

## REACTIONS OF TITANIUM DIOXIDE WITH METAL FLUORIDES

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### Summary

TiO<sub>2</sub> reacts with several condensed-phase metal fluorides at elevated temperatures to form TiF<sub>4</sub> and the metal oxide. Known mixed titanium metal oxides are usually observed as intermediates. FeOF is an intermediate from the system FeF<sub>3</sub> + TiO<sub>2</sub>. With CaF<sub>2</sub> and BaF<sub>2</sub>, the reaction did not proceed beyond the intermediates CaTiO<sub>3</sub> and BaTiO<sub>3</sub>. Reactions usually start at approximately the temperatures predicted from thermochemical data.

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### Introduction

The reaction of TiO<sub>2</sub> 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<sub>2</sub> but there is no evidence for a volatile titanium species in these reactions [2 - 4].

### Experimental

Reagents were purchased commercially (TiO<sub>2</sub>, CuO, CdF<sub>2</sub>, PbF<sub>2</sub>, CaF<sub>2</sub>, BaF<sub>2</sub>, CrF<sub>3</sub> and FeF<sub>2</sub>) or prepared by previously reported methods (TiOF<sub>2</sub> [5], FeF<sub>3</sub> [6], CuF<sub>2</sub> [7], AlF<sub>3</sub> [8], NiF<sub>2</sub> [9], CoF<sub>2</sub> [10], ZnF<sub>2</sub> [10] and MnF<sub>2</sub> [10]).

Thermal analyses (Table 1) were carried out in a 5 cm<sup>3</sup> platinum crucible on a Stanton TR1 or HT5 thermobalance using *m* mol quantities of TiO<sub>2</sub> under nitrogen with a gas flow rate of 400 cm<sup>3</sup> min<sup>-1</sup>. X-Ray diffraction traces were recorded on intermediates and involatile products using a Siemens type-F diffractometer and CuK $\alpha$  radiation. Hygroscopic materials were handled in a dry box over P<sub>2</sub>O<sub>5</sub>.

Reactions (Table 2) in which TiF<sub>4</sub> 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			Intermediates at first minimum of reaction rate				
Fluoride	Oxide	Mole ratio fluoride/oxide	Heating rate (°C h <sup>-1</sup> )(°C) <sup>a</sup>	Temperature range (°C)	Temperatures of minimum reaction rate (°C)	%Mass %Ti in solid products <sup>b</sup> loss	%Ti in solid products <sup>b</sup> Calculated	%Ti in solid products <sup>b</sup> Observed	Solids Calculated	Solids Observed		
AgF	TiO <sub>2</sub>	5:1	270	800	950 <sup>d</sup>	690	21.5	0.0	0.0	Ag, AgF		
CaF <sub>2</sub>	TiO <sub>2</sub>	2:1	400	1280	1350 <sup>d</sup>	46	19.3, 19.6	19.5		(CaTiO <sub>3</sub> , CaF <sub>2</sub> , TiO <sub>2</sub>		
BaF <sub>2</sub>	TiO <sub>2</sub>	2:1	400	1300	1350 <sup>d</sup>	3.8	9.8,10.0	10.0		BaTiO <sub>3</sub> , BaF <sub>2</sub> , TiO <sub>2</sub>		
MnF <sub>2</sub>	TiO <sub>2</sub>	2:1	400	890	940	9.7	18.1, 17.9	15.9		MnF <sub>2</sub> , TiO <sub>2</sub>		
FeF <sub>2</sub>	TiO <sub>2</sub>	2:1	270	600	950	800	41.7	0.7, 0.5	0.6	1.2	Fe <sub>2</sub> O <sub>3</sub> <sup>e</sup>	
CoF <sub>2</sub>	TiO <sub>2</sub>	2:1	400	530	1250	770, 1020, 1150	45.5	6.6, 6.0	6.0	0.0	neg.	
CoF <sub>2</sub>	TiO <sub>2</sub>	2:3	400	530	950 <sup>d</sup>	18.1	31.9, 31.7	31.8		CoTiO <sub>3</sub>		
NiF <sub>2</sub>	TiO <sub>2</sub>	2:1	400	550	1000	740	44.9	0.2, 0.3	* 2	2.1	2.4	NiO
NiF <sub>2</sub>	TiO <sub>2</sub>	2:3	400	620	900		35.6	30.9, 31.0	30.9			TiO <sub>2</sub> , NiTiO <sub>3</sub>
CuF <sub>2</sub>	TiO <sub>2</sub>	3:1	270	400	850		32.6	0.0	0.0	14.0	14.9	CuO, CuF <sub>2</sub>
ZnF <sub>2</sub>	TiO <sub>2</sub>	2:1	400	500	1000	760,810	38.8	2.9, 2.9	2.9	4.6	4.3	ZnO, Zn <sub>2</sub> TiO <sub>4</sub>
ZnF <sub>2</sub>	TiO <sub>2</sub>	2:3	400	620	880		36.7	28.1,28.2	28.1			ZnTiO <sub>3</sub> , Zn <sub>2</sub> Ti <sub>3</sub> O <sub>8</sub>
CdF <sub>2</sub>	TiO <sub>2</sub>	2:1	400	800	850 <sup>d</sup>		10.6	14.0, 14.1	9.5			CdF <sub>2</sub> , TiO <sub>2</sub>
PbF <sub>2</sub>	TiO <sub>2</sub>	2:1	270	700	750 <sup>d</sup>		5.5	8.7, 9.0	6.6			PbF <sub>2</sub> , TiO <sub>2</sub>
AlF <sub>3</sub>	TiO <sub>2</sub>	4:3	270	770	850 <sup>d</sup>		9.2	27.1, 26.9	23.6			AlF <sub>3</sub> , TiO <sub>2</sub>
CrF <sub>3</sub>	TiO <sub>2</sub>	5:3	270	600	850	680	43.8	11.4, 1.5	1.5	15.0	15.4	Cr <sub>2</sub> O <sub>3</sub> , CrF <sub>3</sub> , TiO <sub>2</sub>
FeF <sub>3</sub>	TiO <sub>2</sub>	1:3	270	450	850	630	49.8	0.2, 0.3	0.3	6.0	5.7	Fe <sub>2</sub> O <sub>3</sub> , FeOF, TiO <sub>2</sub>
TiF <sub>4</sub>	CuO	2:1 <sup>g</sup>	270	200	350							(CuO, CuF <sub>2</sub> , TiOF <sub>2</sub>

<sup>a</sup> The temperature ranges are those for which the rate of weight loss was greater than 0.001 g in 5 min.

<sup>b</sup> The calculated analysis figures were obtained from the percentage mass loss by assuming TiF<sub>4</sub> was the only volatile material.

<sup>c</sup> Lines due to an unidentified material were present here.

<sup>d</sup> Reaction held at the maximum temperature for 2 h.

<sup>e</sup> The presence of iron(III) in the solid products is probably due to the inability to completely exclude atmospheric oxygen from the thermobalance.

<sup>f</sup> Intermediates at second minimum of reaction rate, Co<sub>2</sub>TiO<sub>4</sub> and CoF<sub>2</sub>, and at third minimum of reaction rate, CuO, Co<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> and CoF<sub>2</sub>.

<sup>g</sup> The CuO was placed on top of the TiF<sub>4</sub> which sublimed through it.

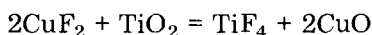
Titanium was analysed by the peroxide titanium yellow method [11] and fluoride by pyrohydrolysis and alkali titration [12].

## Discussion

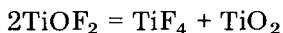
Several condensed-phase metal fluorides react with  $\text{TiO}_2$  at elevated temperatures, only  $\text{PbF}_2$  and  $\text{CdF}_2$  of those investigated showing no evidence of reaction (Table 1).  $\text{TiF}_4$  was isolated from the reactions of  $\text{CuF}_2$  and  $\text{CrF}_3$  with  $\text{TiO}_2$ , and the net weight loss in conjunction with analysis of the residues showed  $\text{TiF}_4$  to be the material volatilising in most other cases. With  $\text{MnF}_2$ ,  $\text{AlF}_3$  and to a lesser extent  $\text{CoF}_2$ , extensive volatilisation of the reacting fluoride occurred in addition to  $\text{TiF}_4$ .

The observed reactions of fluorides with  $\text{TiO}_2$  may be subdivided into three classes: (a) direct formation of  $\text{TiF}_4$  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  $\text{TiF}_4$  and the metal oxide; and (c) reaction *via* oxyfluoride intermediates.

(a) Direct formation of  $\text{TiF}_4$  and the metal oxide: Only in the case of  $\text{CuF}_2 + \text{TiO}_2$  has the simple one-stage reaction been observed.



Only a small excess of  $\text{CuF}_2$  is needed for complete volatilisation of the titanium. The reaction is partly reversible as  $\text{CuO}$  will react with  $\text{TiF}_4$  at lower temperatures to form  $\text{CuO} + \text{TiOF}_2$ . A further stage of the reverse reaction is the known pyrolysis of  $\text{TiOF}_2$  to form  $\text{TiF}_4 + \text{TiO}_2$  [5].



(b) Reaction to form mixed oxides: Mixed oxide formation was observed in the reactions of  $\text{TiO}_2$  with  $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{FeF}_2$ ,  $\text{CoF}_2$ ,  $\text{NiF}_2$  and  $\text{ZnF}_2$ . With  $\text{CaF}_2$  and  $\text{BaF}_2$ , formation of the mixed oxides was incomplete after several hours at  $1350^\circ\text{C}$  and further reaction was not observed. In all other cases further reaction to form the metal oxide occurred, although  $\text{Co}_2\text{TiO}_4$  and  $\text{Zn}_2\text{TiO}_4$  were not completely converted to  $\text{CoO}$  and  $\text{ZnO}$ , respectively. The mixed oxides were not usually obtained free from other reacting materials but by using a deficiency of  $\text{CoF}_2$  it was also possible to prepare  $\text{CoTiO}_3$ . 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,  $\text{Ni}_2\text{Ti}_3\text{O}_8$  and  $\text{Ni}_2\text{TiO}_4$  were not found.

(c) Formation of oxyfluoride intermediates:  $\text{FeF}_3$  reacted with  $\text{TiO}_2$  in two stages,  $\text{FeOF}$  being detected as the intermediate product at the end of the first stage. The reaction of  $\text{CrF}_3$  with  $\text{TiO}_2$  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 $\text{TiF}_4$ produced <sup>a</sup>				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. <sup>b</sup>	Found	Calc. <sup>b</sup>
$\text{CuF}_2$	$\text{TiO}_2$	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
$\text{CrF}_3$	$\text{TiO}_2$	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		

<sup>a</sup> Pure  $\text{TiF}_4$  contains 38.6% Ti and 61.3% F.<sup>b</sup> The calculated analysis figures were obtained from the mass loss by assuming  $\text{TiF}_4$  was the only volatile material.

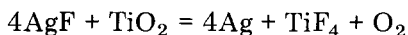
TABLE 3

## Initial reaction temperatures

Fluoride reacting with $\text{TiO}_2$	$\text{AgF}$	$\text{CaF}_2$	$\text{BaF}_2$	$\text{MnF}_2$	$\text{FeF}_2$	$\text{CoF}_2$	$\text{NiF}_2$	$\text{CuF}_2$	$\text{ZnF}_2$	$\text{CdF}_2$	$\text{PbF}_2$	$\text{AlF}_3$	$\text{CrF}_3$	$\text{FeF}_3$
Observed initial reaction temperature (°C) <sup>a</sup>	600	1280	1300	890	600	530	550	400	580	—	—	770	600	450
Calculated initial reaction temperature (°C) <sup>b</sup>	375	1970	2250	550	700	630	640	418	570	810	860	790	280	350 <sup>c</sup>
Calculated initial reaction temperature for formation of the mixed oxide $\text{MTiO}_3$ (°C) <sup>b</sup>			1270	1070										

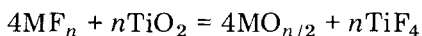
<sup>a</sup> The observed initial reaction temperature was the lowest temperature at which the rate of  $\text{TiF}_4$  loss was greater than 0.001 g in 5 min.<sup>b</sup> The calculated initial reaction temperature was the lowest temperature at which the vapour pressure of  $\text{TiF}_4$  was calculated to be greater than 1/1000 atm.<sup>c</sup> Calculation from estimated data given in ref. 15.

presence of reactants and products. AgF also reacted with  $\text{TiO}_2$  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].

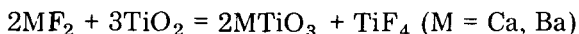


In the first stage of the reaction no titanium was volatilised but there was a small weight loss. Metallic silver and an unidentified material were present in the solids obtained at the end of the first stage. The presence of silver suggests that the volatile material lost was oxygen. If this was so, one oxygen atom was lost for each  $\text{TiO}_2$  molecule reacted. This suggests that the unidentified material was an  $\text{AgF-TiOF}_2$  complex, possibly  $\text{Ag}_2\text{TiOF}_4$  analogous to the known  $\text{K}_2\text{TiOF}_4$  [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



may be estimated from thermochemical data to  $\pm 100^\circ\text{C}$ . The absence of observed reactions of  $\text{CdF}_2$  and  $\text{PbF}_2$  with  $\text{TiO}_2$  is not surprising as both the fluorides are quite volatile at the predicted reaction temperatures. The small extent of reaction with  $\text{AlF}_3$  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  $\text{CaF}_2$  and  $\text{BaF}_2$  with  $\text{TiO}_2$  where stable mixed oxides are formed. If the initial reaction temperature calculations are repeated for the reactions



the reaction temperatures fit much more closely with those observed. The failure to observe the oxides  $\text{CaO}$  and  $\text{BaO}$  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  $\text{CaTiO}_3$  and  $\text{BaTiO}_3$ . Of the remaining significant discrepancies between observed and estimated reaction temperatures, that of the  $\text{MnF}_2 + \text{TiO}_2$  reaction may arise from the particularly large error in the reported heat of formation of  $\text{MnF}_2$  [16] while that of the  $\text{CrF}_3 + \text{TiO}_2$  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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