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Thermodynamic Modeling of the Reaction of Polychlorinated Biphenyls with Sodium Methoxide

T. V. Kulikova[a], A. V. Maiorova[a], K. Yu. Shunyaev[a], T. I. Gorbunova[b], V. I. Saloutin[b], and O. N. Chupakhin[b]

[a] *Institute of Metallurgy, Ural Branch, Russian Academy of Sciences,*
ul. Amundsena 101, Yekaterinburg, 620016 Russia
e-mail: kuliko@gmail.com

[b] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

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Abstract—Thermochemical parameters, like standard enthalpy of formation (ΔH^0_{298}), enthalpy increment from 0 to 298 K ($H^0_{298} - H^0_0$), standard heat capacity (C^0_{p298}) and its temperature dependence [Cp(T)], and entropy (S^0_{298}), were calculated for the gaseous methoxy derivatives formed from polychlotinated biphenyl (PCB) congeners. Thermodynamic modeling and the HSC software were used to evaluate the reactivity of PCB congeners toward sodium methoxide in DMSO, and the calculation results were compared with experimental data.

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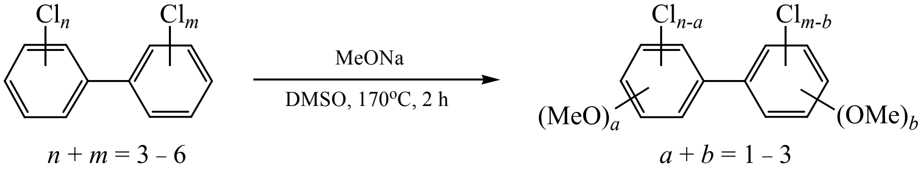
Polychlorinated biphenyls (PCBs) are the most ubiquitous anthropogenic pollutants. The Stockholm Convention (2001) requires PCBs to be completely destroyed by 2025. According to different sources, from 180 to 500 thsd tons of PCB of different trademarks were produced in Russia over the period from 1939 to 1990 [1, 2]. At present no technology capable of destroying all PCB stocks is available. The only way to utilize these toxic wastes is to combine several processing technologies [3–5]. 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, for example, alkoxy groups [4–7]. The procedures of PCB alkoxylation 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 any chemical reaction is hardly predictable.

One of the first PCB alkoxylation processes thoroughly studied by gas chromatography−mass spectrometry is the reaction of the technical mixture Sovol with sodium methoxide in DMSO [8].



Sovol is a mixture of several PCB congener groups: trichlorobiphenyls (~1%), tetrachlorobiphenyls (~22%), pentachlorobiphenyls (~56%), hexachlorobiphenyls (~20%), and heptachlorobiphenyls (~1%) [5]. It was found that the reactivity of PCBs under the process conditions decreases in the order hexa- > penta- > tetra- > trichlorobiphenyl congeners [8] (heptachlorobiphenyls were not considered). Therewith, hexachlorobiphenyls transformed into mono-, di-, and trimethoxy derivatives, pentachlorobiphenyls, into mono-, di-, and trimethoxy derivatives (in trace amounts), and tetrachlorobiphenyls, into mono- and dimethoxy

Table 1. Methoxy PCB derivatives used for modeling the chemical reaction with sodium methoxide

Starting congener (content in Sovol, %)[a]	Methoxy-PCB	
	type	positions of methoxy group/chlorine atoms
PCB 28 (0.4)	$C_{12}H_7Cl_2(OCH_3)$	2- / 4,4'-
	$C_{12}H_7Cl\,(OCH_3)_2$	2,4- / 4'-
	$C_{12}H_7\,(OCH_3)_3$	2,4,4'- / –
PCB 47 (0.5)	$C_{12}H_6Cl_3(OCH_3)$	2- / 2',4,4'-
	$C_{12}H_6Cl_2(OCH_3)_2$	2,2'- / 4,4'-
	$C_{12}H_6Cl(OCH_3)_3$	2,2',4- / 4'-
	$C_{12}H_6(OCH_3)_4$	2,2',4,4'- / –
PCB 118 (11.1)	$C_{12}H_5Cl_4(OCH_3)$	4'- / 2,4,5,3'-
	$C_{12}H_5Cl_2(OCH_3)_2$	5,4'- / 2,4,3'-
	$C_{12}H_5Cl_3(OCH_3)_3$	4,5,4'- / 2,3'-
	$C_{12}H_5Cl(OCH_3)_4$	4,5,3',4'- / 2-
	$C_{12}H_5(OCH_3)_5$	2,4,5,3',4'- / –
PCB 153 (6.1)[b]	$C_{12}H_4Cl_5(OCH_3)$	5'- / 2,4,5,2',4'-
	$C_{12}H_4Cl_4(OCH_3)_2$	5,5'- / 2,4,2',4'-
	$C_{12}H_4Cl_3(OCH_3)_3$	5,4',5'- / 2,4,2'-
	$C_{12}H_4Cl_2(OCH_3)_4$	5,2',4',5'- / 2,4-
	$C_{12}H_4Cl\,(OCH_3)_5$	4,5,2',4',5'- / 2-
	$C_{12}H_4(OCH_3)_6$	2,4,5,2',4',5'- / –
PCB 180 (0.6)	$C_{12}H_3Cl_6(OCH_3)$	4- / 2,3,5,2',4',5'-
	$C_{12}H_3Cl_5(OCH_3)_2$	4,5'- / 2,3,5,2',4'-
	$C_{12}H_3Cl_4\,(OCH_3)_3$	4,5,5'- / 2,3,2',4'-
	$C_{12}H_3Cl_3\,(OCH_3)_4$	4,5,2',5'- / 2,3,4'-
	$C_{12}H_3Cl_2\,(OCH_3)_5$	4,5,2',4',5'- / 2,3-
	$C_{12}H_3Cl\,(OCH_3)_6$	2,4,5,2',4',5'- / 3-
	$C_{12}H_3(OCH_3)_7$	2,3,4,5,2',4',5'- / –

[a] Published data [5]. [b] Total amount of PCB 153 and PCB 132 (these congeners are eluted together).

derivatives (in trace amounts), while trichlorobiphenyls transformed into monomethoxy derivatives (partially). Such tetrachlorobiphenyls as PCB 44 and PCB 52 remained unchanged.

Later we found that an individual pentachlorobiphenyl (PCB 101) under the same conditions transforms exclusively into monomethoxy derivatives to 87.2% [9]. However, in the postreaction mixture of Sovol (which also contains PCB 101) with MeONa we no detected this congener. Consequently, the alkoxylation route depends not only on the reaction conditions but also on other physicochemical factors which can be revealed by calculation methods.

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

The research was performed by means of thermodynamic modeling [10] and the HSC software, which 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.

Calculation of thermodynamic parameters of methoxy derivatives of polychlorinated biphenyls. 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. The following thermochemical parameters are required for thermodynamic modeling of methoxy derivatives of PCBs: standard enthalpy of formation (ΔH^0_{298}), enthalpy increment from 0 to 298 K ($H^0_{298} - H^0_0$), standard heat capacity ($C^0_{p\ 298}$) and its temperature dependence [$C_p(T)$], entropy (S^0_{298}), etc. These data are practically absent from the literature.

The standard enthalpy of formation, entropy, and heat capacity of gaseous methoxy-PCBs were calculated using the ChemBioDraw Ultra 12.0 software and Benson's method [11], which are based on an analysis of the molecular structure. As definite methoxy derivatives we chose compounds derived from those PCB congeners which are really present in Sovol (Table 1). Of each congener group (from tri- to heptachlorinated biphenyls) we chose one compound with the 4 and 4' positions substituted by chlorines, since it is well known that such PCBs are the most reactive in nucleophilic substitution reactions [8, 9]. The order of substitution of chlorines in PCB congeners by methoxy groups is unknown, and it was not taken into account in our calculations.

Table 2 presents an example of treatment of one of the methoxy-PCBs by the method of group additivity. Below we show the numbers of groups for determination of contributions for each group in the structural formulas of methoxy-PCBs.

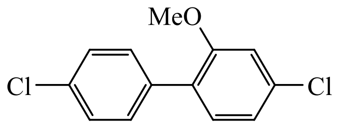
The thermodynamic parameters for the groups (Table 3) were determined on the basis of available reference and published data [12, 13].

Knowing the composition and number of groups comprised in a molecule, as well as the energy contribution of each group, we can calculate thermochemical parameters for the methoxy-PCBs studied by simple summation. Moreover, according to the Benson's method, we should include corrections for positions of the chlorine substituents in biphenyls (Table 3), which hinder the rotation of the benzene rings around the C–C bond. The effect of *ortho*-chlorines is stronger, while the effect of *meta*-chlorines is weaker. *Para*-chlorines have no effect on benzene ring rotation in biphenyls.

Analysis of data in Table 3 shows that some group contributions to standard entropy are lacking. Therefore, the Benson's method of group additivity could be used to calculate the standard enthalpy of formation and heat capacity. The standard entropy was calculated by Eq. (1).

$$\Delta S^0_{298} = (\Delta H^0_{298} - \Delta G^0_{298})/298.15. \qquad (1)$$

Table 2. Division into groups by the method of group additivity by an example of 2-methoxy-4,4'-dichlorobiphenyls



Group[a]	Number of groups in the molecule
C_B–H	7
C_B–C_B	2
C_B–Cl	2
C–O–H_3	1
O–$(C_B)_2$	1
C–(O)–(C_B)–(C_B)	1

[a] The symbol C_B is a commonly accepted denotation of aromatic carbon.

C_B–H	C_B–C_B	C_B–Cl	C–O–H_3	O–$(C_B)_2$	C–(O)–(C_B)–(C_B)
$10 - (x + y)$	2	x	y	y	y

x and y are the numbers of chlorine atoms and methoxy groups in methoxy-PCB, respectively.

The standard enthalpies of formation and Gibbs energies used in Eq. (1) were calculated by the ChemBioDraw Ultra 12.0 software, and the standard entropies of the starting compounds were calculated by Eqs. (2) and (3) using the reference data in [14].

$$\Delta S^0_{298} = S^0_{298\ \text{product}} - \Sigma S^0_{298\ \text{start.comp}}, \qquad (2)$$

$$S^0_{298\ \text{product}} = \Sigma S^0_{298\ \text{start.comp}} + (\Delta H^0 - \Delta G^0)/298.15. \qquad (3)$$

The calculation procedures used in the present work result in well convergent values of standard enthalpies of formation and heat capacities (Table 4). In the thermodynamic modeling we used the mean values of ΔH^0_{298} and $C^0_{p\ 298}$.

Table 3. Benson's group contributions to standard thermodynamic parameters for gaseous methoxy-PCBs [12, 13]

Group	ΔH^0_{298}, kJ mol^{-1}	S^0_{298}, J mol^{-1} K^{-1}	$C^0_{p\ 298}$, J mol^{-1} K^{-1}
C_B–H	13.81 [13] 13.82 [12]	48.31 [13] 48.27 [12]	13.61 [13] 13.56 [12]
C_B–C_B	21.66 [13] 20.77 [12]	–36.57 [13] –36.18 [12]	13.12 [13] 13.94 [12]
C_B–Cl	–17.03 [13] –15.91 [12]	77.08 [13] 79.13 [12]	29.33 [13] 30.98 [12]
C_B–O–H_3	–42.28 [13]	127.33 [13]	25.92 [13]
O–$(C_B)_2$	–88.34 [13]	–	4.56 [13]
C–(O)–(C_B)–(C)–H	–22.47 [13]	–	21.52 [13]
Correction for *ortho*-chlorine	9.50 [13] 9.21 [12]	0	30.80 [13] 2.094 [12]
Correction for *meta*-chlorine	–5.00 [13]	0	0

Table 4. Standard enthalpies of formation (ΔH^0_{298}) and heat capacities ($C^0_{\mathrm{p}\,298}$) for a series of methoxy-PCBs, calculated by the (1) ChemBioDraw Ultra 12.0 software and (2) Benson's group additivity method

Compound	ΔH^0_{298}, kJ mol^{-1}			δ, %	$C^0_{\mathrm{p}\,298}$, J mol^{-1} K^{-1}			δ, %
	1	2	mean		1	2	mean	
$C_{12}H_7Cl_2(OCH_3)$	–36.7	–46.9	–41.8	–24.5	231.5	236.8	234.1	–2.2
$C_{12}H_7Cl\,(OCH_3)_2$	–173.8	–183.0	–178.4	–5.2	256.2	257.8	257.0	–0.7
$C_{12}H_7\,(OCH_3)_3$	–310.8	–319.1	–314.9	–2.6	280.8	278.9	279.8	0.7
$C_{12}H_6Cl_3(OCH_3)$	–63.9	–77.8	–70.8	–19.6	246.8	254.2	250.5	–3.0
$C_{12}H_6Cl_2(OCH_3)_2$	–201.0	–213.8	–207.4	–6.2	271.4	275.3	273.3	–1.4
$C_{12}H_6Cl(OCH_3)_3$	–338.2	–349.9	–344.0	–3.4	296.0	296.3	296.2	–0.1
$C_{12}H_6(OCH_3)_4$	–475.3	–485.9	–480.6	–2.2	320.7	317.3	318.9	1.1
$C_{12}H_5Cl_4(OCH_3)$	–91.1	–108.6	–99.9	–17.5	262.0	271.7	266.8	–3.6
$C_{12}H_5Cl_3(OCH_3)_2$	–228.4	–380.7	–304.6	–50.0	311.3	292.7	301.9	6.2
$C_{12}H_5Cl_2(OCH_3)_3$	–365.4	–244.7	–305.0	39.6	286.6	313.7	300.1	–9.0
$C_{12}H_5Cl(OCH_3)_4$	–502.5	–516.8	–509.6	–2.8	335.9	334.7	335.3	0.4
$C_{12}H_5(OCH_3)_5$	–639.6	–652.9	–646.2	–2.1	360.5	355.7	358.1	1.3
$C_{12}H_4Cl_5(OCH_3)$	–118.3	–139.5	–128.9	–16.4	277.2	289.1	283.2	–4.2
$C_{12}H_4Cl_4(OCH_3)_2$	–255.5	–275.5	–265.5	–7.6	301.9	310.1	305.9	–2.7
$C_{12}H_4Cl_3(OCH_3)_3$	–392.6	–411.6	–402.1	–4.7	326.5	331.1	328.8	–1.4
$C_{12}H_4Cl_2(OCH_3)_4$	–529.7	–547.6	–538.7	–3.3	351.1	352.1	351.6	–0.3
$C_{12}H_4Cl\,(OCH_3)_5$	–666.8	–683.7	–675.3	–2.5	375.8	373.2	374.5	0.7
$C_{12}H_4(OCH_3)_6$	–803.2	–819.8	–811.5	–2.0	400.4	394.2	397.3	1.6
$C_{12}H_3Cl_6(OCH_3)$	–131.3	–170.3	–150.8	–25.9	255.3	306.5	280.9	–18.2
$C_{12}H_3Cl_5(OCH_3)_2$	–295.6	–306.4	–301.0	–3.6	295.2	327.5	311.3	–10.3
$C_{12}H_3Cl_4\,(OCH_3)_3$	–419.8	–442.4	–431.1	–5.3	341.7	348.5	345.1	–1.9
$C_{12}H_3Cl_3\,(OCH_3)_4$	–556.9	–578.5	–567.7	–3.8	366.4	369.5	367.9	–0.9
$C_{12}H_3Cl_2\,(OCH_3)_5$	–694.0	–714.5	–704.3	–2.9	390.9	390.6	390.8	0.1
$C_{12}H_3Cl\,(OCH_3)_6$	–831.1	–850.6	–840.9	–2.3	415.6	411.6	413.6	0.9
$C_{12}H_3(OCH_3)_7$	–968.3	–986.7	–977.5	–1.9	440.3	432.6	436.4	1.8

Table 5. Benson's group contributions to heat capacity for gaseous methoxy-PCBs [11]

Group	C^0_p, cal mol^{-1} K^{-1}					
	300 K	400 K	500 K	600 K	800 K	1000 K
C_B–H	3.24	4.44	5.46	6.30	7.54	8.41
C_B–C_B	3.33	4.22	4.89	5.27	5.76	5.95
C_B–Cl	7.40	8.40	9.20	9.70	10.20	10.40
C–O–H_3	6.19	7.84	9.40	10.79	13.03	14.48
O–$(C_B)_2$	1.09	1.22	1.50	1.99	2.85	3.51
C–(O)–(C_B)–(C_B)	5.14	7.28	9.03	9.41	10.31	10.75

The Benson's method of group additivity [11] was also used to calculate the temperature dependence of heat capacity for gaseous methoxy-PCBs. The group values for calculation of the temperature dependence of heat capacities are listed in Table 5. The resulting data were fitted by the polynomial (4).

$$C_\mathrm{p} = a + b\times10^{-3}T + c\times10^{5}T^{-2} + d\times10^{-6}T^{2}. \qquad (4)$$

The enthalpy increment from 0 to 298 K was calculated by Eq. (5) [17].

$$H^0_{298} - H^0_0 \approx 0.5C^\mathrm{o}_{\mathrm{p}\,298}\cdot 298.15. \qquad (5)$$

The calculated values of all the above-mentioned thermochemical parameters of gaseous methoxy-PCBs are listed in Table 6.

Modeling of chemical reactions of a mixture of PCB congeners with sodium methoxide. Thermodynamic modeling and the HSC 6.1 software were used to model the reaction of 8.2 g (0.025 mol) of the technical PCB mixture Sovol with 5.4 g (0.1 mol) and

Table 6. Thermochemical parameters of gaseous methoxy-PCBs

Compound	ΔH^0_{298}, kJ mol^{-1}	ΔG^0_{298}, kJ mol^{-1}	S^0_{298}, J mol^{-1} K^{-1}	$H^0_{298}–H^0_0$, kJ mol^{-1}	bp, K	$C_p = a + b\times10^{-3}T + c\times10^5T^{-2} + d\times10^{-6}T^2$ J mol^{-1} K^{-1}				$C^0_{p\,298}$, J mol^{-1} K^{-1}
						a	b	c	d	
$C_{12}H_7Cl_2(OCH_3)$	–41.8	125.7	594.4	35.3	662	103.6	688.5	–43.6	–284.8	234.2
$C_{12}H_7Cl\ (OCH_3)_2$	–178.4	41.0	933.9	38.4	670	95.8	820.8	–49.4	–331.8	257.0
$C_{12}H_7\ (OCH_3)_3$	–314.9	–43.7	1273.5	41.6	678	87.7	952.6	–55.4	–378.4	279.8
$C_{12}H_6Cl_3(OCH_3)$	–70.8	104.1	685.8	37.9	705	128.6	670.5	–45.7	–283.3	250.5
$C_{12}H_6Cl_2(OCH_3)_2$	–207.4	19.4	1025.3	41.0	712	120.6	802.8	–51.6	–330.3	273.3
$C_{12}H_6Cl(OCH_3)_3$	–344.0	–65.2	1364.7	44.2	720	112.8	934.6	–57.5	–376.9	296.2
$C_{12}H_6(OCH_3)_4$	–480.6	–149.9	1704.2	47.3	728	104.9	1066.3	–63.4	–423.5	318.9
$C_{12}H_5Cl_4(OCH_3)$	–99.9	82.5	777.2	40.5	747	153.6	652.5	–47.9	–281.9	266.8
$C_{12}H_5Cl_3(OCH_3)_2$	–304.6	–2.1	1116.5	43.6	755	145.6	784.8	–53.7	–328.9	301.9
$C_{12}H_5Cl_2(OCH_3)_3$	–305.0	–86.8	1456.1	46.8	763	137.0	916.6	–59.6	–375.5	300.1
$C_{12}H_5Cl(OCH_3)_4$	–509.6	–171.4	1795.6	49.9	771	129.9	1048.3	–65.6	–422.1	335.3
$C_{12}H_5(OCH_3)_5$	–646.2	–256.1	2135.1	53.0	778	122.1	1180.1	–71.5	–468.7	358.1
$C_{12}H_4Cl_5(OCH_3)$	–128.9	60.9	868.5	43.1	789	178.7	634.5	–50.0	–280.4	283.2
$C_{12}H_4Cl_4(OCH_3)_2$	–265.5	–23.7	1208.0	46.2	797	170.6	766.8	–55.9	–327.4	305.9
$C_{12}H_4Cl_3(OCH_3)_3$	–402.1	–108.3	1547.5	49.4	805	162.8	898.6	–61.8	–373.9	328.8
$C_{12}H_4Cl_2(OCH_3)_4$	–538.7	–192.9	1886.9	52.5	813	154.9	1030.3	–67.7	–420.6	351.6
$C_{12}H_4Cl(OCH_3)_5$	–675.3	–277.6	2226.5	55.6	821	147.1	1162.1	–73.6	–467.2	374.5
$C_{12}H_4(OCH_3)_6$	–811.5	–362.3	2566.6	58.8	829	139.1	1294.4	–79.5	–514.2	397.3
$C_{12}H_3Cl_6(OCH_3)$	–150.8	12.6	1064.2	45.7	820	203.7	616.5	–52.1	–278.9	280.9
$C_{12}H_3Cl_5(OCH_3)_2$	–301.0	–93.7	1448.9	48.8	870	195.6	748.8	–58.0	–325.9	311.3
$C_{12}H_3Cl_4\ (OCH_3)_3$	–431.1	–129.9	1638.9	51.9	848	187.8	880.6	–63.9	–372.5	345.1
$C_{12}H_3Cl_3\ (OCH_3)_4$	–567.7	–214.5	1978.4	55.1	855	179.9	1012.3	–69.9	–419.1	367.9
$C_{12}H_3Cl_2\ (OCH_3)_5$	–704.3	–299.2	2317.8	58.2	863	172.2	1144.1	–75.8	–465.7	390.8
$C_{12}H_3Cl\ (OCH_3)_6$	–840.9	–383.8	2657.3	61.4	871	164.1	1276.4	–81.7	–512.7	413.6
$C_{12}H_3(OCH_3)_7$	–977.5	–468.5	2996.8	64.5	879	156.3	1408.2	–87.6	–559.3	436.4
MeONa [15]	–366.2	–	110.6	9.9	673	42.8	67.1	–0.5	41.9	66.1
DMSO [16]	–151.3	–	306.3	13.2	462	51.9	179.6	–9.0	–61.5	88.6

6.5 g (0.12 mol) of MeONa in 25 ml of DMSO in the temperature range 0−170°C at a total pressure of 1 atm. The input data for the thermodynamic modeling were analogous to the experimental data in [8]. 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). The results of the thermodynamic modeling of the total equilibrium content of the gaseous methoxy-PCBs formed by the reaction of Sovol and MeONa are listed in Table 7. 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. Thus, 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

Table 7. Total equilibrium concentrations (mol %) of gaseous methoxy-PCBs formed in the reaction of Sovol with sodium methoxide (*T* 170°C, *P* 1 atm)

PCB congener				
$C_{12}H_7Cl_3$	$C_{12}H_6Cl_4$	$C_{12}H_5Cl_5$	$C_{12}H_4Cl_6$	$C_{12}H_3Cl_7$
Molar ratio PCB:MeONa = 0.025:0.1				
$C_{12}H_7Cl_3$ 37.60	$C_{12}H_6Cl_4$ 3.14×10^{-6}	$C_{12}H_5Cl_5$ 3.09×10^{-12}	$C_{12}H_4Cl_6$ 2.86×10^{-19}	$C_{12}H_3Cl_7$ 4.73×10^{-27}
$C_{12}H_7Cl_2(OCH_3)$ 9.06×10^{-8}	$C_{12}H_6Cl_3(OCH_3)$ 5.76×10^{-11}	$C_{12}H_5Cl_4(OCH_3)$ 4.86×10^{-14}	$C_{12}H_4Cl_5(OCH_3)$ 4.10×10^{-17}	$C_{12}H_3Cl_6(OCH_3)$ 2.04×10^{-17}
$C_{12}H_7Cl(OCH_3)_2$ 2.22×10^{-4}	$C_{12}H_6Cl_2(OCH_3)_2$ 1.87×10^{-7}	$C_{12}H_5Cl_3(OCH_3)_2$ 1.62×10^{-10}	$C_{12}H_4Cl_4(OCH_3)_2$ 1.33×10^{-13}	$C_{12}H_3Cl_5(OCH_3)_2$ 2.44×10^{-7}
$C_{12}H_7(OCH_3)_3$ 0.70	$C_{12}H_6Cl(OCH_3)_3$ 6.09×10^{-5}	$C_{12}H_5Cl_2(OCH_3)_3$ 5.14×10^{-7}	$C_{12}H_4Cl_3(OCH_3)_3$ 2.13×10^{-11}	$C_{12}H_3Cl_4(OCH_3)_3$ 3.65×10^{-13}
	$C_{12}H_6(OCH_3)_4$ 1.98	$C_{12}H_5Cl(OCH_3)_4$ 1.67×10^{-3}	$C_{12}H_4Cl_2(OCH_3)_4$ 1.41×10^{-6}	$C_{12}H_3Cl_3(OCH_3)_4$ 1.19×10^{-9}
		$C_{12}H_5(OCH_3)_5$ 5.43	$C_{12}H_4Cl(OCH_3)_5$ 5.53×10^{-10}	$C_{12}H_3Cl_2(OCH_3)_5$ 3.86×10^{-6}
			$C_{12}H_4(OCH_3)_6$ 13.40	$C_{12}H_3Cl(OCH_3)_6$ 1.26×10^{-2}
				$C_{12}H_3(OCH_3)_7$ 40.90
Molar ratio PCB:MeONa = 0.025:0.12				
$C_{12}H_7Cl_3$ 10.80	$C_{12}H_6Cl_4$ 1.09×10^{-7}	$C_{12}H_5Cl_5$ 1.29×10^{-14}	$C_{12}H_4Cl_6$ 1.45×10^{-22}	$C_{12}H_3Cl_7$ 2.90×10^{-21}
$C_{12}H_7Cl_2(OCH_3)$ 9.78×10^{-8}	$C_{12}H_6Cl_3(OCH_3)$ 7.52×10^{-12}	$C_{12}H_5Cl_4(OCH_3)$ 7.83×10^{-20}	$C_{12}H_4Cl_5(OCH_3)$ 7.83×10^{-20}	$C_{12}H_3Cl_6(OCH_3)$ 4.73×10^{-20}
$C_{12}H_7Cl(OCH_3)_2$ 9.05×10^{-4}	$C_{12}H_6Cl_2(OCH_3)_2$ 9.23×10^{-8}	$C_{12}H_5Cl_3(OCH_3)_2$ 9.65×10^{-12}	$C_{12}H_4Cl_4(OCH_3)_2$ 9.61×10^{-16}	$C_{12}H_3Cl_5(OCH_3)_2$ 2.13×10^{-10}
$C_{12}H_7(OCH_3)_3$ 10.90	$C_{12}H_6Cl(OCH_3)_3$ 1.13×10^{-3}	$C_{12}H_5Cl_2(OCH_3)_3$ 1.16×10^{-7}	$C_{12}H_4Cl_3(OCH_3)_3$ 3.18×10^{-12}	$C_{12}H_3Cl_4(OCH_3)_3$ 1.20×10^{-15}
	$C_{12}H_6(OCH_3)_4$ 13.90	$C_{12}H_5Cl(OCH_3)_4$ 1.42×10^{-3}	$C_{12}H_4Cl_2(OCH_3)_4$ 1.45×10^{-7}	$C_{12}H_3Cl_3(OCH_3)_4$ 1.48×10^{-11}
		$C_{12}H_5(OCH_3)_5$ 17.40	$C_{12}H_4Cl(OCH_3)_5$ 2.87×10^{-10}	$C_{12}H_3Cl_2(OCH_3)_5$ 1.81×10^{-7}
			$C_{12}H_4(OCH_3)_6$ 19.61	$C_{12}H_3Cl(OCH_3)_6$ 2.23×10^{-6}
				$C_{12}H_3(OCH_3)_7$ 27.30
Molar ratio PCB:MeONa = 0.025:0.15				
$C_{12}H_7Cl_3$ 0	$C_{12}H_6Cl_4$ 0	$C_{12}H_5Cl_5$ 0	$C_{12}H_4Cl_6$ 0	$C_{12}H_3Cl_7$ 0
$C_{12}H_7Cl_2(OCH_3)$ 0	$C_{12}H_6Cl_3(OCH_3)$ 0	$C_{12}H_5Cl_4(OCH_3)$ 0	$C_{12}H_4Cl_5(OCH_3)$ 0	$C_{12}H_3Cl_6(OCH_3)$ 0
$C_{12}H_7Cl(OCH_3)_2$ 0	$C_{12}H_6Cl_2(OCH_3)_2$ 0	$C_{12}H_5Cl_3(OCH_3)_2$ 0	$C_{12}H_4Cl_4(OCH_3)_2$ 0	$C_{12}H_3Cl_5(OCH_3)_2$ 0

Table 7. (Contd.)

PCB congener				
$C_{12}H_7Cl_3$	$C_{12}H_6Cl_4$	$C_{12}H_5Cl_5$	$C_{12}H_4Cl_6$	$C_{12}H_3Cl_7$
Molar ratio PCB:MeONa = 0.025:0.15				
$C_{12}H_7(OCH_3)_3$ 16.60	$C_{12}H_6Cl(OCH_3)_3$ 0 $C_{12}H_6(OCH_3)_4$ 18.50	$C_{12}H_5Cl_2(OCH_3)_3$ 0 $C_{12}H_5Cl(OCH_3)_4$ 0 $C_{12}H_5(OCH_3)_5$ 20.30	$C_{12}H_4Cl_3(OCH_3)_3$ 0 $C_{12}H_4Cl_2(OCH_3)_4$ 0 $C_{12}H_4Cl(OCH_3)_5$ 0 $C_{12}H_4(OCH_3)_6$ 20.10	$C_{12}H_3Cl_4(OCH_3)_3$ 0 $C_{12}H_3Cl_3(OCH_3)_4$ 0 $C_{12}H_3Cl_2(OCH_3)_5$ 0 $C_{12}H_3Cl(OCH_3)_6$ 0 $C_{12}H_3(OCH_3)_7$ 24.50

from 40.9 to 27.3 mol % as the concentration of MeONa increases, while the concentration of unreacted heptachlorobiphenyl therewith increases from 4.73×10^{-27} to 2.90×10^{-21} mol %.

Thermodynamic modeling with 0.15 mol (8.10 g) 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. 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.

The results of thermodynamic modeling allow us to conclude that high-chlorinated PCB congeners are more reactive that low-chlorinated ones, while the composition of the reaction products depends on the initial concentration of MeONa.

The present results are well consistent with the results in [8]: The reactivity data for the congener groups comprised in Sovol are fully coincident. The decrease of the fraction of monomethoxy derivatives of hexachlorobiphenyls at an elevated (150°C) temperature, noted in [8], too, is consistent with the results of thermodynamic modeling (Table 7): The concentration of monomethoxy derivatives decreases from 9.06×10^{-8} to 4.73×10^{-20} mol % at 170°C. At the same time, the unusual behavior of heptachlorobiphenyl in the reaction with MeONa, revealed by thermodynamic modeling, calls for further research, possibly, by other calculation methods.

Thus, 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 obtained in our previous work. Both works gave evidence that the most reactive congeners are hepta-, hexa-, and pentachloro-biphenyls, whereas the least reactive, the trichlorinated congeners. Tetrachlorobiphenyls occupy an intermediate position.

Thus, the reaction of PCB congeners with 0.1 mol of MeONa (*T* 170°C, *P* 1 atm) fails to provide complete detoxication of Sovol. According to the results of thermodynamic modeling, when the initial concentration of MeONa is increased to 0.15 mol, the chlorine substituents in PCB congeners are completely substituted by methoxyls. It was found that, under the chosen conditions of thermodynamic modeling, monomethoxy derivatives of PCBs are almost absent, whereas derivatives with a greater number of methoxy groups are prevailing.

Chemical processing of PCBs with MeONa is suitable not for all commercial mixtures, but only for those mixtures which include congeners containing more than 4 chlorine substituents. In the case of commercial PCB mixtures containing mono- to tetrachlorinated biphenyls, more careful optimization of the starting MeONa concentration is required, because such congeners have a low reactivity.

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.

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