

## Short Communication

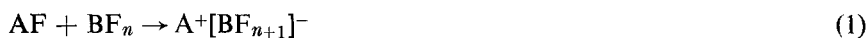
### The interaction of $\text{ClO}_2\text{SO}_3\text{F}$ with $\text{AsF}_5$ and $\text{SbF}_5$

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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:



with AF the donor and  $\text{BF}_n$  the acceptor.

In particular, the pentafluorides  $\text{AsF}_5$  and  $\text{SbF}_5$  have proven to be excellent fluoride-ion acceptors and the hexafluoro anions  $\text{AsF}_6^-$  and  $\text{SbF}_6^-$  or polyanions of the type  $\text{SbF}_6^- \cdot (\text{SbF}_5)_n$ , with  $n$  commonly 1 or 2, are readily formed. A large number of "heterocation"<sup>1</sup> 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<sup>2a, b</sup>,  $\text{ClO}_2\text{SO}_3\text{F}$ , was thought to be a suitable donor for the following reasons: (a)  $\text{ClO}_2\text{SO}_3\text{F}$  is easily synthesized<sup>3</sup> and is a supercooled liquid at room temperature; (b) the chloronium cation,  $\text{ClO}_2^+$ , with  $\text{AsF}_6^-$  or  $\text{SbF}_6^-$ , for example, as counterion, is well characterized by vibrational spectroscopy<sup>4-6</sup>; and (c)  $\text{ClO}_2\text{SO}_3\text{F}$  has been found recently to be a very suitable  $\text{SO}_3\text{F}^-$  donor reacting with tin(IV) tetrakis-(fluorosulfate),  $\text{Sn}(\text{SO}_3\text{F})_4$ , which acts as an acceptor to yield  $[\text{ClO}_2]_2[\text{Sn}(\text{SO}_3\text{F})_6]$ <sup>7</sup>.

Of the expected mixed anion, the two,  $[\text{SbF}_5(\text{SO}_3\text{F})]^-$  and  $[\text{Sb}_2\text{F}_{10}(\text{SO}_3\text{F})]^-$ , have been identified previously<sup>8</sup> by their <sup>19</sup>F NMR spectra only. They are formed by dissolving  $\text{SbF}_5$  in fluorosulfuric acid.  $\text{AsF}_5$  was found to be a far weaker acid than  $\text{SbF}_5$  and evidence for the presence of  $[\text{AsF}_5(\text{SO}_3\text{F})]^-$  rests chiefly on conductivity measurements<sup>8b</sup>, indicating  $\text{AsF}_5$  to be only a very weak acid in  $\text{HSO}_3\text{F}$ . We were interested in a characterization of these and other possible anions by their vibrational spectra.

#### *Experimental*

##### *General*

$\text{AsF}_5$  and  $\text{SbF}_5$  (both from Ozark–Mahoning Company) were purified by repeated distillation, either in a Monel vacuum system ( $\text{AsF}_5$ ) or in a Pyrex apparatus at atmospheric pressure ( $\text{SbF}_5$ ). Chlorylfluorosulfate was obtained by

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condensing a 3–5-fold excess of peroxydisulphuryl 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  $-78^\circ C$  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.  $+38^\circ C$ ) was obtained. Chemical analysis (performed by A. Bernhardt, Elbach, West Germany) together with the weight of product obtained established the composition  $ClO_2SO_3F \cdot AsF_5$ . Analysis: Found: Cl, 10.40; F, 34.10; S, 9.67%.  $ClO_2SO_3F \cdot AsF_5$  (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  $58^\circ C$  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  $ClO_2SO_3F \cdot AsF_5$  are listed in Table 1 together with a tentative assignment. In good agreement with previous reports<sup>4–7, 12</sup> 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  $524\text{ cm}^{-1}$ .

The assignment of the remaining bands is aided by previous assignments for  $SO_3F$  groups in anionic complexes such as  $[Sn(SO_3F)_6]^{2-}$ <sup>7</sup> or  $[Br(SO_3F)_4]^-$ <sup>13</sup> and the square-pyramidal molecules  $BrF_5$  and  $IF_5$ <sup>14</sup>. Again good agreement is found, except for the region of *ca.*  $550\text{--}650\text{ cm}^{-1}$  where ambiguities arise because

of the presence of  $\text{SO}_3$  deformation and As-F stretching modes. No assignment has been attempted in the very low frequency region.

TABLE 1  
RAMAN SPECTRUM OF  $\text{ClO}_2[\text{AsF}_5(\text{SO}_3\text{F})]$

$\Delta\nu/\text{cm}^{-1}$	Int.	Approximate description	$\Delta\nu/\text{cm}^{-1}$	Int.	Approximate description
1359	s	asym. $\text{SO}_2$ stretch	559	m	$\text{SO}_2$ rocking
1307	m	} asym. $\text{ClO}_2^+$ stretch, $\nu_3$	524	s	$\text{ClO}_2^+$ bend, $\nu_3$
1291	mw		451	m,sh	S-F wagging
1205	vs	sym. $\text{SO}_2$ stretch	448	w	S-O*As wagging
1057	s	} sym. $\text{ClO}_2^+$ stretch, $\nu_1$	429	m	$\text{SO}_2\text{F}$ 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	$\nu(\text{AsF}_{\text{ax}})$	298	m,sh	
668	vs	$\nu(\text{AsF}_{\text{eq}})$	272	w	
641	mw	$\nu(\text{AF}_{\text{eq}})$ in phase			
602	m,sh	$\nu(\text{AsF})$ out of phase			
596	m	$\nu(\text{AsO})$ or $\text{S}\delta\text{SO}_2$			

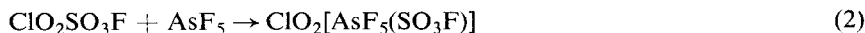
*Abbreviations:* vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, ax = axial, eq = equatorial,  $\delta$  = deformation, O\* = bridging oxygen.

From the above mentioned comparisons, it seems reasonable to regard the reaction product as  $\text{ClO}_2[\text{AsF}_5(\text{SO}_3\text{F})]$ , implying that  $\text{SO}_3\text{F}^-$  abstraction has indeed taken place.

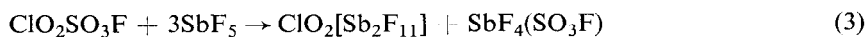
The infrared and Raman data for the  $\text{SbF}_5$  derivative are consistent with the formulation  $\text{ClO}_2[\text{Sb}_2\text{F}_{11}]$ . Vibrational frequencies for the chloronium cation are found at *ca.* 1310, 1050 and  $514\text{ cm}^{-1}$  again in excellent agreement with previous work<sup>4-7</sup>. The remaining bands may be assigned to the polyanion  $\text{Sb}_2\text{F}_{11}^-$ , again using previous work as a basis for comparison<sup>15, 16</sup>.

### Discussion

Whereas  $\text{AsF}_5$  acts as a fluorosulfate-ion acceptor according to



the interaction of  $\text{SbF}_5$  and  $\text{ClO}_2\text{SO}_3\text{F}$  appears to be more complex, *i.e.*



and requires an excess of antimony(V) fluoride. All attempts to obtain a possible complex of composition  $\text{ClO}_2[\text{SbF}_5(\text{SO}_3\text{F})]$  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  $\text{SO}_3\text{F}$  compound into a  $\text{Sb}_2\text{F}_{11}^-$  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 chloryl fluoride,  $\text{FCIO}_2$ , and  $\text{SbF}_5$  has been extensively studied in the past<sup>2a, b, 6, 17</sup>, only  $\text{ClO}_2\text{SbF}_6$  and (very recently)  $\text{ClO}_2\text{Sb}_3\text{F}_{16}$ <sup>6</sup> have been reported.

There appears to be no definite precedent for the ion  $[\text{AsF}_5(\text{SO}_3\text{F})]^-$ . The chloronium compound shows limited thermal stability and decomposition occurs with gradual loss of  $\text{AsF}_5$ . It is interesting in this context that our attempts to obtain an analogous  $[\text{BF}_3(\text{SO}_3\text{F})]^-$  compound resulted in an incomplete uptake of  $\text{BF}_3$  by  $\text{ClO}_2\text{SO}_3\text{F}$  at temperatures between 0 °C and 5 °C. All  $\text{BF}_3$  could be readily removed *in vacuo*. This result was not unexpected when the low thermal stability of  $\text{ClO}_2\text{BF}_4$ <sup>2a, b 4, 6</sup> is taken into consideration.

In all cases  $\text{AsF}_5$  appeared to be a most suitable anion for abstracting the  $\text{SO}_3\text{F}^-$  ion without subsequent side-reactions and this reaction should be capable of extension to other suitable  $\text{SO}_3\text{F}^-$  donors.

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