The +1 Oxidation State of Antimony

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Summary The reaction of antimony with arsenic pentafluoride in liquid SO_2 produces a compound formulated as $(Sb_n^{n+})(AsF_6^-)_n$.

IN a recent communication[1] evidence was presented for the existence of antimony cations with the probable formulations Sb_4^{2+} and Sb_8^{2+}. The latter is presumably analogous to the Bi_8^{2+} cation which is formed in Bi–$BiCl_3$ melts,[2] and which has been isolated[3] as $Bi_8(AlCl_4)_2$ from liquid $NaAlCl_4$. The +1 oxidation state of bismuth can also be produced in molten halide melts where monatomic Bi^+ is thought to be present,[4] but to date there has been no report of the corresponding oxidation state for antimony. We now show that Sb^I can be produced by oxidation of antimony with arsenic pentafluoride.

When finely ground antimony suspended in liquid SO_2 is treated with arsenic pentafluoride in the mole ratio 2 : 3, the suspension changes colour over a period of days, an insoluble white product (I) being formed. On separation from the solvent and removal of volatiles, (I) has the composition $SbAsF_6$. Further oxidation of (I) with AsF_5 in SO_2 gives rise to a product $SbF_3{\cdot}AsF_5$; this can also be prepared directly from antimony trifluoride.[5] The reaction producing (I) can be represented:

$$2Sb + 3AsF_5 \rightarrow 2SbAsF_6 + AsF_3$$

The room-temperature ^{19}F n.m.r. spectrum of (I) in acetone, with which some reaction occurs, shows, at $\phi + 64{\cdot}5$, the characteristic 1 : 1 : 1 : 1 quartet of the AsF_6^- anion (*J ca.* 930 Hz). As confirmation of the nature of the anion in (I), a strong band was observed at 699 cm^{-1} in the i.r. spectrum of a Nujol mull, in the position expected for the ν_3 vibration of AsF_6^-. Compound (I) exhibits a small temperature-dependent paramagnetic susceptibility ($\chi_M' = 132 \times 10^{-6}$ c.g.s. units per formula wt. at 18°), the magnitude of which rules out a bare Sb^+ cation, indicating the cation to be polyatomic.

We conclude that (I) is best formulated as $(Sb_n^{n+})(AsF_6^-)_n$.

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[4] N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, 1967, **6**, 1162.
[5] P. A. W. Dean and R. J. Gillespie, unpublished work.