containing dissolved $Co(NO_3)_2$ and which was colored blue by the cobalt. Eluants used were $LiNO_3$–KNO_3 eutectic and $LiNO_3$–KNO_3 eutectic containing about 20 wt % of an equimolar mixture of LiCl and KCl.

Results

Sodium borate glass of composition $Na_2O \cdot 3B_2O_3$ showed good selectivity between solutes, but a rather slow exchange rate. Good selectivity would be expected of borate glasses in this composition region, since molten sodium borate shows the best selectivity at about this same $Na_2O:B_2O_3$ ratio.[21] Exchange rate measurements with Na^{22}-labeled phases showed that higher temperature and smaller particle size allowed equilibrium to be approached more quickly. However, the exchange rate was not really satisfactory until a borate glass was prepared which had been presaturated with salt while molten. The composition of this glass in mole % was 21.8 Na_2O, 60.2 B_2O_3, and 18.0 NaCl. Na^{22} reached nearly its equilibrium value between molten $NaNO_3$ and this glass of 60–100 mesh size in 45 min at 500°. Table I shows K_d values of the solutes between this glass and molten $NaNO_3$ at 550°. Shown for comparison are equilibrium K_d values of the same solutes between molten borate glass of the same $Na_2O:B_2O_3$ ratio and molten NaCl at 830°.[21]

TABLE I

COMPARISON OF K_d[a] VALUES FOR SALT-SATURATED BORATE GLASS OF $Na_2O:B_2O_3$ RATIO 0.326: SOLID GLASS IN $NaNO_3$ *vs.* LIQUID GLASS IN NaCl

	80–115 mesh glass in $NaNO_3$ at 550°				Liquid borate in NaCl at 830°
Solute	K_d (adsorption)	Equil. time, hr	K_d (desorption)	Equil. time, hr	K_d (equilibrium)[21]
Cs^+	0.0015	0.5	...	...	0.26
Na^+	0.84[b]	...	0.84[b]	...	0.55
Ba^{2+}	1.6	0.5	17	1	2.2
Sr^{2+}	191[c]	2	204	0.5	5.7
Eu^{3+}	3900	1	4000	1	2600

[a] K_d = (moles of solute per gram of glass)/(moles of solute per gram of salt). [b] Calculated from analysis of macro constituents. [c] 450°.

The nitrate eutectic apparently eluted no cobalt from the column but the melt containing chloride promptly removed the blue cobalt, leaving only a small black oxide residue.

Discussion

From even these preliminary results it appears that borate glasses are more generally effective than any other exchanger yet tested in molten salts. They show higher selectivity for solute ions in molten nitrate than do any of the other exchangers for which selectivity has been measured and even show a wider spread of K_d values than do molten borates with molten NaCl.[21]

The manner in which borate glasses show selectivity toward cations is probably the result of the special nature of the functional groups in the borate network. Data obtained so far indicate that the order of selectivity of high-alkali borates, both molten and solid, for uncomplexed cations in fused-salt solvents is that of increasing field strength of the cation. This order and the magnitude of the K_d values suggest a distribution mechanism based on the attraction of unsolvated cations to sites of highly localized negative charge within the borate network. A different selectivity sequence is found with zeolites,[2] where selectivity is based more upon a cation's size than its charge. From the structure of zeolites[23] it may be concluded that the functional groups for ion exchange are $Al(O/2)_4^-$ tetrahedra, where O/2 denotes a shared, bridging oxygen atom. The negative charges on these tetrahedra are not highly localized, and high field-strength cations do not seem to prefer greatly this environment to that of a nitrate melt. In borate glasses, the functional groups probably consist mostly of $B(O/2)_4^-$ and a few $B(O/2)_2O^-$ groups. The negative charge on these groups is more localized than that of the $Al(O/2)_4^-$ group: in the case of $B(O/2)_2O^-$ because the charge is centered on the nonbridging oxygen and in the case of $B(O/2)_4^-$ because this group is smaller than $Al(O/2)_4^-$ and probably not as symmetrical. Actually, the main reason for the high selectivity of borates for highly charged cations may be the pairing of negative charges in polyborate groups. Evidence of such pairing comes from the observation in molten silver borate that the silver ions seem to occur in pairs.[24] Molten and solid borates tend to retain elements of polyborate structural groups which are present and identifiable in crystalline borates.[25] Groups which contain paired negative charges and which may prevail in the borate glasses used here are $B_8O_{13}^{2-}$ and $B_4O_7^{2-}$, evidence for which comes from the treatment of phase diagram data in the Na_2O–B_2O_3 system.[25]

Ion-exchange separations on borate glasses should be possible from a variety of fused-salt solvents. Distribution behavior of individual solutes will differ greatly according to the solvent system and glass formulation.

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Phosphoryl Fluorosulfate

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The new compound phosphoryl fluorosulfate, $PO(OSO_2F)_3$, has been prepared by the reaction of peroxydisulfuryl difluoride with phosphoryl bromide. It

$$POBr_3 + 6S_2O_6F_2 = PO(OSO_2F)_3 + 3Br(OSO_2F)_3$$

appears that phosphoryl fluorosulfate is the first example of a compound in which a fluorosulfate group is

TABLE I

FLUORINE NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

	$PO(OSO_2F)_3$	$POF(OSO_2F)_2$		POF_2OSO_2F		POF_3
δ, ppm	-130	-127	-7.6	-126	1.8	12.4[b]
Type of peak	Singlet	Doublet	2 triplets	Triplet	2 doublets	Doublet
Assignment	S–F	S–F	P–F	S–F	P–F	PF
J_{FF}, cps	...	3.2		3.3		
J_{PF}, cps	...		1100		1085	1055

[a] δ relative to CF_3COOH used as an external reference. [b] A value given in the literature is δ 15.8 ppm.[9]

attached to phosphorus. Various attempts have been made to prepare such compounds by methods including the reaction of phosphorus pentachloride with fluorosulfuric acid,[1] phosphorus trifluoride with peroxydisulfuryl difluoride,[2] and phosphorus trichloride or phosphoryl chloride with peroxydisulfuryl difluoride.[3]

Phosphoryl fluorosulfate is a colorless, slightly volatile liquid melting at approximately −24°. On heating at 100° it decomposes slowly to sulfur trioxide, phosphoryl fluoride, and two new compounds tentatively identified as phosphoryl fluoride di(fluorosulfate), $POF(OSO_2F)_2$, and phosphoryl difluoride fluorosulfate, POF_2OSO_2F.

$$PO(OSO_2F)_3 = POF_{3-x}(OSO_2F)_x + (3 - x)SO_3 \quad x = 0, 1, \text{ or } 2$$

Experimental Section

Reagents.—Peroxydisulfuryl difluoride was prepared by a method described in the literature.[2] Phosphoryl bromide was obtained from a commercial source and was purified by distillation.

Preparation of $PO(OSO_2F)_3$.—The reaction of $S_2O_6F_2$ with $POBr_3$ was carried out many times under a variety of conditions. A specific run which gave good results will be described. Phosphoryl bromide (12.80 g, 0.0446 mole) was distilled into a 100-ml Pyrex bulb fitted with a Fisher–Porter Lab Crest valve having a Teflon stem. The bulb was then flamed off from the vessel containing the main supply of $POBr_3$. A 3.5-g portion of $S_2O_6F_2$ was then added by vacuum transfer to the reactor held at −78° behind a $^1/_8$-in. Plexiglas safety shield. The bulb was transferred directly from the −78° bath to a salt water–ice bath at −15 to −10° (not above −10°) behind the safety shield in a fume hood and allowed to remain at this temperature until the reaction appeared to have stopped (about 1 hr). The bulb was then removed from the bath and permitted to warm to room temperature behind the safety shield in the hood. A safety glass door on the hood was kept closed except when the reaction vessel was being handled with tongs while wearing heavy leather gloves. In cases when the reaction became violent and explosive, even when run on a larger scale than that described here, the Plexiglas shield remained undamaged. The greatest hazard appeared to exist when placing the reaction vessel in the bath at −15 to −10° and until the system had warmed to room temperature. The bulb was later weighed to determine the size of the portion of $S_2O_6F_2$. In preparation for adding the next aliquot the bulb was attached to the vacuum line, cooled to −78°, and evacuated to remove the small amount of oxygen present. The next aliquot of $S_2O_6F_2$ was then added and allowed to react in the manner described above. In the run now being described the successive aliquots after the first had the weights 7.5, 6.3, 9.9, and 27.4 g. This gave a total of 0.276 mole of $S_2O_6F_2$. Danger from explosion was greatest for the first aliquots added. The reaction products then appeared to be $PO(OSO_2F)_3$ and Br_2. The last aliquots were larger because they converted Br_2 to $Br(OSO_2F)_3$ without liberating much heat. It is recommended that a beginner use smaller aliquots during the first stages of this preparation than those indicated above or that the reaction be run on a smaller scale.

A stepwise procedure was used because violent explosions occurred when the required amount of $S_2O_6F_2$ was added at one time to amounts of $POBr_3$ greater than about 3 g. When the reaction was allowed to occur rapidly the following by-products were found: O_2, POF_3, $S_2O_5F_2$, SO_3. After completion of the reaction the product, other than nonvolatile $Br(OSO_2F)_3$, was removed by pumping at room temperature through traps held at −15 and −183°, respectively. The $PO(OSO_2F)_3$ distilled very slowly and collected as an orange liquid in the −15° trap. The material collected at −183° was discarded. The crude $PO(OSO_2F)_3$ had an orange color because of the presence of $BrOSO_2F$. This was removed by adding approximately 2 g of $S_2O_6F_2$ and allowing the mixture to remain at room temperature for a few minutes until the color became less intense. The material was then pumped at room temperature as before through traps at −15 and −183°. The liquid collecting at −15° was again treated with approximately 2 g of $S_2O_6F_2$ and the above process was repeated. After four successive treatments in this manner the liquid collecting in the −15° trap was pure colorless $PO(OSO_2F)_3$. This stepwise method of purification was used because the colored impurity was not completely removed in one step. After each distillation a residue of nonvolatile $Br(OSO_2F)_3$ remained. It appeared that the colored contaminant, $BrOSO_2F$, probably was formed by decomposition of $Br(OSO_2F)_3$. Addition of $S_2O_6F_2$ converted $BrOSO_2F$ back to $Br(OSO_2F)_3$.[4] The amount of $Br(OSO_2F)_3$ formed in the initial reaction was always less than that theoretically possible from the reactants. When the amounts of $Br(OSO_2F)_3$ formed from the purification steps were added to the initial weight of $Br(OSO_2F)_3$, the total weight was close to theoretical (calcd 50.5 g, found 50 g). The yield of $PO(OSO_2F)_3$ after purification was approximately 14.0 g (theoretical 15.3 g).

The addition of 3 moles of $S_2O_6F_2$ per mole of $POBr_3$ to form $PO(OSO_2F)_3$ and $BrOSO_2F$ was an unsatisfactory preparative method because the products could not be separated satisfactorily. The reaction of 1.5 moles of $S_2O_6F_2$ per mole of $POBr_3$ to yield $PO(OSO_2F)_3$ and Br_2 might be a successful method but this process was not tried.

Chemical Analysis.—Phosphoryl fluorosulfate (3.060 g) was allowed to react with excess aqueous sodium hydroxide (3.184 *N*) at 80° for 12 hr, and the remaining OH^- ion in an aliquot of the resulting solution was then titrated with standard hydrochloric acid. Phosphate was determined colorimetrically as phosphovanadomolybdate, sulfate gravimetrically as barium sulfate, and fluoride by titration with standard thorium nitrate after steam distillation.[5] The following reaction occurred on basic hydrolysis.

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$$PO(OSO_2F)_3 + 12OH^- = PO_4^{3-} + 3SO_4^{2-} + 3F^- + 6H_2O$$

Anal. Calcd for $PO(OSO_2F)_3$: P, 9.06; S, 27.89; F, 16.56; moles of OH^- consumed, 12.0. Found: P, 8.97; S, 27.70; F, 16.70; moles of OH^- consumed, 12.4.

Melting Point.—While phosphoryl fluorosulfate had a tendency to form a glass on cooling, it could be made to form white crystals which melted at approximately −24°.

Infrared Spectrum.—The spectrum was studied using a Beckman IR-10 spectrometer with the sample contained in a 10-cm Pyrex glass cell fitted with silver chloride windows and a small trap. Phosphoryl fluorosulfate was distilled under vacuum into the trap. The infrared spectrum of the vapor in equilibrium with the liquid $PO(OSO_2F)_3$ in the trap was then recorded at 22 and ~45°. The spectra at the two temperatures were identical except for increased intensity at the higher temperature. Absorption bands and some probable assignments were as follows (cm^{-1}): 1493 s, S=O asymmetric stretch; 1396 s, P=O stretch; 1253 s, S=O symmetric stretch; 935 s (shoulder at 980), P—O stretch; 845 s, S—F stretch; 720 w; 540 m; 510 m (s, strong; m, medium; w, weak).

Nmr Spectrum.—Spectra were obtained by use of a Varian Model 4311B high-resolution nmr spectrometer with a 40-Mc oscillator. The ^{19}F nmr spectrum for $PO(OSO_2F)_3$ showed a single absorption in the fluorosulfate region at −130 ppm relative to CF_3COOH as an external reference. No spin–spin coupling was observed between phosphorus and the fluorine attached to sulfur.

Decomposition of $PO(OSO_2F)_3$.—During attempts to purify $PO(OSO_2F)_3$ by vacuum fractional distillation at temperatures above room temperature it was found that decomposition occurred slowly. Four major products were found: POF_3, SO_3, and two compounds tentatively identified as $POF(OSO_2F)_2$ and POF_2OSO_2F. While decomposition was slow even at 100°, significant decomposition probably occurred also at somewhat lower temperatures. The above two phosphoryl fluoride fluorosulfates were not isolated in pure form, but infrared spectra, nmr spectra, and vapor densities strongly supported their existence. The infrared spectrum of a mixture of the two showed the following major absorptions (cm^{-1}): 1495, S=O asymmetric stretch;[6] 1380–1400, P=O stretch;[7] 1255, S=O symmetric stretch;[6] 940–980, P=F and P—O stretches;[7,8] 850, S—F stretch;[6] 520.

The ^{19}F nuclear magnetic resonance spectrum of a sample produced by heating $PO(OSO_2F)_3$ for 2 hr at 100° showed in addition to the absorption for $PO(OSO_2F)_3$ others which could be assigned to POF_3, POF_2OSO_2F, and $POF(OSO_2F)_2$. There were two other absorptions in the fluorosulfate region which may have been caused by sulfur oxyfluorides such as sulfuryl fluoride and pyrosulfuryl fluoride. The nuclear magnetic resonance data are given in Table I. The J_{PF} value for POF_3 agrees well with that of Gutowsky, McCall, and Slichter, and the trend for J_{PF} from POF_3 to $POF(OSO_2F)_2$ agrees well with that observed for POF_3 to $POFCl_2$.[9]

Vapor densities were determined for ten successive fractions evaporated from a mixture of the substances considered to be $POF(OSO_2F)_2$ and POF_2OSO_2F. The first five fractions had densities close to 183 g/GMV (theoretical for POF_2OSO_2F, 184). Following that the vapor pressure of the remaining liquid became less as fractions were removed and the vapor density rose to about 260 (theoretical for $POF(OSO_2F)_2$, 264.1).

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Addition of Hexafluoroacetone to Alkoxysilanes

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The reactions of hexafluoroacetone with compounds containing Si–H and Si–OH bonds have been reported recently. The addition of hexafluoroacetone across the Si–H bond of various methylsilanes and trichlorosilane occurred under the influence of ultraviolet irradiation to give alkoxysilanes.[1] The same reactions

$$R_3SiH + R^1{}_2CO \longrightarrow \underset{\text{I}}{R_3SiOCHR^1{}_2}$$

were observed without ultraviolet irradiation with hydrides of silicon, tin, and germanium.[2] Earlier, the reaction of dipropylsilane with hexafluorocyclobutanone to give dipropylbis(hexafluorocyclobutoxy)silane was observed.[3] The spontaneous reaction of trimethylsilanol with hexafluoroacetone was shown to give 2-trimethylsiloxyhexafluoroisopropyl alcohol (II). The

$$(CH_3)_3SiOH + (CF_3)_2CO \longrightarrow \underset{\text{II}}{(CH_3)_3SiOC(CF_3)_2OH}$$

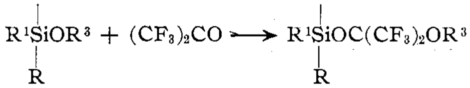
addition of aldehydes (*e.g.*, acetaldehyde, chloral, bromal, etc.) to tributyltin methoxide has been reported to give adducts (III) that are unstable above room temperature and could not be distilled.[4] While

$$\underset{\text{III}}{(C_4H_9)_3SnOCHROCH_3}$$

there is little known about the reaction of perhaloketones with alkoxysilanes, tributyltin methoxide and hexachloroacetone gives the adduct IV, which decomposes at 65°.[5]

$$(C_4H_9)_3SnOCH_3 + (CCl_3)_2CO \rightleftarrows$$
$$(C_4H_9)_4SnOC(CCl_3)_2OCH_3 \longrightarrow (C_4H_9)_3SnCl_3 + CCl_3COOCH_3$$

We have found that the reaction of 1 mole or more of hexafluoroacetone with a wide variety of alkoxysilanes at 100–150° gives 1:1 adducts, V. The adducts are much more stable than the related tin adducts and can be distilled.[5]



$$R^1\overset{\overset{R^2}{|}}{\underset{\underset{R}{|}}{Si}}OR^3 + (CF_3)_2CO \longrightarrow R^1\overset{\overset{R^2}{|}}{\underset{\underset{R}{|}}{Si}}OC(CF_3)_2OR^3$$

V

Va, $R = R^1 = CH_3$; $R^2 = OC_2H_5$; $R^3 = C_2H_5$
Vb, $R = CH{=}CH_2$; $R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$
Vc, $R = C_6H_5$; $R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$
Vd, $R = R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$
Ve, $R = R^1 = OC_2H_5$; $R^2 = (CH_2)_2COOC_2H_5$; $R^3 = C_2H_5$
Vf, $R = R^1 = OCH_3$; $R^2 = (CH_2)_3O\overset{\overset{O}{\|}}{C}C(CH_3){=}CH_2$; $R^3 = CH$
Vg, $R = H$, $R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$

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