

I<sub>54</sub>THE DISSOCIATION OF (SbCl<sub>4</sub>F)<sub>4</sub> IN NON-COORDINATING SOLVENTS

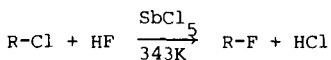
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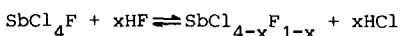
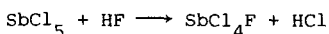
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Antimony pentachloride has been used for over thirty years as the catalyst/solvent for the liquid phase (Swarts) fluorination of chlorocarbons by hydrogen fluoride.



Mixed antimony chloride fluorides are believed to be the active intermediates formed by the reaction of antimony pentachloride with hydrofluoric acid.



SbCl<sub>4</sub>F has been shown by X-ray crystallography to be a tetramer in the solid state, with cis-fluorine bridges between the octahedrally coordinated antimonys (H. Preiss, Z.Chem., 1966, 6(9), 350). Many non-stoichiometric fluorine-rich forms have been characterised over the range SbCl<sub>3</sub>F<sub>2</sub> to SbCl<sub>4</sub>F (J.G. Ballard et al., J.Chem.Soc. (Dalton), 1979, 1, 62; U. Müller, Z.Anorg.All.Chem., 1979, 454, 75) in which the additional fluorines are in terminal Sb-F environments.

This report discusses the nature of stoichiometric and non-stoichiometric (fluorine-rich) SbCl<sub>4</sub>F in the molten state and in the solution phase, using liquid chlorine and bromine as solvents, monitoring the systems by means of infrared and laser Raman spectroscopy.

The Raman spectrum of (SbCl<sub>4</sub>F)<sub>4</sub> in the solid phase, as expected, shows  $\nu(\text{Sb-Cl})$  and  $\delta(\text{Sb-Cl})$  modes of vibration, but no  $\nu(\text{Sb-F}(\text{terminal}))$  modes are detected; this mode is seen, however, in the Raman spectrum of (SbCl<sub>3.6</sub>F<sub>1.4</sub>)<sub>4</sub> in the solid phase, as a weak feature at 660 cm<sup>-1</sup>.

A weak  $\nu(\text{Sb-F}(\text{terminal}))$  feature appears in the Raman spectrum of molten  $(\text{SbCl}_4\text{F})_4$ , the intensity of the signal increasing with temperature over the range 353K (the melting point) to 453K. This suggests that upon heating  $(\text{SbCl}_4\text{F})_4$  above its melting point the tetramer undergoes a ring-opening or dissociation process, leading to the production of species with Sb-F (terminal) bonds. This temperature-dependent process is seen to be reversible; thus the  $\nu(\text{Sb-F}(\text{terminal}))$  feature disappears when the melt is allowed to resolidify below 353K.

The Raman spectrum of  $(\text{SbCl}_4\text{F})_4$  in liquid chlorine shows a very weak but well-defined peak at  $658\text{ cm}^{-1}$  characterising the  $\nu(\text{Sb-F}(\text{terminal}))$  vibration, which implies that a process similar to that proposed for the melt is taking place in solution.

The infrared spectra of solutions of  $(\text{SbCl}_4\text{F})_4$  in liquid bromine provide further evidence for this proposed mechanism, in the form of peaks at  $660\text{ cm}^{-1}$  and  $603\text{ cm}^{-1}$ . The ratio of the areas under these peaks varies with concentration, suggesting that they represent two or more distinct species existing as part of a concentration-dependent equilibrium.

Addition of  $\text{SbCl}_5$  to a solution of  $(\text{SbCl}_4\text{F})_4$  in bromine disrupts this equilibrium leading to significant changes in the ratio of the areas, without diminishing the total area of these absorption bands. Addition of inert solutes, such as  $\text{CH}_2\text{Cl}_2$ , has no apparent effect upon the peak area ratios. This implies that  $\text{SbCl}_5$  coordinates in some way to the dissociated  $\text{SbCl}_4\text{F}$  species, whereas,  $\text{CH}_2\text{Cl}_2$  does not. This coordination, however, appears not to be via Sb-F-Sb linkages, as the overall Sb-F(terminal) bond concentration is unaffected.