

Electrochemical behaviour of organotin compounds

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The results obtained by a systematic electrochemical study of electroreduction of 18 different organostannic compounds of the type R_4Sn , R_3SnX , R_2SnX_2 , $RSnX_3$, $R_2(CH_2Cl)SnX$, R_6Sn_2 , and $R_3R'Sn$ (where $R = CH_3$, C_4H_9 , C_6H_5 , $(CH_3)_3C$) in water, methanol, acetonitrile, and tetrahydrofuran are summarized and discussed in this paper. A general reaction scheme of the electrochemical reduction process has been proposed and the common features as well as peculiarities of individual substances are described.

В работе обсуждаются результаты систематического электрохимического изучения электровосстановления 18 различных оловоорганических соединений типа R_4Sn , R_3SnX , R_2SnX_2 , $RSnX_3$, $R_2(CH_2Cl)SnX$, R_6Sn_2 и $R_3R'Sn$ (где $R = CH_3$, C_4H_9 , C_6H_5 , $(CH_3)_3C$) в воде, метиловом спирте, ацетонитриле и тетрагидрофуране. Была предложена общая схема реакций электрохимического восстановительного процесса и выявлены общие черты и различия отдельных соединений.

Costa [1] was the first to investigate the electrochemical reduction of trialkyltin halides. He ascertained that these substances gave three one-electron diffusion waves. However, he did not identify the products of electrode reactions. *Saikina* [2] found that the electrode reduction of many compounds of this type was, to a great extent, an irreversible process and the half-wave potentials depended on the kind of alkyl. The polarographic behaviour of triethyltin halogenides was thoroughly studied by *Devaud* [3] who stated that these substances were reduced in two one-electron stages. The radical $(C_2H_5)_3Sn^\bullet$ which dimerizes arises in the first stage of reduction. Therefore this author isolated $(C_2H_5)_6Sn_2$ as a product of the first stage of reduction. The second stage involves a rather irreversible process and the hydride $(C_2H_5)_3SnH$ is likely to be its product in a protogenic medium.

Vanachayangkul and *Morris* [4] observed only the first stage of electrochemical reduction of triphenyltin fluoride in aqueous ethanolic medium. *Mehner* and coworkers [5, 6] put forward a mechanism of reduction for tributyltin chloride which is quite different from that suggested by *Devaud* [3] for the ethyl derivative. *Morris* [7] subjected the mechanism put forward in papers [5, 6] to criticism.

Further studies dealing with the trimethyl derivatives [8], tributyl derivatives [8, 9], and triphenyl derivatives [9, 10] confirmed the rightness of the mechanism according to Devaud. The analytical aspects are given attention in papers [9—13].

Riccoboni and *Popoff* [14] found that the cation $(C_2H_5)_2Sn^{2+}$ gave a two-electron reversible wave corresponding to the formation of diethyltin



Morris [15] and *Devaud* [16] thoroughly investigated the polarographic behaviour of the cation $(C_2H_5)_2Sn^{2+}$ in aqueous alcoholic medium. They observed that the polarographic waves were considerably affected by adsorption of the polymer product on the cathode. This product was isolated by Devaud and its composition was $(C_2H_5)_2Sn_6$. A two-electron reduction was also observed by investigating dimethyltin dichloride [17].

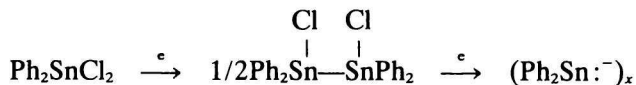
On the other hand, *Flerov*, *Tyurin*, and coworkers [18—20] regard the dimer $R_2Sn(Cl)-Sn(Cl)R_2$ arising on the surface of the electrode by dimerization of the product of one-electron reduction of the depolarizer as the most probable product of electrochemical reduction of dialkyl derivatives. The product, however, could not be identified and the authors assumed them on the basis of the number of electrons taking part in the process.

Fleet and *Fouzder* [21] studied the electrochemical behaviour of the dialkyltin derivatives by different electrochemical techniques. They found that these substances gave three polarographic reduction waves. The first one corresponds to the formation of the ionradical $R_2Sn^{+\bullet}$ which is subsequently reduced to the biradical $R_2Sn^{\bullet\bullet}$. This biradical not only polymerizes but is also reduced to the hydride R_2SnH_2 which decomposes in protogenic solvent and regenerates the depolarizer. Papers [12, 21—24] are concerned with analytical aspects of these problems.

In all above-mentioned studies, water or a mixture of water—lower alcohol was used as solvent. *Allen* [25] used dimethylformamide as a nonaqueous solvent for the study of electrochemical properties of alkyltin halogenides. *Dessy* and coworkers [26] used dimethoxyethane for similar study, found two one-electron waves for both phenyl derivatives (Ph_3SnX and Ph_2SnX_2) and concluded that the electrochemical reduction of these substances proceeded in two steps



or



The authors discuss other possible side reactions of the product with the depolarizer.

The electrochemical properties of methyl, ethyl, and phenyl trichlorostannane were investigated by *Devaud* and coworkers [27—30]. The electrochemical reduction proceeds in a single irreversible three-electron step and the resulting products are polymer alkyltin compounds $(RSn)_n$, which were isolated by *Devaud*. Similar result was also obtained by the authors of paper [6] with butyltin trichloride.

This publication comprehends the results of the systematic research into electrochemical behaviour of organotin compounds at a dropping mercury electrode carried out in the years 1970—1975. On the whole, 18 substances constituting a few homologous series of the organic derivatives of stannane and distannane have been tested. It is a continuation of our earlier papers [8, 17, 31, 32] and simultaneously it completes the above-mentioned publications of other authors treating analogous problems.

Experimental

Methods

The fundamental method employed was the standard classical polarography with a two-electrode vessel according to *Smoler* [33] (for aqueous and aqueous methanolic solutions) or with a three-electrode vessel (for nonaqueous solutions). The normal calomel electrode with aqueous KCl solution was used as a reference electrode. For nonaqueous solutions (methanol, acetonitrile, tetrahydrofuran) this electrode was connected with a salt bridge containing the solution of indifferent electrolyte without depolarizer in particular solvent. (The potential of this reference electrode did not differ from the usual SCE more than by 5 mV.) The dropping mercury electrodes used were so selected that their capillary properties satisfied usual requirements, *i.e.* the flow rate of mercury did not exceed 2 mg s^{-1} and the drop-time was in the interval 2—3 s. If needed, an electromagnetic drop-time controller was used. A large surface platinum electrode served as the auxiliary electrode. The polarograms were recorded with polarographs Radelkis OH 102, Radiometer PO 4 and LP 60 equipped with an electronic recorder EZ 2.

The voltammetric measurements were performed in an analytical vessel of the type Metrohm EA 880 solely with a hanging mercury dropping electrode of the type Metrohm E 410. The surface of this electrode was $1.38 \pm 0.04 \text{ mm}^2$. The normal silver chloride was used as the reference electrode. It was similarly modified as SCE used for polarography. A platinum disc electrode was used as the auxiliary electrode. The source of voltage was a potentiostat Tacussel PRT 20-2X connected with a generator of triangular pulses Tacussel GSTP 2. The voltammograms were recorded by both an X-Y recorder BAK 4T and an oscilloscope Tektronix R 5030.

For controlled potential electrolysis with the large surface mercury cathode a three-electrode vessel was used. It contained a plug-in reference electrode separated from the proper electrolyzed solution by a salt bridge. Furthermore, the cathodic and anodic compartments were separated by fritted glass (S2). The working electrode was the mercury pool at the

bottom of the cathodic compartment. The auxiliary electrode was a rod of pure retort carbon and the reference electrode was SCE. The capillary orifice of the salt bridge with the reference electrode was placed 2–3 mm from the surface of the working electrode. A uniform stirring of the electrolyzed solution in cathodic compartment was ensured by a teflon stirrer of screw form driven by a high-energy motor with constant number of revolutions. A potentiostat according to the construction of L. Němec and I. Holub (development type, Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague) was used as a source of voltage. The value of the transported electric charge was read on an integrator Tacussel IG 5 connected in series. The course of current during electrolysis was recorded with a recorder Vareg. For each electrolysis a coulometric analysis was made by reading the charge transferred. To determine the loss of concentration of the depolarizer, samples of catholyte were taken for polarographic analysis before electrolysis and after electrolysis and sedimentation of the precipitate.

All measurements were carried out in argon atmosphere in the absence of air. Argon was enriched with vapour of the particular solvent in a gas washing bottle before it was introduced into the electrolytic vessel.

Chemicals

n-Bu₄Sn (where Bu = butyl) was the only commercial preparation (Lachema, Brno), the other organotin preparations were synthesized according to the procedures described in the following papers: Ph₄Sn [34] (where Ph = phenyl), Ph₃SnCl [35], Ph₂SnCl₂ and PhSnCl₃ [36], Ph₃SnMe [37] (Me = methyl), PhSnMe₃ [38], Me₄Sn [39], Me₃SnCl, Me₂SnCl₂, Bu₃SnCl, Bu₂SnCl₂ and BuSnCl₃ [40], Me₆Sn₂ and *n*-Bu₆Sn₂ [41], Me₂Sn(CH₂Cl)Cl and *n*-Bu₂Sn(CH₂Cl)Cl [42]. The synthesis of *tert*-Bu₂SnCl₂ by the classical method [43] failed and for this reason, it was performed with the inverse Grignard reagent (prepared in the usual way from magnesium and *tert*-BuCl in tetrahydrofuran) which was added to SnCl₄ in argon atmosphere. The purity of these preparations was checked by elemental analysis and by comparing the melting points and boiling points with tabulated data [44, 45].

Tetrabutylammonium perchlorate (TBAClO₄) was prepared by precipitating a solution of TBAI in 50% ethanol with 20% HClO₄. The precipitate TBAClO₄ was washed with water on a filter and subsequently it was three times recrystallized from tetrahydrofuran. It was dried at 50°C and stored in a vacuum drier. LiClO₄ was twice recrystallized from water and dried to constant weight at 160°C. NaClO₄ and KCl were commercial anal. grade preparations.

Tetrahydrofuran (THF) was purified and deprived of moisture as follows. It was allowed to stay with KOH for a few days owing to which peroxides were eliminated. Then it was distilled, boiled with LiAlH₄ under reflux for a few days and finally it was fractionally distilled. Tetrahydrofuran thus dried was boiled with sodium in an apparatus connected with a vacuum-inert line until the original yellow colour turned to bright blue. The colour indicator was benzophenone and the blue colour indicated the absence of water and oxygen. If tetrahydrofuran was perfectly dried, the technique of Schlenk flasks [46] was used. Methanol, an anal. grade reagent was perfectly dried by the standard method [47]. Acetonitrile, an anal. grade reagent, was dried by repeated fractional distillation with P₂O₅.

Results and discussion

Altogether, we investigated 18 organotin compounds. Their electroactivity and the methods of investigation used are given in Table 1. All chlorostannanes exhibited electroactivity in the sense of electroreduction. Among the compounds which did not contain any halogen only tetraphenyltin was subject to polarographic reduction. Neither distannanes appeared able to undergo electroreduction under given conditions. A survey of experimental results is summarized in Table 2.

In general, it may be stated that the centre of electroactivity of all chlorostannanes is on the atom of tin or on the polar Sn—Cl bond (or the Sn—OH bond of hydrolytic products). Because of the maximum degree of oxidation (Sn(IV)) in these compounds, it is evident that the primary electrochemical process must be a reduction.

The Sn—Cl bond dissociates in polar solvents owing to which the electroactive particle is frequently an organosubstituted cation $R_n\text{Sn}^{(4-n)+}$. In polar solvents, chlorostannanes are frequently subject to solvolysis which brings about a change in the character of reactant.

Table 1

Survey of investigated compounds and used methods

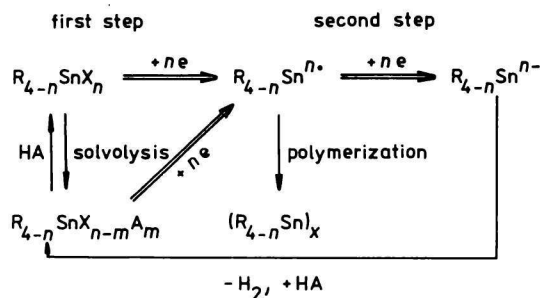
Compound	Method		Controlled potential electrolysis
	Polarography	Voltammetry	
Ph ₄ Sn	+		
Ph ₃ SnCl	+	+	+
Ph ₂ SnCl ₂	+	+	+
PhSnCl ₃	+	+	+
Ph ₃ SnMe	0		
PhSnMe ₃	0		
Me ₄ Sn	0		
Me ₆ Sn ₂	0		
Me ₃ SnCl	+		+
Me ₂ SnCl ₂	+	+	+
Me ₂ Sn(CH ₂ Cl)Cl	+		+
n-Bu ₂ Sn(CH ₂ Cl)Cl	+	+	+
n-Bu ₄ Sn	0		
n-Bu ₆ Sn ₂	0		
n-Bu ₃ SnCl	+	+	+
n-Bu ₂ SnCl ₂	+	+	+
<i>t</i> -Bu ₂ SnCl ₂	+	+	
n-BuSnCl ₃	+	+	

+ Electroactive substance; 0 electroinactive substance.

The character of electrochemical reduction of a certain depolarizer is mainly dependent on the number of the bonded organic radicals or the bonded atoms of chlorine and it is less dependent on the kind of the bonded organic radicals. As for the derivatives of equal constitutional type (*i.e.* with equal number of organic substituents), there are considerable analogies in the character of their electroreduction.

Derivatives with one atom of chlorine and three organic substituents are reduced in two one-electron steps, derivatives with two atoms of chlorine and two organic radicals in two two-electron steps and trichloro derivatives with one organic radical exhibit one three-electron reduction step only. The differences in the image of electroreduction of particular depolarizers of the same constitutional type, *e.g.* in the potential position of particular steps are not very significant. They are likely to obey relationships of the "Hammett" type (influence of the *I* effects of individual substituents).

In spite of a considerable complexity of the whole process, the mechanism of electroreduction of organotin chlorides on mercury electrode may be described by the generalized Scheme 1 where HA is a protogenic solvent. This scheme, however, requires further comments.



Scheme 1

1. The reduction of Ph_4Sn is different from that of organotin chlorides. Its wave occurs in the extreme negative potential region and corresponds to an irreversible step. The height of this wave in comparison with other investigated depolarizers corresponds to a four-electron reduction. No reaction scheme has been put forward in this case.

2. The first stage of reduction appears for all investigated electroactive derivatives and its course may be regarded as reversible or quasireversible in protogenic solvents, which is confirmed by the results obtained with a commutator of the polarization voltage and, in particular, by the voltammetric experiments. The cathodic vertex of the voltammetric curves corresponding to the first stage of

Table 2

Polarographic behaviour of studied organostannanes

Depolarizer	Solvent	Electrolyte	Wave	$E_{1/2}$ (V vs. SCE)	Reduction step	Number of electrons	Characteristics of observed polarographic waves
Ph ₄ Sn	THF	0.1 M-TBAP	1	-2.45 to -2.65		4e	irrev., dif.-kinet.
Ph ₃ SnCl	THF	0.1 M-TBAP	1	-0.92	I	1e	irrev., dif.-kinet.
			2	-2.16	II	1e	irrev., dif.-kinet.
	CH ₃ OH	0.1 M-TBAP	1	-0.92	I	1e	preceding adsorption wave
Ph ₂ SnCl ₂	THF	0.1 M-TBAP	2	-1.02			dif.-kinet.
			3	-1.38	II	1e	dif.-kinet., maximum on ascending part of wave
			2	-1.92	II	2e	irrev., dif.-kinet., of higher conc. of depolarizer, a flat maximum on limiting current
	CH ₃ OH	0.1 M-TBAP	1	-0.50 to -0.55	I	2e	irrev., dif.-kinet., inhibitory effects
			2	-1.4 to -1.9	II	2e	irrev., dif.-kinet., between waves 1 and 2 a broad maximum
	PhSnCl ₃	THF	0.1 M-TBAP	1	-0.35 to -0.40	I	3e
CH ₃ OH		0.1 M-TBAP	1	-0.40	I	3e	dif.-kinet., a deep fall on limiting current because of inhibitory effects
n-Bu ₃ SnCl	THF	0.1 M-TBAP	1	-1.2 to -1.3	I	1e	dif.
	CH ₃ OH	0.1 M-LiClO ₄			II missing		
1			-1.07	I	1e	dif.	
			2	-1.74 to -1.84	II	1e	dif., maximum at the start of wave

Table 2 (Continued)

Depolarizer	Solvent	Electrolyte	Wave	$E_{1/2}$ (V vs. SCE)	Reduction step	Number of electrons	Characteristics of observed polarographic waves
n-Bu ₃ SnCl	60% CH ₃ OH + H ₂ O	0.1 M-LiClO ₄	1	-0.80 to -0.85 -1.19	I	1e	preceding adsorption wave dif.-kinet., slight inhibitory effects
			2				
			3	-1.75 to -1.85	II	1e	dif. to dif.-kinet., maximum on ascending part of wave
n-Bu ₂ SnCl ₂	THF	0.1 M-TBAP	not measured				
			CH ₃ OH	0.1 M-LiClO ₄	1	-0.55	I
	2	-1.8			II	2e	dif.-kinet., maximum on ascending part of wave
	60% CH ₃ OH + H ₂ O	0.1 M-LiClO ₄	1	-0.62	I	2e	dif., inhibitory effects
			2	-1.6	II	2e	dif.-kinet., maximum on ascending part of wave
t-Bu ₂ SnCl ₂	THF	0.1 M-LiClO ₄	1				a deformed wave shifted to neg. potential, irrev., difficult to evaluate
	CH ₃ OH	0.1 M-LiClO ₄	1	-0.65	I	2e	limiting calibration dependence, very intense inhibition of electrode process, deep fall on limiting current
			2	-1.6 to -1.7	II	2e	dif., maximum on ascending part of wave
n-BuSnCl ₃	THF	0.1 M-TBAP	1	-0.55 to -0.60	I	3e	dif., inhibitory effects
	CH ₃ OH	0.1 M-LiClO ₄	1	-0.40 to -0.45	I	3e	dif., at the start the wave complicated by fall (adsorption product of electrode reaction)
Me ₃ SnCl	THF	0.1 M-LiClO ₄	1	-1.2	I II missing	2e	dif.

Table 2 (Continued)

Depolarizer	Solvent	Electrolyte	Wave	$E_{1/2}$ (V vs. SCE)	Reduction step	Number of electrons	Characteristics of observed polarographic waves	
Me_3SnCl	CH_3OH	0.1 M- LiClO_4	1	-1.15 to -1.30	I	1e	dif.-kinet., adsorption effects	
			2	-1.60	II	1e	dif.-kinet., maximum on ascending part of wave preceding adsorption wave	
	H_2O	0.1 M-KCl	1	-1.15	I	1e	dif.-kinet., inhibitory effects, pH dependence of limiting currents of waves 1 and 2	
			2	-1.30				
			3	-1.60	II	1e	dif.-kinet., irrev., maximum on ascending part of wave	
							dif., irrev. inhibitory effects	
Me_2SnCl_2	THF	0.1 M- LiClO_4	1	-0.9	I	2e		
					II missing			
	CH_3CN	0.1 M- NaClO_4	1	-0.8	I	2e	dif.	
			2	-1.6	II	2e	dif.	
	CH_3OH	0.1 M- LiClO_4	1	-0.6 to -0.7	I	2e	dif.-kinet., inhibitory effects	
			2	-1.5 to -1.6	II	2e	dif.-kinet., maximum on ascending part of wave preceding adsorption wave	
	H_2O	0.1 M- NaClO_4	1	-0.68				
			2	-0.8 to -1.2	I	2e	dif.-kinet., adsorption effects, pH dependence of limiting currents of waves 1, 2, 3	
3			-1.38				dif.-kinet., autocatalyt.	
4			-1.68	II	2e	dif.-kinet.		
$\text{Me}_2\text{Sn}(\text{CH}_2\text{Cl})\text{Cl}$	CH_3OH	0.1 M- LiClO_4	1	-1.02	I	2e	dif.-kinet., irrev.	
			2	-1.5 to -1.6	II	2e	dif.-kinet., irrev., maximum on ascending part of wave	
	H_2O	0.1 M-KCl	1	-0.95	I	2e	dif.-kinet., irrev., small maximum at the start of limiting current, grows with conc. of depolarizer	

Table 2 (Continued)

Depolarizer	Solvent	Electrolyte	Wave	$E_{1/2}$ (V vs. SCE)	Reduction step	Number of electrons	Characteristics of observed polarographic waves
$\text{Me}_2\text{Sn}(\text{CH}_2\text{Cl})\text{Cl}$			2	-1.6	II	2e	dif.-kinet., irrev., maximum on ascending part of wave
$\text{Bu}_2\text{Sn}(\text{CH}_2\text{Cl})\text{Cl}$	CH_3OH	0.1 M- LiClO_4	1	-0.64	I	1e + 1e successively	nonlinear conc. dependence, inhibitory effects, starting adsorption current, current drop on the limiting current, finally dif. current
			2	cannot be determined because of broad maximum	II	2e	dif. or dif.-kinet., irrev.

reduction is accompanied at higher potential sweep rates by an opposite practically reversible anodic vertex. A decrease in the sweep rate (approximately $< 0.5 \text{ V s}^{-1}$) brings about disappearance of reversibility. (It is supposed that the potential extent of the inserted voltage pulse has not exceeded the first stage.)

3. The product of the first stage of reduction is a radical which possesses so many nonbonded electrons as are involved in this stage. This radical as an intermediate is the initial reacting particle in the subsequent stage of reduction and simultaneously it reacts as a monomer in a polymerization side reaction to give an oligomer or polymer product. The rate of this polymerization reaction increases with number of the electrons transferred in the first stage of reduction. This reaction is the slowest for monochloro derivatives and the fastest for trichloro derivatives. The product formed is adsorbed on the surface of the electrode (adsorption may be also assumed for monomer) and if it is insoluble in the solvent used, it forms a film on the surface of the electrode which gradually inhibits the proper electrode process. That manifests itself by deformation of the polarographic curve and even by a fall in the region of limiting current. Similar deformations are to be observed in voltammograms. The strongest inhibition was observed with *tert*- Bu_2SnCl_2 . The disappearance of the inhibiting film is nearly consistent with the potential corresponding to the beginning of the second stage of reduction and if a dropping mercury electrode is used in polarographic analysis, a considerable inhomogeneity arises in the vicinity of this electrode, which results in the formation of conspicuous maxima on the rising portion of the second polarographic wave.

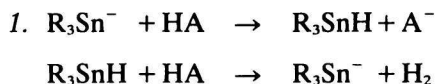
The above-mentioned polymer by-product could also arise in the reaction of the anionic product of the second stage of reduction (in case of monochloro and dichloro derivatives) with the cationic form of the depolarizer. Because of a rather negative potential region of the second stage of reduction, the inhibitory film on the surface of electrode cannot arise any more.

4. In protogenic solvents with higher dielectric constant the electrolytic dissociation and subsequent solvolysis of depolarizer take place. As for the hydrolysis of dimethyltin dichloride and trimethyltin chloride, the reducibility of the hydroxo derivatives formed [8, 17] has been confirmed. Their half-wave potentials are shifted to more negative potentials with increasing pH. As a continuous potential shift appears with the pH change in the first step, we have not regarded the reduction of hydroxo derivatives as a separate step.

Provided an imperfect mobile equilibrium of the dihydroxo derivative and monohydroxo derivative exists, another polarographic wave appears [17].

5. The mono- and dichloro derivatives are subject to the second step of reduction the product of which is an organosubstituted anion with the number of negative charges equal to the number of chlorine atoms in the original depolarizer. The particle formed is strongly basic and reactive and has conspicuous reduction properties. It reacts with protogenic solvents to regenerate the depolarizer (in its basic form) or it may react with the depolarizer to give a polymer. In both cases,

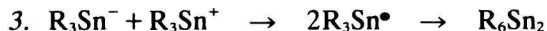
a radical intermediate may temporarily come into existence. The following reaction scheme can be assumed



or



and



The schemes under 1. and 3. are more probable than that under 2., but temporary forming of hydride anions cannot be excluded regarding the strongly negative potential region of the electrode reaction.

On the other hand, the generation of gaseous hydrogen as well as the regeneration of the depolarizer were confirmed and observed during a long-standing electrolysis on a pool mercury electrode.

As for dialkyl derivatives, the regeneration of the depolarizer obeys the following summary equation



The mechanism of this reaction has not been more thoroughly investigated, either. It is without doubt still more complicated than the mechanism in the preceding case.

The regeneration of depolarizer enables us to explain a remarkable effect on voltammetric curves observed with diorgano- and triorganosubstituted derivatives. A cathodic peak appears on the reverse anodic branch of the curve, the magnitude of which increases with decreasing scan rate. This phenomenon may be explained as follows. The product of the second stage of reduction reacts with the solvent and turns into original depolarizer or some of its solvolyzed forms and provided the electrode potential is negative enough in the reverse course, it is subject to repeated reduction.

6. The occurrence of the second stage of reduction is not a universal phenomenon. It exists only if $n \leq 2$. The reason is obvious because further reduction necessitates the radical arising in the first stage. The higher is the number of free uncoupled electrons in the intermediate formed, the higher is the rate of the association side reaction. Thus the associate produced is also sterically more complicated and less soluble. As for compounds of the type RSnCl_3 , the first three-electron reduction step gives rise to a particle $\text{RSn}^{\bullet\bullet\bullet}$. The polymerization of this particle yields a complicated crosslinked polymer compound. This is due to the fact that the second stage of reduction does not exist.

7. The reduction of simple distannanes arising as intermediate in the reduction of trialkyl derivatives is described by Dessy and coworkers [26]. In our experiments we did not observe any electroactivity for the synthetically prepared distannanes (even if tetrahydrofuran was used as solvent and we could work as far as -3.2 V/SCE).

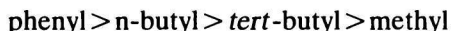
Hexaalkyl distannanes are not, however, absolutely stable. Their Sn—Sn bond splits by the effect of reactive solvents. Older stock solutions of hexaalkyl distannanes give polarograms where the waves corresponding to reduction of the particles R_3Sn^+ appear. These waves grow with time.

8. The constitutional effect on reducibility of the investigated substances is of double kind:

a) The influence of the number of substituents (or bonded halogen atoms) is more significant. The reducibility of substances with equal organic substituents (valuated according to the position of half-wave potential of the first reduction step) decreases with the number of bonded organic substituents in the order



b) The effect of the character of substituent is less significant and corresponds (in most cases) to the order of reducibility



9. The influence of the character of solvent is also remarkable. For solvents with high dielectric constant irrespective if it is a protogenic or aprotic solvent, the half-wave potentials are almost equal or little variable while a marked shift in the half-wave potential of the second step to more negative values (more than 0.5 V) was observed when tetrahydrofuran, a solvent with low dielectric constant, was used. For aliphatic trialkyl radicals, the wave was shifted behind the region of possible investigation, *i.e.* the decomposition potential of indifferent electrolyte. The explanation of this effect is difficult. The potential shift is too great for explanation on the basis of complex formation. The explanation on the basis of acceleration of the chemical side reactions which result in a decrease in surface activity of the radical intermediate is also not plausible.

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