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SHORT PAPER

Polarographic behaviour of some organotin(IV) compounds in dimethyl sulphoxide

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The differential pulse polarographic behaviour in dimethyl sulphoxide (DMSO) of 14 organotin(IV) compounds having the general formula R_3SnX (R = Me, Ph; $X^- = NCS^-, N_3^-, NO_3^-, OH^-, NCO^-$ and OAc^-) and $^nBu_3SnCl$ and $^nBu_2SnCl_2$ has been studied. The peak potential was found to depend markedly on the organic group and to a lesser extent on the nature of the anion X. The phenyltin compounds were reduced at lower potentials than the corresponding methyltin compounds. The data obtained could be used for trace determination of these compounds. Linear calibration curves were obtained over the concentration range of 2.8×10^{-4} to 1.9×10^{-6} mol dm^{-3}.

Keywords: Organotin compounds, determination, differential pulse polarography, dimethyl sulphoxide

INTRODUCTION

Organotin(IV) compounds have found a wide range of applications, especially in recent years. They have been used as stabilizers for PVC plastics (e.g. R_2SnX_2); as fungicides in agriculture (e.g. Ph_3SnX; X = OH, OAc); as general biocides (e.g. R_3SnX; R = Et, nBu, Ph),[1,2] as water repellents (e.g. $nBuSnCl(OH)_2$; as catalysts (e.g. R_4Sn; R = Me, nBu);[3] as anti-tumour agents (e.g. Ph_2SnCl_2.2 DMSO);[4] and as pesticide- and disease-control agents (e.g. nBu_3SnF and nBu_2SnCl_2.bipy).[5]

We recently described the use of differential pulse polarographic techiques for the determination of some organotin(IV) compounds of the general formula R_xSnCl_{4-x} (R = Me, Ph; x = 1,2,3,4).[6] In order to obtain more information about the processes involved in polarographic reduction of organotin(IV) compounds we decided to extend the polarographic studies to a series of organotin(IV) compounds R_3SnX with R = Me or Ph and X^- = isothiocyanate (NCS^-), azide (N_3^-), hydroxide (OH^-), nitrate (NO_3^-) isocyonate (NCO^-), or acetate (OAc^-), and to the compounds nBu_3SnCl and nBu_2SnCl_2 (Tables 1–4).

EXPERIMENTAL

Materials and methods

The compounds Me_4Sn, nBu_3SnCl, Ph_3SnCl and nBu_2SnCl_2 were commercial products (Fluka). The compounds Me_3SnCl and R_2SnCl_2 (R = Me, Ph) were prepared by standard methods.[7,8] The compounds R_3SnX with R = Me or Ph and $X^- = OH^-$, OAc^-, NO_3^-, N_3^-, NCS^-) were prepared from R_3SnCl by reaction with NaOH,[9] AgOAc, $AgNO_3$,[10] NaN_3 and NaNCS,[11] respectively and R_3SnNCO was made from R_3SnOH and urea.[12] All the compounds prepared were purified, and were characterized by their melting points, IR spectra, and ^1H and ^{13}C NMR spectra.[13]

Standard solutions

Stock solutions (10^{-3} mol dm^{-3}) of each of the 14 organotin compounds were freshly prepared by dissolving an appropriate weight of the corresponding tin compounds in dimethyl sulphoxide (DMSO). Dilute solutions were prepared from these stock solutions either by quantitative dilution or by pipetting into the solution used for the polarographic studies. Tetraethylammonium perchlorate ($Et_4N^+ClO_4^-$, 0.10 mol dm^{-3})

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was used as the supporting electrolyte, 0.57 g being dissolved in DMSO (25 cm^3).

Polarographic curves were recorded with a Metrohm Polarecord E 506 polarograph in conjunction with an E 505 polarography stand equipped with a drop timer. A three-electrode combination was used, and consisted of a dropping-mercury electrode (DME) as working electrode; Ag/AgCl; chloride ion in DMSO (a saturated solution of tetraethylammonium chloride in DMSO was used) with a ceramic liquid junction as a reference and a platinum wire as auxiliary electrode. The polarographic cell was maintained at a temperature of 25 ± 0.2° and all sweeps involved a drop time of 2 seconds, a pulse amplitude of 100 mV, and a scan rate of 3 mVs^{-1}. The solution was de-aerated by passing a slow stream of nitrogen through the polarographic cell for *ca* 15 min.

Procedure

The differential pulse polarogram was run between an initial potential of −0.2 V and a final potential of −1.4 V on a de-aerated 25 cm^3 solution containing only the supporting electrolyte. The background current was recorded. To this solution was added a known amount of organotin compound, the solution was again de-aerated for *ca* 5 min and the polarogram recorded. The background current was subtracted from the current observed after the addition of the organotin com-

Differential pulse polarograms in DMSO at pulse amplitude of 100 mV and drop time of 2 s.

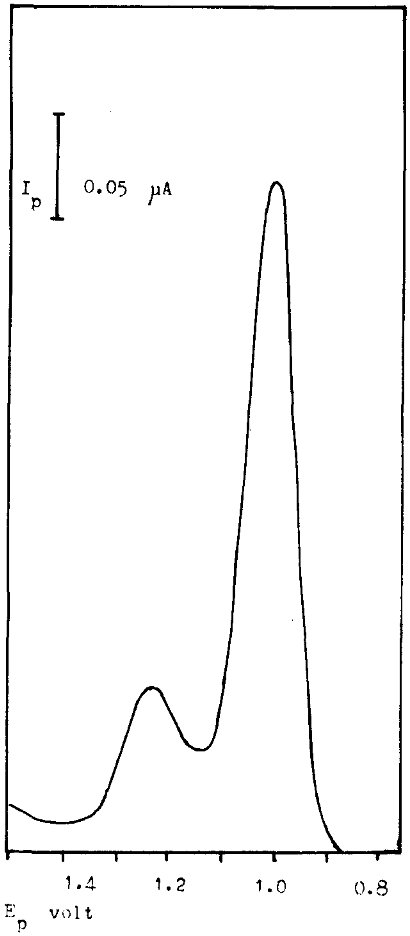

Figure 1 2.8 × 10^{-4} mol dm^3 solution of Me_3SnOH

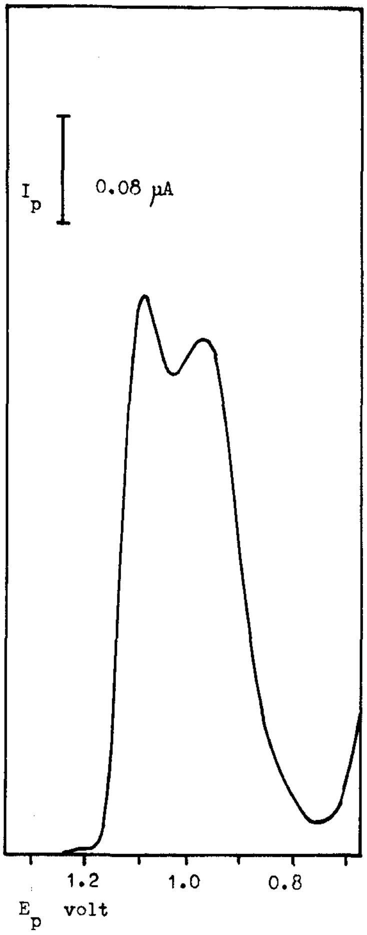

Figure 2 2.8 × 10^{-4} mol dm^3 solution of Ph_3SnOH

pound to give the value for the corrected current. The concentration of the organotin compound was then determined by either the normal method of additions or by the construction of a calibration graph.

RESULTS AND DISCUSSION

Effects of substituent on peak potential

The triorganotin compounds R_3SnX, with R = Me or Ph, X = NCS^-, N_3^-, NO_3^-, OH^-, NCO^-, OAc^- or Cl^-, and R = nBu, X = Cl, give two well-defined differential pulse polarographic peaks, as shown in Figs 1 and 2 for Me_3SnOH and Ph_3SnOH respectively. The peak potentials, measured at a concentration of 7.9×10^{-6} mol dm^{-3}, are shown in Table 1. It is clear from these results that the peak potential (E_p) depends markedly on the organic group and to a lesser extent on the anion present.

Taking the organic groups of R_3SnX with a particular anion, the order of peak potential was found to decrease in the sequence: Me $\geq$ nBu $>$ Ph. This order is expected because of resonance and inductive effects of the organic group (R) attached to tin. On the other hand, the type of anion linked to tin was found to have only a slight effect. For both the trimethyltin and triphenyltin, the compounds with anions NCS^-, OH^- and N_3^- showed very similar reduction potentials, namely 1.2 V for Me_3SnX and 1.05–1.06 V for Ph_3SnX. The compounds containing NO_3^-, OAc^- and NCO^- showed somewhat higher reduction potentials, i.e. 1.27–1.28 V for Me_3SnX and 1.11 V for Ph_3SnX. These effects may be attributed to the differences in electronegativities of the anions.

Table 1 Differential pulse peak potentials for 7.9×10^{-6} mol dm^{-3} solutions of organotin compounds

	R_3SnX			
	R = Me		R = Ph	
X	E_{p1}(V)	E_{p2}(V)	E_{p1}(V)	E_{p2}(V)
NCS	1.22	1.41	1.045	
OH	1.215	1.39	1.045	
N_3	1.21	1.41	1.065	
NO_3	1.28	1.38	1.11	
NCO	1.27	1.335	1.15	
OAc	1.27	1.4	1.07	
Cl[a]	1.15	1.32	0.94	1.12
	R = nBu			
Cl	1.145	1.29		

[a] Data taken from Ref. 6. E_p = peak potential; E_{p1} = peak potential for 1st peak, etc. For nBu_2SnCl_2, E_{p1} and E_{p2} are 1.015 and 1.15 V respectively.

Polarographic behaviour of tributyltin chloride and dibutyltin dichloride

The dc polarographic behaviour of nBu_3SnCl has been studied previously by Tyurin and Flerov[14] for aqueous etheral solutions. They observed two waves at low concentrations. In the present study, the differential pulse polarography of nBu_3SnCl in DMSO showed the appearance of two well-defined peaks at −1.15 and −1.31 V (Fig. 3). The peak current of the first peak (but not that of the second) was found to be linearly dependent on concentration up to 2.18×10^{-4} mol dm^{-3}, and the least-squares plot gave a correlation coefficient of >0.99. The differential pulse polarogram of nBu_2SnCl_2 showed three peaks (Fig. 4), at −0.91, −1.015, and −1.15 V. The peak current of the second peak (but not those of the others) was found to be linearly dependent (correlation coefficient >0.99) on concentration up to 2.18×10^{-4} mol dm^{-3}.

Mechanisms of the reduction of organic compounds in DMSO

From the polarographic measurements of trimethyltin compounds, triphenyltin compounds, nBu_3SnCl and nBu_2SnCl_2 in DMSO, it can be seen that the number of reduction peaks is one greater than the number of anions in the substrate. This supports our previusly suggested mechanism.[6] The routes for organotin compounds, generally formulated R_3SnX (R = Me, nBu, Ph; X = halide or pseudohalide group) follow the sequence:

$$R_3SnX + e^- \longrightarrow R_3Sn^\bullet$$

$$nBu_2SnCl_2 + e^- \xrightarrow{I} nBu_2SnCl^\bullet + e^- \xrightarrow{II} nBu_2Sn:$$

and finally may lead to the formation of the dimeric

Differential pulse polarograms in DMSO at pulse amplitude of 100 mV and drop time of 2 s.

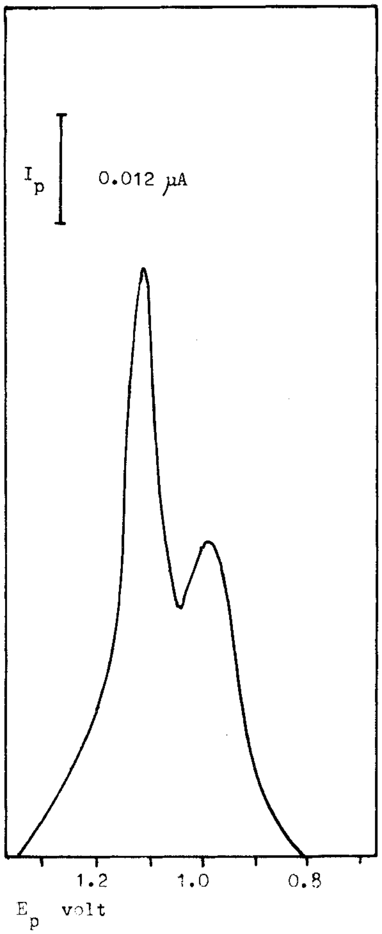

Figure 3 7.9 × 10^{-6} mol dm^{-3} solution of nBu_3SnCl

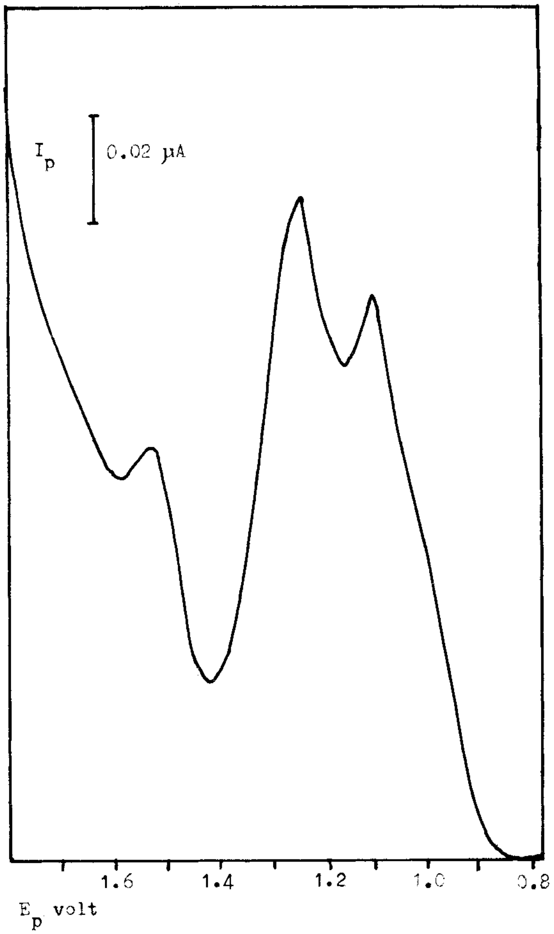

Figure 4 7.9 × 10^{-6} mol dm^{-3} solution of nBu_2SnCl_2

Table 2 Determination of trimethyltin compounds (Me_3SnX)

	Anion, X^-											
	NCS^-		N_3^-		NO_3^-		OH^-		NCO^-		OAc^-	
Concentration of Me_3SnCl (10^{-6} mol dm^{-3})	I_{p1} (10^{-2} µA)	I_{p2} (10^{-3} µA)	I_{p1} (10^{-2} µA)	I_{p2} (10^{-2} µA)	I_{p1} (10^{-3} µA)	I_{p2} (10^{-3} µA)	I_{p1} (10^{-3} µA)	I_{p2} (10^{-3} µA)	I_{p1} (10^{-3} µA)	I_{p2} (10^{-3} µA)	I_{p1} (10^{-3} µA)	I_{p2} (10^{-3} µA)
1.9	1.4	1.2					3.0	3.0			8.8	6.28
3.9	2.3	3.3	1.8	1.6	2.0	2.5	11.0	6.0	6.25	0.75	16.8	11.34
7.9	4.3	7.1	3.4	2.0	3.4	14.7	24.0	10.0	8.82	1.0	32.0	20.56
19.6	9.9	16.8	8.9	2.8	5.7	22.8	75.0	20.0	16.5	3.0	55.2	48.7
38.9	20.0	35.0	17.4	3.1	15.6	43.15	140.0	36.0	36.4	10.0	121.0	94.8
74.0	39.9	71.0	35.5	3.34	30.7	84.0	263.0	46.0	69.6	26.7	206.5	184.0
137.9	76.0	133.9	66.9		58.6	157.1		59.0	140.7	36.0	402.5	
218.7	120.2	206.8	105.5		92.6	248.2		79.0	219.2	57.2	634.1	
285.7	155.5	275.0	135.4		122.6	276.0		57.2	284.5	74.0	767.3	
r^b	0.99	0.99	0.99	0.76^a	0.99	0.98	0.99	0.74^a	0.99	0.98	0.99	0.99

[a] Linearly independent of concentration. I_p = peak current. [b] Correlation coefficients (*r*I were measured on the basis of the least-squares plot (I_p versus concentration): see text. They were deduced from 6–9 points at different concentrations.

Table 3 Determination of triphenyltin compounds (Ph_3SnX)

Concentration of $Ph_3SnX(10^{-6}$ mol $dm^{-3})$	Anion, X^-					
	NCS^-	N_3^-	NO_3^-	OH^-	NCO^-	OAc^-
	$I_{pl}(10^{-2}\ \mu A)$	$I_{pl}(10^{-2}\ \mu A)$	$I_{pl}(10^{-2}\ \mu A)$	$I_{pl}(10^{-2}\ \mu A)$	$I_{pl}(10^{-2}\ \mu A)$	$I_{pl}(10^{-2}\ \mu A)$
3.9	1.6	2.0	10.0	0.8	6.9	0.78
7.9	5.0	4.6	25.7	3.97	13.0	2.25
19.6	12.3	12.0	51.0	8.5	29.0	8.0
38.9	25.5	24.0	103.0	17.7	58.5	14.0
74.0	46.0	45.5	194.0	30.7	112.5	27.5
137.0	86.0	81.0		57.0	208.0	48.0
218.0	136.0				310.0	
285.7					407.0	
r	0.99	0.99	0.99	0.99	0.99	0.99

$(R_3Sn)_2$ and polymeric $(nBu_2Sn)_n$ respectively. The nature of the anion in R_3SnX evidently has no effect on the number of peaks in the reduction process.

Analytical determination of organotin compounds in DMSO

Since the organotin compounds show well-defined differential pulse polarographic peaks, the height of which are linearly dependent on the concentration of the electroactive species, these peaks can be used for the analytical determination of the organotin compounds in DMSO. The optimum condition for analytical determination were found to be at a pulse amplitude of 100 mV, a scan rate of 3 mVs^{-1}, and a drop time of 2 s. Some typical results for quantitative determination of these compounds in DMSO are shwon in Tables 2–4. These solutions were prepared by adding an appropriate amount of the organotin compound to DMSO (25 cm^3) containing tetraethylammonium perchlorate (0.1 mol dm^{-3}) as supporting electrolyte. Good results were obtained. The peak current of the first peak is linearly related to the concentration of the Me_3SnX and Ph_3SnX compounds. The lowest concentration for accurate determination was found to be 1.9×10^{-6} mol dm^{-3}. The peak current of the second peak was also found to be linearly related to the concentration of most of the Me_3SnX compounds except in the case of Me_3SnN_3 and Me_3SnOH, for which the current was independent of the concentration (see Table 2).

For Bu_2SnCl_2, only the second peak was found to be linearly dependent on concentration, (correlation coefficient >0.99).

Table 4 Determination of nBu_3SnCl and nBu_2SnCl_2

Concentration of compound $(10^{-6}$ mol $dm^{-3})$	nBu_3SnCl $I_{pl}(10^{-2}\ \mu A)$	nBu_2SnCl_2 $I_{pl}(10^{-2}\ \mu A)$
3.9	2.0	4.8
7.9	20.0	21.0
19.6	46.0	44.0
38.9	98.0	86.0
74.0	186.0	168.0
137.9	333.0	318.0
218.7	544.0	494.0
r	0.99	0.99

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