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USE OF THE R_6Sn_2/R_3Sn^+ ELECTRODES IN DETERMINING THE DISSOCIATION CONSTANTS OF R_3SnCl SPECIES IN ALCOHOLIC SOLVENTS

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SUMMARY

Reversible redox couples R_6Sn_2/R_3Sn^+ at platinized platinum can be used to measure activities of triorganotin ions. We have used them in a potentiometric determination of the dissociation constant of R_3SnCl species (R = Me and Ph) in methanol or ethanol containing 0.1 *M* $NaClO_4$.

INTRODUCTION

From a survey of the literature it appears that the determination of the dissociation constants of organometallic species, as in the following equilibrium,

$$R_{m-n}MX_n \rightleftarrows R_{m-n}M^{n+} + n\,X^-$$

(R = organic group, M = metal, X = ligand, m = valence state of M and $m > n > 0$), have been carried out by conductometric [1-4], solubility[5], and pH-potentiometric measurements[6-9] or by measuring the ligand activity by the potentiometric method[10,11]. Direct potentiometric measurement of the $R_{m-n}M^{n+}$ species has not been used because of the lack of reversible redox systems suitable for measuring the organometallic cation activity. We have previously pointed out that the R_6Sn_2/R_3Sn^+ systems (R = Me, Et, Bu and Ph) show reversibility at a platinized platinum foil, and thus that platinized platinum electrodes may be used to measure the activity of the R_3Sn^+ cationic species[12,13].

We have now examined the use of these electrodes in the potentiometric determination of the dissociation constants of trimethyl- and triphenyltin chlorides in methanol and ethanol. The data were obtained from EMF measurements on the following cells:

$$\begin{array}{l|l|l|l|l}
\mathrm{Ag} & \mathrm{AgCl,\ satd.} & \mathrm{NaClO_4},\ 0.1\,M & \mathrm{R_6Sn_2, R_3Sn^+} & \mathrm{Pt} \\
 & \mathrm{NaCl},\ z\,M & & \mathrm{NaClO_4},\ 0.1\,M & \\
 & \mathrm{NaClO_4},\ (0.1\text{-}z)\,M & & &
\end{array}$$

in which $z = 0.01$ in methanol and 0.005 in ethanol.

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EXPERIMENTAL

Materials

Hexamethylditin and hexaphenylditin were prepared as previously described[14]. Hexamethylditin was further recrystallized from petroleum ether (60–80°), and had m.p. 23°; hexaphenylditin was recrystallized from chloroform by adding ethanol, and had m.p. 231–232°.

Commercial methanol and ethanol (from C. Erba, Milano, Italy) were purified by standard methods[15]. Sodium perchlorate was prepared by dissolving sodium carbonate in perchloric acid above 50°; the anhydrous salt was obtained by heating under vacuum at 150°. All other materials were reagent grade.

Apparatus

The apparatus is shown in Fig. 1. The compartment b is supplied with two electrodes: a platinized platinum foil e_1 (2.5×2 cm) and a silver wire e_2. The e_1 electrode is connected through a salt bridge to an Ag/AgCl reference electrode a of the "Wilhelm-type"[16]. This permits measurement of the equilibrium potential of the platinized platinum electrode against the reference electrode by means of a Solatron Digital Voltmeter LM 1420. Furthermore the compartment b is jointed through a glass-sintered disc to the compartment c containing a smooth platinum electrode e_3. An electrolysis circuit formed by the silver anode e_2 and the platinum cathode e_3 in conjunction with an amperostat, provides for the generation at constant current of silver ions in the compartment b.

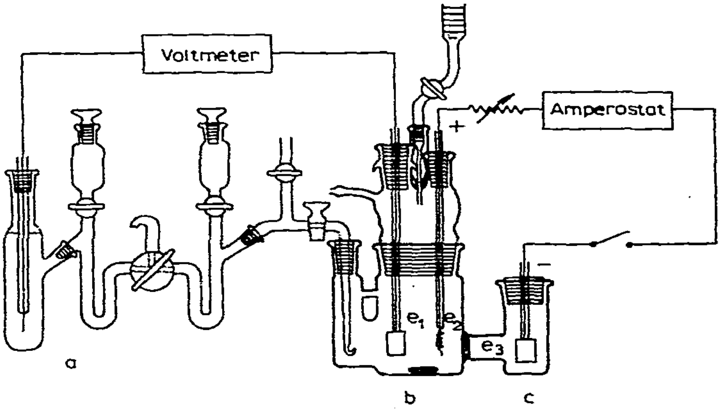

Fig. 1. Apparatus.

The platinum electrode e_1 was platinized as previously described[17]; the Ag/AgCl reference electrode was prepared using a coated platinum wire as described by Ives and Janz[18].

Procedure

Determination of the E_0-values. EMF measurements were made in order to determine the formal standard potentials E_0 *vs.* the utilized Ag/AgCl reference electrodes at 25° ± 0.02° for the systems Me_6Sn_2/Me_3Sn^+ and Ph_6Sn_2/Ph_3Sn^+ in methanol and ethanol: 0.1 *M* $NaClO_4$. The procedure is as previously described [illegible]. The solution in compartment b, degassed with dry nitrogen, contained a known quantity of ditin compound. This was partially oxidized to trialkyl- or triphenyltin ions, silver ions being produced electrolytically by means of the silver anode e_2. The experimental equilibrium potential *E* corresponding to several ratios of reduced and oxidized forms of the considered systems, are related to the E_0-value by the Nernst equation:

$$E = E_0 + 0.0296 \log([R_3Sn^+]^2/[R_6Sn_2]) \qquad (1)$$

that is,

$$E = E_0 + 0.0296 \log(4c) + 0.0296 \log[x^2/(1-x)] \qquad (2)$$

where x represents the percentage of the oxidized organoditin and c is the initial concentration of the ditin compound.

Determination of the dissociation constants. The dissociation constants of the R_3SnCl species (R = Me and Ph) were determined by using the following procedure. A known mixture of reduced (R_6Sn_2) and oxidized (R_3Sn^+) forms of the considered system was prepared electrolytically in the compartment b. Measurements of the assumed equilibrium potential *E* of the platinized platinum electrode e_1 *vs.* Ag/AgCl reference electrode were made after addition from time to time of a known volume of an NaCl alcoholic solution, of the same ionic strength ($[NaClO_4]+[NaCl]=0.1$ *M*) and previously degassed with dry nitrogen. After each addition of sodium chloride solution, the measured EMF attained its equilibrium value within 15 min. Temperature was kept constant at 25° ± 0.02.

Separate experiments, involving potentiometric measurements with a chloride reversible electrode Ag/AgCl, showed that the logarithm of the NaCl concentration is linearly related to the observed EMF values: the Cl^- ligand concentration is taken as equal to the NaCl concentration.

Calculation

On the basis of the dissociation constant relation,

$$K = [R_3Sn^+][Cl^-]/[R_3SnCl] \qquad (3)$$

and eqn. (1), the concentration of each species may be written as the following way:

$$[R_3Sn^+] = 10^{((E-E_0)/0.0592 + \frac{1}{2}\log[R_6Sn_2])} \qquad (4)$$

$$[R_3SnCl] = [R_3Sn^+]_0 - [R_3Sn^+] \qquad (5)$$

$$[Cl^-] = [Cl^-]_0 - [R_3SnCl] = [Cl^-]_0 - [R_3Sn^+]_0 + [R_3Sn^+] \qquad (6)$$

$[R_3Sn^+]_0$ and $[R_6Sn_2]$ represent the initial concentration of these species corrected by the volume change caused by the NaCl solution addition. The $[Cl^-]_0$ represents the total ligand concentration.

Using the relations (4), (5) and (6), eqn. (3) can be written in logarithmic form as follows:

$$\log K = \log([Cl^-]_0 - [R_3Sn^+]_0 + [R_3Sn^+]) + \log[R_3Sn^+] - \log([R_3Sn^+]_0 - [R_3Sn^+]) \qquad (7)$$

that is:

$$\log K = \log A + \log B, \tag{8}$$

where $\log A = \log([\mathrm{Cl}^-]_0 - [\mathrm{R_3Sn^+}]_0 + [\mathrm{R_3Sn^+}])$ and $\log B = \log[\mathrm{R_3Sn^+}] - \log([\mathrm{R_3Sn^+}]_0 - [\mathrm{R_3Sn^+}])$. The log K value can be evaluated graphically by plotting log A against log B. A better fit was obtained by refining the data by a least-squares procedure using an Olivetti Programma 101 desk computer.

RESULTS

Table 1 lists the obtained values of the formal standard potentials E_0 *vs.* Ag/AgCl for the systems $\mathrm{Me_6Sn_2/Me_3Sn^+}$ and $\mathrm{Ph_6Sn_2/Ph_3Sn^+}$ in methanol and ethanol respectively. (It must be remembered that the reference electrode Ag/AgCl was used with 0.01 M NaCl in methanol but 0.005 M NaCl in ethanol.) The experimental slopes which fit the Nernst equation (2) are also listed: these data are in good agreement with the theoretical value, *viz* 0.0296 V at 25°, for a redox equilibrium in which two electrons are exchanged:

TABLE 1

FORMAL STANDARD POTENTIALS E_0 (*vs.* Ag/AgCl)[a] AT 25°
Solvent: alcohol/0.1 M $\mathrm{NaClO_4}$.

Solvent	Redox system	$2.303 \cdot \frac{R \cdot T}{n \cdot F}$ (V)	E_0 (V)	Employed E_0 values (V)
Methanol	$\mathrm{Me_6Sn_2/Me_3Sn^+}$	0.0324 ± 0.0008	−0.139 ± 0.003	−0.139
		0.0298 ± 0.0007	−0.139 ± 0.003	
	$\mathrm{Ph_6Sn_2/Ph_3Sn^+}$	0.0299 ± 0.0010	−0.057 ± 0.004	−0.058
		0.0307 ± 0.0014	−0.059 ± 0.004	
Ethanol	$\mathrm{Me_6Sn_2/Me_3Sn^+}$	0.0292 ± 0.0018	−0.139 ± 0.005	−0.140
		0.0317 ± 0.0008	−0.140 ± 0.003	
	$\mathrm{Ph_6Sn_2/Ph_3Sn^+}$	0.0297 ± 0.0005	−0.068 ± 0.002	−0.068
		0.0292 ± 0.0009	−0.068 ± 0.004	

[a] Ag/AgCl reference electrode; characteristic in methanol: 0.01 M NaCl, 0.09 M $\mathrm{NaClO_4}$; in ethanol: 0.005 M NaCl, 0.095 M $\mathrm{NaClO_4}$.

TABLE 2

EXPERIMENTAL AND CALCULATED DATA FOR RUN 2

$[\mathrm{Me_6Sn_2}]$ mole/l × 10^4	$[\mathrm{Me_3Sn^+}]_0$ mole/l × 10^4	$[\mathrm{Cl^-}]_0$ mole/l × 10^4	E (V)	log A	log B
3.55	2.46	2.23	−0.268	−3.99225	0.01328
3.51	2.43	4.39	−0.283	−3.57643	−0.39976
3.47	2.40	6.48	−0.294	−3.34400	−0.63833
3.40	2.35	10.58	−0.307	−3.07068	−0.89058
3.33	2.30	14.81	−0.317	−2.89654	−1.07188

$$R_6Sn_2 \rightleftarrows 2\,R_3Sn^+ + 2\,e$$

In calculating the concentration of triorganotin ions by means of relation (4) we have employed the E_0 values listed in the last column of Table 1.

Table 2 shows the experimental and calculated data for expt. 2 (*cf.* Table 3) in which the Me_6Sn_2/Me_3Sn^+ system was used to determine the dissociation constant of Me_3SnCl in methanol/0.1 *M* $NaClO_4$. The values of $-\log K$ and the slope were calculated from $\log A$ and $\log B$ values (*cf.* eqn. 8) by a least-squares procedure.

Two sets of measurements were carried out for each compound in both solvents: the obtained values of $-\log K$ and the slopes values related to eqn. (8) are listed in Table 3.

TABLE 3

CALCULATED VALUES OF $-\log K$ AND SLOPES FROM EQN. (8)
Temperature 25°, ionic strength 0.1 M $NaClO_4$.

Run	Solvent	Compound	$-\log K$	Calcd. slope (see eqn. 8)
1	Methanol	Me_3SnCl	3.94±0.06	0.964±0.017
2			3.93±0.03	0.987±0.008
3		Ph_3SnCl	4.57±0.05	1.007±0.052
4			4.55±0.04	1.006±0.012
5	Ethanol	Me_3SnCl	4.82±0.03	1.038±0.050
6			4.83±0.04	1.042±0.036
7		Ph_3SnCl	5.52±0.03	1.007±0.008
8			5.54±0.05	1.009±0.024

CONCLUSION

The results show that the new electrodes can be successfully employed to determine the activity of the triorganotin cations, so that equilibria involving these species can be quantitatively studied. The Me_3SnCl dissociation constant determined

TABLE 4

$-\log K$ VALUES OF INORGANIC AND ORGANOMETALLIC CHLORIDES IN METHANOL AND ETHANOL

Compound	Solvent		Ref.	Method
	Methanol $-\log K_{(M)}$	Ethanol $-\log K_{(E)}$		
LiCl		1.45–1.75	19	Conduct.
NaCl	1.1	1.65–1.9	19	Conduct.
KCl	1.15	2 –2.1	19	Conduct.
CsCl	1.2	2.15	19	Conduct.
Me_3SnCl	3.9	4.8	This work	Potent.
		4.5	1	Conduct.
Me_2CF_3SnCl		4.1	4	Conduct.
Et_3SnCl	3.2		2	Conduct.
Ph_3SnCl	4.5	5.5	This work	Potent.

in ethanol/0.1 M $NaClO_4$, ($-\log K = 4.8$) may be compared with that previously obtained by Kraus and Callis[1] ($-\log K = 4.5$) by use of conductometric measurements. The values (*cf.* Table 4) seem to us to be in agreement bearing in mind that the Kraus value was obtained at infinite dilution.

Table 4 lists the dissociation constant data available in the literature for organotin[1,2,4] and for alkali metal chlorides[19] either in methanol or in ethanol. One can see that the dissociation of the alkali metal chlorides is dependent upon the size of the solvated cation, increasing from cesium to lithium chloride. Similarly with tetraalkylammonium picrates[20], the dissociation in methanol increases on increasing the cation size. The same trend, which is in keeping with the Bjerrum theory[21], is observed for R_3PbCl compounds[5], RHgCl and R_FHgCl compounds[7,9] (R = alkyl group, R_F = perfluoroalkyl group), in which the cation size is important in determining the degree of dissociation in water. Consistently, with the triorganotin chlorides containing alkyl groups (*cf.* Table 4) the dissociation increases with the size of the trialkyltin cation, but triphenyltin chloride shows the smallest dissociation although the Ph_3Sn^+ ion is the largest of those considered. This may be because the trialkyltin ions are more solvated than triphenyltin cation and consequently the solvated Ph_3Sn^+ ion is smaller than the solvated trialkyltin cations.

It is probable that the dielectric constant plays a rôle in the increase of the $-\log K$ values on passing from methanol ($\varepsilon = 32.6$) to ethanol ($\varepsilon = 24.3$).

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