphur(VI) oxide hexafluoroarsenate has been prepared by the reaction of 2ClF, AsF_5, and OSF_2 at room temperature and at −78°.

THE hitherto unreported $OSClF_2^+AsF_6^-$ has been prepared by the reaction of 2ClF, AsF_5, and OSF_2. In a typical reaction 0·075 mmoles of OSF_2 was condensed on to 0·075 mmoles of 2ClF, AsF_5[1] in a Kel-F trap and the mixture was warmed and cooled between −78° and −30° for 2 h. The weight of solid formed corresponded to the formation of 0·075 mmoles of $OSClF_2AsF_6$, consistent with the equation,

$$OSF_2 + 2ClF, AsF_5 = OSClF_2AsF_6 + ClF.$$

When the components were kept at −78° for 1 h, the yield was 70%; overnight, 100%. At ambient temperatures and pressures, the reaction was instantaneous. OSF_3AsF_6 was also formed in these reactions in varying amounts.

The vibrational spectrum of $OSClF_2^+,AsF_6^-$

$OPClF_2$[6] Raman	$OPClF_2$[6] I.r.	$OSClF_2^+AsF_6^-$ Raman	$OSClF_2^+AsF_6^-$ I.r.	Assignment
1358 cm^{-1}	1384 cm^{-1}	1466 cm^{-1}	1470 cm^{-1}	ν(S–O)
948	960	984	980	ν_a(S–F)
895	900	927	925	ν_s(S–F)
			820 (v. weak)	imp?
			690	AsF_6^-
		681		AsF_6^-
618	623	650	638	ν(S–Cl)
		575	580 (weak)	AsF_6^-
		522 (v. weak)		imp?
424	419 412	456	457	$OSClF_2^+$ bending mode
410	406	442	442	$OSClF_2^+$ bending mode
		396 (v. weak)		imp?
		371		AsF_6^-
274	274	308		$OSClF_2^+$ bending mode
		298		

The empirical formula ($OSClF_2AsF_6$) was supported by elemental analysis for sulphur, fluorine, arsenic, and chlorine. The mass spectrum of the solid at 140° by the direct inlet method included peaks attributable to $OS^{37}ClF_2^+$ (2·8), $OS^{35}ClF_2^+$ (6·9), OSF_3^+ (15), OSF_2^+ (41), SF_2^+ (6), OSF^+ (100), SF^+ (16), SO^+ (43), $^{37}Cl^+$ (6), $^{35}Cl^+$ (27), F^+ (16), AsF_4^+ (58), AsF_3^+ (25), AsF_2^+ (50), AsF^+ (8), As^+ (7), consistent with decomposition of $OSClF_2AsF_6$ into $OSClF_3$ and AsF_5. The most abundant ion in the mass spectrum of OSF_4 is OSF_3^+;[2] it is possible that $OSClF_3$, if formed, readily dissociates to OSF_2 and ClF at 140°. The i.r. spectrum of the gaseous products of the reaction $OSClF_2$-AsF_6 and CsF in anhydrous hydrogen fluoride showed the presence of OSF_4, O_2SF_2 (trace), and OSF_2. Chlorine monofluoride, another possible reaction product, was not readily detected because of its weak absorption in the i.r. spectrum. However, the reaction of $OSClF_2AsF_6$ and CsF at 80° in the presence of sulphur dioxide included O_2SClF.

The ^{19}F n.m.r. of $OSClF_2^+AsF_6^-$ in a large excess of anhydrous HF at room temperature showed a single peak at 271 p.p.m. downfield from that of the solvent. The lack of a fluorine resonance attributable to AsF_6^- in similar compounds[3,4] has been attributed to solvent exchange.[3]

The chemical shift of $OSClF_2^+$ is in about the expected region by comparison with OSF_3^+, OPF_3 and $OPClF_2$ assuming δ_{CCl_3F} (HF) = 201 p.p.m.[5]

	δ_{CCl_3F} p.p.m.		δ_{CCl_3F} p.p.m.
OSF_3^+[4]	−32	OPF_3[5]	+94·8
$OSClF_2^+$	−70	$OPClF_2$[5]	+48·6

The laser Raman and i.r. spectra of the solid contain lines that can be assigned to the ions $OSClF_2^+,AsF_6^-$ by comparison with the isoelectronic molecule $OPClF_2$[6] and AsF_6^-.[7]

The addition of "Cl^+" has been effected to the poor donor OSF_2. The reaction of $2ClF,AsF_5$ with other poor donors is under active investigation.

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