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THE FLUORINATION OF URANIUM AND VANADIUM OXIDES WITH SOME METAL FLUORIDES

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SUMMARY

UO_3 reacts with CrF_3 or CuF_2 forming UO_2F_2 and Cr_2O_3 or CuO respectively. Further fluorination occurs above 800°C to form UF_6 though the presence of excess CrF_3 gives mainly UF_4. The fluorination of U_3O_8 with CrF_3 gave UO_2F_2, UF_4 and Cr_2O_3 but with CuF_2 gave UO_2F_2, CuO and Cu_2O. VO_2 reacts with excess CrF_3 forming VF_3, VF_5 and Cr_2O_3. If there is a deficiency of CrF_3 the products are VOF_3, V_3O_5 and Cr_2O_3. CuF_2 and VO_2 form VOF_3, CuO and Cu_2O.

INTRODUCTION

The fluorination of uranium oxides by metal fluorides has not been investigated. The pyrolysis of UOF_4 at 250-500°C [1] producing UF_6 and UO_2F_2 is an oxygen fluorine exchange reaction. The pyrolysis of UO_2F_2 at 700-950°C [2] producing UF_6, U_3O_8 and O_2 and the oxidation of UF_4 by oxygen at 800°C [3] producing UO_2F_2 and UF_6 can be regarded as partly oxygen fluorine exchange reactions. The only fluorination of vanadium oxides by metal fluorides recorded is that of V_2O_5 with CrF_3 above 570°C producing VOF_3 and CrF_3 [4] . The oxidation of VF_3 with oxygen to VOF_3 is also noteworthy [5] .

Two metal fluorides were used for the study of the fluorination of uranium and vanadium oxides. These were CrF_3, chosen as an example of an oxygen fluorine exchange reagent not possessing significant oxidising power, and CuF_2, chosen to show the effect of mild oxidising power on the oxygen fluorine exchange reactions. Most other fluorides had either less favourable oxygen fluorine exchange free energies or were less suitable for studies by thermal analysis.

EXPERIMENTAL

Reagents were purchased commercially (CrF_3) or prepared by previously reported methods CuF_2 [6] , UO_2F_2 [7] , UF_4 [7] , UO_3 [7] , U_3O_8 [7] , UO_2 [7] , V_2O_5 [8] and VO_2 [9]

Thermal analyses (Table 1) were carried out on a Stanton TR1 thermobalance. Millimole quantities of uranium or vanadium oxides were well mixed with the appropriate mole ratio of metal fluoride and placed in a 5 cm^3 platinum crucible on the thermobalance. A heating rate of 270°C hr^{-1} and a dry nitrogen atmosphere with a gas flow rate of 400 cm min^{-1} were used except where otherwise stated. Differential thermal analyses (Table 1) were recorded on a Netzsch 404 instrument. 0.3 cm^3 platinum crucibles were used in a dry nitrogen atmosphere with a heating rate of 10°C min^{-1}. A sample of Al_2O_3 dried at 1000°C was used as the reference standard. X-ray diffraction traces were recorded on a Siemens Type-F diffractometer using copper K-radiation. Hygroscopic materials were handled in a dry box over P_2O_5.

To ascertain the volatile vanadium compounds produced, a second sample of the reaction mixture was heated in a Lawrence Smith platinum crucible of length 90 mm and internal diameter 21 mm. The evolved gases were passed via PTFE connectors to a PTFE cold trap. Excess water was added to the frozen mixture and allowed to react with the vanadium fluorides on warming. The resulting solution was analysed for vanadium and fluorine.

Analyses were made by previously recorded methods; total uranium and uranium(IV) [10] , vanadium [11] , copper [12] and fluorine [13] .

RESULTS AND DISCUSSION

Reactions of uranium containing compounds are recorded in Table 1

UO_3 reacted with CrF_3 at 350-400°C to form mainly UO_2F_2 and Cr_2O_3 (R.12) according to the equation.

$$3\,UO_3 + 2CrF_3 = 3\,UO_2F_2 + Cr_2O_3 \qquad \Delta H = -221\ kJ\ mol^{-1}\ [14] \quad \ldots 1$$

though this was the sole reaction only in the presence of excess inert diluent such as UO_2F_2. If pure UO_3 was reacted with CrF_3 the known endothermic decomposition of UO_3 to U_3O_8 also occurred [15]

$$6\,UO_3 = 2\,U_3O_8 + O_2 \qquad \Delta H = 234\ kJ\ mol^{-1}\ [14] \quad \ldots 2$$

and a complicated two staged reaction was observed in differential thermal analysis.

TABLE 1

Thermal analysis of oxide fluoride reactions involving uranium

Reaction Number (R)	Reactants		Mole Ratio	Differential Thermal Analysis Peaks[a]	Solid Products		Gases evolved[b] (mmol)
	Fluoride	Oxide			Intermediate	Final	
1.1	CrF_3	UO_3[c]	1:1	400 Dex 620 ex 870 end 920 end		Cr_2O_3 $CrUO_4$	UF_6 0.53
1.2	CrF_3	UO_3	2:1	400 Dex 620 ex 870 end 920 end	U_3O_8, UO_2F_2 CrF_3 UO_2F_2, UF_4 Cr_2O_3, CrF_3	Cr_2O_3, UF_4 CrF_3	UF_6 0.90 O_2 0.05
1.3	CrF_3	UO_3	5:1	420 Dex 640 ex 870 end 960 end r			UF_6 0.78 O_2 0.09
1.4	CrF_3	UO_3	7:1	420 Dex 640 ex 840 end 960 end r		Cr_2O_3, UF_4, CrF_3	
1.5	CrF_3	UO_3	9:1	420 Dex 640 ex 780 end 960 end r			
1.6	CrF_3	UO_3	10:1				UF_6 0.09 O_2 0.41
1.7	CrF_3	UO_3	20:1				UF_6 0.07 O_2 0.45
1.8	CrF_3	UO_3	d			No U in CrF_3 layer	
1.9	CrF_3	U_3O_8	6:1	650 ex 880 end 920 end		Cr_2O_3, UF_4, CrF_3	UF_6 0.66 0_2 0.02
1.10	CrF_3	UO_2F_2	2:1	630 ex 880 end 920 end		Cr_2O_3, UF_4, CrF_3	
1.11	CuF_2	UO_3	1:1[e]				UF_6 0.41 O_2 0.40 CuF_2 0.09

Table 1 - continued

Reaction Number (R)	Reactants		Mole Ratio	Differential Thermal Analysis Peaks[a]	Solid Products		Gases evolved[b] (mmol)
	Fluoride	Oxide			Intermediate	Final	
1.12	CuF_2	UO_3	2:1				UF_6 0.70 O_2 0.51 CuF_2 0.04
1.13	CuF_2	UO_3	3:1	220 ex 390 end 680 end r	UO_2F_2, CuO UO_2F_2, CuO CuF_2, UO_3 U_3O_8, CuF_2	UO_2F_2, Cu_2O Cu	UF_6 0.93 O_2 0.53 CuF_2 0.30
1.14	CuF_2	U_3O_8	9:1	680 end r		CuF_2, UO_2F_2 UF_4, Cu_2O	UF_6 0.96 O_2 0.38 CuF_2 0.24
1.15	CuF_2	UO_2F_2	2:1	680 end r			
1.16	CuF_2	UO_2F_2	3:1				UF_6 0.98 O_2 0.55 CuF_2 0.17
1.17	CuF_2	UO_2F_2	15:1			CuF_2, UO_2F_2 Cu_2O	UF_6 0.54 O_2 0.91 CuF_2 2.63
1.18	CuF_2	UO_2F_2	2:1[f]				UF_6 0.18
1.19	CuF_2	UO_2	2:1		CuF_2, Cu_2O, UO_2F_2, UF_4		CuF_2 0.92
1.20	UF_4	CuO	1:3		UO_2F_2, Cu_2O, CuF_2		

Table 1

[a] D double peak
ex exothermic peak
end endothermic peak
r peak reversible on cooling

[b] The gases evolved were inferred by analysis of the solid residues

[c] Weight loss in CrF_3 uranium oxide mixtures commenced at 780°C. The temperature was held steady on reaching 950°C for 2-3 hours to complete the reaction.

[d] A 2:1 mixture of CrF_3:UO_3 was taken in the bottom of the crucible. A further 8 parts of CrF_3 were placed above the reacting mixture so that any UF_6 formed had to sublime through it.

[e] Reactions in the CuF_2 uranium oxide mixtures commenced at 780° C. The temperature was held steady at 890°C for 2-4 hours to complete the reaction.

[f] A dry oxygen atmosphere was used in this experiment

Attempts to stop this reaction at the intermediate stage showed incomplete reaction and no other reaction products. The low temperature of the CrF_3 reaction with UO_3 is noteworthy for CrF_3 - oxide reactions [4] [16] and is perhaps associated with the UO_3 decomposition occurring about this temperature.

UO_3 reacted exothermally with CuF_2 at 210-260° to form UO_2F_2 and CuO (R.1.13) according to the equation

$$CuF_2 + UO_3 = UO_2F_2 + CuO \qquad \Delta H = -59 \text{ kJ mol}^{-1} \quad [14] \qquad \ldots 3$$

though some unreacted UO_3 was observed among the products.

As the CuF_2 used contained small quantities of water a catalytic fluorination mechanism according to the known reactions -

$$CuF_2 + H_2O = CuO + 2HF \qquad [17] \qquad \ldots 4$$

and

$$UO_3 + 2HF = UO_2F_2 + H_2O \qquad [18] \qquad \ldots 5$$

is a possible explanation of the observations. The endothermic reaction observed at 350-400°C (R.1.14) was the decomposition of any unreacted UO_3 to U_3O_8 and O_2.

U_3O_8 required a considerably higher temperature for fluorination than UO_3, reacting at 600-700°C with both CrF_3 and CuF_2 without weight loss (R.1.9). The exothermic reaction with CrF_3 converted the uranium (VI) to UO_2F_2 and the uranium (IV) to UF_4, Cr_2O_3 being the other product according to the equation

$$3\,U_3O_8 + 8\,CrF_3 = 4\,Cr_2O_3 + 3UF_4 + 6UO_2F_2 \qquad \Delta H = -594\ \mathrm{kJ\ mol^{-1}}\ [14] \quad ..6$$

The endothermic reaction of U_3O_8 with CuF_2 was more complex, Cu_2O, UF_4 and UO_2F_2 being identified among the products (R.1.14). The stoicheiometry of the reaction would suggest a Cu(II) U(VI) mixed oxide as the cause of the unidentified X-ray diffraction lines. The same products were observed from a similar temperature reaction if UO_2 was substituted for U_3O_8 in the CuF_2 reaction (R.1.19). CuO also reacted with UF_4 over the same temperature range to give Cu_2O, CuF_2 and UO_2F_2 (R.1.20) only according to the equation

$$3\,CuO + UF_4 = CuF_2 + Cu_2O + UO_2F_2 \qquad \Delta H = -9\ \mathrm{kJ\ mol^{-1}}\ [14] \quad ..7$$

In all these cases there were endothermic peaks in the differential thermal analysis associated with melt formation at 680°C. Pure CuF_2 has M.P. 785°C [19] . The formation of Cu_2O in these reaction products cannot have been due to oxygen loss from CuO as in no case was any weight loss observed. The simple oxide-fluoride metathetical reaction without valency change

$$2\,CuF_2 + UO_2 = UF_4 + 2CuO \qquad \Delta H = -53\ \mathrm{kJ\ mol^{-1}}\ [14] \quad ...8$$

is probably favourable thermodynamically. Thus the presence of UO_2F_2 and Cu_2O among the reaction products of CuF_2 fluorination of U_3O_8 and UO_2 could be accounted for by the initial formation of CuO and UF_4 followed by their further reaction according to equation 7. The absence of a similar redox reactions with CrF_3 and U_3O_8 was probably due to the much more positive free energy needed to remove a mole of oxygen from Cr_2O_3 than from CuO at the same temperature [14] .

Heating of mixtures of UO_3 with CrF_3 (R.1.2) or CuF_2 (R.1.13) to 700°C gave expected products, though in the case of CuF_2 with UO_3 only UO_2F_2 and a little Cu_2O were observed.

Heating either CuF_2 or CrF_3 with UO_3, U_3O_8 or UO_2F_2 above 850°C resulted in a substantial volatilisation of uranium. Attempts to analyse the volatile uranium compounds by the procedure described in the experimental section were unsuccessful. However U and F analyses on the involatile residues left after the reaction indicated that the material volatilised had a composition close to UF_6. As UF_6 is the only uranium-oxygen-fluorine compound known to be readily volatile without decomposition at the reaction temperatures [20] , the volatilisation of UF_6 is assumed.

CuF_2 reacted with UO_2F_2 above 850°C in an endothermic reaction (R.1.15-1.17). Residue analysis indicated volatilisation of UF_6, CuF_2 and some oxygen, while the only involatile reaction products were Cu_2O and Cu. Up to 98% of the uranium present could be volatilised. If an oxygen atmosphere was (R.1.18) used the volatilisation of UF_6 but not the CuF_2 was markedly suppressed. The use of a large excess of CuF_2 had a small suppressing effect on UF_6 volatilisation. Heating of UO_3 mixtures with CuF_2 above 850°C gave the same reaction products (R.1.11 - 1.13)

The volatilisation of some CuF_2 at these reaction temperatures [19] is expected under thermal analysis. The endothermic uranium volatilisation may be explained if simple reactions of CuF_2 with UO_2F_2 are postulated forming UF_6, O_2 and Cu_2O or Cu according to the equations

$$4CuF_2 + 2UO_2F_2 = 2UF_6 + 2Cu_2O + O_2 \qquad \Delta H = 870 \text{ kJ mol}^{-1} \quad [14] \quad ...9$$

$$2CuF_2 + UO_2F_2 = UF_6 + 2Cu + O_2 \qquad \Delta H = 602 \text{ kJ mol}^{-1} \quad [14] \quad ...10$$

The effect of high partial oxygen pressures in suppressing UF_6 volatilisation may be explained it it is assumed the above reactions are reversible. The direct reaction of UO_3 with CuF_2 might be expected to have given rise to some UF_4 via production of U_3O_8 (equation 2) and its subsequent reaction with further CuF_2. The absence of UF_4 is probably explained by the known oxidation reaction at 800°C 3.

$$2UF_4 + O_2 = UO_2F_2 + UF_6 \qquad ...11$$

The less positive free energies required to release oxygen from Cu_2O above 850°C as compared with 600-700°C [14] probably explain the formation of Cu and the absence of UF_4 as products in the high temperature reaction only.

$$2Cu_2O + UF_4 = UO_2F_2 + CuF_2 + 2Cu \qquad \Delta H = +25 \text{ kJ mol}^{-1} \quad 14 \quad ...12$$

Reaction of CrF_3 with uranium oxides and UO_2F_2 was only studied under an inert atmosphere as under oxygen chromium volatilisation was observed [21]. Reaction of CrF_3 with UO_3 above 850°C was endothermic and gave Cr_2O_3 and $CrUO_4$ as the involatile products from a 1:1 mole ratio mixture (R.1.1) but with CrF_3:UO_3 mole ratios of 2:1 or greater UF_4 and Cr_2O_3 were obtained as the involatile products (R.1.2, 1.4). Evidence of a liquid phase above 900°C was obtained. UF_4 melts at 1034°C [22], and an early value for the melting point was 960°C [7]. Analysis indicated that UF_6 and O_2 were the only materials volatilised. For a CrF_3:UO_3 mole ratio of 1:1 all the fluorine was volatised (R.1.1), for 2:1 mole ratio 80% of the uranium was volatilised (R.1.2) but for increasing mole ratios the uranium volatilisation decreased until it fell below 8% for a mole ratio of 15:1 (R.1.3-1.7). Differential thermal analysis indicated reaction below 900°C before much uranium had volatilised, the reaction temperature being lowered by increasing excess of CrF_3 (R.1.2-1.5). The excess CrF_3 had to be present in the reaction mixture as if placed on top of the reaction mixture the UF_6 volatilisation was not suppressed (R.1.8). Similar high temperature reactions were observed for mixtures of CrF_3 with U_3O_8 and UO_2F_2 (R.1.9, 1.10).

Once source of UF_6 could have been the pyrolysis of UO_2F_2 according to the known reaction [2]

$$9\ UO_2F_2 = 2\ U_3O_8 + 3UF_6 + O_2 \qquad \Delta H = +1464\ kJ\ mol^{-1}\ [14] \qquad \ldots 13$$

followed by the fluorination reaction for U_3O_8 (equation 6). This would have given a maximum yield of 60% UF_6 in the equation

$$16CrF_3 + 15UO_2F_2 = 9UF_6 + 6UF_4 + 8Cr_2O_3 + 3O_2 \qquad \ldots 14$$

As, however, yields of up to 80% UF_6 were observed, equation 11 cannot be the sole mechanism of UF_6 production and direct fluorination of UO_2F_2 by CrF_3 is needed according to the equation.

$$4CrF_3 + 3UO_2F_2 = 2Cr_2O_3 + 3UF_6 \qquad \ldots 15$$

The production of $CrUO_4$ [23] in the absence of excess CrF_3 could be explained by combination of Cr_2O_3 with U_3O_8 formed from UO_2F_2 pyrolysis.

$$6\ Cr_2O_3 + 4\ U_3O_8 = 12\ CrUO_4 + O_2 \qquad \ldots 16$$

The suppression of UF_6 volatilisation by excess CrF_3 according to the equation

$$6\ UO_2F_2 + 4CrF_3 = 6UF_4 + 2Cr_2O_3 + 3O_2 \qquad \ldots 17$$

is less easy to explain. It cannot be due to the thermodynamically plausible reactions:

$$6UF_6 + 2Cr_2O_3 = 6UF_4 + 4CrF_3 + 3O_2 \qquad \Delta H = -736\ kJ\ mol^{-1}\ [14] \qquad \ldots 18$$

and

$$6UF_6 + U_3O_8 = 9UF_4 + 4O_2 \qquad \Delta H = -657\ kJ\ mol^{-1}\ [14] \qquad \ldots 19$$

as CrF_3 is not involved as a reactant in these equations. The possible reaction

$$UF_6 + 2CrF_3 = UF_4 + 2CrF_4 \qquad \ldots 20$$

is eliminated as placing the excess CrF_3 above the reacting mixture did not suppress the UF_6 volatilisation (R.1.8). The suppression of the UF_6 volatilisation by the presence of excess CrF_3 is presumably due to a different reaction occurring in the presence of excess CrF_3 as indicated by the lowering of the reaction temperature under differential thermal analysis.

Reactions of vanadium containing compounds are recorded in Table 2. CrF_3 reacted with VO_2 above 570°C in a single stage reaction. The involatile products were Cr_2O_3 and either VF_3 if excess CrF_3 was used or V_3O_5 if excess VO_2 was used. All the vanadium volatilised was in the oxidation state (V) and the fluorine to vanadium ratio varied from 3.05:1 to 4.85:1. As VOF_3 [24] and VF_5 [25] are the only vanadium (V) oxygen-fluorine compounds known to be volatile without decomposition under the reaction conditions, evolution of these two gases in a mixture is assumed. The volatile products were largely VF_5 if excess CrF_3 was used (R.2.1) or only VOF_3 if excess VO_2 was used (R.2.3). By using a reaction mixture containing CrF_3:VO_2 in a 4:9 ratio it was possible to obtain a mixture of VOF_3 and VF_5 as volatile products but only V_3O_5 and Cr_2O_3 in the solid residues (R.2.2).

Only impure VF_3 was available for study but this reacted with VO_2 above 590°C to produce VOF_3 and V_3O_5 (R.2.4) the probably equation being

$$VF_3 + 3VO_2 = V_3O_5 + VOF_3 \qquad \ldots 21$$

The products of the reaction of VO_2 with excess CrF_3 can be regarded as those from a simple oxide fluoride methathetical reaction followed by a disproportionation. The metathetical reaction

$$4CrF_3 + 3VO_2 = 3VF_4 + 2Cr_2O_3 \qquad \ldots 22$$

is analogous to the previously studied reaction of CrF_3 with TiO_2 [16] and would be estimated to go at 540°C at 1/1000th atmosphere pressure [14] assuming that the unknown sublimation energy of VF_4 is similar to that of TiF_4. If VF_4 is produced at elevated temperatures it is known [26] to disproportionate according to the equation

$$2VF_4 = VF_3 + VF_5 \qquad \ldots 23$$

so the overall observed reaction

$$8CrF_3 + 6VO_2 = 4Cr_2O_3 + 3VF_3 + 3VF_5 \qquad \ldots 24$$

may be accounted for.

An alternative sequence of reactions

$$4VO_2 = V_2O_3 + V_2O_5 \qquad \ldots 25$$

$$V_2O_3 + 2CrF_3 = 2VF_3 + Cr_2O_3 \qquad \ldots 26$$

$$3V_2O_5 + 10CrF_3 = 6VF_5 + 5Cr_2O_3 \qquad \ldots 27$$

TABLE 2

Thermal analysis of some oxide-fluoride reactions involving vanadium

Reaction Number (R)	Reactants		Mole Ratio	Solid Products		Gases evolved[a] (mmol)
	Fluoride	Oxide		Intermediate	Final	
2.1	CrF_3	VO_2	4:3[b]		Cr_2O_3, VF_3	VF_5 0.4-0.45 VOF_3 0.05-0.1
2.2	CrF_3	VO_2	2:3		Cr_2O_3, V_3O_5	VF_5 0.33-0.37 VOF_3 0.13-0.19
2.3	CrF_3	VO_2	4:9		Cr_2O_3, V_3O_5	VF_5 0.01 VOF_3 0.50
2.4	VF_3	VO_2	1:3		V_3O_5	VOF_3
2.5	CuF_2	VO_2	5:2[c]			VOF_3 0.76-0.81 CuF_2 0.05
2.6	CuF_2	VO_2	4:2			VOF_3 0.90-0.96 CuF_2 0.07-0.10
2.7	CuF_2	VO_2	3.2:2	CuO+? $Cu_3VO_4xCuF_2$[d]		

[a] Analysis of the volatile products from separate experiments confirmed the assignations

[b] Reactions of CrF_3 with VO_2 started to lose weight at 580°C and had finished by 900°C

[c] Reactions of CuF_2 with VO_2 started to lose weight at 180°C. There was a marked decrease of reaction rate to a minimum at 500-550°C. The overall reaction was complete by 700°C.

[d] Novel X-ray diffraction lines were observed. If these were due to a single material a composition of the form $Cu_3VO_4 \times CuF_2$

is not acceptable as the fluorination of V_2O_5 by CrF_3 only proceeds as far as VOF_3 [4].

The production of VOF_3 as well as VF_5 and the absence of VF_3 in the solid residues from the reaction of CrF_3 with VO_2 in a 4:9 ratio, is plausible as there is evidence for the reaction of VF_3 with VO_2 according to the equation:

$$VF_3 + 3VO_2 = VOF_3 + V_3O_5 \qquad \ldots 21$$

The absence of any VF_5 from the volatile products from the reaction of excess VO_2 with CrF_3 suggests a different reaction sequence in this case, in which presumably oxidation to vanadium (V) occurs before fluorination has reached the VF_4 composition. The evidence for the existence of VOF_2 [27] in this connection is noteworthy.

CuF_2 reacted with VO_2 above 350°C in a sharply differentiated two-stage reaction, the first reaction being complete by 470°C and the second reaction starting at 550°C (R.2.5-2.7). The vanadium was volatilised as VOF_3 only, complete volatilisation of the vanadium being achieved if the initial CuF_2:VO_2 ratio was greater than 3·2. The final involatile reaction products were CuO and Cu_2O only. These results indicate that CuF_2 and VO_2 react according to the overall equation -

$$3CuF_2 + 2VO_2 = CuO + Cu_2O + 2VOF_3 \qquad \ldots 28$$

the oxidising agent producing the vanadium (V) being the CuF_2 rather than the disproportionation of the vanadium (IV) as was observed in the CrF_3 reactions.

X-ray powder diffraction of the reaction products after the first reaction gave only unassignable lines apart from excess unreacted CuF_2. As the mass loss to the end of the first stage was two-thirds the total mass loss, a reaction equation of the form

$$(3+x)CuF_2 + 3VO_2 = Cu_3\ VO_4.xCuF_2 + 2VOF_3 \qquad \ldots 29$$

is likely. Cu_3VO_4 is a known compound [28] so the material prepared was either a new polymorph of Cu_3VO_4 or it contained CuF_2 as well in the crystal.

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