Electrochemical reductive dehalogenation of chlorobenzenes

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Electrochemical dechlorination of 1,2,3,5-tetrachlorobenzene in methanol and chlorobenzene in dimethylsulfoxide with tetraalkylammonium salts as supporting electrolytes was carried out. The extent of dechlorination depends significantly on the electrode composition.

Key words: electrochemical dechlorination, cathodic materials, polychlorobenzenes.

At present, detoxification, destruction, and reprocessing of toxic xenobiotics (mainly, chloroaromatic compounds) into useful products is a challenging problem. Several promising approaches for solving this problem have been proposed and are being intensely developed. One of these approaches is electrochemical reductive dehalogenation, which makes it possible to transform the xenobiotics into less toxic, biodegradable compounds. A number of works deal with electrochemical dehalogenation of polychlorobenzenes (which can be regarded as model compounds), including ecological aspects of the problem.[1—5] However, the effects of the solvent and cathode composition on the elimination of a halogen atom have been studied insufficiently. In the present work we studied the dehalogenation of 1,2,3,5-tetrachlorobenzene (1,2,3,5-TCB) in methanol (MeOH) and chlorobenzene (CB) in dimethyl sulfoxide (DMSO) on cathodes made of titanium, lead, platinum, nickel, copper, and the carbon-based fiber materials: (CFM) Busofit-T (BtT), Viskum-TO15 (V-TO), and Ural-TR3/2 (U-TR), with or without deposited palladium. The choice of the solvents and electrode materials was based on the literature data on the electrochemical stability of protic and aprotic polar media on cathodes made of various materials.[6,7] The use of CFM cathodes was considered necessary for comparing our results with those concerning dehalogenation on metal cathodes, since carbon-based materials are widely used in modern electrochemistry.[8]

Results and Discussion

Electrolysis in methanolic solutions. The results of the experiments on the reduction of 1,2,3,5-TCB in methanol are presented in Fig. 1 as dependences of C/C_0 on the amount of electricity passed, where C and C_0 are the current and starting concentrations of the substrate in solution.

The rate of dehalogenation of 1,2,3,5-TCB only slightly depends on the cathode material. An exception is the lead electrode, which requires three times less electricity to attain the same C/C_0 ratio as the other metals. It has been shown previously[9—11] that alkyl radicals, which result from the reduction of tetraalkylammonium cations on lead, carbon, mercury, and some other cathodes, react with the electrode material to give disperse precipitates of compounds on the surface. These compounds can serve as strong reductants of electrochemically stable substrates, including organochlorine compounds. We observed decomposition of a lead cathode to form a suspension at potentials around −3 V and more negative. This can be due to high intensity of the reaction of alkyl radicals with the cathode surface followed by degradation of the crystal lattice of lead. A sharp increase in the surface of contact of the substrate with the particles of the suspension accelerates the dehalogenation process.

The rate of dehalogenation of 1,2,3,5-TBC on CFM is markedly higher than that on metals and increases with an increase in the absolute value of potential, both in the case of the original CFM (Fig. 1, curves *8*, *10*) and on palladized CFM (curves *5*, *7*). At comparable potentials, an increase in palladium content on CFM results in a noticeable decrease in the rate of 1,2,3,5-TBC dehalogenation.

The nature of the cathode material most considerably affects the qualitative and quantitative composition of the products of electrolysis of 1,2,3,5-TBC. Data on the composition of the electrolysis products formed on different cathode materials are presented in Table 1. The process performed on platinum results in trichlorobenzenes (TCB), while that on nickel gives tri- and dichlorobenzenes (DCB). Noteworthy, nickel was the only material that gave the full set of dichlorobenzenes. The reaction on lead results in almost complete transformation of the substrate into CB. This supports the conclusions made previously[10,11] that the cathode

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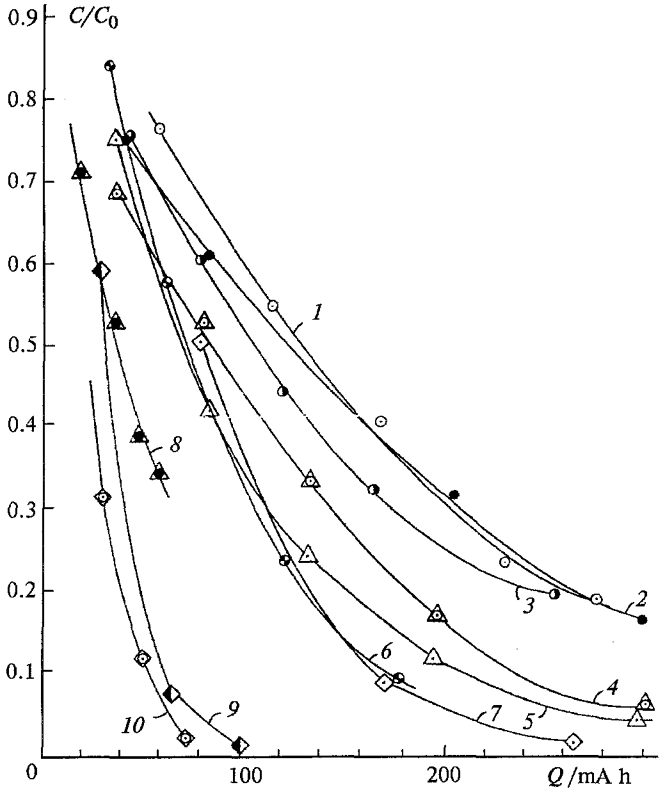

Fig. 1. Dependence of C/C_0 on the amount of electricity passed for a solution of 1,2,3,5-tetrachlorobenzene in MeOH (0.25 *M* TEAB) on different cathodes at various potentials:

Curve	Cathode	Potential/V	$C_0 \cdot 10^2$/mol L^{-1}
1	Platinum	−3.3	1.20
2	Titanium	−4.0	1.14
3	Nickel	−3.3	1.13
4	16 % Pd/BtT	−3.3	1.15
5	6 % Pd/BtT	−3.3	1.05
6	Platinum	−2.2	1.17
7	6 % Pd/BtT	−4.0	1.02
8	BtT	−3.3	1.19
9	Lead	−3.3	1.26
10	BtT	−4.0	1.26

metal reacts with an electrochemically generated radical to give organometallic compounds, which subsequently reduce the substrate according to the general mechanism. This probably explains the predominant formation of chlorobenzene.

When CFM modified by 16 % palladium is used, considerable differences in the distribution of the products of dehalogenation of 1,2,3,5-TBC are observed: the depth of dechlorination of the starting substrate increases, and a noticeable amount of benzene is formed. Such an increase in the degree of dehalogenation with increasing concentration of palladium on CFM originates from the electrocatalytic influence of the metal.[12]

In the absence of deposited palladium, the dehalogenation of the most hardly reducible compound, chlorobenzene, does not occur on CFM in MeOH even at −4.0 V. Benzene is formed only on lead and in a low yield with respect to current (Y_c = 2.1 % at a substrate concentration of *ca.* 10^{-2} mol L^{-1}).

The overall Y_c of the products of substrate reduction, which is the highest on CFM, decreases from 14 to 11 % during electrolysis. These values are 2—3 times lower on other materials. Dechlorination is accompanied by side processes of cleavage of the O—H bond in methanol and reduction of teteraalkylammonium cations. The cathodic current density (Table 2) strongly depends on the electrode material, which is probably due to the overpotential of hydrogen evolution, and the rate of decomposition of the supporting electrolyte. A comparison of Tables 1, 2, and Fig. 1 indicates that the relation between the current density on the electrode, substrate concentration, and degree of its transformation is ambiguous. The low current density on BtT possibly results from predominant decomposition of tetraethylammonium bromide (TEAB). The current density on CFM modified by palladium is 5—10 times higher and is comparable with that on metal electrodes. This probably results from an increase in the rate of methanol decomposition. The degree of conversion on these materials is intermediate between those on metal and CFM electrodes, whereas the depth of transformation increases with increasing content of palladium on CFM. The acceleration of dehalogenation on BtT at a polarization of −4.0 V (Fig. 1, *cf.* curves *8* and *10*) and the weak effect of potential on the conversion on modified electrodes (curves *5*, *7*) possibly result from the ratio between the rates of side processes of hydrogen evolution and reduction of alkyl radicals followed by their reactions with the substrate.

Electrolysis in dimethyl sulfoxide. The BtT carbon material, which showed the best results of electrolysis in methanol, and V-TO and U-TR with and without deposited palladium were used as cathodic materials. Preliminary experiments on the adsorption of *p*-nitroaniline showed that BtT has a considerable adsorptivity (the specific surface of BtT calculated from the adsorption of *p*-nitroaniline is ~900 m^2 g^{-1}), while the two other materials almost do not adsorb *p*-nitroaniline. The high adsorption properties of BtT agree with the literature data.[13]

We chose CB, which is a less reducible compound than polychlorinated benzenes,[3] as the substrate.

Table 3 presents data on the current density for electrodes made of various CFM. These data suggest that cathodic processes occur more intensely in DMSO solutions than in MeOH solutions. The severalfold decrease in the current density on all of the materials in MeOH solutions results from the higher stability of DMSO with respect to electrochemical decomposition,

Table 1. Distribution of the products of electrochemical dehalogenation of 1,2,3,5-tetrachlorobenzene in MeOH (E = −3.3 V) as a function of the cathode material and the amount of electricity passed (Q)

Q	Cathode	Electrolysis products, $C \cdot 10^{-3}$/mol L^{-1}						
/mA h		1,3,5-TCB	1,2,4-TCB	1,2-DCB	1,4-DCB	1,3-DCB	CB	Benzene
50	Platinum	0.65	1.70					
	Nickel	0.90	2.75	0.10	0.10	0.40		
	Titanium*	0.50	1.80		0.15	0.55		
	Lead		0.47		1.00	1.10	2.50	
	BtT	1.30	2.75		1.60	1.85	Traces	
	6% Pd/BtT	0.90	2.25		0.45	1.15	0.20	
	16 % Pd/BtT	0.05	0.60		0.47	0.30	0.30	0.70
150	Platinum	2.00	4.90					
	Nickel	1.25	3.75	0.75	1.30	1.30		
	Titanium*	1.0	3.0		1.12	1.0	0.12	
	Lead						8.20	0.50
	6% Pd/BtT	1.75	4.20		1.30	1.25	0.20	
	16% Pd/BtT	0.40	1.35		2.10	0.65	0.60	2.12

Note. TCB is trichlorobenzene; DCB is dichlorobenzene; CB is chlorobenzene.

* The data for titanium were obtained at −4.0 V.

Table 2. Dependence of current density on the electrode material in 1,2,3,5-TCB—MeOH—TEAB solutions at −3.3 V and Q = 60 mA h

Electrode	Current /mA cm^{-2}
BtT	22
16 % Pd/BtT	216
6 %Pd/BtT	120
Lead	225
Nickel	300
Titanium	270
Platinum	360

Table 3. Dependence of current density on the electrode material in 1,2,3,5-TCB—DMSO—TEAB solutions at −4.0 V and Q = 60 mA h

Electrode	Current /mA cm^{-2}
V-TO	36
BtT	36
U-TR	15
1 % Pd/V-TO	7
6 % Pd/BtT	60
1 % Pd/U-TR	5

and hence a lower contribution of side processes.

The data presented in Fig. 2 suggest that the dehalogenation of CB on all electrode materials gives benzene as the only reduction product. The best and similar results with respect to Y_c and conversion of CB were obtained on cathodes made of BtT, with or without deposited palladium. These characteristics were much worse for the other electrodes.

A comparison of the results presented in Fig. 3 allows us to conclude that Y_c linearly depends on the amount of electricity passed, *i.e.*, in effect, on the current CB concentration in solution. An increase in the concentration of CB in solution (up to $1.20 \cdot 10^{-1}$ mol L^{-1}) decreases the fraction of current consumed for side processes, and hence, Y_c of dehalogenation increases to 60—75 % for various CFM and linearly decreases with an increasing amount of electricity passed. The best results were obtained in the case of BtT. This is probably due to the pronounced adsorption properties of this material.

As follows from the results obtained, electrochemical dechlorination of the substrate on CFM cathodes occurs more intensely in solutions based on aprotic solvents than in protic solvents, due to a decrease in the fraction of side processes. Modification of CFM with palladium makes it possible to increase the degree of substrate dehalogenation without a substantial acceleration of the process.

Experimental

Electrochemical dehalogenation was carried out at 20 °C in a thermostatically controlled diaphragm cell. The potential of the cathode was controlled by a PI-50-1 potentiostat combined with a PR-8 programmer taking into account the *iR* drop of potential. The volume of the electrolyte in each cell was 10 mL. A platinum foil (1 cm^2) was used as the anode. MK-40 and MA-40 ion-exchanging membranes were used as diaphragms. The supporting electrolytes were as follows: tetra-

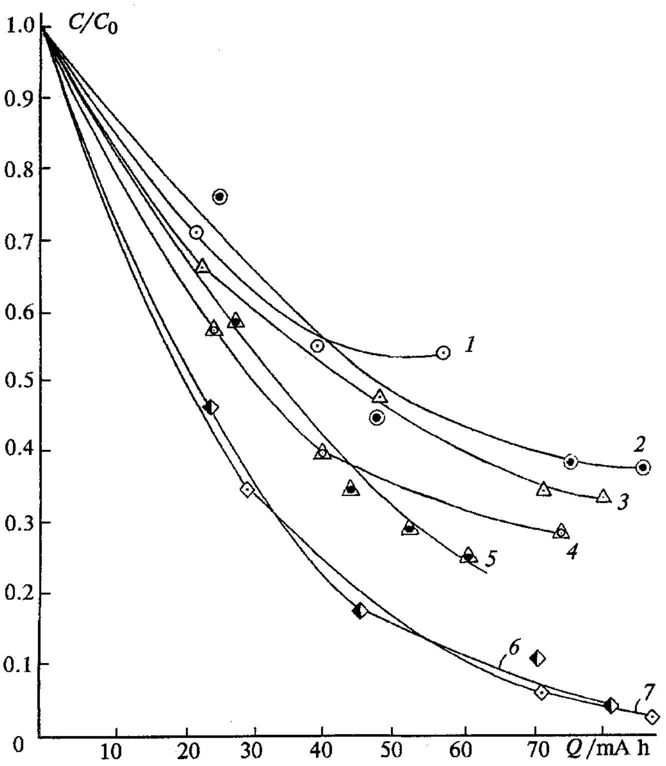

Fig. 2. Dependence of C/C_0 on the amount of electricity passed for a solution of chlorobenzene in DMSO (0.25 *M* TEAB) at −4.0 V on cathodes made of various materials:

Curve	Cathode	$C_0 \cdot 10^2$/mol L^{-1}
1	1 % Pd/U-TR	1.36
2	Platinum	1.44
3	V-TO	1.35
4	U-TR	1.35
5	1 % Pd/V-TO	1.13
6	BtT	1.37
7	6 % Pd/BtT	1.32

ethyl- or tetrabutylammonium bromides as the catholytes, and the same bromides or potassium perchlorates as anolytes (the concentrations were 0.25 *M*). Electrolysis was carried out in the potentiostatic mode at potentials of the discharge of the supporting electrolyte, based on data on the stability of chlorobenzenes at high cathodic polarization.[3] The concentrations of the substrates were $(1.12 \div 1.44) \cdot 10^{-2}$ mol L^{-1}. An EVL-1M1 silver chloride electrode in saturated KCl was used as the reference electrode (0.201 V relative to SHE, 20 °C). "Chemically pure" grade DMSO was used without additional purification. "Chemically pure" grade MeCN and MeOH were distilled. "Pure" grade tetraalkyl-substituted ammonium salts were used without additional purification. All substrates were of "pure" grade. The carbon fiber materials were manufactured by "Khimvolokno" Industrial Association (Svetlogorsk, Belarus'). Palladization of CFM was carried out according to the known procedure.[14]

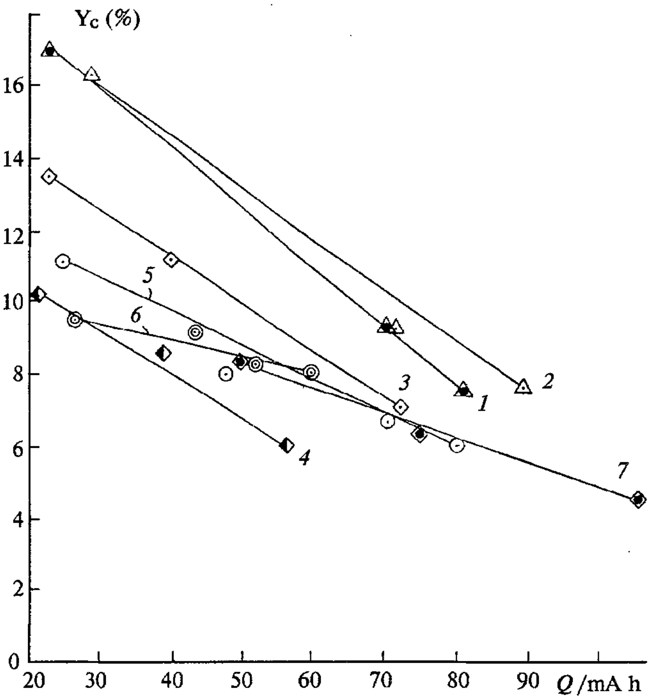

Fig. 3. Dependence of current yield (Y_c) on the amount of electricity passed during the electrolysis of a chlorobenzene solution (C_0 = (1.13—1.44)$\cdot 10^{-2}$ mol L^{-1}) in DMSO at a cathode potential of −4.0 V on different CFM: *1*, BtT; *2*, 6 % Pd/BtT; *3*, U-TR; *4*, 1 % Pd/U-TR; *5*, V-TO; *6*, 1 % Pd/V-TO; *7*, platinum.

The reaction products were analyzed by reversed-phase HPLC on a Milikhrom-4 UF chromatograph using an 80× 2 mm column with Nucleosil-C18, 5 μm. MeCN—water (70 : 30) was used as the mobile phase; the flow rate was 100 mL min^{-1}. The quantitative content of the products was calculated by the absolute graduation method.

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