

The +1 Oxidation State of Antimony

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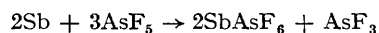
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Summary The reaction of antimony with arsenic pentafluoride in liquid SO₂ produces a compound formulated as (Sb_nⁿ⁺)(AsF₆⁻)_n.

In a recent communication¹ evidence was presented for the existence of antimony cations with the probable formulations Sb₄²⁺ and Sb₈²⁺. The latter is presumably analogous to the Bi₈²⁺ cation which is formed in Bi-BiCl₃ melts,² and which has been isolated³ as Bi₈(AlCl₄)₂ from liquid NaAlCl₄. 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 SO₂ 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

SbAsF₆. Further oxidation of (I) with AsF₅ in SO₂ gives rise to a product SbF₃·AsF₅; this can also be prepared directly from antimony trifluoride.⁵ The reaction producing (I) can be represented:



The room-temperature ¹⁹F n.m.r. spectrum of (I) in acetone, with which some reaction occurs, shows, at $\phi + 64.5$, the characteristic 1 : 1 : 1 : 1 quartet of the AsF₆⁻ 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 AsF₆⁻. 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_nⁿ⁺)(AsF₆⁻)_n.

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

² N. J. Bjerrum and G. P. Smith, *Inorg. Chem.*, 1967, 6, 1958.

³ J. D. Corbett, *Inorg. Chem.*, 1968, 7, 198.

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.