The Reaction of Antimony with Fluorosulphuric Acid and Antimony Pentafluoride

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Summary The colourless monovalent antimony salt $SbSO_3F$ formed from the metal and fluorosulphuric acid, slowly reduces the solvent to sulphur cations (blue and yellow) and eventually to elemental sulphur.

METALLIC antimony dissolves slowly in fluorosulphuric acid at room temperature to give a colourless solution which, contrary to an earlier report,[1] has a conductivity which is considerably greater than that of the pure solvent. The absorption spectrum of the colourless solution has a strong peak at 280 nm which disappears when the solution is subjected to a vacuum for *ca.* 20 min. This peak may be assigned to sulphur dioxide. Clearly antimony metal is oxidized when it dissolves in fluorosulphuric acid and does not dissolve unchanged as appears to have been assumed by Paul *et al.*[1] If the concentration of antimony exceeds 0·08 M a white solid separates out of the solution. Elemental analysis showed that this solid has the composition $Sb(SO_3F)$, and apparently contains antimony in the +1 oxidation state. We have previously found that antimony may be oxidized with arsenic pentafluoride to an analogous Sb^I compound, $SbAsF_6$.[2] It would appear, therefore, that antimony reacts with fluorosulphuric acid at room temperature according to equation (1).

$$2Sb + 4HSO_3F \rightarrow 2Sb(SO_3F) + H_3O^+ + SO_3F^- + SO_2 + HF \qquad (1)$$

Initially colourless solutions of antimony and of $SbSO_3F$ in HSO_3F slowly develop a greenish yellow colour which becomes visible after 12—24 h. These solutions then had absorption bands at 235, 280, 320, 430, 580, and 710 nm and e.s.r. signals with *g* values of 2·014 and 2·027. The *g* values and absorption bands are identical with those found previously for sulphur cations in HSO_3F.[3] Thus the equilibrium mixture of S_{16}^{2+} and S_8^+ in HSO_3F has *g* 2·014 and absorption bands at 235, 350, 430, and 710 nm, the equilibrium mixture of S_8^{2+} and S_4^+ has *g* 2·027 and an absorption band at 580 nm, while a solution of S_4^{2+} has an absorption band at 330 nm and no e.s.r. signal. The 280 nm band is due to SO_2. We conclude, therefore, that antimony metal is first oxidized by HSO_3F to $SbSO_3F$ which is then slowly further oxidized to Sb^{III} while at the same time it reduces HSO_3F to SO_2 and sulphur cations. When a solution of $Sb(SO_3F)$ was left for one month at room temperature a yellow solid was deposited from the solution. This solid was identified by means of its Raman spectrum and its *X*-ray diffraction pattern as rhombic sulphur. Elemental sulphur was also obtained as a sublimate when the solid $SbSO_3F$ was heated at 60° under vacuum for 2—3 days.

When antimony metal is treated with antimony pentafluoride at room temperature a white solid is formed slowly, no colours are observed at any time, and the mixture shows no e.s.r. signals. The white solid is probably a mixture of

$Sb(SbF_6)$ and SbF_3. The absence of any coloured species or of any e.s.r. signals during the course of this reaction is consistent with our assignment of the colours and the e.s.r. signals to sulphur cations and radical cations rather than to antimony cations.

Paul *et al.*[1] have reported that they have obtained blue, green, and yellow solutions on oxidizing Sb with $S_2O_6F_2$ in solution in HSO_3F and they have attributed the formation of these colours to a yellow Sb_4^{2+} species and a blue Sb_8^{2+}. We have been unable to repeat this work and on oxidizing antimony with $S_2O_6F_2$ we have only been able to obtain the white compound $Sb(SO_3F)_3$. The conclusions of Paul *et al.* must be open to doubt until it has been proved that the colours they observed are not due to sulphur cations. The same is true of recent reports by Paul, Malhotra, and their co-workers[4,5] that they have obtained evidence for the formation of a yellow As_4^{2+} species and a blue P_8^{2+} species when arsenic and phosphorus are dissolved in disulphuric acid.

We conclude that the only stable lower oxidation state of antimony which has been definitely established is the +1 state which is known as the compounds $SbAsF_6$ and $SbSO_3F$.

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[1] R. C. Paul, K. K. Paul, and K. C. Malhotra, *Chem. Comm.*, 1970, 453.

[2] P. A. W. Dean and R. J. Gillespie, *Chem. Comm.*, 1970, 853.

[3] R. J. Gillespie, J. Passmore, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, 1971, **10**, 1327.

[4] R. C. Paul, J. K. Puri, K. K. Paul, R. D. Sharma, and K. C. Malhotra, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 725.

[5] R. C. Paul, J. K. Puri, and K. C. Malhotra, *Chem. Comm.*, 1971, 1031.