

Short Communication

Titanium (IV) oxydifluoride

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There is some uncertainty about TiOF_2 in the literature. Vorres and Dutton [1] prepared a material either by hydrolysis of TiF_4 or by dissolving TiO_2 in aqueous HF, followed by evaporation of the resulting solutions to dryness and heating the residues in an oven at 100°C . On the basis of X-ray powder diffraction alone, they assigned the formula TiOF_2 to this material [2]. Dehnicke repeated the preparation and claimed that 50% of the material consisted of OH groups [3]. He suggested that Vorres and Dutton's material was in fact $\text{TiO}(\text{OH})\text{F}$ which would be indistinguishable from TiOF_2 by X-ray powder diffraction. By reaction of Cl_2O with TiF_2Cl_2 , he obtained TiOF_2 as a yellow material [4]. This had the same X-ray powder diffraction pattern as that mentioned above but exhibited no OH band in the infrared [3]. Ravez and Hagenmuller [5] prepared TiOF_2 by Vorres and Dutton's second method, drying the product *in vacuo* at 150°C . They obtained a material with a fluorine content at least 98.5% of that of TiOF_2 .

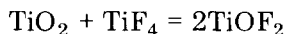
Preparation of TiOF_2 was attempted in the present work by dissolving TiO_2 in 40% HF, evaporating to dryness and removing all volatile materials in a vacuum at 150°C . The analysis of the resulting material (Sample 1 of Table 3) was only slightly low for fluorine, agreeing with the similar preparation and analyses of Ravez and Hagenmuller [5]. The percentage of titanium present was low however, and the infrared spectrum of the material indicated the presence of strong OH bands, agreeing qualitatively with the results of Dehnicke [3].

On heating the material to 450°C , all the OH bands were removed from the IR spectrum but analysis of the resulting product (Sample 2, Table 3) gave too high a value for fluorine content. Heating to higher temperatures resulted in a material of stoichiometry TiOF_2 but X-ray powder diffraction indicated the presence of TiO_2 as well as TiOF_2 .

On heating to 400°C at 0.1 N m^{-2} pressure for 6 h, a white material analysing for TiOF_2 (Sample 3, Table 3) was produced. The IR spectrum of this compound indicated the absence of OH bands and the X-ray powder diffraction pattern was the same as for Vorres and Dutton's material [2].

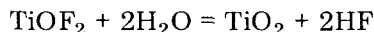
Analyses (Samples 2 and 3, Table 3) indicate that the material giving an X-ray powder diffraction pattern corresponding to TiOF_2 has a range of chemical composition, and can contain more TiF_4 than indicated by the formula TiOF_2 . In this connection, the existence of Ti_2OF_6 is noteworthy [6].

TiOF_2 is also formed by heating finely divided TiO_2 with excess TiF_4 according to the equation



although the reaction is difficult to take to completion. Non-stoichiometric TiF_4 rich in TiOF_2 could be obtained as in the other preparative method. The reaction of TiO_2 with TiF_4 is reversible and pyrolysis of TiOF_2 gives TiO_2 and TiF_4 . The reaction is a single-stage reaction starting at 550°C and complete at 800°C . This indicates that TiOF_2 is much more stable to heat than the other oxydihalides of titanium(IV) [7 - 9]; the latter compounds have also not been prepared by direct reaction between the oxide and the halide. The pyrolysis of TiOF_2 may be conveniently adapted for the preparation of TiF_4 in 80% yield. The resulting product was obtained as long needle-shaped crystals, less deliquescent than commercial TiF_4 .

Pure TiOF_2 is very resistant to hydrolysis either in pure water or with aqueous alkali and hydration to $\text{TiOF}_2 \cdot \text{H}_2\text{O}$ [10] was not observed. Fluorine-rich TiOF_2 (Sample 2, Table 3) was less resistant to hydrolysis and showed an acidic reaction after several weeks in moist air. Application of steam at 200°C or above completely hydrolyses TiOF_2 according to the equation



but the reaction is slow below 500°C . Reaction with molten KOH at 400°C gives $\text{K}_2\text{TiO}_2\text{F}_2$ [11].

In all the chemistry reported here both the anatase and rutile forms of TiO_2 were equally reactive. When formed as products, anatase was obtained below 800°C and rutile above 850°C . The minimum temperature of 200°C for formation of anatase is low but is comparable with that for the pyrolysis of TiOCl_2 [7].

Experimental

Reagents were commercially available to greater than 99% purity. The TiO_2 had an average particle size of $0.2\ \mu\text{m}$.

Thermal analysis and small-scale high-temperature reactions were carried out in a $5\ \text{cm}^3$ platinum crucible on a Stanton TR1 thermobalance under dry oxygen with a flow rate of $400\ \text{cm}^3\ \text{min}^{-1}$. The results obtained are given in Table 1. Large-scale high-temperature reactions were carried out in a nickel boat ($15 \times 2 \times 1.5\ \text{cm}$), situated in a nickel tube ($100\ \text{cm} \times 3\ \text{cm}$) and surrounded by a 25 cm long electric furnace in the region of the nickel boat. An air-cooled portion of the nickel tube projecting 60 cm beyond the electric furnace was used to collect sublimates from the reactions. The results obtained are given in Table 2.

TABLE 1

Thermobalance experiments

Expt.	Reactants		Temperature			Solid products		Nominal composition (%) ^a	X-Ray diffraction composition (%) ^b
	A	Weight (g)	m/mol	Weight (g)	m/mol	range of weight loss (°C)	Weight loss (g)		
1	TiOF ₂ (Sample 1, Table 3)	2.00	19.6			150 - 450	0.129	(Sample 2, Table 3)	
2	TiO ₂ (anatase)	0.101	1.26	TiF ₄	0.232	1.87	0.186	48.5 TiO ₂ 51.5 TiOF ₂	77 TiO ₂ 23 TiOF ₂
3	Solid product from expt. 2	0.132		TiF ₄	0.512	4.13	0.379	87 TiOF ₂ 13 TiF ₄	40 TiO ₂ 60 TiOF ₂
4	Solid product from expt. 3	0.203		TiF ₄	0.101	0.81	0.056	72 TiOF ₂ 28 TiF ₄	10 TiO ₂ 90 TiOF ₂
5	TiO ₂ (rutile)	0.145	1.82	TiF ₄	0.474	3.82	0.374	69 TiO ₂ 31 TiOF ₂	78 TiO ₂ 22 TiOF ₂
6	TiOF ₂ (pure)	0.436	4.28			550 - 850	0.264		
7	TiOF ₂ (pure)	0.249	2.44	KOH	2.64	4.71	0.084	K ₂ TiO ₂ F ₂	

^a This is the composition the material would have had if stoichiometric compounds were produced.^b This is the apparent composition obtained by comparing the observed X-ray diffraction traces with those from mixtures of the pure materials.

TABLE 2

Tube experiments

Expt.	Solid reactants		Atmosphere	Flow rate gas $\text{cm}^3 \text{min}^{-1}$	Temperature ($^{\circ}\text{C}$)	Reaction time (h)	Weight loss (g)	Solid products		Volatile products		Yield (%)
	Weight (g)	m/mol								Quantity m/mol		
1	TiOF ₂ (Sample 1, Table 3)	5.24	51.5	0.1 N m ⁻²	400	6		TiOF ₂ (Sample 3, Table 3)				
2	TiOF ₂ (pure)	80.0	786	O ₂	800		47.0	TiO ₂ (anatase + trace rutile)	TiF ₄ (Sample 4, Table 3)	34.0		81.5
3	TiOF ₂ (pure)	1.226	12.0	H ₂ O	200	9.5	0.244	TiO ₂ (anatase)	HF	24.1		100
4	TiOF ₂ (pure)	1.986	19.5	H ₂ O	400	9	0.587	TiO ₂ (anatase)	HF	39.1		106
5	TiOF ₂ (pure)	2.064	20.2	H ₂ O	500	2.2	0.676	TiO ₂ (anatase)	HF	40.4		100

TABLE 3

Analyses

Sample	Ti(%)	F(%)
1	42.4	36.1
2	45.7	39.5
3	47.0	37.1
4	39.9	60.0
TiOF ₂ (theoretical)	47.0	37.3
TiF ₄ (theoretical)	38.7	61.3

Crude TiOF₂ was prepared by dissolving 50 g TiO₂ (0.625 mol) in 100 cm³ of hot 40% aqueous HF (2.0 mol) in a PTFE beaker. The solution was evaporated to small bulk, 5 cm³ of 6% H₂O₂ was added to destroy reducing impurities, the product evaporated to dryness and heated *in vacuo* for 6 h. The resulting product weighed 60 g (Sample 1, Table 3).

X-Ray diffraction traces were recorded on involatile material using a Siemens type-F diffractometer and CuK α radiation. Infrared spectra were recorded on a Perkin-Elmer 237 grating spectrograph. All handling of solid TiF₄ was undertaken in a Lintott inert atmosphere box.

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