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A SPECIFIC METHOD FOR THE PREPARATION OF MANY TRANSITION METAL AND  
ACTINIDE OXIDE TETRAFLUORIDES

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SUMMARY

A general method for the preparation of many transition metal and actinide oxide tetrafluorides by oxygen-fluorine exchange of their respective hexafluorides using boric oxide is described. This simple procedure affords the preparation of  $\text{MoOF}_4$ ,  $\text{WOF}_4$ ,  $\text{ReOF}_4$ ,  $\text{OsOF}_4$  and  $\text{UOF}_4$  in high yield while reaction of boric oxide with  $\text{IrF}_6$  and  $\text{RuF}_6$  leads to the preparation of lower fluorides of these elements. The preparation of oxide tetrafluorides by reaction of their oxide tetrachlorides with anhydrous HF has also been investigated, as well as a study of some halogen-exchange reactions of the oxide tetrafluorides.

INTRODUCTION

As a class of compounds, transition metal oxide fluorides have received considerable attention of late. However, most of these investigations have involved physical, crystallographic and spectroscopic studies and it is still true to say that very little is known about their chemical properties. More importantly, there are no general methods for the preparation of many of these compounds. All too frequently they have resulted as impurities during the fluorination of metals due to oxide coatings, by the partial hydrolysis of binary fluorides from moisture contamination, or by the reaction of binary

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fluorides with glass storage vessels. In this paper, we shall deal with the preparation and some chemical properties of one type of oxide fluoride, the oxide tetrafluorides.

The oxide tetrafluorides of chromium, molybdenum, tungsten, technetium, rhenium, ruthenium, osmium, uranium, neptunium and plutonium have all been prepared and characterised to some extent [1-16]. Single crystal X-ray studies have also been reported on various polymorphs of  $\text{MoOF}_4$ ,  $\text{WOF}_4$ ,  $\text{TcOF}_4$ ,  $\text{ReOF}_4$  and  $\text{UOF}_4$  [3,12,13], while lattice parameters have been reported for  $\text{OsOF}_4$ ,  $\text{NpOF}_4$  and  $\text{PuOF}_4$  [7,14,16]. However, of all of the above compounds there are very few preparative procedures which are applicable in more than one instance. Examples are, in the case of the actinide oxide tetrafluorides, the controlled hydrolysis of the respective hexafluoride in anhydrous HF [9-16] and in the case of the subgroup VI oxide tetrafluorides,  $\text{MoOF}_4$  and  $\text{WOF}_4$ , either passage of an  $\text{O}_2\text{-F}_2$  mixture over the heated metal under controlled conditions, passage of  $\text{F}_2$  over the corresponding trioxide at elevated temperatures, or halogen-exchange of the oxide tetrachloride with anhydrous HF [1]. Extension of either the fluorination or oxy-fluorination procedures to the preparation of technetium, rhenium and osmium oxide tetrafluorides is not possible as oxidation states higher than six are known for these metals and so result under highly oxidative reaction conditions.

In our investigations we have examined the oxygen-fluorine exchange reactions of several transition metal and actinide hexafluorides with boric oxide ( $\text{B}_2\text{O}_3$ ) as an alternative route to the preparation of transition metal and actinide oxide tetrafluorides. We have also re-investigated the method used originally by Ruff [17,18] involving halogen-exchange of the corresponding oxide tetrachlorides and have examined a selected number of halogen-exchange reactions of some oxide tetrafluorides, similar to the studies on the transition metal and actinide hexafluorides that have been reported by O'Donnell and co-workers [19].

## EXPERIMENTAL

### Apparatus and materials

All reactions were carried out in metal and Kel-F apparatus, similar to that described by Canterford and O'Donnell [20]. The hexafluorides

of molybdenum, tungsten and rhenium were prepared by direct fluorination of their respective metals in a flow system, after prior hydrogenation at 1000°C to remove any oxide coating. Fluorination of rhenium metal in this way produces a mixture of  $\text{ReF}_6$  and  $\text{ReF}_7$  [21]. A pure sample of  $\text{ReF}_6$  was obtained from the mixture by reaction with rhenium metal according to the procedure described by Malm and Selig [21]. Osmium hexafluoride and iridium hexafluoride were prepared by heating their respective metals in a monel reactor at 350-400°C for three hours, in the presence of excess fluorine. Ruthenium hexafluoride was prepared by fluorination of the metal using the procedure of Burns and O'Donnell [22], while uranium hexafluoride was kindly provided by the Australian Atomic Energy Commission. This material had been prepared by the fluorination of uranium dioxide.

The oxide tetrachlorides of molybdenum, tungsten and rhenium were prepared by reaction of  $\text{MoO}_3$ ,  $\text{WO}_3$  and  $\text{Re}_2\text{O}_7$ , respectively, with freshly distilled  $\text{SOCl}_2$  [23-25]. After removal of the excess  $\text{SOCl}_2$  and highly volatile reaction products the oxide tetrachlorides were sublimed under vacuum. Osmium oxide tetrachloride was prepared by oxy-chlorination of the metal at 400°C, as described by Hepworth and Robinson [26].

Anhydrous HF (Matheson grade, 99.8% min. purity) was distilled on a column similar to that described by Shamir and Netzer [27].

All other materials, i.e.,  $\text{BCl}_3$ ,  $\text{BBr}_3$ ,  $\text{CCl}_4$ ,  $\text{B}_2\text{O}_3$  and  $n\text{-C}_6\text{F}_{14}$  (n-perfluorohexane) were of reagent grade purity and, if volatile, were distilled under vacuum before use.

## Reaction procedures

### (a) Metal hexafluoride-boric acid reactions

Typically, a large excess of the hexafluoride (1-2 g) was condensed onto a weighed, powdered and well-dispersed amount of  $\text{B}_2\text{O}_3$  (20-30 mg) at -196°C. The tube and contents were then transferred to an acetone-solid  $\text{CO}_2$  cold bath and subsequently allowed to warm slowly to room temperature. During this time reaction occurred and, to avoid an excessive pressure of the highly volatile  $\text{BF}_3$ , this product was periodically vented into an expansion bulb. Upon reaching room temperature the products were refluxed in the presence of the excess hexafluoride for about one hour to ensure completion of the reaction. In view of the highly exothermic nature of the reactions of  $\text{IrF}_6$  and  $\text{RuF}_6$  [22], with the possibility of thermal

decomposition of the reaction products, the procedure involving these hexafluorides was modified slightly. A medium,  $n\text{-C}_6\text{F}_{14}$ , was employed for the purpose of dissipating the heat generated during these reactions. Thus the  $\text{B}_2\text{O}_3$  was first suspended in this liquid ( $2\text{-}3\text{ cm}^3$ ), and cooled to  $-196^\circ\text{C}$  before introduction of the hexafluoride. The procedure from this point on was as described above, but generally smaller amounts of reactants were used in these reactions.

#### (b) Metal oxide tetrachloride - anhydrous HF reactions

Excess anhydrous HF (2-3 g) was condensed onto a sample of oxide tetrachloride (0.3-0.5 g) at  $-196^\circ\text{C}$  and then allowed to warm slowly to room temperature. Reaction was observed with  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  during this time and the volatile HCl periodically vented into an expansion bulb. No reaction was observed with  $\text{ReOCl}_4$  and  $\text{OsOCl}_4$  even on heating to  $80^\circ\text{C}$  for one hour.

#### (c) Halogen-exchange reactions of the metal oxide tetrafluorides

Halogen-exchange of  $\text{MoOF}_4$ ,  $\text{WOF}_4$ ,  $\text{ReOF}_4$  and  $\text{UOF}_4$  with the reagents  $\text{BCl}_3$ ,  $\text{BBr}_3$  and  $\text{CCl}_4$  was studied by condensing excess halogenating reagent (2-3 g) onto a sample of oxide tetrafluoride (0.2-0.3 g) at  $-196^\circ\text{C}$ . The temperature was then allowed to rise slowly and reaction was usually complete upon reaching room temperature. Excess pressure from the volatile mixed halides of boron or carbon was periodically released into an expansion bulb.

#### Identification of products

After completion of a reaction all of the volatile species were removed under vacuum at room temperature. Careful fractionation enabled the recovery of the excess hexafluoride or reactant in each case and the volatile products of reaction were identified by their infra-red or mass spectra. All solid products were transferred to an argon-filled glove box for subsequent handling and were identified by chemical analysis, X-ray powder photography, infra-red spectroscopy and their physical properties.

Infra-red spectra were recorded on a Perkin-Elmer Grating Infra-red Spectrophotometer Model 457 ( $4000\text{-}250\text{ cm}^{-1}$ ). Volatile samples were con-

tained in a 5 cm monel gas cell while solid samples were mounted as nujol mulls or as powders between CsI or AgCl plates. Mass spectra were recorded on an A.E.I. MS9 instrument. X-ray powder photographs were taken using a Philips Debye-Scherrer camera of diameter 11.46 cm on a Philips Industries Ltd. X-ray generator Model PW 1010/80. Nickel filtered  $\text{Cu-K}_\alpha$  and zirconium filtered  $\text{Mo-K}_\alpha$  radiation were employed for all samples and exposures required from three to four hours.

## RESULTS AND DISCUSSION

### (a) Metal hexafluoride-boric oxide reactions

The products of the reactions of  $\text{MoF}_6$ ,  $\text{WF}_6$ ,  $\text{ReF}_6$ ,  $\text{OsF}_6$ ,  $\text{UF}_6$ ,  $\text{IrF}_6$  and  $\text{RuF}_6$  with  $\text{B}_2\text{O}_3$  are listed in Table 1, while the analytical results on the oxide fluorides that were produced are given in Table 2. In most cases

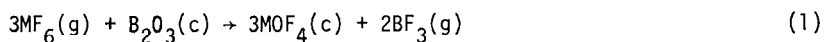
Table 1

### Metal Hexafluoride-Boric Oxide Reactions

Reactant	Products
$\text{MoF}_6$	$\text{MoOF}_4$ , $\text{BF}_3$
$\text{WF}_6$	$\text{WOF}_4$ , $\text{BF}_3$
$\text{ReF}_6$	$\text{ReOF}_4$ , $\text{BF}_3$
$\text{OsF}_6$	$\text{OsOF}_4$ , $\text{BF}_3$
$\text{UF}_6$	$\text{UOF}_4$ , $\text{BF}_3$
$\text{IrF}_6(n\text{-C}_6\text{F}_{14})$	$\text{IrF}_5$ , $\text{BF}_3$ , $\text{O}_2$ (a)
$\text{RuF}_6(n\text{-C}_6\text{F}_{14})$	$\text{RuF}_5$ , $\text{BF}_3$ , $\text{O}_2$ (a)

(a) Other unidentified products were also present.

simple oxygen-fluoride exchange took place, according to equation (1), below, to give the corresponding oxide tetrafluoride.



Only in two cases were oxide tetrafluorides not produced, and these are

Table 2

Analytical Results

Product	Found		Calculated	
	M%	F%	M%	F%
MoOF <sub>4</sub>	50.2	39.8	51.1	40.4
WOF <sub>4</sub>	65.0	27.0	66.7	27.5
ReOF <sub>4</sub>	66.7	26.9	66.9	27.3
OsOF <sub>4</sub>	65.5	25.8	67.4	26.9
UOF <sub>4</sub>	71.8	22.4	72.1	23.0

discussed below. The oxygen-fluorine exchange method using B<sub>2</sub>O<sub>3</sub> therefore offers an alternative procedure for the preparation of oxide tetrafluorides compared to the controlled hydrolysis of metal hexafluorides in anhydrous HF and, indeed, does not require use of this latter reagent.

The reactions of the metal hexafluorides with B<sub>2</sub>O<sub>3</sub> are thermodynamically very favorable. As an indication of this, the standard enthalpy changes for the molybdenum and tungsten reactions may be calculated using the available thermodynamic data for the gaseous hexafluorides, solid oxide tetrafluorides, B<sub>2</sub>O<sub>3</sub>(c) and BF<sub>3</sub>(g) [28,29]. These are -405 and -288 kJ mol<sup>-1</sup> for the molybdenum and tungsten reactions, respectively. However, oxide tetrafluorides are not the only possible products of reaction in that further oxygen-fluorine exchange could occur. The most favorable conditions for the formation of oxide tetrafluorides required the use of finely powdered B<sub>2</sub>O<sub>3</sub> (< 200 mesh) and the presence of a large excess of hexafluoride. Provided that these conditions were employed only oxide tetrafluorides were observed. If a large excess of hexafluoride is not used, then, presumably, localised surface reactions on the B<sub>2</sub>O<sub>3</sub> particles can occur, which may lead to impure or different products. This was observed in a number of investigations where the hexafluoride/B<sub>2</sub>O<sub>3</sub> ratio was ~ 1.

The physical, crystallographic and spectroscopic properties of MoOF<sub>4</sub>, WOF<sub>4</sub>, ReOF<sub>4</sub> and UOF<sub>4</sub> were as described in the literature. With the excep-

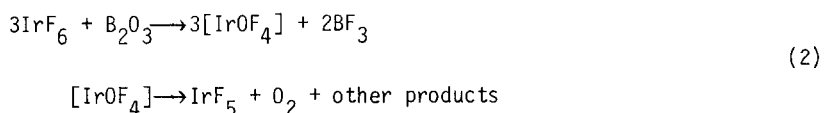
tion of  $\text{UOF}_4$ , all of the oxide tetrafluorides were fairly soluble in their respective hexafluorides and in anhydrous HF. Interestingly, the  $\text{ReOF}_4$  formed by this procedure was light blue in colour and presumably had the recently reported trimeric modification [3] rather than the cis-fluorine bridged chain structure of dark-blue  $\text{ReOF}_4$  [30].

The reaction of  $\text{OsF}_6$  with  $\text{B}_2\text{O}_3$  gave yellow  $\text{OsOF}_4$ , somewhat different in colour to the grey-green and blue-green materials that have been reported by other workers [7,8,31]. Like the other transition metal oxide tetrafluorides,  $\text{OsOF}_4$  proved to be quite soluble in its respective hexafluoride and in anhydrous HF. It was extremely sensitive to moisture, dissolving in water or alkali to give a clear yellow solution and an odour of  $\text{OsO}_4$ . Its hydrolytic behaviour therefore appears to be quite similar to that of  $\text{OsF}_6$  [32]. An X-ray powder photograph of  $\text{OsOF}_4$  was recorded and the pattern could be indexed in terms of the lattice parameters that have been reported by Falconer *et al.* [7]. These had been obtained from measurements on crystals grown from the vapour at about  $100^\circ\text{C}$ . An infra-red spectrum of  $\text{OsOF}_4$  exhibited bands at 1018 (s,sp), 966 (w,br), 735 (m), 705 (m,sh), 657 (s,sh), 648 (s,br), 529 (m), 423 (w), 380 (w), 311 (w), 288 (w), 272 (m,sh) and 263 (s)  $\text{cm}^{-1}$ . The strong, sharp band at  $1018\text{ cm}^{-1}$  may be assigned to the  $\text{Os}=\text{O}$  stretching frequency, and is similar to the  $\text{Os}=\text{O}$  stretching frequency of  $1020\text{ cm}^{-1}$  that has been found for  $\text{OsOCl}_4$  [33]. The bands from 735 to  $648\text{ cm}^{-1}$  may be assigned to osmium-terminal fluorine stretches, those at 529 and  $423\text{ cm}^{-1}$  to the osmium-bridging fluorine stretches and the remaining bands below  $423\text{ cm}^{-1}$  to deformations. On exposure of the sample to air all peaks diminished in intensity and a sharp, intense band appeared at  $960\text{ cm}^{-1}$ . This may be assigned to  $\nu_3$  of  $\text{OsO}_4$ , one of the products of hydrolysis of  $\text{OsOF}_4$ . The  $\text{Os}=\text{O}$  stretching frequency of  $1018\text{ cm}^{-1}$  reported here is somewhat higher than the value of  $1009\text{ cm}^{-1}$  recorded by Falconer *et al.* [31] from a Raman spectrum of their material. This, together with the considerable variations in colour that have been observed for  $\text{OsOF}_4$  suggest that this oxide tetrafluoride, like other oxide tetrafluorides of the transition metals and actinides, is probably polymorphic.

In all of the reactions discussed to this point, oxygen-fluorine exchange has taken place with no evidence of any oxidation-reduction behavior. However, the reactions of  $\text{IrF}_6$  and  $\text{RuF}_6$  with  $\text{B}_2\text{O}_3$  produced solid products containing their respective metals in a lower oxidation state. This was

somewhat surprising in both cases, but especially in the latter instance as  $\text{RuOF}_4$  has been prepared [1,6].

The reaction of  $\text{IrF}_6$  with  $\text{B}_2\text{O}_3$  gave  $\text{IrF}_5$ ,  $\text{BF}_3$ , oxygen and an involatile iridium-containing solid. Formation of the reduced species suggests that the oxide tetrafluoride, which might have been expected to form, is unstable under the experimental conditions. The reaction may perhaps be written as:



although no evidence of an oxide tetrafluoride intermediate could be obtained.

The involatile, iridium-containing solid was dark maroon in colour and quite sensitive to moisture. Chemical analysis was inconclusive, but indicated that the material was a lower oxide fluoride of iridium. The X-ray powder photograph provided no evidence for the presence of any free metal or dioxide in the sample, nor did the pattern show any close resemblances to the patterns of  $\text{IrF}_5$ ,  $\text{IrF}_4$  or  $\text{IrF}_3$  [34-36]. Furthermore, infra-red spectra of the material did not exhibit any bands that could be attributed to  $\text{IrF}_5$  or  $\text{IrF}_4$  [34]. These observations are consistent with the analytical results and it is suggested that the material was probably a lower oxide fluoride of iridium.

The reaction of  $\text{RuF}_6$  with  $\text{B}_2\text{O}_3$  was similar to the above reaction in that  $\text{RuF}_5$ ,  $\text{BF}_3$ , a highly volatile gas (presumably oxygen) and a brown, involatile solid were produced. Unfortunately, no consistent analyses of the latter material could be obtained. The reaction is probably similar to (2) above, but may have been complicated by the formation of some  $\text{RuOF}_4$ . This oxide tetrafluoride has been shown to decompose fairly readily on heating to  $\text{RuF}_4$  and oxygen [6] and this could occur under the experimental conditions in spite of the presence of  $n\text{-C}_6\text{F}_{14}$ , especially since the reactions of its precursor,  $\text{RuF}_6$ , have been found to be extremely exothermic [22].

The formation of lower fluorides in the latter two reactions, as opposed to the formation of oxide tetrafluorides as in the reactions of the other hexafluorides with  $\text{B}_2\text{O}_3$ , can be correlated with the increase in chemical reactivity of the hexafluorides across each transition metal row and



hence with the trends in the thermodynamic stability of the higher oxidation states of these elements [19]. Interestingly, in a recent study of the hydrolysis reactions of a number of transition metal hexafluorides in hydrogen fluoride, Selig *et al.* [37] observed a similar trend in reactivity for these hexafluorides. Hydrolysis of OsF<sub>6</sub> in HF led to the formation of OsOF<sub>4</sub>, but attempted hydrolysis of the more oxidising hexafluorides, IrF<sub>6</sub>, PtF<sub>6</sub> and RuF<sub>6</sub>, gave oxonium salts, H<sub>3</sub>O<sup>+</sup>MF<sub>6</sub><sup>-</sup> (M = Ir, Pt and Ru), according to (3):



The latter reactions therefore involve oxidation of the water by the hexafluoride, rather than oxygen-fluorine exchange, and the trend in reactivity is similar to that observed in this work although the experimental conditions were somewhat different. It is also of interest to note that use of B<sub>2</sub>O<sub>3</sub> contaminated with H<sub>3</sub>BO<sub>3</sub>, or pure H<sub>3</sub>BO<sub>3</sub> itself, provides a source of hydrogen and leads to the formation of oxonium salts in reactions with the more oxidising hexafluorides. This was observed, for example, in some reactions with IrF<sub>6</sub>, which gave H<sub>3</sub>O<sup>+</sup>IrF<sub>6</sub><sup>-</sup> as one of the products of reaction.

#### (b) Metal oxide tetrachloride-anhydrous HF reactions

As an alternative method for the preparation of oxide tetrafluorides, the reactions of their respective oxide tetrachlorides with anhydrous HF were examined. This procedure was used originally by Ruff [17,18] for the preparation of MoOF<sub>4</sub> and WOF<sub>4</sub>, but does not seem to have been extended to the oxide tetrachlorides of technetium, rhenium and osmium, which were unknown at that time.

The reactions of MoOCl<sub>4</sub> and WOCl<sub>4</sub> with anhydrous HF were found to proceed smoothly below room temperature to give MoOF<sub>4</sub> and WOF<sub>4</sub>, as described by Ruff. However, under the same conditions, both ReOCl<sub>4</sub> and OsOCl<sub>4</sub> showed no reaction with anhydrous HF. The oxide tetrachlorides were slightly soluble in this medium to give red-brown and yellow solutions, respectively. Their solubilities increased with temperature, but still no exchange was observed up to 80°C. This is above the melting points of the two oxide tetrachlorides. In view of the lack of reaction of ReOCl<sub>4</sub> with anhydrous HF, no reaction would be expected to TcOCl<sub>4</sub>.

The difference in behaviour between  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  on the one hand and  $\text{ReOCl}_4$  and  $\text{OsOCl}_4$  on the other is a little surprising. The structures of  $\text{WOCl}_4$  [38] and  $\text{ReOCl}_4$  [39] have been studied by single crystal X-ray methods but no data have been reported for  $\text{MoOCl}_4$  and  $\text{OsOCl}_4$ . On the basis of their physical properties, X-ray powder data and infra-red spectra, these latter oxide tetrachlorides would be expected to have similar structures to  $\text{WOCl}_4$  and  $\text{ReOCl}_4$ , respectively. The structural studies indicate that there is only a very small interaction between the essentially  $C_{4v}$  monomeric units in  $\text{ReOCl}_4$ , while in  $\text{WOCl}_4$  there are chains of slightly distorted trans-oxygen bridged octahedra. Thus, there should be no structural factors to hinder exchange. The difference in reactivity may perhaps be related to the extent of metal to chlorine  $d\pi$ - $d\pi$  back-donation, which would be expected to increase from  $\text{MoOCl}_4$  and  $\text{WOCl}_4$ , to  $\text{OsOCl}_4$ . Evidence for this is discussed at greater length by Canterford and Colton [1], and further elaboration is beyond the scope of this paper. It would appear, however, that this type of reaction has only limited applicability for the preparation of oxide tetrafluorides.

(c) Halogen-exchange reactions of the metal oxide tetrafluorides

As pointed out in the Introduction to this paper, there have been very few studies of the chemical reactions of the oxide tetrafluorides, although in many cases their physical and crystallographic properties have been very well-characterised. It was decided, therefore, to look at a selected number of halogen-exchange reactions of some of the oxide tetrafluorides, analogous to those studies that have been made on the corresponding hexafluorides by O'Donnell and co-workers [19].

The results of this limited study are given in Table 4. For the transition metal oxide tetrafluorides, the pattern of reactivity was found to be identical to that of the hexafluorides. That is, if the hexafluoride entered into a halogen-exchange reaction with a particular reagent, then the corresponding oxide tetrafluoride also reacted with this compound. Of course, the products of these reactions were binary halides in the case of the hexafluorides and oxide tetrahalides in the case of the oxide tetrafluorides.

The reactions of the actinide oxide tetrafluoride,  $\text{UOF}_4$ , were somewhat different to those of uranium hexafluoride and to the transition metal oxide tetrafluorides. Uranium oxide tetrafluoride showed no reaction with

Table 4

Halogen-Exchange Reactions of the Metal Oxide Tetrafluorides

Reactants	Products
$\text{MoOF}_4 + \text{BCl}_3$	$\text{MoOCl}_4, \text{BF}_3^{(a)}$
$\text{WOF}_4 + \text{CCl}_4$	No Reaction up to $80^\circ\text{C}$
$\text{WOF}_4 + \text{BCl}_3$	$\text{WOC}_4, \text{BF}_3^{(a)}$
$\text{WOF}_4 + \text{BBr}_3$	$\text{WOB}_4, \text{BF}_3^{(a)}$
$\text{ReOF}_4 + \text{CCl}_4$	$\text{ReOCl}_4, \text{CCl}_3\text{F}$
$\text{ReOF}_4 + \text{BCl}_3$	$\text{ReOCl}_4, \text{BF}_3^{(a)}$
$\text{UOF}_4 + \text{CCl}_4$	No Reaction up to $80^\circ\text{C}$
$\text{UOF}_4 + \text{BCl}_3$	$\text{UCl}_6, \text{B}_2\text{O}_3, \text{BF}_3^{(a)}$
$\text{UOF}_4 + \text{BBr}_3$	$\text{UBr}_5, \text{B}_2\text{O}_3, \text{BF}_3^{(a)}, \text{Br}_2^{(b)}$

- (a) The mixed chloride or bromide fluorides of boron were also present.  
 (b) Other unidentified products were also present.

$\text{CCl}_4$  up to  $80^\circ\text{C}$ , unlike  $\text{UF}_6$ , which has been found to react with this reagent. After standing for several weeks, with occasional heating to  $60\text{--}80^\circ\text{C}$ , a small amount of  $\text{CCl}_3\text{F}$  was detected in the vapour phase by its infra-red spectrum. This is, however, attributed to some disproportionation of the oxide tetrafluoride to  $\text{UF}_6$  and  $\text{UO}_2\text{F}_2$  on heating [10,12], and subsequent reaction of the hexafluoride with  $\text{CCl}_4$ . Uranium oxide tetrafluoride did not undergo simple halogen-exchange with  $\text{BCl}_3$  or  $\text{BBr}_3$  to give the expected oxide tetrahalides, but instead gave  $\text{UCl}_6$  and  $\text{UBr}_5$  plus bromine, respectively, boric oxide and the mixed chloride or bromide fluorides of boron. In the latter reaction, the formation of  $\text{UBr}_5$  and bromine is consistent with the fact that  $\text{UBr}_5$  is the highest known binary bromide of this element. The observed difference in behaviour between the transition metal and actinide oxide tetrafluorides in the above reactions is probably a reflection of the considerable differences in bonding between the respective groups of elements, as has been discussed by O'Donnell [19].

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