ELECTROCHEMICAL DEGRADATION OF POLYCHLORINATED BIPHENYLS

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The feasibility of electrochemical conversion of polychlorinated biphenyls to the parent hydrocarbon in *N,N*-dimethylformamide was studied with respect to the charge and mass efficiency of the process. The process was conducted in two variants, viz. as indirect conversion through pre-electrolysis of an alkali salt solution, and as direct electroreducing splitting of the carbon–chlorine bonds. Mercury served as the working electrode; the suitability of other metals as cathode materials was also examined by slow cyclic voltammetry.

Owing to their excellent physico-chemical properties, polychlorinated biphenyls (PCBs) used to be employed in many industrial applications. Only in many year of their use it was found that PCBs are toxic (e.g. refs[1–3]). Although their use has been banned and their production stopped, there still remain large amounts of half-finished and finished products containing PCBs in high concentrations. These include, for instance, spare electrolytic capacitors with PCBs as the dielectric, which can be found in all plants having their own switching stations. Such spare components actually constitute environmental time bombs.

Among ways of polyhaloaromatics disposal is their transformation to nontoxic or less toxic forms by making use of their electrochemical activity[4,5] or by using some electrode reaction (oxidation or reduction) for the preparation of a reactive intermediate product[5–11] whose reaction with PCBs giving acceptable products is sufficiently fast and attains a high conversion degree. All this should preferably take place in solution at room temperature. Such processes, a survey of which has been presented in our paper[12], are being investigated now; the present paper is a contribution to the study.

EXPERIMENTAL

Methods and Apparatus

Fast speed differential pulse polarography (FSDPP). This method was implemented by using an SMDE1 static mercury drop electrode interfaced to a PA4 polarograph (Laboratorni pristroje, The Czech Republic) at a polarization rate of 50 mV s^{-1} and current sampling period of 0.02 s. The same

instrument was used for cyclic voltammetry measurements (with manual switching of the polarization direction) at polarization rates of 20 to 500 mV s^{-1}. A drop surface area of 1.320 ± 0.005 mm^2 was found in the hanging mercury drop mode. An auxiliary Pt electrode and an Ag/Ag$^+$ reference electrode (a silver wire in 0.1 M AgNO$_3$ in the solvent of choice), separated from the working compartment by a salt bridge, were used. Working metal electrodes obtained by embedding Pb, Cd, Hg, Sn, Zn, Al, Ag, Cu, Fe, Ni, W, Ti, or graphite with a contact in a glass tube by means of an epoxy resin were also used. The geometrical surface area of the electrodes was 0.5 to 4 mm^2. A platinum sheet electrode 0.98 mm^2 working area (Radelkis, Hungary) served the determination of chloride ions released during the electrolysis.

Coulometry. The measurements were performed with an OH 405 potentiostat interfaced to an OH 404 integrator (both Radelkis, Hungary) connected in the auxiliary electrode circuit. The mercury bottom served as the working electrode, the auxiliary electrode – a platinum gauze – was separated from the working compartment by a glass filter. The solution was stirred with nitrogen. The depolarizer loss was monitored polarographically. The observed values were corrected by subtracting charge that was found in the absence of Delor in otherwise identical conditions (potential, time, concentration, supporting electrolyte). The corrected experimental charges are given in Tables I and II as Q_{exp}. The current–time (I–t) curves were recorded on a Vareg 2 recording multimeter (Metra, The Czech Republic). The concentration of chloride ions released during the electrolysis was determined directly in the working solution, voltammetrically, by anodic oxidation on a platinum sheet electrode. The calibration dependence was obtained by using a standard LiCl solution.

AC polarography. The measurements were carried out by using an OH-105 polarograph (Radelkis, Hungary) equipped with an uncontrolled dropping mercury electrode whose drop time in the disconnected circuit was 5.0 ± 0.5 s and flow rate 1.24 mg s^{-1} at a reservoir height of 109 cm. The amplitude of the superimposed alternate voltage was 15 mV, polarization rate 100 mV min^{-1}. All measurements were conducted at 22 °C.

TABLE I

Summary of electrolyses of Delor 103 solutions in DMF in the presence of a sodium salt. Starting chloride (C–Cl bond) concentration was invariably 6.13 mmol l^{-1}; supporting electrolyte cation: Et$_4$N$^+$ (No. 1, 2), Bu$_4$N$^+$ (No. 3, 4)

No.	V ml	$c_{PCB} \cdot 10^3$ mol l^{-1}	$c_{Na^+} \cdot 10^3$ mol l^{-1}	$-E_r$ V	Q_{exp} C	Q_{PCB} C	Q_{Na^+} C	Q_{tot} C	t s	$c_{Cl^-} \cdot 10^3$ mol l^{-1}	$c_{Na^+} \cdot 10^3$ mol l^{-1}
1	21.01	1.94	14.3	2.50	24.90	15.20	12.61	27.81	14 400	4.95	8.08
2	21.01	1.94	14.3	2.84	51.10	24.85	28.99	53.84	7 560	6.10	0
3	20.99	1.94	14.3	2.49	21.00	14.10	11.78	25.88	20 760	4.50	8.48
4	20.99	1.94	14.3	2.84	48.50	24.83	28.95	53.78	7 980	5.83	0

Symbols: V total electrolyzed solutions volume; c_{PCB} starting concentration of Delor 103; c_{Na^+} starting concentration of sodium ions; E_r reduction potential (vs Ag/Ag$^+$ electrode); Q_{exp} true passed charge, corrected as described; Q_{PCB} calculated charge required to release c_{Cl} chloride ions; Q_{Na^+} calculated charge required to reduce the sodium ion concentration to the c_{Na^+} value; $Q_{tot} = Q_{PCB} + Q_{Na^+}$; c_{Na^+} sodium ion concentration after electrolysis; c_{Cl^-} chloride ion concentration in solution after electrolysis; t true time of electrolysis.

Cryoscopic measurements were performed by using a vapour osmometer with a cryoscopic attachment (Knauer, Germany) involving a Peltier cell. A biphenyl solution in benzene served as the standard.

Chemicals

N,N-Dimethylformamide (DMF) (BASF, Germany) was purified and freed from water by the conventional procedure[13]. Water concentration as determined by the Fischer method was lower than 5 mmol l^{-1}. Tetrabutylammonium perchlorate (Bu$_4$NClO$_4$) and tetraethylammonium tetrafluoroborate (Et$_4$NBF$_4$) were prepared and purified following ref.[13], viz. by using tetrabutylammonium iodide and sodium perchlorate (both Lachema, The Czech Republic) as the starting substances in the former case and tetraethylammonium bromide (Fluka, Switzerland) and perchloric acid (Apolda, Germany) in the latter case. Tetramethylammonium iodide (Me$_4$NI), as well as the other chemicals used, viz. AgNO$_3$, LiCl, NaCl, KOH, P$_2$O$_5$, biphenyl and benzene (all Lachema, The Czech Republic), was used as received. All supporting electrolyte salts were kept in a dessicator at 75 °C. The PCB – Delor 103 – was contained in a CCAON-0416.25 electrolytic capacitor (ZSE ZEZ Zamberk, The Czech Republic). Delor 103 (Chemko Strazske, The Slovak Republic – the last digit in the specification gives the mean number of chlorine atoms in a molecule) was further characterized.

In order to enable the current efficiency to be examined and expressed in terms of electron consumption per mole or per mean molecule of Delor or per C–Cl bond, the mean molar mass was determined cryoscopically in benzene; the value obtained was $\overline{M}$ = 263 ± 2.4 g mol^{-1}. The corresponding summary formula is C$_{12}$H$_{6.84}$Cl$_{3.16}$, which is consistent with the manufacturer's specification.

TABLE II
Summary of direct electrolyses of Delor 103 in DMF; α_{Cl} and α_Q are the degrees of C–Cl bond degradation calculated from the observed concentration of chloride ions after electrolysis and from the passed current, respectively; remaining symbols are as in Table I; supporting electrolyte cation: Et$_4$N$^+$ (1–4), Bu$_4$N$^+$ (5, 6)

No.	V ml	$c_{PCB} \cdot 10^3$ mol l^{-1}	$-E_r$ V	t s	Q_{exp} C	Q_{PCB} C	$c_{Cl^-} \cdot 10^3$ mol l^{-1}	α_{Cl} %	α_Q %
1	20.41	2	2.4	8 400	8.2	–	2.09	33.1	33.9
2	20.41	2	2.5	10 860	15.2	–	3.62	57.3	61.1
3	20.41	2	2.66	11 220	24.5	–	5.81	91.9	98.4
4	20.41	2	2.85	5 460	24.1	24.89	6.10	96.5	96.8
5	20.39	2	2.49	18 960	14.1	–	–	–	56.7
6	20.39	2	2.84	7 560	24.1	24.86	–	–	97.8

RESULTS AND DISCUSSION

Basic Electrochemical Characteristics

Typical voltammetric curves of PCBs on a hanging mercury drop electrode using a supporting electrolyte with a variable tetraalkylammonium cation size are shown in Figs 1–3. With regard to the known proportions of the mono-, di-, tri-, tetra-, penta-, and hexachloro derivatives with not very different half-wave potentials[14], it is possible to crudely determine the reduction potential ranges (Fig. 2). The cathodic peak and the corresponding anodic counter-peak at approximately –3.1 V (only in Bu_4NClO_4 solution; mercury drop tearing occurred in solutions of the remaining supporting electrolytes at potentials more negative than ca –3 V, Figs 1 and 2) corresponds to a reversible one-electron reduction of biphenyl to the anion-radical; this was proved by addition of a standard solution of biphenyl (Fig. 3). This well-resolved peak was also employed to determine the concentration of the biphenyl ring system and hence, the total mean concentration of Delor, or its mean molar mass, viz. by using several additions of the standard biphenyl solution. The mean molar mass so obtained was 269 ± 5.9 g mol^{-1}, which is in a good agreement with the value obtained cryoscopically. Owing to the nature of the sample, the resulting CV curves represent a current "envelope" formed by superposition of the partial reduction currents of the individual congeners in dependence on the working electrode potential. Due to this, the explanatory value of the CV curves on their own is not very high. A somewhat better
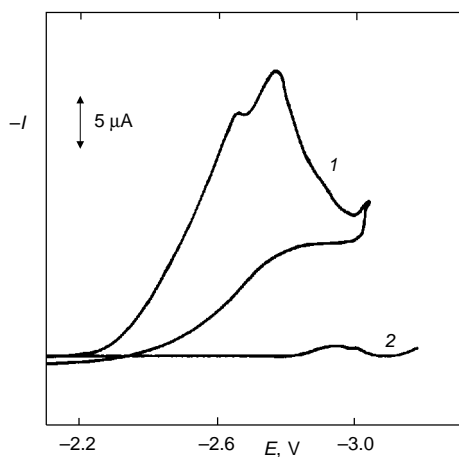

FIG. 1
CV curves on a HMDE in a saturated solution of Me_4NI in DMF, 100 mV s^{-1}; *1* Delor 103 (c = 1.5 mmol l^{-1}), *2* supporting electrolyte
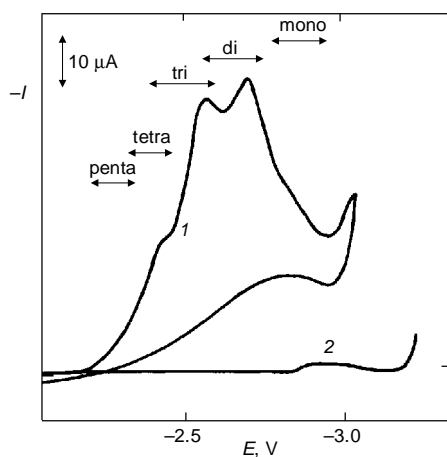

FIG. 2
CV curves on a HMDE in a 0.1 M solution of Et_4NBF_4 in DMF, 100 mV s^{-1}; *1* Delor 103 (c = 2 mmol l^{-1}), *2* supporting electrolyte

current resolution is achieved if the tetrabutylammonium cation is replaced with the less bulky and less adsorbing tetraethylammonium cation. As far as the tetramethylammonium cation is concerned, this is rather low soluble in DMF, so that the concentration of its saturated solution is below 0.1 mol l^{-1}. The CV curves (e.g. Fig. 3) demonstrate that higher-chlorinated isomers are reduced gradually to lower-chlorinated isomers to biphenyl on the mercury drop electrode.

Metals with large differences in hydrogen overvoltage were chosen to examine the effect of the working electrode material, and the CV curves were recorded. The E_{p1} through E_{p4} potential corresponding to the I_{p1} through I_{p4} currents (Fig. 3) along with the a constants in Tafel's equation[16] are given in Table III; the values correspond to the potentials read from the CV curves in the steady state, achieved typically in 5 to 10 cycles. Characteristic CV curves of Delor 103 on some metals are shown in Fig. 4. Table III documents that except for titanium, working electrode material replacement affects only slightly the reduction and oxidation peak potentials of biphenyl (E_{p3}, E_{p4}). The E_{p1} and E_{p2} potentials vary over a span of approximately 200 mV, more positive potentials being observed with metals with high hydrogen overvoltage values. In the metal series of Pb, Cd, Hg, Sn, Al, Ag, Cu, Fe, Ni, and Pt, the E_{p1} and E_{p2} potentials correlate linearly with the a constants in Tafel's equation, the regression equations being as follows (correlation coefficients r are also given):
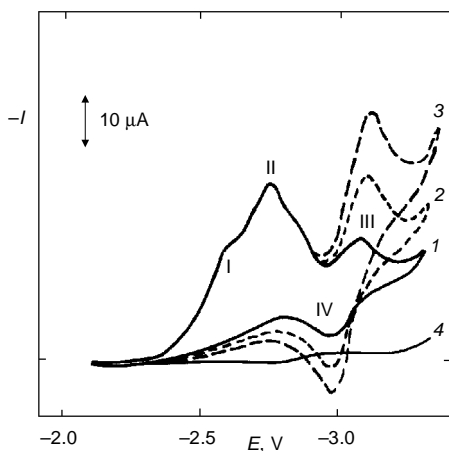

FIG. 3
CV curves on a HMDE in a 0.1 M solution of Bu$_4$NClO$_4$ in DMF, 100 mV s^{-1}; *1* Delor 103 (c = 2 mmol l^{-1}), *2* Delor 103 + biphenyl (2 mmol l^{-1} each); *3* biphenyl (4 mmol l^{-1}); *4* supporting electrolyte; I–IV denote I_{p1} through I_{p4}
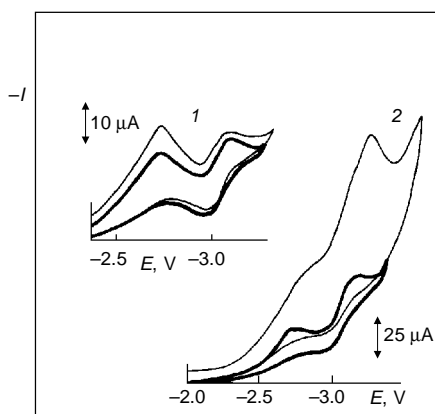
FIG. 4
CV curves of Delor 103 (c = 3.77 mmol l^{-1}) in a 0.1 M solution of Bu$_4$NClO$_4$ in DMF on tin (*1*) and lead (*2*) electrodes; 1st and n-th cycles, 100 mV s^{-1}

$$E_{p1} = -0.102a - 2.72 \ (r = 0.773)$$

$$E_{p2} = -0.119a - 2.90 \ (r = 0.839) \ .$$

In both dependences, the points for W, Ti, and Zn are outliers (Fig. 5). For W and Ti this may be due to the fact that the hydrogen reduction mechanism on them is different from that on the remaining metals (controlled by Heyrovsky's reaction[16]), whereas for Zn the cause of the anomaly is unclear because zinc is among metals exhibiting high hydrogen overvoltage values such as Pb, Sn and Hg, where Volmer's reaction[16] is the controlling phenomenon.

For practical reasons, mercury was selected for subsequent work. The concentration dependences in the CV and FSDPP modes (at pulse amplitudes of –12.5 mV and –100 mV) and in AC polarography were examined over the concentration regions of 2.6 to 1 860 μmol l^{-1} (i.e. 0.7 to 500 μg ml^{-1}). The lower limit of determination by those methods, however, is 5–10 μmol l^{-1} (1.3 to 2.6 μg ml^{-1}). The limiting factors include solvent and supporting electrolyte purity within the potential range examined, viz. –2.4 to –3.2 V (typical curves are reproduced in Figs 6 and 7).
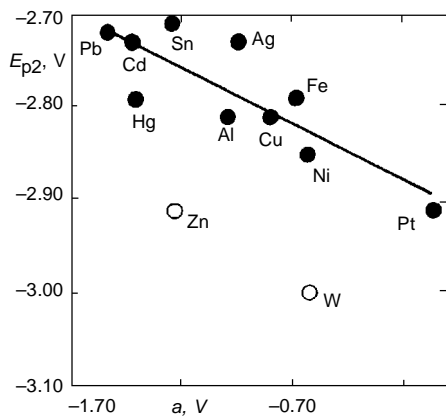

FIG. 5

Plot of the E_{p2} potentials versus a constant in Tafel's equation (Table III); Zn, W and Ti are not included
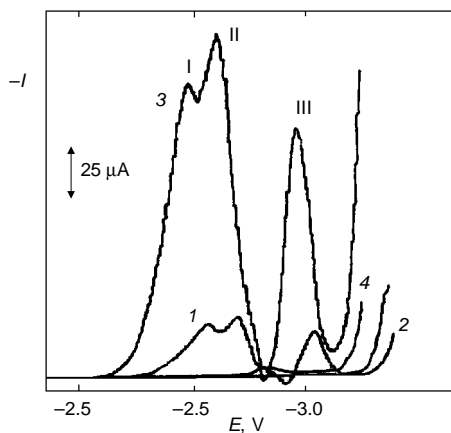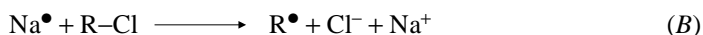

FIG. 6

FSDPP curves of Delor 103 (c = 2 mmol l^{-1}) in a 0.1 M solution of Bu$_4$NClO$_4$ in DMF; 50 mV s^{-1}, sampling period 20 ms. Delor 103 (*1, 3*) and supporting electrolyte (*2, 4*) at pulse amplitudes of –12.5 mV (*1, 2*) or –100 mV (*3, 4*). Peak positions I, II, III correspond to E_{p1}, E_{p2}, E_{p3}, respectively

In many analytical procedures, the C–Cl bond is split with an alkali metal (alkali alcoholate). We supposed that, like hydrogen in statu nascendi, alkali metals prepared by electroreduction of the corresponding salts may exhibit an increased activity for the C–Cl bond. Since from among the alkali metals, sodium ions are electrochemically reduced most positively[15], sodium perchlorate was used for further study. Thus it is conceivable that the sodium ions can play the role of a chemical mediator following the schemes

$$Na^+ + e \; \rightleftharpoons \; Na^\bullet \qquad\qquad (A)$$

on the electrode, and

$$Na^\bullet + R\text{–}Cl \; \longrightarrow \; R^\bullet + Cl^- + Na^+ \qquad\qquad (B)$$

in solution, followed by the processes

$$R^\bullet + H^+ + e \; \longrightarrow \; R\text{–}H \qquad\qquad (C)$$

TABLE III
CV peak potentials of Delor 103 at various electrode materials; a is the constant in Tafel's equation $\eta_H = a + b \log i$ where η_H is hydrogen overvoltage[16] and i is current density. Constants a were taken from ref.[16] (ref.[17] for Ti)

Metal	$-E_{p1}$, V	$-E_{p2}$, V	$-E_{p3}$, V	$-E_{p4}$, V	$-a$, V
Pb	2.55	2.72	3.17	2.97	1.54
Cd	2.55	2.73	3.09	2.95	1.43
Hg	2.63	2.79	3.11	3.00	1.415
Sn	2.57	2.71	3.08	2.96	1.25
Zn	2.76	2.91	3.07	2.95	1.24
Al	2.67	2.81	3.18	3.02	1.0
Ag	2.55	2.73	3.10	2.95	0.95
Cu	2.61	2.81	3.15	3.00	0.8
Fe	2.65	2.79	3.15	3.01	0.69
Ni	2.66	2.85	3.11	2.99	0.64
Pt	2.72	2.91	3.12	2.99	0.07
W	2.82	3.00	3.15	2.98	0.64
Ti	–	3.32	3.4	–	0.94
Graphite		2.55	2.83	3.15	3.00

on the electrode, and

$$R^{\bullet} + SH(solvent) \longrightarrow RH + S^{\bullet} \qquad (D)$$

in solution.

Sodium forms a sodium amalgam when using a mercury working electrode. In the experiment, the sodium perchlorate concentration was double the concentration of the C–Cl bonds. The changes in the sodium ion concentrations were measured directly in the vessel by CV on a hanging mercury drop. Two procedures were applied. In the one procedure, all Na^+ ions were reduced completely at a potential of –2.84 V in the absence of PCBs; the charge consumed corresponded to the theoretical consumption. Spontaneous conversion of sodium back to Na^+ ions was also examined by CV to find that less than 5% sodium converted in an hour (which is roughly the time of electrolysis with PCB). After addition of PCB, 45% sodium recovered to Na^+ in 15 min. The recovery slowed down and ultimately ceased to proceed in an hour; 50% and 34% sodium was so recovered in Et_4N^+ and Bu_4N^+, respectively. Based on the chloride ion concentration, the fractions of degraded C–Cl bonds in the 2 electrolytes can be estimated to 80% and 73%, respectively. The concentration of sodium ions at the end of the experiment, however, was appreciably (by 35%) higher than that of the released chloride anions with respect to the stoichiometry of the equation

$$R{-}Cl + Na \longrightarrow R^{\bullet} + Na^+ + Cl^- \ . \qquad (E)$$
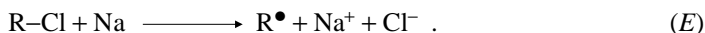
Hence, a fraction of the reduced sodium was converted back to ions by a different reaction (competitive with respect to the C–Cl bond splitting) which, however, requires the presence of PCB. When using Bu_4N^+, the steady state was only attained in 2 h, and
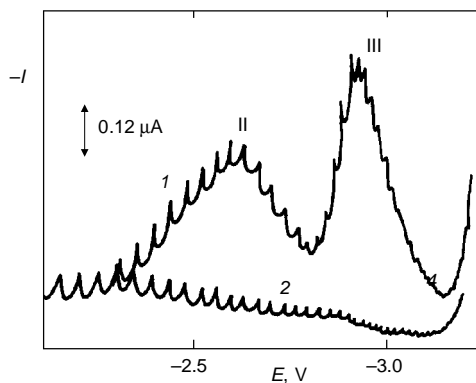

FIG. 7
AC polarographic curves in a 0.1 M solution of Bu_4NClO_4 in DMF; 100 mV s^{-1}, 60 Hz, superimposed alternating voltage amplitude 15 mV; *1* Delor, *2* supporting electrolyte. Peaks II and III correspond to E_{p2} and E_{p3}, respectively

a lower concentration of sodium ions in the solution at the end of the experiment (as compared to Et_4N^+) indicates that the degree of C–Cl bond degradation is lower as well.

In the other procedure using the same starting conditions (sodium ion and PCB concentrations 14.3 and 1.94 mmol l^{-1}, respectively), electrolysis in the two supporting electrolytes was examined at –2.5 V (sodium ion reduction) and at –2.84 V. The results are given in Table I. When reducing the reaction mixture at –2.5 V, competition occurs between the direct electrochemical reduction of higher-substituted PCBs and the degradation by the electrochemically generated sodium in both supporting electrolytes. In times given in Table I, however, the electrolysis virtually ceased to proceed (the current passing during the electrolysis was monitored). This situation is characterized by CV curves indicating a reversible reduction of sodium ions and, more negatively, current due to the reduction of lower-substituted chlorobiphenyls. The process can be conducted as far as a complete vanishing of the PCB and Na^+ peaks during the electroreduction of the reaction mixture at –2.84 V. The charge efficiency can be determined by comparison with the direct electroreduction of PCBs in the absence of the mediator at the given potential.

The results of the third procedure – direct electrolysis – are summarized in Table II. The course was monitored by recording the I–t curves (Fig. 8). A change in the nature of the sample, viz. gradual degradation of higher-substituted PCBs, can also be inferred from the CV curves recorded one by one after finishing the electrolysis at the given potential (Figs 9a, 9b). Biphenyl is also the resulting electroreduction product at
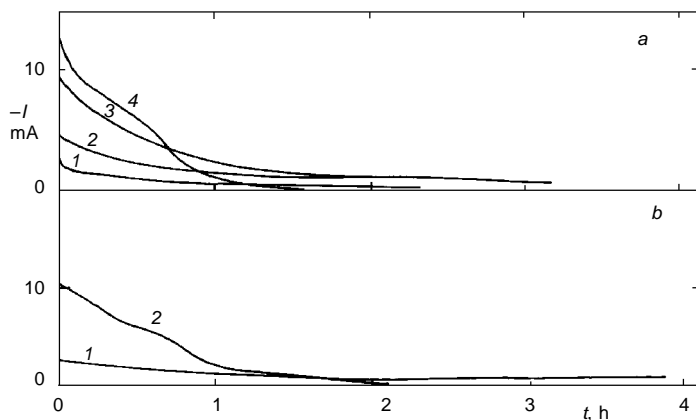

FIG. 8
I–t curves recorded during the electrolysis of Delor 103 in 0.1 M solutions of Et_4N^+ (a) or Bu_4N^+ (b) in DMF. Potential (V): a: 1 –2.4, 2 –2.5, 3 –2.66, 4 –2.85; b: 1 –2.49, 2 –2.84

sufficiently negative potentials. Comparison of the starting concentration of Delor 103 (given the working volume of solution electrolyzed) and of the measured (and corrected as described in Experimental) charge consumption gives evidence that the electrolysis is virtually stoichiometric, associated with the consumption of 2 electrons per C–Cl bond, with the possibility of a quantitative transformation of the PCBs to biphenyl at sufficiently negative potentials. The degradation degree α_{Cl} is given as the concentration ratio of the released chloride ions – found voltammetrically through anodic oxidation of Cl$^-$ ions on a platinum electrode – to the starting C–Cl bonds. Hence, in such conditions the charge (Coulomb) efficiency as well as the mass efficiency of electrodegradation approaches 100% during an exhausting electrolysis.

All the 3 procedures demonstrated the effect of the supporting electrolyte on the dechlorination rate. When using the less bulky and less absorbing Et$_4$N$^+$ supporting electrolyte cation, the process of both indirect and direct electrochemically mediated transformation of Delor 103 is faster and, in the case of dechlorination by the electrochemically prepared sodium amalgam, proceeds to a higher degree of C–Cl bond degradation.

The dependence of the peak potentials of Delor 103 on the working electrode material suggests that the overall process of electrochemical splitting of the C–Cl bond
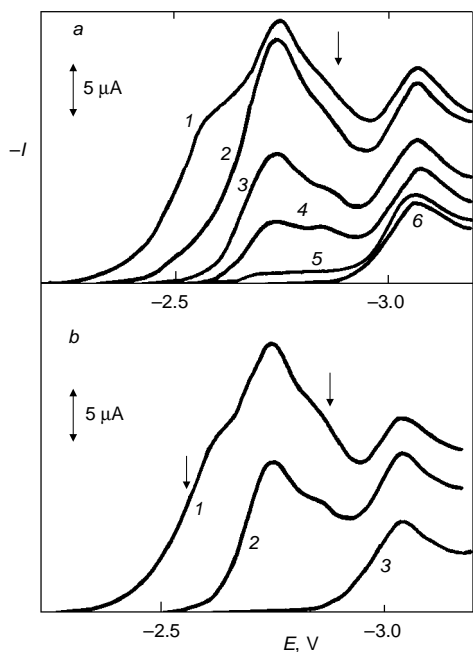

Fig. 9

CV curves of Delor 103 (at a concentration c) on a HMDE during gradual reduction in a 0.1 M solution of Bu$_4$N$^+$; a: E_r = –2.84 V, c = 1.92 mmol l^{-1}, passed charge (in C): 1 0, 2 9.6, 3 15.4, 4 19.0, 5 22.8, 6 24.5 (final state); b: c = 2 mmol l^{-1}, curves: 1 starting state, 2 after complete reduction at E_{r1} = –2.49 V (passed charge 14.1 C), 3 after reduction at E_{r2} = –2.84 V (passed charge 24.3 C). Arrows show potentials of reduction

is affected by adsorption of the PCB molecules, which is more pronounced on metals exhibiting large hydrogen overvoltage values such as lead, cadmium, tin and mercury.

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