Contribution from the Department of Chemistry,
University of Washington, Seattle, Washington 98105

The Reaction of Bromine(I) Fluorosulfate with Some Covalent Chlorides[1]

By DARRYL D. DES MARTEAU[2]

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Bromine(I) fluorosulfate has been shown to react with a variety of nonmetal chlorides according to the general equation $MCl_x + YBrOSO_2F = MCl_{x-y}(OSO_2F)_y + YBrCl$. New compounds obtained in this manner were $[C(O)OSO_2F]_2$, $C(O)ClC(O)OSO_2F$, $CFCl_2OSO_2F$, $CFCl(OSO_2F)_2$, $CCl(OSO_2F)_3$, $C(OSO_2F)_4$, $SO(OSO_2F)_2$, $POCl_2OSO_2F$, and $SiCl_2(OSO_2F)_2$. Some evidence was also found for the compounds CCl_3OSO_2F, $CCl_2(OSO_2F)_2$, $SOClOSO_2F$, and $POCl(OSO_2F)_2$.

The preparation of compounds containing the fluorosulfate group has received considerable attention in recent years. Methods for the preparation of a variety of nonmetal and metal fluorosulfates have been found. The majority of these methods employ fluorosulfuric acid or peroxydisulfuryl difluoride as the fluorosulfonating reagent. This work describes the use of bromine(I) fluorosulfate in the preparation of some new nonmetal fluorosulfates. Previous work has shown that $BrOSO_2F$ is a strong oxidizing agent that adds across the carbon–carbon double bond.[3–5] Because of the positive nature of the bromine atom in $BrOSO_2F$ it was thought that the reaction of $BrOSO_2F$ with covalent chlorides could lead to the formation of bromine monochloride and a fluorosulfate. This has been found to be true and the following reactions were investigated

$$YBrOSO_2F + MCl_x = YBrCl + MCl_{x-y}(OSO_2F)_y$$

where $MCl_x = [C(O)Cl]_2$, $CFCl_3$, CCl_4, $SOCl_2$, $POCl_3$, or $SiCl_4$.

The new fluorosulfates $[C(O)OSO_2F]_2$, $C(O)ClC(O)OSO_2F$, $CFCl_2OSO_2F$, $CFCl(OSO_2F)_2$, $CCl(OSO_2F)_3$, $C(OSO_2F)_4$, $SO(OSO_2F)_2$, $POCl_2OSO_2F$, and $SiCl_2(OSO_2F)_2$ were prepared. Evidence was also found for the existence of CCl_3OSO_2F, $CCl_2(OSO_2F)_2$, $SOClOSO_2F$, and $POCl(OSO_2F)_2$.

Experimental Section

Reagents.—Bromine(I) fluorosulfate was prepared by the method of Roberts and Cady using a slight excess of $S_2O_6F_2$.[3] Peroxydisulfuryl difluoride was prepared in the usual manner.[6,7] The chlorides were obtained from commercial sources and were purified by distillation.

General Methods.—Each reaction was run in a 100-ml Pyrex glass bulb fitted with a Fischer–Porter glass valve closed by a Teflon plug. The reactions were carried out by condensing the chloride onto the $BrOSO_2F$ cooled to −183° and then placing the reaction bulb in a shielded bath at the appropriate temperature. The temperature for each reaction was chosen so that the chloride would be a liquid and so that the reaction was not too vigorous. After reaction was complete the products were separated by trap-to-trap distillation. The yields in the reactions were not determined accurately but appeared to be nearly quantitative in that all of the $BrOSO_2F$ reacted to form BrCl and a fluorosulfate. The reactions are summarized in Table I. More explicit details are given below.

Infrared spectra were taken with a 10-cm Pyrex glass cell fitted with silver chloride windows and a small trap. When the vapor pressure of the compounds was less than a few millimeters at 22°, some of the compound was pumped under vacuum into the trap cooled to the temperature used for separating the compound. The spectrum was then taken of the gas in equilibrium with the liquid in the trap after warming the cell to 22°. Some of the compounds or their decomposition products reacted with the silver chloride windows. For $SOClOSO_2F$, $SO(OSO_2F)_2$, and $SiCl_2(OSO_2F)_2$ the infrared spectra were taken with a thin film of Halocarbon wax (series 1500) on the cell windows. A window with a film of nearly equal thickness was used as a reference.

A Varian Model 4311 B high-resolution nuclear magnetic resonance spectrometer was used to determine the nmr spectra at 40 Mc. Trichlorofluoromethane was used as an internal standard. The nmr samples were prepared by attaching an nmr sample tube to the bottom of a trap. The compound was then pumped under vacuum through the trap cooled to the temperature used to separate the compound. After the appropriate amount of sample had been collected, $CFCl_3$ was condensed in at −183° and the nmr sample tube was sealed under vacuum. Oxalyl fluorosulfate was only slightly soluble in $CFCl_3$ but it was soluble in a mixture of $CFCl_3$ and $[C(O)Cl]_2$. The sample used contained about 25% $CFCl_3$, 25% $[C(O)Cl]_2$, and 50% $[C(O)OSO_2F]_2$.

Molecular weights were determined by Regnault's method for compounds having sufficient vapor pressure at 22°. Determinations were made on successive fractions of each sample.

Melting points were taken in a 1-mm tube using a setup similar to that used for the preparation of nmr samples. The nmr sample tube was replaced by a 1-mm tube at the bottom of a trap and the sample was collected in a similar manner. The temperature was measured using a copper–constantan thermocouple.

Analysis of the compounds was carried out by hydrolyzing a weighed amount with standard aqueous sodium hydroxide (3.1840 *N*) at 100° for 3 hr. Aliquots of the resulting solutions were then analyzed for the amount of base consumed on hydrolysis, sulfate, fluoride, chloride, and phosphate. The determinations were made using standard methods.[8] The analytical results are summarized in Table II.

Preparation of $[C(O)OSO_2F]_2$ and $C(O)ClC(O)OSO_2F$.—Oxalyl chloride (24.0 mmol) was condensed onto an equimolar amount of $BrOSO_2F$. On warming to −2° a smooth reaction took place forming a red-yellow gas and liquid. The reaction mixture was then held at 0° while pumping off the volatile products through traps at −14 and −183°. The infrared spectrum of the material in the −183° trap showed the presence of BrCl and unreacted $[C(O)Cl]_2$ with small amounts of $C(O)Cl_2$ and

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[2] Department of Chemistry, Northeastern University, Boston, Mass. 02115.

[3] J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 352 (1960).

[4] W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2**, 496 (1963).

[5] B. L. Earl, B. K. Hill, and J. M. Shreeve, *ibid.*, **5**, 2184 (1966).

[6] J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, **7**, 124 (1963).

[7] A by-product (SO_3F_2) in the preparation of $S_2O_6F_2$ is explosive: see D. D. Des Marteau and G. H. Cady, *Inorg. Chem.*, **6**, 416 (1967).

[8] S. Charlot and D. Bezier, "Quantitative Inorganic Analysis," 3rd ed, English translation, John Wiley and Sons, Inc., New York, N. Y., 1957, pp 424, 428, 533, 583.

TABLE I

SUMMARY OF $BrOSO_2F$ REACTIONS

Chloride[a]	$Br-OSO_2F$[a]	Temp, °C	Major products[a]
$[C(O)Cl]_2$ (24.0)	24.0	−2	BrCl (24.0), $C(O)ClC(O)OSO_2F$ (13.0), $[C(O)OSO_2F]_2$ (5.6)
$CFCl_3$ (83.0)	30.0	−55	BrCl (30.0), $CFCl_2OSO_2F$ (25.0), $CFCl(OSO_2F)_2$ (2.5)
$CFCl_3$ (20.0)	40.0	−55	BrCl (40.0), $CFCl(OSO_2F)_2$ (20.0)
CCl_4 (8.4)	33.0	−22, 22 (1 hr)	BrCl (33.0), $C(OSO_2F)_4$ (8.2)
CCl_4 (11.0)	33.0	−22	BrCl (33.0), $CCl(OSO_2F)_3$ (11.0)
CCl_4 (6.0)	12.0	−22	BrCl (12.0), $CCl_2(OSO_2F)_2$ (3.0), CCl_3OSO_2F (1.5), $CCl(OSO_2F)_3$ (1.5)
CCl_4 (30.0)	6.5	−22	BrCl (6.5), CCl_3OSO_2F (3.5), $CCl_2(OSO_2F)_2$ (1.5)
$SOCl_2$ (11.0)	22.0	−50	BrCl (22.0), $SO(OSO_2F)_2$ (10.5)
$SOCl_2$ (60.0)	15.0	−50	BrCl (15.0), $SOClOSO_2F$ (7), $SO(OSO_2F)$ (4)
$POCl_3$ (28.0)	25.0	65 (3 days)	BrCl (25.0), $POCl_2OSO_2F$ (24.0)
$POCl_3$ (6.6)	13.0	65 (7 days)	BrCl, $POCl_2OSO_2F$, $POCl(OSO_2F)_2$[b]
$SiCl_4$ (12.0)	24.0	−30	BrCl (24.0), $SiCl_2(OSO_2F)_2$ (11.0)

[a] Millimoles. [b] See Experimental Section.

TABLE II

ANALYTICAL DATA

	% Cl		% F		% S		Moles of OH^-/mole	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$CFCl_2OSO_2F$	35.03	35.05	18.65	18.90	15.80	15.98	7.98	8.00
$CFCl(OSO_2F)_2$	13.50	13.40	20.65	21.53	24.10	24.20	9.93	10.00
$CCl(OSO_2F)_3$	10.85	10.30	15.94	16.53	26.00	27.90	11.86	12.00
$C(OSO_2F)_4$			18.45	18.62	31.30	31.40	14.30	14.00
$C(O)ClC(O)OSO_2F$	18.17	18.63	10.16	9.48	16.30	16.78	5.98	6.00
$[C(O)OSO_2F]_2$			15.23	14.94	24.80	25.20	7.96	8.00
$POCl_2OSO_2F$[a]	34.40	32.70	8.62	8.76	14.43	14.78	8.36	8.00
$SiCl_2(OSO_2F)_2$	23.74	23.84	12.46	12.80	21.20	21.60	8.05	8.00
$SO(OSO_2F)_2$			15.30	15.42	38.20	39.05	7.99	8.00

[a] *Anal.* Calcd for $POCl_2OSO_2F$: P, 14.25. Found: P, 14.21.

$S_2O_5F_2$.[9] Pure $C(O)ClC(O)OSO_2F$ (70%) collected as a colorless liquid in the −14° trap and $[C(O)OSO_2F]_2$ (30%) crystallized in the reactor. The vapor pressures of the compounds were approximately 7 and <1 mm at 22°. Oxalyl fluorosulfate sublimed readily forming large transparent crystals which melted at 57–59° under 1 atm pressure of dry air. Oxalyl chlorofluorosulfate formed white crystals which melted at −17.9 ± 0.5°. Vapor density for $C(O)ClC(O)OSO_2F$: calcd, 190.46; found, 189.5.

Preparation of $CFCl_2OSO_2F$ and $CFCl(OSO_2F)_2$.—Trichlorofluoromethane (83.0 mmol) was condensed onto $BrOSO_2F$ (30.0 mmol) and warmed to −55°. A rapid reaction occurred forming BrCl. The reaction mixture was then held at −25° and pumped through traps at −45 and −183° until approximately 90% of the mixture had distilled. The infrared spectrum of the material collected in the −183° trap indicated large amounts of BrCl and unreacted $CFCl_3$ with small amounts of COClF,[10] $S_2O_5F_2$, and $CFCl_2OSO_2F$. Most of the $CFCl_2OSO_2F$ collected in the −45° trap and was contaminated with BrCl. The latter was removed by repeatedly warming to 22° and then cooling to −35° and pumping on the material momentarily while cold. The products remaining in the reaction bulb were $CFCl_2OSO_2F$ and $CFCl(OSO_2F)_2$. Pure $CFCl(OSO_2F)_2$ was prepared by reaction of $CFCl_3$ (20.0 mmol) with $BrOSO_2F$ (40.0 mmol) at −55°. The reaction products were pumped through traps at −25 and −183°. The infrared spectrum of the material in the −183° trap was that of BrCl with small amounts of $S_2O_5F_2$, COClF, and $CFCl(OSO_2F)_2$. Pure $CFCl(OSO_2F)_2$ collected in the −25° trap.

Chlorofluorobis(fluorosulfato)methane formed a glass on cooling to −100°, but $CFCl_2OSO_2F$ formed white crystals which melted at −90.4 ± 0.5°. The vapor pressures at 22° were approximately 7 and 50 mm, respectively. Vapor density for $CFCl_2OSO_2F$ and $CFCl(OSO_2F)_2$: calcd, 200.96 and 264.57; found, 199.5 and 266.4.

Preparation of $C(OSO_2F)_4$ and $CCl(OSO_2F)_3$.—Carbon tetrachloride (8.4 mmol) was allowed to condense on to $BrOSO_2F$ (33.0 mmol), and the mixture was then warmed to −22°. After initial reaction stopped, the mixture was warmed to 22° and allowed to stand for 1 hr. The products were then pumped under vacuum through traps at 0 and −183°. The products in the −183° trap were BrCl with small amounts of CO_2, $S_2O_5F_2$, and $CO(OSO_2F)_2$.[11] Pure $C(OSO_2F)_4$ collected in the 0° trap.

Pure $CCl(OSO_2F)_3$ was prepared by reaction of CCl_4 (11.0 mmol) with $BrOSO_2F$ (33.0 mmol) at −22°. The products were separated by pumping under vacuum through traps at −15 and −183°. The infrared spectrum of the volatile material in the −183° trap showed the presence of large amounts of BrCl, with a small amount of $COCl_2$, $S_2O_5F_2$, CO_2, and $COClOSO_2F$.[12] Pure $CCl(OSO_2F)_3$ collected as a white solid in the −15° trap. Tetrakis(fluorosulfato)methane and $CCl(OSO_2F)_3$ were colorless liquids which had <1 and ~2 mm vapor pressure at 22°. Both formed white crystalline solids which melted at −11.3 ± 0.5 and −7.0 to −5.7°, respectively.

Formation of $CCl_2(OSO_2F)_2$ and CCl_3OSO_2F.—These compounds could not be obtained pure because of their instability and the difficulty in separating a mixture of $CCl_2(OSO_2F)_2$ and CCl_3OSO_2F. The reaction of $BrOSO_2F$ (12.0 mmol) with CCl_4 (6.0 mmol) at −22° formed about 50% $CCl_2(OSO_2F)_2$, 25% CCl_3OSO_2F, and 25% $CCl(OSO_2F)_3$ based on the F^{19} nmr. The sample was collected by pumping through traps at −22 and −183°. The volatile products in the −183° trap were BrCl with small amounts of $S_2O_5F_2$, $COCl_2$, and CO_2. The reaction of $BrOSO_2F$ (6.5 mmol) with CCl_4 (30.0 mmol) at −30° formed about 70% CCl_3OSO_2F based on the F^{19} nmr. The sample was collected by pumping slowly through traps at −25 and −183°. The products in the −183° trap were shown by infrared analysis to be BrCl and unreacted CCl_4 with small amounts of $COCl_2$, $S_2O_5F_2$, and CO_2.

Preparation of $SO(OSO_2F)_2$ and $SOClOSO_2F$.—Thionyl fluorosulfate was prepared by reaction of $SOCl_2$ (11.0 mmol) with $BrOSO_2F$ (22.0 mmol) at −50°. After the rapid reaction had stopped, the products were pumped through traps at −20 and −183°. The −183° trap contained large amounts of BrCl with some SO_2, $S_2O_5F_2$, and other sulfur oxyhalides. Thionyl fluorosulfate collected as a colorless liquid in the −20° trap. It had <1 mm vapor pressure at 22° and formed a glass when cooled to low temperature.

Thionyl chlorofluorosulfate was not obtained pure. A sample which was about 65% $SOClOSO_2F$ and 35% $SO(OSO_2F)_2$ was prepared by reaction of $SOCl_2$ (60.0 mmol) with $BrOSO_2F$ (15.0 mmol) at −50°. The sample was collected by pumping slowly through traps at −20 and −183°. The products in the −183°

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[9] Spectrum of $S_2O_5F_2$: 1500, 1248, 872, 824, 735, and 550 cm^{-1}.

[10] K. Nakomoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[11] M. Lustig, *Inorg. Chem.*, **4**, 1828 (1965).

[12] R. Cauble and G. H. Cady (unpublished results) give the spectrum as: 1830, 1493, 1250, 1015, 870, 840, and 782 cm^{-1}.

trap were BrCl and unreacted $SOCl_2$ with some SO_2, $S_2O_5F_2$, and other sulfur oxyhalides.

Preparation of $POCl_2OSO_2F$ and $POCl(OSO_2F)_2$.—Phosphoryl chloride (28.0 mmol) was condensed onto $BrOSO_2F$ (25.0 mmol) in the usual manner. On warming to 22°, $BrOSO_2F$ dissolved in the $POCl_3$ forming a viscous yellow solution which slowly evolved BrCl. The mixture was then held at 65° for 3 days. The reaction products were separated by pumping through traps at 0 and −183°. The infrared spectrum of the material in the −183° trap was that of BrCl with some unreacted $POCl_3$ and small amounts of SiF_4, $S_2O_5F_2$, and $POCl_2F$.[13] The $POCl_2OSO_2F$ collected as a pale yellow liquid in the 0° trap. The yellow color was due to impurities but the amount was very small. The vapor pressure of $POCl_2OSO_2F$ was <1 mm at 22°. The substance crystallized with considerable difficulty to a white solid which melted at −58°.

Phosphoryl chlorodi(fluorosulfate) was formed when $POCl_3$ (6.6 mmol) reacted with $BrOSO_2F$ (13.0 mmol) at 65° for 7 days. The reaction mixture was then pumped on at 22° through a trap at −183° until a colorless liquid remained in the bulb. The material collected in the −183° trap was largely BrCl, with some $S_2O_5F_2$, $POCl_2F$, and probably unreacted $POCl_3$ and $BrOSO_2F$. The F^{19} nmr showed that the colorless liquid was approximately an equimolar mixture of $POCl_2OSO_2F$ and $POCl(OSO_2F)_2$ with a small amount of some unidentified impurities. The nmr consisted of a resonance identical with that observed for $POCl_2OSO_2F$ (ϕ −50.4) and another single resonance at ϕ −52.1. The areas were in the approximate ratio of 1:2.

Preparation of $SiCl_2(OSO_2F)_2$.—Silicon tetrachloride (12.0 mmol) was added to $BrOSO_2F$ (24.0 mmol) and warmed to −30°. A reaction took place forming a red-black solid in the liquid $SiCl_4$. The red-black solid reacted slowly at −30° to give a yellow-red solution and gas. After reaction was complete, the products were pumped through traps at −22 and −183°. The infrared spectrum of the material collected in the −183° trap was that of BrCl with small amounts of SiF_4, $S_2O_5F_2$, and other compounds containing Si–F bonds. Dichlorobis(fluorosulfato)silane collected as a colorless liquid in the −22° trap. The vapor pressure of the $SiCl_2(OSO_2F)_2$ was approximately 7 mm at 22°. The compound formed a glass on cooling. Vapor density for $SiCl_2(OSO_2F)_2$: calcd, 297.05; found, 299. Attempts to prepare $SiCl_3OSO_2F$ and $SiCl(OSO_2F)_3$ were unsuccessful.

Results and Discussion

The reaction of $BrOSO_2F$ with covalent chlorides provides a convenient new method for the preparation of compounds containing the fluorosulfate group. Previous attempts have been made to prepare some of the compounds reported (or very similar ones) without success. These attempts have included the reactions of $S_2O_6F_2$ with CCl_4, SOClF,[14] CBr_4,[11] $POCl_3$,[15] and $SiCl_4$,[16] and of $SiCl_4$ with $HOSO_2F$.[17]

Covalent bromides appeared to react in a manner analogous to the chlorides forming bromine. However, the reactions had the disadvantage of being so highly exothermic that frequently the desired product decomposed. Furthermore it was difficult to separate bromine from some of the products.

Several of the compounds reported were unstable at ambient temperature. The decompositions were not studied quantitatively but appeared to be of two types

$$MOSO_2F = MF + SO_3$$

$$M(OSO_2F)_2 = MO + S_2O_5F_2$$

Table III

Infrared Spectra (cm⁻¹)

	S=O Asym	S=O Sym	S—F	Other
$[C(O)OSO_2F]_2$	1490 s	1250 s	840 s	1850, 1825 m (C=O), 1180 m, br, 520 m
$ClC(O)C(O)OSO_2F$	1498 s	1253 s	840 s	1823, 1740 s (C=O), 1140 s, 920 s, 782 m, 555 s
$CFCl_2OSO_2F$	1490 s	1250 s	846 s	1137 sh, 1115 s, 1083 m, 997 s, 937 s, 693 m, 603 m, 575 s, 545 w, 510 w
$CFCl(OSO_2F)_2$	1493 s	1253 s	838 s	1170 m, 1150 m, 1055 s, 1030 s, 930 w, 795 m, 725 w, 640 w, 567 m
$C(OSO_2F)_4$	1502 s	1260 s	843 s	1090 s (C—O), 624 s, 585 m
$CCl(OSO_2F)_3$	1494 s	1252 s	835 s	1042 s (C—O), 1020 sh, 782 m, 642 m, 610 w, 570 w, 550 m
$CCl_2(OSO_2F)_2$[a,b]	1490 s	1250 s	835 s	990 s (C—O), 550 s
CCl_3OSO_2F[a,b]	1485 s	1245 s	840 s	955 s (C—O), 560 s
$SiCl_2(OSO_2F)_2$	1473 s	1243 s	835 s	989 s (Si—O), 645 s (Si—Cl), 515 s
$SO(OSO_2F)_2$[b]	1451 s	1245 s	845 s	550 s
$SOClOSO_2F$[a,b]	1470 s	1235 s	830 s	670 m, 500 m, 450 s
$POCl_2OSO_2F$	1480 s	1241 s	847 s	1345 s (P=O), 907 s (P—O), 725 m, 630 s (P—Cl), 535 s
$POCl(OSO_2F)_2$[a]	1480 s	1240 s	840 s	1370–1390 m (P=O), 920 s (P—O), 640 m (P—Cl), 540 s

[a] From an impure sample contaminated with preceding compound. [b] A good infrared spectrum was very difficult to obtain because decomposition products were always present. The data presented here are a composite of many different spectra, and some weaker absorptions are probably absent.

Table IV

Nuclear Magnetic Resonance Data

	ϕ	Assignment
$[CO(O)OSO_2F]_2$	−48.2	SF
$ClC(O)C(O)OSO_2F$	−47.0	SF
$CFCl_2OSO_2F$	−49.2, 14.5	SF, CF[a]
$CFCl(OSO_2F)_2$	−51.4, 31.6	SF, CF[b]
$C(OSO_2F)_4$	−51.9	SF
$CCl(OSO_2F)_3$	−50.9	SF
$CCl_2(OSO_2F)_2$[d,h]	−50.7	SF
CCl_3OSO_2F[d,h]	−50.5	SF
$SiCl_2(OSO_2F)_2$[e]	−46.6	SF
$SO(OSO_2F)_2$[f]	−52.7	SF
$SOClOSO_2F$[f,h]	−50.1	SF
$POCl_2OSO_2F$	−50.2	SF[c]
$POCl(OSO_2F)_2$[g,h]	−52.1	SF

[a] Doublet of doublets, J_{FF} = 8.85 cps. [b] Doublet and a triplet, J_{FF} = 9.55 cps. [c] Doublet, J_{PF} = 3.8 cps. [d] After 20 hr at 22° an additional resonance at ϕ −49.0 appeared. [e] Other resonances of low and varying intensity at ϕ −45.1, −47.3, −47.9, 149.5, 150.0, and 157 appeared in various samples. [f] After 20 hr at 22° several additional resonances appeared at ϕ −49.7 to −50.8 and −75.0 and −77.0 [ϕ −77.0 was absent for $SO(OSO_2F)_2$]. [g] Other small resonances at ϕ −50.6, −50.9, and −17.4 (doublet). [h] Contaminated with preceding compound.

The first type was observed for $SiCl_2(OSO_2F)_2$ and the second type for $CCl_{4-x}(OSO_2F)_x$ (x = 1–4). Both modes of decompositions appeared to take place with $SO(OSO_2F)_2$ and $SOClOSO_2F$. The decompositions were observed by the infrared and nmr spectra taken at 22° as a function of time. The rates of decomposition were very slow for $C(OSO_2F)_4$ and $CCl(OSO_2F)_3$ but moderate for the other unstable compounds.

The infrared spectra of the new compounds are summarized in Table III. All of the compounds showed bonds characteristic of the fluorosulfate group. In

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agreement with other fluorosulfates, the S=O symmetric and asymmetric and S—F stretching frequencies occurred over a narrow range.[4,11,14,18,19] Some other tentative assignments are also given.

The F^{19} nmr results are summarized in Table IV. All of the compounds showed an F^{19} resonance in the fluorosulfate region at about ϕ −50.[20] The F^{19} resonance for the fluorosulfate group was shifted downfield as successive replacement of chlorine by fluorosulfate occurred. For the thionyl fluorosulfates the S–F resonance was slightly broadened. For $SiCl_2(OSO_2F)_2$ the high-resolution nmr showed a sharp resonance with a broad resonance slightly downfield.

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CONTRIBUTION FROM THE CLIMAX MOLYBDENUM COMPANY OF MICHIGAN,
RESEARCH LABORATORY, ANN ARBOR, MICHIGAN 48105

Molybdovanadophosphoric Acids and Their Salts.
I. Investigation of Methods of Preparation and Characterization

BY GEORGE A. TSIGDINOS AND C. J. HALLADA

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By the use of improved procedures, the free heteropoly acids $H_4[PMo_{11}VO_{40}]\cdot 34H_2O$, $H_5[PMo_{10}V_2O_{40}]\cdot 32H_2O$, and $H_6[PMo_9V_3O_{40}]\cdot 34H_2O$ were prepared reproducibly as orange crystalline solids. Potentiometric titration measurements showed that the number of replaceable hydrogen ions in these free acids is four, five, and six, respectively. The salts $Na_4[PMo_{11}VO_{40}]\cdot 8H_2O$ and $(NH_4)_3H[PMo_{11}VO_{40}]\cdot 7.5H_2O$ were prepared for the first time. The molybdovanadophosphate anion had unusually high hydrolytic stability. Infrared, visible, and ultraviolet spectra were obtained for these salts. Thermogravimetric and differential thermal analyses were performed on $H_4[PMo_{11}VO_{40}]\cdot 32H_2O$ and $Na_4[PMo_{11}VO_{40}]\cdot 8H_2O$. Potentiometric titration measurements with methanol as the solvent and $NaOCH_3$ as the titrant showed that the $H_4[PMo_{11}VO_{40}]$ acid is tetraprotic in solvents with low dielectric constants.

Introduction

The heteropolymolybdovanadates constitute an important class of heteropoly compounds on which only limited research has been conducted. The most well known of these heteropolymolybdovanadates is the 10-molybdo-2-vanadophosphate(V) anion prepared by Kokorin.[1] In 1964, Souchay and co-workers[2-4] were able to replace molybdenum in the 12-molybdophosphate anion structure by up to three pentavalent vanadium atoms,[2] but the compounds prepared were not fully characterized and no analytical data were given.[4]

In work published in 1964, Krivy and Krtil[5] assigned a basicity of 3 to the 10-molybdo-2-vanadophosphoric acid on the basis of radiometric titration studies employing cesium-137. They gave the salt the formula $Cs_3H_4[P(Mo_2O_7)_5V_2O_6]$.

The present work elucidates the properties of the free acids and salts of the anions $[PMo_{11}VO_{40}]^{4-}$, $[PMo_{10}V_2O_{40}]^{5-}$, and $[PMo_9V_3O_{40}]^{6-}$. The desired free acids were obtained in a reproducible manner by using detailed, improved procedures. Further characterization of the properties of these anions was accomplished by physicochemical means discussed in this paper.

Experimental Section

Prepurified grade sodium metavanadate containing 2% water (Matheson Coleman and Bell) was used without further purification. All other reagents used were Baker Analyzed grade.

Preparation of Compounds. (a) **11-Molybdo-1-vanadophosphoric Acid.**—Na_2HPO_4, 7.1 g, was dissolved in 100 ml of water and mixed with 6.1 g of sodium metavanadate that had been dissolved by boiling in 100 ml of water. The mixture was cooled and acidified to a red color with 5 ml of concentrated sulfuric acid. To this mixture was added a solution of 133 g of $Na_2MoO_4\cdot 2H_2O$ dissolved in 200 ml of water. Finally, 85 ml of concentrated sulfuric acid was added slowly with vigorous stirring of the solution. With this addition the dark red color changed to a lighter red. The heteropoly acid was then extracted with 400 ml of ethyl ether after the water solution was cooled. In this extraction, the heteropoly etherate was present as a middle layer; the bottom layer (water) was yellow and probably contained vanadyl species. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The orange solid that remained was dissolved in 50 ml of water, concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulfuric acid, and then allowed to crystallize further. The orange crystals that formed were filtered, washed with water, and air dried. The yield was 28 g. The crystalline acid effloresces slowly at room temperature; thus the amount of water of crystallization varied slightly from sample to sample. *Anal.* Calcd for $H_4[PMo_{11}VO_{40}]\cdot 32.5H_2O$: P, 1.31; Mo, 44.60; V, 2.15; H_2O, 24.71. Found: P, 1.31; Mo, 44.54; V, 2.68; H_2O (based on Mo), 24.86. The molar ratios are Mo to P, 10.97 to 1.00; and V to P, 1.24 to 1.00. Similar analyses were

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