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Preliminary Note

Ionization in the SO_3–BrF_3 system

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The recent communication of Gross and Meinert[1] in which they identified BrF_2^+ and SO_3F^- ions in BrF_3-SO_3 by shifts in the ^{19}F magnetic resonance prompts us to record further chemical evidence we have obtained on ionization in this system and to point out that the redox range differs from that in BrF_3.

The original preparation of silver fluorosulphate was an indirect one. Silver and nitrosyl pyrosulphate were mixed in BrF_3 rather than silver and sulphur trioxide[2]. The latter route was not described because the product was always off-white. A re-examination of the reaction of silver with a BrF_3–SO_3 mixture shows that the product is mainly argentic fluorosulphate which can be thermally decomposed to white argentous fluorosulphate. A similar argentic state was also encountered in the anodic oxidation of silver fluoride in fluorosulphuric acid[3] when the black anodic deposit corresponded to a 70:30 mixture of Aρ (II) and Aρ (I). The brown solid reported from the reaction of $XeF_2(SO_3F)_2$ and silver chloride[4] is probably similar. Thus in BrF_3–SO_3 the fluorosulphate ion, generated *in situ*, can stabilize Aρ (II); whereas in BrF_3 the trifluoride is oxidised and only the Aρ (I) salts can be obtained from solution. Other oxidations which proceed differently in BrF_3–SO_3 mixtures than in BrF_3–Br_2 or BrF_3 can be turned to practical account.

The ionization of sulphur trioxide in BrF_3 is also shown by calorimetric measurements. The heat of solution is close to that of SbF_5 in BrF_3 (92.80 ± 0.75 and 92.38 ± 0.33 kJ mol^{-1} of solute respectively) and greater than that of weaker "acids" such as TaF_5 and SnF_4[5]. The heat of formation of potassium fluorosulphate (-1166.5 ± 6.3 kJ mol^{-1}) derived from the heat of "neutralization" of BrF_3–SO_3 mixture with a deficiency of potassium fluoride is in good agreement with the heats of formation measured in fluorosulphuric acid[6] (-1161.5 kJ mol^{-1}). These results are compatible with a primary ionization of SO_3–BrF_3 mixtures to BrF_2^+ and SO_3F^- ions as originally suggested.

A small practical point should be mentioned in connection with BrF_3–SO_3 mixtures to avoid future misunderstanding. Solids are sometimes formed on evaporating these mixtures as well as the more usual liquids. This is caused by polymerisation of sulphur trioxide to its asbestos form, and is more likely to occur when excess trioxide is added to the trifluoride because of traces of moisture.

With excess trifluoride we have been able to store a liquid solution at room temperature over two years without solid deposition. On heating these solutions bromine, possibly bromine fluorosulphates, and polysulphuryl fluorides are formed.

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