The Trifluorosulphur(VI) Oxide Cation, SOF_3^+

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Summary It is shown that the adducts $SOF_4{\cdot}AsF_5$ and $SOF_4{\cdot}SbF_5$ have the ionic structure $SOF_3^+MF_6^-$ in the solid state and in solution in hydrogen fluoride: the vibrational spectrum of the SOF_3^+ ion is assigned and the bonding in the ion is discussed.

SOLID 1 : 1 complexes of SOF_4 with SbF_5, AsF_5, and BF_3 were reported by Seel and Detmer[1] who suggested an ionic structure for these compounds, *e.g.*, $SOF_3^+AsF_6^-$, but they gave no experimental evidence in support of this. We have prepared the 1 : 1 adducts of SOF_4 with AsF_5 and SbF_5 and we report here some of the results of a detailed investigation of these compounds.

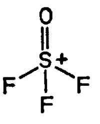
Solutions of $SOF_4{\cdot}AsF_5$ have conductivities in anhydrous HF that are very close to those of $SF_3^+BF_4^-$ and $SF_3^+SbF_6^-$ (ref. 2) indicating essentially complete ionization to SOF_3^+ and AsF_6^-. A solution of SOF_4 in HF had a very low conductivity indicating that it behaves as a very weak electrolyte. In solution in hydrogen fluoride SOF_4 gave a ^{19}F n.m.r. resonance at δ (CCl_3F) -75 p.p.m. in addition to the solvent resonance. The ^{19}F n.m.r. spectrum of $SOF_4{\cdot}AsF_5$ in HF had two signals in addition to that of the solvent, a very weak peak at δ (CCl_3F) -75 p.p.m. which can be assigned to SOF_4 and a strong peak at δ (CCl_3F) -32 p.p.m. which we assign to SOF_3^+. On cooling the solution, the solvent peak split into a doublet which at $-40°$ had a splitting of 526 Hz which did not increase on further cooling. This splitting is due to hydrogen–fluorine coupling in the HF molecule, and its observation indicates that fluorine exchange between solvent molecules in the solution is very slow and that the solution must therefore be exactly neutral,[3] *i.e.*, $[HF_2^-] = [H_2F^+]$ as the exchange is catalysed by amounts of either HF_2^- or H_2F^+ in small excess. The slight traces of water that are usually present in HF produce a slight excess of HF_2^- that is sufficient to collapse the H–F coupling. Presumably this slight excess of HF_2^- is removed by reaction with SOF_3^+ to give SOF_4 and this also accounts for the presence of the SOF_4 peak in the spectrum. Solutions of $SOF_4{\cdot}SbF_5$ in HF gave very similar spectra. The spectrum of a solution of $SOF_4{\cdot}AsF_5$ in HF containing an excess of AsF_5 did not show the SOF_4 peak and the solvent signal was a sharp singlet. On the other hand addition of an excess of F^- to the $SOF_4{\cdot}AsF_5$ solution increased the intensity of the SOF_4 peak but the solvent peak still remained a doublet at low temperatures. It must be concluded therefore that the system $SOF_3^+ : SOF_4$ acts as a buffer and the solution remains sufficiently neutral, *i.e.*, $[HF_2^-] = [H_2F^+]$, so that the H–F coupling can be observed.

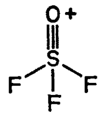
The laser Raman spectra of the solid adducts $SOF_4{\cdot}AsF_5$ and $SOF_4{\cdot}SbF_5$ contain, in addition to lines that can be assigned to the anions, six bands that by comparison with the known spectra of POF_3[4] and NSF_3[5] can unambiguously be assigned to SOF_3^+ as shown in the Table. The SO stretching frequency of 1536 cm.$^{-1}$ in $SOF_3^+SbF_6^-$ is the highest that has been observed for this bond, and this corresponds to a force constant of 14·7 mdyne cm.$^{-1}$. (In SOF_4 the force constant of the SO bond has been calculated[6] to be 11·7 mdyne cm.$^{-1}$.) Using the relationships given by Gillespie and Robinson[6] one can calculate a bond length of 1·38 Å and a bond order of 2·3 for SOF_3^+. This high bond order can be accounted for if it is assumed that the structure can be described by the important resonance structures (I) and (II). A similar high bond order has been found for the PO bond in the isoelectronic POF_3 molecule.[7] The S–F frequencies of 1063 and 909 cm.$^{-1}$ are the highest that have been observed for any S–F bond. This presumably results from the positive charge on sulphur which increases its effective electronegativity and also probably from some contribution from structures such as (III). The effect of a positive charge on sulphur on the S–F stretching frequency is illustrated by the values of 723 and 738 cm.$^{-1}$ for SF_4 and the values of 928 and 943 cm.$^{-1}$ for SF_3^+.[2]

SOF_3^+ *Vibrational frequencies*

$SOF_3{\cdot}AsF_6$	$SOF_3{\cdot}SbF_6$	POF_3	NSF_3	Assignment
391	387	345	342	ν_6 $\delta(S{=}O)$
497	508	485	429	ν_5* $\delta(SF)$
513	535	473	521	ν_3* $\delta(SF)$
911	909	873	775	ν_2 $\nu_s(SF)$
1057 1063	1063	990	811	ν_4 $\nu_a(SF)$
1529 1538	1532 1540	1415	1515	ν_1 $\nu(SO)$

* These assignments are not quite certain and possibly could be reversed.


(I)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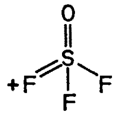
(III)

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