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Reactivity of polychlorinated biphenyls in nucleophilic and electrophilic substitutions

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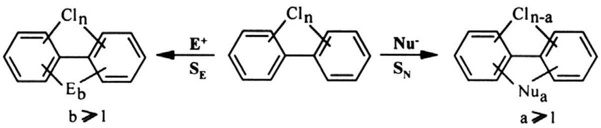
HIGHLIGHTS

- Quantum chemical calculations were carried out for PCBs congeners.
- Calculated descriptors were used to explain the PCBs reactivity in S_N and S_E substitutions.
- Obtained data were used to estimate the PCBs reactivity in the S_N reactions.
- Calculated descriptors were insufficient to explain the PCBs reactivity in the S_E reactions.
- New neutralization methods of the large-capacity PCBs were discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

To explain the chemical reactivity of polychlorinated biphenyls in nucleophilic (S_N) and electrophilic (S_E) substitutions, quantum chemical calculations were carried out at the B3LYP/6-31G(d) level of the Density Functional Theory in gas phase. Carbon atomic charges in biphenyl structure were calculated by the Atoms-in-Molecules method. Chemical hardness and global electrophilicity index parameters were determined for congeners. A comparison of calculated descriptors and experimental data for congener reactivity in the S_N and S_E reactions was made. It is shown that interactions in the S_N mechanism are reactions of *the hard acid–hard base* type, these are the most effective in case of highly chlorinated substrates. To explain the congener reactivity in the S_E reactions, correct descriptors were not established. The obtained results can be used to carry out chemical transformations of the polychlorinated biphenyls in order to prepare them for microbiological destruction or preservation.

1. Introduction

The problem of disposal of technogenic polychlorinated biphenyls (PCBs) is still relevant for many countries. The burning of PCBs is the only technologically developed and effective method using a turbojet engine [1]. This method is a highly power-input process as it is necessary to follow the rule of "three T" (reaction time (τ) is nearly 2–3 s; reaction temperature (T) is 2000–3000 °C; turbulence (t) is very high). The burning of PCBs also requires a large amount of oxygen (4–6 tons for burning of each PCBs ton). According to various data, the amount of PCBs exceeds 1 million tons in the world. All PCBs cannot be burned. Microbiological and chemical methods of PCBs processing are an alternative to burning.

At present microbiological methods of PCBs destruction are gaining importance due to selection of new effective strain destructors. The most successful studies in the field of the PCBs biodestruction are those that use lowly chlorinated congeners [2–5]. From their results it was established that the PCBs biodegradability increases with a decrease in the amount of chlorine atoms

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in the initial substrates. At the same time, there is still considerable interest to search for surfactants for solubilization of more hydrophobic highly chlorinated congeners in aqueous medium in order to create stable emulsions where strains decompose the PCBs effectively [6–8].

Among the chemical methods of PCBs neutralization, hydrodechlorination is developing most intensively [9]. As a rule, Pd catalysts have the most positive effect on hydrodechlorination. Depending on the Pd catalyst, the source of hydrogen can be both hydrogen generator and hydrogen obtained *in situ*. In the former the Pd catalysts modified by inert catalyst carriers, such as C and SiO_2, are applied [10–14], whereas in the latter the Pd catalysts are used with active metals such as Fe and Mg [15–23].

It should be noted that each of the 209 PCBs congeners has individual reactivity, and there is no uniform methodological approach to chemical transformations of all the PCBs. This conclusion concerns commercial mixtures substantially. For example, hydrodechlorination of the decachlorobiphenyl (PCB 209) using Pd/C at 209–230 °C leads to the formation of biphenyl and benzene. But the commercial mixture of PCBs Arochlor 1254 in the same conditions at 130 °C is transformed into biphenyl, benzene, toluene, styrene and propylbenzene mixture [12]. As was shown in Ref. [21], the use of Pd/Mg catalyst for the hydrodechlorination of the 4-chlorobiphenyl (PCB 3) and the 2,3,4,5,2′,3′,4′-heptachlorobiphenyl (PCB 170) in H_2O–MeOH medium leads to complete removal of chlorine atoms from the initial substrates after 10 min. A similar effect for Aroclor 1260 is not observed. Lowly chlorinated PCBs and biphenyl formed initially are then adsorbed on the Pd catalyst surface. Following this reaction the process is slowed down. *Ortho*-substituted congeners are the most difficult to hydrodechlorinate.

In Ref. [24] “selective rules” for hydrodechlorination of commercial mixture Delor 103 were determined. Even for tri- and tetrachlorinated congeners from the Delor 103 the authors do not give a definite answer about the advantages of the hydrodechlorination of several C—Cl bonds. Other commercial mixtures consisting of more highly chlorinated congeners lead to more complicated results. In general, for them the selective rules are not known.

When investigating chemical transformations of PCBs, we encounter problems of an incomplete conversion of congeners and the absence of reaction selectivity [25]. The purpose of the present work is to explain the reactivity of the PCBs congeners in nucleophilic (S_N) and electrophilic (S_E) substitutions by means of obtained experimental results and quantum chemical non-empirical (*ab initio*) calculations. The results of interactions between commercial mixture of the PCBs and MeO^- (S_N) and $NO_2{}^+$ (S_E) are considered.

2. Experimental

2.1. Chemicals

The object of the research is Russian industrial PCBs mixture Sovol (analog of commercial mixture Arochlor 1254 (USA)). Sodium methoxide (MeONa, cp grade, Russia), dimethyl sulfoxide (DMS, cp grade, Russia), toluene (cp grade, Russia), calcium chloride ($CaCl_2$, cp grade, Russia), nitric acid (HNO_3) (cp grade, Russia) and oleum (H_2SO_4 (20% SO_3), cp grade, Russia) were used.

2.2. Chemical experiments

Interaction of PCBs mixture Sovol with sodium methoxide was described [26]. Interaction of PCBs mixture Sovol with nitric acid and oleum was reported [27].

2.3. Analytical methods

The PCBs products were analyzed by a GC equipped with a flame ionization detector (FID) (Shimadzu, GC-2010) or GC/MS (Agilent 7890A MS 5975C Inert XL) [26–28]. The quantitative estimation was carried out by internal normalization.

2.4. Quantum chemical calculations

Quantum chemical non-empirical calculations were performed using the Gaussian 09 software package [29]. The structural parameters were fully optimized in the approximation of the Density Functional Theory at the RB3LYP/6-31G(d) level in gas phase. The reliability of the minimum of the localized stationary points is confirmed with Hessian’s calculation. For all compounds imaginary vibrational frequencies are absent.

The used B3LYP/6-31G(d) basis set is small. But literature analysis shows that it yields quite reliable and adequate results in agreement with experimental data for some aromatic substrates [30–34]. There are positive examples of the basis used to calculate the values for biphenyl derivatives [35] and PCBs [36,37].

To estimate the reactivity of congeners in the mixture Sovol in the S_N reaction the following descriptors were chosen: highest occupied molecular orbital energies (E_{HOMO}), lowest unoccupied molecular orbital energies (E_{LUMO}), chemical hardness (η) and global electrophilicity index (ω). The two last parameters were calculated using Eqs. (1)–(5) [36,38–42]:

$$\eta = \frac{1}{2}(\mathrm{IP} - \mathrm{EA}) \qquad (1)$$

IP is the ionization potential and EA is the electron affinity.

$$\mathrm{IP} = -E_{\mathrm{HOMO}} \qquad (2)$$

$$\mathrm{EA} = -E_{\mathrm{LUMO}} \qquad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \qquad (4)$$

μ is the chemical potential, eV.

$$\mu = -\frac{1}{2}(\mathrm{IP} + \mathrm{EA}) \qquad (5)$$

To calculate the charge values (q) on the carbon atoms in the biphenyl structure Bader’s theory “Atoms-in-Molecules” (AIM) was used [43] as well as the wave function obtained by the RB3LYP/6-31G(d) method. The AIM method was applied to carry out calculations using the AIMAll software package [44].

The basis B3LYP/6-31G(d) used in the present work is very convenient for q calculations within the Mulliken’s scheme. We carried out such calculations but the q values were not satisfactory. For example, the q values for the carbon atoms at C—Cl bonds were negative but the q values for the carbon atoms at C—H bonds were positive.

The torsion angle between benzene cycles upon rotation with respect to the simple C—C-bond (φ) was determined within the framework of the RB3LYP\6-31G(d) method. The scaling factor for the B3LYP/6-31G(d) level is 0.9945 with respect to the experiment [45].

3. Results and discussion

3.1. Making mixture Sovol

The composition of the commercial mixture Sovol was represented in an earlier paper [25]. It was determined that the Sovol is a mixture of 35 congeners; the contents of tetra-, penta-, and hexachlorobiphenyls are 22, 56 and 20%, respectively. Minor amounts