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Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Sulfinyl Fluoride: A Reagent for Fluorination and Introduction of the –S(O)F Group

TARIQ MAHMOOD and JEAN'NE M. SHREEVE*

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Sulfinyl fluoride reacts to replace active hydrogen with fluorine in P–H and C–H bonds. However, with >N–H bonds, >NS(O)F is formed, e.g., with piperidine, 2,6-dimethylpiperidine, 2,2,6,6-tetramethylpiperidine, morpholine, 3,5-dimethylmorpholine, and thiomorpholine. Fluorination occurs with oxidatively unsaturated compounds, such as trialkylphosphines and trialkyl phosphites to form difluorophosphoranes. The yields are reduced by side reactions of the phosphorus(III) species with the sulfur and sulfur dioxide that form concomitantly with the fluorination reaction. Sulfinyl fluoride and carbonyl fluoride are compared as fluorinating agents.

Introduction

Current methods for introducing fluorine into a wide range of chemical environments suffer from many major drawbacks. These fluorination processes often require low temperature and special handling, which may involve special equipment. Elemental fluorine or reagents whose preparation require the use of elemental fluorine are hazardous and demand special techniques and equipment. Some reagents also form products that are dangerous or that may be difficult to separate from the desired compound, thus making purification time consuming and sometimes impossible.

We have reported recently the utilization of carbonyl fluoride (COF_2) as a versatile and nondestructive fluorine-transfer reagent.[1] In the present work we report a comparison study of the relative efficacy of sulfinyl fluoride (SOF_2) with that of carbonyl fluoride as a fluorinating agent. A distinct advantage of both reagents is that elemental fluorine is not required in the preparation of either.[2]

Results and Discussion

To learn about the versatility of sulfinyl fluoride as a fluorinating reagent, we have examined its behavior with a variety of oxidatively unsaturated phosphorus(III) compounds as well as with compounds that contain reactive element–hydrogen bonds, such as P–H, N–H, and C–H.

Although PF_3, PCl_3, and $P(OCH_2CF_3)_3$ are oxidatively unsaturated, sulfinyl fluoride, under the mild conditions employed in this study, does not fluorinate or react with them in any way. This lack of reactivity is also noted for COF_2 with PF_3 and PCl_3.[1]

In fact, there is a remarkable similarity in the fluorinating capabilities of these two simple acid fluorides. But because of the inherent difference in the stabilities and reactivities of the byproducts, i.e., CO vs. SO, the number of products from any one system in addition to the fluorinated moiety is interesting and varied with SOF_2. As a consequence, the yields from SOF_2 fluorination may be reduced.

Consider the reaction of SOF_2 with trialkyl phosphites

$$3(RO)_3P + SOF_2 \xrightarrow[25\ ^\circ C,\ 10\ h]{CH_2Cl_2}$$
$$(RO)_3PF_2 + (RO)_3PO + (RO)_3PS + (RO)_2P(O)H\ (tr) \quad (1)$$
$$R\ (\text{yield of } (RO)_3PF_2) = C_2H_5\ (25\%),\ n\text{-}C_4H_9\ (22\%)$$

while with COF_2

$$(RO)_3P + COF_2 \xrightarrow[25\ ^\circ C]{CH_2Cl_2} (RO)_3PF_2 + CO$$
$$R\ (\text{yield}) = C_2H_5\ (72\%),\ n\text{-}C_4H_9\ (70\%)^1$$

The products $(RO)_3PO$ and $(RO)_3PS$ from the reaction of SOF_2 suggest that SO_2 is formed and reacts further with the trialkyl phosphite. In a separate reaction, SO_2 was reacted with $(RO)_3P$ under the same conditions. The products were identified from the reported ^{31}P NMR spectral data.[3]

$$3(RO)_3P + SO_2 \xrightarrow[25\ ^\circ C]{CH_2Cl_2} (RO)_3PS + 2(RO)_3PO$$
$$R = C_2H_5,\ n\text{-}C_4H_9$$

Sulfur dioxide and sulfur result from the disproportionation of sulfur oxide. Since no sulfur was recovered in these reactions, the trialkyl phosphites were mixed with elemental sulfur to determine reactivity. Oxidation of phosphorus(III) to phosphorus(V) occurred quantitatively:[4]

$$(RO)_3P + S \xrightarrow[25\ ^\circ C]{CH_2Cl_2} (RO)_3PS$$
$$R = C_2H_5,\ n\text{-}C_4H_9$$

The trace amounts of the dialkyl phosphonate, $(RO)_2P(O)H$, that are observed in reaction 1 must arise from hydrolysis of $(RO)_3PO$. Reactions of trialkyl phosphites ($R = C_2H_5$, n-C_4H_9) with oxygen gave $(RO)_3PO$ with trace amounts of the hydrolysis product, $(RO)_2P(O)H$.

On the basis of the yields of the products obtained and the SOF_2 recovered in the trialkyl phosphite/SOF_2 reaction, the stoichiometry is 3:1. The difluorophosphoranes that are formed undergo Michaelis–Arbuzov reactions readily at 45 °C:

$$(RO)_3PF_2 \xrightarrow{45\ ^\circ C} (RO)_2P(O)F + C_2H_5F$$
$$R = C_2H_5,\ n\text{-}C_4H_9$$

The behavior of SOF_2 with $(CH_3)_3P$ is similar to that with $(RO)_3P$:

$$3(CH_3)_3P + SOF_2 \rightarrow \underset{25\%}{(CH_3)_3PF_2} + (CH_3)_3PO + (CH_3)_3PS$$

The fact that only a single phosphoryl product is formed supports the premise that oxygen is not a reactive intermediate in these reactions with SOF_2. This assumption is based on earlier work[5] where it was shown that, e.g., tributylphosphine when reacted with elemental oxygen gave $(Bu)_3PO$ (42%), $(Bu)_2P(O)OBu$ (49%), $BuP(O)(OBu)_2$ (6%), and $(BuO)_3PO$ (3%). The products were identified by using vapor-phase chromatography. In our reaction of trimethylphosphine with oxygen, four products were also obtained and identified on the basis of ^{31}P NMR data as $(CH_3)_3PO$, $(CH_3)_2P(O)OCH_3$, $CH_3P(O)(OCH_3)_2$, and $(CH_3O)_3PO$.[3] Sulfur with trimethylphosphine gave rise to only $(CH_3)_3PS$. However, $(C_6H_5)_3P$ with oxygen resulted in only $(C_6H_5)_3PO$, which is in keeping with the low reactivity of arylphosphines with oxygen.[4] Under similar conditions, COF_2 fluorinated $(CH_3)_3P$ to $(CH_3)_3PF_2$ in 72% yield.[1]

Only two phosphorus-containing products were obtained when SOF_2 was reacted with $(C_6H_5)_3P$:

$$(C_6H_5)_3P + SOF_2 \xrightarrow[25\ ^\circ C,\ 10\ h]{CH_2Cl_2} \underset{44\%}{(C_6H_5)_3PF_2} + (C_6H_5)_3PO + S$$

However, a similar lack of reaction of $(C_6H_5)_3P$ with sulfur is observed in its reaction with SF_4.[6] Although the yield of the

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phosphorane was 50% greater when SF_4 was employed as the fluorinating reagent, the experimental conditions were harsher and separation of the product from the solvent benzene was troublesome. Thionyl fluoride may be used at room temperature in ordinary Pyrex glass apparatus.

$$2(C_6H_5)_3P + SF_4 \xrightarrow[6\ \mathrm{h}]{150\ °\mathrm{C}} 2(C_6H_5)_3PF_2 + S$$

In reactions with dialkyl phosphonates, the active hydrogen is displaced readily by fluorine:

$$(RO)_2P(O)H + SOF_2 \xrightarrow[\substack{CH_2Cl_2 \\ 25\ °\mathrm{C},\ 10\ \mathrm{h}}]{Et_3N} (RO)_2P(O)F + S + (Et_3N{\cdot}SO_2 + Et_3NHF)$$

$$R\ (\mathrm{yield}) = C_2H_5\ (100\%),\ n\text{-}C_4H_9\ (68\%)$$

For the reaction with COF_2,[1] R (yield) = C_2H_5 (65%) and n-C_4H_9 (60%), with CO and Et_3NHF also obtained. Triethylamine is reported to form an adduct with SO_2,[7] which again results from the disproportionation of SO. Thus, Et_3N plays a dual role in tying up the HF and the SO_2 that are formed.[8,9]

Sulfinyl fluoride fluorinates $(C_6H_5)_3CH$ readily to give $(C_6H_5)_3CF$ in 60% yield apparently via the same mechanism as that for $(RO)_2P(O)H$. Thus it is as effective as COF_2 in this reaction.

Although SOF_2 has not been studied previously as a fluorinating reagent, its reactions have, of course, been examined. It has demonstrated a varying ability to introduce the $-S(O)F$ group into compounds, e.g., reacting with $[(CH_3)_2N]_3P$ to give unstable products

$$SOF_2 + [(CH_3)_2N]_3P \xrightarrow{CH_3CN} FS(O)N(CH_3)_2 + \mathrm{solids}^{10}$$

or with HNF_2 to give a moderately stable species

$$SOF_2 + HNF_2{\cdot}KF \xrightarrow{-23\ °\mathrm{C}} FS(O)NF_2^{11}$$

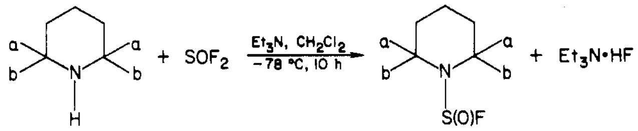
or under forcing conditions across olefinic double bonds to form stable perfluoroalkylsulfinyl fluorides.[12,13]

$$(>C{=}C<)_f + SOF_2 \xrightarrow[\Delta]{CsF} R_fS(O)F$$

$$(>C{=}C<)_f = C_2F_4,\ C_3F_6$$

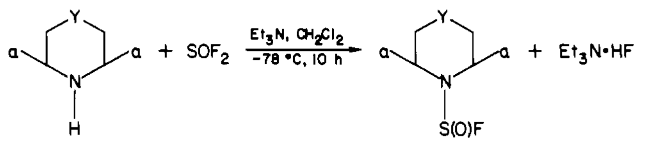
Since we had shown that carbonyl fluoride was useful in converting piperidine to N-fluoropiperidine,[1] it was of interest to examine the behavior of SOF_2 with that system. Thus, we have studied the reactions of SOF_2 with piperidines, morpholines, and thiomorpholine. Invariably, the $-S(O)F$ group displaces the active hydrogen to give products of varying stability.

The stability of the sulfinyl fluoride products increases as the degree of substitution on the piperidine ring increases, viz.



a	a	b	b	% yield	state	stability
H	H	H	H	70	col liq	<25 °C
CH_3	CH_3	H	H	71	col liq	<25 °C
CH_3	CH_3	CH_3	CH_3	75	solid	25 °C

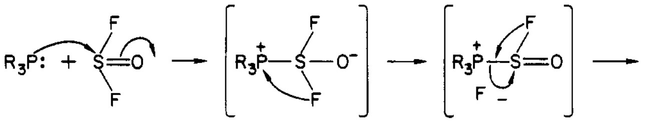
A similar case is noted with the morpholines although the presence of a second heteroatom in the ring gives sulfinyl fluorides of very limited stability.



Y	a	a	% yield	state	stability
O	H	H	68	col liq	<0 °C
O	CH_3	CH_3	65	col liq	<0 °C
S	H	H	50	col liq	<0 °C

With a secondary acyclic amine, $(CH_3)_2NH$, in the presence of triethylamine, the N–H bond was replaced by an N–S bond to form $(CH_3)_2NS(O)F$. This reaction at −78 °C was reported in the literature,[14] but we found quantitative conversion when it was carried out at 22 °C over a period of 30 min. In keeping with the stability of substituted cyclic amine–S(O)F derivatives, $(CH_3)_2NS(O)F$ was more stable than the piperidine or dimethylpiperidine derivatives. With COF_2, $(CH_3)_2NF$[1] was found.

The routes by which these reactions occur may be as follows: for phosphines and phosphites

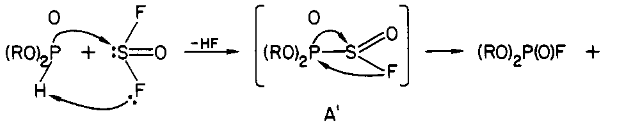


A

$$R_3PF_2 + [SO]$$

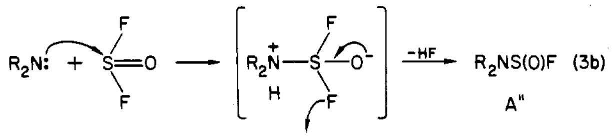
$$2[SO] \longrightarrow S + SO_2$$
$$R_3P + S \longrightarrow R_3PS$$
$$3R_3P + SO_2 \longrightarrow R_3PS + 2R_3PO \qquad (2)$$

for compounds with active hydrogen



A'

[SO] (3a)



Intermediates A and A′ in (2) and (3a), respectively, are destabilized by the driving force to form the very strong P–F bond. A similar driving force is also present in the case where a C–H bond is replaced by a C–F bond as in $(C_6H_5)_3CH$. However, the stability of A″ in (3b) is not influenced by a similar force since the N–F is appreciably weaker. In the case of cyclic and acyclic primary amines, the stability of the $>N-S(O)F$ derivatives is a function of the number of electron-donating substituents on the carbon atom α to the nitrogen, e.g., the tetramethylpiperidine–S(O)F compound is stable while the dimethyl derivative and the piperidine–S(O)F compound are stable only below 0 °C. The presence of CH_3 groups enhances the stability of the N–S bond via a greater degree of pπ–dπ bonding. On the basis of the fact that no oxygenated species other than R_3PO is found in the reaction of trialkylphosphine and SOF_2, it appears likely that the unstable SO intermediate must decompose first to S + SO_2, which in turn react with R_3P. Otherwise other oxygenated species such as those cited above would be found.

In summary, sulfinyl fluoride is as effective as carbonyl fluoride in displacing active hydrogen from P–H and C–H to form P–F and C–F bonds. With N–H, only N–S(O)F species are formed. However, with oxidatively unsaturated systems, SOF_2 is less ef-

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ficient because of the reactions of SO (SO_2 + S) with the systems to be fluorinated. Addition of Et_3N to these reactions does not reduce the yields of products resulting from starting materials interacting with the byproducts from SOF_2.

Experimental Section

Materials. Sulfinyl fluoride was prepared according to the literature method.[2] Starting materials were obtained and treated as follows: $(C_2H_5O)_3P$ and $(n\text{-}C_4H_9O)_3P$ (Aldrich) were used after distilling over sodium; $(C_2H_5O)_2P(O)H$ and $(n\text{-}C_4H_9O)_2P(O)H$ (Aldrich) were distilled over $PbCO_3$ before use; $(CH_3)_3P$ (Strem), $(C_6H_5)_3P$, PCl_3, $C_5H_{11}N$, $C_7H_{15}N$, $C_9H_{19}N$, $C_6H_{13}NO$, C_4H_9NS, $(C_6H_5)_3CH$, $(CF_3CH_2O)_3P$ (Aldrich), C_4H_9NO (Sigma), and PF_3 (Ozark-Mahoning) were used as received. Dichloromethane was stored over molecular sieves as was triethylamine after it was distilled from KOH.

General Procedure. A conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge was used for manipulation of gases and volatile liquids. Trap-to-trap distillation using a vacuum-line apparatus was carried out to accomplish separation of volatile products. Reactions carried out at −78 or 25 °C were contained in 25-mL round-bottomed flasks equipped with Teflon stopcocks. Infrared spectra were obtained on a Perkin-Elmer 599B spectrometer by using a 10-cm cell fitted with KBr windows for gases, KBr disks for liquids, and KBr pellets for solids. ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a JEOL FX90Q FT NMR spectrometer with $(CH_3)_4Si$, CCl_3F, or H_3PO_4 as external reference. Deuterated chloroform was the solvent. Negative values are assigned to signals that are upfield of the reference. Mass spectra were recorded on a VG HS7070 mass spectrometer. Mixtures were separated with a Kugelrohr apparatus.

Reaction of $(C_2H_5O)_2P(O)H$ with SOF_2. Freshly distilled $(C_2H_5O)_2P(O)H$ (3 mmol) was transferred with a syringe in a nitrogen atmosphere into a dry 50-mL round-bottomed flask that was equipped with a Teflon stopcock and a magnetic stirring bar. Into the evacuated flask at −196 °C were transferred CH_2Cl_2 (3 mL) and Et_3N (3 mmol). The contents of the flask were warmed to 25 °C and the three liquids allowed to mix. The flask was recooled to −196 °C, and SOF_2 (3.5 mmol) was introduced. The flask was allowed to warm slowly to 25 °C and the mixture then stirred for 10 h. The contents were separated by trap-to-trap distillation. In the trap at −40 °C was found $(C_2H_5O)_2P(O)F$ (3 mmol, 100%). Remaining in the flask were sulfur (soluble in CS_2) and Et_3NHSO_2F ($Et_3NHF{\cdot}SO_2$). The ^{19}F NMR spectrum contains a doublet centered at ϕ −80.00 (J_{P-F} = 981.3 Hz), and the ^{31}P NMR spectrum has a doublet centered at δ −13.20 (H decoupled).

Reaction of $(C_4H_9O)_2P(O)H$ with SOF_2. This reaction was carried out as above. Separation of $(C_4H_9O)_2P(O)F$ (68%) from S and Et_3NHSO_2F was accomplished via a Kugelrohr apparatus at 45 °C. The ^{19}F NMR spectrum contains a doublet centered at ϕ −79.34 (J_{P-F} = 976.1 Hz), and the ^{31}P NMR spectrum has a doublet centered at δ −13.39 (H decoupled). When the reaction was carried out at −78 °C for 10 h, the yield of $(C_4H_9O)_2P(O)F$ was 30%; for 30 h, the yield was 47%.

Reaction of $(C_2H_5O)_3P$ with SOF_2. This reaction was carried as above without Et_3N. Upon Kugelrohring at 40 °C, $(C_2H_5O)_3PF_2$ was obtained in 25% yield. The ^{19}F NMR spectrum contains a doublet centered at ϕ −57.89 (J_{P-F} = 722.7 Hz), and the ^{31}P NMR spectrum has a triplet centered at δ −74.78. The ^{31}P NMR spectrum of the material left in the Kugelrohr flask shows a peak at δ 68.34 (s) for $(C_2H_5O)_3PS$, a peak at δ −0.28 (s) for $(C_2H_5O)_3PO$, and a peak for $(C_2H_5O)_2P(O)H$ (trace) at δ 7.9 (s) (H decoupled).

Reaction of $(C_4H_9O)_3P$ with SOF_2. The reaction was run as above without Et_3N. The yield of $(C_4H_9O)_3PF_2$ was 22%. The doublet in the ^{19}F NMR spectrum is centered at ϕ −5[illegible].51 (J_{P-F} = 727.7 Hz), and the triplet in the ^{31}P NMR spectrum is centered at δ −75.23. The ^{31}P NMR spectrum of the material left in the Kugelrohr flask shows a peak at δ 68.4 (s) for $(n\text{-}C_4H_9O)_3PS$, a peak at δ −0.3 (s) for $(n\text{-}C_4H_9O)_3PS$, a peak at δ −0.3 (s) for $(n\text{-}C_4H_9O)_3PO$, and a peak for $(n\text{-}C_4H_9O)_2P(O)H$ at δ 7.8 (s) (H decoupled).

Reaction of $(C_6H_5)_3P$ with SOF_2. The reaction was run at 25 °C in CH_2Cl_2 in a 2:2.5 millimolar $(C_6H_5)_3P$:SOF_2 ratio. The yield of $(C_6H_5)_3PF_2$ was 44%. The ^{19}F NMR spectrum contains a doublet centered at ϕ −38.54 (J_{P-F} = 667.8 Hz), and the ^{31}P NMR spectrum has a triplet centered at δ −55.52. With Kugelrohring, sulfur sublimed out of the flask at 45 °C, and $(C_6H_5)_3PO$, at 60 °C, leaving $(C_6H_5)_3PF_2$ behind.

Reaction of $(CH_3)_3P$ with SOF_2. The reaction was carried out neat in a ratio of 2 mmol of $(CH_3)_3P$ to 2.5 mmol of SOF_2. Trap-to-trap distillation gave $(CH_3)_3PF_2$ (25%) in the trap at −78 °C. The ^{19}F NMR spectrum contains a doublet centered at ϕ −5.74 (J_{P-F} = 547.7 Hz), and the ^{31}P NMR spectrum has a triplet centered at δ −13.4. The mass spectrum contains *m/e* 113 (M − 1⁺) and 95 (M − F⁺) as the base peak. After Kugelrohring at 40 °C, $(CH_3)_3PO$ (δ 31.3 (s)) sublimed to leave $(CH_3)_3PS$ (δ 41.38 (s)) in the flask (H decoupled).

Chart I

reactants		products[3]
$(C_2H_5O)_3P$ (2.5 mmol)	O_2 (excess)	$(C_2H_5O)_3PO$, $(C_2H_5O)_2P(O)H$ (tr)
$(n\text{-}C_4H_9O)_3P$ (2.5 mmol)	O_2 (excess)	$(n\text{-}C_4H_9O)_3PO$, $(n\text{-}C_4H_9O)_2P(O)H$ (tr)
$(CH_3)_3P$ (2.5 mmol)	O_2 (excess)	$(CH_3)_3PO$, $(CH_3O)_3PO$, $(CH_3)_2P(O)(OCH_3)$, $CH_3P(O)(OCH_3)_2$
$(C_6H_5)_3P$ (2.5 mmol)	O_2 (excess)	$(C_6H_5)_3PO$
$(C_2H_5O)_3P$ (2.5 mmol)	S (2.5 mmol)	$(C_2H_5O)_3PS$
$(n\text{-}C_4H_9O)_3P$ (2.5 mmol)	S (2.5 mmol)	$(n\text{-}C_4H_9O)_3PS$
$(CH_3)_3P$ (2.5 mmol)	S (2.5 mmol)	$(CH_3)_3PS$
$(C_2H_5O)_3P$ (2.5 mmol)	SO_2 (2.5 mmol)	$(C_2H_5O)_3PO$, $(C_2H_5O)_3PS$
$(n\text{-}C_4H_9O)_3P$ (2.5 mmol)	SO_2 (2.5 mmol)	$(n\text{-}C_4H_9O)_3PO$, $(n\text{-}C_4H_9O)_3PS$

Reaction of PCl_3, PF_3, or $P(OCH_2CF_3)_3$ with SOF_2. Each of these reactions was attempted with or without solvent (CH_2Cl_2) by using essentially equimolar amounts of reactants at 25 °C. No reaction occurred in any case.

Reaction of $(C_6H_5)_3CH$ with SOF_2. This reaction was carried out as with $(C_2H_5O)_2P(O)H$ above. The millimolar ratio of $(C_6H_5)_3CH$:Et_3N:SOF_2 was 2:2:2.5 in 5 mL of CH_2Cl_2. Trap-to-trap distillation led to CH_2Cl_2 in a trap at −98 °C and excess SOF_2 at −196 °C. The solid residue in the flask was sublimed under vacuum at 40 °C to remove $Et_3N{\cdot}HF$ and SO_2 and at 45 °C to remove sulfur. The material that did not sublime at this temperature was $(C_6H_5)_3CF$ in 60% yield. The ^{19}F NMR spectrum contains a singlet at ϕ −128.4. The ^1H NMR spectrum contains only ring proton signals.

Reactions of Phosphites and Phosphines with Oxygen, Sulfur, or Sulfur Dioxide. In general, the reactions, shown in Chart I, were run neat except when the reactant was a solid and CH_2Cl_2 was used. The reactions of each of the heterocycles were carried out essentially the same as the reaction between $(C_2H_5O)P(O)H$ and SOF_2 except that the reaction temperature was −78 °C.

(a) Piperidine with SOF_2. Piperidine (3 mmol), Et_3N (3 mmol), SOF_2 (3.5 mmol), and CH_2Cl_2 (5 mL) were held at −78 °C for 10 h. After the excess SOF_2 and CH_2Cl_2 were removed, a white residue remained, which was extracted with dry *n*-hexane. The $C_5H_{10}NS(O)F$ (70% yield) dissolved, leaving $Et_3N{\cdot}HF$ behind. The ^{19}F NMR spectrum contains a singlet at ϕ 51.9, and the ^1H NMR spectrum shows ring protons. The infrared spectrum has bands at 2924 vs, 2834 s, 1454 s, 1212 vs, br ($\nu_{S=O}$), and 864 m (ν_{S-F}) cm^{-1}. The CI (positive) mass spectrum contains a molecular ion (M^+ + H) at *m/e* 152 as well as other peaks at *m/e* 132 (M − F^+), 7.0%), 114 ($C_5H_8NS^+$, 9.7%), 98 ($C_4H_4NS^+$, 7.9%), 86 ($C_3H_9NS^+$), 46.2%), 84 ($C_5H_{10}N$, 100%), 81 ($NSOF^+$, 0.97%), and 65 ($C_5H_5{}^+$, 22.6%).

(b) 2,6-Dimethylpiperidine with SOF_2. *n*-Hexane extraction gave a 71.3% yield of $C_7H_{14}NSOF$. The ^{19}F NMR spectrum contains a singlet at ϕ 64.2, and the ^1H NMR spectrum contains signals for ring protons. The infrared spectrum has bands at 2970 vs, 2880 vs, 1450 m, 1220 vs, br ($\nu_{S=O}$), and 870 vs (ν_{S-F}) cm^{-1}. The mass spectrum (positive CI) has peaks at *m/e* 180 ($C_7H_{14}NSOFH^+$, 3.7%), 160 ($C_7H_{14}NSO^+$, 18.9%), 145 ($C_6H_{11}NSO^+$, 2.6%), 130 ($C_5H_8NSO^+$, 3.0%), 112 ($C_7H_{14}N^+$, 100%), 98 ($C_6H_{12}N^+$, 38.8%), 97 ($C_6H_{11}N^+$, 2.6%), 82 ($C_5H_8N^+$, 1.74%), 68 ($C_5H_8{}^+$, 3.4%), and 65 ($C_5H_5{}^+$, 17.8%).

(c) 2,2,6,6-Tetramethylpiperidine with SOF_2. Sublimation at 25 °C and 0.2 torr permitted separation of the white solid $C_9H_{18}NSOF$ (75.4% yield) from the less easily sublimed $Et_3N{\cdot}HF$. The ^{19}F NMR spectrum contains a singlet at ϕ 65.2, and the ^1H NMR spectrum has ring protons signals. The infrared spectrum has bands at 2986 s, 2840 m, 1460 s, 1204 s ($\nu_{S=O}$), and 930 m (ν_{S-F}) cm^{-1}. The positive EI mass spectrum has peaks at *m/e* 207 ($C_9H_{18}NSOF^+$, 0.80%), 192 ($C_8H_{15}NSOF^+$, 8.0%), 158 ($C_7H_{12}NSO^+$, 0.76%), 140 ($C_9H_{18}N^+$, 1.64%), 126 ($C_8H_{16}N^+$, 97.8%), 111 ($C_7H_{13}N^+$, 2.75%), 110 ($C_7H_{12}N^+$, 5.4%), 96 ($C_6H_{10}N^+$, 3.1%), 95 ($C_6H_9N^+$, 3.78%), 81 ($C_5H_7N^+$, 7.72%), 80 ($C_5H_6N^+$, 0.96%), 67 (SOF^+, 9.1%), 66 ($C_4H_4N^+$, 3.63%), and 48 (SO^+, 5.62%).

Anal. Calcd for $C_9H_{18}NSOF$: C, 52.17; H, 8.69; N, 6.76; S, 15.45. Found: C, 51.50; H, 8.71; N, 6.80; S, 14.27.

(d) Morpholine with SOF_2. *n*-Hexane extraction gave a 68.2% yield of $C_4H_8NSO_2F$. The ^{19}F NMR spectrum contains a singlet at ϕ 47.9, and the ^1H NMR spectrum has ring proton signals. The infrared spectrum has bands at 2974 m, 2860 s, 1457 s, 1217 vs ($\nu_{S=O}$), and 857 w

(ν_{S-F}) cm^{-1}. The positive CI mass spectrum has peaks at *m/e* 134 ($C_4H_8NSO_2^+$, 91.3%), 86 ($C_4H_8NO^+$, 92.4%), 72 ($C_4H_8O^+$, 4.5%), 70 ($C_4H_8N^+$, 42.2%), and 67 (SOF^+, 2.58%).

(e) 3,5-Dimethylmorpholine with SOF_2. *n*-Hexane extraction gave a 65% yield of $C_6H_{12}NSO_2F$. The ^{19}F NMR spectrum contains a singlet at ϕ 47.3, and the ^1H NMR spectrum has ring proton signals. The infrared spectrum has bands at 2983 s, 2877 s, 1457 s, 1212 vs ($\nu_{S=O}$), and 851 m (ν_{S-F}) cm^{-1}. The positive CI mass spectrum has peaks at *m/e* 162 ($C_6H_{12}NSO_2^+$, 34.9%) 114 ($C_6H_{12}NO^+$, 100%), 99 ($C_5H_9NO^+$, 9%), 98 ($C_5H_8NO^+$, 90.1%), 84 ($C_4H_6NO^+$, 5%), 70 ($C_4H_6O^+$, 22%), 68 ($C_4H_6N^+$), and 67 (SOF^+, 3.27%).

(f) Thiomorpholine with SOF_2. *n*-Hexane extraction gave a 50% yield of $C_4H_8NS_2OF$. The ^{19}F NMR spectrum contains a singlet at ϕ 55.8, and the ^1H NMR has ring proton signals. The infrared spectrum has bands at 2962 m, 2855 m, 1450 vs, 1206 vs ($\nu_{S=O}$), and 821 w (ν_{S-F}) cm^{-1}. The positive CI mass spectrum has peaks at *m/e* 150 ($C_4H_8NS_2O^+$, 20.66%), 102 ($C_4H_8NS^+$, 56.15%), 88 ($C_4H_8S^+$, 9.47%), 70 ($C_4H_8N^+$, 2.74%), and 67 (SOF^+, 1.42%).

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Registry No. SOF_2, 7783-42-8; $(C_2H_5O)_2P(O)H$, 762-04-9; $(C_2H_5O)_2P(O)F$, 358-74-7; S, 7704-34-9; Et_3NHFSO_2, 95552-60-6; $(C_4H_9O)_2P(O)H$, 1809-19-4; $(C_4H_9O)_2P(O)F$, 674-48-6; $(C_2H_5O)_3P$, 122-52-1; $(C_2H_5O)_3PF_2$, 55422-04-3; $(C_2H_5O)_3PS$, 126-68-1; $(C_2H_5O)_3PO$, 78-40-0; $(C_4H_9O)_3P$, 102-85-2; $(C_4H_9O)_3PF_2$, 91223-81-3; $(C_4H_9O)_3PS$, 78-47-7; $(C_4H_9O)_3PO$, 126-73-8; $(C_6H_5)_3P$, 603-35-0; $(C_6H_5)_3PF_2$, 845-64-7; $(C_6H_5)_3PO$, 791-28-6; $(CH_3)_3P$, 594-09-2; $(CH_3)_3PF_2$, 661-42-7; $(CH_3)_3PO$, 676-96-0; $(CH_3)_3PS$, 2404-55-9; PCl_3, 7719-12-2; PF_3, 7783-55-3; $P(OCH_2CF_3)_3$, 370-69-4; $(C_6H_5)_3CH$, 519-73-3; $(C_6H_5)_3CF$, 427-36-1; $(CH_3O)_3PO$, 512-56-1; $(CH_3)_2P(O)(OCH_3)$, 14337-77-0; $CH_3P(O)(OCH_3)_2$, 756-79-6; piperidine, 110-89-4; 1-piperidinesulfinyl fluoride, 455-33-4; 2,6-dimethylpiperidine, 504-03-0; 2,6-dimethyl-1-piperidinesulfinyl fluoride, 95533-39-4; 2,2,6,6-tetramethylpiperidine, 768-66-1; 2,2,6,6-tetramethyl-1-piperidinesulfinyl fluoride, 95533-40-7; morpholine, 110-91-8; 4-morpholinesulfinyl fluoride, 60094-26-0; 3,5-dimethylmorpholine, 123-57-9; 3,5-dimethyl-4-morpholinesulfinyl fluoride, 95533-41-8; thiomorpholine, 123-90-0; 4-thiomorpholinesulfinyl fluoride, 95533-42-9.

Contribution from Physical Chemistry 1,
Chemical Center, University of Lund, S-220 07 Lund, Sweden

Halide-Exchange Reactions of Mixed Chloro–Bromo–Iodo Trihalides. 1. Equilibria in the Chloro–Iodo System

LARS-FRIDE OLSSON

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Formation of the trihalide anions Cl_3^-, ICl_2^-, I_2Cl^-, and I_3^- from the parent halogen molecules has been studied in methanol. Equilibrium constants have been determined by spectrophotometric and potentiometric measurements at temperatures below 0 °C, with an ionic strength of 1 M ($LiCl/LiBF_4$) and under restricted illumination. Iodide has a considerably higher affinity than chloride toward halogen molecules. Reaction between iodide and halogen involves such large electron displacements that they are best described as redox reactions, whereas the reaction with chloride is a simple addition. The reaction between iodide and chlorine, $2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$, is a multistep process that involves species such as the dichloroiodate(I) and, for excess chlorine, tetrachloroiodate(III) ion. Spectra of all the trihalides display large absorption maxima between 225 and 290 nm with molar absorptivities around 5×10^4 cm^{-1} M^{-1}.

Introduction

This paper reports equilibrium constants in methanol for the formation of trihalide anions from the parent halogen or interhalogen compound and the halide ion (eq 1–6) together with

$$Cl^- + Cl_2 \rightleftarrows Cl_3^- \tag{1}$$

$$I^- + Cl_2 \rightleftarrows ICl_2^- \tag{2}$$

$$Cl^- + ICl \rightleftarrows ICl_2^- \tag{3}$$

$$I^- + ICl \rightleftarrows I_2Cl^- \tag{4}$$

$$Cl^- + I_2 \rightleftarrows I_2Cl^- \tag{5}$$

$$I^- + I_2 \rightleftarrows I_3^- \tag{6}$$

constants for the halide-exchange reactions according to eq 7–9.

$$I^- + Cl_3^- \rightleftarrows ICl_2^- + Cl^- \tag{7}$$

$$I^- + ICl_2^- \rightleftarrows I_2Cl^- + Cl^- \tag{8}$$

$$I^- + I_2Cl^- \rightleftarrows I_3^- + Cl^- \tag{9}$$

The overall reaction can be written as the redox equilibrium (10).

$$3I^- + Cl_2 \rightleftarrows I^-_3 + 2Cl^- \tag{10}$$

The equilibrium constants for all the reactions are known with water as solvent.[1-3] In nonaqueous solvents (methanol in this study) only the triiodide equilibrium (eq 6) has been determined.[2,4-11] This equilibrium constant is larger by a few powers of ten in nonaqueous solvents[1,2] as compared to in water. The variation of this constant with solvent has been reported.[11] An estimate of the dichloroiodide equilibrium (eq 3) has also been reported.[12] Of the constants reported here, K_1, K_3, K_5, K_6, K_8, and K_9 have been determined spectrophotometrically. The absorption spectra of the relevant species are all known in water (cf. ref 13 and references therein) and, except for I_2Cl^-, also in methanol.[12] The spectra are very similar in these two solvents. The trihalide ions exhibit high absorption maxima in the UV spectral region,[12,14] with molar absorptivities around 5×10^4 M^{-1} cm^{-1}. Of the halide ions, only iodide has a maximum in the same region (cf. Figure 2b).

The constants according to eq 2 and 7 were determined potentiometrically. A proper combination of eq 2–5 leads to the simple redox equation (11). The electrode potentials in methanol for the redox couples Cl_2/Cl^- and I_2/I^- are known.[15]

$$2I^- + Cl_2 \rightleftarrows I_2 + 2Cl^- \tag{11}$$

The aim of this study is to give the necessary spectral and equilibrium data for a planned stopped-flow kinetic study of

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