1147. *Tin(II) Acetates.*

By J. D. DONALDSON, W. MOSER, and W. B. SIMPSON.

The solid phases obtained from solutions of tin or tin(II) compounds in acetic acid have been studied. *X*-Ray diffraction data, and complete analysis, show that two distinct phases exist: tin(II) acetate and tin(II) acetate–2-acetic acid. The preparations of the pure materials are described and their solubility in various solvents reported. Their thermal decomposition has been studied in detail. Tin(II) acetate sublimes *in vacuo* at 150—155°, but at higher temperatures or pressures decomposes to give blue-black tin(II) oxide, acetone, and carbon dioxide. Tin(II) acetate–2-acetic acid decomposes when heated *in vacuo* to give the same products and acetic acid, but at 295° at 1 atm. pressure gives instead tin(IV) oxide, acetone, carbon dioxide, and hydrogen. Tin(II) acetate–2-acetic acid is poorly soluble but otherwise stable in water, but tin(II) acetate is hydrolysed to blue-black tin(II) oxide or hydrous tin(II) oxide. *X*-Ray diffraction data for both compounds are reported and the bonding in tin(II) acetates is discussed.

IN view of the conflicting reports[1-7] of the preparation of tin(II) acetates from solutions of tin or tin(II) compounds in acetic acid, we have studied the materials obtained from such solutions. We find that two distinct phases, the normal acetate, $Sn(CH_3 \cdot CO_2)_2$, and a

[1] J. D. Donaldson, W. Moser, and W. B. Simpson, *Analyst*, 1961, **86**, 619.
[2] A. Ditte, *Ann. Chem. Phys.*, 1882, **27**, 115.
[3] F. W. Bury and J. R. Partington, *J.*, 1922, 1998.
[4] B. Glassman, *Ber.*, 1908, **41**, 36.
[5] E. Elöd and F. Kolbach, *Z. anorg. Chem.*, 1927, **164**, 297.
[6] E. Colonna, *Gazzetta*, 1904, **85**, 224.
[7] E. M. Baker and F. C. Tompkins, *J.*, 1952, 4518.

solvated acetate, $Sn(CH_3 \cdot CO_2)_2, 2CH_3 \cdot CO_2H$, can be obtained. Methods for preparing each of these in a pure form are reported together with data on their physical and chemical properties. It is also shown that the precipitates formed by the action of alkalis on solutions of tin(II) acetate are not a basic acetate phase.

EXPERIMENTAL

Preparation of Normal Tin(II) *Acetate.*—Three methods for preparing normal tin(II) acetate were studied.

(i) *Action of acetic acid on tin*(II)*oxide.* This method is an improved modification of one previously described by us.[1] Pure blue-black tin(II) oxide (25 g.) was refluxed under nitrogen with 50% v/v acetic acid (200 ml.) to give a yellowish-brown solution which was filtered and evaporated to dryness in a vacuum rotary evaporator. The white product (30 g.) was powdered and kept *in vacuo* over potassium hydroxide until dry and free from acetic acid. The crude tin(II) acetate was then purified by vacuum sublimation at 150°. This material was used in subsequent work. The infrared spectrum of this material has been studied,[8] and the distortion of the carboxylate ion in it explained on the basis of the outer electronic configuration of tin. Hydrous tin(II) oxide, in place of the oxide, gives the same product, which is also obtained if glacial acetic acid or acetic anhydride is used as solvent and the solution evaporated in a vacuum rotary evaporator until 10—20 ml. of liquid remains.

The methods of preparing blue-black tin(II) oxide described previously do not give consistently good products and the material used in the above preparation was obtained as follows. A solution of pure tin(II) sulphate, filtered as described[9] but not concentrated or crystallised, was placed immediately in a 3-necked round-bottom flask under oxygen-free nitrogen. 10N-Sodium hydroxide was added until the milky suspension gave a bright-red colour with phenolphthalein indicator (approx. 80 ml. of NaOH). The suspension was then boiled, lustrous blue-black tin(II) oxide being deposited. (Second and subsequent preparations in any given round-bottom flask proved invariably more successful than the first.) The oxide (*ca.* 16 g.) was washed by decantation, collected on a Buchner funnel, washed with acetone, and sucked dry.

(ii) *Action of acetic acid on metallic tin.* The product of this reaction depends upon the relative concentrations of tin and acetic acid. Tin(II) acetate is obtained when finely divided tin (90 g.) is refluxed under nitrogen with glacial acetic acid for 80—90 hr., but the product obtained on refluxing for a shorter time (*ca.* 50 hr.) is the solvated acetate, $Sn(CH_3 \cdot CO_2)_2, 2CH_3 \cdot CO_2H$.

(iii) *Preparation from copper*(II) *acetate.* Poor yields of tin(II) acetate were obtained by replacing the copper in solutions of copper(II) acid in acetic acid with metallic tin and evaporating the solution obtained.

Preparation of Tin(II) *Acetate–2-Acetic Acid*, $Sn(CH_3 \cdot CO_2)_2, 2CH_3 \cdot CO_2H$.—Tin(II) acetate–2-acetic acid can be prepared by refluxing tin metal with glacial acetic acid for 50 hr. as described in (ii) above. The material was, however, more conveniently prepared by the following method: Tin(II) acetate (10 g.) was dissolved in glacial acetic acid (100 ml.), and the solution evaporated to 70 ml. under nitrogen. The white crystalline product obtained on cooling was washed with the minimum of water and dried *in vacuo* over potassium hydroxide.

We determined stannous and total tin in the tin(II) acetates by Donaldson and Moser's[10] method. For acetate assay we refluxed the materials with a methanolic solution of sodium hydroxide, removed the excess of methanol, refluxed the solution with concentrated sulphuric acid and distilled off the free acetic acid which was then determined by titration with standard sodium hydroxide. The acetate assays were checked by carbon and hydrogen analysis [Found, on three typical samples of resublimed normal tin(II) acetate: Sn(II), 50·2, 50·0, 50·2; total Sn, 50·1, 50·0, 50·1; acetate, 49·9, 50·1, 50·1; C, 20·3, 20·4, 20·4; H, 2·5, 2·5, 2·4. Tin(II) acetate, $Sn(CH_3 \cdot CO_2)_2$, requires Sn(II), 50·2; acetate, 49·8; C, 20·3; H, 2·5%] [Found, on three typical samples of tin(II) acetate–2-acetic acid: Sn(II), 32·9, 32·8, 32·9; Sn total, 33·3, 33·2, 33·3; acetate, 66·4, 66·6, 66·5; C, 27·0, 27·2, 27·0; H, 4·0, 4·0, 4·1. Acid tin(II) acetate, $Sn(CH_3 \cdot CO_2)_2, 2CH_3 \cdot CO_2H$, requires Sn(II), 33·3, acetate, 66·2; C, 26·9; H, 3·9%].

Solubility of Tin(II) *Acetates.*—The solubility of the normal and the solvated acetate in four common solvents (see Table 1) under a non-oxidising atmosphere at various temperatures, was measured by titrating[10] the stannous tin in solution.

[8] J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, 1965, **21**, 215.
[9] J. D. Donaldson and W. Moser, *J.*, 1960, 4000.
[10] J. D. Donaldson and W. Moser, *Analyst,* 1959, **84**, 10.

TABLE 1.

Solubility (g. per 100 ml. of solution) of tin(II) acetate [$Sn(OAc)_2$] and tin(II)
acetate–2-acetic acid [$Sn(OAc)_2,2HOAc$]

Solvent	Compound	Temp.				
		25°	40°	50°	70°	100°
Water	$Sn(OAc)_2$	d	d	d	d	d
	$Sn(OAc)_2,2HOAc$	1·89	1·26	0·64	0·41	0·29
Ethyl alcohol	$Sn(OAc)_2$	2·87	9·04	11·84	n.d.	—
	$Sn(OAc)_2,2HOAc$	1·36	2·30	3·05	n.d.	—
Acetone	$Sn(OAc)_2$	1·36	2·30	3·05	—	—
	$Sn(OAc)_2,2HOAc$	1·66	2·96	3·11	—	—
2N-Acetic acid	$Sn(OAc)_2$	33·3	39·2	42·7	44·6	45·6
	$Sn(OAc)_2,2HOAc$	6·41	3·90	3·20	2·52	2·17

d = decomposed   n.d. = not determined.

Stability of Normal Tin(II) *Acetate.*—Tin(II) acetate can be stored for several months in contact with air, and much longer in the dark under a vacuum, with no alteration in appearance, analytical composition, or *X*-ray diffraction pattern. The first sign of impurity is the formation of small yellow areas near the walls of the container. This colour gradually spreads through the sample and is presumably caused by the formation of tin(IV); certainly all yellowish samples of tin(II) acetate contain about 4% of stannic tin.

Tin(II) acetate melts at 182·5—183° and boils, with some decomposition, at 239—241° under an atmosphere of oxygen-free nitrogen. The material can be sublimed *in vacuo* at 150—155° to give a 95—98% yield of pure tin(II) acetate.[1] Increase in the sublimation temperature or pressure results in partial decomposition of tin(II) acetate to blue-black tin(II) oxide (*X*-ray data), acetone, and carbon dioxide (infrared and chemical characterisation).

Stability of Tin(II) *Acetate–2-Acetic Acid.*—Tin(II) acetate–2-acetic acid can be kept for several months without change but it gradually becomes yellow, due to formation of tin(IV), and loses acetic acid on prolonged storage.

When heated at 1 atm. pressure under oxygen-free nitrogen the material was non-volatile and decomposed, without melting, at 295° to give tin(IV) oxide (*X*-ray data), acetone, and carbon dioxide (infrared and chemical characterisation), and hydrogen (the gas not condensed in a liquid-nitrogen trap was absorbed on metallic palladium; *X*-ray diffraction powder pattern of the metal then showed the presence of palladium hydride[11]). Proof of the stoicheiometry of the decomposition of tin(II) acetate–2-acetic acid to tin(IV) oxide at 1 atm. pressure was obtained by igniting the solid decomposition product at 700° in oxygen. Since tin(IV) oxide is the only tin compound which is unchanged under these conditions, any impurity in the decomposition product would result in an alteration in weight. However, when six samples of the decomposition product (0·1196—0·1756 g.) were ignited, the maximum weight change was 0·3%. The decomposition of tin(II) acetate–2-acetic acid at 1 atm. is thus $Sn(CH_3 \cdot CO_2)_2, 2CH_3 \cdot CO_2H \rightarrow SnO_2 + 2(CH_3)_2CO + 2CO_2 + H_2$.

Thermal decomposition of tin(II) acetate–2-acetic acid under a vacuum, however, gave a gaseous product, a white sublimate, and a black residue. The gaseous products contained only acetic acid, acetone, and carbon dioxide (infrared and chemical characterisation), the sublimate was tin(II) acetate (analysis and *X*-ray identification), and the residue was blue-black tin(II) oxide (*X*-ray data). The decomposition under vacuum must, therefore, take place in two stages: (1) the loss of the solvating acetic acid; and (2) the subsequent decomposition of normal tin(II) acetate. It was found that the bands in the infrared spectrum of the gaseous product due to acetic acid diminished in intensity with increasing pressure, as did the percentage of tin(II) in the solid residue.

N_2 pressure (mm. Hg)	<1	30	109	300	507	694	754
Sn(II)/total Sn (%)	99·3	80·0	52·1	18·7	6·6	0·11	0·03

Attempted Preparation of Basic Tin(II) *Acetate.*—When a solution of 2N-sodium hydroxide was added to a solution of tin(II) acetate (15 g.) in acetic acid (60 ml.), precipitation of a gelatinous material began at pH 5·16. The change in composition of the precipitate with pH was studied by adding varying amounts of 2N-sodium hydroxide and analysing the precipitates obtained. Those obtained between pH values of 5·3 and 6·2 have a mean analytical composition of Sn(II), 32·4;

[11] L. W. McKeechan, *Phys. Rev.* 1923, **20**, 82.

total Sn, 33·7; $CH_3CO_2^-$, 49·9; H_2O, 9·7; Na, 6·2.   This is not a basic phase and is almost certainly a complex acetate, possibly $NaSn(CH_3 \cdot CO_2)_3, 2H_2O$ which requires Sn(II), 33·5; $CH_3CO_2^-$, 49·9; H_2O, 10·1; Na, 6·5.   Increase in the pH above 6·3 results in the production of some hydrous tin(II)

TABLE 2.

X-Ray diffraction powder data for tin(II) acetates, (s, m, w etc., denote relative intensities)

Tin(II) *acetate*

dÅ	Index of refn.	Calc. d spacings	dÅ	dÅ
11·80 ms	011	11·80	2·96 m	1·803 mw
10·68 s	002	10·68	2·92 w	1·784 vvw
8·59 mw	012	8·52	2·84 w	1·778 mw
7·06 m	020	7·06	2·78 m	1·766 m
6·33 s	013	6·35	2·74 vvw	1·731 vww
5·85 m	022	5·89	2·66 ms	1·696 vvw
5·34 vs	004	5·34	2·61 vw	1·675 w
4·95 vvw	100	4·96	2·54 m	1·666 w
4·56 s	111	4·56	2·49 ms	1·629 vvw
4·36 vvw	032	4·32	2·43 vvw	1·622 vw
4·31 mw	112	4·29	2·37 w	1·578 mw
4·21 vvw	024	4·25	2·34 m	1·557 w
4·07 s	{ 103	4·07	2·32 m	1·538 vvw
	{ 120	4·06	2·27 mw	1·453 w
4·01 vvw	121	3·99	2·24 mw	1·431 w
3·90 vw	113	3·90	2·21 vw	1·417 mw
3·65 vw	025	3·63		1·387 vw
	{ 040		2·18 mw	1·376 vw
3·53 vvs	{ 034	3·53		1·318 w
	{ 123		2·14 mw	1·294 vvw
3·50 mw	114	3·52	2·11 w	1·264 vvw
3·35 vs	{ 131	3·37	2·09 vvw	1·210 vw
	{ 042	3·35	2·05 m	1·193 w
3·23 w	{ 105	3·23	2·03 vm	1·181 vw
	{ 124		2·00 m	1·143 vvw
	{ 043		1·965 w	1·126 vvw
3·16 mw	{ 026, 115	3·17	1·944 vm	1·094 vw
	{ 035	3·16	1·908 m	
3·07 vvw	113	3·08	1·863 w	

Tin(II) *acetate–2-acetic acid*

dÅ	Index of refn.	Calc. d spacings	dÅ
9·35 ms	020	9·35	1·635 vvw
8·73	011	8·70	1·573 w
7·39 ms	110	7·41	1·543 vw
6·91 mw	120	6·90	1·507 vw
5·94 vvw	111	5·92	1·498 w
4·88 m	002	4·88	1·471 vw
4·65 vvw	040	4·67	1·436 vw
4·40 vw	131	4·41	1·410 vvw
4·04 vvw	140	4·05	1·351 vvw
3·84 w	122	3·84	1·308 vw
3·65 vw	211	3·64	1·291 w
3·38 w	150	3·39	1·277 mw
3·20 vw	202	3·18	1·218 vvw
3·11 vvs	{ 151	3·12	1·171 w
	{ 142	3·11	1·160 vvw
2·95 vvw	222	2·94	1·140 vw
2·89 vvw	241	2·91	1·119 vvw
2·50 ms	162	2·50	1·064 vw
2·42 vvw	004	2·43	1·028 vw
2·35 vw	080	2·34	1·008 vvw
2·20 s	262	2·19	0·991 vvw
2·18 ms	350	2·18	
2·01 m	400	2·01	
1·975 vvw	191	1·972	
1·925 vvw	064	1·923	
1·913 vvw	430	1·912	

oxide (analytical and X-ray evidence).[12] Similar results are obtained if 2N-potassium hydroxide or a 1 : 1 ammonia (d 0·88)–water solution is used as precipitant.

Hydrolysis of Tin(II) Acetates.—Normal tin(II) acetate decomposed slowly to blue-black tin(II) oxide when kept under water for several hours. This decomposition was rapid in boiling water and in alkaline solution. Under certain conditions, however, a white hydrolysis product was obtained. When a suspension of tin(II) acetate (3·5 g.) in alkali-free deærated distilled water (100 ml.) was shaken mechanically for 30 min., the product was a white powder that had an X-ray powder pattern identical with that of hydrous tin(II) oxide.[12] All attempts to obtain red tin(II) oxide[13] by hydrolysis of chloride-free tin(II) acetate suspensions in an acetic acid–sodium acetate buffer (pH 5·73) and in the presence of sodium phosphite failed. A surface layer of red tin(II) oxide (X-ray identification) is, however, obtained when powdered tin(II) acetate is exposed to an atmosphere containing hydrogen chloride. Tin(II) acetate–2-acetic acid is stable towards hydrolysis even in boiling water.

Tin(II) Acetate as a Reducing Agent.—Normal tin(II) acetate is a useful reducing agent and in certain circumstances can act both as a reducing and an acetylating agent. The conversion of naphthaquinone into diacetoxynaphthalene is a two-stage process if the usual reducing agent, tin(II) chloride, is used, but can be carried out in one stage with tin(II) acetate. 1,4-Naphthaquinone (0·5 g.) was refluxed for 20 min. with tin(II) acetate in acetic anhydride (15 ml.) or glacial acetic acid. Water was added to the cooled solution and the crystalline product, 1 : 4-diacetoxynaphthalene, filtered off and recrystallised from ethanol (yield 0·59 g., 75%).

Crystallography.—(1) Resublimed tin(II) acetate consists of acicular fibres which show parallel extinction and positive elongation; it has $n > 1·74$ and high birefringence. Attempts to obtain single crystals of the material were unsuccessful; even the thinnest fibres (5 μ) were bundles of fibrous crystallites.

Crystal data: $Sn(CH_3 \cdot CO_2)_2$, $M = 236·7$, Orthorhombic, $a = 4·96 \pm 0·01$, $b = 14·11 \pm 0·03$, $c = 21·35 \pm 0·04$Å, $U = 1493$ Å^3, $D_m = 2·31$ g./c.c. (by suspension in a mutual solution of thallous formate and thallous malonate in water), $Z = 8$, $D_c = 2·11$ g./c.c. Filtered Cu–K_α radiation, single-crystal rotation and Weissenberg photographs about the fibre axis a.

(2) Tin(II) acetate–2-acetic acid consists of acicular crystals, which show parallel extinction and have $n > 1·74$, negative elongation, and high birefringence. X-ray data show that the crystals are orthorhombic with needle axis a and cleavage (010).

Crystal data: $Sn(CH_3 \cdot CO_2),2CH_3 \cdot CO_2H$, $M = 356·7$, Orthorhombic, $a = 8·03 \pm 0·02$, $b = 18·70 \pm 0·03$, $c = 9·75 \pm 0·02$ Å, $U = 1464$ Å^3, $D_m = 1·63$ g./c.c. (by suspension in a mutual solution of thallous formate and thallous malonate in water), $Z = 4$, $D_c = 1·62$ g./c.c. space group $Pnnm$, (D_{2h}^{12} No. 58) or $Pnn2,(C_{2v}^{10}$ No. 34). Filtered Cu–K_α radiation, single-crystal rotation and Weissenberg photographs about all three axes.

Table 2 contains the X-ray diffraction powder data of tin(II) acetate and tin(II) acetate–2-acetic acid, obtained by using an 11·64-cm. camera and a Phillips X-ray diffractometer with filtered Cu–K_α radiation. The d spacings longer than 3·00 Å for tin(II) acetate and 1·90 Å for tin(II) acetate–2-acetic acid have been indexed by comparison of single-crystal and powder photographs and by calculation from the unit-cell dimensions.

DISCUSSION

Two distinct solid phases, tin(II) acetate and tin(II) acetate–2-acetic acid can be obtained from solutions of tin(II) in acetic acid. Tin(II) acetate can be obtained pure by vacuum sublimation and is a suitable primary standard for tin analysis[1] and a valuable reducing agent. Its exceedingly fibrous nature and generally poor solubility would indicate a linear polymer, breaking down to monomeric or low polymeric species under the action of heat (sublimation) or suitable donor solvents (acetic acid, DMF). The i.r. spectrum,[8] however, provides no real evidence for polymer-type bonding.

Oxygen-containing tin(II) compounds in which the anion is a strong donor towards tin decompose thermally to tin(II) materials. Tin(II) acetate, like tin(II) formate[14] and tin(II) phosphite,[15] decomposes in this way. Tin(II) acetate–2-acetic acid, on the other hand,

[12] J. D. Donaldson and W. Moser, *J.*, 1961, 835.
[13] J. D. Donaldson, W. Moser, and W. B. Simpson. *J.*, 1961, 839.
[14] J. D. Donaldson and J. F. Knifton, *J.*, 1964, 4801.
[15] J. D. Donaldson, W. Moser, and W. B. Simpson, *J.*, 1964, 323.

decomposes thermally to tin(IV) oxide under normal conditions and therefore it seems likely that an oxygen from the solvate is also bonded to the tin. The resistance of the material to attack by water is consistent with such a structure because all of the likely bonding orbitals on tin(II) are used. Tin(II) acetate–2-acetic acid does, however, lose its solvated acetic acid if heated under a vacuum and any tin–solvent oxygen bond must therefore be weaker than the tin–acetate bonds.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, OLD ABERDEEN.
[Present Addresses: (J. D. D.) CHELSEA COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.3. (W. B. S.) THE UNIVERSITY, NOTTINGHAM.]   [*Received, June 2nd*, 1964.]