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# Reactivity of Congeners of Sovol Technical Mixture of Polychlorinated Biphenyls toward Sodium Methoxide

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**Abstract**—The reaction of Sovol technical mixture of polychlorobiphenyls with sodium methoxide in bipolar aprotic solvents was studied. The reactivity of polychlorobiphenyls was evaluated using gas chromatography and gas chromatography–mass spectrometry.

With adoption in 2001 of the Stockholm Convention on Persistent Organic Pollutants, which prohibited the use of technical polychlorobiphenyls (PCBs), the number of papers concerning these pollutants increased. Primary attention is given to detection of PCBs in various natural objects and biological media, determination of pollution levels, and elucidation of pathways of PCB transformations and metabolism in living bodies. Considerably less attention was given to development of new procedures for rendering PCBs harmless, which is largely due to wide use of efficient methods involving complete breakdown of PCBs (e.g., thermolysis). Other possible procedures for PCB treatment are often considered to be of low promise, either because of incomplete conversion or because of possible formation of more toxic polychlorodibenzofurans and polychlorodibenzodioxins in side reactions.

The major drawback of alternative pathways of rendering PCBs harmless is that it is impossible to predict reliably the behavior of particular PCB congeners in the processes, since technical PCBs contain up to 50–70 congeners differing in the number of chlorine atoms and their mutual positions in aromatic structures [1, 2].

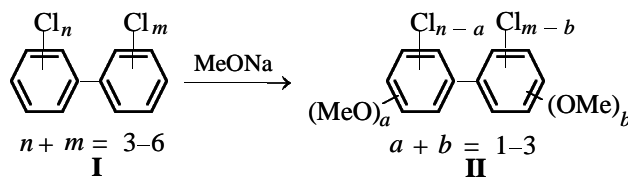
Previous studies of reagent (chemical) processing of PCBs showed that reactions of PCBs with various sodium or potassium alcoholates formally result in substitution of two aryl-bonded chlorine atoms by alkoxy groups [3]. These conclusions were confirmed by elemental analysis, IR spectroscopy, and some data on the solubility of the resulting derivatives. The reactivity of PCB congeners present in the mixture was not discussed.

In this context, our goal was to determine the

chemical composition of mixtures obtained by reaction of Sovol PCB mixture with sodium methoxide, to evaluate the reactivity of PCB congeners in this mixture, and to find conditions ensuring the most complete conversion of the starting compounds.

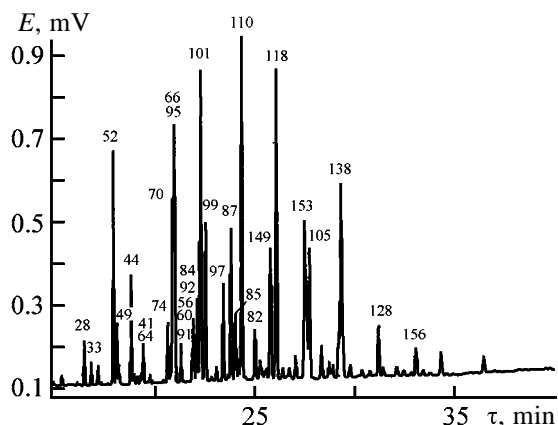
Previously we determined the composition and content of PCB congeners in Sovol and identified more than 30 components; the total contents of tetra-, penta-, and hexachlorobiphenyls were found to be about 20, more than 50, and about 20%, respectively; minor amounts of trichloro- and heptachlorobiphenyls were also detected [2]. A typical chromatogram of Sovol is shown in Fig. 1. The IUPAC designations of all the possible PCB congeners are given in [1]; the components of Sovol are listed in Table 1.

Published data on nucleophilic substitutions in PCB aromatic systems **I** are virtually lacking. The reaction of technical PCB mixture **I** with sodium methoxide can formally be described by the scheme



Our first goal was to find the optimal conditions for nucleophilic substitution of aryl-bonded chlorine atoms by methoxy group: solvent, reactant ratio, temperature, and time.

Mixtures **II** obtained from the reactions were analyzed by capillary gas–liquid chromatography with flame-ionization (GLC–FID) and mass-spectrometric (GLC–MSD) detectors. The trends in variation of the



**Fig. 1.** Chromatogram of Sovol technical mixture of polychlorinated biphenyls: (*E*) potential and ( $\tau$ ) time; the same for Figs. 2.

retention times and the relative intensities of peaks were evaluated under optimal conditions of GLC–FID analysis.

### EXPERIMENTAL

The reaction progress was monitored with a Shimadzu GC-17A gas chromatograph [flame-ionization detector; MDN 5S (30 000  $\times$  0.25 mm) quartz capillary column coated with 0.25  $\mu$ m 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;

**Table 1.** Major congeners of Sovol technical mixture of polychlorinated biphenyls

IUPAC no.	Positions of Cl atoms	IUPAC no.	Positions of Cl atoms
33	2', 3, 4	101	2, 2', 4, 5, 5'
28	2, 4, 4'	99	2, 2', 4, 4', 5
52	2, 2', 5, 5'	97	2, 2', 3', 4, 5
49	2, 2', 4, 5'	87	2, 2', 3, 4, 5'
47	2, 2', 4, 4'	85	2, 2', 3, 4, 4'
44	2, 2', 3, 5'	110	2, 3, 3', 4', 6
41	2, 2', 3, 4	82	2, 2', 3, 3', 4
64	2, 3, 4', 6	149	2, 2', 3, 4', 5', 6
74	2, 4, 4', 5	118	2, 3', 4, 4', 5
70	2, 3', 4', 5	153	2, 2', 4, 4', 5, 5'
66	2, 3', 4, 4'	132	2, 2', 3, 3', 4, 6'
95	2, 2', 3, 5', 6	105	2, 3, 3', 4, 4'
91	2, 2', 3, 4', 6	138	2, 2', 3, 4, 4', 5'
56	2, 3, 3', 4'	128	2, 2', 3, 3', 4, 4'
60	2, 3, 4, 4'	156	2, 3, 3', 4, 4', 5

solvent toluene; sample volume 0.2  $\mu$ l].

The compounds were identified with a Fisons gas chromatograph–mass spectrometer [MD 800 detector; HP-5 (25 000  $\times$  0.25 mm) quartz capillary column coated with 0.25  $\mu$ m 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.

Quantitative calculations were performed by the internal normalization method.

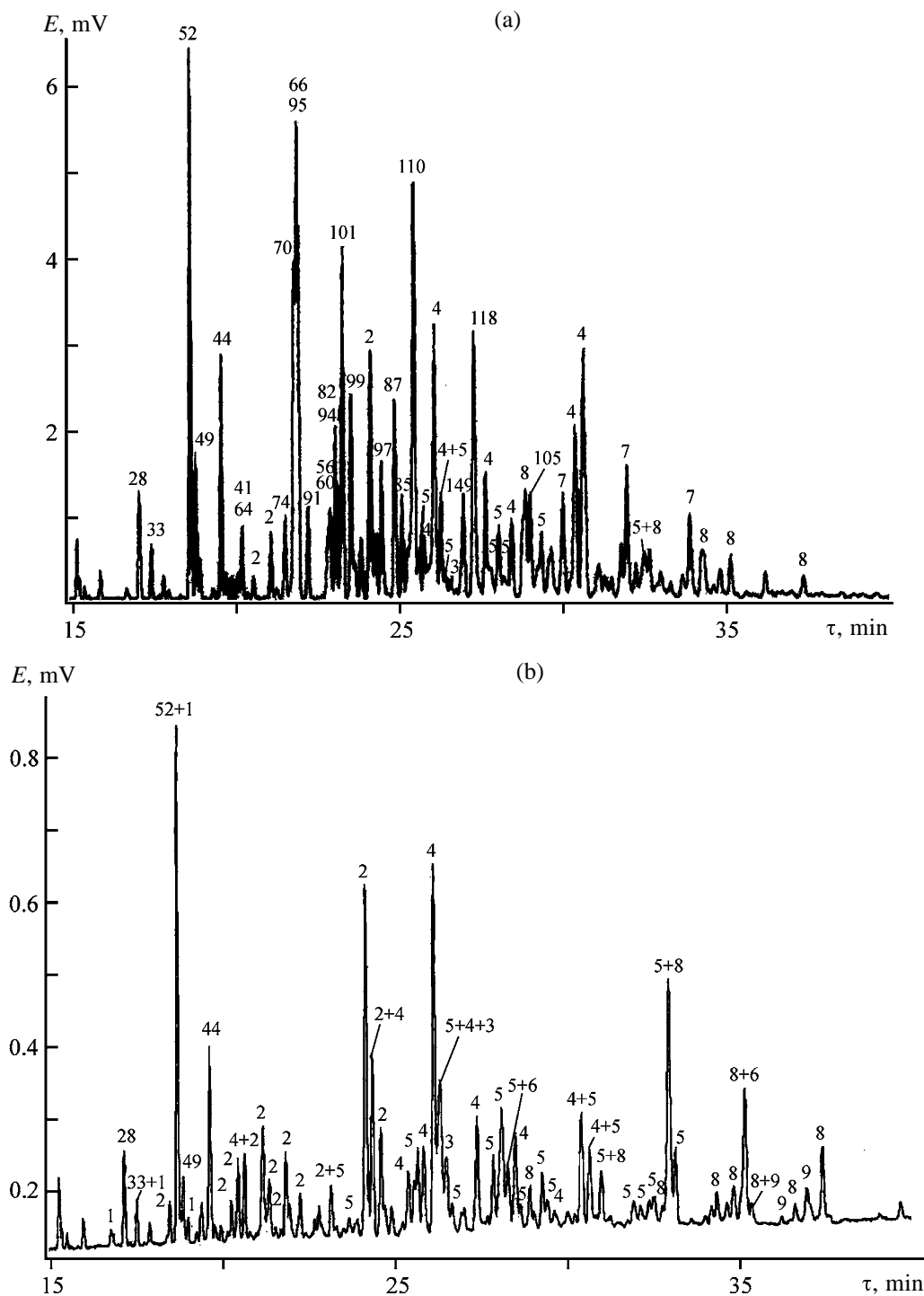
### Reaction of PCB I with sodium methoxide.

A round-bottomed flask equipped with an air condenser and a CaCl<sub>2</sub> tube was charged with 5.4 g (0.1 mol) of freshly dried MeONa and 25 ml of dimethyl sulfoxide (DMSO) dried over molecular sieves. The flask was heated on a Wood's alloy bath for 5–10 min at 165–170°C with shaking. Then 8.2 g (0.025 mol) of PCB I was added, and the mixture was heated on a Wood's alloy bath at 170°C for 25 min with shaking. After cooling, the mixture was diluted with 100 ml of water and transferred into a separating funnel. The homogeneous mixture was extracted with toluene (2  $\times$  20 ml); the toluene extracts were combined, washed with water (5  $\times$  100 ml), filtered, and dried over CaCl<sub>2</sub>; the solvent was evaporated, and the residue was kept in a vacuum. The resulting yellow oily mass was analyzed.

The reaction of PCB I with sodium methoxide was performed in bipolar aprotic solvents: DMSO, dimethylformamide (DMF), sulfolane, *N*-methyl-2-pyrrolidone, diglyme, and 1,4-dioxane. Under similar conditions [the same PCB concentration, PCB : MeONa ratio 1 : 4, 25 min, boiling point of the solvent], the best results were obtained in DMSO, DMF, sulfolane, and *N*-methyl-2-pyrrolidone.<sup>1</sup> In diglyme and 1,4-dioxane, no reaction of PCB I with MeONa was observed. Thus, the requirements to solvents for this process are high polarity and high electron density on the oxygen atom ( $\epsilon > 15$ ) [4]. Such properties ensure strong interaction of Na<sup>+</sup> ions with the solvent, enhancing the reactivity of MeO<sup>-</sup>.

The degree of conversion was evaluated from a decrease in the areas of the peaks of the starting PCBs I and increase in the areas of the peaks of methoxy derivatives II. Figures 2a and 2b show chromatograms of mixtures obtained from the reactions.

<sup>1</sup> The reactions of PCB I with sodium methoxide in sulfolane and *N*-methyl-2-pyrrolidone were performed at 175–180°C.



**Fig. 2.** Chromatogram of reaction products **II**. 170°C, DMSO, 25 min. **I**: MeONa: (a) 1 : 1 and (b) 1 : 4. Peak assignment: (1)  $C_{12}H_7Cl_2OCH_3$ , (2)  $C_{12}H_6Cl_3OCH_3$ , (3)  $C_{12}H_6Cl_2(OCH_3)_2$ , (4)  $C_{12}H_5Cl_4OCH_3$ , (5)  $C_{12}H_5Cl_3(OCH_3)_2$ , (6)  $C_{12}H_5Cl_2(OCH_3)_3$ , (7)  $C_{12}H_4Cl_5OCH_3$ , (8)  $C_{12}H_4Cl_4(OCH_3)_2$ , and (9)  $C_{12}H_4Cl_3(OCH_3)_3$ ; for other designations, see Table 1.

The reactions in DMSO, DMF, sulfolane, and *N*-methyl-2-pyrrolidone gave qualitatively and quantitatively similar results. The composition of mixtures **II** was complex, with increased number of chromato-

graphic peaks. Under the optimal conditions, 8–15% of the starting PCBs **I** (mainly tri- and tetrachlorobiphenyls) remained unchanged.

The chemical composition of mixtures **II** and de-

gree of conversion of PCBs **I** were determined by GLC-MSD. To do this, we reconstructed the mass chromatograms for particular ions characteristic of the starting tri-, tetra-, penta-, and hexachlorobiphenyls and thus estimated the relative content of unchanged PCBs **I**. Then, as far as possible, we studied the mass spectra of all the detected products.

Synthesis of individual monomethoxypolychlorobiphenyls by cross coupling of the corresponding monoaromatic systems and the fragmentation patterns of these compounds under electron impact were reported in [5, 6]. A specific feature of the mass spectra of pure monomethoxypolychlorobiphenyls is the presence of strong molecular peaks. No such data are available in mass-spectrometric databases on di- and trimethoxypolychlorobiphenyls. We have revealed in the mass spectra of **II** strong molecular peaks belonging to monomethoxydi(tri-, tetra-)chlorobiphenyls, dimethoxydi(tri-, tetra-)chlorobiphenyls, and trimethoxydi(tri-)chlorobiphenyls.

Reconstruction of the mass chromatograms for the molecular peaks of PCB methoxy derivatives **II** allowed us to assign the peaks and reveal the cases of joint elution of the derivatives. Since the columns used in GLC-FID and GLC-MSD experiments were similar, we obtained similar chromatograms, which allowed peak assignment in the chromatograms obtained by GLC-FID (Fig. 2).

As described previously for monomethoxypolychlorobiphenyls [5, 6], the fragmentation pattern of such compounds under electron impact depends on the position of the methoxy groups. However, their position in components of **II** cannot be determined from the available data.

For example, *p*-monomethoxy derivatives of PCBs show the peaks  $[M - 15]^+$  ( $M - \text{CH}_3$ ) and  $[M - 43]^+$  ( $M - \text{CH}_3 - \text{CO}$ ); *o*-isomers, the peaks  $[M - 35]^+$  ( $M - \text{Cl}$ ) and strong peaks  $[M - 50]^+$  ( $M - \text{CH}_2\text{Cl}$ ); and *m*-isomers, medium-intensity peaks  $[M - 43]^+$  and  $[M - 50]^+$ . All the three types of fragmentation were detected in our study.

The characteristic peaks of dimethoxy derivatives of PCBs were  $[M - 65]^+$  ( $M - \text{CH}_3 - \text{CH}_2\text{Cl}$ ),  $[M - 93]^+$  ( $M - \text{CH}_2\text{Cl} - \text{CH}_3 - \text{CO}$ ), and  $[M - 156]^+$  ( $M - \text{CH}_2\text{Cl} - \text{CH}_3 - \text{CO} - \text{COCl}$ ). In some cases, we also detected the peaks  $[M - 15]^+$  and  $[M - 43]^+$ , and in other cases, the peaks  $[M - 50]^+$  and  $[M - 65]^+$ , which may be associated with the location of the two methoxy groups.

The mass spectra of PCB trimethoxy derivatives contain peaks characteristic of monomethoxy ( $[M -$

$15]^+$ ,  $[M - 43]^+$ ,  $[M - 50]^+$ ) and dimethoxy ( $[M - 65]^+$ ,  $[M - 93]^+$ ) derivatives.

To evaluate the reactivities of PCB congeners, we studied in more detail the reaction of **I** with sodium methoxide in DMSO; we varied the reaction temperature and time and the molar ratio of the reactants. The results are listed in Table 2.

Quantitative treatment of the chromatographic data for mixtures **II** shows that the reactivity of PCB congeners grows with increasing number of chlorine atoms.

Hexachlorobiphenyls (PCB 149, PCB 153, PCB 138, PCB 128) started to transform at a relatively low temperature (60°C), mainly into monomethoxy derivatives  $\text{C}_{12}\text{H}_4\text{Cl}_5\text{OCH}_3$  (Figs. 2a, 2b, peak 7). Their reactivity increased with temperature, methoxylation proceeded further, and, starting from 150°C, monomethoxypentachlorobiphenyls were no longer detected; the reaction yielded dimethoxy  $[\text{C}_{12}\text{H}_4\text{Cl}_4 \cdot (\text{OCH}_3)_2]$ , 8) and trimethoxy  $[\text{C}_{12}\text{H}_4\text{Cl}_3(\text{OCH}_3)_3]$ , 9) derivatives, with dimethoxytetrachlorobiphenyls prevailing. The starting hexachlorobiphenyls were not detected in the reaction products. These results were obtained in all the four solvents: DMSO, DMF, sulfolane, and *N*-methyl-2-pyrrolidone.

Pentachlorobiphenyls started to react with sodium methoxide at 60°C, and their reactivity also increased with temperature. The major products were monomethoxy ( $\text{C}_{12}\text{H}_5\text{Cl}_4\text{OCH}_3$ , 4) and dimethoxy  $[\text{C}_{12}\text{H}_5 \cdot \text{Cl}_3(\text{OCH}_3)_2]$ , 5) derivatives. Minor amounts of trimethoxy derivatives  $[\text{C}_{12}\text{H}_5\text{Cl}_2(\text{OCH}_3)_3]$ , 6) were also detected by GLC-MSD. PCB 85, PCB 99, PCB 105, and PCB 118 containing chlorine atoms in both *p*-positions appeared to be more reactive. These congeners entered into the reaction earlier than the other pentachlorobiphenyls.

Tetrachlorobiphenyls were characterized by relatively low degree of reaction with sodium methoxide, with predominant formation of monomethoxytrichlorobiphenyls ( $\text{C}_{12}\text{H}_6\text{Cl}_3\text{OCH}_3$ , 2); minor amounts of dimethoxydichlorobiphenyls 3 also formed. PCB 47, PCB 60, PCB 66, and PCB 74 containing two chlorine atoms in the *p*-positions showed high reactivity; PCB 41, PCB 49, PCB 64, and PCB 70 containing one chlorine atom in the *p*-position appeared to be less reactive.

Tetrachlorobiphenyls PCB 52 and PCB 44 containing no chlorine in *p*-positions did not noticeably react under the experimental conditions. Trichlorobiphenyls PCB 28 and PCB 33 containing one chlorine in *p*-position under the optimal conditions partially trans-

**Table 2.** Conditions of the reaction of PCBs I with sodium methoxide in DMSO and transformation products

Reaction conditions				PCB transformations products			
$T$ °C	$\tau$ , min	PCB : NaOMe ratio	content of un- changed PCB congeners, %	trichloro- ( $C_{12}H_7Cl_3$ )	tetrachloro- ( $C_{12}H_6Cl_4$ )	pentachloro- ( $C_{12}H_5Cl_5$ )	hexachloro- ( $C_{12}H_4Cl_6$ )
60	25	1 : 4	87	Unchanged	Unchanged	$C_{12}H_5Cl_4OCH_3$	$C_{12}H_4Cl_5OCH_3$
80	25	1 : 4	62	"	"	$C_{12}H_5Cl_4OCH_3$	$C_{12}H_4Cl_5OCH_3$
100	25	1 : 4	28	"	$C_{12}H_6Cl_3OCH_3$	$C_{12}H_5Cl_3(OCH_3)_2$	$C_{12}H_4Cl_4(OCH_3)_2$
150	25	1 : 4	23	$C_{12}H_7Cl_2OCH_3$	$C_{12}H_6Cl_2(OCH_3)_2$	$C_{12}H_5Cl_4OCH_3$	$C_{12}H_4Cl_4(OCH_3)_2$
170	10	1 : 4	40	Unchanged	$C_{12}H_6Cl_3OCH_3$	$C_{12}H_5Cl_3(OCH_3)_2$	$C_{12}H_4Cl_3(OCH_3)_3$
170	25	1 : 4	13	$C_{12}H_7Cl_2OCH_3$	$C_{12}H_6Cl_2(OCH_3)_2$	$C_{12}H_5Cl_4OCH_3$	$C_{12}H_4Cl_4(OCH_3)_2$
170	25	1 : 6	11	$C_{12}H_7Cl_2OCH_3$	$C_{12}H_6Cl_3OCH_3$	$C_{12}H_5Cl_4OCH_3$	$C_{12}H_4Cl_4(OCH_3)_2$
170	25	1 : 1	59	Unchanged	$C_{12}H_6Cl_2(OCH_3)_2$	$C_{12}H_5Cl_3(OCH_3)_2$	$C_{12}H_4Cl_3(OCH_3)_3$
170	120	1 : 4	10	$C_{12}H_7Cl_2OCH_3$	$C_{12}H_6Cl_3OCH_3$	$C_{12}H_5Cl_4OCH_3$	$C_{12}H_4Cl_4(OCH_3)_2$
					$C_{12}H_6Cl_2(OCH_3)_2$	$C_{12}H_5Cl_3(OCH_3)_2$	$C_{12}H_4Cl_3(OCH_3)_3$

formed into monomethoxydichlorobiphenyls  $C_{12}H_7Cl_2OCH_3$  (1).

Thus, we have revealed the features of chemical transformations of PCB (Sovol) congeners under the action of sodium methoxide, as influenced by the number of chlorine atoms in the molecule, their relative location, and reaction conditions.

### CONCLUSIONS

(1) Reaction of Sovol mixture of polychlorobiphenyls with sodium methoxide is the most efficient in bipolar aprotic solvents (dimethyl sulfoxide, dimethylformamide, sulfolane, *N*-methyl-2-pyrrolidone).

(2) Among Sovol congeners, the most reactive toward sodium methoxide are hexa- and pentachlorobiphenyls; tetra- and trichlorobiphenyls are less reactive.

(3) Reaction of polychlorobiphenyls with sodium methoxide (170°C, 25–120 min, PCB : MeONa 1 : 4)

in various solvents does not ensure complete conversion of the main pollutants.

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