Regularity of Boiling Points.—A comparison of the boiling points of isocyanates with those of the corresponding chlorides shows interesting regularities. The difference between the boiling points of PCl₃ and P(NCO)₃ divided by the number of halogenoid groups is 31.9° − (169.3 − 73.5)/3. When PO(NCO)₃, As(NCO)₃, and Si(NCO)₄ are included, the average increment is 31.0°. The only volatile *cyanate*, Si(OCN)₄, yields a higher increment, 47.4°.

Upon comparing the *thiocyanate* series with the corresponding chlorides, the increment is also found identical; P(SCN)₃, PO(SCN)₃, and Si(SCN)₄ yield an average increment of 64.1°. All of these three thiocyanates have been shown to be thiocyanates, not isothiocyanates.

Further work in this field is planned. The author is much indebted to Professor George S.

Forbes, of this Laboratory, for valuable suggestions during the experimental work.

Summary

1. Phosphoryl isocyanate, PO(NCO)₃, arsenic isocyanate, As(NCO)₃, and antimony isocyanate, Sb(NCO)₃, have been prepared by the action of silver (iso)cyanate with the appropriate chloride.

2. Thermal transformations of these volatile isocyanates into the corresponding non-volatile cyanates have been observed.

3. Phosphoryl thiocyanate has been isolated; arsenic thiocyanate, provisionally reported by Miquel, has been found non-volatile.

4. Various physical properties have been investigated quantitatively and an apparent regularity of boiling points has been observed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

The Preparation and Properties of Potassium Oxalatostannate[1]

BY HOBART H. WILLARD AND TAFT Y. TORIBARA[2]

Previous workers[3] prepared and studied the complex oxalatostannates. Pechard[3b] claimed to have isolated a complex oxalatostannic acid, but he made no investigation of it. Hausmann and Löwenthal[3a] and Rosenheim and Platsch[3c] found that such an acid of constant composition could not be obtained.

Pechard prepared a potassium salt by dissolving stannic acid in potassium bioxalate solution and reported a formula K₂SnO(C₂O₄)₂·7H₂O. Rosenheim and Platsch repeated Pechard's work but got entirely different results and reported a formula K₆Sn₂(C₂O₄)₇·5H₂O. They state that the usual qualitative reactions for stannic tin and for oxalic acid are completely concealed and attribute this to the formation of a complex.

In connection with some proposed studies on oxalatothiostannates, further studies were made on the oxalatostannates.

Experimental

Preparation of Oxalatostannates.—The previous use of stannic acid in preparing solutions of oxalatostannates was

tedious as well as undesirable because of the introduction of adsorbed impurities. For this reason a scheme was devised for preparing a solution of stannic tin in excess of oxalic acid only. Attempts to isolate an oxalatostannic acid proved unsuccessful as previous workers had found. The potassium salt was prepared and studied.

A mixture of 25 g. of metallic tin (30-mesh) and 125 g. of oxalic acid in 800 ml. of distilled water was cooled in an ice–salt-bath to about 5°. With continuous mechanical stirring, 150 ml. of 30% hydrogen peroxide (superoxol) was gradually added, and the reaction mixture was kept cool until all the tin had dissolved. Such a procedure required six hours or more. The excess of hydrogen peroxide was decomposed by adding 40 mg. of finely divided platinum black, and the solution was kept cool in an ice–salt bath during this procedure to prevent hydrolysis of the tin. The platinum was removed by filtration and the filtrate was the desired solution of oxalatostannic acid in excess of oxalic acid.

To prepare the potassium salt, the solution was analyzed for total oxalate and for tin. Allowing two moles of oxalate per mole of tin, the excess oxalic acid was neutralized by adding the calculated quantity of solid potassium bicarbonate. The solution was cooled to 0°, and the solid was filtered off. To recrystallize the salt obtained, it was dissolved in the smallest amount of water at 60°, allowed to cool to room temperature and then cooled to 0°. This salt was found to be very stable, and the air-dried solid gave a very definite composition, K₆Sn₂(C₂O₄)₇·4H₂O. The potassium was determined gravimetrically as the perchlorate after first removing the tin by dropping hydrobromic acid into a boiling perchloric acid solution. The tin was determined gravimetrically as stannic oxide, using

(1) From a dissertation submitted by Taft Y. Toribara in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, 1942.

(2) Florence Fenwick Memorial Fellow, 1939–1942.

(3) (a) Hausmann and Löwenthal, *Ann.*, **89**, 104 (1854); (b) Pechard, *Compt. rend.*, **116**, 1513 (1893); (c) Rosenheim and Platsch, *Z. anorg. Chem.*, **20**, 308 (1899).

ammonium hydroxide to precipitate the tin after the oxalate had been removed with concentrated sulfuric acid. The quantity of stannic oxide after ignition was determined by difference, using solid ammonium iodide in the second ignition. The amount of oxalate present was determined gravimetrically by oxidizing it to carbon dioxide with permanganate and absorbing the gas on ascarite.

Anal. Calcd.: K, 20.22; Sn, 20.46; C_2O_4, 53.11; H_2O, 6.21. Found: K, 20.23, 20.18; Sn, 20.41, 20.46, 20.51; C_2O_4, 53.13, 53.16, 53.20; H_2O, 6.21, 6.21.

It will be noticed that the formula obtained is identical with that of Rosenheim and Platsch[3c] with the exception of the water of hydration. In this work the water of hydration was determined directly by driving it off by heat and absorbing it on dehydrite. Previous workers determined the amount of water by difference. In order to make certain that the tetrahydrate was the solid phase in equilibrium with a saturated solution at 25°, a solution of the salt was evaporated at that temperature until the solid precipitated out. This solid was then centrifuged and analyzed immediately for water. Analyses gave 6.27% and 6.24% of water as compared to 6.21% theoretical for a tetrahydrate.

Titration of $K_6Sn_2(C_2O_4)_7$ by Alkali.—It was noticed in preparing the salt that the pH was low even after the calculated quantity of potassium bicarbonate had been added. A water solution of the pure compound gave the same acidic solution. Standard potassium hydroxide was added, and the pH change was followed with a glass electrode. The titration curve is shown in Fig. 1.
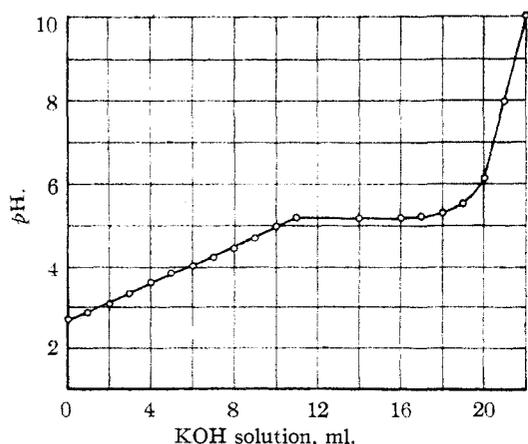

Fig. 1.—Titration of $K_6Sn_2(C_2O_4)_7$ solution with alkali.

The pH increased uniformly with the addition of the base until a value of 5.2 was attained. At the point where the solution became turbid from the precipitation of stannic hydroxide, the ratio $KOH/K_6Sn_2(C_2O_4)_7$ was 4.0. The pH remained constant until nearly all the tin had been precipitated and then increased rapidly. At the point where the steep rise in the curve occurs, the ratio $KOH/K_6Sn_2(C_2O_4)_7$ is 8.0, or just enough potassium hydroxide to precipitate all the tin in the compound as stannic hydroxide. The low value of the pH of a water solution of the compound may be explained on the basis of the hydrolysis of the tin.

The System $K_2C_2O_4$-$Sn(C_2O_4)_2$-H_2O.—The compound $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ may be considered as composed of $3K_2C_2O_4$, $2Sn(C_2O_4)_2$ and $4H_2O$. Rosenheim and Platsch[3c] reported the composition of the barium salt as $Ba_2Sn(C_2O_4)_4 \cdot 8H_2O$. For these reasons it appeared as if a complex might result from other combinations of $K_2C_2O_4$, $Sn(C_2O_4)_2$ and H_2O.

The system was studied at 25°. In order to obtain true equilibrium between the solid phase and the saturated liquid phase, the solid was caused to precipitate out of the liquid phase at the temperature desired by slow evaporation. This was accomplished by the use of an isothermal evaporator constructed by attaching a number of side-arms just below the neck of a one-liter round-bottom flask. Rubber stoppers were placed on the side-arms so that 8-inch test-tubes containing the solutions could be attached. Sulfuric acid was placed in the flask as the desiccant, and the system was evacuated to hasten evaporation.

The solutions were made by adding appropriate quantities of potassium oxalate to a properly neutralized oxalatostannate solution with an oxalate to tin ratio of 2.9 and to a nearly saturated solution of potassium oxalatostannate. When a sufficient amount of solid phase had been deposited, the tubes were removed from the evaporator and allowed to stand a few days in the thermostat to ensure equilibrium between the solid and liquid phases. Samples of the solution were measured in weight pipets and the wet solid in weighing bottles. Both solution and solid were analyzed for total oxalate and tin; the water was determined by difference. The composition of the solid in equilibrium with the liquid was determined by the well-known residue method of F. A. H. Schreinemakers.[4]

The data in Table I are shown plotted on triangular coördinates in Fig. 2.

(4) Schreinemakers, *Z. physik. Chem.*, **11**, 75–109 (1893).

TABLE I

THE SYSTEM $K_2C_2O_4$–$Sn(C_2O_4)_2$–H_2O AT 25°

Wt. in liquid phase		Wt. in wet residue	
$K_2C_2O_4$	$Sn(C_2O_4)_2$	$K_2C_2O_4$	$Sn(C_2O_4)_2$
1.90	5.54	24.06	37.84
1.80	2.14	24.91	29.32
4.11	0.79	28.31	33.04
7.44	0.72	30.99	34.79
13.64	1.41	36.53	40.19
22.37	0.79	38.57	38.81
27.25	2.81	69.94	2.82
27.80	1.25	71.20	0.29
27.21	0.54	68.16	0.47
27.12	0.00	$K_2C_2O_4 \cdot H_2O$	

The tie lines indicate that only two solid phases, $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ and $K_2C_2O_4 \cdot H_2O$, were found in the region of oxalate to tin ratio greater than 3.5, showing that tin does not form any complex with potassium oxalate in which the oxalate to tin ratio is greater than this. Since the purified product obtained from a neutralized oxalatostannate solution with an oxalate to tin ratio less than 3 was $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$, there is reason to believe that it is the only compound formed from a combination of the three components.

That point on the isotherm representing the solubility of pure potassium oxalatostannate in water, was determined from both under- and super-saturation; equilibrium was reached very slowly from the latter direction, but the results obtained were in close agreement, giving an average of 3.94% of the anhydrous salt as the solubility. The aqueous solubility of potassium oxalate at 25° here reported, 27.12% (averaged from 6 determinations ranging between 27.09 and 27.15), differs somewhat from previous values: 27.40,[5] 27.36,[6] 27.2,[7] 27.40.[8] Equilibrium in this work was approached from both sides. The disagreement may result from the difference in analytical methods: whereas previous workers used the permanganate titration, oxalate was here de-

(5) Foote and Andrew, *Am. Chem. J.*, **34**, 153 (1905).
(6) Hartley, Drugman, Vlieland and Bourdillon, *J. Chem. Soc.*, **103**, 1747 (1913).
(7) Rivett and O'Conner, *ibid.*, **115**, 1346 (1919).
(8) Woskressenskaja, *Z. anorg. allgem. Chem.*, **155**, 115 (1926).
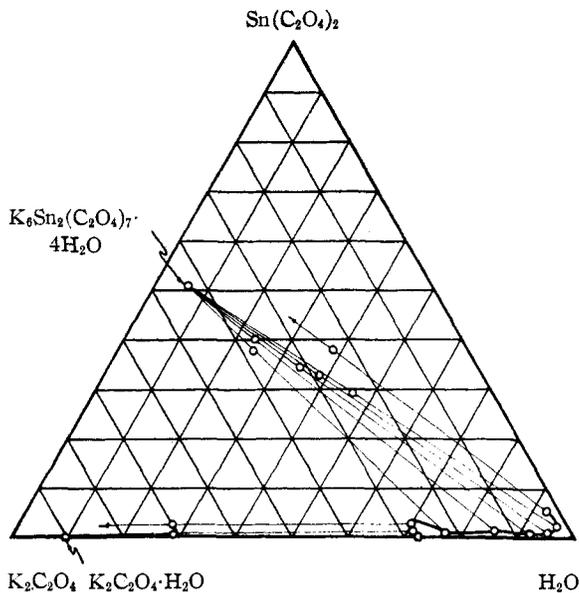
$Sn(C_2O_4)_2$

$K_6Sn_2(C_2O_4)_7 \cdot$
$4H_2O$

$K_2C_2O_4$ $K_2C_2O_4 \cdot H_2O$ H_2O

Fig. 2.—The system $K_2C_2O_4$–$Sn(C_2O_4)$–H_2O at 25°.

termined gravimetrically as already described. Because of the absence of interferences and because larger samples may be used, the precision of the gravimetric method is greater than that of the volumetric method, which must be carried out under carefully controlled conditions. The density 25°/4° of the potassium oxalate solution, 1.2135, agrees with Rivett and O'Conner's value, 1.215.

Summary

1. Tin was dissolved directly in oxalic acid, using hydrogen peroxide as an oxidizing agent.

2. Crystallized potassium oxalatostannate was shown to have the formula $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$.

3. The titration of a solution of potassium oxalatostannate was followed by pH measurements.

4. The solubility relations in the system, $K_2C_2O_4$–$Sn(C_2O_4)_2$–H_2O at 25° were determined, and the only solid phases present in the region of oxalate to tin ratio greater than 3.5 were $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ and $K_2C_2O_4 \cdot H_2O$.