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Short Communication

The interaction of ClO_2SO_3F with AsF_5 and SbF_5

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The chemical literature abounds in examples where a fluoride-ion donor and a suitable fluoride acceptor interact with fluoride-ion transfer, according to:

$$AF + BF_n \rightarrow A^+[BF_{n+1}]^- \qquad (1)$$

with AF the donor and BF_n the acceptor.

In particular, the pentafluorides AsF_5 and SbF_5 have proven to be excellent fluoride-ion acceptors and the hexafluoro anions AsF_6^- and SbF_6^- or polyanions of the type $SbF_6^- \cdot (SbF_5)_n$, with n commonly 1 or 2, are readily formed. A large number of "heterocation"[1] complexes have been synthesized by this route.

We became interested in extending this method by attempting the transfer of fluorosulfate ion to these two acceptors. Chlorylfluorosulfate[2a, b], ClO_2SO_3F, was thought to be a suitable donor for the following reasons: (a) ClO_2SO_3F is easily synthesized[3] and is a supercooled liquid at room temperature; (b) the chloronium cation, ClO_2^+, with AsF_6^- or SbF_6^-, for example, as counterion, is well characterized by vibrational spectroscopy[4–6]; and (c) ClO_2SO_3F has been found recently to be a very suitable SO_3F^- donor reacting with tin(IV) tetrakis-(fluorosulfate), $Sn(SO_3F)_4$, which acts as an acceptor to yield $[ClO_2]_2[Sn(SO_3F)_6]$[7].

Of the expected mixed anion, the two, $[SbF_5(SO_3F)]^-$ and $[Sb_2F_{10}(SO_3F)]^-$, have been identified previously[8] by their ^{19}F NMR spectra only. They are formed by dissolving SbF_5 in fluorosulfuric acid. AsF_5 was found to be a far weaker acid than SbF_5 and evidence for the presence of $[AsF_5(SO_3F)]^-$ rests chiefly on conductivity measurements[8b], indicating AsF_5 to be only a very weak acid in HSO_3F. We were interested in a characterization of these and other possible anions by their vibrational spectra.

Experimental

General

AsF_5 and SbF_5 (both from Ozark–Mahoning Company) were purified by repeated distillation, either in a Monel vacuum system (AsF_5) or in a Pyrex apparatus at atmospheric pressure (SbF_5). Chlorylfluorosulfate was obtained by

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condensing a 3–5-fold excess of peroxydisulfuryl difluoride, $S_2O_6F_2$, on to ClO_2 in a Pyrex flask fitted with a Teflon stem stopcock. The mixture reacted while being warmed up from −78 °C to room temperature overnight. Both starting materials, ClO_2[9] and $S_2O_6F_2$[10], were prepared by literature methods.

Vibrational spectra were obtained on a Cary 81 Raman spectrophotometer equipped with a Spectra Physics Model 125 He–Ne laser and on a Perkin–Elmer 457 grating infrared spectrophotometer. For the IR samples, AgCl, AgBr and KRS-5 (all from Harshaw Chemicals) windows were employed. Moisture-sensitive materials were handled in an inert-atmosphere box and stored under dry nitrogen.

Reaction of ClO_2SO_3F with AsF_5

In a typical preparation, 345 mg (2.08 mmol) of ClO_2SO_3F was reacted with an excess of AsF_5 at a pressure of *ca.* 300 mmHg in a Pyrex flask fitted with a Teflon stem stopcock and attached to the vacuum line. With the reactor at room temperature, a yellow liquid was formed over a period of 4 h. After removal of all excess AsF_5 and cooling, a yellow solid (m.p. +38 °C) was obtained. Chemical analysis (performed by A. Bernhardt, Elbach, West Germany) together with the weight of product obtained established the composition $ClO_2SO_3F{\bullet}AsF_5$. Analysis: Found: Cl, 10.40; F, 34.10; S, 9.67%. $ClO_2SO_3F{\bullet}AsF_5$ (1:1 complex) requires Cl, 10.54; F, 33.89; S, 9.53%.

Reaction of ClO_2SO_3F with SbF_5

When a 3–5-fold excess of SbF_5 was added to 1021 mg (6.14 mmol) of ClO_2SO_3F at room temperature in a similar Pyrex reactor to that described above, a yellowish-white solid was formed immediately in addition to a colourless, moderately volatile liquid. After all volatiles were removed *in vacuo*, 3190 mg of a white solid melting at 58 °C was left behind. Qualitative and infrared analysis indicated the complete absence of fluorosulfate while quantitative analysis indicated the presence of $ClO_2Sb_2F_{11}$. Analysis: Found: Sb, 46.51; F, 40.26%. $ClO_2Sb_2F_{11}$ requires Sb, 46.74; F, 40.31%. The infrared spectrum of the volatile material, run as liquid between two window plates, indicated the presence of $SbF_4(SO_3F)$[11] together with SbF_5.

Vibrational spectra

The observed Raman frequencies for $ClO_2SO_3F{\bullet}AsF_5$ are listed in Table 1 together with a tentative assignment. In good agreement with previous reports[4–7, 12] and aided by the observation of ^{35}Cl and ^{37}Cl isotope splittings, the presence of the ClO_2^+ cation may be clearly identified by bands at 1300, 1060 and 524 cm^{-1}.

The assignment of the remaining bands is aided by previous assignments for SO_3F groups in anionic complexes such as $[Sn(SO_3F)_6]^{2-}$ [7] or $[Br(SO_3F)_4]^-$ [13] and the square-pyramidal molecules BrF_5 and IF_5[14]. Again good agreement is found, except for the region of *ca.* 550–650 cm^{-1} where ambiguities arise because of the presence of SO_3 deformation and As–F stretching modes. No assignment has been attempted in the very low frequency region.

TABLE 1

RAMAN SPECTRUM OF $ClO_2[AsF_5(SO_3F)]$

$\Delta\nu/cm^{-1}$	Int.	Approximate description	$\Delta\nu/cm^{-1}$	Int.	Approximate description
1359	s	asym. SO_2 stretch	559	m	SO_2 rocking
1307	m	asym. ClO_2^+ stretch, ν_3	524	s	ClO_2^+ bend, ν_3
1291	mw		451	m,sh	S–F wagging
1205	vs	sym. SO_2 stretch	448	w	S–O*As wagging
1057	s	sym. ClO_2^+ stretch, ν_1	429	m	SO_2F torsion
1060	w,sh		382	m	As–F bending
1034	m	S–O*As stretch	366	m,sh	
856	w	S–F stretch	353	s	
849	m		315	m	
700	s	$\nu(AsF_{ax})$	298	m,sh	
668	vs	$\nu(AsF_{eq})$	272	w	
641	mw	$\nu(AF_{eq})$ in phase			
602	m,sh	$\nu(AsF)$ out of phase			
596	m	$\nu(AsO)$ or $S\delta SO_2$			

Abbreviations; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, ax = axial, eq = equatorial, δ = deformation, O* = bridging oxygen.

From the above mentioned comparisons, it seems reasonable to regard the reaction product as $ClO_2[AsF_5(SO_3F)]$, implying that SO_3F^- abstraction has indeed taken place.

The infrared and Raman data for the SbF_5 derivative are consistent with the formulation $ClO_2[Sb_2F_{11}]$. Vibrational frequencies for the chloronium cation are found at *ca.* 1310, 1050 and 514 cm^{-1} again in excellent agreement with previous work[4–7]. The remaining bands may be assigned to the polyanion $Sb_2F_{11}^-$, again using previous work as a basis for comparison[15, 16].

Discussion

Whereas AsF_5 acts as a fluorosulfate-ion acceptor according to

$$ClO_2SO_3F + AsF_5 \rightarrow ClO_2[AsF_5(SO_3F)] \qquad (2)$$

the interaction of SbF_5 and ClO_2SO_3F appears to be more complex, *i.e.*

$$ClO_2SO_3F + 3SbF_5 \rightarrow ClO_2[Sb_2F_{11}] + SbF_4(SO_3F) \qquad (3)$$

and requires an excess of antimony(V) fluoride. All attempts to obtain a possible complex of composition $ClO_2[SbF_5(SO_3F)]$ by using excess chlorylfluorosulfate resulted in the formation of complex reaction mixtures.

Very little can be said at this point regarding a detailed mechanism for reaction (3); however, the conversion of a SO_3F compound into a $Sb_2F_{11}^-$ salt may be extended to other fluorosulfates. Work in this direction is at present under way.

It is interesting to note that even though the reaction of chlorylfluoride, $FClO_2$, and SbF_5 has been extensively studied in the past[2a,b,6,17], only ClO_2SbF_6 and (very recently) $ClO_2Sb_3F_{16}$[6] have been reported.

There appears to be no definite precedent for the ion $[AsF_5(SO_3F)]^-$. The chloronium compound shows limited thermal stability and decomposition occurs with gradual loss of AsF_5. It is interesting in this context that our attempts to obtain an analogous $[BF_3(SO_3F)]^-$ compound resulted in an incomplete uptake of BF_3 by ClO_2SO_3F at temperatures between 0 °C and 5 °C. All BF_3 could be readily removed *in vacuo*. This result was not unexpected when the low thermal stability of ClO_2BF_4[2a,b 4,6] is taken into consideration.

In all cases AsF_5 appeared to be a most suitable anion for abstracting the SO_3F^- ion without subsequent side-reactions and this reaction should be capable of extension to other suitable SO_3F^- donors.

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