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# Electrochemical Reduction of Trichlorobiphenyls: Mechanism and Regioselectivity

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Abstract—The regioselectivity of electrochemical reduction of four trichlorobiphenyls (PCB 28–30 and PCB 37) was studied by cyclic voltammetry and bulk electrolysis. The number of stages and mechanism of electrochemical reduction of each of the examined substrate were inferred on the basis of the experimental electron transfer coefficients and calculated (DFT) bond lengths and potential energy surface sections. GC/MS analysis of the controlled potential electrolysis products showed that chlorine atom in the disubstituted ring of trichlorobiphenyls is reduced more readily than in the monosubstituted ring and that the rate of chlorine reduction changes in the series o-Cl > p-Cl > m-Cl.

Keywords: polychlorobiphenyls, cyclic voltammetry, preparative electrolysis, DFT calculations, electron transfer mechanism

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Nowadays, the problem of environmental pollution with persistent organic pollutants (POPs) is considered by the United Nations to be a priority environmental problem. The group of persistent organic pollutants consists of 12 chemical compounds, including polychlorinated biphenyls (PCBs) [1, 2]. The Stockholm Convention on Persistent Organic Pollutants signed in 2001 was aimed at not only elimination of the production and use of POPs but also disposal of the existing stocks of these compounds.

Commercial PCBs are complex mixtures consisting of 50–70 individual compounds (congeners) with different numbers and positions of chlorine atoms in their molecules. Up to now, various methods for remediation of PCBs have been proposed; they include biochemical [3, 4], oxidative [5, 6], and reductive methods [6–12] and those based on nucleophilic substitution of chlorine by other functional groups (e.g., methoxycarbonylation [13] or solvolysis [14–19]). Utilization of PCBs is possible only via reduction and nucleophilic substitution or a combination of these methods. Biphenyl or its functional derivatives thus formed can be used as starting compounds in industrial organic synthesis. In order to develop scientifically substantiated recommendations on the use of one or another method for remediation of PCBs, it is necessary to consider the problem of the reduction regioselectivity, which has been insufficiently studied. Taking into account that many reduction and substitution processes involve intermediate formation of radical anions [7, 20], it seemed important to study radical anion reactions of PCBs.

One of the most obvious ways to study radical anion reactions of PCBs consists of generation of radical anions in an electrochemical cell. Furthermore, in recent years electroreductive decontamination of water and soils from halogenated POPs has gained researchers' attention [21], which further increases the importance of studying electrochemical hydrodechlorination of PCBs.

Electrochemical reduction of polychlorinated biphenyls and naphthalenes is often performed by cyclic voltammetry [22]. It should be noted that the presence of aromatic radical anion mediators such as biphenyl and naphthalene increases the rate of reduction of PCBs [23]. We have recently studied by cyclic voltammetry regioselective electrochemical reduction





of dichlorobiphenyls, and the results of these studies allowed us to analyze the kinetic and mechanistic aspects of the process [24, 25]. Electrochemical reduction of PCBs involves dissociation of the C-Cl bond, which gives rise to the corresponding aryl radical according to either stepwise (path a) or concerted mechanism (path b; Scheme 1). The relative rates of the two reduction stages, electron transfer and bond cleavage, determine the reduction mechanism. If the bond dissociation rate is lower than the rate of the electron transfer stage (with account taken of solvation shell reorganization), the reaction follows the stepwise path. Otherwise (i.e., when the bond dissociation stage is faster), the concerted mechanism is operative. The neutral radical formed after departure of chloride ion is reduced at a lower potential than that required for the reduction of the initial compound. The resulting aryl anion abstracts a proton (mostly from a solvent molecule) [26] to produce hydrodechlorination product.

Theoretical calculations can also be used to understand the reaction mechanism. For example, the C–X bond lengths before and after electron transfer and spin density on the carbon atom linked to halogen in the radical anion can be successfully used as indicators of the reaction mechanism. Even a more important indicator is the occurrence of local minima and transition states on the potential energy surface, which points out the formation of stable radical anions. Herein we report the kinetic and mechanistic features of successive hydrodechlorination of four trichlorobiphenyls which were studied by complementary methods including cyclic voltammetry, structure determination of controlled potential electrolysis products, and DFT quantum chemical calculations. The substrates were four PCB congeners 1-4 with 3:0 (2, 3) and 2:1 substitution patterns (1, 4) and different numbers of chlorine atoms in the *ortho* positions.

Cyclic voltammetry. The cyclic voltammograms for the reduction of PCBs 1-4 were recorded at a potential scan rate of 0.1-10 V/s. The cyclic voltammograms of PCBs 28, 29, and 37 (1, 2, 4) displayed three irreversible electrochemical reduction peaks (Fig. 1) corresponding to dissociation of three different C-Cl bonds. The peak potentials are given in Table 1. The reduction peaks remained irreversible even at high potential scan rates, which indicated fast decomposition of radical anions into neutral aryl radical and chloride ion. At a potential scan rate of 0.1 V/s, distinct peaks were observed for PCB 37, whereas those for PCB 29 and PCB 28 were less distinct. The peak potential separation between the first and second peaks of PCB 37 was 180 mV, and between the second and third peaks, 159 mV. Only two irreversible peaks were observed for PCB 30, and the peak potential separation was small (105 mV).

The other two parameters important for understanding the mechanism of electrochemical reduction [27] are the peak width  $(E_{p/2} - E_p)$  and the dependence of the peak potential on the potential scan rate  $\partial E_p/\partial \log v$ . Their values are also given in Table 1. The peak width was calculated as the difference between the peak potential  $E_p$  and half-peak potential  $E_{p/2}$ . For the accurate determination of the second and third peak parameters, the procedure for recording baseline for multicomponent systems was applied [28]. The width of the first peak for PCB 29 and PCB 30 were 123.5 and 155.7 mV, respectively, whereas the calculated

#### Scheme 2.



peak widths of the second and third peaks exceeded 200 mV. These findings suggest that the reaction rate is controlled by electron transfer. The width of the first peak of PCB 28 was 49.4 mV, and that of PCB 30, 95.0 mV. The calculated peak widths of the second and third peaks widths ranged from 63.8 to 266.8 mV, indicating that the reaction rate is controlled by both processes.

The  $\partial E_p/\partial \log v$  values for trichlorobiphenyls 1, 2, and 4 ranged from 78.2 to 111.3 mV; this means that the rate-determining stage is the initial electron transfer. A conclusion on the reaction mechanism can be drawn on the basis of the electron transfer coefficients [29]:

$$\alpha = \frac{1.856RT}{F(E_{\rm p/2} - E_{\rm p})}$$

The electron transfer coefficients  $\alpha$  (Table 1) for PCB 28 (first peak) and PCB 37 (first and second peaks) are higher than 0.5, indicating stepwise mechanism of the electrochemical reduction, whereas the  $\alpha$  values are lower than 0.5 for PCB 29 and PCB 30 (all peaks), which suggests concerted mechanism of the process.

Controlled potential electrolysis (bulk electrolysis). Controlled potential electrolysis was performed to estimate regioselectivity of the reduction of C-Cl bonds in PCBs 1-3 possessing a chlorine atom in the ortho position with respect to the bridging bond. In all cases, the substrate conversion did not exceed 2% in order to determine which chlorine atom is cleaved primarily. The electrolysis products were analyzed by GC/MS, and the resulting dichlorobiphenyls were identified by comparing their retention times with those of reference compounds. No monochlorobiphenyls were detected in the reaction mixtures, which indicated stability of the dichlorobiphenyls under the electrolysis conditions. The regioselectivity of the reduction in the first stage is illustrated by Scheme 3.

Obviously, elimination of chlorine from the *ortho* position was preferred in all cases. These data are very consistent with the selectivity observed in other radical anion reactions of PCBs studied previously, in particular chemical reduction with a sodium–naphthalene complex [30], electrochemical reduction of dichlorobiphenyls [24, 25], and methoxycarbonylation of PCB 28 [13].

Parameter	PCB 28 (1)			PCB 29 (2)			PCB 30 ( <b>3</b> ) <sup>a</sup>		PCB 37 (4)		
	$Cl^1$	Cl <sup>2</sup>	Cl <sup>3</sup>	Cl <sup>1</sup>	$Cl^2$	Cl <sup>3</sup>	$Cl^1$	$Cl^2$	Cl <sup>1</sup>	$Cl^2$	Cl <sup>3</sup>
$E_{\rm r}, V$ $(v = 0.1 \text{ V/s})$	-2.252	-2.379	-2.483	-2.248	-2.397	-2.549	-2.391	-2.496	-2.215	-2.395	-2.554
$E_{p/2}$ – $E_p$ , mV	49.4	240	266.8	155.7	258.4	309–410	123.5	201.4	95	63.8	231.1
$\partial E_{\rm p}/\partial \log v$ , mV	82.3	88.2	111.3	95.6	103.3	99.7	—	-	78.2	92.3	87.9
α	0.972	0.199	0.179	0.306	0.185	0.154	0.386	0.237	0.501	0.747	0.206

Table 1. Parameters of the electrochemical reduction of trichlorobiphenyls 1–4 (voltammetric analysis)

<sup>a</sup> Parameters for the Cl<sup>3</sup> atom cannot be determined.



-60

-75

-3.0

**Fig. 1.** Cyclic voltammograms with subtracted background current for the reduction of (a) 2,4,5-trichlorobiphenyl (PCB 29), (b) 2,4,6-trichlorobiphenyl (PCB 30), (c) 2,4,4'-trichlorobiphenyl (PCB 28), and (d) 3,4,4'-trichlorobiphenyl (PCB 37) recorded against 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> in MeCN; v = 0.1 V/s. **Quantum chemical calculations.** During the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 28, PCB 37) give rise to stable  $\pi$ -type radical animality of the past 37 give rise to stable  $\pi$ -type radical animality of the past 38 give rise to stable  $\pi$ -type radical animality of the past 38 give rise to stable  $\pi$  stables  $\pi$  stables  $\pi$  stables  $\pi$  stables  $\pi$  st

-1.5

-2.0

Potential, V (vs. Ag/Ag<sup>+</sup>)

two decades quantum chemical calculations. During the past increasingly used to analyze dissociation processes with electron transfer in organic halogen derivatives [31–35]. These calculations make it possible to answer two important questions: (1) does electrochemical reduction follow stepwise or concerted mechanism and (2) what is the regioselectivity of the reaction. For this purpose it is necessary to estimate the relative stabilities of radical anions, bond lengths therein, and effective charges on the departing halogen atoms [36].

-2.5

0

-20

-40

-60

-80

-100

-25

-50

-75

-100

-125

-150

-3.0

Ι, μΑ

*Ι*, μΑ

Table 2 contains the corresponding parameters calculated for PCBs 1–4. Geometry optimization of radical anions showed that PCB congeners containing no more than two chlorine atoms in a single ring (PCB

28, PCB 37) give rise to stable  $\pi$ -type radical anions (Fig. 2) which occupy local energy minima on the potential energy surface (the corresponding Hessian matrix contains no imaginary frequencies). This means that PCB 28 and PCB 37 should react according to the stepwise mechanism (path *a* in Scheme 1).

-2.5

-2.0

Potential, V (vs. Ag/Ag<sup>+</sup>)

-1.5

We also calculated potential energy surface sections along the reaction coordinate (C–Cl distance) for the radical anions derived from PCB 28 and PCB 37 (Fig. 3). Obviously, dissociation of the C–Cl bond in radical anions requires overcoming an energy barrier corresponding to the transition state between  $\pi$ -radical anion and aryl radical/chloride ion couple. The activation barriers  $\Delta E^{\neq}$  are given in Table 2. The following trends in the variation of  $\Delta E^{\neq}$  may be noted.





Elimination of the *ortho*-chlorine atom from the disubstituted ring of PCB 28 requires an energy lower by 4-11 kJ/mol than elimination of the other chlorine atoms. Elimination of chlorine from the monosubstituted ring is least probable for both PCB 28 and PCB 37 (activation barrier 13-18 kJ/mol). In addition, Table 2 contains some structural parameters of neutral PCB 28 and PCB 37 molecules and radical anions derived therefrom. The lowest activation barrier was found for that C–Cl bond in the  $\pi$ -radical anion which is elongated most relative to the corresponding bond in the neutral molecule. Change of the charge on the chlorine atom (calculated according to both Mulliken and NBO method) in going from the neutral molecule to its radical anion cannot be used to determine the regioselectivity of the radical anion reduction of PCBs.

A relation between the potential barrier and thermodynamic stability of biphenyl radical formed as a result of dissociation of the C–Cl bond was observed for PCB 28 (Table 2). In other words, both kinetic and thermodynamic parameters suggest preferential elimination of chlorine from the *ortho* position of the disubstituted ring. In the case of PCB 37, the activation barrier changes in the opposite direction to the thermodynamic stability of the product; however, the differences in the thermodynamic stabilities of biphenylyl radicals are insignificant (2.4 kJ/mol). Obviously, this is reflected in the reduced selectivity of the first stage of preparative electrolysis (Scheme 3).

Our results are analogous to those obtained previously for dichlorobiphenyls [24, 25]. The calculated activation barriers are consistent with the regioselectivity observed in the preparative electrolysis of PCB 28 and PCB 37. In both cases, the regioselectivity correlates with the activation barrier. Furthermore, the theoretical regioselectivity conforms to the regioselectivity observed experimentally in another radical anion reaction of PCB 28, namely methoxycarbonylation [13].

Attempted geometry optimization of  $\pi$ -radical anions derived from PCB 29 and PCB 30 possessing three chlorine atoms in the same ring led to structures whose Hessian matrices contained one imaginary frequency; i.e., these structures are transition states rather than intermediate products. Therefore, the reduction of PCB 29 and PCB 30 is a concerted process. Comparison of the results of calculations with

	1			2		3	4		
Parameter	molecule	radical anion	molecule	radical anion (TS)	molecule	radical anion (TS)	molecule	radical anion	
C-Cl bond length, Å	1.763 ( <i>o</i> ) 1.760 ( <i>p</i> ) 1.764 ( <i>p</i> ')	1.790 ( <i>o</i> ) 1.773 ( <i>p</i> ) 1.777 ( <i>p</i> ')	1.760 ( <i>o</i> ) 1.748 ( <i>p</i> ) 1.749 ( <i>m</i> )	1.787 (o) 1.763 (p) 1.773 (m)	1.759 ( <i>o</i> ) 1.756 ( <i>p</i> ) 1.758 ( <i>o</i> )	1.807 ( <i>o</i> ) 1.781 ( <i>p</i> ) 1.797 ( <i>o</i> )	1.753 (m) 1.751 (p) 1.764 (p')	1.774 (m) 1.764 (p) 1.777 (p')	
NBO charge on the chlorine atom, a.u.	0.004 ( <i>o</i> ) 0.000 ( <i>p</i> ) -0.013( <i>p</i> ')	-0.065 ( <i>o</i> ) -0.062 ( <i>p</i> ) -0.070 ( <i>p</i> ')	0.012 (o) 0.032 (p) 0.028 (m)	-0.058 ( <i>o</i> ) -0.040 ( <i>p</i> ) -0.040 ( <i>m</i> )	0.018 ( <i>o</i> ) 0.014 ( <i>p</i> ) 0.018 ( <i>o</i> )	-0.098 ( <i>o</i> ) -0.074 ( <i>p</i> ) -0.070 ( <i>o</i> )	0.019 (m) 0.020 (p) -0.013(p')	-0.039 (m) -0.038 (p) -0.070 (p')	
Mulliken charge on the chlorine atom, a.u.	0.192 (o) 0.211 (p) 0.193 (p')	0.075 ( <i>o</i> ) 0.104 ( <i>p</i> ) 0.098 ( <i>p</i> ')	0.226 (o) 0.271 (p) 0.244 (m)	0.095 ( <i>o</i> ) 0.108 ( <i>p</i> ) 0.134 ( <i>m</i> )	0.198 (o) 0.239 (p) 0.199 (o)	-0.040 ( <i>o</i> ) 0.065 ( <i>p</i> ) 0.088 ( <i>o</i> )	0.209 (m) 0.250 (p) 0.196 (p')	0.153 (m) 0.159 (p) 0.114 (p')	
φ, <sup>a</sup> deg	57	28	58	31	90	44	38	0	
$\Delta E^{\neq, b}$ kJ/mol		1.9 ( <i>o</i> ) 6.0 ( <i>p</i> ) 13.1 ( <i>p</i> ')						2.7 (p) 13.2 (m) 17.9 (p')	
$\Delta E$ , <sup>c</sup> kJ/mol		0 ( <i>o</i> ) min 16.3 ( <i>p</i> ) 16.3 ( <i>p</i> ')		0 (o) min 8.6 (p) 9.4 (m)		0 (o) min 8.2 (p)		0 (m) min 2.4 (p) 2.4 (p')	
$\Delta G$ (electron transfer), eV		-2.05		-2.06		-1.96		-2.23	

**Table 2.** Selected structure and energy parameters of trichlorobiphenyls 1–4 and  $\pi$ -radical anions derived therefrom determined by quantum chemical calculations (solvent acetonitrile)

<sup>a</sup> Dihedral angle formed by the benzene rings. <sup>b</sup> Energy barrier to the fragmentation of radical anion. <sup>c</sup> Relative energy of radical.

the experimental data on the regioselectivity of preparative electrolysis showed that relative thermodynamic stability of the electrolysis products is the main factor responsible for the regioselectivity.

Thus, in keeping with the theoretical data, the electrochemical reduction of not all of the examined trichlorobiphenyls follows the stepwise mechanism. Congeners containing chlorine atoms in both rings (PCB 28 and PCB 37) give rise to stable  $\pi$ -radical anions as intermediate species, and the reduction is a stepwise process. Electron transfer to PCB 29 and PCB 30 molecules leads to barrierless formation of orthobiphenvlvl radical/chloride ion couple. The regioselectivity of the reduction of PCB 28 and PCB 37 is determined by the activation barrier to dissociation of the C-Cl bond in intermediate radical anion, which increases in going from ortho- to para- and then to meta-chlorine atom. In the case of PCB 29 and PCB

30, the regioselectivity depends on the thermodynamic stability of the aryl radical formed as a result of elimination of chloride ion.

In summary, by using four different trichlorobiphenyls as substrates we showed that electrochemical reduction provides a convenient method for selective hydrodechlorination of PCBs. The chlorine atom in the *ortho* position with respect to the bridging bond is reduced most readily, and next follows *para*and then *meta*-chlorine atom. The data were obtained in the framework of a complementary approach including electrochemical measurements, preparative electrolysis, and quantum chemical calculations. The validity of this approach is confirmed by similarity of the conclusions on the regioselectivity and relative reactivity, which were drawn on the basis of the results obtained by different methods.



Fig. 2. Optimized geometric structures and HOMO isosurfaces of  $\pi$ -radical anions derived from PCBs (a) 1 and (b) 4.

#### **EXPERIMENTAL**

Pure trichlorobiphenyls PCB 28 (1), PCB 29 (2), PCB 30 (3), and PCB 37 (4) and dichlorobiphenyls (authentic samples and internal standards for GLC) were synthesized by the Suzuki reaction from the corresponding substituted iodobenzenes and arylboronic acids according to the procedure described in [18] using a carbene palladium complex [37, 38] as catalyst. The other reagents and solvents were commercial products (Aldrich) which were used without additional purification.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance II+ spectrometer [400.13 (<sup>1</sup>H), 100.61 MHz (<sup>13</sup>C)] at room temperature using CDCl<sub>3</sub>

as solvent. GC/MS analysis was performed on a Shimadzu GCMS QP-2010 SE instrument [electron impact, 70 eV; a.m.u. range 35-500 Da; ion source temperature 200°C; Rtx-5MS column, 30 m×0.32 mm, film thickness 0.25 µm; carrier gas argon, flow rate 0.8 mL/min; oven temperature programming from 50°C (2 min) to 250°C at a rate of 25 deg/min, 20 min at 250°C]. GLC analysis was performed with a Khromatek Crystall 5000.2 chromatograph equipped with a flame ionization detector and an Optima 1 capillary column (25 m×0.32 mm, film thickness 0.35 µm). Electrochemical measurements were carried out on a CHI 660A workstation (CH Instruments, USA) using a glassy carbon working electrode with a diameter of 3 mm (CH Instruments, USA), a platinum auxiliary electrode, and an Ag/Ag<sup>+</sup> (10 mM) reference pseudo-



Fig. 3. Potential energy surface cross sections along the reaction coordinate for the fragmentation of  $\pi$ -radical anions of PCBs (a) 1 and (b) 4.

electrode. The glassy carbon electrode was polished with alumina and ultrasonically treated prior to use. The cyclic voltammograms were recorded using a single-compartment electrochemical cell at 298 K. Uncompensated resistance of the solution was measured before each run, and the ohmic drop was compensated to a residual value of ~35  $\Omega$ .

**Bulk electrolysis.** A four-necked electrolysis cell was filled with a solution of trichlorobiphenyl (30 mM) and tetrabutylammonium perchlorate (0.2 M) in anhydrous acetonitrile (20 mL), and the solution was purged with argon of ultrapure grade. A constant potential (-2.6 V vs. Ag/Ag<sup>+</sup>) was applied to the working electrode under continuous stirring and slowly bubbling argon through the solution. The electrolysis was terminated when the current decreased to a background value. The mixture was poured into water (30 mL) and extracted with *n*-hexane (30 mL). The organic phase was separated, washed with brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and analyzed by GC/MS.

**Quantum chemical calculations** were performed in terms of the density functional theory using B3LYP functional and 6-31+G(d) basis set (Gaussian 09 [39]). Open and closed shell models were applied to calculate radical anions and neutral molecules, respectively. Energy minimization was conducted until a state without imaginary frequencies was obtained. Solvent effects were included in terms of the polarizable continuum model. The potential energy surfaces for radical anions were scanned with respect to the C–C1 bond length through a step of 0.05 Å with full geometry optimization at each step.

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## CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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