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REACTIONS OF TITANIUM DIOXIDE WITH METAL FLUORIDES

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Summary

TiO_2 reacts with several condensed-phase metal fluorides at elevated temperatures to form TiF_4 and the metal oxide. Known mixed titanium metal oxides are usually observed as intermediates. FeOF is an intermediate from the system FeF_3 + TiO_2. With CaF_2 and BaF_2, the reaction did not proceed beyond the intermediates $CaTiO_3$ and $BaTiO_3$. Reactions usually start at approximately the temperatures predicted from thermochemical data.

Introduction

The reaction of TiO_2 with condensed-phase metal fluorides has been little investigated. Titanium has been volatilised by heating the oxide with fluorides at high temperatures for spectroscopic studies [1]. Potassium fluoride will react with TiO_2 but there is no evidence for a volatile titanium species in these reactions [2 - 4].

Experimental

Reagents were purchased commercially (TiO_2, CuO, CdF_2, PbF_2, CaF_2, BaF_2, CrF_3 and FeF_2) or prepared by previously reported methods ($TiOF_2$ [5], FeF_3 [6], CuF_2 [7], AlF_3 [8], NiF_2 [9], CoF_2[10], ZnF_2 [10] and MnF_2 [10]).

Thermal analyses (Table 1) were carried out in a 5 cm^3 platinum crucible on a Stanton TR1 or HT5 thermobalance using *m* mol quantities of TiO_2 under nitrogen with a gas flow rate of 400 cm^3 min^{-1}. X-Ray diffraction traces were recorded on intermediates and involatile products using a Siemens type-F diffractometer and Cu$K\alpha$ radiation. Hygroscopic materials were handled in a dry box over P_2O_5.

Reactions (Table 2) in which TiF_4 was collected were carried out *in vacuo* in a Lawrence Smith platinum crucible (length 90 mm, internal diameter 21 mm). The exit gases were passed via PTFE connectors to a cold-finger condenser. The products collected on the cold finger were purified by sublimation.

TABLE 1

Thermal analysis experiments

Reactants			Reaction conditions				Products						
Fluoride	Oxide	Mole ratio $\frac{\text{fluoride}}{\text{oxide}}$	Heating rate (°C h^{-1})	Temperature range (°C)[a]		Temperatures of minimum reaction rate (°C)	%Mass loss	%Ti in solid products[b]		%F in solid products”		Solids	Intermediates at first minimum of reaction rate
								Observed	Calculated	Observed	Calculated		
AgF	TiO_2	5.1	270	R00	950[d]	690	21 5	0 0	0.0			Ag, AgF	Ag, AgF[c]
CaF_2	TiO_2	2 1	400	1280	1350[d]		4 6	19 3, 19.6	19 5			$CaTiO_3$, CaF_2, TiO_2	
BaF_2	TiO_2	2:1	400	1300	1350[d]		3.8	9.8, 10 0	10.0			$BaTiO_3$, BaF_2, TiO_2	
MnF_2	TiO_2	2:1	400	890	940		9.7	18 1, 17 9	15 9			MnF_2, TiO_2	
FeF_2	TiO_2	2:1	270	600	950	800	41.7	0.7, 0 5	0 6	1.2	1.5	Fe_2O_3[e]	$FeTiO_3$, Fe_2O_3[e]
CoF_2	TiO_2	2.1	400	530	1250	770, 1020, 1150	45 5	6.6, 6.0	6 0	0 0	neg.	CoO, Co_2TiO_4	[f]
CoF_2	TiO_2	2:3	400	530	950[d]		18.1	31 9, 31 7	31.8			$CoTiO_3$	
NiF_2	TiO_2	2:1	400	550	1000	740	44.9	0.2, 0.3	“ 2	2 1	2.4	NiO	
NiF_2	TiO_2	2.3	400	620	900		35 6	30 9. 31.0	30.9			TiO_2, $NiTiO_3$	
CuF_2	TiO_2	3:1	270	400	850		32 6	0 0	0.0	14.0	14.9	CuO, CuF_2	
ZnF_2	TiO_2	2:1	400	500	1000	760,810	38 8	2 9. 2.9	2.9	4.6	4.3	ZnO, Zn_2TiO_4	
ZnF_2	TiO_2	2:3	400	620	880		36.7	28.1, 28 2	28.1			$ZnTiO_3$, $Zn_2Ti_3O_8$	
CdF_2	TiO_2	2 1	400	800	850[d]		10 6	14 0, 14 1	9.5			CdF_2, TiO_2	
PbF_2	TiO_2	2:1	270	700	750[d]		5.5	8.7, 9 0	6.6			PbF_2, TiO_2	
AlF_3	TiO_2	4:3	270	770	850[d]		9.2	27.1, 26.9	23.6			AlF_3, TiO_2	
CrF_3	TiO_2	5:3	270	600	850	680	43 8	1 1 , 1 5	1 5	15 0	15.4	Cr_2O_3	Cr_2O_3, CrF_3, TiO_2
FeF_3	TiO_2	1:3	270	450	850	630	49.8	0.2, 0.3	0.3	6.0	5.7	Fe_2O_3	Fe_2O_3, FeOF, TiO_2
TiF_4	CUO	2:1[g]	270	200	350							CuO, CuF_2, $TiOF_2$	

[a] The temperature ranges are those for which the rate of weight loss was greater than 0 001 g in 5 min.

[b] The calculated analysis figures were obtained from thr percentage mass loss by assuming TiF_4 was the only volatile material

[c] Lines due to an unidentified material were present here.

[d] Reaction held at the maximum temperature for 2 h.

[e] The presence of iron(III) in the solid products is probably due to the inability to completely exclude atmospheric oxygen from the thermobalance

[f] Intermediates at second minimum of reaction rate, Co_2TiO_4 and CoF_2, and at third minimum of reaction rate, CoO, Co_2TiO_4 and CoF_2

[g] The CuO was placed on top of thr TiF_4 which sublimed through it.

Titanium was analysed by the peroxide titanium yellow method [11] and fluoride by pyrohydrolysis and alkali titration [12].

Discussion

Several condensed-phase metal fluorides react with TiO_2 at elevated temperatures, only PbF_2 and CdF_2 of those investigated showing no evidence of reaction (Table 1). TiF_4 was isolated from the reactions of CuF_2 and CrF_3 with TiO_2, and the net weight loss in conjunction with analysis of the residues showed TiF_4 to be the material volatilising in most other cases. With MnF_2, AlF_3 and to a lesser extent CoF_2, extensive volatilisation of the reacting fluoride occurred in addition to TiF_4.

The observed reactions of fluorides with TiO_2 may be subdivided into three classes: (a) direct formation of TiF_4 and of the metal oxide without the formation of observable intermediates; (b) reaction to form mixed oxides, with possible further reaction of the fluoride with the mixed oxides to form more TiF_4 and the metal oxide; and (c) reaction *via* oxyfluoride intermediates.

(a) Direct formation of TiF_4 and the metal oxide: Only in the case of $CuF_2 + TiO_2$ has the simple one-stage reaction been observed.

$$2CuF_2 + TiO_2 = TiF_4 + 2CuO$$

Only a small excess of CuF_2 is needed for complete volatilisation of the titanium. The reaction is partly reversible as CuO will react with TiF_4 at lower temperatures to form $CuO + TiOF_2$. A further stage of the reverse reaction is the known pyrolysis of $TiOF_2$ to form $TiF_4 + TiO_2$ [5].

$$2TiOF_2 = TiF_4 + TiO_2$$

(b) Reaction to form mixed oxides: Mixed oxide formation was observed in the reactions of TiO_2 with CaF_2, BaF_2, FeF_2, CoF_2, NiF_2 and ZnF_2. With CaF_2 and BaF_2, formation of the mixed oxides was incomplete after several hours at 1350 °C and further reaction was not observed. In all other cases further reaction to form the metal oxide occurred, although Co_2TiO_4 and Zn_2TiO_4 were not completely converted to CoO and ZnO, respectively. The mixed oxides were not usually obtained free from other reacting materials but by using a deficiency of CoF_2 it was also possible to prepare $CoTiO_3$. In those cases in which several mixed oxides were formed, increasing the reaction temperature tended to increase the metal content of the mixed titanium oxide. In the case of cobalt, the various stages of the thermal analysis could be reasonably assigned to the formation of particular mixed oxides. Usually all the known metal titanium oxides were observed as reaction intermediates but, in the case of nickel, $Ni_2Ti_3O_8$ and Ni_2TiO_4 were not found.

(c) Formation of oxyfluoride intermediates: FeF_3 reacted with TiO_2 in two stages, FeOF being detected as the intermediate product at the end of the first stage. The reaction of CrF_3 with TiO_2 showed a similar two-stage reaction. X-Ray diffraction studies on the intermediate stage however only showed the

TABLE 2

Preparative experiments

Reactants				Reaction conditions			Analysis of TiF_4 produced[a]				Analysis of solid residues			
Fluoride	Oxide	Mole ratio fluoride: oxide	Weight of sample (g)	Temp. (°C)	Time(min)	Mass loss (g)	g	%	Ti(%)	F(%)	Ti(%)		F(%)	
											Found	Calc.[b]	Found	Calc.[b]
CuF_2	TiO_2	5:2	6.656	850	60	2.610	1.390	53	38.6, 38.6	60.2, 61.0	0.0	0.0	8.8, 8.7	8.7
CrF_3	TiO_2	4:3	0.672	850	60	0.3052	0.131	40	38.6, 38.5	60.9, 60.5	7.3, 7.5	7.5		

[a] Pure TiF_4 contains 38.6% Ti and 61.3% F.

[b] The calculated analysis figures were obtained from the mass loss by assuming TiF_4 was the only volatile material.

TABLE 3

Initial reaction temperatures

Fluoride reacting with TiO_2	AgF	CaF_2	BaF_2	MnF_2	FeF_2	CoF_2	NiF_2	CuF_2	ZnF_2	CdF_2	PbF_2	AlF_3	CrF_3	FeF_3
Observed initial reaction temperature (°C)[a]	600	1280	1300	890	600	530	550	400	580	—	—	770	600	450
Calculated initial reaction temperature (°C)[b]	375	1970	2250	550	700	630	640	418	570	810	860	790	280	350[c]
Calculated initial reaction temperature for formation of the mixed oxide $MTiO_3$ (°C)[b]		1270	1070											

[a] The observed initial reaction temperature was the lowest temperature at which the rate of TiF_4 loss was greater than 0.001 g in 5 min.

[b] The calculated initial reaction temperature was the lowest temperature at which the vapour pressure of TiF_4 was calculated to be greater than 1/1000 atm.

[c] Calculation from estimated data given in ref. 15.

presence of reactants and products. AgF also reacted with TiO_2 in a two-stage reaction. The final solid product was merely metallic silver, presumably formed from the decomposition of silver oxide which is unstable at the reaction temperature [13].

$$4AgF + TiO_2 = 4Ag + TiF_4 + O_2$$

In the first stage of the reaction no titanium was volatilised but there was a small weight loss. Metallic silver and an unidentified material were present in the solids obtained at the end of the first stage. The presence of silver suggests that the volatile material lost was oxygen. If this was so, one oxygen atom was lost for each TiO_2 molecule reacted. This suggests that the unidentified material was an $AgF–TiOF_2$ complex, possibly Ag_2TiOF_4 analogous to the known K_2TiOF_4 [14].

Comparison of the observed reaction temperatures with those predicted from thermochemical data is interesting (Table 3). If it is assumed that the first detectable mass loss in the thermal analysis occurred at *ca.* 1/1000 atm pressure, the initial reaction temperature of the metathetical reactions

$$4MF_n + nTiO_2 = 4MO_{n/2} + nTiF_4$$

may be estimated from thermochemical data to ±100 °C. The absence of observed reactions of CdF_2 and PbF_2 with TiO_2 is not surprising as both the fluorides are quite volatile at the predicted reaction temperatures. The small extent of reaction with AlF_3 may be similarly understood. For other fluorides, the observed reaction temperatures show a rough correspondence with those calculated. The largest deviations are for the reactions of CaF_2 and BaF_2 with TiO_2 where stable mixed oxides are formed. If the initial reaction temperature calculations are repeated for the reactions

$$2MF_2 + 3TiO_2 = 2MTiO_3 + TiF_4 \ (M = Ca, Ba)$$

the reaction temperatures fit much more closely with those observed. The failure to observe the oxides CaO and BaO as reaction products in these systems is also accounted for. In other cases where mixed oxides are formed, a lowering of the observed reaction temperature is also observed. In the absence of thermochemical data, it is not possible to estimate the initial reaction temperatures. The relatively small lowering of the observed reaction temperatures, coupled with the observation of further fluorination of the mixed metal titanium oxides, suggests that the heats of formation of these mixed oxides from their constituent metal oxides are small compared with those of $CaTiO_3$ and $BaTiO_3$. Of the remaining significant discrepancies between observed and estimated reaction temperatures, that of the $MnF_2 + TiO_2$ reaction may arise from the particularly large error in the reported heat of formation of MnF_2 [16] while that of the $CrF_3 + TiO_2$ reaction is possibly associated with the slow reaction kinetics frequent with chromium(III) compounds [17]. As AgF initially reacts with evolution of oxygen, the calculation is not applicable to this system.

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