Reactions of Tin(II) Halides with Tellurium(IV) Halides: A New Route to Subhalides of Tellurium

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Reactions of SnX_2 with TeX_4 (X = Cl, Br, or I) have been monitored by differential thermal analysis in closed tubes, and the products identified by their *X*-ray powder patterns. In the course of the reactions, Sn^{II} is always oxidized to Sn^{IV}. In the chloride system, Te^{IV} is reduced to elemental Te, whereas in the bromide system the subhalide Te_2Br and in the iodide system the subhalide TeI (α and/or β modification) are formed. An excess of Sn^{II} causes further reduction of the subhalides to elemental Te.

HALIDES of tellurium have only recently been the subject of detailed investigations. The formal oxidation state of tellurium in these compounds is VI, IV, II, or an average of ≤I. The tetrahalides and those compounds of formal tellurium oxidation state ≤I (subhalides) are crystalline solids at room temperature (Table 1). Tellurium dihalides do not appear in the solid state,[1-3], but are stable in the vapour phase.[4]

TABLE 1

Sub- and tetra-halides of tellurium [a]

	Formal oxidation state of Te in			
	Te_yX ($y \geqslant 1$)			TeX_4
X	0.5	0.66	1	4
F				TeF_4 (130) [b]
Cl	Te_2Cl [7]	Te_3Cl_2 (239) [7]		$TeCl_4$ (223) [c]
Br	Te_2Br (225) [7]			$TeBr_4$ (388) [c]
I	Te_2I [7]		α-TeI (185) [7] β-TeI [7]	TeI_4 (280) [d] TeI_4 [e]

[a] Values in parentheses represent melting temperatures (°C) of phases which belong to the respective Te–X phase diagrams.[1,2] The literature cited (except *e*) refers to the corresponding crystal-structure analysis. [b] A. J. Edwards and F. I. Hewaidy, *J. Chem. Soc.* (*A*), 1968, 2977. [c] B. Buss and B. Krebs, *Inorg. Chem.*, 1971, **12**, 2795. [d] B. Krebs and V. Paulat, *Acta Cryst.*, 1976, **B32**, 1470. [e] R. Kniep and D. Mootz, *Chem. Exp. Didakt.*, 1975, **7/8**, 199.

The formation of $TeCl_2$ was reported [5] to take place by reaction (1) of tellurium(IV) chloride with tin(II) chloride.

$$SnCl_2 + TeCl_4 \rightleftharpoons SnCl_4 + TeCl_2 \qquad (1)$$

In the course of our work on compounds of oxidation state IV, VI, or VII and especially on subhalides of tellurium we became interested in reaction (1) because we supposed that the formation of a tellurium subchloride should be much more likely than the formation of the dichloride. So we decided to examine reactions of SnX_2 with TeX_4 (X = Cl, Br, or I) by differential thermal analysis (d.t.a.) in order to obtain further insight into this type of reaction.

RESULTS AND DISCUSSION

D.T.A. and X-Ray Investigations.—D.t.a. diagrams of the reactions of Sn^{II} with tellurium(IV) halides are shown in Figures 1—3. *X*-Ray powder patterns of subhalides of tellurium are given in Table 2. The

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[1] R. Kniep, A. Rabenau, and H. Rau, *J. Less-Common Metals*, 1974, **35**, 325.

[2] A. Rabenau and H. Rau, *Z. anorg. Chem.*, 1973, **395**, 273.

[3] G. C. Christensen and J. Alstad, *Radiochem. Radioanalyt. Letters*, 1973, **13**, 227.

[4] H. Oppermann, G. Stöver, and E. Wolf, *Z. anorg. Chem.*, 1974, **410**, 179.

[5] V. V. Safonov, A. V. Konov, and B. G. Korshunov, *Izvest. Vysshikh Uchebn. Zavedenii Tsvetn. Met.*, 1969, **12**, 83.

reactions are rather slow at room temperature and become faster with increasing temperature. In the course of the reactions Sn^{II} is oxidized to the respective tin(IV) halide. The reduction of Te^{IV} to lower formal oxidation states is dependent on the participating halogen.

TABLE 2

X-Ray powder patterns of tellurium subhalides

d/Å obs.	*d*/Å calc.	I/I_0	*hkl*
	Te_3Cl_2		
5.410	5.390	7	011
4.510	4.480	2	111
4.330	4.320 4.310	5	020 210
3.463	3.458	8	002
3.229	3.237	5	$30\bar{1}$
3.103	3.098	6	310
2.919	2.912	6	112
2.708	2.699	2	022
2.657	2.660 2.657	10	311 031
2.534	2.537 2.534	2	$31\bar{2}$ $22\bar{2}$
2.068	2.084	3	$30\bar{3}$
1.866	1.863	4	402
1.827	1.832 1.831 1.827 1.825	1	042 $52\bar{1}$ 501 412
1.777	1.777 1.776	3	$23\bar{3}$ $24\bar{2}$
	Te_2Br		
3.584	3.582	9	410
2.927	2.925 2.907	10	031 510
2.870	2.872	5	131
2.806	2.806	3	321
2.512	2.515	8	421
2.119	2.116	2	160
2.081	2.080	2	441
1.919	1.919	3	541
1.862	1.862	1	711
1.748	1.748	2	412
	Te_2I		
3.673	3.682	10	410
3.054	3.059	9	031
2.989	3.000 2.985	7	131 510
2.905	2.903	2	321
2.605	2.595	4	421
2.415	2.418 2.413	2	511 350
2.261	2.257 2.256	2	160 151
2.061	2.062	3	002
1.997	1.996	4	541
1.959	1.959	2	451
1.911	1.911	2	800 711 222 302
1.797	1.799	3	412
	β-TeI		
3.525	3.523	3	$40\bar{3}$
3.183	3.183	10	$31\bar{2}$
3.146	3.148	8	003
3.025	3.027	1	400
2.944	2.945	5	202
2.484	2.483	3	311
2.453	2.454 2.449	5	$60\bar{4}$ $51\bar{3}$
2.096	2.096 2.091	5	510 020
2.054	2.054	3	$31\bar{5}$
1.872	1.872	1	$80\bar{5}$
1.799	1.780	1	$80\bar{2}$
1.777	1.777	1	313
1.742	1.742	2	023
1.711	1.711	1	$60\bar{7}$
	α-TeI		
3.767	3.766	2	020
3.255	3.253	2	$3\bar{1}0$
3.231	3.230	2	300
3.190	3.192	9	012
3.165	3.167 3.165	10	$20\bar{2}$ $02\bar{2}$
3.059	3.062 3.057	3	$3\bar{1}1$ $30\bar{1}$
2.512	2.511	4	030
2.120	2.120	1	312
1.885	1.884 1.883	4	$32\bar{3}$ 040
1.822	1.820	1	340
1.792	1.792	2	330
1.780	1.783 1.782 1.781 1.780	2	$5\bar{1}2$ $51\bar{1}$ 313 510

In the chloride system, Te^{IV} is reduced to elemental tellurium [equation (2)]. The ΔT curve in Figure 1 shows a broad exothermic peak for reaction which is superimposed on the endothermic effect of vaporization of $SnCl_4$ (lit.,[6] b.p. 114 °C). The reaction is complete at 205 °C. Depending on the extent of filling of the sample tubes, the latter burst at temperatures >300 °C because of the internal pressure. Cooling from *ca.* 300 °C takes place without significant thermal effects. At room temperature the sample tube contains liquid $SnCl_4$ and crystalline tellurium. Tellurium was identified by its *X*-ray powder pattern which was checked against the known tellurium pattern (ASTM 4/0554). No dichloride[5] and/or other intermediate chlorides (*e.g.* subchlorides Te_2Cl or Te_3Cl_2[7]) are formed by this reaction either at lower temperatures or by using an excess of $SnCl_2$ or $TeCl_4$.

$$2SnCl_2 + TeCl_4 \longrightarrow Te + 2SnCl_4 \qquad (2)$$

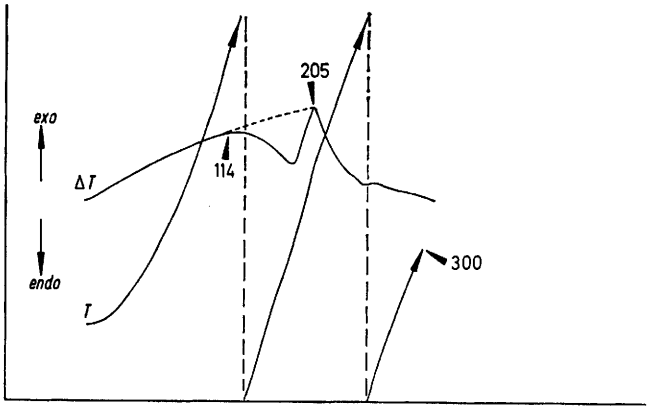

FIGURE 1 Reaction of $SnCl_2$ with $TeCl_4$ monitored by d.t.a. The broken line completes the broad exothermic peak for reaction, which would be observed in the absence of endothermic boiling of $SnCl_4$. Numbers are temperatures in °C

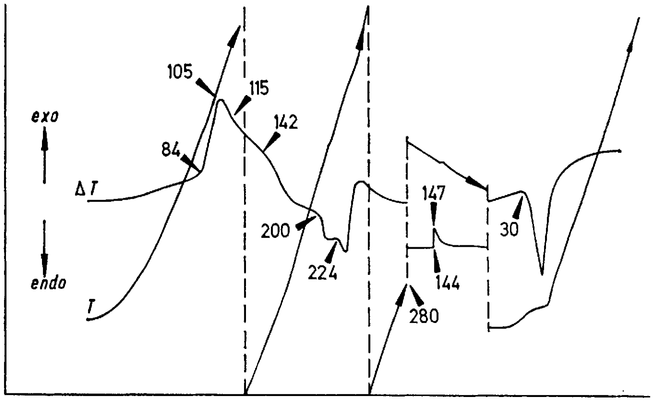

FIGURE 2 Reaction of $SnBr_2$ with $TeBr_4$ monitored by d.t.a. Other details as in Figure 1

In the bromide system, reduction of Te^{IV} takes place as in equation (3). The ΔT curve in Figure 2 shows a

$$7SnBr_2 + 4TeBr_4 \longrightarrow 2Te_2Br + 7SnBr_4 \qquad (3)$$

[6] R. C. Weast 'Handbook of Chemistry and Physics,' 54th edn., CRC Press, Cleveland, Ohio, 1973—1974.

[7] R. Kniep, D. Mootz, and A. Rabenau, *Z. anorg. Chem.*, 1976, **422**, 17.

very exothermic reaction between 84 and 105 °C which continues slowly up to 142 °C. At 200 °C endothermic boiling of $SnBr_4$ (lit.,[6] b.p. 202 °C) starts and is followed by melting of Te_2Br (lit.,[2] m.p. 225 °C) at 224 °C. During cooling, supercooled crystallization of Te_2Br occurs from 144 to 147 °C. Solidification of $SnBr_4$ is not observed down to room temperature because of supercooling. A quenched sample shows endothermic melting of $SnBr_4$ (lit.,[6] m.p. 31 °C) at 30 °C. At room temperature the sample tube contains Te_2Br crystals (up to 3 mm in length) in a supercooled $SnBr_4$ melt. Ditellurium bromide was identified by its X-ray powder pattern (Table 2). Variation of the upper limit of temperature of the reaction does not favour the formation of products other than Te_2Br. If an excess of $TeBr_4$ is used, $TeBr_4$ remains in the reaction product. If an excess of $SnBr_2$ is used, further reduction of Te_2Br takes place [equation (4)]. The elemental tellurium

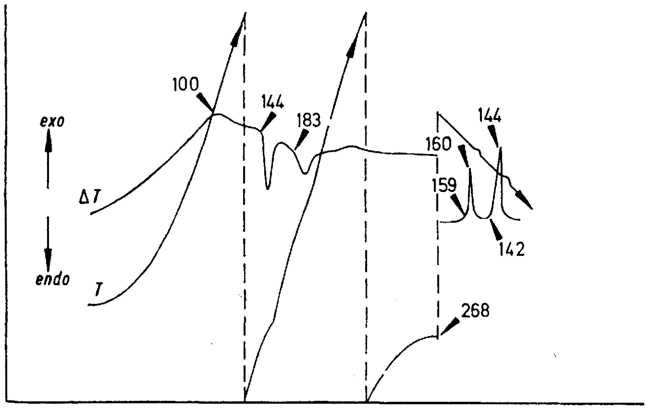

FIGURE 3 Reaction of SnI_2 with TeI_4 monitored by d.t.a. Other details as in Figure 1

$$SnBr_2 + 2Te_2Br \longrightarrow 4Te + SnBr_4 \qquad (4)$$

formed was again identified by its powder pattern (ASTM 4/0554).

In the iodide system, Te^{IV} is reduced to tellurium of average oxidation state I [equation (5)]. The ΔT curve

$$3SnI_2 + 2TeI_4 \longrightarrow 2TeI + 3SnI_4 \qquad (5)$$

in Figure 3 shows a broad exothermic peak for reaction between room temperature and 100 °C. At 144 °C endothermic melting of SnI_4 (lit.,[6] m.p. 145 °C) takes place and melting of TeI (lit.,[1] m.p. 185 °C) starts at 183 °C. During cooling from the melt, supercooled solidification of TeI from 159 to 160 °C is followed by only slightly supercooled solidification of SnI_4 from 142 to 144 °C. The crystalline subiodide formed by cooling from the melt was shown to be the β-TeI modification[7] by its X-ray powder pattern (see Table 2). Crystals of β-TeI were up to 4 mm in length. When the reaction was stopped before the first melting of SnI_4 was observed, the subiodide was a mixture of the α- and β-TeI phases. After annealing a mixture of SnI_2 and TeI_4 at 100 °C for 2 weeks, the subiodide formed was α-TeI without any β-TeI. These observations are in agreement with investigations of the Te–TeI_4 system:[1] β-TeI is a metastable phase which is formed by cooling from the melt and which can be transformed into α-TeI by annealing. An excess of TeI_4 results in its remaining in the reaction product. If an excess of SnI_2 is used, further reduction of TeI to elemental tellurium takes place [equation (6)]. The presence of

$$SnI_2 + 2TeI \longrightarrow 2Te + SnI_4 \qquad (6)$$

elemental tellurium besides the respective TeI phase after reaction with an excess of SnI_2 was indicated by X-ray powder investigations (see Table 2 and ASTM 4/0554).

Systematics.—Table 3 summarizes the results of the reduction of Te^{IV} by Sn^{II} in the respective halide systems. The change in formal oxidation state of Te^{IV} decreases with increasing atomic number of the participating halogen. Reaction in the iodide system takes place in the solid state. In the bromide and chloride systems participation of the liquid phases ($SnBr_4$, $SnCl_4$), which may act as a solvent for the respective tellurium(IV) halides, is not excluded. Whereas in the chloride system reduction invariably yields elemental tellurium, in the bromide system the subbromide Te_2Br and in the iodide system the subiodide TeI (β and/or α modification) is formed and only tin(II) halide in excess causes further reduction to elemental tellurium. Application of this type of reaction to tetrahalides of selenium as a possible route to subhalides of this element has been started.

TABLE 3

Formal oxidation states of tellurium in the course of the reduction of Te^{IV} by tin(II) halides (SnX_2)

X	Change in tellurium oxidation state
Cl	$4 \longrightarrow 0$
Br	$4 \longrightarrow 0.5 \longrightarrow 0$
I	$4 \longrightarrow 1 \longrightarrow 0$

EXPERIMENTAL

Materials.—The compounds $TeCl_4$ and $TeBr_4$ (99%, Pierce Inorganics) were purified by sublimation; TeI_4 was prepared by thermal decomposition of freshly crystallized $H_2TeI_6 \cdot 10$—$12H_2O$. (Details of this method of preparation as well as a crystal-structure determination of $H_2TeI_6 \cdot 10$—$12H_2O$ will be reported in a later paper.) Tin(II) chloride was prepared by dehydration of $SnCl_2 \cdot 2H_2O$, and $SnBr_2$ by reaction of Sn with HBr.[8] Tin(II) iodide was prepared from the elements and purified by transport through the vapour phase.[9] The purity of all the materials was checked by d.t.a. (melting point) and X-ray analysis.

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[8] G. Brauer, 'Handbuch der präparativen Anorganischen Chemie,' Ferdinand Enke Verlag, Stuttgart, 1954.

[9] A. A. Yarovoi, G. E. Revzin, and L. M. Petrova, *Inorg. Materials*, 1971, **7**, 385.

D.T.A. and X-*Ray Powder Investigations*.—Reactions for d.t.a. were carried out in sealed tubes using an M. Braun d.t.a. apparatus (R. Kniep) and a constant heating rate of 3.8 °C min^{-1}. The reference material was elemental tellurium.

X-Ray investigations were made by the Guinier method (film technique, Enraf Nonius FR4 camera) using monochromated nickel-filtered Cu-K_{α_1} radiation. The powder patterns of the tellurium subhalides (Table 2) were calculated from the known crystal structures[7] and experimentally confirmed by the Guinier technique. Intensities given were estimated by eye from the photographs.

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