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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 TiO(OH)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 precentage 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

$$TiO_2 + TiF_4 = 2TiOF_2$$

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 $TiOF_2 \cdot H_2O$ [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

$$TiOF_2 + 2H_2O = TiO_2 + 2HF$$

but the reaction is slow below 500 °C. Reaction with molten KOH at 400 °C gives $K_2TiO_2F_2$ [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 μm.

Thermal analysis and small-scale high-temperature reactions were carried out in a 5 cm^3 platinum crucible on a Stanton TR1 thermobalance under dry oxygen with a flow rate of 400 cm^3 min^{-1}. The results obtained are given in Table 1. Large-scale high-temperature reactions were carried out in a nickel boat (15 × 2 × 1.5 cm), situated in a nickel tube (100 cm × 3 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 range of weight loss (°C)	Solid products			
	A	Weight (g)	m/mol	B	Weight (g)	m/mol		Weight loss (g)	X-Ray diffraction	Nominal composition (%)[a]	X-Ray diffraction composition (%)[b]
1	$TiOF_2$ (Sample 1, Table 3)	2.00	19.6				150 - 450	0.129	$TiOF_2$	(Sample 2, Table 3)	
2	TiO_2 (anatase)	0.101	1.26	TiF_4	0.232	1.87	190 - 260	0.186	TiO_2 (anatase) + $TiOF_2$	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	190 - 260	0.379	TiO_2 (anatase) + $TiOF_2$	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	200 - 260	0.056	TiO_2 (anatase) + $TiOF_2$	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	200 - 260	0.374	TiO_2 (rutile) + $TiOF_2$	69 TiO_2 31 $TiOF_2$	78 TiO_2 22 $TiOF_2$
6	$TiOF_2$ (pure)	0.436	4.28				550 - 850	0.264	TiO_2 (anatase and rutile)		
7	$TiOF_2$ (pure)	0.249	2.44	KOH	2.64	4.71	150 - 450	0.084	$K_2TiO_2F_2$		

[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 ($cm^3 min^{-1}$)	Temperature (°C)	Reaction time (h)	Weight loss (g)	Solid products	Volatile products		
		Weight (g)	*m*/mol								Quantity *m*/mol	Yield (%)
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	10	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_2O	2000	200	9.5	0.244	TiO_2 (anatase)	HF	24.1	100
4	$TiOF_2$ (pure)	1.986	19.5	H_2O	2000	400	9	0.587	TiO_2 (anatase)	HF	39.1	106
5	$TiOF_2$ (pure)	2.064	20.2	H_2O	2000	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 $TiOF_2$ was prepared by dissolving 50 g TiO_2 (0.625 mol) in 100 cm^3 of hot 40% aqueous HF (2.0 mol) in a PTFE beaker. The solution was evaporated to small bulk, 5 cm^3 of 6% H_2O_2 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 Cu$K\alpha$ radiation. Infrared spectra were recorded on a Perkin-Elmer 237 grating spectrograph. All handling of solid TiF_4 was undertaken in a Lintott inert atmosphere box.

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