ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 3, pp. 486–495. © Pleiades Publishing, Ltd., 2014.
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Polychlorinated Biphenyls: Correlation between Experimental Data and Quantum-Chemical Simulation

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Received July 22, 2013

Abstract—In order to comprehend the data on reactivity of polychlorinated biphenyls of the Sovol mixture in nucleophilic substitution reactions we have performed quantum-chemical simulation using the RB3LYP\6-31G(d) gas phase approximation. Using the "Atoms-in-Molecules" approach, we have computed charges on the biphenyl carbon atoms adjacent to chlorine; furthermore, absolute chemical hardness and global electrophilicity index have been determined for the studied chlorobiphenyls. The calculated descriptors have been correlated with experimentally determined reactivity of the biphenyls in the hard acid–hard base nucleophilic reactions. The higher reactivity of more chlorinated substrates has been confirmed.

DOI: 10.1134/S107036321403013X

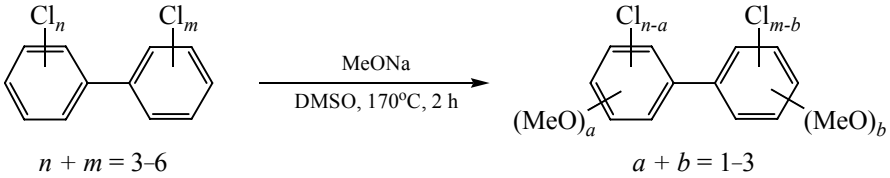
Development of approaches to disposal of technogenic polychlorinated biphenyls (PCBs) is still a topical issue. The only efficient process technologically developed so far has been apparetyly their combustion in rocket engines [1]. This process, however, suffers from significant drawbacks: it is highly energy-demanding, oxygen consumption is quite high (4–6 tons per ton of the biphenyl), and certain technical requirements are posed on the process: the oxidized biphenyl should be retained in the reaction zone during 2–3 s at 2000–3000°C and high turbulence. Therefore, it is impossible to destroy all the produced PCBs via combustion.

Alternative approaches to the biphenyls combustion is their chemical processing. One of the most rapidly developing approaches is hydrodechlorination to give less chlorinated biphenyls [2], biphenyl [3–16], benzene derivatives [5, 17–19], dicyclohexyl [20], etc. Another approach is the nucleophilic substitution of chlorine atoms with other functional groups leading to less chlorinated compounds as well. The so prepared new derivatives of PCBs can be further decomposed via microbiologic methods. Such two-stage procedure is efficient in the case of highly chlorinated biphenyls that cannot be directly decomposed by bacteria [21, 22].

One of the common problems to implement the process of nucleophilic substitution to disposal of technical mixtures of PCBs is incomplete conversion of some of the biphenyls [23–26]. In this work we attempted to understand the reactivity of chlorobiphenyls in a real commercial mixture in nucleophilic substitution reactions by combined analysis of existing experimental data and results of non-empirical quantum-chemical simulation.

The studied object was Russian commercial mixture of polychlorinated biphenyls Sovol (analog of Aroclor 1254) containing 35 congeners: trichlorinated (1%), tetrachlorinated (22%), pentachlorinated (56%), hexachlorinated (20%), and heptachlorinated (1%) biphenyls [23, 26]. The model reaction studied was the interaction of the biphenyls with sodium methoxide MeONa (see Scheme). The choice of model reaction was due to a large volume of experimental data on methoxylation of Sovol mixture [24] as well as of individual polychlorinated biphenyls [25]. Furthermore, MeONa as the simplest alkoxide was expected to have minor steric influence on nucleophilic substitution. Results of Sovol mixture interaction with other aliphatic alcohols were similar [26]. Methoxylated derivatives were identified by GC-MS method in the previous works [24, 25]; chromatogram

of products of Sovol mixture interaction with MeONa is shown in the figure. PCBs and their derivatives were enumerated following IUPAC recommendations and [27].

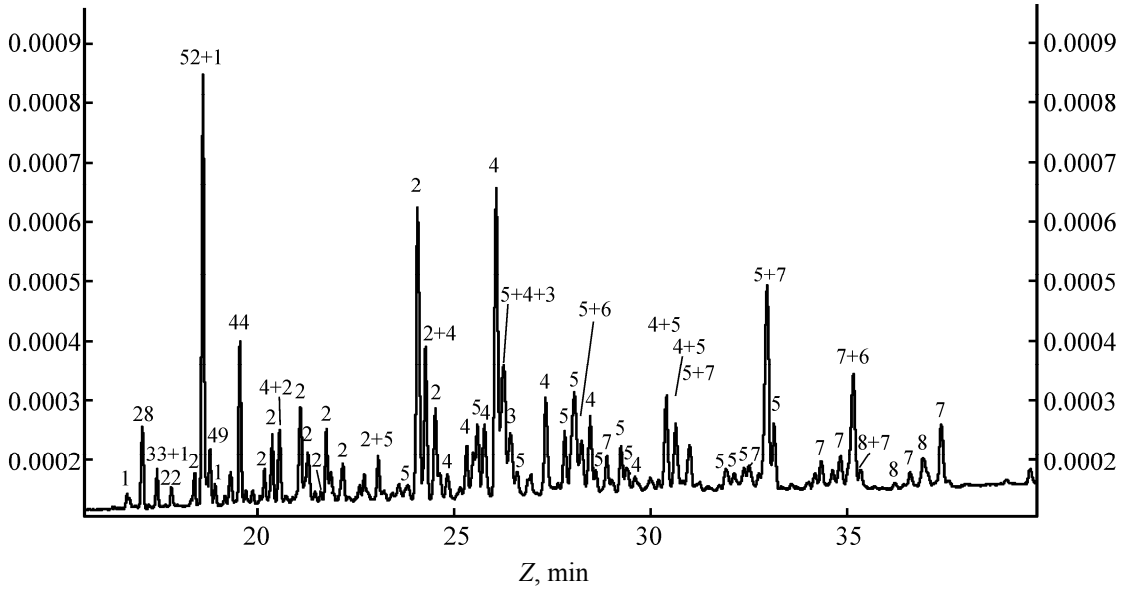


GC-MS study of each of the chromatogram peaks (decay at 70 eV) showed that intense peaks of molecular ions were typical of all methoxylated derivatives. From GC-MS data we were able to determine numbers of chlorine and methoxy substituents in each of the reaction products; however, the positions of the substituents in the biphenyl structure could not be elucidated. Methoxylated derivatives of heptachlorobiphenyls (nos. 170 and 180) were not found in the reaction mixture and, therefore, were not shown in the scheme.

Sovol mixture contained three trichlorobiphenyls: nos. 22, 28, and 33. In the course of the reaction with MeONa, their conversion was not complete, and all the biphenyls yielded at least four monomethoxydichlorobiphenyls (5%) (see figure) [23, 24].

11 isomeric tetrachlorobiphenyls of Sovol mixture gave monomethoxylated (21%, at least 13 compounds) and dimethoxylated (4%, at least 2 compounds) derivatives upon reaction with MeONa (see figure) [23, 24]. The conversion of three compounds (nos. 44, 49, and 52) was not complete; others were fully transformed into MeO-derivatives.

13 isomeric pentachlorobiphenyls of Sovol mixture were converted into monomethoxylated (24%, at least 12 compounds), dimethoxylated (19%, at least 19 compounds), and trimethoxylated (3%, at least 2 compounds) derivatives in the reaction with MeONa (see figure) [23, 24]. For convenience, the pentachlorobiphenyls were divided into groups according to chlorine positions in one of biphenyl rings: 2,3,6-trichloro (group I, nos. 84, 91, 95, and 110), 2,4,5-



Chromatogram of products of polychlorinated biphenyls of Sovol mixture with MeONa. (1) monomethoxylated dichlorinated biphenyls [$C_{12}H_7Cl_2(OCH_3)$]; (2) monomethoxylated trichloro biphenyls [$C_{12}H_6Cl_3(OCH_3)$]; (3) dimethoxylated dichlorinated biphenyls [$C_{12}H_6Cl_2(OCH_3)_2$]; (4) monomethoxylated tetrachloro biphenyls [$C_{12}H_5Cl_4(OCH_3)$]; (5) dimethoxylated trichloro biphenyls [$C_{12}H_5Cl_3(OCH_3)_2$]; (6) trimethoxylated dichlorinated biphenyls [$C_{12}H_5Cl_2(OCH_3)_3$]; (7) dimethoxylated tetrachloro biphenyls [$C_{12}H_4Cl_4(OCH_3)_2$]; (8) trimethoxylated trichloro biphenyls [$C_{12}H_4Cl_3(OCH_3)_3$]. Two figure Arabic numbers designate unreacted polychlorinated biphenyls.

trichloro (group II, nos. 97, 99, 101, and 118), 2,3,4-trichloro (group III, nos. 82, 85, 87, and 105), and PCB no. 92.

6 Isomeric hexachlorobiphenyls of Sovol were converted into dimethoxylated (10%, at least 10 compounds) and trimethoxylated (5%, at least three compounds) derivatives in the reaction with MeONa (see figure) [23, 24]. Of the hexachlorobiphenyls, those with 2,3,4-trichloro substitution in one of the rings formed group IV of PCB (nos. 128, 132, 138), whereas the substitution pattern of PCBs nos. 149, 153, and 156 (group V) did not show common features.

The above-described experimental data showed that the less chlorinated compounds (tri- and tetrachlorobiphenyls) were less reactive in nucleophilic substitution as compared with more chlorinated ones (penta- and hexachlorobiphenyls). The fact of different substitution with chlorine was not sufficient for the understanding of the PCBs reactivity from common structural considerations. However, their reactivity could be estimated by means of quantum-chemical simulation.

The simulation was performed using GAUSSIAN 09 software package [28]. The structures were optimized under density functional theory approximation [RB3LYP\6-31G(d) basis set, gas phase]. Validity of the localized stationary points was confirmed by the Hessian calculation: in the cases of all compounds imaginary vibration frequencies were absent.

The following descriptors were chosen in order to estimate the compounds reactivity: energy of frontier orbitals (E_{HOMO} and E_{LUMO}), absolute chemical hardness (η), and global electrophilicity index (ω). The latter two parameters (η and ω) were calculated according to Eqs. (1)–(5) [29–33]:

$$\eta = S\,(IP - EA), \quad (1)$$

$$IP = -E_{HOMO}, \quad (2)$$

$$EA = -E_{LUMO}, \quad (3)$$

$$\omega = \mu^2/2\eta, \quad (4)$$

$$\mu = -S(IP - EA), \quad (5)$$

where *IP* standing for ionization potential (eV), *EA* is the electron affinity (eV), and μ is the chemical potential (eV).

To explain the direction of nucleophilic substitution at the aromatic ring, we analyzed the charges at carbon atoms (*q*) in the biphenyls molecules. The charges were determined utilizing the "Atoms-in-Molecules" Beider theory [34] and the wave function derived with the RB3LYP\6-31G(d) basis set; the computations were performed using AIMAll software [35].

The torsion angle between the benzene rings at the rotation around C–C bond (φ) computed in the frame of the RB3LYP\6-31G(d) method served as additional descriptor to determine the electron density distribution in the molecules and, hence, their reactivity.

Values of E_{HOMO} and E_{LUMO}. Analysis of additional descriptors. Values of E_{HOMO} and E_{LUMO} calculated using AIM method are given in Table 1. In most cases, E_{LUMO} of trichlorobiphenyls was higher than that of hexachlorobiphenyls; thus, electrophilicity of more chlorinated congeners was higher. Therefore, highly chlorinated biphenyls of Sovol mixture should be more reactive than their less chlorinated analogs.

Similar conclusion follows from the computed values of ω (Table 1): in the cases of trichlorobiphenyls this parameter was higher than in the cases of hexachloro analogs; this indicats the increase in the electrophilicity with the deeper chlorination of biphenyl. The trend was confirmed by experimental data [24, 25]: tri- and tetrachlorobiphenyls were not completely converted in the reaction with MeONa and formed mono- and dimethoxylated derivatives, whereas more chlorinated substrates were completely converted to more methoxylated products.

According to HSAB theory [36], "efficient" reactions occur between soft base and soft acid or hard base and hard acid. As methoxide ion MeO^- was a hard base [36], its interaction should have been more complete in the case of relatively hard acid PCBs. Calculated values of η for constituents of Sovol mixture (Table 1) revealed that the parameter increased with deeper chlorination of biphenyl. Hence, highly chlorinated biphenyls (tetra-, penta-, and hexachloro derivatives) were harder acids than the less chlorinated biphenyls (trichloro derivatives), and interaction of the latter with MeO^- should have been less efficient. The computed values of η correlated well with the experimental data [24]: in the studied reaction with MeONa, trichlorobiphenyls gave exclusively monomethoxylated derivatives, tetrachlorobiphenyls yielded mono- and dimethoxylated derivatives, pentachlorobiphenyls were converted into mono-, di-, and trimethoxylated compounds, and hexachlorobiphenyls gave rise to di- and tri-

Table 1. E_{HOMO}, E_{LUMO}, absolute chemical hardness (η), and global electrophilicity index (ω) values of polychlorinated biphenyls (PCB) present in Sovol mixture

PCB no.	E_{HOMO}, a. u.	E_{LUMO}, a. u.	ΔE, eV	η, eV	ω, eV
Trichlorobiphenyls					
22	–0.242	–0.044	5.396	2.698	2.794
28	–0.239	–0.046	5.268	2.634	2.857
33	–0.241	–0.045	5.350	2.675	2.827
Tetrachlorobiphenyls					
41	–0.254	–0.036	5.921	2.956	2.617
44	–0.250	–0.037	5.780	2.890	2.638
47	–0.250	–0.044	5.600	2.800	2.868
49	–0.250	–0.040	5.737	2.868	2.710
52	–0.250	–0.041	5.683	2.842	2.757
56	–0.247	–0.051	5.352	2.676	3.066
60	–0.244	–0.051	5.265	2.633	3.050
64	–0.251	–0.040	5.748	2.874	2.724
66	–0.245	–0.053	5.249	2.625	3.128
70	–0.247	–0.053	5.267	2.633	3.169
74	–0.244	–0.054	5.182	2.591	3.162
Pentachloro biphenyls					
Group I					
84	–0.254	–0.041	5.787	2.893	2.789
91	–0.255	–0.042	5.798	2.899	2.830
95	–0.251	–0.043	5.664	2.832	2.818
110	–0.255	–0.044	5.732	2.866	2.892
Group II					
97	–0.255	–0.045	5.714	2.857	2.914
99	–0.254	–0.051	5.537	2.769	3.102
101	–0.254	–0.047	5.611	2.806	2.990
118	–0.250	–0.060	5.161	2.580	3.430
Group III					
82	–0.258	–0.041	5.901	2.950	2.788
85	–0.258	–0.042	5.879	2.939	2.850
87	–0.253	–0.044	5.701	2.851	2.858
105	–0.250	–0.057	5.262	2.631	3.305
92	–0.254	–0.046	5.669	2.834	2.937

Table 1. (Contd.)

PCB no.	E_{HOMO}, a. u.	E_{LUMO}, a. u.	ΔE, eV	η, eV	ω, eV
Hexachlorobiphenyls					
Group IV					
128	–0.261	–0.048	5.815	2.908	3.042
132	–0.258	–0.045	5.782	2.891	2.939
138	–0.258	–0.050	5.674	2.837	3.092
Group V					
149	–0.256	–0.047	5.703	2.852	2.980
153	–0.260	–0.050	5.712	2.856	3.116
156	–0.253	–0.064	5.164	2.582	3.597

methoxylated derivatives. In the cases of PCBs nos. 60, 66, 70, 74, 118, 105, and 156 values of η were comparable to those of trichloro biphenyls, or even lower. However, the experiment demonstrated that the above-listed group of PCBs was methoxylated exhaustively, in contrast to the trichloro congeners [24, 25].

Despite some deviations, the presented analysis of computed indices allowed preliminary estimation of reactivity of constituents of Sovol mixture and its prediction in the cases of other PCBs.

Charges and torsion angles. The assumed "hard acid–hard base" type of PCBs interaction with MeO^- along with the calculated large energy gap (ΔE) between E_{HOMO} and E_{LUMO} (Table 1) showed that those reactions were charge-controlled [37]. Therefore the regioselectivity of the studied reaction may be predicted by the analysis of charge distribution in the molecules.

Values of q together with values of φ (related to the molecule stability under the reaction conditions) may also be useful for the estimation of the PCBs reactivity; these descriptors are collected in Table 2.

According to the simulation, in the cases of trichlorobiphenyls, carbon atoms adjacent to chlorine in the more substituted ring were more positively charged as compared with those of the less substituted ring. The monomethoxylated products obtained from compounds nos. 22, 28, and 33 were likely formed via MeO^- attack at the more substituted ring. The higher reactivity of more substituted aromatic fragments was also demonstrated previously [1, 23]. Close values of q at different atoms of the same molecule led to non-selective nucleophilic substitution and explained formation of at least four monomethoxylated derivatives from three trichloro biphenyls.

Computed values of φ in the cases of trichloro-biphenyls were relatively low and ranged between 52.2° and 58.4°, thus pointing at higher delocalization of electron density between two aromatic rings. Therefore, compounds nos. 22, 28, and 33 should be highly stable and less reactive; this coincided with the experimental findings [24].

In the case of unsymmetrical tetrachloro biphenyls nos. 44 and 49 the higher values of q were found in more substituted rings, the values of φ were relatively high. The highest q values were found at C^2 atoms; hence, MeO^- should attack the substrates at these positions. That could not be directly confirmed, as experimental data on pure PCBs nos. 44 and 49 with MeONa were not available.

Symmetric compound no. 52 (2,5,2',5'-tetrachloro-biphenyl) possessed even lower values of q but a high value of φ. On the one hand, the presence of two chlorine atoms in the *ortho* positions should destabilize the structure and increase the C–Cl bonds reactivity. On the other hand, the absence of chlorine atoms in *para* positions should complicate the removal of chlorine in the course of nucleophilic substitution [38] and the compound would be relatively inert towards MeONa; that was actually found in the experiment [24].

Table 2. Charge on the carbon atom adjacent to chlorine atom (q) and dihedral angle (φ) of PCBs of Sovol mixture[a]

PCB no.	q, elementary charge										φ, deg [39]
	2	3	4	5	6	2'	3'	4'	5'	6'	
Trichlorobiphenyls											
22	**0.067**	**0.067**	–	–	–	–	–	0.039	–	–	58.4/59.4
28	0.054	–	**0.056**	–	–	–	–	0.047	–	–	55.4/56.4
33	–	**0.068**	**0.068**	–	–	0.036	–	–	–	–	52.2/56.4
Tetrachlorobiphenyls											
44	**0.076**	0.070	–	–	–	0.046	–	–	0.052	–	83.9/82.9
49	**0.064**	–	0.058	–	–	0.057	–	–	0.053	–	78.2/81.3
52	**0.053**	–	–	0.046	–	**0.053**	–	–	0.046	–	87.3/81.3
47	**0.052**	–	0.051	–	–	**0.052**	–	0.051	–	–	70.6/83.0
56	0.068	0.068	–	–	–	–	**0.070**	**0.069**	–	–	58.5/59.3
66	0.049	–	0.050	–	–	–	**0.071**	**0.069**	–	–	52.5/55.7
70	0.046	–	–	0.043	–	–	**0.071**	**0.070**	–	–	52.5/55.7
41	0.082	**0.098**	0.076	–	–	0.044	–	–	–	–	88.0/82.9
60	0.075	**0.097**	0.075	–	–	–	–	0.040	–	–	58.7/59.3
64	**0.081**	0.077	–	–	0.059	–	–	0.049	–	–	88.6/88.8
74	0.052	–	**0.079**	0.073	–	–	–	0.041	–	–	51.8/55.7
Pentachlorobiphenyls											
Group I											
84	**0.084**	0.074	–	–	0.059	0.081	0.071	–	–	–	91.9/91.1
91	**0.084**	0.075	–	–	0.058	0.063	–	0.052	–	–	89.5/91.0
95	**0.085**	0.075	–	–	0.059	0.057	–	–	0.049	–	89.5/91.0
110	**0.083**	0.078	–	–	0.060	–	0.077	0.075	–	–	88.4/89.5
Group II											
97	0.062	–	**0.080**	0.075	–	0.076	0.070	–	–	–	82.6/83.0
99	0.057	–	**0.080**	0.075	–	0.054	–	0.052	–	–	72.6/81.0
101	0.070	–	**0.085**	0.079	–	0.059	–	–	0.054	–	77.2/81.0
118	0.059	–	**0.084**	0.078	–	–	0.076	0.071	–	–	52.1/55.1
Group III											
82	0.083	**0.099**	0.076	–	–	0.075	0.070	–	–	–	92.4/86.5
85	0.082	**0.099**	0.077	–	–	0.057	–	0.051	–	–	86.2/83.0
87	0.084	**0.099**	0.077	–	–	0.051	–	–	0.047	–	85.0/83.0
105	0.076	**0.098**	0.076	–	–	–	0.072	0.070	–	–	55.6/59.4
92	**0.081**	**0.081**	–	0.057	–	0.053	–	–	0.048	–	84.6/83.0

Table 2. (Contd.)

PCB no.	*q*, elementary charge										φ, deg [39]
	2	3	4	5	6	2'	3'	4'	5'	6'	
Hexachlorobiphenyls											
Group IV											
128	0.081	**0.099**	0.077	–	–	0.081	**0.099**	0.077	–	–	83.2/89.4
132	0.089	**0.101**	0.078	–	–	0.085	0.074	–	–	0.059	91.1/90.9
138	0.081	**0.099**	0.077	–	–	0.081	–	0.077	0.015	–	84.3/83.1
Group V											
149	**0.085**	0.075	–	–	0.059	0.067	–	**0.082**	0.078	–	89.4/90.8
153	0.061	–	**0.081**	0.076	–	0.061	–	**0.081**	0.076	–	88.6/81.1
156	0.080	**0.105**	**0.106**	0.080	–	–	0.072	0.071	–	–	59.0/59.2

[a] Preferential sites of nucleophilic attack are marked in bold.

The opposite behavior in the reaction with MeONa was found in the case of symmetric 2,4,2',4'-tetrachlorobiphenyl no. 47 with the value of *q* at C^2 (*q* 0.0521) comparable to that in 2,5,2',5'-tetrachlorobiphenyl (*q* 0.0525) and lower φ value as compared with the same isomer. However, compound no. 47 was not found in the reaction mixture after interaction with MeONa. Evidently, chlorine atoms in *para* positions favored complete conversion of this congener thus confirming the classical findings on easy nucleophilic substitution in the aromatic ring in the presence of electronegative groups in the *para* position [38]. Thus, in the cases of compounds nos. 52 and 47 the charge factor was less important in determination of nucleophilic attack site.

Compounds nos. 56, 66, and 70 possessed relatively low values of φ. They were well correlated with the previously reported results of simulation in the extended basis set [39]. At the same time, these compounds showed higher *q* values in the aromatic rings of similar structure, and their reactivity was practically the same. Previously we found that pure compound no. 70 gave six products (three mono- and three dimethoxylated ones) under the studied reaction conditions [25]. As was mentioned above, it was impossible to elucidate the substitution pattern of the products by means of GC-MS. By analogy with no. 70 [25], compounds nos. 56 and 66 could give mono- as well as dimethoxylated derivatives in the reaction with MeONa. The monomethoxylated products were likely formed via nucleophilic attack at positions 3' and 4' as well as at the carbon atom with the highest *q* value in the other aromatic ring. The presented simulation data did not allow a prediction of the posi-tions of substituents in the dimethoxylated derivatives.

Compounds nos. 41, 60, 64, and 74 showed the highest values of *q* at the carbon atom in the trichloro ring. Computed values of φ for those structures indicated that PCBs nos. 41 and 64 were the most reactive. In compounds nos. 41 and 60 the C^3 atom had the highest *q* value; in no. 64 the C^2 atom was the most positive; and in no. 74, the highest charge was found on C^4. Neglecting steric factors, MeO^- should have occurred at these positions. Evidently, in the cases of these compounds the dimethoxylated derivatives could be formed via attack at the carbon atom with the highest *q* values.

All pentachlorobiphenyls of group I possessed high *q* values at C^2. Of those compounds the highest values of *q* at C^2 were found when chlorine atom was present at 2' position, the *q* value was higher when the second chlorine atom was closer to $C^{2'}$. The relatively high values of φ (88.4–91.9°) correlated well with data of [39]. The simulation data showed that compounds nos. 84, 91, 95, and 110 should be highly reactive; that was confirmed by the experiment [25]: under similar conditions, the mixture of PCBs 105, 107, 110, and 118 was converted into di- (88.8%) and trimethoxylated (11.2%) derivatives, the monomethoxylated ones were absent.

All compounds of group II showed high *q* values at C^4. Values of φ were high as well, however, being lower than those of group I compounds. Hence, compounds nos. 97, 99, 101, and 118 were less reactive than PCBs of group I. For all the group II compounds, C^4 was the preferential site of the nucleophilic attack, another reactive site being C^5; those compounds could yield mono- and dimethoxylated derivatives [25].

Among pentachlorobiphenyls, compounds of group III possessed higher values of *q* at C^3. At the same time, chlorine in position 3 was surrounded by *ortho* and *para* chlorine atoms, the adjacent carbon atoms possessing high *q* values as well (the charge at C^2 was higher than that at C^4). Computed values of φ were finely correlated with data of [39], being close to the respective parameter of group I compounds. Thus, in the case of PCBs of group III, the preferential site of nucleophilic attack was C^3; C^2 , and C^4 were reactive as well (steric factors being ignored).

The computed values of *q* were high in the case of PCB 92, they were approximately equal at C^2 and C^3. Hence, primary nucleophilic attack should yield both mono- and dimethoxylated derivatives. no. 92 was a highly reactive substrate, as confirmed by relatively high φ value.

Hexachlorobiphenyls possessed *q* values comparable to those in the case of pentachlorobiphenyls of group III, and high values of φ. Hence, we assumed high reactivity of compounds nos. 128, 132, 138, 149, and 153. In the previously reported study, GC-MS did not reveal monomethoxylated pentachlorobiphenyls (products of hexachlorobiphenyls substitution) in the reaction products [24]. Evidently, di- and trimethoxylated derivatives were the most probable products of hexachlorobiphenyls reaction with MeONa. Distribution of chlorine atom was even in the cases of above-listed biphenyls: three chlorine atoms in each ring. However, group V contained a compound no. 156 with another chlorine atoms distribution (2+4), affecting the descriptors values. No. 156 had the *r* highest *q* values at C^3 and C^4, and the φ value was the lowest of all hexachloro biphenyls. Thus, the reactivity prediction was contradictory. According to the experiment [25], pure no. 156 formed monomethoxylated derivatives (62.9%) in the reaction with MeONa; they were not detected in Sovol modification products [24]. Evidently, the formed methoxylated products could not be detected due to low content of no. 156 in the mixture (0.9%) [23, 26] and, probably, because of joint elution of some of the products. Nevertheless, compound no. 163 with even distribution of chlorine atoms between the aromatic rings did not form monomethoxylated derivative in the reaction with MeONa [25]. Hence, the even distribution of chlorine atoms favored deeper conversion of hexachlorobiphenyls.

To conclude, analysis of parameters *q* and φ allowed the estimation of PCBs reactivity and the prediction of possible sites of primary nucleophilic attack.

It should be noted that the correctness of computed values of *q* could be confirmed by ^{13}C NMR data [40] of Sovol mixture components. Their analysis consisted in correlation of the most downfield signals of chlorine-adjacent carbon atoms to the highest values of *q*. For instance, in the case of no. 28 the most downfield signal was assigned to C^4 showing the highest value of *q* (Table 2) [41, 42]. The following biphenyl derivatives revealed the best correlation of highest positive charge at chlorine-adjacent carbon atom with the most downfield signal in ^{13}C NMR spectrum: trichloro no. 33 [42], tetrachloro nos. 52 [43] and 70 [41], pentachloro no. 101 [41, 43], and hexachloro no. 153 [41, 43]. The cited references [41–43] contained spectral data on other components of Sovol mixture; they did not meet the above-described criterion. However, the difference between the most downfield chemical shift and that of the carbon atom with the highest *q* value (Table 2) was as low as several hundredths of ppm, thus confirming good correlation between computed value of *q* and experimental ^{13}C chemical shifts of PCBs.

To conclude, correlation of experimental data and quantum-chemical simulation indicated that the interaction of PCBs with MeO^- was of the "hard acid–hard base" type. Chemical hardness (η) of PCBs increased with growing number of chlorine atoms in the substrate confirming the higher reactivity of the deeper chlorinated compounds.

The direction of nucleophilic substitution in the aromatic ring of PCBs was governed by the charge distribution due to the sufficiently high energy gap between the frontier orbitals. Charge at carbon atom adjacent to chlorine (*q*) was the decisive descriptor to determine the reactive site of primary attack of (MeO^-). The experimentally found higher reactivity of more substituted aromatic rings was due to the higher charge

on the carbon atoms and, therefore, their higher electrophilicity in the case of more chlorinated biphenyls. When several sites of similar electrophilicity were found in the substrate, the formation of di- and trimethoxylated derivatives could be anticipated. The low selectivity of PCBs nucleophilic substitution was due to the close values of charges at chlorine-substituted carbon atoms.

Low reactivity of tri- and (in some cases) tetrachlorobiphenyls was well consistent with the insufficient acid hardness of the substrate and by relatively low charges at the sites of nucleophilic attack. Torsion angle values (φ) were not decisive in determination of PCBs reactivity.

ACKNOWLEDGMENTS

This work was financially supported by Ural Branch of Russian Academy of Sciences (project no. 12-M-34-2036) and by Russian Foundation for Basic Research (project no. 12-03-31574 mol_a).

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