

# Thermodynamic Modeling of the Stage of Polychlorinated Biphenyls Preparation to Thermal Decomposition

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**Abstract**—The reaction of Sovol (technical mixture of polychlorinated biphenyls) with sodium methoxide in dimethyl sulfoxide and methanol has been studied using the thermodynamic modeling method. The optimal process conditions have been elaborated: 1 atm, 115°C, 0.25 mol of dimethyl sulfoxide, 0.085 mol of methanol, the polychlorinated biphenyls : sodium methoxide molar ratio = 1 : 4. Experimental data on the interaction of the polychlorinated biphenyls with sodium methoxide under the theoretically determined conditions have revealed a range of positive effects: savings of the reactants, complete conversion, and the formation of potentially less toxic compounds. The studied interaction can serve as a stage for the pretreatment of toxic polychlorinated biphenyls for the pyrolytic destruction.

**Keywords:** polychlorinated biphenyls, chemical pretreatment, thermodynamic modeling, pyrolytic method

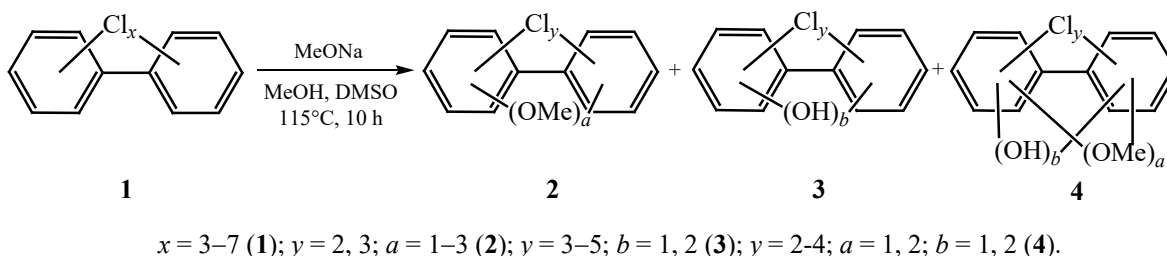
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Development of methods of wastes utilization or disposal should aim at the technology ensuring minimal production of additional useless products and complete conversion of the starting materials. In the case of hazardous wastes which should be exclusively disposed, the technological requirements are even more strict: the absence of any side products and complete conversion of the disposed materials. Polychlorinated biphenyls (PCB) belong to persistent organic pollutants and should have been disposed by 2028, according to the Stockholm Convention (2001). Russia (ratified the Convention in 2011) currently stores about 35000 tons of these wastes as PCBs mixtures Sovol and Sovtol-10 (21000 tons in total) and Triklorbifenil (14000 tons) [1]. The Sovol mixture of PCBs is the largest-scale grade of hazardous wastes among technical PCBs. According to the State Standard 7821-2000 developed basing on the Sovol mixture (OST 6-01-24-75), the product consists of 35 congeners including tri- (2.1%), tetra- (19.1%), penta- (51.5%), hexa- (17.9%), and heptachlorinated biphenyls (1.9%) [2].

Pyrolytic method has been recognized as the only sufficiently developed and efficient approach to PCBs disposal [3]. However, burning of these chloroaromatic compounds in air yields highly toxic products: chlorine, nitrogen oxides, phosgene, polychlorinated dibenzofurans, and polychlorinated dibenzodioxins [4]. It is reasonable to suggest that the mixtures of PCBs should be completely or partially dechlorinated prior to burning in order to minimize the formation of toxic compounds during disposal. This is possible via chemical hydrodechlorination [5]. However, these reactions occur in a solution in the presence of expensive catalyst (usually Pd-based) which should be separated and regenerated after the use, therefore large-scale pretreatment of PCBs via reductive dichlorination is cost-inefficient. Another approach to elimination of chlorine from PCBs congeners takes advantage of nucleophilic substitution with the groups introduction of which in the biphenyl structure would reduce the toxicity of the burning products.

The simplest procedures for nucleophilic substitution ( $S_N$ ) of chlorine in PCBs congeners is the interaction

Scheme 1.



with alkoxides of alkali metals [6]. However, practical application of this reaction is hampered by the complex composition of the PCBs mixtures, since the reactivity of individual congeners is different and depends on the number and position of the chlorine atoms in the structure, as shown by quantum-chemical simulation of nucleophilic substitution [7, 8]. This can be a reason of incomplete conversion during the interaction of Sovol mixture with alkali metals alkoxides:  $\text{MeO}^-$  [9],  $\text{EtO}^-$ ,  $\text{PrO}^-$ ,  $i\text{-PrO}^-$ ,  $n\text{-BuO}^-$ ,  $sec\text{-BuO}^-$ , and  $tert\text{-BuO}^-$  [10]. Thermodynamic modeling [11] has allowed elaboration of the conditions of complete conversion of the Sovol PCBs with  $\text{MeO}^-$  [12]: Sovol :  $\text{MeONa}$  molar ratio 1 : 5, temperature  $170^\circ\text{C}$ , and pressure 1 atm in DMSO medium.

Moreover, further development of the experimental techniques has allowed complete conversion of Sovol mixture **1** under the action of  $\text{MeO}^-$  (1 :  $\text{MeONa}$  molar ratio 1 : 5) at much lower temperature ( $114\text{--}115^\circ\text{C}$ ) owing to the introduction of anhydrous methanol to the reaction mixture, to enhance the solubility of chloroarenes in the mixed solvent [13, 14]. The formation of methoxy (**2**, 21.5%), hydroxy (**3**, 51.0%), and methoxyhydroxy (**4**, 27.5%) derivatives of PCBs has been observed after the reaction during 8 h (Scheme 1).

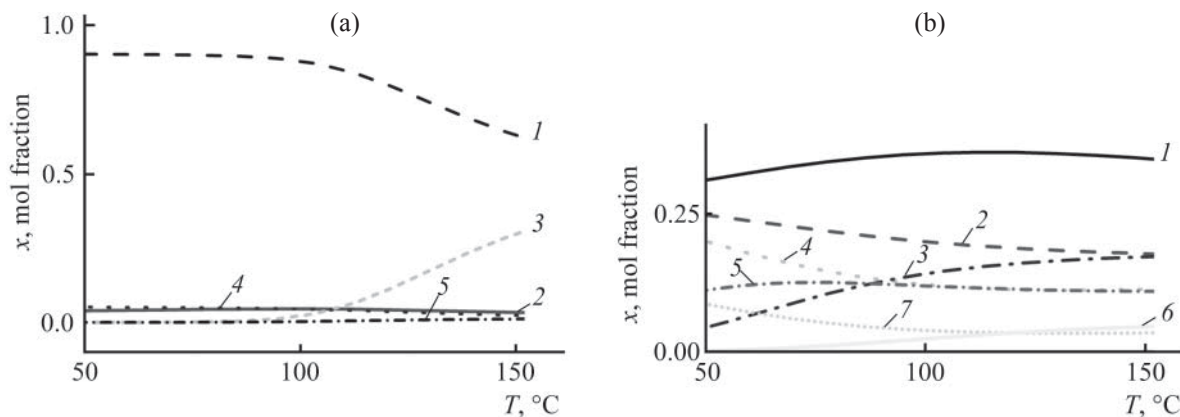
Thermodynamic modeling has not been applied to this interaction, even though it has been demonstrated [15, 16] that the marked theoretical approach can be used for elaboration of the conditions allowing the increase in the starting PCBs congeners conversion, minimization of the toxic products formation, and significant saving of the consumables, labor, and electricity.

This study aimed to investigate the interaction of Sovol mixture with  $\text{MeONa}$  in DMSO–MeOH medium by means of thermodynamic modeling and to verify the obtained data by comparison with the experimental results in order to develop a method of chemical pretreatment of the toxic PCBs before burning.

**Thermodynamic modeling of chemical interaction of Sovol mixture 1 with  $\text{MeONa}$  in DMSO–MeOH medium.** Availability of the database of thermochemical properties of the studied compounds is a prerequisite for thermodynamic modeling. The following thermochemical parameters of methoxy (**2**), hydroxy (**3**), and methoxyhydroxy (**4**) derivatives of PCBs were required to apply the thermodynamic modeling method: standard enthalpy of formation ( $\Delta H_{298}^\circ$ ), enthalpy increase between 0 and 298 K ( $H_{298}^\circ - H_0^\circ$ ), standard heat capacity ( $C_p^\circ$ ) and its temperature dependence [ $C_p(T)$ ], and entropy ( $S_{298}^\circ$ ). The thermochemical properties of the methoxy (**2**) and hydroxy (**3**) derivatives have been calculated and reported by us earlier [18, 19]. The data on the methoxyhydroxy derivatives **4** have not been available.

The missing thermochemical properties of derivatives **4** were calculated using the earlier developed algorithm based on the structure analysis [20]. The calculations were performed in HSC 8.2.0 software suite including Benson Estimation module. The calculated thermochemical parameters of the derivatives **4** (Table 1) were imported in the HSC 8.2.0 database and used in the modeling of the interaction between the components of Sovol mixture **1** with  $\text{MeONa}$  in DMSO–MeOH medium.

The interaction of Sovol mixture **1** (0.025 mol) with  $\text{MeONa}$  (0.025–0.15 mol) in DMSO (0.25 mol) in the absence and in the presence of the cosolvent MeOH (0.085 mol) was investigated by means of thermodynamic modeling using Equilibrium Composition module of HSC suite. It has been shown that the boiling point of the considered DMSO–MeOH mixed solvent is of  $114\text{--}115^\circ\text{C}$  [13, 14]. Thermodynamic modeling was performed over the  $50\text{--}150^\circ\text{C}$  temperature range at atmospheric pressure. The following products were added to the model:  $\text{NaCl}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ ; their thermochemical properties were taken from the HSC database. The algorithm of calculation of the equilibrium composition in HSC software suite has been detailed elsewhere [17].



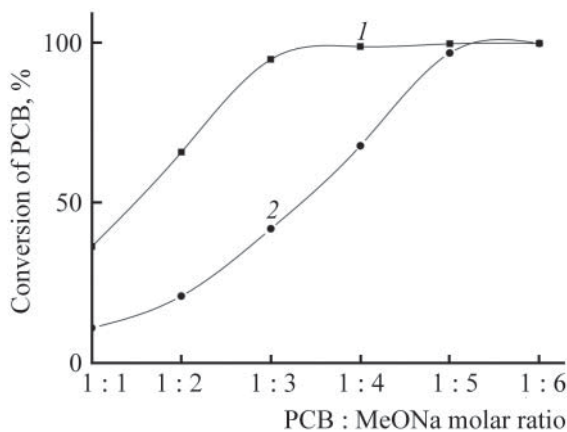
**Fig. 1.** Equilibrium composition of polychlorinated biphenyls and congeners as function of temperature. Starting composition: (a) 0.025 mol of Sovol mixture **1**, 0.025 mol of MeONa, 0.25 mol of DMSO; (b) 0.025 mol of Sovol mixture **1**, 0.025 mol of MeONa, 0.25 mol of DMSO, 0.085 mol of MeOH (50–150°C, 1 atm). Sum of molar fraction of the congeners and polychlorinated biphenyls derivatives is unity. (a), (1)  $C_{12}H_7Cl_3$ , (2)  $C_{12}H_6Cl_4$ , (3)  $C_{12}H_3Cl_5(OCH_3)_2$ , (4)  $C_{12}H_5Cl_5$ , (5)  $C_{12}H_3Cl_6(OCH_3)$ . (b) (1)  $C_{12}H_7(OCH_3)_3$ , (2)  $C_{12}H_7Cl(OCH_3)_2$ , (3)  $C_{12}H_7Cl_2(OCH_3)$ , (4)  $C_{12}H_7Cl(OH)_2$ , (5)  $C_{12}H_7Cl_3$ , (6)  $C_{12}H_7Cl_2(OH)$ , (7)  $C_{12}H_7(OH)_3$ .

Figure 1 displays the equilibrium composition of the system obtained via thermodynamic modeling of the interaction of equimolar amounts of Sovol mixture **1** with MeONa. In the absence of MeOH, the resulting products majorly contained the unreacted trichlorinated (up to 0.9 molar parts) as well as tetra- and pentachlorinated biphenyls (Fig. 1a). The increase in temperature resulted in the decrease in the starting PCBs **1** concentration and the increase in the content of the methoxy derivatives **2**. The introduction of MeOH as cosolvent (Fig. 1b) led to sharp decrease in the concentration of the starting congeners at temperature as low as 50°C, the reaction products containing considerable amounts of the methoxy (**2**) and hydroxy (**3**) derivatives. The concentration of the methoxyhydroxy derivatives **4** was not significant, not exceeding

$10^{-7}$  molar parts. The obtained data showed that the methoxyhydroxy derivatives **4** were thermodynamically unstable (intermediate) products. The equilibrium mixture of the nucleophilic substitution products contained majorly the methoxy (**2**) and hydroxy (**3**) derivatives.

It should be noted that the excess of MeOH (a protic solvent) could hinder the substitution. It has been earlier found that the optimal DMSO : MeOH ratio not leading to the studied reaction inhibition was 1 : 7 (mass) or 1 : 3 (molar) [13]. That ratio was used hereafter.

Figure 2 displays the results of thermodynamic modeling performed to optimize the MeONa–mixture **1** molar ratio ensuring complete substitution of chlorine in the PCBs congeners with methoxy and hydroxy groups. It was found that the substitution was complete at the mixture **1**–MeONa molar ratio of 1 : 4 (in the presence of MeOH) and 1 : 6 (in the absence of MeOH). Hence, the addition of the cosolvent to DMSO sharply reduced the concentration of the PCBs congeners of mixture **1** which were converted into the methoxy **2** and hydroxy **3** derivatives. The amount of MeONa required for complete conversion of Sovol mixture **1**.



**Fig. 2.** Conversion of polychlorinated congeners of Sovol mixture **1** with respect to (1 : MeONa) molar ratio: (1) 0.085 mol of MeOH, (2) without MeOH. Conditions: 115°C, 1 atm.

The obtained results of thermodynamic modeling should be considered as the highest conversion possible, disregarding the catalytic and kinetic effects. The real process occurring within finite time can be kinetically hampered even being allowed thermodynamically. The optimal conditions of the interactions in terms of the highest conversion of mixture **1** in the reaction with MeONa were found as follows: MeOH : DMSO molar ratio 1 : 3, temperature 115°C (highest possible due to the

**Table 1.** Calculated thermochemical properties of derivatives of polychlorinated biphenyls 4

Compound	$\Delta H_{298}^{\circ}$ , J/mol	$S^{\circ}$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G_{298}^{\circ}$ , kJ/mol	$H_{298}^{\circ} - H_0^{\circ}$ , kJ/mol	$C_p = a + b \times 10^{-3}T + c \times 10^5 T^{-2} + d \times 10^{-6}T^2$ , J mol <sup>-1</sup> K <sup>-1</sup> [17]			
					<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
C <sub>12</sub> H <sub>6</sub> Cl <sub>2</sub> (OCH <sub>3</sub> )OH	-214.01	530.27	-28.97	37.19	71.672	702.524	-8.778	-279.123
C <sub>12</sub> H <sub>5</sub> Cl <sub>3</sub> (OCH <sub>3</sub> )OH	-241.22	557.41	-50.53	39.46	90.750	679.174	-6.722	-269.650
C <sub>12</sub> H <sub>5</sub> Cl <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> OH	-378.34	573.81	-135.18	43.13	75.971	799.516	-0.013	-313.966
C <sub>12</sub> H <sub>4</sub> Cl <sub>4</sub> (OCH <sub>3</sub> )OH	-268.43	584.55	-72.09	41.73	109.828	655.813	-4.667	-260.176
C <sub>12</sub> H <sub>4</sub> Cl <sub>3</sub> (OCH <sub>3</sub> ) <sub>2</sub> OH	-405.55	600.95	-156.74	45.41	111.171	717.944	-2.043	-230.627
C <sub>12</sub> H <sub>4</sub> Cl <sub>3</sub> (OCH <sub>3</sub> )(OH) <sub>2</sub>	-418.53	583.77	-205.15	42.14	102.636	681.342	-4.770	-268.246
C <sub>12</sub> H <sub>3</sub> Cl <sub>4</sub> (OCH <sub>3</sub> )(OH) <sub>2</sub>	-445.74	610.91	-226.71	44.41	121.714	657.882	-2.715	-258.832
C <sub>12</sub> H <sub>5</sub> Cl <sub>2</sub> (OCH <sub>3</sub> )(OH) <sub>2</sub>	-391.32	556.63	-183.59	39.87	83.558	704.803	-6.826	-277.780
C <sub>12</sub> H <sub>6</sub> Cl(OCH <sub>3</sub> )(OH) <sub>2</sub>	-364.11	529.49	-162.03	37.58	64.480	728.263	-8.881	-287.253
C <sub>12</sub> H <sub>6</sub> (OCH <sub>3</sub> )(OH) <sub>3</sub>	-514.21	528.71	-295.09	38.00	57.288	753.992	-8.985	-295.383
C <sub>12</sub> H <sub>6</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	-501.23	545.89	-246.68	41.25	59.446	813.581	-4.641	-286.924
C <sub>12</sub> H <sub>6</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH)	-488.25	563.06	-198.27	44.53	78.746	811.481	-4.645	-199.924
C <sub>12</sub> H <sub>5</sub> Cl(OCH <sub>3</sub> )(OH) <sub>3</sub>	-541.42	555.85	-316.65	40.27	76.366	730.531	-6.929	-285.910
C <sub>12</sub> H <sub>5</sub> (OCH <sub>3</sub> )(OH) <sub>4</sub>	-691.52	555.07	-449.71	40.68	69.174	756.260	-7.033	-294.040
C <sub>12</sub> H <sub>5</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>3</sub>	-678.54	572.24	-401.30	43.94	69.393	822.838	-2.198	-294.462
C <sub>12</sub> H <sub>5</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH) <sub>2</sub>	-665.56	589.42	-352.89	47.21	106.040	758.213	-6.593	-127.987
C <sub>12</sub> H <sub>5</sub> (OCH <sub>3</sub> ) <sub>4</sub> (OH)	-652.58	606.60	-304.48	50.48	92.483	874.442	1.732	-191.523
C <sub>12</sub> H <sub>4</sub> Cl <sub>2</sub> (OCH <sub>3</sub> )(OH) <sub>3</sub>	-568.63	582.99	-338.21	42.54	95.444	707.071	-4.874	-276.436
C <sub>12</sub> H <sub>4</sub> Cl(OCH <sub>3</sub> )(OH) <sub>4</sub>	-718.73	582.21	-471.27	42.95	88.252	732.800	-4.977	-284.566
C <sub>12</sub> H <sub>4</sub> (OCH <sub>3</sub> )(OH) <sub>5</sub>	-868.63	582.10	-604.33	43.35	81.060	758.529	-5.081	-292.696
C <sub>12</sub> H <sub>4</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>4</sub>	-855.85	598.60	-555.92	46.62	73.473	853.242	1.733	-328.883
C <sub>12</sub> H <sub>4</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub>	-842.87	615.85	-507.53	49.88	65.888	948.056	8.545	-365.069
C <sub>12</sub> H <sub>4</sub> (OCH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>	-829.89	632.96	-459.10	53.15	58.300	1042.769	15.358	-401.256
C <sub>12</sub> H <sub>4</sub> (OCH <sub>3</sub> ) <sub>5</sub> (OH)	-816.91	650.14	-410.69	56.42	50.713	1137.483	22.171	-766.482
C <sub>12</sub> H <sub>4</sub> Cl <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	-555.65	600.50	-289.90	45.81	87.857	801.785	1.939	-312.623
C <sub>12</sub> H <sub>4</sub> Cl <sub>2</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH)	-542.67	532.74	-241.39	49.08	80.270	896.598	8.752	-348.809
C <sub>12</sub> H <sub>4</sub> Cl(OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>3</sub>	-705.75	599.38	-422.86	46.21	80.665	827.513	1.836	-320.753
C <sub>12</sub> H <sub>4</sub> Cl(OCH <sub>3</sub> ) <sub>3</sub> (OH) <sub>2</sub>	-692.77	616.56	-374.45	49.48	91.037	857.595	4.098	-274.659
C <sub>12</sub> H <sub>4</sub> Cl(OCH <sub>3</sub> ) <sub>4</sub> (OH)	-679.79	633.74	-326.04	52.75	65.492	1017.041	15.462	-393.126
C <sub>12</sub> H <sub>5</sub> Cl(OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	-528.44	573.03	-268.24	43.54	68.779	825.245	-0.116	-322.096
C <sub>12</sub> H <sub>5</sub> Cl(OCH <sub>3</sub> ) <sub>3</sub> (OH)	-515.46	590.20	-219.83	46.81	61.192	920.059	6.697	-358.283
C <sub>12</sub> H <sub>3</sub> Cl <sub>4</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH)	-419.78	509.19	-129.89	50.94	114.127	752.595	4.098	-295.019
C <sub>12</sub> H <sub>3</sub> Cl <sub>3</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH)	-569.88	644.48	-262.95	51.35	99.348	873.138	10.808	-339.336
C <sub>12</sub> H <sub>3</sub> Cl <sub>3</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	-582.86	627.31	-311.36	48.08	106.935	778.324	3.995	-303.149
C <sub>12</sub> H <sub>3</sub> Cl <sub>3</sub> (OCH <sub>3</sub> )(OH) <sub>3</sub>	-595.84	610.13	-359.77	44.81	92.278	763.789	2.818	-368.878
C <sub>12</sub> H <sub>3</sub> Cl <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>3</sub>	-732.96	625.95	-444.25	48.48	99.743	804.053	3.891	-311.279
C <sub>12</sub> H <sub>3</sub> Cl <sub>2</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH) <sub>2</sub>	-719.98	643.70	-396.01	51.75	92.156	898.867	10.704	-347.466
C <sub>12</sub> H <sub>3</sub> Cl <sub>2</sub> (OCH <sub>3</sub> ) <sub>4</sub> (OH)	-707.00	660.88	-347.6	55.02	84.978	992.109	17.414	-381.782
C <sub>12</sub> H <sub>3</sub> Cl <sub>2</sub> (OCH <sub>3</sub> )(OH) <sub>4</sub>	-745.94	609.35	-492.83	45.22	107.330	709.339	-2.922	-275.092
C <sub>12</sub> H <sub>3</sub> Cl(OCH <sub>3</sub> )(OH) <sub>5</sub>	-896.04	608.57	-625.89	45.62	100.138	735.068	-3.025	-283.222
C <sub>12</sub> H <sub>3</sub> Cl(OCH <sub>3</sub> ) <sub>5</sub> (OH) <sub>1</sub>	-844.12	677.28	-432.25	58.69	69.995	1113.287	24.175	-447.194
C <sub>12</sub> H <sub>3</sub> Cl(OCH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>	-857.1	660.10	-480.66	56.46	77.378	1019.309	17.414	-391.782
C <sub>12</sub> H <sub>3</sub> Cl(OCH <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub>	-870.07	642.95	-529.07	52.04	84.965	924.595	10.601	-355.596
C <sub>12</sub> H <sub>3</sub> Cl(OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>4</sub>	-883.06	625.74	-577.48	48.75	92.551	829.782	3.788	-319.409
C <sub>12</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>2</sub> (OH) <sub>5</sub>	-1033.16	624.96	-710.54	49.29	85.360	855.511	3.684	-327.539
C <sub>12</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH) <sub>6</sub>	-1046.14	607.79	-758.95	46.03	68.253	849.803	3.129	-404.488
C <sub>12</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>6</sub> (OH)	-981.24	693.67	-516.9	62.36	55.012	1234.465	30.936	-472.285
C <sub>12</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>5</sub> (OH) <sub>2</sub>	-994.22	676.49	-565.31	59.09	62.905	1138.648	24.046	-434.696
C <sub>12</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>4</sub> (OH) <sub>3</sub>	-1007.2	659.32	-613.72	55.83	70.186	1045.038	17.310	-399.912
C <sub>12</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>3</sub> (OH) <sub>4</sub>	-1020.18	642.14	-662.13	52.56	77.773	950.324	10.497	-363.726

**Table 2.** The products of interaction between Sovol mixture **1** with MeONa in DMSO in the presence of MeOH (115°C, 10 h)

Compound no.	Number of substituents	Molecular ion, $m/z$	Number of isomers	Relative content, %
2	$y = 2, a = 1$	252	2	1.5
2	$y = 2, a = 2$	282	11	12.0
2	$y = 3, a = 1$	286	7	5.8
3	$y = 3, b = 1$	272	4	4.9
2	$y = 2, a = 3$	312	5	1.7
2	$y = 3, a = 2$	316	2	0.5
3	$y = 3, b = 2$	288	5	0.9
3	$y = 4, b = 1$	306	15	31.1
4	$y = 2, a = 2, b = 1$	298	6	2.6
4	$y = 3, a = 1, b = 1$	302	17	19.9
3	$y = 4, b = 2$	322	11	11.2
3	$y = 5, b = 1$	340	3	0.7
4	$y = 3, a = 1, b = 2$	318	1	0.1
4	$y = 3, a = 2, b = 1$	332	5	1.5
4	$y = 4, a = 1, b = 1$	336	10	3.4
4	$y = 4, a = 1, b = 2$	352	1	2.1
3	$y = 5, b = 2$	356	1	0.1
			Total:	100

solvent boiling), mixture **1** : MeONa molar ratio 1 : 4, and pressure 1 atm. The reaction duration could be found only in the experiment.

**Experimental investigation of chemical interaction of Sovol mixture 1 with MeONa in DMSO–MeOH medium.** The experiment conditions corresponded to the results of the optimization by means of thermodynamic modeling. The reaction duration (10 h) was selected for comparison with the data obtained earlier in the study of the same reaction in the absence of MeOH [12]. The moment when the glycerol bath temperature reached 114–115°C after the reagents mixing was considered the reaction start. The reaction mixture was sampled each 2 h, treated as described in Experimental section, and analyzed by means of GC–FID and GC–MS. The analysis revealed the formation of over 100 of new derivatives; their relative content is given in Table 2.

The obtained results showed that the interaction of PCBs mixture **1** with MeONa in DMSO–MeOH medium

occurred as a series of reactions differing in the rate and the products, depending on the starting congener structure. The methoxy (**2**), hydroxy (**3**), and methoxyhydroxy (**4**) derivatives of PCBs could be formed simultaneously or in sequence, in line with the earlier discussed data [12, 13]. The discrepancy between the results of thermodynamic modeling and the experiments (regarding the concentration of the formed methoxyhydroxy derivatives **4**) was due to impossibility to take into account the kinetic factors during the modeling. When the reaction was performed under the conditions elaborated via the modeling, complete conversion of the starting mixture **1** was reached within 10h, yet the required MeONa was reduced in comparison with the study in Ref. [12], which is a positive result. Furthermore, the Sovol **1** contained 44.28% of C, 1.65% of H, and 54.07 of Cl (elemental analysis data) whereas the mixture of products **2–4** isolated after the reaction contained 53.73% of C, 4.60% of H, and 27.26% of Cl. The twofold decrease in the chlo-



rine content upon the chemical treatment can potentially reduce the amount of hazardous products of burning as compared to burning of the starting mixture **1** [4].

In summary, thermodynamic modeling gave the optimized conditions of the interaction between the PCBs Sovol mixture **1** with MeONa in DMSO–MeOH medium. Performing the treatment under the elaborated conditions afforded complete conversion of the starting compounds saving the reagents and, potentially, to the reduced toxicity of the compounds **2–4** and the products of their further burning in comparison with Sovol mixture **1**. The obtained results are important in view of the comprehensive approach to disposal of PCBs via chemical and pyrolytic methods.

## EXPERIMENTAL

The following substances were used: technical mixture of polychlorinated biphenyls Sovol (OST 6-01-24-75), sodium metal, freshly dried and distilled MeOH ( $d_4^{20} = 0.7917 \text{ g/mL}$ ), and DMSO ( $d_4^{20} = 1.10 \text{ g/mL}$ ). The chemicals were of “chemical pure” grade if not stated otherwise.

**Interaction of Sovol mixture with MeONa in DMSO–MeOH medium.** A mixture of 2.3 g (0.1 mol) of sodium and 30.0 mL ( $V_0$ ) of anhydrous MeOH was stirred until the complete formation of MeONa (0.1 mol). Excess of MeOH was distilled off to frothing of the mixture. The volume of distilled MeOH was measured ( $V_1$ ), and the required amount of DMSO was calculated. To do so, we calculated the amount of MeOH required for the *in situ* formation of MeONa [ $V_2$ , Eq. (1)].



Then the amount of unreacted MeOH ( $V_3$ ) was determined using Eq. (2).

$$V_3 = V_0 - (V_1 + V_2). \quad (2)$$

Having determined  $V_3$ , the amount of DMSO corresponding to MeOH–DMSO molar ratio 1 : 3 was calculated.

The experimentally determined values were as follows:  $V_1 = 22.5 \text{ mL}$  ( $m = 17.78 \text{ g}$ ),  $V_2 = 4 \text{ mL}$  ( $m = 3.20 \text{ g}$ ),  $V_3 = 3.5 \text{ mL}$  ( $m = 2.77 \text{ g}$ , 0.085 mol). The amount of DMSO added to the mixture was 19.25 g (0.25 mol, 17.5 mL). The reaction mass was stirred at 115°C during 0.1 h, and then 8.2 g (0.025 mol) of Sovol mixture **1** was added (**1** : MeONa = 1 : 4). The reaction was performed at that temperature during 10 h at vigorous stirring. When the reaction was complete, the mixture was cooled, 50 mL of dilute HCl was added (to pH < 7), and the mix-

ture was extracted with toluene ( $4 \times 20 \text{ mL}$ ). The extract was analyzed by means of GC–MS.

**Qualitative and quantitative analysis of the products.** The reaction products were identified using an Agilent GC 7890A MSD 5975C inert XL EI/CI chromatogram–mass spectrometer equipped with an HP-5MS quartz capillary column (length 25 m, inner diameter 0.25 mm, stationary phase film thickness 0.25  $\mu\text{m}$ , polydimethylsiloxane with 5% of grafted phenyl groups) and a quadrupole mass spectrometry detector (GC–MS). Carrier gas: helium, split ratio 1 : 50, column temperature: 40°C (starting, isotherm 3 min), heating at 10 deg/min to 280°C (isotherm 50 min), evaporator temperature 250°C, detector temperature 300°C.

Relative amount of the products was determined by means of internal normalization (the contribution of individual compounds into the overall peak area was calculated, and the products amount was estimated from the calculated peaks area). Processing of the GC–MS chromatograms included the reconstruction by the selective ions which allowed identification of individual compounds under co-elution conditions. The data on the content of the unreacted congeners were confirmed by the analysis in the scanning over selective ions mode.

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## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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