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THE REVERSIBLE REDOX SYSTEMS R_6Sn_2/R_3Sn^+ ON PLATINIZED PLATINUM ELECTRODE*

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SUMMARY

Electrochemical reversibility has been found for organometallic redox couples R_6Sn_2/R_3Sn^+. Formal standard potentials E_0 at a platinized platinum electrode have been determined for the systems having R = Me, Et, Bu and Ph in methanol and in methanol/benzene.

The presence of R_3Sn radicals at the platinized platinum electrode–solution interface seems to be responsible for the reversibility. The E_0 values obtained under different conditions, are discussed.

INTRODUCTION

Interest in organometallic electrochemistry has lately increased: polarography, electrolysis and triangular voltammetry have been applied to organometallic compounds. Dessy *et al.*[1] carried out remarkable work on the triangular voltammetry of organometallic species such as Ph_6Sn_2, Ph_3Sn^+ and Ph_3Sn^-. They suggest the existence of triphenyltin radicals in order to account for the electrochemical behaviour of the above mentioned species. Radical species have been proposed[2-9] as intermediates in several electrochemical processes dealing with organometallic compounds, for instance in the electrolytical reduction of some ions such as RHg^+, Et_3Pb^+, Et_3Sn^+ etc. Nevertheless no experimental evidence has been put forward for the electrochemical reversibility of the reduction steps. If radicals are actually present as intermediates, it seems reasonable to think that under particular conditions reversibility must arise in such systems.

In order to demonstrate that organometallic redox processes can be reversible, we have studied the reaction

$$R_3Sn{-}SnR_3 \rightleftarrows 2\,R_3Sn^+ + 2\,e$$

(R = Me, Et, Bu and Ph), and found that the R_6Sn_2/R_3Sn^+ species form conjugate redox couples. Measurements of the equilibrium potentials at a platinized platinum electrode were carried out in methanol and in a methanol/benzene mixture. The biamperometric technique was also successfully applied to these systems.

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EXPERIMENTAL

Materials

Ditin compounds were prepared and purified according to the literature[10]. Commercial methanol and benzene (C. Erba, Milano, Italy) were furtherly purified[11]. Commercial lithium nitrate was recrystallized and dried by the Joon's method[12]. The platinum electrode used (platinum foil 2.5×2 cm) was platinized before each measurement[13].

Procedure and calculation

In a half-cell consisting of a platinized platinum electrode immersed in methanol (or methanol/benzene, 75:25 v/v) $LiNO_3$ 0.5 *M* solution, previously degassed with dry nitrogen, a known quantity of the relevant ditin compound was oxidized to trialkyl- or triphenyltin ions, silver ions being produced electrolytically by means of a silver anode[14] dipped in the same half-cell. The assumed equilibrium potential of the platinum electrode against SCE could be measured at 25° for several ratios of reduced and oxidized forms of the considered systems. A Solartron Digital Voltmeter was used.

Since E represents the experimental equilibrium potential *vs.* SCE, c the initial concentration of the ditin compound and x the percentage of the oxidized organoditin compound, the relation.

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

has been applied in order to calculate the formal standard potential E_0. Calculations by means of an Olivetti Programma 101 desk computer, give maximum standard deviations for E_0 of ± 0.004 V and for the slope value of 0.0296 ± 0.0020 V.

Biamperometric titrations were carried out by using two platinized platinum wire electrodes (12 mm long, 1 mm diameter) and by adding hexamethylditin to trimethyltin ions or *vice versa*. The constant potential difference applied across the two electrodes were 50, 70 or 100 mV.

The solutions of trimethyltin ions were prepared by adding an equivalent amount of silver nitrate to trimethyltin chloride.

RESULTS

As an example, we report in Table 1 the values of E_0 calculated from the x values and the corresponding experimental equilibrium potentials E for the Me_6Sn_2/Me_3Sn^+ redox couple in methanol/0.5 *M* $LiNO_3$. The data for the other runs concerning the other systems investigated are omitted for brevity. The calculated formal standard potentials E_0 for all the systems studied in methanol and methanol/benzene mixture are given in Table 2 and 3, respectively.

Fig. 1 represents the biamperometric behaviour of the Me_6Sn_2/Me_3Sn^+ system. Fig. 1a shows the plot obtained when amounts of trimethyltin ions are added to a known quantity of the ditin compound. The plot in Fig. 1b represents behaviour when amounts of hexamethylditin are added to a known quantity of trimethyltin ions.

TABLE 1

CALCULATED VALUES OF E_0 FROM x VALUES AND EXPERIMENTAL EQUILIBRIUM POTENTIALS FOR THE SYSTEM Me_6Sn_2/Me_3Sn^+
Solvent: methanol/0.5 *M* $LiNO_3$; temp. 25°; initial concentration of Me_6Sn_2: 12.23×10^{-4} *M*.

x^a	E (V)	E_0 (calcd.) (V)
0.0296	−0.296	−0.137
0.0537	−0.279	−0.138
0.0806	−0.269	−0.139
0.1344	−0.256	−0.139
0.1792	−0.247	−0.139
0.2329	−0.239	−0.138
0.2777	−0.234	−0.138
0.3225	−0.229	−0.139

[a] Fraction of organoditin oxidized.

TABLE 2

FORMAL STANDARD POTENTIALS E_0 (*vs.* SCE) AT 25°
Solvent: methanol/0.5 *M* $LiNO_3$

Redox system	Concentration organoditin (c) ($M \times 10^4$)	$2.303\frac{RT}{nF}$ (V)	E_0 (V)
Me_6Sn_2/Me_3Sn^+	12.23	0.0290	−0.139
	9.30	0.0329	−0.144
	7.40	0.0300	−0.141
Et_6Sn_2/Et_3Sn^+	9.51	0.0300	−0.135
	9.19	0.0302	−0.136
	8.29	0.0294	−0.135
Bu_6Sn_2/Bu_3Sn^+	15.73	0.0304	−0.140
	11.10	0.0298	−0.144
	5.90	0.0296	−0.144
Ph_6Sn_2/Ph_3Sn^+	0.31	0.0297	−0.048
	0.20	0.0295	−0.050
	0.72	0.0290	−0.054

DISCUSSION

It is well known that R_6Sn_2 compounds are very reactive towards electrophilic reagents such as halogens, heavy metal ions[10,15,16] etc., leading in most cases to breaking of the metal–metal bond and formation of R_3Sn^+ or R_3SnX species, depending upon the solvents used. For example, the reaction

$$R_3Sn{-}SnR_3 + 2\,Ag^+ \rightleftarrows 2\,R_3Sn^+ + 2\,Ag$$

may be considered a redox process in which tin may be formally considered to pass from oxidation level 3+ to 4+.

In a previous paper[16] we have shown that this reaction may occur by electron transfer in an electrolytic cell consisting of a silver electrode immersed in an alcoholic

TABLE 3

FORMAL STANDARD POTENTIALS E_0 (*vs.* SCE) AT 25°
Solvent: methanol/benzene (75:25 v/v)/0.5 *M* $LiNO_3$

Redox system	Concentration organoditin (*c*) ($M \times 10^4$)	$2.303 \frac{RT}{nF}$ (V)	E_0 (V)
Me_6Sn_2/Me_3Sn^+	8.63	0.0314	−0.196
	7.70	0.0291	−0.193
	6.16	0.0303	−0.192
Et_6Sn_2/Et_3Sn^+	8.39	0.0306	−0.222
	7.28	0.0300	−0.217
	5.82	0.0302	−0.216
Bu_6Sn_2/Bu_3Sn^+	9.50	0.0292	−0.205
	5.70	0.0303	−0.218
	4.50	0.0294	−0.212
Ph_6Sn_2/Ph_3Sn^+	4.37	0.0300	−0.038
	3.30	0.0302	−0.038
	3.34	0.0300	−0.039

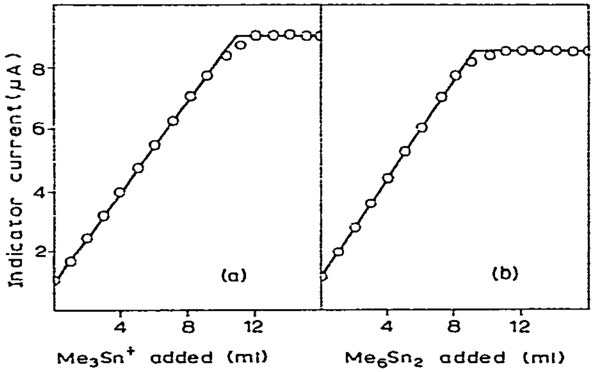

Fig. 1. Biamperometric titrations of (a) 10 ml of Me_6Sn_2 solution with Me_3Sn^+ and (b) 10 ml of Me_3Sn^+ solution with Me_6Sn_2. Applied potential difference 70 mV. $C(Me_6Sn_2)=0.08544$ coulombs/ml and $C(Me_3Sn^+)=0.07770$ coulombs/ml (concentrations have been given in coulombs/ml on the basis of the biamperometric titrations of the R_6Sn_2 compounds by means of silver ions[14]); (a) calcd. end point 11 ml, found 10.6 ml, (b) calcd. end point 9.1 ml, found 8.9 ml.

solution of silver nitrate and of a metallic electrode dipped in an alcoholic solution of R_6Sn_2. The reaction was not reversible in the presence of mercury or smooth platinum electrodes, whereas it was reversible when working with a platinized platinum electrode. On the basis of the previous findings and of the present results, the redox couple R_6Sn_2/R_3Sn^+ displays a behaviour similar to the system:

$$H_2 \rightleftharpoons 2\,H^+ + 2\,e$$

In fact, in both cases, reversibility results from the catalytic properties of the platinum black. This property can be attributed to the ability of the platinized platinum electrode to increase the rate of radical formation in the process

$$R_6Sn_2 \rightleftharpoons 2\,R_3Sn^\bullet \tag{1}$$

followed by the electron transfer

$$2\,R_3Sn^{\cdot} \rightleftharpoons 2\,R_3Sn^+ + 2\,e \qquad (2)$$

On this basis process (1) become very important and represents the determining step of the whole process.

The use of platinized platinum electrodes allows one to utilize such systems also under dynamic conditions, for instance, in the biamperometric technique. As shown in Fig. 1 the current produced by the redox system Me_6Sn_2/Me_3Sn^+ increases linearly up to the molar ratio $Me_6Sn_2/Me_3Sn^+ = 0.5$ and remains constant for larger molar ratios. The plateaux represent regions in which the current is controlled either (see Fig. 1a) by the constant concentration of the ditin compound, or by the constant concentration of the trimethyltin ions (see Fig. 1b).

Such plot can be obtained also by operating with a small potential difference (50 mV) applied across the two wire electrodes. The analogy of this electrochemical behaviour with typical reversible redox systems employed in biamperometric technique[17], shows that the system under consideration is characterized by a very high reversibility.

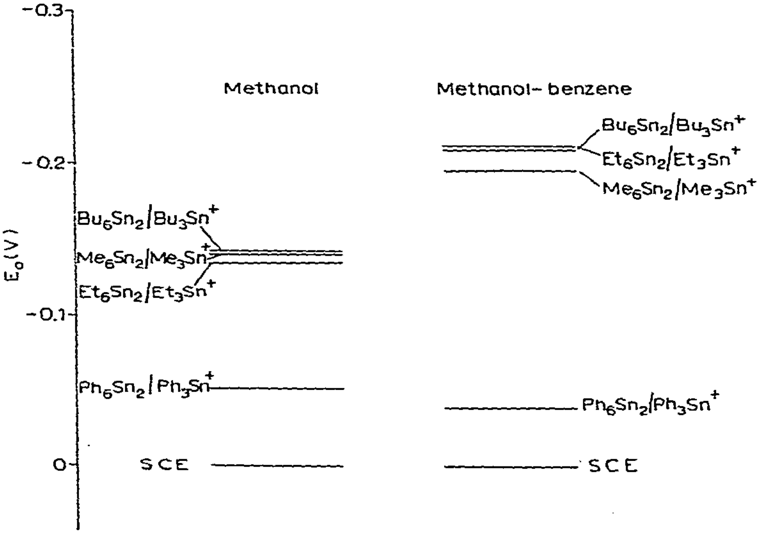

Fig. 2. E_0 potential levels diagram.

In Fig. 2 the potential level diagrams of the obtained E_0 values are given. It appears that in methanol the redox systems containing alkyl groups have practically the same E_0 values, whereas the Ph_6Sn_2/Ph_3Sn^+ system presents a more positive value. In methanol/benzene media the systems containing alkyl groups show no substantial difference in the E_0 values, but these are more negative by about 0.060 V in respect to the values found for the same systems in methanol.

The E_0 potential for the Ph_6Sn_2/Ph_3Sn^+ system remains practically the same in both media. The fact that the phenyl system is characterized by a reducing power lower than that of the other systems agrees with the assumption that radical species are present at the electrode–solution interface. It seems likely that the lower reducing power of this redox couple as compared to the R_6Sn_2/R_3Sn^+ systems (R=alkyl group) is a consequence of the greater stabilization by delocalization of the unpaired electron on to the three phenyl groups in the $Ph_3Sn^\bullet$. The E_0 values for these systems are practically the same, presumably because the stability of the R_3Sn radicals must be little affected by change in the R chain-length.

In conclusion, it seems reasonable to think that the lower stabilization of the radical is related to an increased reducing power of the system. Considering the sets of values obtained for alkyl systems in each media, it appears that on passing from methanol to methanol/benzene media the reducing power increases. By taking into account that alcohol stabilizes radicals by forming hydrogen bonds with the unpaired electron[18], stabilization of the radicals in methanol/benzene media probably decreases because the distances between the alcohol molecules are increased and complexes formed by hydrogen bonding break down.

The small solvent effect on the E_0 value for the Ph_6Sn_2/Ph_3Sn^+ system is opposite to that observed for systems containing alkyl groups and could be due to difference in the liquid–junction potential. In fact owing to the greater stability of the $Ph_3Sn^\bullet$, the additional stabilization by the solvent is likely to be negligible for this radical.

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