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Short Communication

Reaction of hydrogen fluoride with manganese(III) oxide

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Methods of preparing MnF_3 using F_2 directly or indirectly *via* BrF_3 are well established[1]. No routes are known to MnF_3 which completely avoid the use of F_2. Thermodynamic data, however, suggest the reaction

$$Mn_2O_3 + 6HF = 2MnF_3 + 3H_2O \qquad (1)$$

might be possible[2]. In an aqueous phase, this reaction is known to produce $MnF_3{\cdot}2H_2O$[3]. Two different methods for fluorination of Mn_2O_3 with anhydrous HF have been investigated, one method using a vapour-phase reaction the other a liquid-phase reaction.

HF gas was passed over Mn_2O_3 at temperatures slowly rising from 25 °C to 500 °C over a period of 3–4 h. The product contained $>80\%$ MnF_3 by analysis, the main impurity being MnF_2. The presence of MnF_2 as an impurity is not surprising as MnF_3 was shown to react with Mn_2O_3 above 360 °C according to the equation

$$8MnF_3 + 2Mn_2O_3 = 12MnF_2 + 3O_2 \qquad (2)$$

The product was a strong fluorinating agent reacting with Se at 250 °C and CH_4 at 550 °C. The use of $MnF_3{\cdot}2H_2O$ as a starting material did not improve the yields.

Liquid HF was refluxed over Mn_2O_3 in a fractionating column. The method was based on the preparation of conductivity HF by fractionation of HF distillates[4] and the low solubility of MnF_3 in HF[5]. The HF reacted with the Mn_2O_3 exothermically to give a red product nearly insoluble in HF. A similar, less exothermic reaction was observed with $MnF_3{\cdot}2H_2O$. Even on repeated HF treatment, the product always contained a few per cent of water and strong heating gave low yields of anhydrous MnF_3.

Experimental

Mn_2O_3 was prepared by heating $MnSO_4{\cdot}4H_2O$ to 775 °C in air for 24 h[6]. $MnF_3{\cdot}2H_2O$ was prepared by dissolving Mn_2O_3 in 40% HF and evaporating to small bulk[3].

X-Ray diffraction traces were recorded on a Siemens Type F Goniometer. Thermal analysis was carried out on a Stanton STA HT5 thermobalance. MnF_3 samples were analysed for total Mn by titration with EDTA, oxidising power by reacting with aqueous KI and fluorine content by NaOH fusion and conversion of the NaF formed to HF by ion exchange.

Reactions with gaseous HF

Reactions were carried out in a Ni tube (90 cm × 3 cm), the sample (9–11 g) being contained in an Ag or Pt boat (Table 1). The tube was heated by a small electric furnace. HF gas was passed over the sample for a period of 4 h while the temperature rose steadily from 25–500 °C. Experimental results are shown in Table 1, runs 1–3.

TABLE 1

Run	Starting material	HF state	Container type	Mn^{3+} (%)	Mn^{2+} (%)	F^- (%)	Volatiles (%)	MnF_3 (%)
1	Mn_2O_3	Gas	Ag boat [a]	42.1	8.5	48.2		83.1
2	Mn_2O_3	Gas	Pt boat [b]	42.4	8.8	47.4		81.1
3	$MnF_3 \cdot 2H_2O$	Gas	Pt boat	27.7	26.1	44.5		53.6
4	Mn_2O_3	Liquid	Polypropylene tube	42.9	0.2	50.1	12.3	
5	$MnF_3 \cdot 2H_2O$	Liquid [c]	Polypropylene tube	47.7	0.3	44.0	5.6	
6	Product run 5	Liquid [c]	Polypropylene tube	47.3	0.7	48.0	3.3	
7	Product run 6	Liquid [c]	Polypropylene tube	47.3	0.7	48.0	3.7	

[a] Ag boat 13 cm × 2 cm × 1 cm.

[b] Pt boat 7.5 cm × 2 cm × 1 cm.

[c] One sample treated three times with fresh liquid HF. Final run constituted a reflux period of 9 h.

Reactions with liquid HF

The apparatus was built in five sections from polypropylene interconnected with PTFE joints. The lowest section was used to boil HF by warming to 30 °C. Above this was a fractionating column (30 cm × 1.2 cm) packed with Cu turnings. The third section (25 cm × 1.2 cm) contained the sample (3–5 g) supported on PTFE swarf. The fourth section was a polypropylene coiled condenser cooled with water. The fifth section was a similar polypropylene condenser cooled to −78 °C to protect the apparatus from atmospheric moisture. About 40 cm^3 of liquid HF in the boiler were gently refluxed through the column. Any water from the reaction of Mn_2O_3 with HF was returned to the boiler in the downward HF stream, so that the reacting material was continuously in an environment of anhydrous HF. When the reaction was complete, the product was evacuated at 80 °C for 30 min. Experimental results are shown in Table 1, runs 4–7.

Thermal analysis

0.964 g of the product of run 2, Table 1, containing 0.782 g MnF_3 (6.97 mmol) was heated with 0.329 g Mn_2O_3 (2.08 mmol) in a 5 cm^3 Pt crucible in a nitrogen atmosphere on a thermobalance. Reaction started at 360 °C and was complete at 700 °C. The weight loss was 0.0842 g. Reaction (2) above should give 0.0838 g weight loss for the sample. The solid residues were MnF_2 and excess unreacted Mn_2O_3 only.

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