# 925. *Tin*(II) *Formate.*

By J. D. DONALDSON and J. F. KNIFTON.

The preparation and analysis of pure tin(II) formate are described. Its solubility in various solvents is reported. Its thermal decomposition has been studied in detail; the decomposition temperature is 198—200° and the products are tin(II) oxide, trioxymethylene, formaldehyde, and carbon dioxide. It was not possible to obtain an acid tin(II) formate from concentrated formic acid solutions. Hydrous tin(II) oxide (analytical composition $5SnO,2H_2O$) is obtained free from tin(IV) impurities by the controlled hydrolysis of tin(II) formate. The unit cell dimensions, cell contents, and *X*-ray diffraction powder data of tin(II) formate are also reported.

THE preparation of tin(II) formate has been described,[1-3] but the reports contain little information on the purity or on the properties of the products. Goldschmidt [3] obtained the material by dissolving a paste of freshly prepared hydrous tin(II) formate in formic acid, in the absence of oxygen, and evaporating the solution. The white crystalline product had the normal properties of a tin(II) compound and decomposed between 100 and 180° to tin(II) oxide, formaldehyde, and carbon dioxide. The infrared spectrum of tin(II) formate has been studied,[4] and the distortion of the carboxylate ion in the material explained on the basis of the outer electronic configuration of tin. The only other reports of tin(II) formate in the literature concern its use as a catalyst in the preparation of polyethylene tetraphthalate [5] and as a stabiliser for organic acid esters of cellulose.[6]

We have prepared pure tin(II) formate in good yields and studied some of its properties.

## EXPERIMENTAL

*Preparation.*—Four possible methods for preparing tin(II) formate were studied and the yield, purity, and crystal size of the products were compared.

(1) *Action of formic acid on tin*(II) *oxide.* Tin(II) oxide (10 g.) was refluxed with 60% w/w aqueous formic acid (250 ml.) at 100—105° under oxygen-free nitrogen until it dissolved (*ca.* 1½ hr.) and the solution filtered and cooled. The white crystalline product was filtered off, washed with acetone followed by ether, and dried *in vacuo* over potassium hydroxide pellets. This method gave the pure crystalline product in good yield (*ca.* 85%) and was used in subsequent work.

The conditions of this preparation were varied by using different concentrations of aqueous formic acid (30—100% w/w). The product was always tin(II) formate, but, in low concentrations of acid, the yields were poor, because of the low solubility of tin(II) oxide, and in high concentration of acid, they were also poor, because of low solubility of the product.

(2) *Action of formic acid on hydrous tin*(II) *oxide.* A paste of freshly prepared hydrous tin(II) oxide was refluxed with aqueous formic acid of various concentrations (150 ml. of 30—100% w/w) under oxygen-free nitrogen until it dissolved (*ca.* 2 hr.). The solution was filtered hot and cooled, and the white crystalline product filtered off, washed, and dried as in method (1). Pure crystalline tin(II) formate was obtained by this method but the yields (maximum 50%) were poor.

(3) *Preparation from copper*(II) *formate.* Copper(II) formate (10 g.) was dissolved in 50% w/w aqueous formic acid (250 ml.). This copper formate solution was heated with tin (30 g.) until the reduction of cupric ions to copper was completed (*ca.* 2 hr.). The clear solution, when filtered and concentrated in a vacuum rotary evaporator, gave a poor yield (40%) of small yellow crystals of tin(II) formate containing 1—2% of tin(IV) impurity. Varying the concentration of aqueous formic acid (30—80% w/w) did not improve the yield or the quality of the product.

---

[1] Liebig, *Ann. Pharm.*, 1836, **17**, 75.
[2] Grobel, " Gmelin's Hand. Org. Chem.," **4**, 236.
[3] Goldschmidt, *Chem. Ztg.*, 1907, **48**, 608.
[4] Donaldson, Knifton, and Ross, *Spectrochim. Acta*, 1964, **20**, 847.
[5] Chemstrand Corp., B.P. 791,790/1958.
[6] Hiatt and Williams, U.S.P. 2,614,914/1952.

(4) *Action of formic acid on tin.* Tin metal was refluxed with concentrated formic acid solutions for long periods but no solid product was obtained on evaporating the solution.

*Attempted preparation of an acid tin*(II) *formate.* An acid tin(II) acetate, $\mathrm{Sn(CH_3COO)_2{\cdot}2CH_3COOH}$ [8] can be prepared by boiling a solution of tin(II) acetate (10 g.) in glacial acetic acid, under a non-oxidising atmosphere, until the volume is about 70 ml. and then cooling the solution. Under similar conditions, however, tin(II) formate was unchanged ($X$-ray diffraction powder data and analysis).

*Analyses.*—We have found that formate does not interfere with determinations of stannous tin and total tin by Donaldson and Moser's method,[9] which was used in the present work. A sample of tin(II) oxide was analysed for stannous and total tin in the presence of varying amounts of sodium formate (0·2—2·0 g.) and the results were shown to be identical within the limits of experimental error.[9] We determined formate by oxidising a known weight of sample in dilute (2$N$) hydrochloric acid solution with lead tetra-acetate and weighing the carbon dioxide liberated. Three typical samples of tin(II) formate prepared by method (1) gave: Sn(II), 56·6, 56·6, 56·7; total Sn, 56·8, 56·7, 56·7; and $\mathrm{HCOO^-}$, 43·5, 43·6, 43·6% [tin(II) formate, $\mathrm{Sn(HCOO)_2}$, requires Sn(II), 56·9, $\mathrm{HCOO^-}$, 43·1%].

*Solubility of Tin*(II) *Formate.*—The solubility of tin(II) formate in five common solvents (see Table 1) under a non-oxidising atmosphere at various temperatures was measured by titrating [9] the tin(II) in solution.

TABLE 1.

Solubility (g. per 1. of solution) of tin(II) formate.

| Solvent/Temp. | 25° | 40° | 50° | 70° |
|---|---|---|---|---|
| Water | 4·09 | 4·42 | 4·90 | d |
| 2$N$ formic acid | 14·3 | 22·8 | 25·9 | 30·8 |
| Acetone | 0·131 | 0·219 | 0·270 | — |
| Ethanol | 0·131 | 0·174 | 0·200 | 0·235 |
| 2$N$ sodium hydroxide | d | d | d | d |

d = decomposed.

*Stability of Tin*(II) *Formate.*—Tin(II) formate can be kept for several months in contact with air, and for longer periods if stored in the dark under a vacuum. The first sign of impurity is a change in colour of the sample to pale yellow and a loss of crystallinity. The colour gradually spreads in the sample and is presumably due to the formation of tin(IV); certainly, all yellowish samples of the formate contain up to 2% of quadrivalent tin.

The thermal stability of tin(II) formate was studied by using a melting point and a vacuum grid apparatus. The material decomposes without melting at 198—200° (pressure range 5—760 mm.) with evolution of carbon dioxide and formaldehyde (infrared and chemical characterisation). A sublimate, trioxymethylene ($X$-ray and infrared characterisation) is also obtained and the residue consists of blue-black tin(II) oxide ($X$-ray values).

The stoicheiometry of the decomposition of tin(II) formate to tin(II) oxide was determined by heating known weights of formate in an evacuated Thunberg tube to about 240°, dissolving the product in the minimum of concentrated hydrochloric acid and titrating [9] the bivalent tin in solution. It was found that more than 96% of the tin(II) formate was converted to tin(II) oxide.

*Hydrolysis of Tin*(II) *Formate.*—Tin(II) formate decomposed slowly to blue-black tin(II) oxide when kept under water for 6—7 days; 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) formate (1 g.) in alkali-free deaerated distilled water (250 ml.) was shaken mechanically for 1—2 hr., the product was a white powder that had an $X$-ray powder pattern identical with that of hydrous tin(II) oxide.[7] Three typical samples of the product of hydrolysis gave Sn(II), 83·5, 83·4, 83·5; total Sn, 83·7, 83·4, 83·4; and $\mathrm{H_2O}$, 5·03, 5·04, 5·07%. Hydrous tin(II) oxide,[7] analytical composition $\mathrm{5SnO,2H_2O}$ requires Sn(II), 83·7, $\mathrm{H_2O}$, 5·07%.

*Crystallography of Tin*(II) *Formate.*—Tin(II) formate consists of white plates, which show extinction at 52° to the $a$ axis and have $n > 1{\cdot}74$ and high birefringence.

$\mathrm{Sn(HCOO)_2}$, M = 208·7, Triclinic, $a = 10{\cdot}56 \pm 0{\cdot}2$ Å, $b = 10{\cdot}56 \pm 0{\cdot}2$ Å, $c = 8{\cdot}81 \pm 0{\cdot}2$ Å,

---

[7] Donaldson and Moser, *J.*, 1961, 835.

[8] Donaldson, Moser, and Simpson, unpublished work.

[9] Donaldson and Moser, *Analyst*, 1959, **84**, 1 0.

$\alpha = 82° 50' \pm 5'$, $\beta = 82° 50' \pm 5'$, $\gamma = 74° 50' \pm 5'$, $U = 937{\cdot}6$ Å,$^3$ $D_m = 2{\cdot}98$ g./c.c. (displacement of various organic solvent). $Z = 4$, $D_c = 2{\cdot}96$ g./c.c. Filtered Cu-$K_\alpha$ radiation, single crystal rotation and Weissenberg photographs about all three axes.

Table 2 contains the *X*-ray diffraction powder data for tin(II) formate obtained by using 11·64 cm. cameras with Cu-$K_\alpha$ radiation. The spacings longer than 2·50 Å have been indexed on the basis of the unit cell dimensions.

TABLE 2.

*X*-Ray powder data for tin(II) formate.

| *d* (Å) | RI * | Index of refl. | $d_{calc.}$ | *d* (Å) | RI * | Index of refl. | $d_{calc.}$ |
|---|---|---|---|---|---|---|---|
| 8·57 | m | 001 | 8·71 | 3·18 | vs | $20\bar{2}$ | 3·18 |
| 6·98 | w | 101 | 6·70 | | | 320 | 3·19 |
| 5·48 | vs | $1\bar{1}\bar{1}$ | 5·46 | 3·06 | vs | $\bar{3}01$ | 3·06 |
| 4·77 | vs | $1\bar{1}1$ | 4·84 | 2·92 | w | 003 | 2·91 |
| 4·28 | mw | 121 | 4·28 | 2·84 | mw | $11\bar{3}$ | 2·84 |
| 4·11 | mw | 102 | 4·12 | 2·73 | s | $\bar{2}2\bar{2}$ | 2·73 |
| 3·79 | m | 112 | 3·79 | 2·60 | ms | 410 | 2·60 |
| 3·68 | ms | 221 | 3·66 | 2·53 | w | $2\bar{3}0$ | 2·53 |
| 3·49 | ms | 130 | 3·47 | | | 400 | 2·53 |
| 3·38 | w | 300 | 3·38 | | | | |

| *d* (Å) | RI * | *d* (Å) | RI * | *d* (Å) | RI * | *d* (Å) | RI * |
|---|---|---|---|---|---|---|---|
| 2·44 | w | 1·84 | vw | 1·473 | m | 1·193 | vvw |
| 2·40 | ms | 1·82 | w | 1·457 | mw | 1·183 | vvw |
| 2·22 | w | 1·81 | w | 1·444 | vw | 1·177 | vvw |
| 2·20 | s | 1·78 | mw | 1·425 | vw | 1·164 | vvw |
| 2·14 | ms | 1·73 | vw | 1·387 | w | 1·150 | vvw |
| 2·12 | w | 1·68 | m | 1·371 | w | 1·146 | vvw |
| 2·07 | mw | 1·64 | mw | 1·326 | mw | 1·109 | vvw |
| 1·99 | s | 1·59 | vw | 1·282 | vw | 1·094 | vvw |
| 1·94 | mw | 1·567 | m | 1·261 | vw | 1·050 | vw |
| 1·88 | mw | 1·548 | mw | 1·220 | vvw | 1·024 | vvw |

## DISCUSSION

Tin(II) compounds containing oxygen can decompose thermally to give tin(II) or tin(IV) material. The product obtained depends upon the donor strength of the anionic part of the compound towards the tin. With weak donors, the product is tin(IV) oxide, and materials such as tin(II) oxide,[7] tin(II) sulphate,[10] and most basic salts,[11] decompose in this way. With strong donors, the product is a tin(II) oxide, and compounds such as tin(II) formate, tin(II) acetate,[8] and tin(II) phosphite [12] decompose in this way.

Hydrous tin(II) oxide cannot be obtained free from tin(IV) or from basic salt by precipitation [7] with a solution of an alkali, because contamination and a basic salt phase occurs below pH 6·3 and oxidation of some of the tin(II) above pH 6·3. In the controlled hydrolysis of tin(II) formate, however, there is no basic salt phase, the maximum pH is about 5·5 and a pure tin(II) material is obtained. Analysis of the hydrous oxide prepared by hydrolysis confirmed that the analytical composition of the material was $5SnO{\cdot}2H_2O$.[7]

Tin(II) formate can be obtained as a pure material, and, since formate and tin(II) are good reducing agents, the use of the material in various reductions merits investigation.

One of us (J. F. K.) is grateful to the International Tin Research Council for a research grant.

DEPARTMENT OF CHEMISTRY,
CHELSEA COLLEGE OF SCIENCE AND TECHNOLOGY,
MANRESA ROAD, LONDON S.W.3.

[*Received, February 3rd,* 1964.]

[10] Donaldson and Moser, *J.*, 1960, 4000.

[11] Donaldson and Moser, *J.*, 1961, 1996; Donaldson, Moser, and Simpson, *J.*, 1963, 1727.

[12] Donaldson, Moser, and Simpson, *J.*, 1964, 323.