A NEW PREPARATION OF PEROXYDISULFURYL DIFLUORIDE

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Cady and Dudley (1) first reported the preparation of peroxydisulfuryl difluoride $(S_2O_6F_2)$ via the catalytic fluorination of SO_3 with F_2 over AgF_2 at 100°. More recently it was shown that XeF_2 will react with SO_3 to form $S_2O_6F_2$ (2).

We now wish to report another route to $S_2^{0}{}_6F_2$. Chromium pentafluoride reacts quantitatively with SO_3 according to the following equation:

 $CrF_5 + 5SO_3 \longrightarrow S_2O_6F_2 + Cr(SO_3F)_3$ Pure $S_2O_6F_2$ is removed from the reaction mixture at -22°.

 $Cr(SO_3F)_3$, which has not been previously reported, is an amorphous light green solid soluble in DMSO. The infrared spectrum was measured neat between KRS5 windows and is listed along with its assignments in Table I.

TABLE I

Infrared Spectra of $Cr(SO_3F)_3$

Band (cm^{-1})		Approximate		Assignment	
1485	(vw)	Vasym	^{S0} 2	Α'	(stretch)
1355	(s)	ん	S0	A''	(stretch)
1210	(s)	Jasym	so ₂	Α'	(stretch)
1100 1005	(s,b) (s)	v_{sym}	^{SO} 2	Α'	(stretch)
855	(m,vb)	ປ	SF	Α'	(stretch)
628	(m)	ſ	^{so} 2	A'	(bend)
555	(m)	δ	SF	A'	(wag)
410	(w)	δ	so2	A''	(rock)
340	(w)	δ		A'	(torsion)

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The sulfur-oxygen stretching, bending, and deformation bands for $Cr(SO_3F)_3$ are similar to those reported for $(CH_3)_2Sn(SO_3F)_2$ and $IO_2(SO_3F)_2$ (3) in which bridging fluorosulfate groups are present. The i.r. spectrum and the amorphous powder spectrum of $Cr(SO_3F)_3$ suggest a polymeric structure with bridging fluorosulfate groups. Attempts to obtain a Raman spectrum were unsuccessful.

The ultraviolet spectrum of $Cr(SO_3F)_3$ in DMSO was found to exhibit bands at 272 nm / \mathcal{E} = 110/, 445 nm / \mathcal{E} = 42/, 647 nm / \mathcal{E} = 43/, typical of other chromium (III) compounds (4). The ¹⁹F nuclear magnetic resonance spectrum of $Cr(SO_3F)_3$ in DMSO consists of a singlet at -36 ppm (external standard CFCl₃). The magnetic susceptibility for $Cr(SO_3F)_3$ at 26° is 3.90 B.M.

Experimental

 CrF_5 was prepared by the method of Slivnik and Zemva (5) and the sulfur trioxide was obtained from the Allied Chemical Company as Sulfan B and was twice distilled.

Infrared spectra were recorded with a Perkin-Elmer model 467 infrared spectrometer using a 8.25 cm cell fitted with AgCl windows for gases or KRS5 windows for solids. Fluorine nmr spectrum was obtained with a Varian HA-100 nmr spectrometer. The electronic spectrum was recorded on a Cary Model 14 recording spectrometer (path length of cell was 1.00 cm). The magnetic susceptibility value was obtained by the Gouy method. Measurements were made at a field strength of about 5KG using an Alpha AL 7500 water cooled magnet with a 1.5 in. air gap. Diamagnetic corrections were made with Pascal's constants. The calibrant was HgCo(SCN)₄. X-ray result was obtained using an XRD-5 General Electric powder camera. The samples were contained in 0.5 mm capillaries.

In a typical reaction, 2.93 mmol of CrF_5 and 11.0 mmol of SO_3 were condensed at -196° in a 40 ml quartz reactor equipped with a Kel-F Kontes stopcock. The reaction was initiated by brief heating to 55° and was complete after 2 days at r.t. The reaction vessel was cooled to -22° and the $S_2^{0}{}_{6}F_2$ (2.11 mmol, yield of 96%) was pumped away through a trap cooled to -196°. At r.t. excess CrF_5 (.72 mmol) was pumped away leaving the pale green solid $Cr(SO_3F)_3$ (2.19 mmol)

Analysis

Cr(SO₃F)₃ Calcd: Cr, 14.89; S, 27.50; F, 16.3. Found: Cr, 15.13; S, 27.26; F, 16.0.

The infrared spectrum of $S_2O_6F_2$ was identical to that reported by Qureshi et al. (6). The $S_2O_6F_2$ was quantitatively converted to $NOSO_3F$. The $NOSO_3F$ was characterized by its m.p. 155-157° [lit. 156-157°; (7)] and its fluorine analysis (Calcd: F, 14.7; Found: F, 14.3). The vapor phase molecular weight of $S_2O_6F_2$ was found to be 199 (theor. 198).

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References

- 1. F.B. DUDLEY and G.H. CADY, J. Amer. Chem. Soc., 1957, 79, 513.
- 2. N. BARTLETT and F.O. SLADKY, J.C.S. Chem. Comm., 1968, 1046.
- 3. H.A. CARTER and F. AUBKE, Inorg. Chem., 1971, 10, 2296.
- 4. D.W. MEEK, R.S. DRAGO and T.S. PIPER, Inorg. Chem., 1962, 1, 285.
- 5. J. SLIVNIK and B. ZEMVA, Z. Anorg. Allg. Chem., 1971, 385, 137.
- A.M. QURESHI, L.E. LEVICHUCK and F. AUBKE, Can. J. Chem., 1971, <u>49</u>, 2544.
- 7. J.E. ROBERTS and G.H. CADY, J. Amer. Chem. Soc., 1960, 82, 353.