ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 4, pp. 800–808. © Pleiades Publishing, Ltd., 2010.
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Reduction of Mono- and Dichlorobiphenyls with Sodium-Naphthalene Complex

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Received September 5, 2009

Abstract—Reactivity of low-chlorinated congeners of polychlorinated biphenyls in relation to sodium-naphthalene complex in THF was studied. It was shown that the rate of reduction of these substrates weakly depended on their structure. The regioselectivity of the first stage of reduction of dichlorobiphenyls may be caused by relative stability of the intermediately formed aryl radicals. Kinetic analysis of the processes taking place in the system showed that sodium-naphthalene complex alongside with one-electron reduction of dichlorobiphenyls is involved also in the multi-electron reduction leading directly to biphenyl avoiding the stage of formation of monochlorobiphenyl.

DOI: 10.1134/S1070363210040201

One of the results of rapid development of chemical industry in the middle of the XX century is the problem of elimination of the stable organic contaminants disastrous for human beings in the environment. To this group belong 12 types of chemical substances including polychlorinated biphenyls containing from one to ten atoms of chlorine in the molecule. Commercial polychlorinated biphenyls are complex mixtures consisting of 50–70 individual compounds, the so-called congeners. Mullins et al. [1] identified all 209 possible congeners. Their physicochemical properties such as thermostability, high boiling point, non-flammability, stability to chemical decomposition, low solubility in water, miscibility with organic solvents and plastics determined the application of polychlorinated biphenyls in various branches of industry [2–4]. Nowadays production of these substances is cut off, but because of leakages from various technical devices they continue to contaminate the environment.

Natural decomposition of polychlorinated biphenyls proceeds by different pathways under the aerobic as well as anaerobic conditions. Only low chlorinated congeners are oxidized by microorganisms under the aerobic conditions [5, 6], but their content in technical mixtures is usually low. Besides because of low solubility in water polychlorinated biphenyls appearing in waste water are concentrated in the bottom deposits. Hence, their natural biodegradation takes place mainly under the anaerobic conditions characteristic of bottom deposits. It proceeds according to the pathway of reductive dechlorination with the successive formation of less chlorinated congeners [7]. Highly chlorinated polychlorobiphenyls are destructed in the same manner, moreover, their reactivity is higher as compared to that of low chlorinated congeners [7].

As is known [8], many microorganisms can assimilate the chlorinated compounds enzymatically transferring electrons to these substances. For example, *Desulfomonile tiedjei* obtain ATP necessary for their growth using the reductive hydrodechlorination as the source of energy [9].

Considerable part of methods of reprocessing of polychlorinated biphenyls and some other stable organic contaminants based on the reactions of substitution of chlorine atoms with hydrogen or any functional group include the stage of electron transfer. First of all it is the reductive dechlorination of polychlorobiphenyls by alkali metals (for example, sodium) in the presence of compounds characterized as good hydrogen donors (hexane, cyclohexane) [10–13]. Note further the reduction of polychlorinated biphenyls

under the action of alkali metals in the presence of such solvents as ammonia, amines, alcohols or esters (the so-called "solvated electron" technology) [14]. And finally, it is a recently developed method of carbonylation of polychlorobiphenyls using the effective catalytic systems on the basis of the epoxide-modified cobalt carbonyl in the alkaline ethanol medium [15, 16].

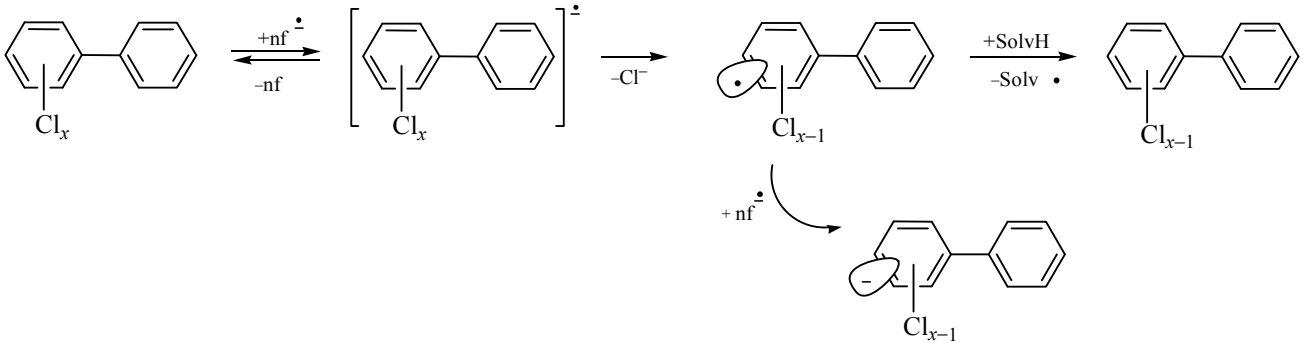
Hence, the key stage of a series of methods of reprocessing of polychlorobiphenyls is the radical anion activation of these inert molecules.

No less important for biodegradation of the compounds under study taking place in the nature is the stage of electron transfer. It explains the interest to establishing the laws of the radical anion reactions in the series of polychlorobiphenyls. At the same time the data on the intersubstrate selectivity in the radical anion reduction of polychlorinated biphenyls is practically absent, and the positional selectivity is studied insufficiently [17]. That is why it seems important to study the hydrodechlorination of polychlorinated biphenyl congeners.

In this work the hydrodechlorination of low chlorinated congeners, mono- and dichlorobiphenyls, is studied. In this case comparatively simple mixtures of the products are formed considerably facilitating the establishment of the reaction rules. The reduction with the alkali metal–naphthalene complex was chosen as the most widespread (alongside with the reduction with a solution of sodium in liquid ammonia) chemical method of one-electron reduction of organic halides [17].

1. Studies of relative reactivity of polychlorinated biphenyls. The first step in solving the problem under investigation was the evaluation of relative reactivity of monochlorobiphenyls and some of dichlorobiphenyls in the reduction with sodium–naphthalene complex dissolved in THF. This reaction proceeds according to the following scheme (Scheme 1) [18]:

Scheme 1.



nf is naphthalene.

If the concentration of naphthalene radical anions in the solution is very small, the formation of the reduction products may proceed by the abstraction of the hydrogen atom from the solvent. When THF is used as a solvent this stage is quick because THF is a good donor of hydrogen atom for the aryl radical [19]. At the significant concentrations of naphthalene radical anions in solution aryl radical undergoes the preferable reduction to aryl anion because the transfer of electron from the naphthalene anion radical to the aryl radical proceeds with the diffusion rate [20]. Aryl anion may further form the reaction product by the abstraction of a proton from the solvent during the workup of the reaction mixture or may undergo further reduction.

The reaction was carried out at 20–22°C by three methods. In the first one the formation of sodium-naphthalene complex took place *in situ* at the excess of sodium and naphthalene in THF (procedure I). In the second one solution of substrate in THF was treated with the previously prepared solution of sodium-naphthalene complex in THF (procedure II). In the third case solution of the substrate in 1,2-dimethoxyethane was treated with the previously prepared solution of lithium–naphthalene complex dissolved in 1,2-dimethoxyethane (procedure III). The data obtained are listed in Table 1.

While using the previously prepared sodium-naphthalene (procedure II) or lithium-naphthalene complex (procedure III) reaction with aryl halides proceeds very fast (in several seconds after mixing of solutions). It is accompanied by the disappearance of the intense dark-green color of the solution of the

Table 1. Dependence of composition of the reaction mixture in hydrodechlorination of 3,4-dichlorobiphenyl on the experimental conditions (molar % according to GLC, for procedures and relative error see Experimental)

Component of the reaction mixture	Procedure I	Procedure II	Procedure III
3,4-Dichlorobiphenyl	68	93	94
3-Chlorobiphenyl	7	0.4	0.3
4-Chlorobiphenyl	<0.01	<0.01	<0.01
Biphenyl	25	4.7	5.2

complex. The analysis of samples taken at different times after the addition of reagent to the substrate showed that the conversion achieved during the first 20–30 seconds did not increase later. While using the excess of sodium and naphthalene with respect to alkyl chloride and the formation of complex *in situ* (procedure I) the conversion of the substrate increases in the course of several hours what agrees with the reported data on the rate of formation of the complex [21]. In this case the last process determines evidently the rate of reduction of aryl chloride. The resemblance of the results obtained while using a solution of sodium-naphthalene complex in THF and a solution of lithium-naphthalene complex in dimethoxyethane (known as better chelating agent in relation to lithium cations) (procedure III) shows that the variation in the complex solvation under the reaction conditions does not affect its reducing properties.

By the method of competing reactions the relative rates of consumption of substrates were evaluated. The studies were carried out according to the procedure I because this method of evaluation requires a significant (more than 30%) conversion. Obtained $(k_{obs})_{rel}$ values are listed in Table 2 together with the reported data on the values of the reducing potentials of the corresponding aryl halides.

It may be suggested that the rate of one-electron reduction of the aryl halides under the reaction conditions is determined by the rate of the formation and fragmentation of the radical anion, and the abstraction of hydrogen atom from the molecule of solvent by the aryl radical (the last stage in the Scheme 1) is fast. In the opposite case by-products of recombination of the aryl radicals or of their reaction with naphthalene should have formed, but no such data was obtained. Material balance was preserved even at the significant conversion of substrate (Table 1, procedure I).

Table 2. Relative rate constants of the reduction of mono- and dichlorobiphenyls with sodium-naphthalene complex, procedure I

Substrate	$(k_{obs})_{rel}$	$-E_{1/2}$,[a] V [22]
2-Chlorobiphenyl	1.0	2.092
3-Chlorobiphenyl	0.79±0.04	2.108
4-Chlorobiphenyl	1.09±0.03	2.056
2,3-Dichlorobiphenyl	0.90±0.05	1.956
2,4-Dichlorobiphenyl	1.14±0.05	1.983
2,5-Dichlorobiphenyl	1.17±0.06	1.942
3,4-Dichlorobiphenyl	0.95±0.02	1.871
4,4'-Dichlorobiphenyl	1.11±0.04	2.000

[a] Half-wave potentials of polarographic reduction against the standard calomel electrode.

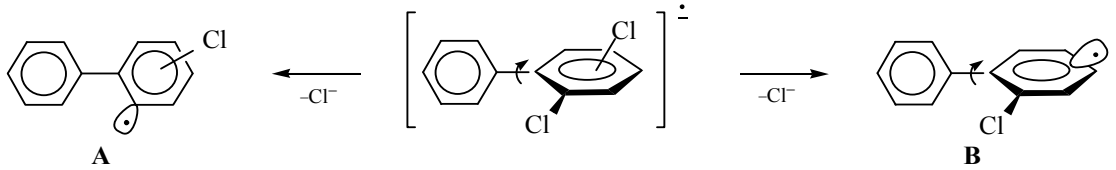
In its turn the rate of fragmentation of the radical anion depends on its energy of formation in a complex manner. Standard reducing potential of the aryl halide may be used as its quantitative characteristic. On the one hand, a less negative value of the reducing potential of substrate, the aryl halide, corresponds to a higher concentration of radical anion, and due to that to the increase in the rate of its fragmentation. On the other hand, the fragmentation of the radical anion having lower energy of formation under the equal condition must proceed slower according to the Bell-Evans-Polanyi principle. Such dependence of the rate constant of fragmentation of radical anions on the energy of its formation was really observed for the series of aryl halides [23, 24].

Evidently just the opposite trend in the two above-mentioned factors leads to the fact that for mono- and dichlorobiphenyls under study relative reactivity of substrates in the reduction with sodium-naphthalene complex occurs to be equal and independent of the reducing potential of the aryl halide. It is somehow unusual for the radical anion reactions.

2. Regioselectivity of fragmentation of radical anions of dichlorobiphenyls. Similar reactivity of mono- and dichlorobiphenyls under investigation in the reactions of the one-electron reduction gives no opportunity to establish how the position of chlorine atom in the molecule of aryl halide affects the rate of fragmentation of the radical anion. It compelled us to develop an approach to the investigation of the regioselectivity problem of this reaction from another side. It is evident that while using as the substrate the

unsymmetrically substituted dichlorobiphenyl the abstraction of chloride anion from two different positions of the radical anion is possible. The greatest interest presents the reduction of polychlorobiphenyls having one chlorine atom in *ortho*-position in relation to the C–C bond between the phenyl rings (Scheme 2).

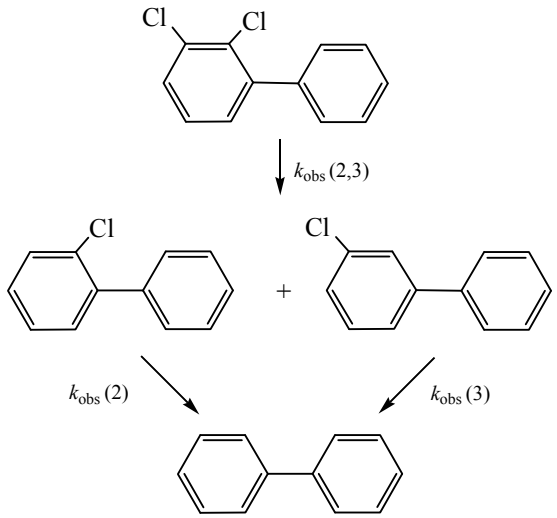
Scheme 2.



The radicals **A** and **B** abstract hydrogen atom from the molecule of solvent and give a mixture of monochlorobiphenyls, the products of the one-electron reduction of the starting substrate. Monochlorobiphenyls formed in their turn may take part in the reduction leading finally to biphenyl.

The assumed kinetic scheme of reduction of the unsymmetrically substituted dichlorobiphenyl without the consideration of possible formation of the aryl anion is presented below for the case of 2,3-dichlorobiphenyl (Scheme 3):

Scheme 3.



Here k_{obs} is the observed rate constant of reduction of this congener.

In agreement with the Scheme 3 and basing on the data on the relative reactivity of various mono- and dichlorobiphenyls (Table 2) it could be expected that in the early stages of the reaction when the concentration of starting dichlorobiphenyl exceeds significantly the concentrations of monochlorobiphenyls formed only the starting substrate and the products of its one-electron reduction will be present in the reaction mixture. In this case the regioselectivity of fragmentation of the radical anion will be quantitatively characterized by the ratio of concentrations of monochlorobiphenyls formed.

For the evaluation of regioselectivity of the process of one-electron reduction a series of dichlorobiphenyls was reduced to a small conversion (5–6%) using the procedure II. The results obtained are presented in Table 3. It follows from these data that even at a small (<5%) conversion of starting substrate the system in all the cases together with monochlorinated substances contains significant amount of unsubstituted biphenyl exceeding the amounts of monochlorobiphenyls. This fact together with the data on relative reactivity of mono- and dichlorobiphenyls in the reduction with sodium-naphthalene complex disagree with the above-presented kinetic scheme.

This contradiction can be eliminated by an assumption that alongside the one-electron reduction the multi-electron reduction process takes place.

$$Ar_2Cl_2 \rightarrow (Ar_2Cl_2)^{\cdot-} \rightarrow (Ar_2Cl)^{\cdot} \rightarrow (Ar_2Cl)^{-} \rightarrow \ldots \rightarrow Ar_2H_2$$

Such multi-electron processes are well known for the electrochemical reduction [20] when the radical formed by fragmentation has no time to leave the cathode space and is reduced further to monoanion or even dianion in the case of the presence in it of several functional groups.

In this case considering the above-presented experimental data on the relative reactivity of mono- and dichlorobiphenyls kinetic scheme of the process may be descibed as follows (by an example of 2,3-dichlorobiphenyl, Scheme 4).

It follows from Scheme 4 and the data presented in the Tables 2, 3 that practically all biphenyl under the conditions of the experiment (conversion of starting

Table 3. Composition of the reaction mixture of hydrodechlorination of some dichlorobiphenyls at low conversions (mol %, GLC data)

Substrate	Product of one-electron reduction[a]	Biphenyl
2,3-Dichlorobiphenyl	3-Chlorobiphenyl (2.8)	3.2
2,4-Dichlorobiphenyl	4-Chlorobiphenyl (1.0)	3.8
2,5-Dichlorobiphenyl	3-Chlorobiphenyl (0.6)	3.6

[a] In all cases only one monochlorobiphenyl was found. Second possible product, 2-chlorobiphenyl, was absent. Detection limit was 0.007–0.01 mol % with respect to the taken dichlorobiphenyl as was evaluated specially by addition of the given amount of 2-chlorobiphenyl to the reaction mixture.

2,3-dichlorobiphenyl < 5–6%) is formed by multi-electron reduction of dichlorobiphenyl. Hence, the contribution of the multi-electron reduction expressed as the ratio of the amount of biphenyl obtained to the summary conversion of substrate in the course of hydrodechlorination with sodium–naphthalene complex in THF solution is sufficiently high (Table 4).

Constants k_5 and k_6 are diffusion constants [20], that is why in this case $k_5 = k_6$. Considering the correction taking into account the part of multi-electron process and regarding the constants k_3 and k_4 as close in value we evaluated the regioselectivity of the one-electron reduction by the kinetic Scheme 4 and the data of the Table 3 (see Table 4).

From the data presented it is evident that for all dichlorobiphenyls having one chlorine atom in the *ortho*-position to the C–C bond between two aromatic rings (mono-*ortho*-substituted dichlorobiphenyls) the fragmentation by this position is preferred. The regioselectivity of hydrodechlorination in this case may be affected by different stability of the products formed in the stage of fragmentation, that is, of aryl radicals, connected with the specific features of their spatial arrangement. Possible pathways of fragmentation of radical anion formed from mono-*ortho*-substituted dichlorobiphenyl are shown in Scheme 2. The quantum chemical calculation of geometry of starting dichlorobiphenyl molecules and the aryl radicals formed from them (Gaussian 03 program [25]) was carried out by the density functional DFT

Scheme 4.

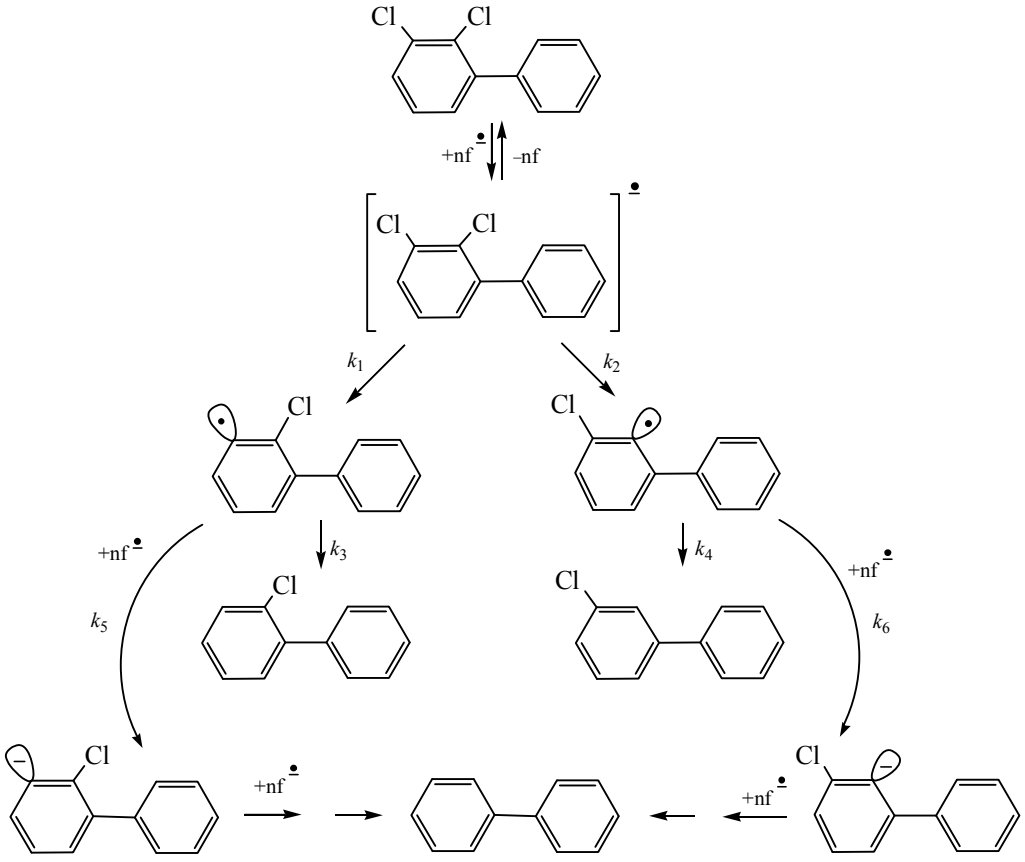


Table 4. The contribution of the process of multi-electron reduction and regioselectivity of one-electron reduction of dichlorobiphenyls in the hydrodechlorination with sodium-naphthalene complex

Substrate	Part of multi-electron reduction, %	k_1/k_2[a]
2,3-Dichlorobiphenyl	53	<0.0035
2,4-Dichlorobiphenyl	79	<0.010
2,5-Dichlorobiphenyl	86	<0.017

[a] k_2 is the rate constant of fragmentation of dichlorobiphenyl radical anion by the C–Cl bond located in *ortho*-position to the bond between the phenyl rings, k_1 is the rate constant of fragmentation of dichlorobiphenyl radical anion by the alternative C–Cl bond.

Table 5. Values of dihedral angles, deg., between the planes of phenyl rings in the radicals formed during the decomposition of radical anions of dichlorobiphenyls, and difference in energies of these radicals according to the data of calculations by the density functional method DFT B3LYP/6-31+G(d,p) (Gaussian-03 [25])

Dichlorobiphenyl	φ, deg		$\Delta E_{\mathbf{A-B}}$, kJ mol^{-1}
	Radical of type **A**	Radical of type **B**	
2,3-Dichlorobiphenyl	25	56	16
2,4-Dichlorobiphenyl	27	56	13
2,5-Dichlorobiphenyl	28	57	14

B3LYP/6-31+G(d,p). The results obtained are listed in Table 5. If in mono-*ortho*-chlorosubstituted dichlorobiphenyls dihedral angles between the planes of aromatic rings are sufficiently large and reach 56°–60°, in the corresponding radicals **A** (Scheme 2) this parameter decreases to 25°–28°. It improves significantly the conjugation of π-orbitals of aromatic rings that significantly stabilizes radical **A** as compared to the radical **B**.

The energy gain during the abstraction of chloride ion from the position 2 of the radical anion of mono-*ortho*-substituted dichlorobiphenyls compared to the alternative pathway according to our calculations is about 13–14 kJ mol^{-1}. That is why in the fragmentation of radical anion formed from mono-*ortho*-substituted dichlorobiphenyl the abstraction of chloride ion from the position 2 is preferred.

For the reaction of fragmentation of radical anions of the aryl halides the Markus-Hush model [24,26,27] connecting the activation energy $\Delta G^{\#}$ with the reaction energy ΔG_0 [Eq. (1) in the Scheme 5] is applicable.

Scheme 5.

$$RX^{\cdot-} \rightarrow R^{\cdot} + X^{-},$$

$$\Delta G^{\#} = \frac{(\Delta G_0)^2}{16\Delta G_0^{\#}} + \frac{\Delta G_0}{2} + \Delta G_0^{\#}. \qquad (1)$$

Here $\Delta G^{\#}_0$ is the internal barrier of free energy equal to $(D_{RX^-})/4$; D_{RX^-} is the energy of dissociation of the carbon-halogen bond in the radical anion.

It follows from Eq. (1) that the established difference in the reaction energy (13–16 kJ mol^{-1}) must lead to the difference in the rate constants of fragmentation of one radical anion according to different pathways in several tens times even at the unlimitedly large $\Delta G_0^{\#}$. At the decrease in the internal barrier the difference will increase still more. Besides, $\Delta G_0^{\#}$ will also decrease with the decrease in energy of the aryl radical formed in the course of fragmentation. Hence, the preferred fragmentation of the chloride ion from the position 2 of mono-*ortho*-substituted dichlorobiphenyl arises from the lower energy of the corresponding aryl radical.

On the whole the studies performed showed that the intersubstrate selectivity in the reactions of mono- and dichlorobiphenyls with sodium-naphthalene complex in THF is not high. At the same time the regionselectivity of the reduction for all mono-*ortho*-substituted dichlorobiphenyls is significant. The abstraction of the chlorine atom located in the *ortho*-position to the C–C bond between two aromatic rings is preferred.

Note also that sodium-naphthalene complex is not only the one-electron reducing agent as it was considered before. In the reduction of polychlorobiphenyls together with the one-electrion reduction the multielectron process takes place, and its contribution is rather large.

EXPERIMENTAL

GLC analysis was carried out on a Chrom-5 chromatograph equipped with the flame-ionization detector, carrier gas argon, flow rate 20–30 ml min^{-1}. Two types of glass columns were used, 2500×3 mm filled with 10% of SE-30 on Chromaton N-Super (80–100 mesh), and 2500×3 mm filled with 5% of OV-225 on Chromaton N-Super. Evaporator temperature 200°C, oven temperature 200°C.

Calculation of concentrations of the aryl chlorides and biphenyl was carried out according to the formula

$$\frac{C_X}{C_X^0} = \frac{S_X/}{S_X^0/S_{st}^0}, \quad (2)$$

where C_X and C_X^0 are the concentrations of the evaluated substance after performing the reaction and the initial one respectively, S_X and S_X^0, S_{st} and S_{st}^0 are the areas of peaks of the evaluated substance and the internal standard (docosane) after performing the reaction and the initial ones. Each probe was analyzed three times and the mean square deviation of the evaluated square ratio was established. In the case of square deviation being more than 2% the sample was analyzed several times more until the achievement of the above-mentioned value of deviation. Hence, relative deviation of analysis in all the cases was no more than 8% at the exclusion of the specially marked ones.

General Procedures of Reduction

Procedure I. Reduction with sodium-naphthalene complex formed *in situ*. THF, 2 ml, 500 mg of naphthalene, and 30 mg of sodium were placed in a 5 ml Schlenk flask equipped with a magnetic stirrer and a reflux condenser. The flask was flushed with argon and heated to boiling. Dark green color marked the beginning of formation of sodium–naphthalene complex. After that the mixture was cooled to 20–22°C and a solution of 0.4–0.6 mmol of substrate[1] and the internal GLC standard (docosane) in 2 ml of THF was added. Reaction was carried out until the 30–70% conversion. Reaction progress was controlled by the analysis of samples taken each 5–10 min.

Procedure II. Reduction with the preliminary formed sodium-naphthalene complex (shortage of complex). *a. Preparing the solution of sodium-naphthalene complex*. THF, 12 ml, 150–210 mg of naphthalene, and 50–60 mg of sodium were placed in a 25 ml Schlenk flask equipped with a magnetic stirrer and a reflux condenser. The flask was flushed with argon and heated to boiling. The appearance of the dark green color marked the beginning of formation of sodium–naphthalene complex [solution (1)]. Reaction mixture was refluxed for 2 h. Under these conditions the conversion of naphthalene to the sodium complex was complete [21, 28]. The reaction mixture was cooled to room temperature to give the solution 1 with the calculated concentration of complex 0.10–0.13 mol l^{-1}.

***b. Performing the reduction*.** A solution of 0.08–0.12 g of dichlorobiphenyl and the internal GLC standard (docosane) in 2 ml of THF was prepared in a 10 ml Schlenk flask equipped with a magnetic stirrer, and the apparatus was flushed with argon. A 1.0 ml sample of solution (1) (sodium–naphthalene complex content 0.10–0.13 mmol) was added at 20-22°C under argon to the reaction mixture. One minute after addition of sodium-naphthalene complex a sample was taken and treated according to the general procedure.

Procedure III. Reduction with the preliminary formed lithium-naphthalene complex (shortage of complex). *a. Preparing the solution of lithium-naphthalene complex*. 1,2-Dimethoxyethane, 12 ml, 150–210 mg of naphthalene, and 30–40 mg of lithium were placed in a 25 ml Schlenk flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was flushed with argon and heated to boiling. The appearance of dark green color marked the beginning of the formation of lithium–naphthalene complex [solution (1)]. Reaction mixture was refluxed for 2 h and cooled to room temperature (concentration of complex 0.10–0.13 mol l^{-1}).

b. Performing the reduction. A solution of 0.08–0.12 g of dichlorobiphenyl and the internal GLC standard (docosane) in 2 ml of 1,2-dimethoxyethane was prepared in a 10 ml Schlenk flask equipped with a magnetic stirrer and flushed with argon. Solution (1), 1 ml (lithium–naphthalene complex content 0.10–0.13 mmol) was added under argon to the reaction mixture. After 1 min a sample of the reaction mixture was taken and treated according to the general procedure.

Procedure for Preparing GLC Samples

A sample of the reaction mixture, 0.2–0.3 ml, was added to 3 ml of the hexane–water mixture. The mixture obtained was shaken intensely, and after the separation of layers the organic layer was taken for analysis.

Evaluation of Relative Rates of the Reduction of Polychlorobiphenyls

Evaluation of relative rates of the reduction of polychlorobiphenyls was carried out by the competing reactions method according to the procedure I. Calculation of the rate constant values was carried out

[1] In concurrent reactions two substrates were used in a ratio about 1:1.

Table 6. Evaluation of relative rate constant of reduction for the pair 2-chlorobiphenyl–3-chlorobiphenyl

Amounts loaded, mmol			C_1/C_1^0	C_2/C_2^0	$(k_{obs})_2/(k_{obs})_1$[a]
1 2-chloro biphenyl	2 3-chloro biphenyl	internal standard docosane)			
0.25	0.26	0.15	0.64	0.72	0.74
			0.58	0.65	0.79
			0.53	0.60	0.80
0.30	0.28	0.16	0.63	0.70	0.77
			0.56	0.61	0.85
			0.43	0.53	0.77

[a] $(k_{obs})_2/(k_{obs})_1 = 0.79\pm0.04$.

on the basis of consumption of starting substrates according to the formula:

$$(k_{obs})_{rel} = (k_{obs})_2/(k_{obs})_1 = \ln (C_2/C_2^0)/\ln (C_1/C_1^0),$$

where $(k_{obs})_1$ and $(k_{obs})_2$ are the rate constants of reduction of polychlorobiphenyls, C_1^0 and C_2^0 are concentrations of polychlorobiphenyls at the initial moment, C_1 and C_2 are their concentrations in the sample.

Following pairs of substrates were used: 2-chlorobiphenyl and 3-chlorobiphenyl, 2-chlorobiphenyl and 4-chlorobiphenyl, 2-chlorobiphenyl and 3,4-dichlorobiphenyl, 2-chlorobiphenyl and 4,4'-dichlorobiphenyl, 2,4-dichlorobiphenyl and 3,4-dichlorobiphenyl, 2,5-dichlorobiphenyl and 3,4-dichlorobiphenyl, 2,3-dichlorobiphenyl and 3,4-dichlorobiphenyl. Evaluation of the relative rate constant was carried out twice for each pair of polychlorobiphenyls. In each experiment 3-4 samples were taken and the relative rate constant was evaluated for each sample independently.

In the Table 6 an example of evaluation of the relative rate constant for the pair 2-chlorobiphenyl–3-chlorobiphenyl is presented.

ACKNOWLEDGMENTS

The work was carried out with the financial support of Russian Fundation for Basic Research (grant no. 08-03-91301-IND_a).

REFERENCES

1. Mullins, M.D., Pochini, C.M., Mc-Crindle, S., Romkes, M., Safe, S.H., and Safe, L.M., *Environ. Sci. Technol.*, 1984, vol. 18, no. 6, p. 468.
2. Ivanov, V. and Sandell, E., *Environ. Sci. Technol.*, 1992, vol. 26, no. 10, p. 2012.
3. Kannan, N., Schulz-Bull, D.E., Petrick, G., and Duinker, J.C., *Intern. J. Environ. Anal. Chem.*, 1992, vol. 47, p. 201.
4. Safe, S., *Critical Rev. Toxicol.*, 1984, vol. 13, p. 319.
5. Triska, J., Kuncova, G., Mackova, M., Novakova, H., Paasivirta, J., Lahtipera, M., and Vrchotova, N., *Chemosphere*, 2004, vol. 54, p. 725.
6. Havel, J. and Reineke, W., *FEMS Microbiol. Lett.*, 1991, vol. 78, p. 163.
7. Tiedje, J.M., Quesen, J.F., and Chee-Sanford, J., *Biodegradation*, 1993, vol. 4, no. 7, p. 231.
8. Dolfing, J., *Arch. Microbiol.*, 1990, vol. 153, p. 264.
9. Mohn, W.W. and Tiedje, J.M., *Arch. Microbiol.*, 1991, vol. 157, p. 1.
10. Ariizumi, A., Otsuka, T., Kamiyama, M., and Hosomi, M., *J. Environ. Chem.*, 1997, vol. 7, p. 793.
11. Suzuki, H., *Environ. Manag.*, 1997, vol. 33, p. 889.
12. Noma, Y., Mitsuhara, Y., Matsuyama, K., and Sakai, S., *Organohalogen Compounds*, 2003, vol. 63, p. 280.
13. Miyoshi, K., Nishio, T., Yasuhara, A., and Morita, M., *Chemosphere*, 2000, vol. 41, p. 819.
14. Pittman, C.U. and He, J., *J. Hazard. Mater.*, 2002, vol. 92, no. 1, p.51.
15. Boyarskii, V.P., Zhesko, T.E., Lanina, S.A., and Tereshchenko, G.F., *Zh. Prikl. Khim.*, 2007, vol. 80, no. 7, p. 1120.
16. Lanina, S.A., Boyarskii, V.P., Zhesko, T.E., Nikiforov, V.A., and Bart, T.Ya., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 1, p. 127.
17. Hawari, J., *J. Organomet. Chem.*, 1992, vol. 437, nos. 1–2, p. 91.
18. Sargent, G.D., *Tetrahedron Lett.*, 1971, vol. 12, no. 35, p. 3279.
19. Jing, L., Nash, J.J., and Kenttmaa, H.I., J. *Am. Chem. Soc.,* 2008, vol. 130, no. 52, p. 17697.
20. Amatore, C., Combellas, C., Lebbar, N.-E., Thiebault, A., and Verpeaux, J.-N., *J. Org. Chem.*, 1995, vol. 60, p. 18.

21. Scott, N.D., Walker, J.F., and Hansley, V.L., *J. Am. Chem. Soc*., 1936, vol. 58, no. 12, p. 2442.
22. Farwell, S.O., Beland, F.A., and Geer, R.D., *Anal. Chem*., 1975, vol. 47, p. 895.
23. Enemaerke, R.J., Christinsen, T.B., Jensen, H., and Daasbjerk, K., J. *Chem. Soc., Perkin Trans. 2*, 2001, no. 9, p. 1620.
24. Saveant, J.M., *J. Phys. Chem*., 1994, vol. 98, no. 14, p. 3716.
25. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuceria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Vreven, Jr.T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Menucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ocherski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, A.D., Daniels, M.C., Strain, O., Farkas, D.K., Malick, S., Rabuck, A.D., Raghavachari, K., Forsmann, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Lacham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonsalez, C., and Pople, J.A., *Gaussian03*, Ver.5, Gaussian Inc., Pittsburg P.A., 2003.
26. Takeda, N., Poliakov, P.V., Cook, A.R., and Miller, J.R., *J. Am. Chem. Soc*., 2004, vol. 126, no. 13, p. 4301.
27. Prasad, M.A. and Sangaranarayanan, M.V., *Chem. Phys. Lett*., 2006, vol. 421, p. 193.
28. Sargent, G.D., Cron, J.A., and Bank, S., *J. Am. Chem. Soc*., 1966, vol. 88, no. 22, p. 5363.