URANIUM (V) FLUORIDES

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Rhenium and uranium hexafluorides oxidise iodine in iodine pentafluoride at ambient temperature to give the I_2^+ cation. With UF_6 additional reaction occurs to give β-uranium pentafluoride as one product (J.A. Berry, A. Prescott, D.W.A. Sharp, and J.M. Winfield, J. Fluorine Chem., 1977, 10, 247). Further work on the latter reaction together with an electronic spectroscopic study of the oxidation of I_2 by phosphorus pentafluoride in IF_5, suggests that the fate of the I_2^+ cation depends on the nature and quantity of the oxidising agent. Oxidation of I_2 by PF_5 can be conveniently followed by monitoring its visible spectrum. The reaction occurs over several hours and eventually an apparent equilibrium between I_2 and I_2^+ results. Formation of $I_2^+UF_6^-$ is rapid and, with the mole ratio $UF_6:I_2 > 10:1$, UF_5 is precipitated rapidly from solution, I_2^+ being oxidised further, apparently to IF_5. With a smaller $UF_6:I_2$ mole ratio UF_5 is contaminated by I_2, the latter is presumed to result from the disproportionation of an I^I or I^{III} fluoride.

β-UF_5 is very soluble in acetonitrile and reacts with thallium(I) fluoride in this solvent to give Tl^IUF_6. It reacts with trimethyl(methoxo)silane to give $(CH_3)_3SiF$, $U(OCH_3)_5$, and an insoluble solid, believed to be a mixture of U^V methoxide, fluorides. Both reactions are conveniently followed by near i.r. spectroscopy.