POLAROGRAPHIC STUDY OF TRIMETHYLTIN CHLORIDE*

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Trimethyltin chloride gives in aqueous medium two polarographic one-electron waves depending on pH and on the presence of surface active substances. Characteristics of these waves and of the electrode process are presented and discussed.

Electrochemical reduction of trialkyltin halides in aqueous ethyl alcohol was first studied by Costa[1], however the reduction mechanism proposed by him was not fully substantiated[2,3]. Devaud[4] followed the dependence of polarographic waves of these substances in the same medium on pH, found two one-electron reduction steps and isolated the product of the first step — hexaethyldistannane. The second reduction step was irreversible, appeared only in sufficiently alkaline medium and its product was probably triethyltin hydride. Another, more complicated mechanism of the electroreduction of tributyltin chloride giving hexabutyldistannane and tetrabutyltin was mentioned by Mehner and coworkers[5] who studied also the behaviour of butyl derivatives of tin(IV) chloride by a.c. polarography[6,7]. An analytical method to determine these substances (also one in the presence of another) oscillopolarographically was elaborated by Geyer and Rotermund[8]. Kočkin and coworkers[9,10] studied polarographically trialkyltin derivatives containing oxygen. With all mentioned compounds the R_3Sn^+ cation undergoes a two-step reduction.

The authors chose different conditions and criteria of their work and arrived at different results which do not enable us to find a unique scheme of the electrochemical behaviour of the studied organometallic compounds. It was therefore desirable to supplement the available information, mainly in the case of compounds not studied hitherto.

EXPERIMENTAL

Trimethyltin chloride was prepared according to ref.[11] and its purity was controlled by the standard method[12]; another sample furnished by Dr R. Goel (Guelph University, Canada) behaved polarographically in the same way. The supporting electrolyte was either 0·1M-KCl or a Britton–Robinson buffer aqueous solution with constant concentration of K^+ ions equal to 0·1M. Polarographic analyses were carried out in the absence of oxygen in a Smolei vessel[13]

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with a normal calomel electrode, the capillary had a rate of flow $m = 2.02$ mg/s and drop time $t_1 = 2.62$ s at a height of mercury column 70 cm. Polarographic curves were recorded with an LP 60 or Radelkis OH 102 type polarograph. The dependences of the mean current on the drop time were obtained with the aid of an electromagnetic drop time controller. The pH values were measured with a Metrohm E 388 pH meter with a glass electrode of a combined type. Current––time curves were studied with an electronic oscilloscope of the type Křižík D 581 and a potentiostat according to Holub and Němec (designed and constructed in the J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague). Electrocapillary curves were measured by the dynamic method, *i.e.*, from the dependence of drop time on potential. Coulometric electrolyses at controlled potential on a mercury pool electrode were carried out during vigorous stirring in an electrolytic vessel with three compartments enabling to use besides the mercury electrode a calomel reference and a platinum counter electrode. The current source was either the mentioned potentiostat or a Tacussel PRT 20-2-XM type potentiostat. The charge consumed was determined by an iodine coulometer with platinum electrodes and 5% KI aqueous solution. The concentration of the depolarizer prior to and after electrolysis was checked polarographically.

RESULTS

Trimethyltin chloride gives two waves: wave *1* is preceded by a small adsorption prewave *1a*, and the rising portion of wave *2* is accompanied by a sharp maximum (Figs 1 and 2). The waves depend on pH and concentration of the depolarizer. In acidic medium only wave *1* appears while wave *2* coincides with the evolution of hydrogen. The half-wave potential of wave *1* is shifted with rising pH to more negative
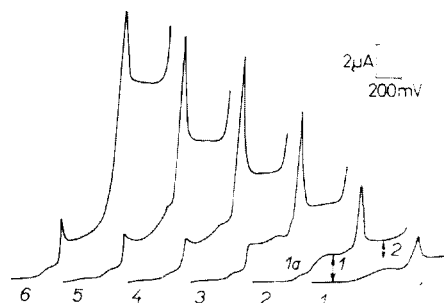

FIG. 1

Concentration Dependence of the Wave of Trimethyltin Chloride

0.1M-KCl, N.C.E., from -0.80 V, 100 mV/absc. Depolarizer concentration: *1* $4 . 10^{-4}$M; *2* $7 . 10^{-4}$M; *3* $1 . 10^{-3}$M; *4* $1.6 . 10^{-3}$M; *5* $2.1 . 10^{-3}$M; *6* $3.0 . 10^{-3}$M.
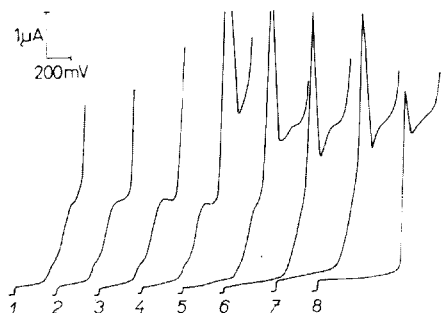
FIG. 2

Influence of pH on the Form and Position of Trimethyltin Chloride Waves

$5 . 10^{-4}$M-$(CH_3)_3SnCl$, from -0.80 V (N.C.E.), 100 mV/absc. Britton–Robinson buffer, pH: *1* 2·45; *2* 3·36; *3* 4·70; *4* 6·26; *5* 8·39; *6* 9·73; *7* 11·20; *8* 12·38.

values. Wave *2* is well developed at pH $\geq$ 6·5. whereas wave *1* at the same condition becomes less distinct and eventually fuses with the former. The half-wave potential of wave *2* remains constant up to pH 11·5; at higher pH values it is shifted similarly as wave *1*. In the pH region where these waves are well developed, their height is independent of pH. To observe both waves simultaneously, a nonbuffered medium is most suitable (Fig. 3). At concentrations of the depolarizer smaller than 0·001M, the prewave *1a* is formed first whose concentration dependence tends to a limit, and the wave *1*, which at a concentration of about 0·001M splits into two steps, *1b* and *1c*, the first being of constant height and the second increasing with the depolarizer concentration. This can be well observed if the solution contains surface active substances, which suppress the current maximum and counteract the inhibition of the electrode process by the products (Fig. 4), however they also suppress the prewave *1a*. A small, sharp maximum which is formed at higher concentrations of the depolarizer on the rising portion of the wave *1* can be eliminated by shortening the drop time.

The character of the limiting currents follows from their dependences on the corrected height of the mercury column, $i = \text{const.}\ h^y$, and on the drop time, $i = \text{const.}\ t_1^{\gamma}$, and from $i-t$ curves. The exponents y and γ measured both in buffered and non-
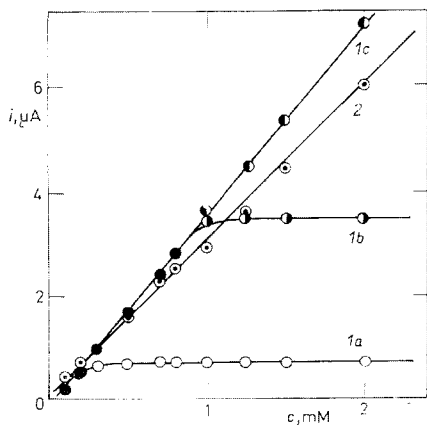

FIG. 3

Calibration Dependence for Trimethyltin Chloride in 0·1M-KCl with 0·04% Gelatin
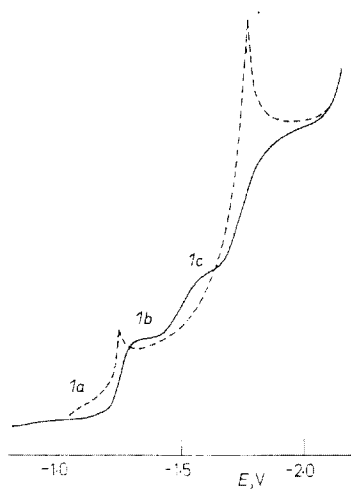

FIG. 4

Influence of Gelatin on the Wave of Trimethyltin Chloride

2 . 10^{-3}M-$(CH_3)_3$SnCl in 0·1M-KCl with 0·04% gelatin; from -0.80 V (N.C.E.), 100 mV/absc. Dashed curve refers to the absence of gelatin.

buffered media are summarized in Table I. The $i–t$ curves for the prewave *1a* are characteristic for an adsorption current; for the wave *1* they are obviously influenced by an inhibition effect and are not monotonous. In the region of the maximum, complicated $i–t$ curves with oscillations were observed. Only at potentials corresponding to the wave *2*, $i–t$ curves with an exponential course were obtained with the exponent $\gamma = 0{\cdot}41$ on the rising portion of the wave and $\gamma = 0{\cdot}24$ on the limiting current. The maximum on the wave *2* can be suppressed by a surface active substance, but it does not disappear at low flow rates of mercury. Microscopic examination revealed the existence of streaming of the electrolyte from the bottom to the neck of the drop (at $-1{\cdot}60$ V).

Electrocapillary curves were measured in $0{\cdot}1$M-H_2SO_4, $0{\cdot}1$M-KCl and $0{\cdot}1$M-KOH in the presence of the depolarizer. In the first two cases a decrease of the surface tension takes place in the potential region corresponding approximately to the wave *1*; this effect disappears before the potential of $-1{\cdot}5$ V is reached. In alkaline medium the decrease of the surface tension was not observed since the depolarizer is reduced at potentials more negative than $-1{\cdot}5$ V, beyond the region of the electrocapillary measurement.

To investigate the influence of OH^- ions on the behaviour of trimethyltin chloride, we determined the titration curve of this compound with a solution of sodium hydroxide. The dependence of pH on the amount of the titration agent has the usual sigmoidal course and its inflexion point indicates that one equivalent of OH^- anions is bound to the equivalent of the titrated compound.

Coulometric electrolysis of a solution of $1{\cdot}5 \cdot 10^{-3}$M $(CH_3)_3$ SnCl in at $-1{\cdot}4$ V (N.C.E.) (limiting current of the wave *1*) indicates that the electrode process corresponding to the wave *1* requires the transfer of one electron. During the electrolysis, the electrode surface became covered with a carmine-red deposit which turned black after some time. Electrolysis under similar conditions at $-1{\cdot}8$ V (limiting current of the wave *2*) revealed the number of electrons $n = 1{\cdot}9$. During the electrolysis, the electrode became covered with a dark red or black-red deposit, the solution turned opaque and gas bubbles were formed on the electrode surface. The electrolysed solution became alkaline (its pH being shifted from 4·8 to 10·7); after it was standing in the absence of air, the depolarizer concentration measured polarographically increased and so did the value of pH. Electrolysis at -1.8 V in the medium of $0{\cdot}5$M--NaOH gave the number of electrons $n = 2{\cdot}0$ and the pH value was constant.

DISCUSSION

From the polarographic behaviour of trimethyltin chloride it can be concluded that the wave *1a* is an adsorption prewave due to adsorption of the electrode reaction product. The wave *1* changes its character according to the depolarizer concentration and pH. At low concentrations, it has a diffusion-kinetic or pure diffusion character.
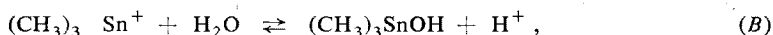
TABLE I

Characteristics of Individual Waves

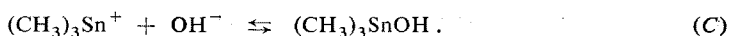| Wave	pH	Depol. conc. M	y	γ
1a	$3 \cdot 69^a$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 66$	$-0 \cdot 13$
	$7 \cdot 34^a$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 75$	$-0 \cdot 25$
	$8 \cdot 96^a$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 92$	$-0 \cdot 26$
	nonbuf.^{a}	$5 \cdot 10^{-4}$	$0 \cdot 68$	$-0 \cdot 13$
	nonbuf.^{a}	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 63$	$0 \cdot 0$
1	$3 \cdot 60^b$	$5 \cdot 10^{-4}$	$0 \cdot 45$	$0 \cdot 26$
	$7 \cdot 20^b$	$5 \cdot 10^{-4}$	$0 \cdot 48$	—
	$8 \cdot 96^c$	$5 \cdot 10^{-4}$	$0 \cdot 24$	$0 \cdot 38$
	$3 \cdot 69^d$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 81$	$-0 \cdot 11$
	$7 \cdot 34^d$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 65$	$0 \cdot 21$
	$8 \cdot 96^d$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 53$	$0 \cdot 25$
	nonbuf.^{c}	$5 \cdot 10^{-4}$	$0 \cdot 26$	$0 \cdot 33$
	nonbuf.^{d}	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 62$	$-0 \cdot 08$
2	$7 \cdot 20^b$	$5 \cdot 10^{-4}$	$0 \cdot 54$	—
	$8 \cdot 96^b$	$5 \cdot 10^{-4}$	$0 \cdot 64$	$0 \cdot 21$
	$12 \cdot 30^b$	$5 \cdot 10^{-4}$	$0 \cdot 47$	$0 \cdot 21$
	$7 \cdot 34^b$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 51$	$0 \cdot 22$
	$8 \cdot 96^b$	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 45$	$0 \cdot 19$
	nonbuf.^{b}	$4 \cdot 10^{-4}$	$0 \cdot 67$	$0 \cdot 12$
	nonbuf.^{b}	$1 \cdot 5 \cdot 10^{-3}$	$0 \cdot 49$	$0 \cdot 22$

^{a} Adsorption; ^{b} diffusion; ^{c} diffusion-kinetic character of the wave; ^{d} inhibition effects.

At higher concentrations, it is influenced by inhibition of the electrode reaction by a surface film of an insoluble product. The small maximum on the rising portion of the wave *1* occurring at higher concentrations of the depolarizer can be also attributed to the formation of an insoluble electroreduction product according to Majranovskij[14].

The splitting of the wave *1* at depolarizer concentrations above 10^{-3}M into two steps, *1b* and *1c*, can be explained if we consider the formation of the corresponding hydroxo form and the slow hydrolytic equilibrium of the depolarizer in aqueous medium:

$$(CH_3)_3SnCl \rightleftharpoons (CH_3)_3Sn^+ + Cl^-, \tag{A}$$

$$(CH_3)_3 Sn^+ + H_2O \rightleftharpoons (CH_3)_3SnOH + H^+, \tag{B}$$

or

$$(CH_3)_3Sn^+ + OH^- \rightleftharpoons (CH_3)_3SnOH. \tag{C}$$

The cation is reduced at more positive (step *1b*) and the hydroxo form at more negative potentials (step *1c*), since the rate of its dissociation is small.

The coulometric measurements substantiated the one-electron reduction assumed by Devaud[4], which leads in both cases to the formation of a radical:

$$(CH_3)_3Sn^+ + e \rightarrow (CH_3)_3Sn^{\cdot}, \quad (CH_3)_3SnOH + e \rightarrow (CH_3)_3Sn^{\cdot} + OH^- .$$

$$(D), (E)$$
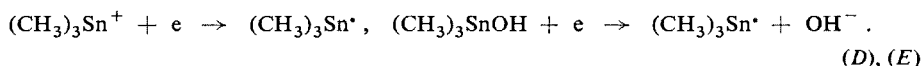
The formation of the wave *1a* is doubtless caused by adsorption of this radical. Hydroxyl ions formed during reduction of the hydroxo form accelerate its formation; this is manifested by an autocatalytic character of the wave *1c*. The radical undergoes dimerization:

$$2(CH_3)_3Sn^{\cdot} \rightarrow (CH_3)_3Sn.Sn(CH_3)_3 .$$

$$(F)$$

The product, hexamethyldistannane, is insoluble in water and we found it to be electroinactive up to the potential of -2.7 V (in the medium of tetrahydrofurane); it is surface active and forms very probably a film on the mercury electrode inhibiting the electrode process corresponding to the wave *1*. Especially at higher concentrations of the depolarizer the inhibition of the electrode process is strong and the form of the wave *1* or its steps *1b* and *1c* is considerably distorted. The inhibition can be diminished or eliminated by concurrent adsorption of gelatin; both steps can then be better distinguished.

The wave *2* is typically irreversible and is not influenced by adsorption of the reduction product, which takes place in the potential range of the wave *1*. It follows from our coulometric measurements that the wave *2* is a single-electron one; we assume that it corresponds to the following reaction:

$$(CH_3)_3Sn^{\cdot} + e \rightarrow (CH_3)_3Sn^- .$$

$$(G)$$
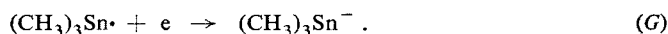
The anion formed undergoes protonation in either of two ways:

$$(CH_3)_3Sn^- + H^+ \rightarrow (CH_3)_3SnH ,$$

$$(H)$$

$$(CH_3)_3Sn^- + H_2O \rightarrow (CH_3)_3SnH + OH^-$$

$$(I)$$
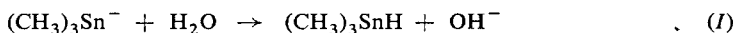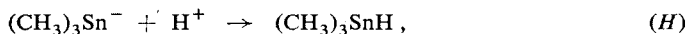
in accord with our observation that the solution becomes appreciably alkaline after a long-time electrolysis. The evolved gas (apparently hydrogen) at the mercury surface is an evidence for the instability of the hydride, which reacts with water. Other authors arrived at similar conclusions for the reduction of triethyltin chloride[4] and triphenyltin chloride[15]. The following reaction of the anion with the original cation can also lead to the formation of distannane:

$$(CH_3)_3Sn^+ \dotplus (CH_3)_3Sn^- \rightarrow (CH_3)_6Sn_2 \,. \qquad (J)$$
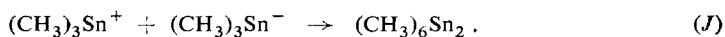
Another reaction scheme, analogous to that proposed by Dessy and coworkers[16] for the reduction of triphenyltin chloride, assuming reduction of distannane in the second step, cannot be considered possible in view of the above-mentioned findings.

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