POLAROGRAPHIC BEHAVIOUR OF HALOGEN DERIVATIVES OF ALKYL- AND ARYLSTANNANES. I.

STUDY OF DIMETHYLDICHLOROSTANNANE

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Dimethyldichlorostannane gives in aqueous solution an anodic polarographic wave due to chloride anions and three to four cathodic waves beginning at a potential of -0.8 V (N.C.E.). The basic electrode process involves two electrons; the number, size and shape of the cathodic waves depend on the depolarizer concentration and on pH. A scheme of the electrode process is proposed.

The polarographic behaviour of tin organic compounds was investigated first by Riccoboni and Popoff[1] who found that diethyldichlorostannane was reduced in a two-electron wave to diethyltin. Toropova and Saikina[1] studied the electroreduction of alkylhalogenostannanes in 40% C_2H_5OH at various pH values and found that the reduction became more difficult in the substituent series ethyl-propyl-butyl. Geyer and Seidlitz[3] studied the influence of alkyl substituents on reduction of compounds of the type R_2Sn^{2+} and constructed a calibration curve for their analysis with special regard to $(C_4H_9)_2Sn^{2+}$ and $(C_8H_{15})_2Sn^{2+}$ used technically as stabilizers.

The cation $(C_2H_5)_2Sn(H_2O)_4^{2+}$ in aqueous acid solution gives a reversible polarographic two-electron wave[4] distorted by the formation of an insoluble polymer product, $[(C_2H_5)_2Sn]_n$, on the electrode surface. Well-defined waves were obtained at a concentration of the depolarizer of 10^{-4}M; at higher concentrations the wave was splitted into more steps. Similarly, diethyl-dichlorostannane in aqueous methanolic solutions gives a two-electron reduction wave[5] depending on pH. At higher concentrations of the depolarizer, the wave is splitted into three steps: and adsorption prewave, a wave due to reduction and limited by adsorption of a polymer product[7], and a wave due to desorption. The polymer product was isolated[5] and its composition determined as $[(C_2H_5)_2Sn]_x$.

Other authors[6] obtained also a reduction wave of diethyldichlorostannane or dibutyldichlorostannane in aqueous methanolic solutions; the wave was splitted into two at higher depolarizer concentrations, higher drop times and lower concentrations of supporting electrolyte: an adsorption prewave and a reduction wave. However, they consider the dimer, $(R_2SnCl)_2$, as the most probable product of one-electron reduction of the depolarizer.

Most papers deal with the electroreduction of the diethyl derivative and their results are difficult to compare owing to different conditions and criteria used. Since no unambiguous survey of the electrochemical behaviour of compounds of the type R_2SnCl_2 ($R = $ alkyl) can be made, we decided to investigate them and to begin with the most simple one — the dimethyl derivative.

EXPERIMENTAL

Apparatus

The polarographic curves were recorded with an LP-60 type polarograph with a pen recorder EZ-2 (Laboratorní přístroje, Prague). A Kalousek cell with a normal calomel reference electrode and a straight capillary ($m = 4.05$ mg/s, $t_1 = 2.4$ s at a height of mercury column 70 cm) were used. An electromagnetic drop time controller served to study the dependence of mean current on drop time. Temperature dependences were measured with the aid of an ultrathermostat of the type NBE (Prüfgeräte, Medingen/Dresden) with a contact thermometer and a relay. The dependences of instantaneous current on drop time (i–t curves) were recorded with the aid of a potentiostat according to Němec and Holub (designed and constructed in J. Heyrovský Institute of Polarography, Prague) and an oscilloscope D 581 (Křižík, Prague) or a string galvanometer Stylo A 80 (Kipp and Zonen, Delft) with a half-period of 1/60 s and sensitivity 3.75 . $. 10^{-9}$ A/mm at a scale distance of 75 cm. Solutions in the polarographic cell were always deaerated by bubbling nitrogen and their pH was measured with a pH-meter Compensator E 388 (Metrohm, Herisau) with a glass electrode.

Reagents

The compound $(CH_3)_2SnCl_2$ was prepared by methylation of tin tetrachloride with Grignard reagent, CH_3MgI, according to Edgell and Ward[8]. Its purity was checked by quantitative analysis according to Neumann[9]. All solutions were prepared in water and were sufficiently stable regardless of pH (no change was observed even after five hours). A solution of $0.1N$-$NaClO_4$ (or sometimes $0.1N$-K_2SO_4) was used in measurements without buffer; otherwise citrate–phosphate, borate, carbonate and phosphate buffers were used and contained always $0.1N$-Na^+ or K^+ in the form of an indifferent electrolyte. All chemicals were of reagent grade.
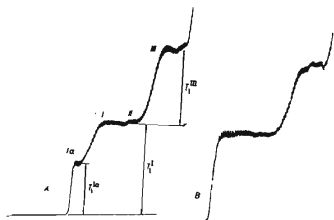

Fig. 1

Polarographic Curve of $7 . 10^{-4}M$-$(CH_3)_2$. .$SnCl_2$ in $0.1M$-$NaClO_4$

A Without gelatin, beginning from 0 V; *B* with 0.005% gelatin, beginning from -0.5 V. Sens. 1 : 100, *h* 80 cm, 100 mV/absc.
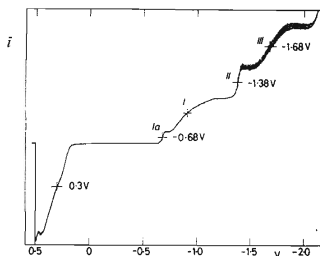
Fig. 2

Polarographic Curve of $3 . 10^{-3}M$-$(CH_3)_2$. .$SnCl_2$ in $0.1M$-$NaClO_4$

Sens. 1 : 1 000, *h* 65 cm.

RESULTS

Dimethyldichlorostannane in unbuffered solutions gives three cathodic waves, the shape and height of which depend on the depolarizer concentration (Fig. 1, curve *A*, and Fig. 2). After addition of an electroinactive surface active substance, the first wave attains its limiting height at more positive potentials (Fig. 1, curve *B*).

In buffered solutions the mentioned three waves do not appear simultaneously; their form and position depend on pH. At pH 2–7, waves *I* and *Ia* are observed, and wave *II* appears at pH 4·5 and higher. At pH 7–10, the current i_1^{II} of the wave *II* increases with pH at the expense of the current i_1^I of the wave *I* which decreases to zero (Fig. 3). Both these waves almost fuse together in alkaline medium and their currents are difficult to distinguish. Wave *III* appears at pH 8 and higher and its height is independent of pH.

The half-wave potential $E_{1/2}^I$ of the wave *I* is shifted with increasing pH to more negative values first slowly, then (in alkaline medium) more rapidly until it becomes equal to $E_{1/2}^{II}$ of the wave *II* (Fig. 4). The latter attains its most positive value at pH 9·5–10, otherwise it is more negative. The value of $E_{1/2}^{III}$ of the wave *III* is independent of pH.

In unbuffered medium, where the waves *I–III* are observed simultaneously, the currents i_1^I and i_1^{Ia} increase with the depolarizer concentration first linearly, then approach a limit (Fig. 5). The current i_1^{II} increases with the depolarizer concentration first slowly, then (when i_1^I approaches its limiting value) more rapidly and linearly, so that the slope of this dependence becomes equal to the initial slope of the
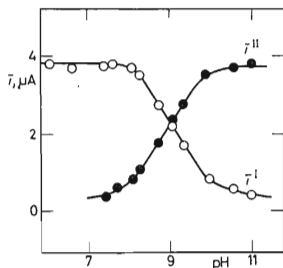

FIG. 3

Dependence of Mean Currents i^I and i^{II} on pH

$6 . 10^{-4}$ M-$(CH_3)_2SnCl_2$ + $0·1$M-Na$^+$ in buffers.
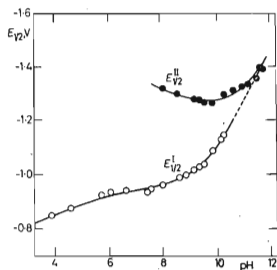
FIG. 4

Dependence of Half-Wave Potentials $E_{1/2}^I$ and $E_{1/2}^{II}$ on pH

$6 . 10^{-4}$ M-$(CH_3)_2SnCl_2$ + $0·1$M-Na$^+$ in buffers.

dependence of i_1^I on concentration. The sum $i_1^I + i_1^{II}$ increases linearly with the depolarizer concentration; the same applies for i_1^{III} in the whole concentration range studied.

In a buffered medium, the dependence of the currents i_1^I, i_1^{Ia} (at pH 2·39, 6·60 and 9·11) and i_1^{III} (at pH 9·11 and 11·42) on the depolarizer concentration is similar as in unbuffered solutions. However, the dependence of i_1^{II} on concentration is influenced by pH (Fig. 6): in acid solutions it is analogous as in an unbuffered medium whereas at pH 10 it is linear.

The character of individual waves was determined from the dependence on the height of mercury column h, on drop time t_1 and temperature and from the $i–t$ curves. The corresponding exponents y, γ and γ_{i-t} and the activation energy Q_i are summarized in Table I.

Electrocapillary curves measured both in 0·1M-H_2SO_4 and 0·1M-NaOH are characteristic for adsorption phenomena. In acid medium, adsorption takes place only together with electroreduction, but in alkaline medium adsorption occurs already at more positive potentials at which the reduction does not proceed.

Gelatin in concentrations as small as 0·005% eliminates the wave *Ia* whereas the wave *I* is fully developed (Fig. 1). The wave *III* is also fully suppressed by addition of gelatin.

The number of electrons involved in electroreduction was determined from the drop of the limiting current during polarographic electrolysis by the method of Gilbert and Rideal[10]: *a*) The decrease of the wave *I* (7 . 10^{-4}M-$(CH_3)_2SnCl_2$ + + 0·1M-NaClO$_4$) (electrolysis at −1·20 V *vs* N.C.E. for 2 hours) gives $n = 2·12$.
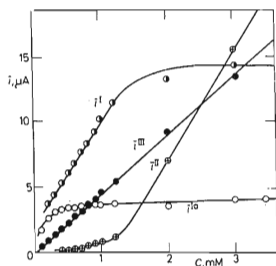

FIG. 5

Dependence of Currents i_1^{Ia}, i_1^I, i_1^{II} and i_1^{III} on Concentration of $(CH_3)_2SnCl_2$ in 0·1M-NaClO$_4$
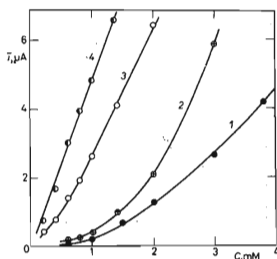
FIG. 6

Dependence of Current i_1^{II} on $(CH_3)_2$. . SnCl$_2$ Concentration at Various pH Values pH: *1* 4·0, *2* 6·6, *3* 9·1, *4* 11·4.

b) The decrease of the sum of the waves *I* and *II* $(1.5 \cdot 10^{-3}\text{M-(CH}_3)_2\text{SnCl}_2 +$ $+ 0.1\text{N-K}_2\text{SO}_4)$ (electrolysis at -1.42 V for 2 h) gives also $n = 2.12$. *c*) The decrease of the wave *II* $(6 \cdot 10^{-4}\text{M-(CH}_3)_2\text{SnCl}_2 + 0.1\text{M-NaOH})$ (electrolysis at -1.70 V for 2 h) gives $n = 1.89$. The "logarithmic analysis" of the wave is in accord with these results: The wave of $7 \cdot 10^{-4}\text{M-(CH}_3)_2\text{SnCl}_2 + 0.1\text{M-NaClO}_4 + 0.005\%$ gelatin has a logarithmic slope $\beta_I = 0.0285$ V and the wave of $3 \cdot 10^{-3}\text{M-(CH}_3)_2.\text{SnCl}_2 +$ $+ 0.1\text{M-NaClO}_4$ gives $\beta_{II} = 0.029$ V.

TABLE I

Character of Individual Waves and Calculated Activation Energies

Wave	pH	conc., M	y	γ	γ_{i-t}	Q_i, kcal
Ia	nonbuf.[c]	$5 \cdot 10^{-4}$	0.92	-0.28	—	0
	nonbuf.[c]	$3 \cdot 10^{-3}$	1.08	-0.22	-0.33	0
	2,39[c]	$7 \cdot 10^{-4}$	0.85	-0.29	-0.44	—
	2,39[c]	$4 \cdot 10^{-3}$	—	—	-0.33	—
I	nonbuf.[d]	$5 \cdot 10^{-4}$	0.58	0.23	—	2.5
	nonbuf.[d]	$3 \cdot 10^{-3}$	0.47	0.15	0.26	3.7
	2,39[d]	$7 \cdot 10^{-4}$	0.52	0.18	0.20—0.21	—
	2,39[d]	$4 \cdot 10^{-3}$	—	—	0.15—0.16	—
	9,11[e]	$7 \cdot 10^{-4}$	0.40	0.39	0.38—0.56	—
	9,11[e]	$4 \cdot 10^{-3}$	—	—	0.28—0.32	—
II	nonbuf.[e]	$5 \cdot 10^{-4}$	—[b]	—[b]	—	
	nonbuf.[e]	$3 \cdot 10^{-3}$	0.43	0.29	0.39	—
	9,11[e]	$7 \cdot 10^{-4}$	0.50	0.21	—	—
	9,11[e]	$4 \cdot 10^{-3}$	—	—	0.23—0.27	—
	11,42[d]	$7 \cdot 10^{-4}$	0.52	0.22	0.18—0.20	—
	11,42[d]	$4 \cdot 10^{-3}$	—	—	0.17—0.21	—
III[a]	nonbuf.	$5 \cdot 10^{-4}$	0	0.58	—	—
	nonbuf.[e]	$3 \cdot 10^{-3}$	0	0.56	—	—
	9,11[e]	$7 \cdot 10^{-4}$	0.23	0.51	—	—
	9,11[e]	$4 \cdot 10^{-3}$	—	—	—	—
	11,42[e]	$7 \cdot 10^{-4}$	0.23	0.52	—	—
	11,42[e]	$4 \cdot 10^{-3}$	—	—	—	—
	nonbuf.[d]	$5 \cdot 10^{-4}$	0.48	0.22	—	1.1
	nonbuf.[d]	$3 \cdot 10^{-3}$	0.55	0.21	0.25	2.6

[a] In first six cases measured on the rising portion of wave *III*, in last two cases on its limiting current. [b] Cannot be evaluated. [c] Adsorption, [d] diffusion, [e] diffusion-kinetic character of the wave.

DISCUSSION

The wave Ia is apparently a part of the wave I; its dependence on the height of mercury column and drop time as well as the $i-t$ curves are an evidence for its adsorption character both in buffered and unbuffered solutions. The position of the wave Ia and the electrocapillary curve in acidic solution show that the reduction product is adsorbed — the drop surface is covered with a film inhibiting more or less the electrode process. The $i-t$ curves at -0.72 V are characteristic for adsorption. Their complicated form in the range from -0.8 to -0.95 V can be attributed to two concurrent effects: weakening or removal of the inhibiting film due to weakening of the adsorption forces, and formation of the inhibiting film due to the rapid electroreduction. Alternative removal and formation of the film results in abrupt changes of the mass transport and oscillations of the instantaneous current.

The influence of gelatin on the waves I and Ia can be — in view of the above explanation — attributed to concurrent adsorption: gelatin covers the surface of the mercury drop and does not allow the reaction product to form an adsorbed inhibiting film.

The dependences of the mean current i_i^I on the height of mercury column and drop time and the $i-t$ curves are in accord with a diffusion character of the wave I. Only in weakly alkaline buffered medium where the wave II is markedly increased at the expense of the wave I, both waves have a mixed diffusion-kinetic character. In a strongly alkaline buffered medium (where the wave I is nearly entirely suppressed), the wave II is controlled by diffusion. Hence the electrode reaction responsible for this is apparently more rapid in alkaline medium, or the chemical reaction generating the corresponding depolarizer form is more rapid.

From the pH dependence it follows that the original wave I is due to an acid form of the depolarizer. The potentiometric titration of dimethyldichlorostannane with sodium hydroxide (Fig. 7) shows two inflexions, the first one rather flat with equi-
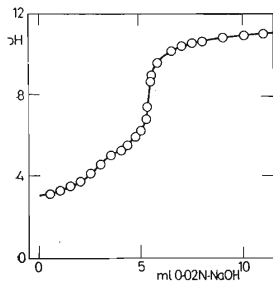

FIG. 7
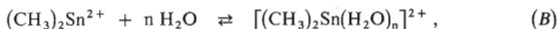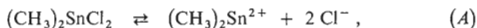Titration Curve of $1 . 10^{-4}$ M-$(CH_3)_2SnCl_2$

valence point about pH 4·5, the second one steep at pH 8·0. The ratio of equivalents of the titration agent added is about 1 : 2 indicating a consecutive addition of two OH^- anions to the original compound. Since the latter dissociates in aqueous solutions we assume the formation of $[(CH_3)_2SnOH]^+$ and $(CH_3)_2Sn(OH)_2$.

From the pH range in which the wave *II* appears it follows that this wave is due to reduction of the dihydroxo form which (in contrast to the divalent cation) is adsorbable as evidenced by the electrocapillary curves. Its adsorption causes inhibition of the whole electrode process in the whole potential range of adsorption resulting in a shift of the polarographic wave to more negative potentials, its rising portion being discontinuous ("cutting off" of the wave).

The sum of the waves *I* and *II* is somewhat higher than the wave *I* when occurring without *II*. This may be due to a smaller diffusion coefficient of the $(CH_3)_2Sn^{2+}$ cation in its hydrated form.

The dependences of the height of waves *I* and *II* on pH intersect at pH 9·05 which is more alkaline than the pK value for the reaction $R_2Sn(OH)^+ + OH^- \rightleftarrows R_2Sn(OH)_2$. This difference can be explained in terms of kinetics of formation of $R_2Sn(OH)_2$ preceding the electrode process. However, the corresponding rate constants were not calculated.

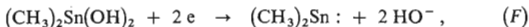We conclude that the reactions in solution are as follows:

$$(CH_3)_2SnCl_2 \;\rightleftarrows\; (CH_3)_2Sn^{2+} + 2\,Cl^- , \qquad (A)$$

$$(CH_3)_2Sn^{2+} + n\,H_2O \;\rightleftarrows\; [(CH_3)_2Sn(H_2O)_n]^{2+} , \qquad (B)$$

$$(CH_3)_2Sn^{2+} + H_2O \;\rightleftarrows\; [(CH_3)_2SnOH]^+ + H^+ , \qquad (C)$$

$$[(CH_3)_2SnOH]^+ + H_2O \;\rightleftarrows\; (CH_3)_2Sn(OH)_2 + H^+ . \qquad (D)$$

Since we have to deal with a two-electron reduction, we accept the scheme proposed by Devaud[5]:

$$(CH_3)_2Sn^{2+} + 2\,e \;\rightleftarrows\; (CH_3)_2Sn : \qquad (E)$$
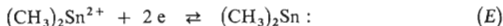
The radical polymerizes in a subsequent step. Similarly we assume

$$(CH_3)_2Sn(OH)_2 + 2\,e \;\rightarrow\; (CH_3)_2Sn : + 2\,HO^- , \qquad (F)$$

or

$$(CH_3)_2Sn(OH)_2 + 2\,H^+ + 2\,e \;\rightarrow\; (CH_3)_2Sn : + 2\,H_2O . \qquad (G)$$

(This is in accord with the observed increase of pH during electrolysis on a mercury pool cathode.)

Thus, it is possible to explain the sometimes simple concentration dependence. The fact that the wave *II* appears only at higher depolarizer concentrations and the

sum of the waves *I* and *II* gives a straight line which coincides with that for the wave *I* (Fig. 5) can be explained so that at higher concentrations the equilibriums (*C*) and (*D*) are shifted gradually in favour of the product owing to the increasing rate of the corresponding reaction, whereas at low concentrations this reaction is so slow that the equilibrium is shifted markedly in favour of the original nonhydrolyzed cations. This may be also caused by the fact that the electrolyzed solution is initially acidic owing to hydrolysis; the pH value increases during electrolysis whereby the electrode reaction is accelerated. We consider an autocatalytic effect.

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Note added in proof: The wave III is likely due to the reduction of the biradical $(CH_3)_2Sn$: which further proceeds under partial regeneration of the depolarizer.