from one sample to another; the formation of some of the lactone in the process of isolating triethyl isocitrate accounts for all the observed results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Intermediate States of Oxidation of Stannous Chloride[1]

BY T. R. BALL, WALTER WULFKUEHLER AND R. E. WINGARD

In studying the reduction of chromic acid by various reducing agents, including stannous chloride, Ball and Crane[2] found evidence for the existence of tin trichloride in solutions partially oxidized. The magneto-optic apparatus of Dr. Fred Allison was used in the previous and the present investigation.

The evidence for the tervalent state of tin is very positive and conclusive in the field of organometallic compounds. Several compounds analogous to triphenylmethyl have been prepared. In dilute solutions in organic solvents, the molecular weights approach those of trialkyl tin compounds containing one tin atom. A few of the more important references are cited.[3]

In the inorganic field the evidence for tin sesquioxide appears to be quite strong. Von Fuchs[4] reduced ferric chloride with stannous chloride and as soon as the solution became green, added calcium carbonate and thus prepared tin sesquioxide. From this he got tin trichloride by solution in hydrochloric acid. However, Mellor[5] states that this is "probably a mixture of stannous and stannic chlorides." Berzelius[6] mixed solutions of stannous and ferric chlorides, each neutralized with ammonia just short of the point of precipitation. The mixture gradually lost its color and a precipitate formed which, upon drying in an atmosphere of carbon dioxide, yielded brownish-black Sn_2O_3. It was soluble in ammonia and was, therefore, not a mixture of stannous and stannic oxides.

Experimental

Procedure.—One-tenth normal stannous chloride was made by dissolving tin in concentrated hydrochloric acid and was kept in tightly stoppered bottles. By a fifty-fold dilution with 3 N hydrochloric acid, 0.002 N solutions were prepared; 250 ml. portions of the dilute solution were partially oxidized with 0.10 N potassium dichromate, added from a micro buret, care being taken to have the stannous chloride in excess at all times. In general, a fresh solution was prepared for each day's work. Observations were made on the magneto-optic apparatus and minima were found at the following positions on the scale (Allison units): 23.56, 23.67, 23.73, 23.83, 23.90, 24.03, 24.12, 24.24, 24.33, 24.39, 24.46. These are attributed to $SnCl_3$ as will be shown later. Blanks were run on the hydrochloric acid and the potassium dichromate and no minima were observed in this region of the scale. These results were obtained by Mr. Wulfkuehler and were later checked by Mr. R. E. Wingard with almost perfect agreement. He had no knowledge of the previous results, other than the fact that minima had been observed between 23 and 25 on the scale. This fact is mentioned because the statement has frequently been made that the minima are purely subjective. In order to ascertain the approximate concentrations of tin trichloride in the solutions studied, one of us (R. E. W.) made a sensitivity curve by the method of Nicol rotation such as was used by Bishop and Dollins[7] in their quantitative determination of calcium. A series of stannic chloride solutions was prepared and the angle through which the analyzing Nicol had to be rotated to cause the disappearance of the minima of the most abundant isotope was determined for each concentration. From these data a sensitivity curve was constructed in which log $1/c$ was plotted against the angular rotation. Solutions of trivalent tin were then prepared and the angle again determined. The concentration was read off on the curve, assuming that the curve would apply to the trivalent ion. The original unoxidized solutions had a total tin concentration of about 6 parts in 10^5 of solution. After partial oxidation with dichromate, the maximum concentration of $SnCl_3$ observed in any of the tests was about 2 parts in 10^9. From this it may be calculated that only about 0.01% of the tin was in the trivalent form.

Discussion

Slack[8] and MacPherson[9] have stated that the

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[2] Ball and Crane, THIS JOURNAL, **55**, 4860 (1933).

[3] (a) Ladenburg, *Ber.*, **4**, 19 (1871); (b) Rügheimer, *Ann.*, **364**, 51 (1909); (c) Kraus, *Rec. trav. chim.*, **42**, 588 (1923); (d) Böeseken and Rutgers, *ibid.*, **42**, 1017 (1923); (e) Kraus and Sessions, THIS JOURNAL, **47**, 2361 (1925).

[4] Von Fuchs, *J. prakt. Chem.*, [1] **5**, 318 (1835).

[5] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1927, Vol. VII, p. 424.

[6] Berzelius, *Pogg. Ann.*, **28**, 443 (1833).

[7] Bishop, Dollins and Otto, THIS JOURNAL, **55**, 4365 (1933).

[8] Slack, *J. Franklin Inst.*, **218**, 445 (1934). This paper contains a complete bibliography of publications on the magneto-optic method.

[9] MacPherson, *Phys. Rev.*, **47**, 254 (1935).

distribution of minima observed on the magneto-optic apparatus is merely one of chance. In a recent paper[10] one of us has attempted to answer this by presenting distribution curves of 1698 minima taken from work done in this Laboratory,[11] including the present investigation. Of all minima read, 84.2% fall within the limits of experimental error of a peak in the curve and 30.1% fall on a peak. Of the 629 readings taken in this study, 77.2% are within experimental limits. From these data one could scarcely conclude that there is chance distribution only.

The justification for attributing the observed minima to tin trichloride is based upon the following considerations. First, we have checked Allison's results for stannous and stannic chlorides and find eleven minima for each, corresponding to the isotopes of tin. Since the equivalent weight of the cation determines the position of the minima in a series of salts having a common anion, the minima for $SnCl_3$ should fall about midway between those of $SnCl_2$ and $SnCl_4$. Table I shows that the newly observed minima fall in this range. Other salts of equivalent weights between $SnCl_2$ and $SnCl_4$ are also included. In computing the scale readings all the minima for a given salt were averaged. This method of tabulation is open to the objection that the scale readings are unweighted averages, whereas the chemical equivalents are weighted with respect to isotopic abundance. Work is now in progress which shows promise of giving an improved method of correlating scale readings with factors other than equivalent weight. We hope to present this at some future date.

TABLE I

SCALE READINGS AS A FUNCTION OF EQUIVALENT WEIGHT

Salt	Equiv. wt. cation	Av. scale rdg.
$CoCl_2$	29.47	20.09[a]
$SnCl_4$	29.67	20.26[a,b]
$CuCl_2$	31.78	20.57[b]
$ZnCl_2$	32.69	21.56[b]
KCl	39.10	22.79[b]
$SbCl_3$	40.59	23.48[b]
$SnCl_3$	39.60	24.00[a]
$SrCl_2$	43.81	24.47[b]
$NdCl_3$	48.09	24.59[c]
$CdCl_2$	56.20	25.69[b]
$SnCl_2$	59.35	29.10[a,b]

[a] This Laboratory. [b] Allison. [c] Hopkins.

With the exception of the relationship to antimony trichloride, the tin trichloride fits into the tabulation quite satisfactorily.

Second, the minima in the 23.50 to 24.50 range may be made to disappear if an excess of potassium dichromate is added, indicating that they are due to oxidizable material.

Third, the number of minima corresponds with that of all tin salts which have been studied by this method. It also agrees with the number of isotopes attributed to tin as determined by Aston's positive ray method.

There is, however, one other possibility which would account for the data obtained. The minima might be due to stannous chlorostannate. This salt should show eleven minima which should disappear upon complete oxidation. Since nothing is known as to the effect of anions of this type upon the positions of minima, it is impossible at this time to predict where such a salt would be evidenced on the scale. It would be a peculiar coincidence if it should give minima midway between those of stannous and stannic chlorides.

Summary

Evidence has been presented to show that the distribution of observed minima in the magneto-optic method of analysis is not one of chance.

Trivalent tin is an intermediate state in the oxidation of stannous chloride with potassium dichromate. Not more than 0.01% of the tin was found in the trivalent state.

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[10] Ball, *Phys. Rev.*, **47**, 548 (1935).

[11] Ball and Cooper. THIS JOURNAL, **55**, 3207 (1933); see also Ref. 2.