Preparation of Uranium Oxide Tetrafluoride

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Summary The new compound, UOF_4, has been prepared by the reaction of UF_6 with H_2O in a HF slurry.

The oxide fluorides of U^{VI} constitute a poorly understood system. Uranyl fluoride has been known for many years, but the only other definitely characterised member of the system is $U_3O_5F_8$.[1] There have been reports of the preparation of UOF_4 by the fluorination of UO_3 with SeF_4,[2] but this has not been successfully repeated.[1]

Reagents used in the preparation were UF_6, HF, and water. The UF_6 was prepared by fluorination of UO_2.[3] The HF was a commercial product. Both the UF_6 and the HF were distilled twice before use. The equipment used has been described elsewhere.[3] The reaction was carried out in the following manner: 50 mg of water was placed by syringe into a Kel-F tube and diluted with 7 ml of anhydrous HF. This mixture was thoroughly stirred to ensure homogeneity; 1 g of UF_6 was then distilled into the mixture. The resultant slurry was vigorously shaken over the next 30 min. At first no change was observed but after 10 min there was a definite change in colour. No further reaction seemed to occur after 20 min when the mixture was bright orange. The mixture was allowed to stand another 10 min to ensure that the reaction was complete and then excess UF_6 and HF were removed by distillation. A bright orange free-flowing powder remained.

The powder was characterised by a number of techniques. Chemical analysis was used to establish the empirical formula of the compound as UOF_4 [% calc. for UOF_4: U, 72·1; O, 4·9; F. 23·0. Found: U, 71·4; O (difference) 5·6; F, 23·0]. The diffuse reflectance spectrum in the visible region showed only a smooth curve of high absorbance at 300 nm decreasing to low absorbance at wave lengths above 500 nm. The *X*-ray powder diffraction pattern was obtained but has not yet been analysed. However, the pattern showed that the compound is unique and in particular that it is not $U_3O_5F_9$ or $U_2O_3F_6$.[1] The i.r. spectrum of the compound showed only bands at 460 (b), 550 and 655 cm^{-1}. There was also usually a small band at 940 cm^{-1}. This is probably due to UO_2F_2 contamination produced by hydrolysis of UOF_4 during the period the sample was being prepared and the spectrum run. The spectrum was obtained by the KBr disc technique because the compound reacted with Nujol. The strong bands are in the region expected for uranium oxide halides.[4]

The chemical properties of UOF_4 have received some study. UOF_4 is hygroscopic and must be handled in a dry box. It dissolves completely in water producing a clear solution which confirms that the uranium is in the U^{VI} form. A precipitate of UF_4 would appear if the compound contained uranium in the U^{IV} or U^{V} form. The compound is not soluble in benzene, diethyl ether, acetone, acetonitrile, or chloroform. It is slowly decolorised by methyl alcohol but it is not known whether this is due to an alcoholysis reaction or to reaction with the hydrocarbon portion of the solvent. UOF_4 is thermally unstable. At temperatures above 150 °C it decomposes rapidly to give UF_6 and UO_2F_2. It decomposes slowly even at room temperature, but it can be stored for some weeks before decomposition becomes appreciable.

The properties described above, combined with the analysis and method of preparation, provide sufficient evidence to establish that the compound is UOF_4. A number of studies are in progress to obtain quantitative data regarding the properties and structure of UOF_4.

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