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Reactions of Bromine and Chlorine with Osmium Hexafluoride

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SUMMARY

Osmium hexafluoride combines with bromine to form Br_2OsF_6. Solutions of OsF_6 in liquid chlorine are strongly blue or blue violet in colour, and charge transfer interactions are indicated.

INTRODUCTION

The reactions of osmium hexafluoride with bromine and chlorine have recently been studied in these laboratories as part of an investigation into the behaviour of metal hexafluorides towards non-metallic halides

RESULTS and DISCUSSION

Osmium hexafluoride reacts immediately with excess of liquid bromine in an FEP reaction vessel to give a cherry red solid below a reddish-brown solution. This solution gives a Raman spectrum (Kr laser) with principal absorptions at 316, 382, and 660 cm^{-1}, which may be assigned, respectively, to Br_2 [1], Br_2^+ [1], and OsF_6^-. The Br_2^+ ion is also identified by its absorption frequency in the visible region at 495 nm (cf. 510 nm) [1]. The reddish-brown solid which results when the solvent has been removed under a vacuum is the salt Br_2OsF_6 (Found: equiv. wt. 462; calculated, for

the change from OsF_6 to Br_2OsF_6; 464.0. Found: Br, 34.2. Calc. for Br_2OsF_6; Br, 34.4%). The mass spectrum shows OsF_6^+, OsF_5^+, OsF_4^+, OsF_3^+, $OsOF_2^+$, OsF_2^+, $OsOF^+$, OsF^+, Os^+, and Br_2^+ fragments of which the $OsOF^+$ and $OsOF_2^+$ fragments may be ascribed to hydrolysis in the mass spectrometer, and the infrared spectrum of the solid shows the presence of an OsF_6^- absorption frequency at about 620 cm^{-1}. The effective magnetic moment of the compound, determined at 298 K, is 3.82, which is well above the expected value for OsF_5 (2.06) [2] or OsF_6^- (3.2 - 3.3) [3], but is in reasonable accord with the presence of Br_2^+ and OsF_6^- together. The compound Br_2OsF_6 is very sensitive to moisture, and liberates bromine on dissolution in water.

The reaction between OsF_6 and liquid chlorine takes a different course. OsF_6 dissolves in liquid chlorine at -78° to give a blue solution, which on cooling yields a grass-green solid. If the solution is allowed to warm to 25° in a sealed tube, the colour becomes blue-violet, and shows strong absorption peaks at 640, 495, and 395 nm. On allowing the excess of liquid chlorine to boil off from the solution at atmospheric pressure, the osmium hexafluoride is recovered nearly quantitatively.

The only solid compound containing Br_2^+ which appears to have been isolated hitherto is the complex salt $Br_2Sb_3F_{16}$ [4]. In the present work, curiously, there appears to be no evidence for the related diamagnetic Br_3^+ cation even in the bromine solution, in contrast to the situation observed by Gillespie and Morton in fluorosulphuric acid [1].

It is not expected that OsF_6 would be a sufficiently strong oxidising agent to convert Cl_2 to Cl_2^+, but the strong colourations suggest charge-transfer. We note that IrF_6 reacts with Cl_2 in a complicated manner but that in this case also the Cl_2^+ ion is not isolated as a stable entity [5].

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