A Study of Tin Oxides by X-Ray Diffraction Method

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There are various reports available for the occurrence and stability of tin oxides: stannous oxide, β-stannous oxide, tritin tetroxide and stannic oxide. Most of these reports are in accord with one another on the point that stannous oxide decomposes into tin and stannic oxide at higher temperatures, though various temperatures have been reported for the decomposition such as 400°C[1], 510°C[2], 385°C[3] and 300°C.[4] Weiser and Milligan[5], however, showed that heating of stannous oxide in vacuo at 500°C gives a product which is neither stannous oxide, nor tin and stannic oxide and which they called β-stannous oxide.

According to Spandau and Kohlmeyer[6,7] stannous oxide decomposes into tin and tritin tetroxide over the temperature range from about 400°C to 1040°C, the melting point of stannous oxide. On the other hand, Platteeuw and Meyer[4] have recently reported that stannous oxide on heating in vacuo at 300°C and 550°C completely decomposed into tin and stannic oxide.

Owing to the results of the measurements on equilibria of $Sn—SnO_2—CO—CO_2$[8] and $Sn—SnO_2—H_2—H_2O$[9] the existence of β-stannous oxide and tritin tetroxide as stable compounds is improbable in the temperature range about 550°C to 850°C. But Fraenkel and Snipischski[2] deduced from an equilibrium measurement that some compound other than stannous oxide and stannic oxide existed above 900°C.

The thermodynamic data obtained by Veselovsky[10] indicate that stannous oxide (solid) is stable only within temperature range about 300° to 600°K. But recent calorimetric determination of the heat of formation of the tin oxides performed by Humphrey and O'Brien[11] indicates that stannous oxide (solid) is unstable over all temperature ranges.

In this work, a change of stannous oxide by heating, observed by X-ray diffraction methods, is reported and discussion is offered as to the existence of β-stannous oxide or tritin tetroxide and the decomposition of stannous oxide.

Experimental

Materials.—Stannous oxide was prepared by adding sodium hydroxide solution to a hydrochloric acid solution of stannous chloride until the solution became slightly alkaline and by boiling the resulting mixture until the precipitate turned black. The black stannous oxide precipitate was decanted until it became free from chloride; then it was dried at 110°C for eighteen hours. Stannic oxide was prepared by drying and calcining the white metastannic acid obtained by the reaction of concentrated nitric acid with metallic tin. X-ray diffraction patterns obtained from these two oxides were in agreement with the previous data, and no other impurities were observed.

Heating of stannous oxide, and tin-

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2) W. Fraenkel and K. Snipischski, ibid., **125**, 235 (1922).
3) C. G. Fink and C. L. Mantel, *J. Phys. Chem.*, **32**, 103 (1928).
4) J. C. Platteeuw and G. Meyer, *Trans. Faraday Soc.*, **52**, 1066 (1956).
5) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **36**, 3039 (1932).
6) H. Spandau and E. G. Kohlmeyer, *Z. anorg. u. allgem. Chem.*, **254**, 65 (1947).
7) H. Spandau, *Z. angew. Chem.*, **A/60**, 73 (1948).
8) E. D. Eastman and R. Robinson, *J. Am. Chem. Soc.*, **50**, 1106 (1928).
9) P. H. Emmett and J. F. Shultz, ibid., **55**, 1390 (1933).
10) B. K. Veselovsky, *J. Appl. Chem.* (U. S. S. R.), **16**, No. 9/10, 397 (1943); *Chem. Abst.*, **38**, 6148 (1944).
11) G. L. Humphrey and C. J. O'Brien, *J. Am. Chem. Soc.*, **75**, 2805 (1953).

stannic oxide mixture.—One- to two-tenths grams of sample were sealed in Pyrex tube in vacuo at 100°C or in nitrogen gas at 1/3 atmosphere. Each tube was heated in an electric furnace for a given time, then quenched to room temperature and cut for opening. The contents were examined by X-ray diffraction method, using Cu$K\alpha$ ray in a Debye-Scherrer camera of 90 mm. diameter.

High temperature X-ray diffraction.—A high temperature camera (Rigaku-Denki Co.) was used to obtain the patterns at elevated temperature by using Cu$K\alpha$-ray. The samples were sealed in a Pyrex capillary in vacuo.

Results

The diffraction patterns obtained from the quenched samples are illustrated in Fig. 1, A—C, corresponding to No. 6—8 in Table I. In Table I, the results of analysis of patterns, which were obtained from the sample quenched after treatment at various temperatures (column 3) and durations (column 4), are listed. No other compounds than tin, stannous oxide and stannic oxide were observed. Results of heating in nitrogen agree with those in vacuo.

TABLE I

RESULTS OF HEATING OF SnO AND A MIXTURE OF Sn AND SnO_2

Sample No.	Initial Sample	Temperature °C	Time min.	Detected Substances SnO	Sn	SnO_2
1	SnO	550	3	−	##	##
2	〃	〃	10	−	##	##
3	〃	〃	75	−	##	##
4	〃	〃	180	−	##	##
5	Sn+SnO_2	〃	75	−	##	##
6	SnO	500	5	##	+	+
7	〃	〃	10	+	+	+
8	〃	〃	15	−	##	##
9	〃	450	60	+	##	##
10	〃	〃	120	−	##	##
11	〃	400	600	##	+	+
12	Sn+SnO_2	〃	〃	−	##	##

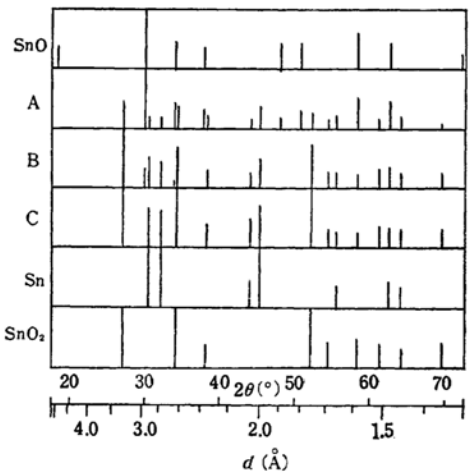

Fig. 1. X-ray powder diagrams of SnO heated at 500°C.

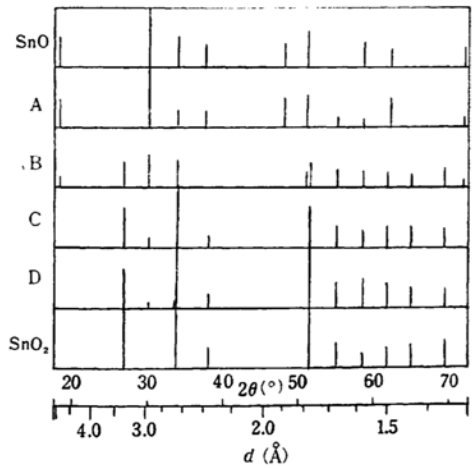

Fig. 2. X-ray powder diagrams of SnO heated at 445°C and 500°C, obtained by high temperature camera.

The patterns obtained by the high temperature camera are shown in Fig. 2. Fig. 2-D gives schematic pattern for thirty minutes of exposure at 500°C, where the material was ascertained only as stannic oxide. Fig. 2-A, -B and -C are patterns which were obtained step-by-step at 445°C. At each step forty minutes of exposure are needed. The pattern 2-A reveals the presence of monoxide and a small amount of dioxide; 2-B, monoxide and a comparable amount of dioxide; and 2-C, dioxide and a very small amount of monoxide, respectively.

Discussion

When stannous oxide is heated at 550°C in vacuo, the decomposition reaction,

$$2SnO \rightarrow Sn + SnO_2$$

is completed in a relatively short time. The reaction is also completed in the same manner at 500°C and 450°C, though the reaction time is prolonged. At 400°C, a certain small amount of stannous oxide still remains even after a considerably long time of heating. But reverse reaction started from tin and stannic oxide does not proceed at all. From these facts, it is deduced that the decomposition reaction may be completed even at 400°C, though the reaction velocity is very slow.

TABLE II

COMPARISON BETWEEN β-SnO* AND A MIXTURE OF Sn, SnO_2 AND SnO

β-SnO*		Sn		SnO_2		SnO		Corresponding Substance
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	
						(4.81	1)	
3.38	10	—	—	3.34	10	—	—	SnO_2
2.99	5	—	—	—	—	2.97	4	SnO
2.92	5	2.91	7	—	—	—	—	Sn
2.88	9	2.80	5	—	—	—	—	Sn ?
2.66	9	—	—	2.64	7	2.66	1	SnO_2
				(2.36	2)	(2.39	f)	
2.08	1	2.05	2	—	—	—	—	Sn
2.02	4	2.01	5	—	—	—	—	Sn
						(1.89	f)	
1.77	8	—	—	1.75	7	1.79	1	SnO_2
1.67	2	1.65	2	1.67	2	—	—	Sn & SnO_2
1.59	2	—	—	1.58	1	1.59	2	SnO_2 & SnO

* Obtained by Weiser and Milligan.

d: Spacing *I*: Intensity f: Faint

The patterns obtained by the high temperature X-ray diffraction camera show that the quenched samples sufficiently represent the high temperature state. In this temperature tin exists in liquid phase and hence gives no lines.

The conclusion is that, in the temperature range from 550°C to 400°C stannous oxide is thermodynamically unstable and decomposes into tin and stannic oxide.

As shown in Table II, the pattern of β-stannous oxide which was obtained by Weiser and Milligan is very similar to that of a mixture of tin, stannous oxide and stannic oxide except for minor disagreements. However, the pattern of stannous oxide reported by the same authors is found to be slightly inconsistent with the other authors' data. Further, Weiser and Milligan found the color of β-stannous oxide to be gray. This color is the same as that of the mixture of tin, stannous oxide and stannic oxide, but does not agree with the deep orange color of β-stannous oxide, which was prepared by two different methods by Partington and Moser[12]. It is presumed, therefore, that β-stannous oxide observed by Weiser and Milligan was not a new phase, but substantially a mixture of tin, stannous oxide and stannic oxide.

The existence of tritin tetroxide in equilibrium, which was deduced by Spandau at high temperatures, is rather open to question, since stannous oxide completely decomposes into tin and stannic oxide at high temperatures. Since patterns other than those of stannous oxide and stannic oxide were observed and no change in lattice-spacings was detected in the patterns obtained by a high temperature camera, it is clear that the coexistence of tin, stannous oxide and stannic oxide is not stable, and that they form neither a new phase nor a solid solution. The experiments by Spandau were carried out in a nitrogen-gas stream. But it is hardly probable that nitrogen has any influence on the decomposition, since the results of heating of stannous oxide in nitrogen agree with those in vacuo.

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12) J. R. Partington and W. Moser, *Nature*, **154**, 643 (1944).