

Chlorodifluorosulphur(vi) Oxide Hexafluoroarsenate(v), $\text{OSClF}_2^+ \text{AsF}_6^-$

By C. LAU and J. PASSMORE*

(Department of Chemistry, University of New Brunswick, Fredericton, N.B., Canada)

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

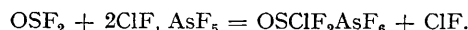
THE hitherto unreported $\text{OSClF}_2^+ \text{AsF}_6^-$ has been prepared by the reaction of 2ClF , AsF_5 , and OSF_2 . In a typical reaction 0.075 mmoles of OSF_2 was condensed on to 0.075 mmoles of 2ClF , AsF_5 in a Kel-F trap and the mixture was

chlorine. The mass spectrum of the solid at 140° by the direct inlet method included peaks attributable to $\text{OS}^{37}\text{ClF}_2^+$ (2.8), $\text{OS}^{35}\text{ClF}_2^+$ (6.9), OSF_3^+ (15), OSF_2^+ (41), SF_2^+ (6), OSF^+ (100), SF^+ (16), SO^+ (43), $^{37}\text{Cl}^+$ (6), $^{35}\text{Cl}^+$ (27), F^+ (16), AsF_4^+ (58), AsF_3^+ (25), AsF_2^+ (50), AsF^+ (8), As^+ (7), consistent with decomposition of $\text{OSClF}_2\text{AsF}_6$ 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,

The vibrational spectrum of $\text{OSClF}_2^+ \text{AsF}_6^-$

OSClF_2^+		$\text{OSClF}_2^+ \text{AsF}_6^-$		Assignment
Raman	I.r.	Raman	I.r.	
1358 cm^{-1}	1384 cm^{-1}	1466 cm^{-1}	1470 cm^{-1}	$\nu(\text{S-O})$
948	960	984	980	$\nu_a(\text{S-F})$
895	900	927	925	$\nu_s(\text{S-F})$
			820 (v. weak)	imp?
		681	690	AsF_6^-
		650	638	AsF_6^-
618	623	575	580 (weak)	$\nu(\text{S-Cl})$
		522 (v. weak)		AsF_6^-
424	419	456	457	imp?
	412			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		

warmed and cooled between -78° and -30° for 2 h. The weight of solid formed corresponded to the formation of 0.075 mmoles of $\text{OSClF}_2\text{AsF}_6$, consistent with the equation,



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 empirical formula ($\text{OSClF}_2\text{AsF}_6$) was supported by elemental analysis for sulphur, fluorine, arsenic, and

readily dissociates to OSF_2 and ClF at 140° . The i.r. spectrum of the gaseous products of the reaction $\text{OSClF}_2\text{AsF}_6$ 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 $\text{OSClF}_2\text{AsF}_6$ and CsF at 80° in the presence of sulphur dioxide included O_2SClF .

The ^{19}F n.m.r. of $\text{OSClF}_2^+ \text{AsF}_6^-$ 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 $\delta_{\text{CCl}_3\text{F}}(\text{HF}) = 201$ p.p.m.⁵

$\delta_{\text{CCl}_3\text{F}}$ p.p.m.		$\delta_{\text{CCl}_3\text{F}}$ 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 com-

parison 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 $2\text{ClF}, \text{AsF}_5$ with other poor donors is under active investigation.

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