termined by titration back to perrhenate with ceric sulfate. The results ranged from Re(4.01) to Re(4.68) though duplicate determinations on any one solution agreed to within 0.02 unit. Since the violet solutions have also been obtained on oxidation of Re(V), it would appear from these low values that the solutions contained some reducing impurity. The fact that higher values were generally obtained with the more concentrated violet solutions also indicated that this was the case. Such a reducing impurity might possibly be formed by the rhenium-catalyzed reduction of sulfuric acid during the electrolytic reductions of the perrhenate.

Studies of the cathodic reduction of the violet solutions revealed that a definite reduction step started at approximately −0.4 v. and could be completed at −0.2 v. This reduction step gave amber solutions showing the absorption spectrum reproduced in Fig. 3. The amber solutions, which were identical with those formed by the action of hydrogen sulfide on the violet solutions, were rapidly oxidized by air back to the violet. Coulometric measurements made during five reductions of three different violet solutions gave 0.49 ± 0.02 as the oxidation state difference between the violet and amber species. This half-unit oxidation state difference suggests that the violet and amber species are dimers, one of which contains rhenium in two different oxidation states. Dilutions of the violet solutions in 10 *M* HCl appeared to be stable, but similar dilutions of the amber exhibited after several days a nearly pure Re(V) chloride spectrum. This result indicates that the amber is a Re(V) and the violet a mixed Re(V)–Re(VI) species; however definite assignment of oxidation states will not be possible until pure solutions of the species have been obtained.

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The Electrolytic Dissociation of Dimethyltin Dichloride

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The dissolution of dimethyltin dichloride in water produces chloride ions and doubly-charged dimethyltin ions, together with their hydrolysis products. The degree of dissociation and the hydrolysis constant have been determined, and a study of the further hydrolysis of dimethyltin dichloride in basic solution has been made.

The electrolytic behavior of several organometallic halides has been studied intensively during the past ninety-three years[2–12] but there has been no report on dimethyltin dichloride. This compound now is readily available,[13] and its stability and wide range of solubility make it an interesting substance to study. We are concerned here with its dissociation in water, the extent of its hydrolysis in pure water, and its further hydrolysis in basic solutions.

Experimental

Preliminary Tests.—Dimethyltin dichloride is a volatile, covalent substance which melts at 106°, boils at 190°, and readily sublimes at room temperature. It is very soluble in benzene, cyclohexane and other hydrocarbon solvents to give non-conducting solutions. It also dissolves readily in water to the extent of 1200 g. or more per liter, forming a colorless solution without precipitation of oxide or hydroxide.[14] The aqueous solutions are highly conducting, and show the usual reactions for chloride ion. Positive ions were detected by their metathetic reactions and also were retained by an ion-exchange column. We may write the dissociation as

$$(CH_3)_2SnCl_2 + nH_2O = (CH_3)_2Sn(H_2O)_n^{++} + 2Cl^- \quad (1)$$

The solutions also are acid in all concentrations, so some hydrolysis must occur

$$(CH_3)_2Sn(H_2O)_n^{++} + H_2O = (CH_3)_2Sn(H_2O)_{n-1}\,OH^+ + H_3O^+ \quad (2)$$

The extent of dissociation by reaction with water was sought, and also the degree of hydrolysis in solutions of comparable concentration.

Cryoscopic Measurements.—If equation (1) is correct, the van't Hoff *i* factor at infinite dilution should be 3.0 in the absence of any hydrolysis or other reaction. The freezing points of three solutions were determined, relative to water: (a) 1.5698 g. $(CH_3)_2SnCl_2$ in 42.202 g. H_2O; molality 0.1693. Observed ΔT = 0.823°; calculated for complete ionization as in eq. (1) 0.945°, for no ionization 0.315°; i = 2.61. (b) 0.9993 g. subs. in 43.687 g. H_2O; molality 0.1041. Observed ΔT = 0.521°, i = 2.69. (c) 0.6023 g. subs. in 42.9013 g. H_2O; molality 0.0639. Observed ΔT = 0.340°, i = 2.86.

Hydrolysis Constant.—The *p*H values of dilute solutions of $(CH_3)_2SnCl_2$ were measured at 24.8° with a Beckman *p*H meter. A 2.05×10^{-3} *M* solution had a *p*H of 3.025 (H^+ concn. = 9.44×10^{-4} *M*), and a 9.16×10^{-4} *M* solution had a *p*H of 3.27 (H^+ concn. = 5.37×10^{-4} *M*). By equation (2), at equilibrium

$$K_h = \frac{[Me_2Sn(H_2O)_{n-1}OH^+][H_3O^+]}{[Me_2Sn(H_2O)_n{}^{++}]} = \frac{[H_3O^+]^2}{[Me_2SnCl_2] - [H_3O^+]}$$

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[1] Ethyl Corporation Fellow at Harvard University, 1952–1953.

[2] A. Cahours, *Ann.*, **114**, 367 (1860).

[3] G. Bredig, *Z. physik. Chem.*, **13**, 303 (1894).

[4] N. Zelinsky and S. Krapiwin, *ibid.*, **21**, 47 (1896).

[5] Werner and Pfeiffer, *Z. anorg. Chem.*, **17**, 82 (1898).

[6] C. A. Kraus and W. N. Greer, THIS JOURNAL, **45**, 2946 (1923).

[7] C. A. Kraus and C. C. Callis, *ibid.*, **45**, 2624 (1923).

[8] F. Hein and H. Meininger, *Z. anorg. Chem.*, **145**, 95 (1925).

[9] I. B. Johns, *et al.*, *J. Phys. Chem.*, **34**, 2218 (1930).

[10] W. Evans and F. Lee, THIS JOURNAL, **55**, 1474 (1933); **56**, 654 (1934).

[11] W. Klemm, FIAT Report of Inorganic Chemistry, Part II, p. 169.

[12] K. Gingold, E. G. Rochow, D. Seyferth, A. C. Smith and R. West, THIS JOURNAL, **74**, 6306 (1952).

[13] Our dimethyltin dichloride was prepared by the direct reaction of methyl chloride with molten tin containing copper and zinc as catalysts (A. C. Smith and E. G. Rochow, report in preparation). A similar method, developed independently, is reported by F. A. Smith in U. S. Patent 2,625,559 (Jan. 13, 1953).

[14] In this respect $(CH_3)_2SnCl_2$ resembles $(CH_3)_2GeCl_2$, and both differ markedly from $(CH_3)_2SiCl_2$, which hydrolyzes rapidly and completely.

Substituting the respective concentrations

$$K_h = 7.6 \times 10^{-4} \text{ at } 2.05 \times 10^{-3} M$$
$$= 8.05 \times 10^{-4} \text{ at } 9.16 \times 10^{-4} M$$

Using an average value of 7.8×10^{-4} for K_h, the extent of hydrolysis of a 0.063 M (0.064 molal) solution of $(CH_3)_2SnCl_2$ at 24.8° would be 10.5%.

Further Hydrolysis with Base.—Dimethyltin oxide had been prepared by Cahours[2] and Harada[15] by the addition of ammonia to a solution of dimethyltin diiodide. It is a white powder, insoluble in water but soluble in strong alkali (to form a salt) and in phenol (to form a phenoxide). We found that the addition of 0.5 N NaOH to 4.4 g. of $(CH_3)_2SnCl_2$ in 150 ml. of water precipitated no oxide until a *p*H of 5.7 was reached, at which time the oxide formed rather slowly and the *p*H *decreased* to 5.32. Further addition of base precipitated all of the oxide, which remained in suspension until the *p*H rose to 11.5. Between 11.52 and 11.55 the oxide completely dissolved as disodium salt. It was found best to prepare dimethyltin oxide for other experiments by adding a calculated amount of sodium hydroxide to a solution of the dichloride, or by adding a solution of the dichloride to an excess of alkaline buffer at *p*H 8–9 (1 M NH_4Cl with added NH_3), precipitating a fine white powder that could be washed by centrifugation.

In order to follow the hydrolysis in basic solution more closely, a 0.1016 N solution of $(CH_3)_2SnCl_2$ (standardized with silver nitrate) and a 0.09763 N solution of NaOH (standardized with potassium acid phthalate) were compared in a titrimeter equipped with a magnetic stirrer and a *p*H electrode. Fifty-four observations of *p*H *vs.* ml. of base added lead to the curve shown in Fig. 1, which shows a plot of *p*H *vs.* milliequivalents of base per milliequivalent of $(CH_3)_2SnCl_2$. The precipitation of the oxide followed a course similar to that in the previous experiment: when almost one equivalent of base had been added (*p*H 6.80), solid began to form and the precipitation continued without further addition of base, lowering the *p*H to 6.76 after two minutes, 6.53 after four minutes, 6.28 after six minutes, 6.15 after eight minutes, and a constant value of 6.06 after ten minutes. This is regarded as supersaturation of the solution in oxide followed by rather slow crystallization; the delay probably persists to a lesser extent throughout the rest of the titration. The oxide dissolved in two mols of base, indicating the reaction

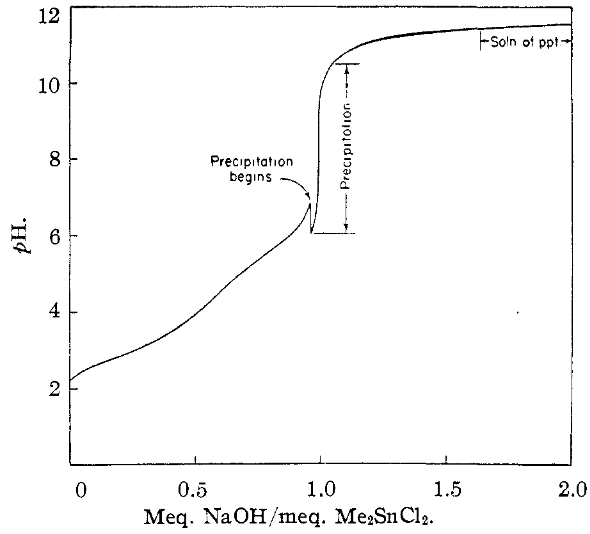

Fig 1.

$$(CH_3)_2Sn(H_2O)_n^{++} + 4OH^- = (CH_3)_2Sn(OH)_4^{=} + nH_2O \quad (3)$$

in which the value of n probably is four but may be six.

Isolation of Ions.—A sample of 0.4135 g. of $(CH_3)_2SnCl_2$ was dissolved in 30 ml. of water and run through a column of 50 cc. of Dowex 50 cation-exchange resin. The effluent was neutral and gave no precipitate with a saturated solution of K_2CrO_4 (dimethyltin dichloride is precipitated completely as a yellow basic chromate by K_2CrO_4). The column was washed free of chloride ion (the amount of wash water needed having been determined in a parallel experiment), and the amount of chloride ion in the effluent plus washings was determined by titration with a standardized solution of silver nitrate, using dichlorofluorescein as indicator. *Anal.* Calcd. for $(CH_3)_2SnCl_2$: Cl, 32.28. Found: Cl, 32.21. The adsorbed cations were eluted with approximately 8 N sulfuric acid, and neutralization of the acid precipitated white dimethyltin oxide.

Discussion

The degree of hydrolysis of a solution of dimethyltin dichloride according to equation (2) may be calculated from the hydrolysis constant and the relation

$$K_h = cx^2/(1 - x)$$

where x is the degree of hydrolysis and c is the concentration of the solution. Using an average value of 7.8×10^{-4} for K_h, a 0.000916 M solution would be 59% hydrolyzed, a 0.00205 M solution 47.5%, and a 0.063 M solution 10.5%. The most dilute solution used in the cryoscopic measurements was 0.0639 molal. Since the freezing point measurements were made near 0° and the hydrolysis constants were measured at 24.8°, we may expect that the degree of hydrolysis of the most dilute solution was somewhat under 10%. Under such conditions n molecules of $(CH_3)_2SnCl_2$ would give $3.1n$ particles when completely ionized, rather than $3n$ particles as assumed in the calculations of dissociation. Since the depression of freezing point is directly proportional to the number of particles, we can calculate by simple proportion the depression due to $3n$ particles when we actually have measured that due to $3.1n$ particles

$$3.1/3 = 0.340/\Delta T_{3n}$$
$$\Delta T_{3n} = 0.329$$

Hence the corrected i factor for this most dilute solution is 2.76, instead of 2.86. The change in the i values at higher concentration will be still less. The increase of i with decreasing concentration to a value approaching three indicates that equation (1) describes the "dissociation," which of course is really a reaction of the covalent substance with water.[16] The withdrawal of hydrated $(CH_3)_2Sn^{++}$ ions, either by reaction or by adsorption on a cation-exchange resin, displaces the equilibrium until the reaction is complete. The same process may be followed during the titration of dimethyltin dichloride with base.

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[15] T. Harada, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, **35**, 290 (1939).

[16] For analogous solvolytic dissociations, see Kraus and Greer, ref. 6.