

NEW ROUTES TO TELLURIUM(IV) FLUORIDE

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SUMMARY

Three new routes, all indirectly using hydrogen fluoride as the source of fluorine, have been shown to give good yields of TeF_4 . These were: reaction of elemental tellurium with CuF_2 or FeF_3 , reaction of TeO_2 with these fluorides and the thermal decomposition of NaTeF_5 and KTeF_5 . All of these reactions afford satisfactory yields of TeF_4 , but the reaction of FeF_3 and TeO_2 appears to be the most satisfactory.

INTRODUCTION

Previously, the most convenient synthesis¹ of TeF_4 involved the reaction of SeF_4 and TeO_2 at 80°. Other reactions have been reviewed². These involve the use of a fluorine source and generally give small yields of TeF_4 . The work reported here was undertaken to see if convenient synthetic routes to TeF_4 existed which avoided the use of elemental fluorine at any stage. That such routes might exist was suggested by the moderate heat of formation³ of TeF_4 , $-994.2 \text{ kJ mol}^{-1}$, which also indicated that it would not be formed by reaction of hydrogen fluoride on elemental tellurium. The reaction of hydrogen fluoride with TeO_2 has been reviewed² and also does not appear to be suitable for preparation of TeF_4 .

EXPERIMENTAL

Reactants were prepared by previously reported methods, thus: CuF_2 ^{4,5}, FeF_3 ⁶, NaTeF_5 and KTeF_5 ^{7,8} and copper(II) tellurite⁹.

Preparations of TeF_4 (Table 1) were carried out in a cold-finger sublimation apparatus containing a platinum crucible 1.7 cm in diameter and with an outer silica jacket heated by a small electric furnace. The receiving cold finger was also made of platinum. Reactants (A) and (B) [see Table 1] were mixed and the volatile product handled in a dry box over P_2O_5 . A layer of dried, finely powdered CaF_2

TABLE 1
PREPARATIVE EXPERIMENTS

Reactant weight		B		Reaction conditions		TeF ₄ produced		Analysis*	
A	g	mol	g	Temp. (°C)	Time (min)	g	mol	Free Te (%)	Combined F Te (%)
CuF ₂	1.617	15.9	Te	800	90	0.468	2.30	2.7	62.7
FeF ₃	0.708	6.26	TeO ₂	700	90	0.333	1.63	<0.1	62.8
NaTeF ₅	1.363	5.55	—	700	90	0.594	2.92	1.9	62.6

* The weight of elemental Te in the product was subtracted from the weight of the impure TeF₄ before calculating the percentage of combined Te and F. Pure TeF₄ contains 62.7% combined Te and 37.3% F.

was spread over the mixed reactants in the crucible to prevent sputtering during the reaction. Thermal analyses (Table 2) were carried out on a Stanton TR1 thermobalance under nitrogen, with a gas flow rate of $400 \text{ cm}^3 \text{ min}^{-1}$, using crucibles as indicated in Table 2. X-ray diffraction traces were recorded on intermediates and involatile products using a Siemens Type F diffractometer, using $\text{CuK}\alpha$ radiation.

Samples of TeF_4 were analysed by dissolving them in molar KOH solution, any residual tellurium being filtered off and weighed. The solution was then reduced by SO_2 and the precipitated tellurium was also weighed. Fluoride ion in the same solution was determined by ion exchange using Zeocarb 225 resin, the liberated hydrofluoric acid being titrated with standard alkali.

RESULTS AND DISCUSSION

Three different types of reaction have been investigated for the preparation of TeF_4 , all indirectly using only hydrogen fluoride as the source of fluorine:

- (i) Reaction of elemental tellurium with inorganic fluorides.
- (ii) Reaction of TeO_2 with inorganic fluorides.
- (iii) Thermal decomposition of alkali metal pentafluorotellurate(IV) complexes.

In (i) and (ii) excess of the metal fluoride was used, as otherwise reactions were found to proceed to completion extremely slowly and, where elemental tellurium was present, the platinum crucible became badly corroded. Satisfactory preparative yields of TeF_4 were obtained by each method, but in every case the product contained a little elemental tellurium. Chemical analysis (Table 1) indicated that no other materials were present in the volatile product.

Thermal analyses were carried out (Table 2) to ascertain the maximum amount of TeF_4 available from any reaction and to detect possible intermediate stages.

Reaction of CuF_2 with elemental tellurium was shown to be quantitative below 860° , producing TeF_4 as the only volatile product. The best preparative yield of TeF_4 was 68%. Thermal analysis indicated a complex decomposition. A single marked arrest in the reaction rate was observed at $450\text{--}480^\circ$, corresponding closely to a composition of Cu_4Te_3 , identified previously from phase studies¹⁰. However, X-ray diffraction patterns obtained from mixtures held in this temperature range indicated the presence of Cu_2Te and not Cu_4Te_3 . Subsequent reaction of the copper telluride intermediate with CuF_2 was slower than the initial reaction of CuF_2 with tellurium. The residue from thermal analysis experiments contained Cu_2O , presumably obtained by oxidation of the copper by atmospheric oxygen, which it was not possible to exclude completely from the thermobalance. The overall reaction was

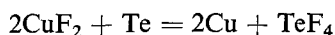


TABLE 2
THERMAL ANALYSIS EXPERIMENTS

Reactant weight			B		mol		Reaction conditions			Cumulative Products	
A	g	mol	g	mol	Crucible ^a	Heating rate (°C h ⁻¹)	Temperature range ^b (°C)	weight loss (g)	TeF ₄ mol	Intermediates	Others
									%		
CuF ₂	0.422	4.16	Te	0.262	Pt	200	320-430	0.172	0.85	Cu ₄ Te ₃ , Cu ₂ Te	Cu, Cu ₂ O
FeF ₃	0.462	4.09	Te	0.120	Pt	270	430-860	0.414	2.04		
CuF ₂	0.445	4.38	TeO ₂	0.312	Pt	70	520-775	0.142	0.70		FeF ₂
							370-480	0.117	0.57	CuTeO ₃	
							500-950	0.384	1.89		
CuF ₂	0.705	6.95	CuTeO ₃	0.258	Pt	270	505-890	0.217	1.07		Cu ₂ O, CuO
FeF ₃	0.525	4.65	TeO ₂	0.315	Pt	230	420-530	0.114	0.56		Cu ₂ O, CuO
							530-800	0.401	1.97		
NaTeF ₅	0.428	1.74			Au	310	455-960	0.333	1.64		α-Fe ₂ O ₃
KTeF ₅	0.284	1.09			Au	300	570-900	0.260			NaF
KTeF ₅	0.965	3.68			C	270	570-850	0.416	2.04		KF
KSbF ₆	0.252	0.92			Pt	270	700-900	0.134	e		KF ^d
									e		KF

^a The crucible diameters were: Pt, 1.7 cm; Au, 1.2 cm; C (vitreous), 1.4 cm.

^b The temperature ranges are those for which the rate of decomposition was greater than 0.001 g in 5 min.

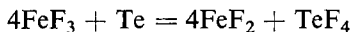
^c Some KF also volatilised.

^d This decomposition was allowed to proceed only until the overall composition of the residue was K₂TeF₆.

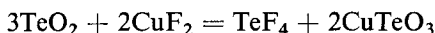
^e This corresponds to a loss of 0.62 mmol, 67% of presumed SbF₅.

The reverse of the reaction between CuF_2 and copper telluride to give TeF_4 and copper has been reported by Nichols³ as occurring at 185° .

Reaction of FeF_3 and elemental tellurium was briefly investigated. Thermal analysis showed the reaction to be slow and a mass loss corresponding to a yield of 74% of TeF_4 could be obtained below 800° . Above this temperature FeF_3 was volatile. The reaction was

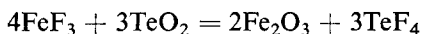


Reaction of CuF_2 and TeO_2 was shown to give a good yield of TeF_4 by thermal analysis. The single reaction arrest corresponded to the formation of copper(II) tellurite as an intermediate according to the equation



The second reaction temperature range (Table 2) corresponded to that found for reaction of CuF_2 with a prepared sample of CuTeO_3 , the products being the same. The poor crystallinity of all samples of CuTeO_3 precluded the use of X-ray diffraction in these studies.

Reaction of FeF_3 and TeO_2 gave quantitative formation of TeF_4 as the only volatile product, as shown by thermal analysis. The sample of TeF_4 obtained preparatively contained a visible but unweighable quantity of elemental tellurium. Thermal analysis showed a distinct reaction arrest to occur after a mass loss corresponding to 28% of the available TeF_4 . The composition of the residue at this stage was close to $\text{Fe}_2\text{O}_3 \cdot 4\text{TeO}_2$ and unreacted FeF_3 . X-ray diffraction showed that all of the TeO_2 had reacted, but the powder pattern lines not due to FeF_3 did not correspond to those of a known iron tellurite or FeOF . On further heating, the overall mass loss was as expected from the equation



Potassium pentafluorotellurate(IV) is recorded as being stable to decomposition¹¹ at 450° , in agreement with our observation that decomposition commences at 570° . No evidence of intermediates in the decomposition was obtained by either thermal analysis or X-ray diffraction examination of the partly decomposed material. Thus the reaction proceeds according to the simple equation



This agrees with the earlier work of Edwards *et al.*¹¹, who found no evidence for the formation of K_2TeF_6 on heating an equimolar mixture of KF and KTeF_5 . Before complete decomposition occurs there is some volatilisation of KF , rendering the reaction unsuitable for the preparation of TeF_4 . The high temperature of the decomposition is noteworthy as being only 130° lower than that of potassium hexafluoroantimonate(V) run under comparable conditions (Table 2). This suggests that TeF_4 has considerable affinity for the fluoride ion.

Sodium pentafluorotellurate(IV) decomposed at a lower temperature (Table 2) and gave a satisfactory yield of TeF_4 without any volatilisation of the only other product, NaF. The higher decomposition temperatures of complex potassium fluorides compared to the corresponding sodium compounds is known for other systems¹². Attempts to prepare the presumably less stable complex LiTeF_5 by the same method as the sodium and potassium salts were unsuccessful.

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