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MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Optimization of the Reaction of Polychlorobiphenyls with a Binucleophile by Thermodynamic Modeling

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Abstract—The reaction of congeners of Sovol commercial mixture of polychlorinated biphenyls with 2-aminoethanol in the presence of potassium hydroxide was studied. The results of thermodynamic modeling show that only hydroxy derivatives of polychlorobiphenyls should be formed. The optimum conditions for complete dechlorination of the congeners were determined: 1 atm, 170°C, molar ratio polychlorobiphenyls : 2-aminoethanol : potassium hydroxide = 1 : 8 : 6. The experimental data obtained using the theoretically chosen initial conditions for the reaction of polychlorobiphenyls with 2-aminoethanol show that the conversion increases from 82 to 96%.

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Polychlorinated biphenyls (PCBs) belong to the group of compounds extremely hazardous for the environment and human health, namely, to the group of persistent organic pollutants (POPs). Their storage or improper disposal leads to the formation of still more hazardous chlorinated organic substances, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF). Polychlorinated biphenyls exhibit unique physical and chemical properties such as excellent insulating properties, inertness to acids and alkalis, thermal stability, and high adhesive power [1]. Therefore, these compounds were widely used as dielectrics in transformers and capacitors, lubricating oils, solvents, liquid coolants, components of varnishes, paints, and adhesives, etc. [1, 2]. In 2001, many countries signed the Stockholm Convention [3] according to which all the PCBs should be taken off from operation by 2015 and eliminated by 2028.

There are many procedures for rendering PCBs harmless: oxidation, pyrolysis, dechlorination, photolysis, radiolysis, electrochemical and biotechnological methods, etc. [4]. However, there are still no versatile methods allowing safe elimination of the whole existing amount of PCBs.

The number of complex approaches to PCB elimination tends to increase. The combined method of mineralization of chlorinated aromatic compounds is the most promising. This approach is based on primary chemical functionalization of PCBs to obtain new derivatives that are later broken down by degrading bacterial strains. The mineralization of PCB derivatives with degrading strains yields the simplest chemical compounds: carbon dioxide, water, and hydrogen chloride [5, 6]. The necessary condition for the efficient mineralization of PCB derivatives under the conditions of a microbiological process is their delivery to the medium populated with bacteria. This problem is successfully solved by introducing surfactants [6] and by preparing hydrophilic water-soluble PCB derivatives [5].

A promising route to hydrophilic PCB derivatives is nucleophilic substitution of chlorine atoms in PCB structures by other substituents decreasing the toxicity of the compounds [7–11]. As a rule, reactions of PCB congeners with alkali metal alcoholates or with alcohols in the presence of alkalis are performed. Such processes often yield products of a competing reaction, hydroxy derivatives of PCBs, which positively influence the solubility of the whole mixture of PCB derivatives in an aqueous medium. For example, the reaction of PCBs with polyethylene glycols in the presence of KOH yields a water-soluble mixture of products, the main of which are poly(ethylene glycol)oxy and hydroxy derivatives [5]. As shown in [6], the mixture of products formed by the reaction of PCB congeners with 2-aminoethanol (2-AE) in the presence of KOH, consisting of 2-aminoethoxy, hydroxy, and (2-aminoethoxy)hydroxy derivatives, is insoluble in water. Both water-soluble [5] and water-insoluble [6] PCB derivatives are characterized by positive dynamics of bacterial degradation under the action of *Rhodococcus wratislaviensis* KT112-7 strain (*R. wratislaviensis* KT112-7), yielding the products of complete mineralization [5, 6]. However, the transport of water-insoluble PCB derivatives [6] to the medium populated by the bacteria required the use of either a solvent (acetone) or a surfactant, which affected the rate of the microbiological process. Among the components of a mixture of PCB derivatives described in [6], hydroxy derivatives are the most hydrophilic. Therefore, increasing the content of hydrophilic hydroxy derivatives in nucleophilic substitution products leads to saving of additional reagents and reduction of the time required for complete mineralization of PCB derivatives under the conditions of the microbiological method of their degradation.

Thermodynamic modeling (TDM) aimed at finding conditions ensuring the formation of the maximal amount of hydrophilic PCB in nucleophilic substitution reactions is a topical problem. The use of TDM allows significant saving of materials, labor, and time and reduces to a minimum the contact of researchers with toxic substances. TDM allows finding complete equilibrium chemical composition of the system at the preset thermodynamic parameters (e.g., temperature and pressure). HSC program for calculating the multicomponent high-temperature equilibrium is used for these purposes [12]. The TDM method was successfully used previously for calculating the composition of products formed by chemical and thermal reprocessing of toxic PCBs [13–15].

In this study, we examined by TDM the conditions of the reaction of congeners of Sovol commercial PCB mixture with a binucleophile (2-AE) in the presence of KOH with the aim of obtaining the maximal amount of the hydroxy derivatives. The results obtained were verified experimentally, and the efficiency of using TDM for optimization of the process conditions was evaluated.

EXPERIMENTAL

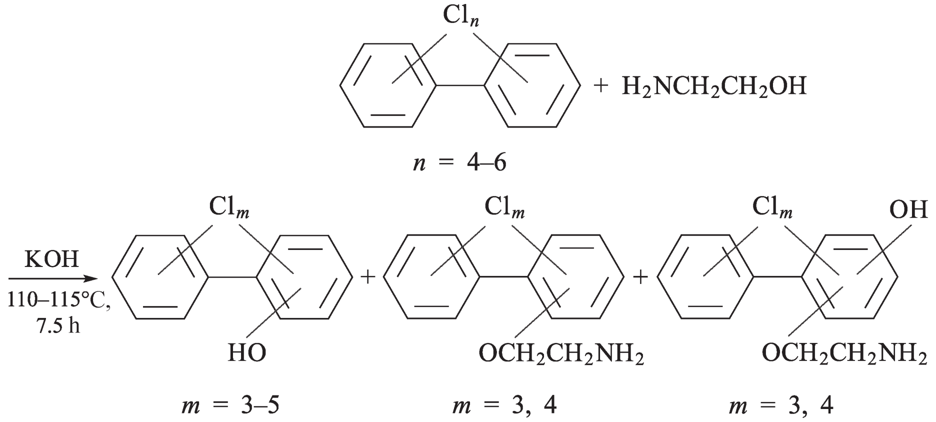
The necessary condition for performing TDM is the availability of a database on the thermochemical properties of the compounds in question. The following thermochemical properties of aminoethoxy and hydroxy derivatives of PCBs should be known for performing TDM: standard enthalpy of formation ΔH°_{298}, enthalpy increment from 0 to 298 K ($H^\circ_{298} - H^\circ_0$), standard heat capacity C°_{p298} and its temperature dependence $C_p(T)$, and entropy S°_{298}. Such data are lacking.

The thermochemical properties of the PCB derivatives were calculated using the previously developed algorithm based on analysis of the molecular structure [11–13, 16]. We used for analysis the HSC 8.2.0 program complex containing the Benson Estimation module. The calculated thermochemical parameters of the PCB derivatives were introduced into the HSC 8.2.0 database and used in modeling of the reaction of PCB congeners present in Sovol mixture with 2-AE in the presence of KOH.

In the experimental studies, the reaction progress and the completeness of the conversion of the base PCBs were monitored with a Shimadzu GC 2010 gas chromatograph (Japan) equipped with a flame ionization detector (GC-FID conditions) and a ZB-5 quartz capillary column (polydimethylsiloxane, 5% phenyl groups) 30 m long, 0.25 mm i.d., with the film thickness of 0.25 μm. The initial column temperature was 40°C (keeping for 3 min), after which the column was heated at a rate of 10 deg min^{-1} to 280°C and kept at the final temperature for 30 min. The injector temperature was 250, and the detector temperature, 300°C. The carrier gas was nitrogen (flow split ratio 1 : 30, flow rate through the column 1.0 mL min^{-1}).

Mass-spectrometric analysis was performed with an Agilent GC 7890A MSD 5975C inert XL EI/CI gas chromatograph/mass spectrometer (the United States) equipped with a quadrupole mass-spectrometric detector (GC-MS conditions) and an HP5-MS quartz capillary column (polydimethylsiloxane, 5% phenyl groups) 30 m long, 0.25 mm i.d., with the film thickness of 0.25 μm. The initial column temperature was 40°C (keeping for 3 min), after which the column was heated at a rate of 10 deg min^{-1} to 290°C and kept at the final temperature for 30 min. The temperatures in the device were as follows, °C: injector 250, transfer line 280, source 230, and quadrupole 250. The carrier gas

Scheme. Reaction of the congeners of Sovol PCB mixture with 2-AE in the presence of KOH.



was helium (flow split ratio 1 : 50, flow rate through the column 1.0 mL min^{-1}). Scanning was performed in the range 20–1000 Da with electron impact ionization (70 eV). The compound concentrations were estimated from the peak areas in the chromatograms using the internal normalization method.

Reaction of PCB with 2-AE in the presence of KOH. A three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel was charged with 3.36 g (0.06 mol) of KOH and 25 mL (25.55 g, 0.42 mol) of 2-AE. The reactor was placed on a magnetic stirrer and heated until a finely dispersed suspension was obtained. Then, 3.26 g (0.01 mol) of Sovol commercial mixture was added, and the mixture was refluxed with stirring (~170°C) for 2–16 h. After the reaction completion, the reaction mass was cooled to room temperature, dilute HCl was added to pH 1–2, and the mixture was extracted with toluene (2 × 10 mL). The toluene extract was dried over $CaCl_2$ and analyzed under the GC-FID and GC-MS conditions.

RESULTS AND DISCUSSION

Thermodynamic modeling of the chemical reaction of PCB congener mixture with 2-aminoethanol in the presence of KOH. Sovol commercial PCB mixture (an analog of Aroclor-1254) is a mixture of several types of congeners: tri- (~1%), tetra- (~22%), penta- (~56%), hexa- (~20%), and heptachlorobiphenyls (~1%) [17, 18]. As found previously, the reaction of Sovol PCB mixture with 2-aminoethanol in the presence of KOH, performed at 110–115°C for 7.5 h, yields 2-aminoethoxy (15%), hydroxy (63%). and (2-aminoethoxy)hydroxy PCB derivatives (<4%) [6] (see scheme). Tetra- and pentachlorobiphenyls partially remain unchanged in the reaction (~18%); i.e., the conversion of Sovol PCB mixture under the chosen reaction conditions is moderate [6]. Tri- and heptachlorobiphenyl derivatives initially present in the Sovol mixture were not detected in the reaction mixture.

The nucleophilic substitution was studied by TDM to reveal conditions ensuring the formation of the maximal amount of the hydrophilic hydroxy derivatives.

The calculated thermochemical properties of PCB derivatives, introduced into the database of the HSC Chemistry program complex, are given Table 1.

Using TDM and the HSC program complex, we modeled the reaction of 0.05 mol of Sovol PCB mixture with 2-AE taken in an amount of 0.15 to 0.50 mol and with KOH (0.1 to 0.45 mol).

It is known that the boiling point of 2-AE is 171°C, and on heating over 200°C the probability of the formation of toxic PCDD/PCDF increases. Therefore, TDM was performed for temperatures of up to 200°C. When creating a file for TDM, we included into the set of decomposition products calcium chloride, carbon monoxide and dioxide, water, and hydrogen chloride. The thermochemical properties of these substances were taken from the HSC database. The modeling was performed at atmospheric pressure. The algorithm for calculating the equilibrium composition using HSC program complex is described in detail in [12].

Figure 1 shows the calculated equilibrium composition of the reaction products in the system consisting of 0.05 mol of Sovol PCB congeners, 0.15 mol of 2-AE, and 0.1 mol of KOH.

Figure 1 shows that the major reaction products are hydroxy PCB derivatives. The content of 2-aminoe-

Table 1. Calculated thermochemical properties of PCB derivatives

Compound	ΔH°_{298}, kJ mol^{-1}	S°_{298}, J mol^{-1} K^{-1}	H°_{298}–H°_0, kJ mol^{-1}	$C_p = a + b \times 10^{-3}\,T + c \times 10^5\,T^{-2} + d \times 10^{-6}\,T^2$, J mol^{-1} K^{-1} [12]			
				a	*b*	*c*	*d*
$C_{12}H_7Cl_2(OH)$	–54.40	493.77	31.59	113.20	572.09	–40.02	–242.11
$C_{12}H_7Cl(OH)_2$	–203.46	493.69	32.14	114.96	587.45	–42.41	–245.99
$C_{12}H_7(OH)_3$	–352.52	493.55	32.75	116.73	602.81	–44.79	–249.87
$C_{12}H_6Cl_3(OH)$	–83.43	521.79	33.90	138.22	554.10	–42.17	–240.63
$C_{12}H_6Cl_2(OH)_2$	–232.49	521.69	34.51	139.98	569.46	–44.57	–244.52
$C_{12}H_6Cl(OH)_3$	–381.55	521.595	35.12	141.74	584.82	–46.94	–248.39
$C_{12}H_6(OH)_4$	–530.61	521.49	35.73	143.51	600.18	–49.33	–252.28
$C_{12}H_5Cl_4(OH)$	–112.45	549.82	36.20	163.24	536.11	–44.31	–239.16
$C_{12}H_5Cl_3(OH)_2$	–336.56	550.77	36.81	165.00	551.47	–46.70	–243.04
$C_{12}H_5Cl_2(OH)_3$	–335.52	550.07	37.12	166.76	566.83	–49.09	–246.92
$C_{12}H_5Cl(OH)_4$	–559.63	549.52	37.85	168.53	582.19	–51.48	–250.79
$C_{12}H_5(OH)_5$	–708.69	549.42	38.41	170.29	597.55	–53.87	–254.68
$C_{12}H_4Cl_5(OH)$	–141.48	577.84	38.51	188.26	518.12	–46.46	–237.68
$C_{12}H_4Cl_4(OH)_2$	–290.54	577.74	39.19	190.02	533.48	–48.85	241.56
$C_{12}H_4Cl_3(OH)_3$	–439.60	577.65	39.62	191.78	548.84	–51.24	–245.44
$C_{12}H_4Cl_2(OH)_4$	–588.66	577.55	40.17	193.54	564.19	–53.62	–249.32
$C_{12}H_4Cl(OH)_5$	–737.72	577.45	40.38	195.31	579.56	–56.01	–253.20
$C_{12}H_4(OH)_6$	–886.78	577.01	41.27	197.07	594.91	–58.39	–257.08
$C_{12}H_3Cl_6(OH)$	–170.50	605.88	40.82	213.27	500.13	–48.61	–236.19
$C_{12}H_3Cl_5(OH)_2$	–319.56	605.77	41.01	215.04	515.49	–50.99	–240.08
$C_{12}H_3Cl_4(OH)_3$	–468.62	600.64	41.92	216.79	530.85	–53.38	–243.96
$C_{12}H_3Cl_3(OH)_4$	–617.68	605.57	42.47	218.56	546.21	–55.77	–247.84
$C_{12}H_3Cl_2(OH)_5$	–766.74	605.47	43.03	220.32	561.56	–58.16	–251.72
$C_{12}H_3Cl(OH)_6$	–915.80	605.37	43.58	222.09	576.92	–60.55	–255.60
$C_{12}H_3(OH)_7$	–1064.86	605.27	44.13	223.85	592.28	–62.93	–259.48
$C_{12}H_7Cl_2(O(CH_2)_2NH_2)$	–26.65	602.73	41.48	91.380	918.12	–46.140	–369.419
$C_{12}H_7Cl(O(CH_2)_2NH_2)_2$	–147.07	713.82	51.95	46.638	1328.3	–39.177	–526.698
$C_{12}H_7(O(CH_2)_2NH_2)_3$	–267.49	824.88	62.42	1.895	1738.49	–32.215	–683.977
$C_{12}H_6Cl_3(O(CH_2)_2NH_2)$	–55.68	630.1	43.79	124.24	884.419	–53.179	–359.545
$C_{12}H_6Cl_2(O(CH_2)_2NH_2)_2$	–176.10	741.19	54.26	79.504	1294.60	–46.216	–516.823
$C_{12}H_6Cl(O(CH_2)_2NH_2)_3$	–296.52	852.28	64.73	34.762	1704.79	–39.254	–674.102
$C_{12}H_6(O(CH_2)_2NH_2)_4$	–416.94	963.37	75.20	–81.92	2302.32	–46.079	–964.299
$C_{12}H_5Cl_4(O(CH_2)_2NH_2)$	–84.70	657.5	46.10	157.11	850.718	–60.218	–349.670
$C_{12}H_5Cl_3(O(CH_2)_2NH_2)_2$	–205.12	768.59	56.57	112.37	1260.90	–53.256	–506.948
$C_{12}H_5Cl_2(O(CH_2)_2NH_2)_3$	–325.54	879.68	67.04	67.628	1671.09	–46.293	–664.227
$C_{12}H_5Cl(O(CH_2)_2NH_2)_4$	–445.96	990.77	77.51	22.886	2081.28	–39.331	–821.506
$C_{12}H_5(O(CH_2)_2NH_2)_5$	–566.38	1101.86	87.97	–111.7	2725.64	–49.603	–1144.93
$C_{12}H_4Cl_5(O(CH_2)_2NH_2)$	–113.73	684.9	48.41	189.97	817.017	–67.257	–339.795
$C_{12}H_4Cl_4(O(CH_2)_2NH_2)_2$	–234.15	795.99	58.88	145.23	1227.20	–60.295	–497.073
$C_{12}H_4Cl_3(O(CH_2)_2NH_2)_3$	–354.57	907.08	69.35	100.49	1637.39	–53.332	–654.352
$C_{12}H_4Cl_2(O(CH_2)_2NH_2)_4$	–474.99	1018.17	79.82	55.752	2047.58	–46.370	–811.631
$C_{12}H_4Cl(O(CH_2)_2NH_2)_5$	–595.41	1129.26	90.29	11.010	2457.77	–39.407	–968.909
$C_{12}H_4(O(CH_2)_2NH_2)_6$	–715.83	1240.35	100.8	–33.73	2867.96	–32.445	–1126.18
$C_{12}H_3Cl_6(O(CH_2)_2NH_2)$	–142.75	712.3	50.72	222.84	783.315	–74.297	–329.920

Table 1. (Contd.)

Compound	ΔH°_{298}, kJ mol^{-1}	S°_{298}, J mol^{-1} K^{-1}	$H^\circ_{298}-H^\circ_0$, kJ mol^{-1}	$C_p = a + b \times 10^{-3}\, T + c \times 10^{5}\, T^{-2} + d \times 10^{-6}\, T^2$, J mol^{-1} K^{-1} [12]			
				a	*b*	*c*	*d*
$C_{12}H_3Cl_5(O(CH_2)_2NH_2)_2$	–263.17	823.39	66.33	178.10	1193.50	–67.334	–487.198
$C_{12}H_3Cl_4(O(CH_2)_2NH_2)_3$	–383.59	934.48	76.80	133.36	1603.69	–60.372	–644.477
$C_{12}H_3Cl_3(O(CH_2)_2NH_2)_4$	–504.01	1045.57	87.27	88.619	2013.88	–53.409	–801.756
$C_{12}H_3Cl_2(O(CH_2)_2NH_2)_5$	–624.43	1156.66	97.74	43.876	2424.07	–46.447	–959.034
$C_{12}H_3Cl(O(CH_2)_2NH_2)_6$	–744.85	1267.75	108.2	–0.866	2834.26	–39.484	–1116.31
$C_{12}H_3(O(CH_2)_2NH_2)_7$	–865.27	1374.84	118.7	–45.60	3244.44	–32.522	–1273.59
$C_{12}H_7Cl(OH)(O(CH_2)_2NH_2)$	–175.265	603.755	42.05	80.799	957.875	–40.794	–386.344
$C_{12}H_6Cl_2(OH)(O(CH_2)_2NH_2)$	–204.295	631.44	44.9	109.742	932.03	–45.393	–380.672
$C_{12}H_6(OH)_2(O(CH_2)_2NH_2)_2$	–473.775	742.43	55.47	30.795	1451.25	–47.704	–608.289
$C_{12}H_5Cl_3(OH)(O(CH_2)_2NH_2)$	–270.84	659.68	46.69	138.685	906.185	–49.978	–374.994
$C_{12}H_5Cl(OH)_2(O(CH_2)_2NH_2)_2$	–502.795	770.145	57.68	95.708	1331.735	–45.407	–536.148
$C_{12}H_4Cl_4(OH)(O(CH_2)_2NH_2)$	–262.345	686.865	49.04	167.625	880.34	–54.572	–127.757
$C_{12}H_4Cl_2(OH)_2(O(CH_2)_2NH_2)_2$	–531.825	797.86	59.99	124.646	1305.885	–49.995	–530.476
$C_{12}H_4(OH)_3(O(CH_2)_2NH_2)_3$	–801.305	908.68	71.04	81.67	1731.435	–45.418	–691.63
$C_{12}H_3Cl_5(OH)(O(CH_2)_2NH_2)$	–291.365	714.58	53.67	196.57	854.495	–59.162	–363.639
$C_{12}H_3Cl_3(OH)_2(O(CH_2)_2NH_2)_2$	–560.845	825.57	64.87	153.5895	1280.045	–54.589	–524.798
$C_{12}H_3Cl(OH)_3(O(CH_2)_2NH_2)_3$	–830.325	936.56	75.89	110.612	1705.59	–50.017	–685.955

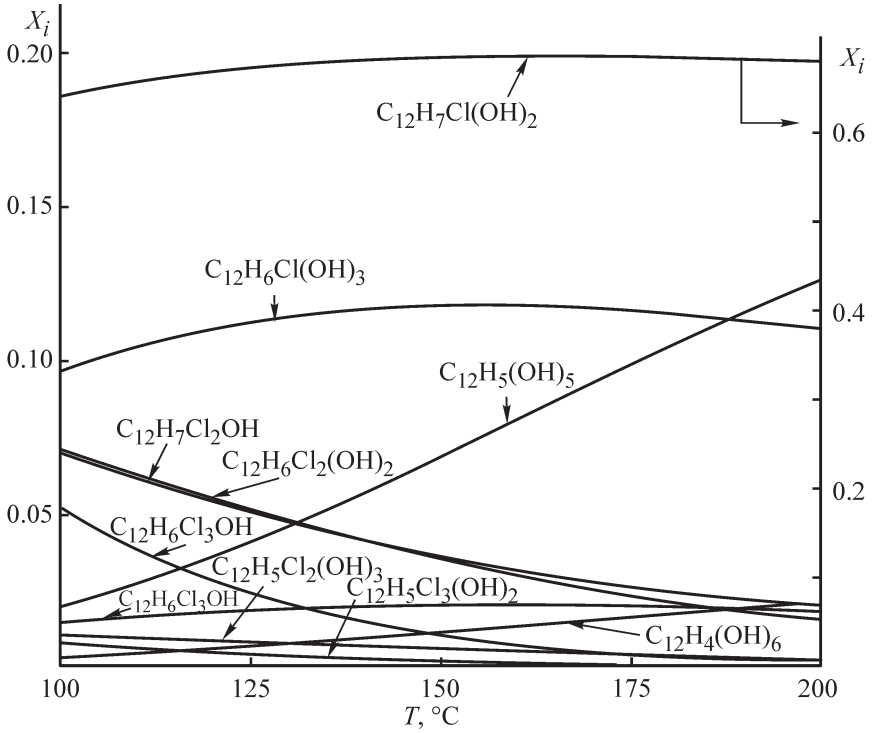


Fig. 1. Equilibrium composition of PCB congeners and derivatives (mole fractions X_i) as a function of temperature T. Initial composition, mol: Sovol PCB mixture 0.05, 2-AE 0.15, and KOH 0.1; the sum of the mole fractions of all the PCB congeners and derivatives is 1.

Table 2. Comparative analysis of products formed in the reaction of Sovol PCB mixture with 2-AE in the presence of KOH

Compound	Content, %				
	reaction time, h (conditions 1)				conditions 2
	2	11	13	16	
$C_{12}H_7Cl_3$	2.1	1.1	0.8	0.6	1.0
$C_{12}H_6Cl_4$	18.9	8.9	3.4	3.1	16.2
$C_{12}H_5Cl_5$	0.2	–	–	–	1.7
$C_{12}H_4Cl_6$	–	–	–	–	–
$C_{12}H_6Cl_3OH$	7.6	9.7	16.8	18.5	2.9
$C_{12}H_5Cl_4OH$	65.4	58.0	46.4	47.0	56.0
$C_{12}H_4Cl_5OH$	2.2	1.7	0.6	0.3	4.1
$C_{12}H_5Cl_3(OH)_2$	1.2	5.3	14.4	14.6	–
$C_{12}H_4Cl_4(OH)_2$	2.4	15.2	14.6	14.9	–
$C_{12}H_4Cl_3(OH)_3$	–	–	<3.0	<1.0	–
$C_{12}H_6Cl_3OCH_2CH_2NH_2$	–	–	–	–	4.3
$C_{12}H_5Cl_4OCH_2CH_2NH_2$	–	–	–	–	10.4
$C_{12}H_4Cl_5OCH_2CH_2NH_2$	–	–	–	–	–
$C_{12}H_4Cl_4(OCH_2CH_2NH_2)_2$	–	–	–	–	–
$C_{12}H_5Cl_3(OCH_2CH_2NH_2)OH$	–	–	–	–	2.7
$C_{12}H_4Cl_4(OCH_2CH_2NH_2)OH$	–	–	–	–	0.7
Conversion, %	80	90	96	96	82

thoxy PCB derivatives in the reaction products is very low (mole fraction 10^{-10}), and (2-aminoethoxy)hydroxy PCB derivatives were not detected in the reaction products at all. With increasing temperature, the amount of unchanged PCB congeners decreases, and that of the derivatives increases. The initial amounts of 0.15 mol of 2-AE and 0.1 mol of KOH were found to be insufficient for complete conversion of the Sovol PCB mixture, because unchanged trichlorobiphenyl ($C_{12}H_7Cl_3$) remained in the products.

The modeling results show that, at the initial amounts of 2-AE and KOH increased to 0.4 and 0.3 mol, respectively, the conversion of PCB congeners becomes complete, and the hydrophilic derivatives $C_{12}H_5(OH)_5$ and $C_{12}H_4(OH)_6$ are formed. Further increase in the reagent amounts does not alter the modeling results.

Thermodynamic analysis is a tool for finding conditions at which certain substances are formed in minimal or maximal amounts or are not formed at all. Thus, the calculation results should be considered as maximum possible values of conversion, which do not take into account catalytic and kinetic effects. A real process occurring within a definite time interval, even being thermodynamically allowed, can be kinetically suppressed because of extremely low reaction rate. The TDM results allow a conclusion that, to reach the maximal conversion of PCB in the reaction with 2-AE in the presence of KOH, the process temperature should be 170°C (maximum possible because of 2-AE boiling) at the PCB : 2-AE : KOH molar ratio of 1 : 8 : 6 and pressure of 1 atm. The reaction time can be chosen only experimentally.

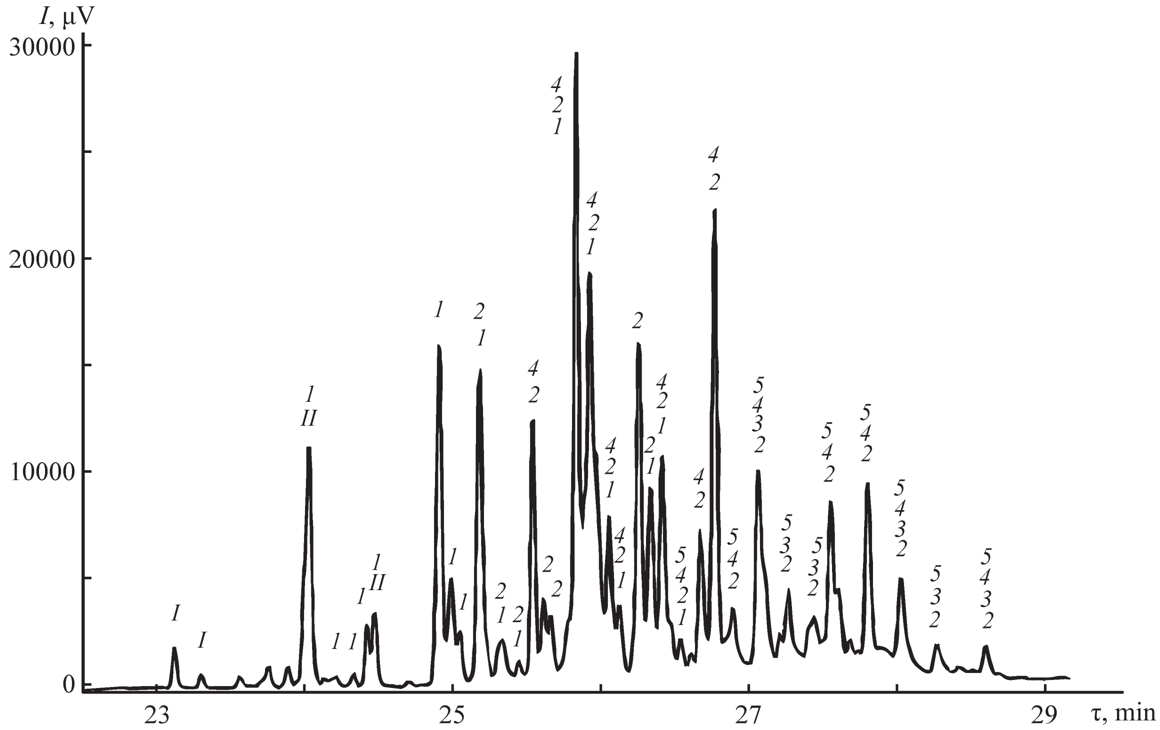


Fig. 2. Chromatogram of products formed in the reaction of Sovol commercial PCB mixture with 2-AE. T = 170°C, PCB : 2-AE : KOH = 1 : 8 : 6, pressure 1 atm, 13 h. (*I*) Intensity and (τ) time. (*I*) $C_{12}H_7Cl_3$ and (*II*) $C_{12}H_6Cl_4$; (*1*) $C_{12}H_6Cl_3(OH)$, (*2*) $C_{12}H_5Cl_4(OH)$, (*3*) $C_{12}H_4Cl_5(OH)$, (*4*) $C_{12}H_5Cl_3(OH)_2$, and (*5*) $C_{12}H_4Cl_4(OH)_2$.

Experimental studies of the reaction of Sovol PCB congeners with 2-AE in the presence of KOH. The reaction conditions corresponded to the TDM results: T = 170°C, molar ratio PCB : 2-AE : KOH = 1 : 8 : 6, pressure 1 atm. The reaction time was varied from 2 to 16 h.

The moment of mixing the reactants was taken as the start of the reaction. Samples of the reaction mixture was taken, treated as described in Experimental, and analyzed under GC-FID and GC-MS conditions.

Figure 2 shows as an example the chromatogram of the reaction products after the 13-h reaction. Numerous products are manifested in the chromatogram, and with time the number of the detected derivatives increases.

Five types of PCB derivatives were identified in products of the reaction of PCB congeners with 2-AE in the presence of KOH (Table 2). All the derivatives obtained were conventionally subdivided into three groups depending on the number of chlorine atoms in the initial PCB (tetra-, penta-, or hexachlorobiphenyls). For quantitative estimation, we scanned the total ion current and, using the GC-MS software, recorded the areas of the chromatographic peaks corresponding to the specific PCB derivatives. We calculated the content of each product in a chromatographic peak from the intensities of the base ion peaks in the mass spectra corresponding to these peaks. Then, we calculated the content of each derivative within the corresponding group depending on the initial PCB and on the total amount of the products.

Data on the products of the reaction of Sovol PCB mixture with 2-AE in the presence of KOH, performed under different conditions, are given in Table 2. Two kinds of conditions were used:

– at 170°C, ratio PCB : 2-AE : KOH = 1 : 8 : 6, pressure of 1 atm, and reaction time of 2, 11, 13, and 16 h (conditions 1);

– at 110–115°C, ratio PCB : 2-AE : KOH = 1 : 3 : 3, pressure of 1 atm, and reaction time of 7.5 h [6] (conditions 2).

The results obtained show that the interaction of PCB with 2-AE in the presence of KOH involves a series of reactions occurring at different rates and yielding different sets of final products (see scheme). Both 2-aminoethoxy and hydroxy PCB derivatives can be formed simultaneously or successively. The conversion of components of Sovol PCB mixture under the conditions of [6] was about 82%, whereas under the conditions found by TDM it varied from 80 to 96% depending on the reaction time. Under the experimental conditions of [6], 2-aminoethoxy, hydroxy, and (2-aminoethoxy)hydroxy PCB derivatives are formed, whereas under the conditions found by TDM only hydroxy PCB derivatives are formed. As the reaction time is increased from 2 to 13 h, the conversion of the initial PCBs increases to 96%. Further increase in the reaction time (to 16 h) does not alter the results.

The results of the experimental study show that the use of the theoretically chosen dechlorination conditions leads to an increase in the conversion of the initial congeners of the Sovol PCB mixture relative to the data of [6]. The reaction products are hydrophilic hydroxy derivatives that are capable to dissolve in water and undergo mineralization under the action of degrading bacterial strains.

CONCLUSIONS

(1) The use of thermodynamic modeling and HSC 8.2.0 program complex allowed choosing the optimum conditions for complete dechlorination of polychlorinated biphenyl congeners: $T = 170°C$, molar ratio biphenyls : 2-aminoethanol : KOH = 1 : 8 : 6, and pressure of 1 atm.

(2) Under the conditions chosen on the basis of the thermodynamic modeling results, only hydroxy derivatives of polychlorinated biphenyls are formed. These compounds can be subsequently mineralized using degrading bacterial strains.

(3) The experimental data obtained under the theoretically chosen conditions for nucleophilic substitution of chlorine atoms in the structures of polychlorinated biphenyls show that the conversion increases from 82 [6] to 96%. The reaction products contain only hydroxy derivatives of polychlorinated biphenyls.

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