

Thermodynamic Aspects for the Reaction of Polychlorinated Biphenyls with Sodium Methoxide in Ethanol and Dimethyl Sulfoxide Solution

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Abstract—The reaction of Sovol technical-grade mixture of polychlorinated biphenyls with sodium methoxide in dimethyl sulfoxide and ethanol medium has been studied for the first time by thermodynamic modeling. The addition of ethanol co-solvent to dimethyl sulfoxide has been found to result in the emergence of solvolysis process. The optimal conditions for nucleophilic substitution reaction have been found. Using these reactions, derivatives of polychlorinated biphenyls with decreased chlorine content have been synthesized. A high conversion of initial polychlorinated biphenyl congeners of Sovol mixture has been reached. The studied reaction can serve as a pretreatment stage for the destruction of toxic polychlorinated biphenyls by thermal methods.

Keywords: polychlorinated biphenyls, nucleophilic substitution, thermodynamic modeling, thermal method

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At present time, the disposal of polychlorinated biphenyls (PCBs) remains an important and urgent task [1, 2]. Only the use of cross-disciplinary approaches can provide the development of efficient methods for the destruction of these toxic chlorine-containing wastes.

To prevent the formation of gaseous ecotoxins (polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) [3, 4]) on the thermal disposal of PCB technical mixtures, the maximal removal of chlorine from a congener structure (to obtain pre-products) is necessary. This goal can be achieved using nucleophilic substitution (S_N) reaction. The known procedures for chlorine removal from commercial PCB mixtures show low conversion of initial compounds [5, 6], the complete functionalization of congeners is a challenging task because of multicomponent composition of the mixture.

Thermodynamic modeling (TDM) [7] is an efficient method to search for conditions of chemical reaction resulting in complete transformation of con-

geners of PCB mixtures. The method was used previously to optimize the reaction of Sovol PCB mixture in reaction with sodium methoxide (MeONa) in dimethyl sulfoxide (DMSO) solution [8]. In the synthesis under conditions proposed by TDM, the conversion of initial congeners considerably rises but this procedure is not safe for environment because of PCDF formation.

We prevented PCDF formation by adding methanol co-solvent to DMSO followed by optimization of synthesis conditions using TDM [9, 10]. Reaction products were a mixture of methoxy, hydroxy, and methoxyhydroxy PCB derivatives. The obtained pre-products are less thermally stable compounds as compared with the initial congeners of Sovol mixture and their thermolysis leads to their evaporation and degradation to the simplest volatile products [11].

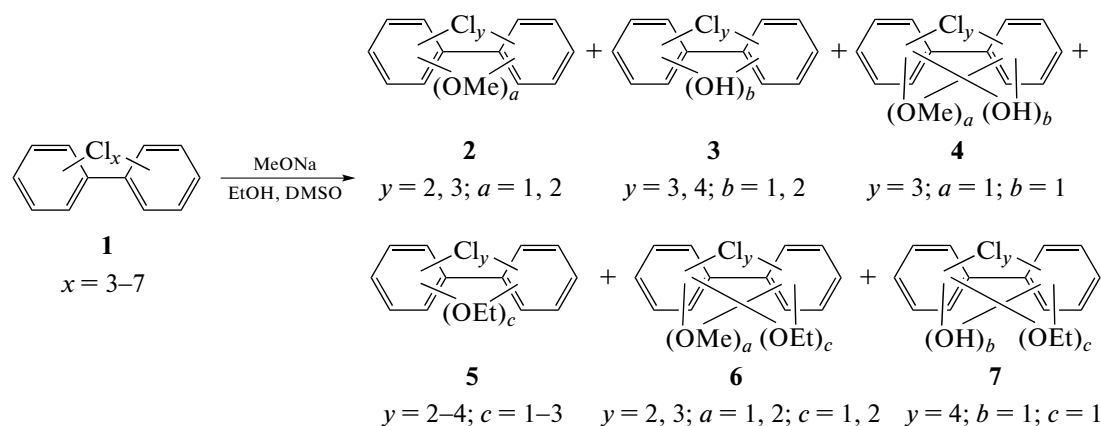
It has been found that an increase in the temperature of the nucleophilic substitution reaction enhances the conversion of initial congeners of PCB mixtures [8, 10]. Therefore, we proposed to use a mixture with molar ratio DMSO : EtOH = 3 : 1 ($T_b = 145^\circ\text{C}$) instead of a mixture with DMSO : MeOH = 3 : 1 ($T_b = 115^\circ\text{C}$). The thermal destruction of pre-products with decreased chlorine content obtained due to larger conversion of initial PCB congeners probably leads to decrease of emission of gaseous and volatile chlorine-containing ecotoxins (PCDFs and PCDDs, chlorine and phosgene oxides).

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Scheme 1.

In this work, we performed TDM for the first time to optimize the reaction of Sovol 1 PCB mixture with MeONa in DMSO and EtOH solution. We supposed and experimentally confirmed that this reaction results in a mixture of products of six types: compounds 2–7 (Scheme 1).

A similar algorithm for the calculation of thermochemical properties of compounds has been described in [12]. The thermochemical properties for methoxy, hydroxy, and methoxyhydroxy PCB derivatives (compounds 2–4, respectively) have been previously calculated by us [8, 10, 12]. There are no literature data for ethoxy (5), ethoxymethoxy (6), and ethoxyhydroxy derivatives (7). Taking into account all types of functional groups in compounds 5–7 (chlorine atoms, hydroxy, methoxy, and ethoxy groups) and their number, the list of all hypothetically possible compounds 5–7 includes 125 structures. The calculated properties of these 125 derivatives of compounds 5–7 have been introduced in the database of HSC Chemistry software package; the computations in this program are based on the minimization of Gibbs free energy of the system. Table 1 shows the thermochemical properties

of three randomly selected possible derivatives of compounds 5–7 as an example.

We performed modeling for the reaction of Sovol PCB mixture 1 (0.01 mol) with MeONa (0.01–0.06 mol) in a DMSO solution (0.26 mol) in the absence and in the presence of EtOH co-solvent (0.087 mol). Using CEMCAD software, we established and experimentally confirmed that the boiling point of the DMSO–EtOH mixture with the specified molar ratio is about 130–150°C. TDM was performed in an extended temperature range from 50 to 200°C. The calculation of equilibrium mixture compositions obtained by modeling for the reaction of Sovol PCB congeners 1 with MeONa in a DMSO–EtOH solution was performed for molar compositions from 1 : 1 to 1 : 6.

Figure 1 exemplifies the results of TDM for equilibrium composition at molar ratio 1 : 4 in the absence and in the presence of EtOH co-solvent.

Figure 1a shows that the reaction of Sovol PCB mixture 1 with MeONa without EtOH additive leads to a mixture containing the highest concentration of trichlorobiphenyl ($C_{12}H_7Cl_3$) among unreacted con-

Table 1. Calculated thermochemical properties of PCB derivatives 5–7

Compound	$C_{12}H_7Cl_2(OC_2H_5)$ 5	$C_{12}H_6Cl_2(OC_2H_5)OCH_3$ 6	$C_{12}H_3(OC_2H_5)_3(OH)_4$ 7
ΔH_{298}° , kJ/mol	–57	–222	–1082
S_{298}° , J/mol K	542	586	758
ΔG_{298}° , kJ/mol	134	28	–637
$H_{298}^\circ - H_0^\circ$, kJ/mol	38	44	63
$C_p = a + b \times 10^{-3}T + c \times 10^5T^{-2} + d \times 10^{-6}T^2$, J/mol K	a	49	117
	b	818	883
	c	–6.9	15.1
	d	–339	–624

geners. Increasing the temperature of the process leads to a decrease in the $C_{12}H_7Cl_3$ concentration in reaction products and an increase in of the contribution of methoxy PCB derivatives **2**. The content of PCB hydroxy derivatives **3** in the products was minimal: less than 1×10^{-5} mole fraction. The use of a DMSO–EtOH solvent mixture led to detection in reaction products of not only methoxy but also ethoxy and hydroxy PCB derivatives **2**, **5**, and **3**, respectively (Fig. 1b). There were no initial PCB congeners. The concentration of intermediates **4**, **6**, and **7** was less than 1×10^{-10} mole fraction. Probably, they transformed during substitution reaction from PCB derivatives **4** and **6** into compounds **3** and from PCB derivatives **7** into compounds **2**, which are more thermodynamically stable (have larger negative values of standard Gibbs energy). The presence of ethoxy PCB derivatives **5** results from solvolysis reaction when solvent behaves simultaneously as a nucleophilic agent. This feature explains the decrease in the MeONa amount necessary for the complete conversion of Sovol mixture **1** (Fig. 1b). However, as established in the course of this study, subsequent uncontrolled increase in the amount of the cosolvent is impossible. It has been experimentally found that an excess of the protic solvent EtOH leads to inhibition of substitution reactions with MeONa. The optimal molar ratio, at which there is no inhibition of the interaction, is DMSO : EtOH = 3 : 1. This ratio was used in further studies.

Experimental reaction conditions corresponded to the optimal data obtained by TDM (molar ratio PCB **1** mixture : MeONa = 1 : 4, 0.087 mol EtOH, 0.26 mol DMSO, $T_b = 145^\circ C$). Product composition for the reaction of Sovol congeners mixture **1** with MeONa in neat DMSO [8] and in a DMSO–EtOH solvent mixture was compared after 10-h reaction. The analysis of the reaction products by GC–MS revealed more than 80 new derivatives. Their average relative content according to the results of three experiments is given in Table 2, root-mean-square deviation was not larger than 3%.

The obtained data showed that the reaction of PCB **1** mixture with MeONa in a DMSO–EtOH mixture concurrently or consecutively could result in the formation of PCB derivatives **2–7**. The content of derivatives **4**, **6**, and **7** in reaction products is insignificant as compared with the content of the corresponding initial derivatives **2**, **3**, and **5**. The obtained results coincide with TDM data that the main derivatives are also substitution products **2**, **3**, and **5**, while intermediates **4**, **6**, and **7** are thermodynamically unstable compounds.

The conversion of the initial congeners of Sovol PCB mixture **1** in the reaction with MeONa in the presence of DMSO and DMSO–EtOH was 100 [8] and 99.7% (Table 2), respectively. When the reaction was conducted in the presence of ethanol, no forma-

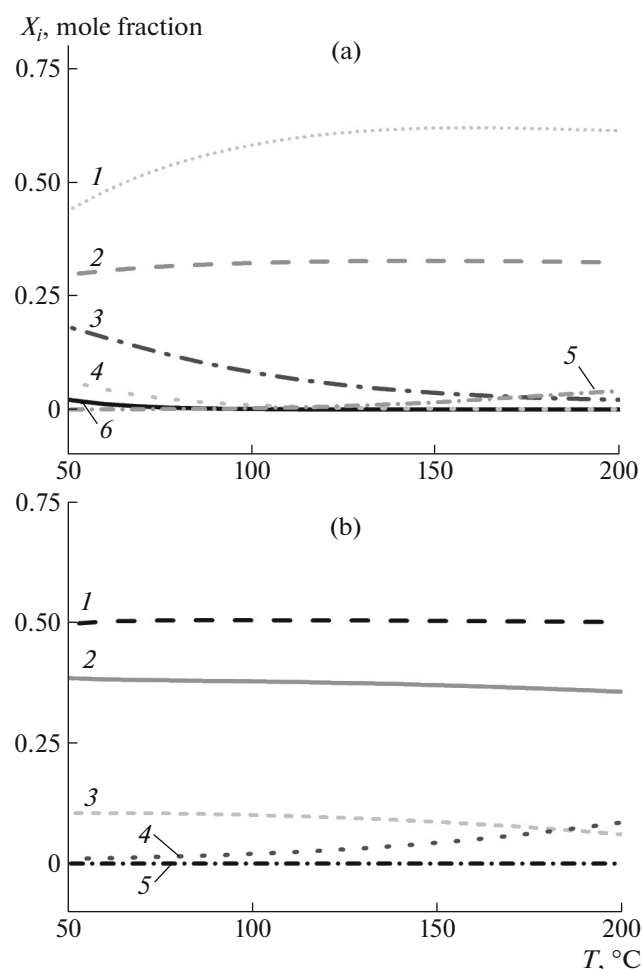


Fig. 1. Temperature dependence for the equilibrium composition of congeners and PCB derivatives. Initial composition: (a) 0.01 mol PCB Sovol **1** mixture, 0.04 mol of MeONa, 0.26 mol DMSO; (b) 0.01 mol Sovol PCB mixture **1**, 0.1 mol MeONa, 0.26 mol DMSO, 0.087 mol EtOH. $T = 50\text{--}200^\circ C$, $P = 1$ atm. The sum of mole fractions of all PCB congeners and derivatives is 1. (a) (1) $C_{12}H_4(OCH_3)_6$, (2) $C_{12}H_7Cl_3$, (3) $C_{12}H_5(OCH_3)_5$, (4) $C_{12}H_6(OCH_3)_4$, (5) $C_{12}H_7(OCH_3)_3$, (6) $C_{12}H_3Cl(OCH_3)_6$; (b) (1) $C_{12}H_4Cl_2(OCH_3)_4$, (2) $C_{12}H_7(OH)_3$, (3) $C_{12}H_5(OC_2H_5)_5$, (4) $C_{12}H_7(OCH_3)_3$, and (5) $C_{12}H_5Cl_2(OCH_3)_3$.

tion of PCDFs was detected, while the amount of necessary MeONa was lower than stoichiometric.

According to elemental analysis data, the chlorine content in the obtained synthesis products **2–7** is 1.6 times lower than in the initial Sovol PCB mixture **1**.

Thus, using the results of theoretical calculation, we selected for the first time the conditions of nucleophilic substitution reaction of Sovol congener mixture **1** with MeONa in a DMSO–EtOH solvent. This approach allowed experimentally safe preparation of pre-products **2–7**, because chlorine content in them is 1.6 times lower. The obtained PCB derivatives **2–7** are

Table 2. Data for reaction products for PCB Sovol **1** mixture treatment with MeONa in DMSO and EtOH solution at $T = 145^\circ\text{C}$, reaction time of 10 h

Compound no. according to Scheme 1	Molecular formula	Molecular ion, m/z	Number of isomers	Relative content, %
1	$\text{C}_{12}\text{H}_8\text{Cl}_2$	222	2	0.05
1	$\text{C}_{12}\text{H}_7\text{Cl}_3$	256	2	0.10
1	$\text{C}_{12}\text{H}_6\text{Cl}_4$	290	1	0.14
2	$\text{C}_{12}\text{H}_7\text{Cl}_2(\text{OCH}_3)$	252	1	0.11
2	$\text{C}_{12}\text{H}_6\text{Cl}_3(\text{OCH}_3)$	286	2	1.34
2	$\text{C}_{12}\text{H}_5\text{Cl}_3(\text{OCH}_3)_2$	316	2	0.97
3	$\text{C}_{12}\text{H}_6\text{Cl}_3(\text{OH})$	272	4	1.43
3	$\text{C}_{12}\text{H}_5\text{Cl}_4(\text{OH})$	306	10	26.65
3	$\text{C}_{12}\text{H}_4\text{Cl}_3(\text{OH})_2$	322	2	1.31
4	$\text{C}_{12}\text{H}_5\text{Cl}_3(\text{OCH}_3)(\text{OH})$	302	1	0.27
3	$\text{C}_{12}\text{H}_7\text{Cl}_2(\text{OC}_2\text{H}_5)$	266	2	0.48
5	$\text{C}_{12}\text{H}_6\text{Cl}_3(\text{OC}_2\text{H}_5)$	300	7	9.88
5	$\text{C}_{12}\text{H}_5\text{Cl}_4(\text{OC}_2\text{H}_5)$	334	7	11.24
5	$\text{C}_{12}\text{H}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2$	310	3	3.49
5	$\text{C}_{12}\text{H}_5\text{Cl}_3(\text{OC}_2\text{H}_5)_2$	344	14	19.16
5	$\text{C}_{12}\text{H}_4\text{Cl}_4(\text{OC}_2\text{H}_5)_2$	378	2	0.16
5	$\text{C}_{12}\text{H}_5\text{Cl}_2(\text{OC}_2\text{H}_5)_3$	354	5	6.01
5	$\text{C}_{12}\text{H}_4\text{Cl}_3(\text{OC}_2\text{H}_5)_3$	388	3	0.21
6	$\text{C}_{12}\text{H}_6\text{Cl}_2(\text{OC}_2\text{H}_5)(\text{OCH}_3)$	296	3	2.82
6	$\text{C}_{12}\text{H}_5\text{Cl}_3(\text{OC}_2\text{H}_5)(\text{OCH}_3)$	330	5	4.21
6	$\text{C}_{12}\text{H}_5\text{Cl}_2(\text{OC}_2\text{H}_5)_2(\text{OCH}_3)$	340	2	1.30
6	$\text{C}_{12}\text{H}_4\text{Cl}_3(\text{OC}_2\text{H}_5)(\text{OCH}_3)_2$	360	2	2.13
7	$\text{C}_{12}\text{H}_4\text{Cl}_4(\text{OC}_2\text{H}_5)(\text{OH})$	350	7	6.55
Total				99.72

less toxic for the further research in the processes of their thermal disposal.

EXPERIMENTAL

Initial chemicals used in this work were Sovol technical PCB mixture (Standard 6-01-24-75), sodium metal, freshly dried and distilled MeOH (d_{20}^4 0.7918), EtOH (d_{20}^4 0.7917), and DMSO (d_{20}^4 1.1004).

A procedure for the reaction of Sovol mixture **1** with MeONa in a DMSO and EtOH solution was similar to that for the reaction of MeONa in a DMSO–MeOH mixture described in [14].

Identification and quantitative assessment of reaction products was performed using an Agilent GC 7890A MSD 5975C inert XL EI/CI gas chromatograph–mass spectrometer with an HP-5MS quartz capillary column and a quadrupole mass spectrometric (GC–MS) detector. Scanning over full ionic cur-

rent was carried out in the mass range 20–1000 Da in electron ionization mode with an ionizing voltage of 70 eV.

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