Journal of Fluorine Chemistry, 15 (1980) 435–439

Received: August 10, 1979

SHORT COMMUNICATION

The Bromine Catalysed Oxidation of Arsenic Trifluoride by Antimony Pentafluoride

JACK PASSMORE, W. A. SHANTHA NANDANA, E. KEITH RICHARDSON and PETER TAYLOR

Chemistry Department, University of New Brunswick, Fredericton, N.B.,
E3B 5A3 (Canada)

Antimony pentafluoride dissolves in excess arsenic trifluoride presumably with the formation of $AsF_3 \cdot SbF_5$ [1,2] and possibly $(AsF_3)_nSbF_5$ n = 2, [3], 3, [4], in equilibrium with one another and the solvent. However, O. Ruff [5] found in 1906 that in the presence of bromine, antimony pentafluoride oxidises arsenic trifluoride to arsenic pentafluoride with formation of a solid he suggested was $SbBrF_4$. In the course of our work we investigated this reaction and found that trace quantities of bromine (<0.1 mole per cent) catalyse the formation of arsenic pentafluoride and $SbF_3 \cdot SbF_5$ [6], according to equation (1).

$$AsF_3 + 2SbF_5 = AsF_5 + SbF_3 \cdot SbF_5 \qquad (1)$$

Reaction (2) is endothermic to the extent of ca. 33 Kcals $mole^{-1}$ [7-9], but reaction (1) occurs spontaneously in presence of bromine, being more favourable than reaction (2) by the heat of reaction (3).

$$AsF_3 + SbF_5 = AsF_5 + SbF_3 \qquad (2)$$

$$SbF_3 + SbF_5 = SbF_3 \cdot SbF_5 \qquad (3)$$

It has been proposed [10] that the reaction between AsF_3, Br_2 and SbF_5 is water catalysed; however, we took considerable care to dry our reagents and apparatus and suggest that the reaction proceeds via BrF, produced in small amounts, according to equilibrium (4).

$$2SbF_5 + Br_2 \leftrightharpoons 2BrF + SbF_3 \cdot SbF_5 \qquad (4)$$

Bromine monofluoride may then oxidise arsenic trifluoride with regeneration of the catalyst bromine, as shown in equation (5).

$$2BrF + AsF_3 = Br_2 + AsF_5 \qquad (5)$$

Reactions (4) and (5) sum to give net oxidation of AsF_3 by SbF_5 given by equation (1).

The occurrence of equilibrium (4), with bromine monofluoride as an intermediate in the overall reaction, is supported by the formation of SO_2BrF and lesser amounts of SO_2F_2 and SOF_2, from sulphur dioxide, antimony pentafluoride and bromine. The same products were obtained by the reaction of bromine trifluoride, bromine (leading to BrF), and sulphur dioxide [11]. The reaction of arsenic pentafluoride, bromine and sulphur dioxide gave SO_2BrF at a much slower rate.

The reaction of $Br_3^+AsF_6^-$ with arsenic trifluoride to give bromine and arsenic pentafluoride [12] may also proceed via bromine monofluoride intermediate produced via equilibrium (6).

$$Br_3^+AsF_6^- \leftrightharpoons Br_2 + BrF + AsF_5 \qquad (6)$$

Iodine does not catalyse the oxidation of arsenic trifluoride by antimony pentafluoride [13,14], and fluoroantimonate and some fluoroarsenate salts of iodine polyatomic cations [13-16] are stable in arsenic trifluoride solutions, suggesting that equilibria such as (7) and (8) lie far to the left, consistent with the general greater stability of iodine polyatomic cations relative to those of bromine [15].

$$I_3^+AsF_6^- \leftrightarrows I_2 + IF + AsF_5 \quad (7)$$

$$2I_2^+Sb_2F_{11}^- \leftrightarrows I_2 + 2IF + 4SbF_5 \quad (8)$$

EXPERIMENTAL

Apparatus, reagents and techniques are described in refs. [13,14].

In a typical reaction, SbF_5 (67.84 mmol) was allowed to react with Br_2 (0.05 g) and AsF_3 (97.25 mmol) for 14 hr. at r.t. The colour of the product indicated the presence of bromine. The volatiles, including AsF_5, were removed leaving 13.48 g or 34.08 mmol of $SbF_3 \cdot SbF_5$ identified by X-ray powder diffraction, and infrared and Raman spectroscopy [6,17]. In another experiment SbF_5 (6.8 mmol) oxidised AsF_3 (15.6 mmol) with Br_2 (0.04 g), yielded (3.6 mmol) $SbF_3 \cdot SbF_5$ in 2 hr. and in another SbF_5 (36.86 mmol), AsF_3 (71.74 mmol) and Br_2 (0.06 g) in 16 hr. yielded 7.58 g solid, or, 19.16 mmol $SbF_3 \cdot SbF_5$ (probably contains traces $AsF_3 \cdot SbF_5$), and 14.56 mmol AsF_5 (isolated).

Antimony pentafluoride (11.5 mmol) was allowed to react with Br_2 (6.1 mmol) in SO_2 (8.6 mmol), and the infrared spectra of the volatiles was recorded after 4 hr., 18 hr., and 4 d. The spectrum obtained after 4 hr. showed the presence of SO_2BrF as the major product, with small amounts of SOF_2, and SO_2F_2. The relative intensities of the SOF_2 and SO_2F_2 peaks were greater in the spectra obtained after the longer reaction times. The volatiles were removed leaving 2.00 g (solid) or 5.1 mmol $SbF_3 \cdot SbF_5$.

Arsenic pentafluoride (16.0 mmol) was allowed to react with SO_2 (17.5 mmol) and Br_2 (18.7 mmol) for 5 d. The infrared spectrum of the gases above the highly coloured mixture (indicating Br_2) showed the presence of SO_2 and AsF_5, and lesser quantities of SO_2BrF and AsF_3, as well as traces of SO_2F_2.

ACKNOWLEDGMENT

We thank the Natural Sciences and Engineering Research Council (Canada) for financial support and for a Fellowship (E.K.R.).

REFERENCES AND NOTES

1 A. J. Edwards and R. J. C. Sills, J. Chem. Soc. (A), (1971) 942.

2 T. K. Davies and K. C. Moss, J. Chem. Soc. (A), (1970) 1054.

3 The cation $As_2F_5^+$ has been identified in the gas phase (C. E. Doiron and T. McMahon, Inorg. Chem. Submitted for publication,) therefore, $As_2F_5^+SbF_6^-$ or $(AsF_3)_2SbF_5$, is a possible component of AsF_3/SbF_5 solutions.

4 $(SbF_3)_3SbF_5$ has been identified by X-ray crystallography and shown to be $Sb_3F_8^+SbF_6^-$, therefore $(AsF_3)_3SbF_5$ is a possible component of AsF_3/SbF_5 solutions. (W. A. S. Nandana, J. Passmore, N. Swindells, P. S. White, and P. Taylor. To be submitted for publication.)

5 O. Ruff and H. Graf, Chem. Ber., 39 (1906) 67.

6 R. J. Gillespie, D. R. Slim, J. E. Vekris, J. C. S. (Dalton), (1977) 971.

7 P. A. G. O'Hare and W. N. Hubbard, J. Phys. Chem., 69 (1965) 4358.

8 J. Bousquet, J. Carre, M. Kollmannsberger and P. Barberi, J. Chem. Phys. Phys.-Chim. Biol., 72 (1975) 280.

9 R. D. W. Kemmitt and D. W. A. Sharp, "Advances in Fluorine Chemistry", 4, Edited by M. Stacey et al, London, Butterworths, p. 142, 1965.

10 H. M. Dess and R. W. Parry, J. Amer. Chem. Soc., 78 (1956) 5735.

11 P. R. Reed and R. W. Lovejoy, Spectrochim. Acta, 24A (1968) 1795.

12 W. V. F. Brooks, J. Passmore and E. K. Richardson, Can. J. Chem. In press.

13 J. Passmore and P. Taylor, J. C. S. (Dalton), (1976) 804.

14 J. Passmore, E. K. Richardson and P. Taylor, J. C. S. (Dalton), (1976) 1006.

15 R. J. Gillespie and J. Passmore, in "Advances in Inorganic Chemistry and Radiochemistry", Eds. H. J. Emeléus and A. G. Sharpe, Academic Press, 17 (1975) 49.

16 J. Passmore, P. Taylor, T. Whidden and P. S. White, Can. J. Ghem., 57 (1979) 968.

17 T. Birchall, P. A. W. Dean, B. Della Valle and R. J. Gillespie, Can. J. Chem., 15 (1973) 667.