

# THE REACTION OF POLYCHLORINATED BIPHENYLS WITH SODIUM METHOXIDE

A.V. Maiorova<sup>1</sup>, T.V. Kulikova<sup>1</sup>, K.Yu. Shunyaev<sup>1</sup>, V.A. Bykov<sup>1</sup>,  
A.S. Ivashev<sup>1</sup>, T.I. Gorbunova<sup>2</sup>, M.G. Pervova<sup>2</sup>, K.A. Plotnikova<sup>2</sup>

<sup>1</sup>*Institute of Metallurgy of Ural Branch of Russian Academy of Sciences, 101, Amundsena St., Ekaterinburg, Russian Federation,*  
<sup>2</sup>*Postovskii Institute of Organic Synthesis of Ural Branch of Russian Academy of Sciences, 22 Sofia Kovalevskaya St., Ekaterinburg, Russian Federation*  
*imeturoran@mail.ru*

## Introduction

Unique technological and physicochemical properties of polychlorinated biphenyls (PCBs), a huge volume of their production, considerable volatility and solubility, and extreme chemical inertness have led to the world-wide spread of PCB-containing equipment and materials, resulting in the universal contamination with these substances. In Russia, the most common method used for destruction of PCBs are their incineration with the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), which are among the most hazardous chemical substances known to the mankind [1].

As often happens, the hazard of PCBs has been underestimated for long time. With respect to their severe toxicological effect, PCBs are reckoned among substances with high class of hazard. Since these substances are so toxic, they have been assigned low toxicological standards, which impose special requirements on the organization of processes assuming formation of these substances (the so-called dioxinogenic processes) so that industrial emissions meet the norms.

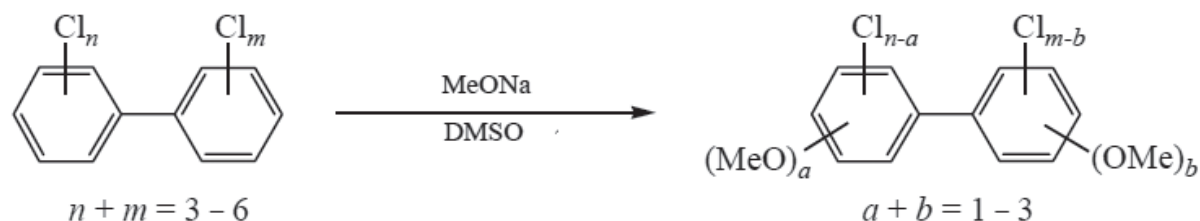
Promising technologies for detoxification of PCBs or their pretreatment for the subsequent destruction are based on chemical reactions of PCBs. The most widespread of such technologies involves nucleophilic substitution of aromatically bound chlorine atoms in PCBs by other substituents. The procedures of PCB nucleophilic substitution are simple to realize and do not require special equipment. However, in view of the fact that any commercial PCB trademark is a mixture of several tens of congeners, and the behavior of each congener in one or another chemical reaction is hardly predictable (for example, Sovol). Sovol is a mixture of several PCB congener groups: trichlorobiphenyls (~1%), tetrachlorobiphenyls (~22%), pentachlorobiphenyls (~56%), hexachlorobiphenyls (~20%), and heptachlorobiphenyls (~1%).

The volume of experimental research can be significantly reduced by using thermodynamic modeling. The research, performed by using of thermodynamic modeling, provide information on the composition of reaction products and ways of their formation, as well as behavior of different substances over a wide range of temperatures and pressures.

The aim of the present work was to study the reactivity of PCB congeners in their reaction with sodium methoxide (MeONa) in DMSO by means of computer modeling and compare the calculation results with experimental data.

### Experiment

The reaction of technical PCB mixture Sovol with MeONa in DMSO can formally be described by the scheme (Fig.1):



**Fig. 1.** The reaction of technical PCB mixture with MeONa in DMSO

The necessary condition for the realization of the aims of our research is the availability of a database of thermochemical parameters of the compounds of interest.

Thermochemical parameters, such as standard enthalpy of formation ( $\Delta H_{298}^\circ$ ), enthalpy increment from 0 to 298 K ( $H_{298}^\circ - H_0^\circ$ ), standard heat capacity ( $C_{p,298}^\circ$ ) and its temperature dependence [ $C_p(T)$ ], and entropy ( $S_{298}^\circ$ ) were calculated for the gaseous of methoxy derivatives of PCBs formed from polychlorinated biphenyl (PCB) congeners [2] and are listed in Table 1.

The thermochemical properties, which were taken as reliable, were added to the HSC database and were used for thermodynamic simulation of reactivity of PCB congeners in their reaction with sodium methoxide (MeONa) in DMSO.

Experimental research and the reaction progress was monitored with a Shimadzu GC-2010 gas chromatograph (flame-ionization detector; GsBP-5MS (30000  $\times$  0.25 mm) quartz capillary column coated with 0.25  $\mu\text{m}$  of dimethylpolysiloxane stationary phase containing 5% grafted phenyl groups; carrier gas nitrogen; flow division ratio 1 : 30; column temperature: 40  $^\circ\text{C}$ , 3 min; heating to 280  $^\circ\text{C}$ , 10 deg  $\text{min}^{-1}$ ; vaporizer temperature

Table 1

## Thermochemical parameters of gaseous methoxy-PCBs

Compound	$\Delta H_{298}^{\circ}$ kJ/mol	$S_{298}^{\circ}$ J/mol K	$H_{298}^{\circ} - H_{0}^{\circ}$ kJ/mol	$T_{bp}^{\circ}$ K	$C_p = a + b \cdot 10^{-3} T + c \cdot 10^5 T^{-2} + d \cdot 10^{-6} T^2$ J/mol K			
					a	b	c	d
$C_{12}H_7Cl_2(OCH_3)$	-41.8	594.4	35.3	662	103.6	688.5	-43.6	-284.8
$C_{12}H_7Cl(OCH_3)_2$	-178.4	933.9	38.4	670	95.8	820.8	-49.4	-331.8
$C_{12}H_7(OCH_3)_3$	-314.9	1273.5	41.6	678	87.7	952.6	-55.4	-378.4
$C_{12}H_6Cl_3(OCH_3)$	-70.8	685.8	37.9	705	128.6	670.5	-45.7	-283.3
$C_{12}H_6Cl_2(OCH_3)_2$	-207.4	1025.3	41.0	712	120.6	802.8	-51.6	-330.3
$C_{12}H_6Cl(OCH_3)_3$	-344.0	1364.7	44.2	720	112.8	934.6	-57.5	-376.9
$C_{12}H_6(OCH_3)_4$	-480.6	1704.2	47.3	728	104.9	1066.3	-63.4	-423.5
$C_{12}H_5Cl_4(OCH_3)$	-99.9	777.2	40.5	747	153.6	652.5	-47.9	-281.9
$C_{12}H_5Cl_3(OCH_3)_2$	-304.6	1116.5	43.6	755	145.6	784.8	-53.7	-328.9
$C_{12}H_5Cl_2(OCH_3)_3$	-305.0	1456.1	46.8	763	137.	916.6	-59.6	-375.5
$C_{12}H_5Cl(OCH_3)_4$	-509.6	1795.6	49.9	771	129.9	1048.3	-65.6	-422.1
$C_{12}H_5(OCH_3)_5$	-646.2	2135.1	53.0	778	122.1	1180.1	-71.5	-468.7
$C_{12}H_4Cl_5(OCH_3)$	-128.9	868.5	43.1	789	178.7	634.5	-50.0	-280.4
$C_{12}H_4Cl_4(OCH_3)_2$	-265.5	1208.0	46.2	797	170.6	766.8	-55.9	-327.4
$C_{12}H_4Cl_3(OCH_3)_3$	-402.1	1547.5	49.4	805	162.8	898.6	-61.8	-373.9
$C_{12}H_4Cl_2(OCH_3)_4$	-538.7	1886.9	52.5	813	154.9	1030.3	-67.7	-420.6
$C_{12}H_4Cl(OCH_3)_5$	-675.3	2226.5	55.6	821	147.1	1162.1	-73.6	-467.2
$C_{12}H_4(OCH_3)_6$	-811.5	2566.6	58.8	829	139.1	1294.4	-79.5	-514.2
$C_{12}H_3Cl_6(OCH_3)$	-150.8	1064.2	45.7	820	203.7	616.5	-52.1	-278.9
$C_{12}H_3Cl_5(OCH_3)_2$	-301.0	1448.9	48.8	870	195.6	748.8	-58.0	-325.9
$C_{12}H_3Cl_4(OCH_3)_3$	-431.1	1638.9	51.9	848	187.8	880.6	-63.9	-372.5
$C_{12}H_3Cl_3(OCH_3)_4$	-567.7	1978.4	55.1	855	179.9	1012.3	-69.9	-419.1
$C_{12}H_3Cl_2(OCH_3)_5$	-704.3	2317.8	58.2	863	172.2	1144.1	-75.8	-465.7
$C_{12}H_3Cl(OCH_3)_6$	-840.9	2657.3	61.4	871	164.1	1276.4	-81.7	-512.7
$C_{12}H_3(OCH_3)_7$	-977.5	2996.8	64.5	879	156.3	1408.2	-87.6	-559.3

250 °C; detector temperature 300 °C) and Shimadzu GC-17A gas chromatograph (flame-ionization detector; MDN 5S (30000 × 0.25 mm) quartz capillary column coated with 0.25 μm of methylphenylsilicone stationary phase containing 5% grafted phenyl groups; carrier gas nitrogen; flow division ratio 1 : 30; column temperature: 100°C, 1 min; heating to 200°C, 10 deg min<sup>-1</sup>; heating to 300°C, 2 deg min<sup>-1</sup>; vaporizer temperature 250°C; detector temperature 280°C; solvent toluene; sample volume 0.2 μl).

The compounds were identified with a Fisons gas chromatograph-mass spectrometer (MD 800 detector; HP-5 (25 000 × 0.25 mm) quartz capillary column coated with 0.25 μm of stationary phase; carrier gas helium; flow division ratio 1 : 20; column temperature: 100 °C, 1 min; heating to 200 °C, 10 deg min<sup>-1</sup>; heating to 300 °C, 2 deg min<sup>-1</sup>; vaporizer temperature 250 °C; ionization by electron impact, 70 eV; scanning

rate 1 mass spectrum per second; scanning of total ion current in the range 20 -700 amu), (Agilent GC7890A MSD 5975C inert XL EI/CI; HP-5MS (25 000 × 0.25 mm) quartz capillary column coated with 0.25 μm of dimethylpolysiloxane stationary phase; carrier gas helium; flow division ratio 1 : 50; column temperature: 40°C, 3 min; heating to 290°C, 10 deg min<sup>-1</sup>; vaporizer temperature 250°C; transition chamber temperature 280 °C; MS-source temperature 230°C; quadrupole temperature 150 °C; ionization by electron impact, 70 eV; scanning of total ion current in the range 20 -1000 amu).

## Results and discussion

### *Modeling of chemical reactions of a mixture PCB congeners with MeONa in DMSO*

Thermodynamic modeling and the HSC 6.1 software were used to model the reaction of 0.025 mol of the technical PCBs mixture Sovol with 0.1 – 0.15 mol of MeONa in 25 ml of DMSO in the temperature range 25–170 °C at a total pressure of 1 atm. The input data for the thermodynamic modeling were analogous to the experimental data in [3]. In the modeling we took into account formation of NaCl, as well as carbon monoxide and dioxide, water, and HCl (decomposition products of PCB congeners).

Thermodynamic modeling with different initial contents of MeONa showed that at the increased concentration of MeONa the concentrations of all starting congeners in the final gas phase decrease, for example, the concentration of trichlorobiphenyl decreases from 37.6 to 10.8 mol %, while the concentration of the products of complete chlorine substitution by methoxy groups much increases. The increase in temperature from 25 to 170 °C also leads to an increase in the degree of conversion of PCB congeners.

Thus, at 170 °C the concentration of trimethoxybiphenyl increases from 0.7 to 10.9 mol %, tetramethoxybiphenyl, from 1.98 to 13.9 mol %, pentamethoxybiphenyl, from 5.43 to 17.4 mol %, and hexamethoxybiphenyls, from 13.4 to 19.6 mol %. An exception is heptamethoxybiphenyl, the concentration of which in the gas phase decreases from 40.9 to 27.3 mol % as the concentration of MeONa increases, while the concentration of unreacted heptachlorobiphenyl there with increases from  $4.73 \times 10^{-27}$  to  $2.90 \times 10^{-21}$  mol %.

Thermodynamic modeling with 0.15 mol of MeONa under the same conditions established that increasing the concentration of MeONa results in that the final gas phase contains no starting PCB congeners, and the prevalent reaction products are methoxy derivatives of hepta-, hexa-,

and pentamethoxybiphenyls as the products of exhaustive substitution of chlorine by methoxy groups. Consequently, less reactive PCB congeners (for example, trichlorobiphenyls), too, readily enter the methoxylation reaction as the quantity of MeONa is increased. The results of thermodynamic modeling allow us to conclude that high-chlorinated PCB congeners are more reactive than low-chlorinated ones, while the composition of the reaction products depends on the initial concentration of MeONa.

However, the calculated starting amount of MeONa of 0.15 mol should be considered as an arbitrary value, and an exact amount of this reagent can only be determined experimentally, because thermodynamic modeling does not include kinetic factors for example, the reaction time.

### ***The experimental studies of the interaction of PCBs with MeONa in DMSO***

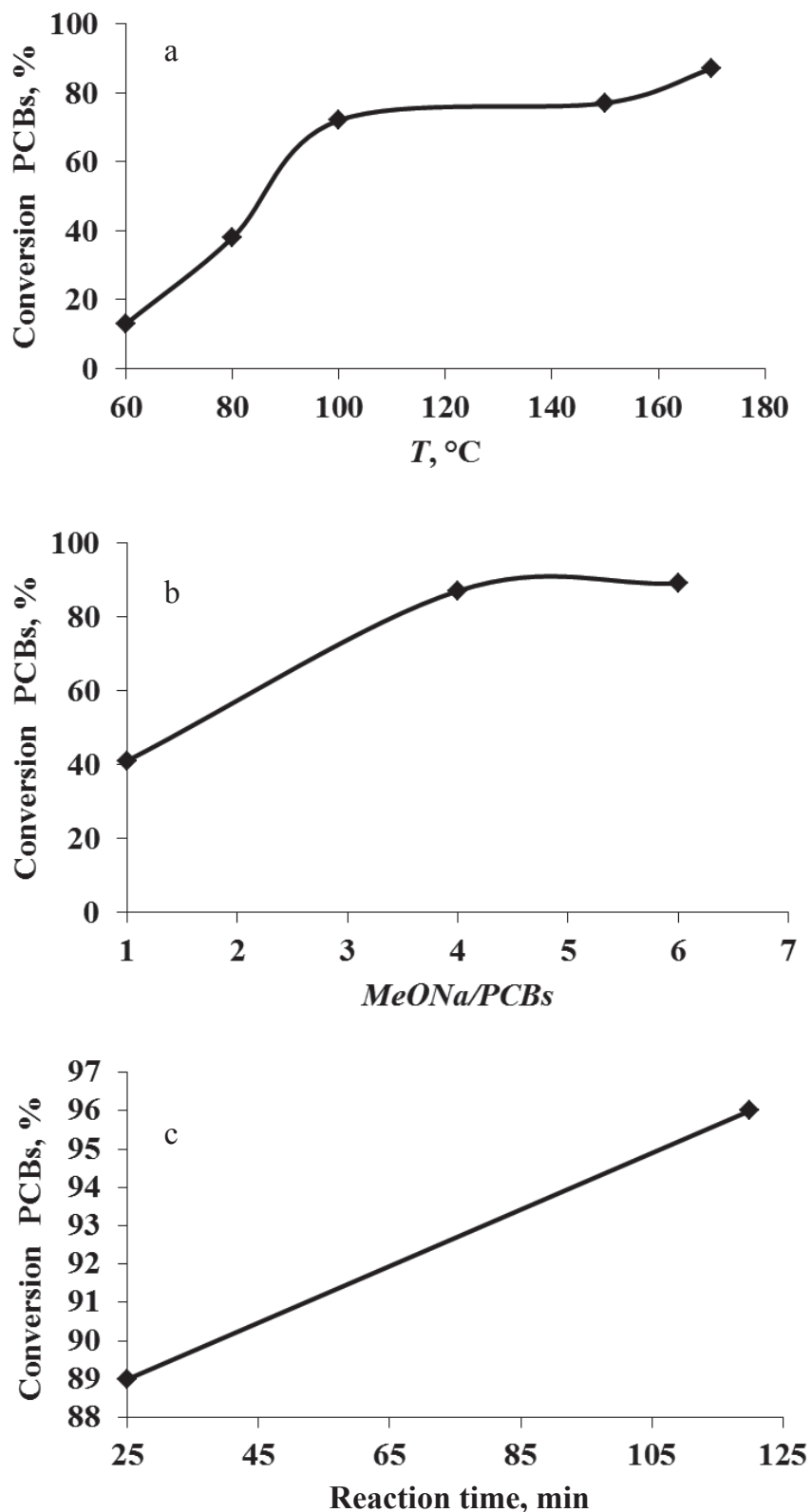
The experimental studies of the interaction of a mixture of PCBs Sovol with MeONa in DMSO were carried within temperature 60 - 170 °C, at reaction time 10, 25, 120 min and molar excess MeONa/ PCBs = 1/1, 4/1, 6/1. The results of the experimental studies are listed in Fig. 2.

Fig. 2 (a) shows that 25 to 170 °C the degree of conversion of congeners of a mixture Sovol increases and at temperature 170 °C is 87%. The increases of the fraction of methoxy- derivatives at an elevated (170 °C) temperature is consistent with the results of thermodynamic modeling.

Fig. 2 (b) shows the degree of conversion of PCB congeners by the reaction with MeONa in DMSO at temperature - 170 °C and reaction time – 25 min at a different molar excess MeONa/ PCBs. It shows, that the maximum the degree of conversion of PCBs Sovol is reached at molar excess MeONa/PCBs= 6/1 is equal to 89 %. The main products of the reaction are methoxy- derivatives PCBs (mono-, di-, three methoxy derivatives).

Fig. 2 (c) shows the degree of conversion of PCB congeners at temperature 170 °C and MeONa/PCBs =6/1 at a different time of interaction. It shows, that the maximum the degree of conversion of PCBs Sovol with MeONa in DMSO is reached at time of interaction 120 min is equal to 96 %.

The experimental research showing that the most reactive congeners are hepta-, hexa-, and pentachlorobiphenyls, where as the least reactive of trichlorinated congeners. Tetrachlorobiphenyls occupy an intermediate position. Trichlorobiphenyls were characterized by relatively low degree of reaction with sodium methoxide, with predominant formation of monomethoxydichlorobiphenyls. The reactivity data for the congener



**Fig. 2.** The degree of conversion of PCB congeners by the reaction of 0.025 mol Sovol with MeONa in 25 ml DMSO vs: a) temperature, at reaction time 25 min, MeONa/PCBs= 4/1; b) MeONa/PCBs, at reaction time 25 min and temperature 170 °C; c) reaction time, at temperature 170 °C, MeONa/PCBs= 6/1, a total pressure of 1 atm

groups comprised in Sovol are fully coincident with result of thermodynamic modeling.

### **Conclusion**

The results of thermodynamic modeling of the reactions of the PCB congeners comprised in the Sovol mixture, with MeONa in DMSO well reproduce the experimental data. The maximum the degree of conversion of PCBs Sovol with MeONa in DMSO is reached at time of interaction 120 min,  $T=170\text{ }^{\circ}\text{C}$ , MeONa/PCB=6/1 is equal to 96%. The main products of the reaction are methoxy-derivatives PCBs (mono-, di-, tri- methoxy derivatives).

Both works gave evidence showing that the most reactive congeners are hepta-, hexa-, and pentachlorobiphenyls, whereas the least reactive of trichlorinated congeners. Tetrachlorobiphenyls occupy an intermediate position.

The thermodynamic modeling performed in the present work seems to be a useful and promising tool for predicting the behavior of PCB congeners in reactions with other reagents.

### **Acknowledgements**

The work was supported by the RFBR (grant № 16-33-00314).

### **References**

1. Maisterenko V.N., Klyuev N.A. *Environmental Analytical Monitoring of Persistent Organic Pollutants*, Moscow: INOM, 2004.
2. Kulikova T.V., Maiorova A.V., Shunyaev K.Yu., Gorbunova T.I., Saloutin V.I., Chupakhin O.N. *Thermodynamic modeling of the reaction of polychlorinated biphenyls with sodium methoxide // Russian Journal of General Chemistry*. 2013. V. 83. №. 5. P. 893–900.
3. Zabelina O. N., Gorbunova T. I., Pervova M. G., Kirichenko V. E., Zapevalov A. Ya., Saloutin V. I., Chupakhin O. N. *Reactivity of Congeners of Sovol Technical Mixture of Polychlorinated Biphenyls toward Sodium Methoxide // Russian Journal of Applied Chemistry*. V. 77. № 9. 2004. P. 1523-1527.