

CCCLXXVI.—*The Reactions of Hydrogen Chloride with the Dioxides of Selenium and Tellurium between 0° and 170°.*

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SELENIUM dioxide has been stated by Ditte (*Compt. rend.*, 1876, 83, 56) to absorb hydrogen chloride exothermally, forming, (1) at the ordinary temperature, an amber-coloured liquid,  $\text{SeO}_2, \text{HCl}$ , stable below  $26^\circ$ , but evolving hydrogen chloride on warming, and (2) at low temperatures, a transparent yellow solid,  $\text{SeO}_2, 2\text{HCl}$ , which reverts to  $\text{SeO}_2, \text{HCl}$  on rise of temperature. The formation of  $\text{SeO}_2, 2\text{HCl}$  was confirmed by Lenher (*J. Amer. Chem. Soc.*, 1920, 42, 2498), who, however, did not specify the temperature; by the action of either phosphoric oxide or calcium chloride on this compound, followed by distillation, he prepared selenium oxychloride.

The present authors find that a pale yellow solid approximating closely to  $\text{SeO}_2, 4\text{HCl}$  is formed at  $0^\circ$ ; when warmed, this loses hydrogen chloride, liquefies completely at  $35^\circ$ , and at  $100^\circ$  is a yellow liquid containing slightly more hydrogen chloride than required by  $\text{SeO}_2, 2\text{HCl}$ . If the reaction is started at  $18^\circ$ , the resulting material is partly liquid, has the composition  $\text{SeO}_2, 2.6\text{HCl}$ , and behaves like the preceding product when heated to  $100^\circ$ ; whereas at  $100^\circ$  material identical with the previous final product is obtained. At  $140$ — $170^\circ$  an amber-coloured liquid is formed of composition  $\text{SeO}_2, 1.3\text{HCl}$ , which on distillation partly decomposes into selenium dioxide and hydrogen chloride, the resulting clear yellow liquid, b. p.  $160$ — $170^\circ$ , *d* 2.45, having the composition  $\text{SeO}_2, 1.8\text{HCl}$ . Redistillation of the liquid in a vacuum is accompanied by a further partial decomposition, producing a distillate, b. p.  $70$ — $80^\circ/15$  mm., the analysis of

which agrees with  $\text{SeO}_2 \cdot 2\text{HCl}$ . We therefore conclude that there are two addition compounds, *viz.*, (1)  $\text{SeO}_2 \cdot 4\text{HCl}$ , a yellow solid stable at  $0^\circ$ , and (2)  $\text{SeO}_2 \cdot 2\text{HCl}$ , a yellow liquid, stable up to and partly distillable at  $170^\circ$ . This liquid dissolves hydrogen chloride in amounts varying with temperature.

Ditte (*Compt. rend.*, 1876, **83**, 336) considered that an addition compound,  $2\text{TeO}_2 \cdot 3\text{HCl}$ , was formed by passing dry hydrogen chloride over tellurium dioxide at  $-10^\circ$ , which dissociated at the ordinary temperature, yielding  $\text{TeO}_2 \cdot \text{HCl}$ , but he obtained no evidence of  $\text{TeO}_2 \cdot 2\text{HCl}$  at an intermediate stage;  $\text{TeO}_2 \cdot \text{HCl}$  was described as beginning to lose water at  $110^\circ$  and yielding at  $300^\circ$  tellurium oxychloride,  $\text{TeOCl}_2$ , a yellow liquid setting to a crystalline solid. Lenher (*J. Amer. Chem. Soc.*, 1909, **31**, 243) found that the dioxide and hydrogen chloride combined to form  $\text{TeO}_2 \cdot 3\text{HCl}$  at  $0^\circ$ , and that this was successively converted into  $\text{TeO}_2 \cdot 2\text{HCl}$  and  $\text{TeCl}_4$  on heating, but he obtained no evidence of the formation of tellurium oxychloride in any reaction. At  $280$ – $300^\circ$  tellurium dioxide was completely volatilised in a stream of hydrogen chloride, presumably as tetrachloride and steam. The present investigation shows that at  $0^\circ$  hydrogen chloride is absorbed in varying quantities by the dioxide, giving a product, obviously not homogeneous, which loses water continuously with rising temperature when heated in a stream of the gas. There is no evidence that tellurium dioxide forms a definite addition compound within the range  $0$ – $150^\circ$ , the experimental data according more closely with the anticipated behaviour of basic chlorides in the presence of hydrogen chloride.

#### EXPERIMENTAL.

*Tellurium.*—The dioxide was prepared by adding successive small quantities of finely powdered tellurium to boiling concentrated nitric acid, decanting the excess of acid, washing the oxide well with water, and drying it first on a steam-bath and then at  $110^\circ$  (Found: Te, 77.4. Calc. for  $\text{TeO}_2$ : 79.9%). This material was used in the preliminary runs, but for the later work it was just fused and then allowed to crystallise, the central portions of the melt being used (Found: Te, 79.3%). Hydrogen chloride, dried and purified by passing successively through concentrated sulphuric acid and a cotton-wool filter, was led into a horizontal glass tube containing the dioxide (1–3 g.) in a porcelain boat at laboratory temperature. The oxide first turned yellow, then moist, and finally separated into yellow liquid and white solid layers; the solid lost 1.4% of moisture in a desiccator, but gained 12% on exposure to the air, dirty white friable solids being produced in each case. After various periods of passage of gas, the increase in weight of the contents of the boat

was irregular and neither the liquid nor the solid was of definite composition (see Table I).

TABLE I.

Run.	Time, hrs.	Increase in weight, %.	Empirical com- position calc. from increase.	Liquid.		Solid.	
				Te %.	Cl %.	Te %.	Cl %.
1	5	38.4	TeO <sub>2</sub> ,1.68HCl	30.7	29.0	—	—
2	7	35.8	TeO <sub>2</sub> ,1.57HCl	30.6	26.1	59.9	—
3	7	44.7	TeO <sub>2</sub> ,1.96HCl	—	—	—	—

Further experiments were made with the oxide in a stoppered U-tube at laboratory temperature and at 100°. Pure, dry hydrogen chloride was passed first through a weighed stoppered U-tube (*A*) with a filling of phosphoric oxide, then through the reaction tube, and finally through a second, weighed, stoppered U-tube (*B*) filled in like manner. The drying-tubes were filled with hydrogen chloride before all weighings and the weight of the reaction tube was corrected for the change from air to hydrogen chloride. Baker (J., 1898, 73, 422) has shown that unless phosphoric oxide is pure it absorbs small quantities of hydrogen chloride, and accordingly the difference between the increase in tubes *A* and *B* was taken as the amount of water leaving the reaction tube. Run 4 confirms Baker's observations, but in runs 5 and 6, carried out at 100°, it is obvious that the course of the reaction has changed; little hydrogen chloride has been absorbed, and some water, presumably that produced in the reaction, has been arrested by tube *B*. In these runs there was evidence of a slight reaction, the surface of the solid becoming greenish-yellow whilst a trace of brown sublimate was carried a little way up the limb of the reaction tube.

TABLE II.

Run.	Time, hrs.	Temp.	Weight of TeO <sub>2</sub> , g.	Increase in weight, %.	Empirical composition calc. from increase.	Change in weight (g.) in	
						<i>A</i> .	<i>B</i> .
4	5	18°	0.5564	40.4	TeO <sub>2</sub> ,1.77HCl	+0.0130	+0.0156
5	12	100	1.0420	6.3	TeO <sub>2</sub> ,0.27HCl	+0.0126	+0.0290
6	2.5	100	1.4154	9.3	TeO <sub>2</sub> ,0.41HCl	-0.0002	+0.0324

Three further runs (7, 8, 9) were carried out exactly as above in order to ascertain the change taking place in the material formed at 0° when it was subsequently heated in a stream of the gas. The reaction tube was first surrounded by a brine bath maintained at 0° ± 1° and gas was passed through the material for 5 hours. After the three U-tubes had been weighed the product was warmed to 100°, and subjected to the action of hydrogen chloride for a further 3 hours, and the tubes were re-weighed; finally, the temperature

was raised to 150°, and gas passed for a further 2 hours, after which the last weighings were made. The results are shown in Table III, from which it is clear that at the higher temperatures there is a loss of water and a nearly equal gain of chlorine.

TABLE III.

Temp.	Run	7.	8.	9.	10.
0°	TeO <sub>2</sub> , g.	0.8320	0.8922	0.3580	0.8086
	Increase, %.	35.9	26.2	40.2	32.1
	HCl/TeO <sub>2</sub> (mols.)*	1.57	1.15	1.76	1.40
	Increase in A, g.	0.0408	0.0870	0.0830	0.0068
	Increase in B, g.	0.0790	0.0996	0.0936	0.0008
100°	Increase, %.	35.7	29.7	47.7	41.5
	HCl/TeO <sub>2</sub> (mols.)*	1.56	1.30	2.09	1.82
	Increase in A, g.	0.0082	0.0590	0.0682	0.0030
	Increase in B, g.	0.0370	0.1018	0.1014	0.0302
150°	Increase, %.	33.8	30.7	51.3	47.0
	HCl/TeO <sub>2</sub> (mols.)*	1.48	1.34	2.24	2.05
	Increase in A, g.	0.0310	0.0438	0.0726	0.0012
	Increase in B, g.	0.1152	0.1348	0.1216	0.0364

\* Calculated from increase.

At the highest temperature, water carried forward by the gas stream was observed to condense in droplets in the connecting tubes. In run 10, which confirms the results in runs 7—9, drying tubes filled with calcium chloride were used to confirm the conclusion that the increase recorded in the *A* tube when phosphoric oxide was used is due to the cause indicated above.

Tellurium was estimated by dissolving weighed amounts of the compounds in hot concentrated hydrochloric acid and adding successively a saturated solution of sulphur dioxide, a 15% solution of hydrazine hydrate in hydrochloric acid, and finally more sulphurous acid; the resulting black colloidal tellurium was granulated by boiling for 10 minutes and then weighed on a Gooch crucible (compare Gutbier and Huber, *Z. anal. Chem.*, 1914, **53**, 430).

*Selenium.*—Crude dioxide was purified by solution in concentrated nitric acid, evaporation to dryness, and gentle ignition. Calcium chloride drying-tubes were used, and runs were conducted exactly as above at 0°, with change to 100°; at laboratory temperature, with change to 100°; and at 100° throughout. At 0° a very light yellow solid was produced which developed a considerable pressure of hydrogen chloride at the ordinary temperature, and there was no change in the weight of the *B* tube; on being heated to 100° this solid melted to a dark yellow liquid, and an increase was noted in the *B* tube, but it appeared to be due, not to water, but to the distilling forward of the undecomposed compound, for the tube became yellow, and, moreover, when the increase in weight of the *B* tube was added to the increase in the reaction tube, the sum always

indicated the presence of a substance having a composition very close to  $\text{SeO}_2 \cdot 2\text{HCl}$ . At laboratory temperature a mixture of liquid and solid was produced which gave precisely similar results when heated to  $100^\circ$  in a current of hydrogen chloride. The product obtained directly at  $100^\circ$  behaved similarly. The results are given in Table IV.

TABLE IV.

Run.	$\text{SeO}_2$ (g.).	Increase %		$\text{HCl}/\text{SeO}_2$ (mols.).	Increase at $100^\circ$ , %.	$\text{HCl}/\text{SeO}_2$ (mols.).
		at $0^\circ$ .	at $20^\circ$ .			
11	0.3220	126.5	—	3.85	60.3	1.83
12	0.3142	131.9	—	4.02	66.7	2.03
13	0.1576	134.6	—	4.10	70.9	2.16
14	0.1620	127.7	—	3.89	81.9	2.50
Mean		130.2	—	3.97	70.0	2.13
15	0.1364	—	79.1	2.41	75.2	2.29
16	0.1468	—	90.2	2.75	(45.6)	(1.39)
Mean			84.7	2.58	75.2	2.29
17	0.1760	—	—	—	71.5	2.18
18	0.1574	—	—	—	70.7	2.15
Mean					71.1	2.17
General mean at $100^\circ$						2.16

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