Journal of Fluorine Chemistry, *44* (1989) 177–185
Received: October 12, 1988; accepted: January 22, 1989

FLUORINATION OF OXIDES OF URANIUM AND THORIUM BY AMMONIUM HYDROGENFLUORIDE

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SUMMARY

UO_2, U_3O_8 and ThO_2 were fluorinated by NH_4HF_2 either alone or in conjunction with NH_4F at room temperature to $[NH_4]_4UF_8.2H_2O$, $[NH_4]_3UO_2F_5.H_2O$ and $[NH_4]_4ThF_8.2H_2O$ respectively. The TG/DTA and powder XRD techniques were employed to study the thermal decomposition of these compounds and identify the final residues as UF_4, $UO_2F_2.2H_2O$ and ThF_4. This appears to be a simple route to the tetrafluorides.

INTRODUCTION

NH_4HF_2 has been used [1-3] as a fluorinating agent at room temperature or close to room temperature to prepare fluoro and oxyfluoro anionic compounds of V(III), V(V), Nb(V) and Ta(V). More recently [4,5] it has found application in introducing fluorine in place of oxygen in complex oxides such as 1,2,3 superconducting oxide $YBa_2Cu_3O_{6+\delta}$. Sanlaville [6] has shown that reaction between ammonium hydrogenfluoride and oxides of uranium can be used to prepare different fluorides/ oxyfluorides. The mechanism of the reaction was not investigated. In this communication, we report the reaction of ammonium hydrogenfluoride with three oxides, viz., UO_2, U_3O_8 and ThO_2.

EXPERIMENTAL

The materials employed in this study are: UO_2 and ThO_2 of nuclear grade and U_3O_8 with an oxygen to metal ratio of 2.655, as determined according to the technique described by Menilly and Chikalla [7]. The NH_4HF_2 is of BDH LR quality. All the reactions were conducted by intimate grinding together of the constituents in polythene bags. The TG/DTA equipment was a ULVAC SINKU RIKO TGD model 7000RHP. The heating/cooling rate was $8K.min^{-1}$, the atmosphere is static air and the sample size is 30mg. XRD powder pattern was run using a nickel filtered $Cu\text{-}K_\alpha$ radiation.

Reaction With UO_2

A mechanical mixture of UO_2 and NH_4HF_2 in 1:4 proportion was mixed for about 15 minutes. The powder XRD pattern of the resultant mixture taken immediately shows no reaction between the constituents. However, on keeping the mixture for about 2 hours the colour of the mixture changed from black to green and showed a total absence of NH_4HF_2 and UO_2 peaks in the XRD pattern showing reaction between the two reactants. The products, however, were not crystalline. The product was dried at 100C and its XRD pattern, which became crystalline agreed reasonably well with that reported [8] for $[NH_4]_4UF_8$. The TG/DTA runs of the mixture are shown in figure 1. While the TG shows three clear, though overlapping steps, the DTA exhibits three endotherms with 1:2:1 areas. The thermal data are summarised in Table 1. The residue in both TG/DTA at 400C is UF_4. All the thermal data may be quantitatively explained in terms of the following steps.

$$UO_2 + 4NH_4HF_2 \xrightarrow[80\,°C]{RT} [NH_4]_4UF_8 . 2H_2O \tag{1}$$

$$[NH_4]_4UF_8 . 2H_2O \longrightarrow [NH_4]_4UF_8 + 2H_2O \tag{2}$$

$$[NH_4]_4UF_8 \longrightarrow [NH_4]_3UF_7 + NH_4F \tag{3}$$

$$[NH_4]_3UF_7 \longrightarrow [NH_4]UF_5 + 2NH_4F \tag{4}$$

$$[NH_4]UF_5 \longrightarrow UF_4 + NH_4F \tag{5}$$

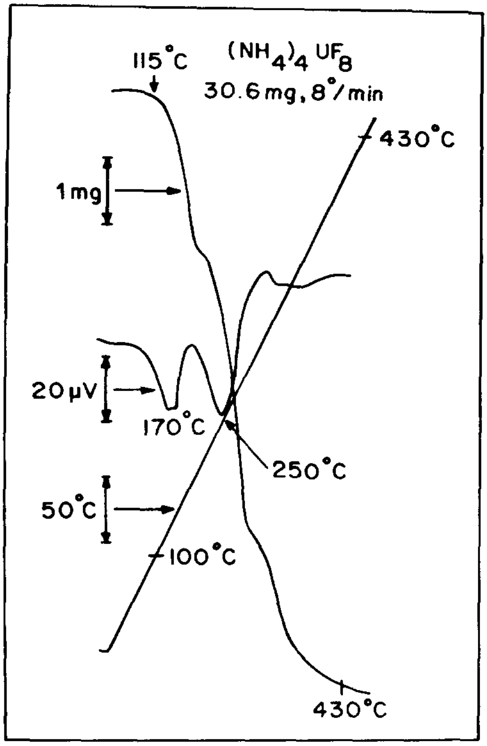


Fig. 1. Simultaneous TG/DTA of $(NH_4)_4UF_8$ in air.

TABLE I

SUMMARY OF TG/DTA RESULTS

Compound	TG						DTA Peak Temp		
	Step Temperature interval			Weight Loss in Steps					
	First	Second	Third	First	Second	Third	First	Second	Third
	(C)			Obsd(Calc) Percent			(C)		
1. $[NH_4]_4UF_8 \cdot 2H_2O$	115-190	190-285	285-430	7.8(8.0)	16.0(16.0)	7.5(8.0)	170	250	360
2. $[NH_4]_3UO_2F_5 \cdot 2H_2O$	170-300	335-420	-------	20.0(17-25)	4.5(4.0)	------	250	375	----
3. $[NH_4]_4ThF_8 \cdot 2H_2O$	50-130	130-220	220-300	13.3(15.0)	13.6(15.0)	11(7.3)	100	190	275

The first equation represents the reaction between the reactants. The second step denotes dehydration at 100C which makes the material crystalline as was mentioned above.. The three steps in TG and DTA correspond to equations (3), (4) and (5).

Reaction with U_3O_8

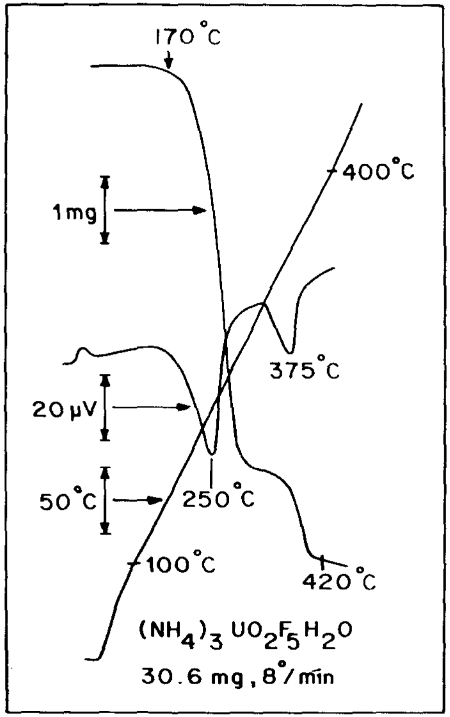
The black oxide, NH_4HF_2 and NH_4F were mixed in the proportion 0.33:2:1 for about half-an-hour. The product was green coloured and the XRD pattern of the product agreed well with that reported [9] for $[NH_4]_3UO_2F_5.H_2O$ without any left over reactants. The TG/DTA runs of this compound are given in figure 2 and the thermal data summarised in Table 1. The TG shows two steps consistent with loss of three moles of NH_4F in the first step and loss of one mole of water in the second. The corresponding DTA shows a strong peak for the first followed by a weak one for the second. The final product in both the cases is UO_2F_2 which readily picks up moisture to the dihydrate. In this case since the uranium oxide is non-stoichiometric, it is not possible to balance the equation for the reaction (1). However, the course of reaction and thermal degradation can be represented as follows:

$$1/3U_3O_8 + 2NH_4HF_2 + NH_4F \xrightarrow{RT} [NH_4]_3UO_2F_5.H_2O \quad (6)$$

$$[NH_4]_3UO_2F_5.H_2O \longrightarrow UO_2F_2.H_2O + 3NH_4F \quad (7)$$

$$UO_2F_2.H_2O \longrightarrow UO_2F_2 + H_2O \quad (8)$$

The thermal data given in Table 1 are consistent with this scheme.



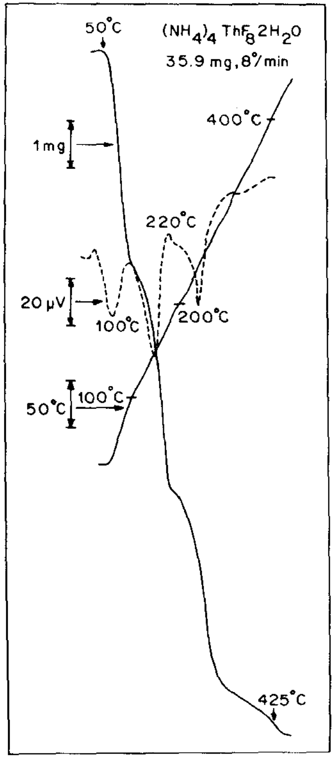


Fig.2. Simultaneous TG/DTA of $(NH_4)_3UO_2F_5$ in air. Fig.3. Simultaneous TG/DTA of $(NH_4)_4ThF_8$ in air.

Reaction with ThO_2

The reaction between ThO_2 and NH_4HF_2 in 1:4 proportion was attempted as in the case of UO_2. The product after keeping for two hours at room temperature did not show the presence of starting materials. Its XRD pattern agrees with that reported by Ryan [10] for $[NH_4]_4ThF_8$ but for the total absence of the reported reflection with d=8.15A. The TG/DTA of the compound are given in figure 3. The TG shows three steps, the first two with loss of $2NH_4F$ each and the third with loss of $2H_2O$ with simultaneous hydrolysis. The corresponding DTA shows three endotherms. If the compound is heated at 100C the product is assumed to be $[NH_4]_2ThF_6.2H_2O$, the thermal data in Table 1 can be summarised in terms of the following equations:

$$ThO_2 + 4NH_4HF_2 \xrightarrow{RT} [NH_4]_4ThF_8.2H_2O \quad (9)$$
$$[NH_4]_4ThF_8.2H_2O \longrightarrow [NH_4]_2ThF_6.2H_2O + 2NH_4F \quad (10)$$
$$[NH_4]_2ThF_6.2H_2O \longrightarrow ThF_4.2H_2O + 2NH_4F \quad (11)$$
$$ThF_4.2H_2O \longrightarrow ThO_2 + 4HF \quad (12)$$

A doubt arises whether water absorbed by ammonium hydrogenfluoride is responsible for the so called solid state reactions that take place with ease at room temperature. In order to confirm this, the reaction with UO_2 was performed with ammonium hydrogenfluoride dried by heating at 80C and further dried over P_2O_5 overnight. No reaction took place over 2hrs. The mixture was then kept at room temperature over P_2O_5 in a desiccator for 24hrs under dry condition. The reaction did take place under these conditions showing that even in the absence of moisture, reaction takes place.

It is worth noting that reaction of ammonium hydrogenfluoride was very slow with U(IV) compared to that with U(VI) and Th(IV). Similarly, removal of water of reaction was more difficult in last two cases compared to U(IV).

Both uranium and thorium are in +4 oxidation state in their dioxides and hence the products of fluorination of these oxides, $[NH_4]_4U/ThF_8$, are also in the same oxidation state. In the non-stoichiometric oxide U_3O_8, however, uranium is in +6 oxidation state with oxygen vacancies in the lattice and hence the product of fluorination, $[NH_4]_3UO_2F_5$, is in +6 oxidation state.

CONCLUSION

From the foregoing, we find that NH_4HF_2 reacts with UO_2 / ThO_2 to give $[NH_4]_4U/ThF_8$ compounds while it reacts with U_3O_8 to give $[NH_4]_3UO_2F_5$. These three compounds, on heating to about 400C give U/ThF_4 and $UO_2F_2.2H_2O$.

It may be added that the usual mode of preparation of UF_4 from UO_2 is by reaction with anhydrous HF at about 400C. It appears that the present method of using NH_4HF_2 for making UF_4 is simpler.

ACKNOWLEDGEMENTS

We sincerely thank Dr Satya Brat and Shri Z A Khan of Process Engineering and Instrumentation Division, BARC for TG/DTA data. We are grateful to Dr N C Jayadevan, Radiochemistry Division, BARC for determining O/U ratio in U_3O_8 sample.

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