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Chemical methods of transformation of polychlorobiphenyls

T I Gorbunova, V I Saloutin, O N Chupakhin

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Abstract. Modern methods for detoxication of production waste containing polychlorobiphenyls are considered. The reactivities of some congeners (individual components) and technological mixtures of polychlorobiphenyls in various types of reactions are analyzed. Possible fields of application of polychlorobiphenyl derivatives are considered. The bibliography includes 123 references.

I. Introduction

The Stockholm Convention on persistent organic pollutants (POP) adopted in May 2001 provides for elimination of the action of polychlorobiphenyls (PCB) on humans and the environment. With respect to PCB, the International Convention should be implemented in two steps including universal elimination of PCB and PCB-containing materials from all production fields (before 2015) and their complete elimination (before 2025).

Whereas the first step is a solvable problem, realization of the second step requires carrying out scientific research. This situation is due to inhomogeneous compositions of the PCB to be eliminated and a variety of methods developed for their elimination, detoxication or pretreatment for elimination. Chemical methods used to this end differ from one another in many parameters (energy consumption, conversion, yield, type of final reaction products). Therefore, it is difficult to give an unambiguous answer to the question about the most efficient method for PCB detoxication. A review[1] summarizes information on chemical methods for detoxication (processing) of PCB and PCB-containing materials available before 1998 and concludes that rational processing of toxic waste requires a combination of two or more methods. The choice of particular methods for processing of PCB is determined by the aggregation state of the material to be detoxicated, the PCB concentration and the engineering and environmental features of the processes realized.

There is a variety of PCB detoxication techniques, *viz*., pyrolysis, oxidation methods, substitutive dechlorination, reductive dechlorination (hydrodechlorination), photolysis, radiolysis, electrochemical and biotechnology methods, *etc*. A priority position is occupied by pyrolysis, because under particular conditions (temperatures above 2000 °C; the residence time in the reaction zone 2 – 3 s, high turbulence of the reaction mass) it leads to complete mineralization of PCB and the pyrolysis products contain no polychlorodibenzodioxins (PCDD) or polychlorodibenzofurans (PCDF). However, owing to high energy expenditure, colossal oxygen consumption (4 – 6 tonnes per tonne of PCB) and low selectivity, this process is suitable for elimination of small amounts of highly concentrated PCB. In addition, a large number of studies analyzed in Ref. 1 were carried out ignoring control of competing formation of PCDD and PCDF. Information on even higher toxicity of the PCDD and PCDF derived from PCB was generalized in a monograph.[2]

Recent, studies on the detoxication of PCB and PCB-containing materials do not cover a variety of approaches. There is almost no new scientific information on pyrolysis of technological chloroaromatic materials and on the electrochemical and oxidation methods for processing of PCB. Contrary to this, the proportion of studies on the reductive and substitutive dechlorination of PCB abruptly increased. The development of the methods for reductive dechlorination of chloroaromatic materials is first of all due to the possibility of utilizing novel types of catalysts prepared using nanomaterials and nanotechnologies. The use of cheaper reactants based on alkali-earth metal oxides com-

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pared to the alkali and alkali-earth metals gave an impetus to the development of PCB dechlorination methods resulting in the formation of new C–C bonds. In addition, studies devoted to the chemical methods of PCB processing and carried out in the last decade are characterized by more stringent analytical control of the side formation of PCDD and PCDF and of the isomeric composition of the starting reactants and final reaction products.

This review is devoted to the newest methods of detoxication (elimination) of PCB and PCB-containing materials, developed in the last decade.

II. Reductive dechlorination

1. Reactions in the presence of palladium catalysts

Reductive dechlorination using modified Pd-catalysts is one of the most rapidly developing fields of organic synthesis. Usually, the content of palladium in such catalysts is at most 10% by mass. Depending on the Pd-catalyst, one can use hydrogen gas from a bottle or hydrogen evolved *in situ*. In the former case, Pd-catalysts modified with inert supports (mainly coal and SiO_2) are used,[3–7] while Pd-catalysts modified with active metals, *e.g.*, Fe and Mg,[8–15] are utilized in the latter case. Therefore, successful reductive dechlorination of chloroaromatic compounds in the presence of Pd-catalysts diluted with inert substrates requires that the process be conducted under anhydrous conditions. And *vice versa*, if reductive dechlorination is carried out in the presence of Pd-catalysts with active metals, water is needed for *in situ* formation of hydrogen.[16] In this case, the active metal (*e.g.*, Fe) counterpart of Pd plays the role of reactant rather than catalyst.

$$Fe^0 \longrightarrow Fe^{2+} + 2e^-,$$

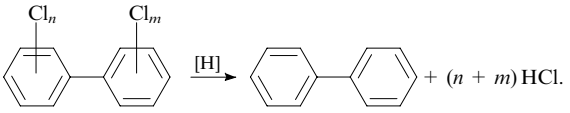
$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^-,$$

$$Fe^0 + 2H_2O \longrightarrow Fe^{2+} + H_2\uparrow + 2OH^-,$$

$$RCl + H_2\uparrow \longrightarrow RH + HCl$$

R is organic residue.

It is desired that reductive dechlorination of PCB results in chlorine-free biphenyl.



a. Palladium catalysts supported on inert substrates

In our opinion, the published data on the use of Pd-catalysts supported on inert substrates in the reaction of reductive dechlorination of PCB cast some doubt and this process cannot be recommended for hydrodechlorination of all technical PCB. The reasons are as follows. First, only a number of particular PCB congeners are used in the reactions; second, the results obtained to date; third, a relatively high cost of Pd-catalysts; finally, difficulties in the determination of complete material balances of the reactions due to adsorption of the resulting mixtures of products on solid catalysts.

For instance, a successful reductive dechlorination of 2-, 3- and 4-chlorobiphenyls (PCB 1, PCB 2 and PCB 3, respectively) using an external source of hydrogen and a Pd/C-catalyst was reported.[3] According to gas chromatography with mass spectrometric detection (GC–MS) data, the reaction results in unsubstituted biphenyl. It was pointed out that the dechlorination of the *ortho*-isomer (PCB 1) proceeds much slower than that of the *meta*- (PCB 2) and *para*- (PCB 3) isomers of monochlorobiphenyl. This order of reductive dechlorination was corrected[4] to give the following series of the reactivity of the C–Cl bond in PCB:

meta > *para* ≫ *ortho*.

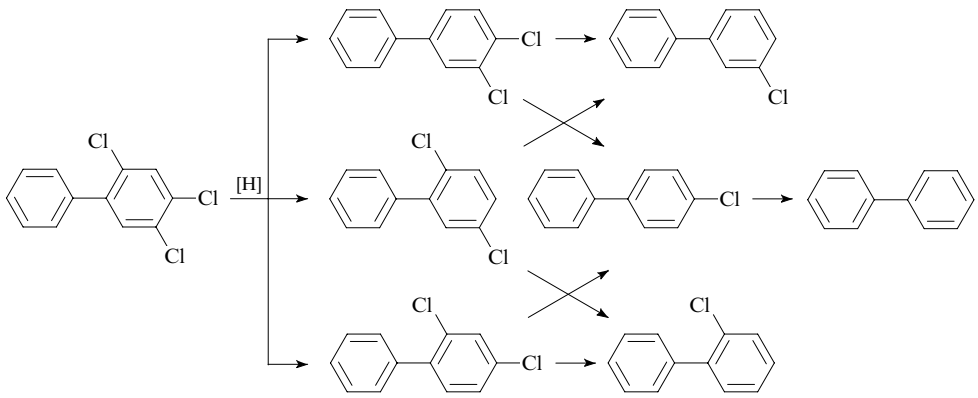
However, this order of hydrodechlorination of PCB by a heterogeneous mixture of $NH_2NH_2 \cdot HCl$ and Pd(10%)/C in hexane was proved in the studies of only two substrates, *viz.*, 2,4,5-trichloro- (PCB 29) and 2,5-dichlorobiphenyl (PCB 9) ignoring mutual influence of chlorine atoms localized in different positions. The consumption of Pd(10%)/C was 9.4×10^{-5} mol per 0.05 mol of PCB 29 or PCB 9 (Scheme 1).

It was emphasized[4] that the most pronounced effect in hydrodechlorination of PCB 29 and PCB 9 is attained at 60 °C and/or when the reaction mass is exposed to microwave radiation or sonicated to accelerate the main heterogeneous reaction. This technique was successfully used for purification of PCB-contaminated industrial oils; indeed, the oil can be completely cleaned from chlorine-containing products. The conclusions drawn in Ref. 4 were formulated based on the GC data.

Studies on reductive dechlorination of technical PCB mixtures are of greatest interest.

Removal of aromatic chlorine atoms from Aroclor 1254 mixture in the presence of Pd(5%)/C or Pd(5%)/SiO_2 was studied.[5] For comparison, the authors of Ref. 5 investigated the hydrodechlorination of perchlorinated biphenyl

Scheme 1



(decachlorobiphenyl, PCB 209). Hydrogen gas from a bottle was used as reducing agent; all stages of hydrodechlorination were carried out at atmospheric pressure, which undoubtedly attracts considerable attention to the experimental methods employed. The degree of dechlorination of substrates was determined by an ion-selective electrode for Cl^- ions; the final mixtures of reaction products were not isolated.

The main distinctive feature of the hydrodechlorination of Aroclor 1254 and PCB 209 is the temperature regime of the reaction with hydrogen in the presence of catalysts. Namely, the reaction temperature is 130 °C for the Aroclor 1254 substrate (a liquid under normal conditions) and 230 °C for solid PCB 209. The difference in the aggregation state has a pronounced effect on the results of reductive dechlorination under the conditions specified. PCB 209 undergoes a complete conversion while the reaction with Aroclor 1254 is accompanied by evaporation of less chlorinated congeners from the reaction mass, which precludes construction of complete material balance of PCB hydrodechlorination for this technical mixture. The PCB hydrodechlorination is accompanied by competing destruction reactions; as a result, the final mixtures contain some low-molecular-mass compounds. In particular, reductive dechlorination of PCB 209 on the Pd/C-catalyst results in diethylbenzene as side product, while Aroclor 1254 is transformed to a mixture of biphenyl, diethylbenzene, toluene, styrene and propylbenzene under similar conditions.

The activity of the Pd-containing catalysts was compared with those of modified Ni-based catalysts.[5] All catalysts have porous structures with pore sizes ranging from 10 to 50 nm. Porous structures favour more efficient hydrodechlorination of PCB that can adsorb and desorb hydrogen present in the reaction mass. The experimentally established order of catalytic activity is as follows:

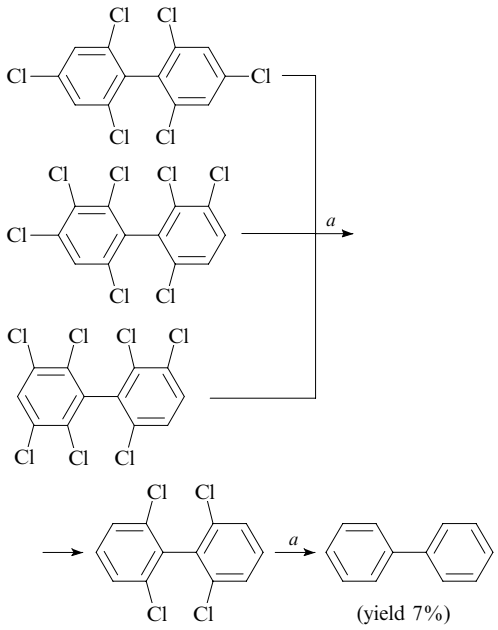
$$Pd(0.5\%)/C > Ni(3\%)/C > Ni(7\%)/C > Ni(7\%)/SiO_2 .$$

Different catalytic activities of these catalysts manifest themselves in the results of thermal destruction of PCB 209, namely, the reductive dechlorination in the presence of Ni/C is accompanied by the formation of propylbenzene and toluene. The compositions of side products formed in the reaction with the Aroclor 1254 technical mixture in the presence of Ni-containing catalysts remains unchanged as in the case of the reaction on Pd/C.

The best example of hydrodechlorination of PCB including technical PCB is provided by the results obtained in Ref. 6. Reductive dechlorination of PCB was carried out at room temperature in MeOH using hydrogen gas from a bottle in the presence of a Pd(10%)/C catalyst (2.3×10^{-3} mol of catalyst per 7.7×10^{-5} mol of PCB) and Et_3N. The introduction of Et_3N into the reaction mass is due to the need for binding HCl formed in the reaction. After completion of the reaction, the reaction mass contained the solvent, the catalyst, biphenyl and $Et_3N \cdot HCl$. The PCB conversion and the yield of biphenyl were determined from GC–MS data. A total of 15 PCB congeners were used including monochlorinated: PCB 1, PCB 2; dichlorinated: 2,2′–dichlorobiphenyl (PCB 4), 2,3-dichlorobiphenyl (PCB 5), 2,4-dichlorobiphenyl (PCB 7), 2,5-dichlorobiphenyl (PCB 9), 2,6-dichlorobiphenyl (PCB 10), 3,3′-dichlorobiphenyl (PCB 11), 3,4-dichlorobiphenyl (PCB 12), 3,5-dichlorobiphenyl (PCB 14), 4,4′-dichlorobiphenyl (PCB 15); trichlorinated PCB 29; 3,3′,4,4′-tetrachlorobiphenyl (PCB 77); 3,3′,4,4′,5-pentachlorobiphenyl (PCB 126) and 3,3′,4,4′5,5′-hexachlorobiphenyl (PCB 169). In all cases, hydrodechlorination went to completion and the chromatographic yield of unsubstituted biphenyl was 100%.

Different results were obtained in the study of reductive dechlorination of completely *ortho*-substituted congeners including 2,2′,4,4′,6,6′-hexachlorobiphenyl (PCB 155), 2,2′,3,3′,4,6,6′-heptachlorobiphenyl (PCB 176) and 2,2′,3,3′,5,6,6′-heptachlorobiphenyl (PCB 179) (Scheme 2). Reactions under similar conditions led to removal of the chlorine atoms in *meta*- and *para*-positions and the formation of 2,2′,6,6′-tetrachlorobiphenyl (PCB 54) as the major reaction product. A prolonged multistep treatment of PCB 54 (> 24 h) results in a low yield of biphenyl (7%).

Scheme 2



(*a*) Pd(10%)/C, Et_3N, MeOH, H_2.

At the same time, it was reported that the formation of PCB 54 during the synthesis of technical PCB is sterically hindered.[6] Therefore, it is hardly probable that commercially available PCB contain PCB 54 and the proposed hydrodechlorination technique enables an almost complete detoxication of technical PCB mixtures.

This method was successfully applied to technical PCB mixtures including Aroclor 1254, Aroclor 1248 and capacitor PCB. Complete reductive dechlorination of all technical PCB congeners was observed and conversion of the starting products was 100%.[6]

The one and only problem of this method of hydrodechlorination of particular congeners and technical PCB is related to the isolation of the final product, biphenyl, whose yield varies from 51% to 88%. Adsorption of biphenyl from the solution on the catalyst surface causes the product yield and the catalyst activity to decrease. A comparison of the degree of PCB conversion in the presence of a multiply used and reduced catalyst showed that the catalytic activity of Pd/C decreases.[6]

The use of zirconium phosphate supported palladium and rhodium catalysts of reductive dehalogenation of technical PCB from contaminated soil was reported.[7] Technological waste (Aroclor 1260 and Aroclor 1254) desorbed from the solid matrix by a hexane/acetone mixture (1 : 1 by

volume) reacted with hydrogen in the presence of palladium (3.2% – 4%) or rhodium (3.8% – 5.5%) catalyst and Et_3N. The reactions were carried out in an autoclave (50 °C, 0.5 MPa, 12 h). GC-analysis of final mixtures showed that the major reaction product is biphenyl; the degree of conversion of the starting PCB was 99%.

b. Complexes of palladium and active metals

A review of studies on the hydrodechlorination of PCB in the presence of Pd-catalysts modified with active metals showed that such methods are useful for complete removal of chlorine atoms from aromatic substrates. On the one hand, successful reductive dechlorination of PCB requires Pd-catalysts with a low content of the noble metal because the reaction proceeds under anhydrous conditions and provides high values of both conversion of the starting PCB and the yield of biphenyl. On the other hand, the amounts of water, organic solvents (co-solvents) and hydrogen liberated *in situ* are interrelated and so do the pore size of the Pd-catalyst and the adsorption capacity of reaction products on the surface of catalysts. Taking into account these facts, a thorough optimization of reaction conditions is required.

Despite the fact that in this case the active metal plays the role of hydrogen 'source', success of the PCB hydrodechlorination is due to the presence of palladium which adsorbes the reducing agent (gas).[8] This leads to a high surface concentration of hydrogen. Independent data also confirm the need for palladium as a component of complex catalysts. For instance, a comparison of the catalytic activity of Pd/Fe (iron particle size about 10^{-6} m) and nanosized iron in PCB hydrodechlorination revealed a higher rate of the reaction using the former catalyst.[9]

The method also requires water and a polar solvent. According to calculations, if there is water deficiency or in the presence of a nonpolar solvent the dielectric constant of the reaction medium decreases, thus leading to an abrupt decrease in the catalytic activity of palladium and retardation of the reductive dechlorination of PCB.

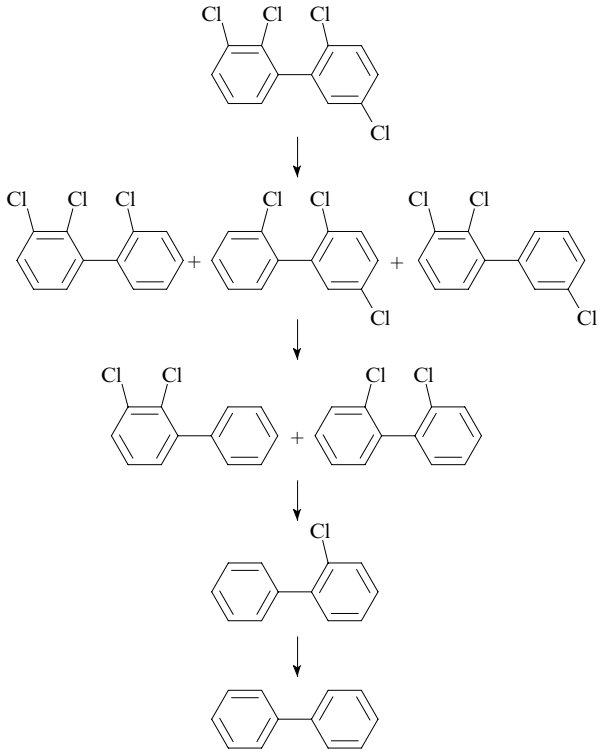
A study[10] of the reductive dechlorination of PCB 1, PCB 2 and PCB 3 in aqueous methanol solution in the presence of Pd(0.585%)/Fe revealed a somewhat different order of the reactivities of congeners compared to that presented above, *viz.*:

para > *meta* > *ortho*.

If the MeOH concentration in the mixture is higher than 10%, the rate of hydrodechlorination of all PCB abruptly decreases. The reaction is also strongly affected by the temperature regime, *viz.*, the PCB conversion and the yield of biphenyl increase with the temperature (reductive dechlorination of PCB was studied in the temperature range from 4 to 60 °C). The reaction is accompanied by high adsorption of PCB and biphenyl on the catalyst. The reaction time is also of crucial importance to the hydrodechlorination of PCB 1, PCB 2 and PCB 3. The initial reaction rate is high. In this stage, iron undergoes corrosion in the presence of moisture and vigorous evolution of hydrogen begins. This is followed by the formation of a passivating iron oxide layer on the iron surface and slower production of hydrogen and, correspondingly, slower hydrodechlorination of PCB. Therefore, the catalytic activity of the Pd/Fe-catalyst decreases. In any case, all series of experiments (duration from 10 min to 24 – 216 h) revealed no 100% conversion of the starting PCB.[10] Note that Pd^0 used was obtained by reduction from a solution of $(AcO)_2Pd$ in EtOH and supported on the surface of activated iron. In this case, the consumption of Pd(0.585%)/Fe was rather high, *viz.*, 1.9×10^{-3} mol of catalyst for the reductive dechlorination of $(2-19) \times 10^{-6}$ mol of PCB in solution.

Taking 2,2′,3,5′-tetrachlorobiphenyl (PCB 44) as an example, the order of reactivity of the chlorine atoms in the *ortho* and *meta* positions (Scheme 3) was revised.[8] Chlorine atoms in the *meta*-position are more prone to hydrodehalogenation in aqueous alcohols in the presence of Pd(10%)/Fe, as was reported by Lowry and Johnson.[9] Experiments[8,9] were carried out using highly dilute solutions of PCB congeners.

Scheme 3



A similar procedure using the Aroclor 1260 technical mixture extracted from a PCB-contaminated system is successfully completed in 9 h; however, isolation of the final biphenyl is complicated due to its adsorption on the surface of the Pd-catalyst.[8]

A (nanoscale Pd)/Fe catalyst supported on polymer matrix is highly active in the room-temperature reductive dechlorination of PCB 77.[11] However, in spite of a 100% conversion of the starting chloroaromatic compound, the reaction results in a mixture of biphenyl and low-chlorinated PCB.

Yet another procedure for the preparation of the Pd-catalyst was proposed.[12] Initially, the *in situ* formation of Pd/Fe in the reaction mass containing Fe, K_2PdCl_6, PCB, MeOH (or Me_2CO) and water is followed by the beginning of the reductive dechlorination of PCB. Then, Mg, K_2PdCl_6, hexane and a PCB internal reference is added. In this stage, Pd/Mg is formed and the PCB hydrodechlorination continues. After completion of the reaction and extraction with hexane, only biphenyl was detected among the reaction products (GC data). The authors of that study noted that the yield of biphenyl obtained from high-chlorinated PCB decreases when Pd(1%)/Mg is used as catalyst.

A similar trend is observed if the reaction mass contains no organic solvents favouring solubilization of the starting PCB in the aqueous solution. The loss of biphenyl can be due to the volatility of low-molecular-mass products obtained from radical intermediates formed as a result of reductive dechlorination of high-chlorinated PCB. This follows from the results obtained in studies of the reactions of technical mixtures including Aroclor 1221, Aroclor 1248 and Aroclor 1260. However, the final products were not isolated and the material balances of the reactions were incomplete.[12]

The preparation of a series of Pd/Mg catalysts with different Pd content was reported.[13] X-Ray diffraction data showed that if the catalyst is prepared as recommended in Ref. 12, it may contain palladium nanoparticles; this improves the PCB hydrodechlorination conditions and favours a decrease in the palladium content in the catalyst. Unfortunately, experimental data[13] refer to the PCB 2 substrate only. Room-temperature treatment of PCB 2 by the Pd/Mg-catalyst in aqueous alcohol solution demonstrated a successful reductive dechlorination. Experiments with a series of catalysts containing from 0.11% to 1.62% of palladium revealed a linear correlation between the conversion of PCB 2 and the palladium content in the catalyst, *viz*., the higher the palladium content of the catalyst the higher the conversion of PCB 2.

Hydrodechlorination of PCB 3 and 2,2′,3,3′,4,4′,5-heptachlorobiphenyl (PCB 170) in a water–methanol solution (10% MeOH) in the presence of Pd(0.01%)/Mg leads to complete removal of chlorine atoms from substrates after 10 min.[14] This effect was not observed for Aroclor 1260. Low-chlorinated PCB and biphenyl formed in the initial stage of hydrodechlorination of Aroclor 1260 are adsorbed on the catalyst surface and the reaction slows down. This to a greater extent concerns *ortho*-substituted PCB whose reductive dechlorination requires more severe conditions. The material balance of the corresponding reaction using Aroclor 1260 is far from 100%.

A similar method is suitable for remediation of soil contaminated with Aroclor technical PCB provided thorough extraction of biphenyl.[15]

Modern technologies allow reductive dechlorination to be carried out using osmosis of PCB solutions through membranes with bimetallic catalysts based on palladium and active metals.[17,18]

Recently, the expensive noble metal is 'diluted' with cheaper active and inert components to reduce the cost of the Pd-catalysts. Novel catalytic systems for hydrodechlorination of chloroaromatic compounds were reported. An example is provided by a series of multicomponent Pd-catalysts ($PdFe_4$/C, Pd_4Fe/C, Pd_4Fe_2/C, *etc*.), which enable successful reductive dechlorination of polychlorobenzenes and 2,4,8-trichlorodibenzofuran.[19]

Researchers are aimed at using nanosized Pd-catalysts for reductive dechlorination of PCB. This is completely justified because the reaction efficiency is improved,[5,8,11] the reaction temperature decreases and a smaller amount of catalyst is required. However, even at high conversion of the starting PCB one cannot completely isolate the hydrodechlorination products from the reaction mass owing to their adsorption on the surface of solid porous catalyst structures.

Summing up, mention may be made of Ag-containing catalysts as possible alternative to bimetallic Pd-catalysts because the former are cheaper. For instance, reductive dechlorination of polychlorobenzenes in the presence of Ag(1%)/Fe was reported.[20]

2. Reactions in the presence of iron nanoparticles

The advantages of using iron nanoparticles for neutralization of soil and water contaminated with technical PCB have been considered in detail in a review.[21] First of all, mention should be made of a low cost, availability, large surface area, high reactivity, and the possibility of *in situ* preparation of iron nanoparticles.

Analysis of the results reported in a comparative study[9] showed that hydrodechlorination of PCB 4; 3,4′-dichlorobiphenyl (PCB 13); 2,3,4-trichlorobiphenyl (PCB 21); PCB 44; 2,2′,4,5′-tetrachlorobiphenyl (PCB 49) and PCB 77 using 50-nm iron nanoparticles and Pd/Fe as catalysts leads to similar results, *viz*., the reductive dechlorination results in low-chlorinated congeners. Small differences are observed in the duration of hydrodechlorination in the presence of iron nanoparticles and Pd/Fe-catalyst.

As in the case of palladium, iron nanoparticles can be supported on inert, highly porous substrates. Reductive dechlorination of 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153) is carried out in the presence of a Fe/C-catalyst.[22] Hydrodechlorination of PCB 153 at 350 °C was studied in air and in inert (N_2) atmosphere. It was shown that the degree of chlorine removal from PCB 153 is higher for the reaction conducted in air (30 min). The reaction products include mixtures of tetra- and trichlorobiphenyls and the degree of conversion of the starting compound is as high as 99.9%. As to the reaction in nitrogen atmosphere, analysis of reaction products after 120 min revealed only tetrachlorobiphenyls; the degree of conversion of the starting compound was 97.1%. Successful hydrodechlorination of PCB in air in the presence of iron nanoparticles as a step in neutralization of contaminated soil was reported.[16] Iron nanoparticles exhibit high catalytic activity towards PCB 209.[23]

3. Other catalysts based on metals or metal oxides and reduction systems

In this Section we will dwell on some rarely used complex catalysts based on metals or metal oxides[24–26] and on novel reduction systems.[27,28]

A catalyst $Ni-Mo/Al_2O_3$ is efficient in hydrodechlorination of dichlorobiphenyls (290 °C, H_2, 3 MPa).[24] It was assumed that the reaction involves successive formation of monochlorinated biphenyls and biphenyl. The reactivity of dichloro-containing congeners reduces in the order

PCB 7 ≈ PCB 9 > PCB 5.

The maximum conversion attained under the reaction conditions is 89% for PCB 5, 92% for PCB 9 and 93% for PCB 7.

Complex catalysts based on TiO_2 were also used.[16,25] A comparative study[16] of the catalytic activity of iron nanoparticles and V_2O_5/TiO_2 in the hydrodehalogenation of PCB 153 under identical conditions revealed that both catalysts are equally efficient if the reaction is carried out in air.

Warning information was reported in a study[25] on reductive dechlorination of 2,3,3′,4′,5,5′-hexachlorobiphenyl (PCB 162) and 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB 138) in the presence of the catalytic system V_2O_5/

WO_3-TiO_2. The formation of toxic PCDF was detected in the temperature range from 150 to 200 °C (10% O_2, 70% N_2, 20% H_2O, 2 h). Therefore, efficient reductive dechlorination of PCB 162 and PCB 138 requires higher temperatures.

The catalytic system V–Ni–W enables complete oxidation (combustion) of PCB and other supertoxic chlorine-containing compounds in the temperature interval 260–340 °C at high O_2 content.[26]

A new catalytic system for neutralization of soil contaminated with Aroclor 1242 was used.[27] The catalyst is based on SmI_2; samarium cation exhibits the properties of a reducing agent ($Sm^{2+} \rightarrow Sm^{3+}$). Room-temperature hydrodechlorination of PCB in inert atmosphere in aqueous THF solution with additives of a coordinating agents (1,8-diazabicyclo[5.4.0]undec-7-ene, tetramethyl glycol, triethylamine) did not lead to 100% conversion of the technical PCB. The best result (100% conversion) was attained at 230 °C in the presence of hexamethylphosphorus triamide. The final mixture contained biphenyl, mono- and dichlorobiphenyls. The reaction products were ready for further biodegradation.

Hydrodechlorination of PCB using the reduction systems $NiCl_2$–2,2′-bipyridyl(or 1,10-phenanthroline)–Zn proceeds efficiently; however, chlorine atoms are not quantitatively removed from the PCB molecules.[28] It was shown that PCB 209 is transformed to less chlorinated biphenyls under the action of this system in the presence of DMF and water additives (80 °C, 6 h)

$$C_{12}Cl_{10} \longrightarrow \underset{(0.4\%)}{C_{12}H_5Cl_5} + \underset{(38.5\%)}{C_{12}H_4Cl_6} + \underset{(47.5\%)}{C_{12}H_3Cl_7} + \underset{(13.7\%)}{C_{12}H_2Cl_8}$$

The advances of the reduction system $NiCl_2$–2,2′-bipyridyl(or 1,10-phenanthroline)–Zn include its availability, high efficiency of PCB hydrodechlorination and reproducibility of results. This creates prerequisites for further progress in studies of dechlorination using this catalytic system and in search for novel reduction systems for PCB destruction.

4. Reactions in the presence of hydrides, boron hydrides and aluminium hydrides

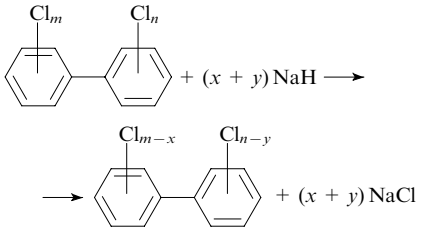
A few studies on reductive dechlorination of PCB under the action of hydrides and boron hydrides have been reported in the last decade. Hydrodechlorination of PCB using only hydrides or boron hydrides is of limited use because the reagents are expensive, hazardous and provide a low rate of the main reaction at relatively low temperatures.

In particular, dechlorination of the Aroclor 1016 mixture under the action of more than sixfold excess of $NaBH_4$ in anhydrous diglyme (boron hydride : diglyme ratio of about 1 : 4) at 162 °C leads to a 65% conversion of PCB after 180 h.[29] At the same time, the reaction using tetraglyme (boron hydride : tetraglyme ratio of about 1 : 2) at 310 °C results in 99% conversion after 2 h. These examples demonstrate that $NaBH_4$ is inefficient in dechlorination of technical PCB. This also to the full extent holds for $LiAlH_4$.[30]

It is much more efficient to carry out hydrodechlorination of chloroaromatic compounds using systems containing not only hydrides or boron hydrides but also metal salts capable of reducing *in situ*. Therefore, a hydride or boron hydride are necessary for initial reduction of metal cations to zero-valent metals, while in the subsequent reaction stages the metals themselves promote the evolution of hydrogen from solvents with mobile protons. As a consequence, the temperature of the reductive dechlorination decreases and the conversion of chloroaromatic compounds increases. Reductive dechlorination under the action of systems containing hydrides or boron hydrides and metal salts is highly selective; the selectivity-determining stage is the oxidative addition of aryl halide to the catalyst (complex of zero-valent metal).[30, 31]

Most often, divalent nickel salts are used for hydrodechlorination of PCB. It was shown[31] that treatment of a solution of PCB 15 in THF with a colloidal suspension prepared in advance by the reaction of a solution of $Ni(OAc)_2$ in THF with a mixture of NaH, THF and Bu^tOH in inert atmosphere results in a 93% conversion and quantitative yield of biphenyl under normal conditions after 110 h.

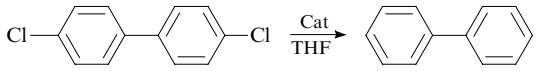
A similar result was obtained in the dechlorination of dichlorobiphenyls (conversion 99.9%) and transformer oils contaminated with PCB (conversion 89.8%).[32] Reductive dechlorination of PCB was carried out using nanosized NaH and a solution of $Ni(OAc)_2$ in Pr^iOH in inert (argon) atmosphere (68 °C, 8 h).



$x \leqslant m \leqslant 5$, $y \leqslant n \leqslant 5$.

High conversion of a technical PCB mixture (Delor 103) was attained using divalent nickel and cobalt pentadionates as catalysts in the presence of $NaAlH_2(OCH_2CH_2OMe)_2$.[33] The reaction carried out in toluene or in a mixture of a mineral oil with toluene in the presence of a threefold excess of this aluminium hydride (nitrogen atmosphere, 110 °C) results in biphenyl as the sole product (GC–MS data). After less than 60 min, the conversion of the starting PCB becomes as high as 99.5%.

For comparison, mention may be made of the hydrodechlorination of PCB 15 in the presence of aluminium acetyl acetonate



Cat = Bu^tOH, NaH, $Al(acac)_3$, $Ni(OAc)_2$, N_2,

which is needed to form a cluster compound Ni–Al in the first stage. The particle size of the *in situ* formed cluster is about 10 nm.[31] The cluster type and size have a pronounced effect on the results of reductive dechlorination of PCB 15, *viz.*, the reaction time is 6 h, the conversion is 100% and the yield of biphenyl is 95%.

At least equally interesting is the use of nickel complexes with phosphorus-containing ligands for hydrodechlorination of PCB.[34] A rather simple procedure involves the introduction of a solution of $NiCl_2L_2$ (L is a phosphorus-containing ligand) in THF into the reaction mixture containing boron hydride [$NaBH_2(OCH_2CH_2OMe)_2$], THF and PCB. The reaction proceeds at the boiling temperature

of the solvent and after its completion the dechlorination products are extracted by organic solvents. This reduction system is efficient in the hydrodechlorination of individual low-chlorinated congeners, being inefficient when applied to high-chlorinated (including technical) PCB. For instance, reductive dechlorination of PCB 3 and PCB 10 in the presence of a nickel-based catalytic system leads to a 99% conversion to biphenyl after 12 h. The conversion of PCB 209 under similar conditions is only 65% after 6 h, the yield of biphenyl is only 25% while other reaction products represent a mixture of di-, tri- and tetrachlorobiphenyls. Possible routes of formation of chlorine-containing products in the course of hydrodechlorination of PCB 209 using the catalytic system mentioned above are as follows:[34]

ligand migration

$$NiL_4 \longrightarrow NiL_3 + L,$$

oxidative addition

$$C_{12}Cl_{10} + NiL_3 \longrightarrow C_{12}Cl_9NiL_2Cl + L,$$

reductive elimination

$$C_{12}Cl_9NiL_2Cl + H^- + L \longrightarrow C_{12}Cl_9H + Cl^- + NiL_3,$$

partial hydrodechlorination

$$C_{12}Cl_{10} + n\,H^- \longrightarrow C_{12}Cl_{10-n}H_n + n\,Cl^-,$$

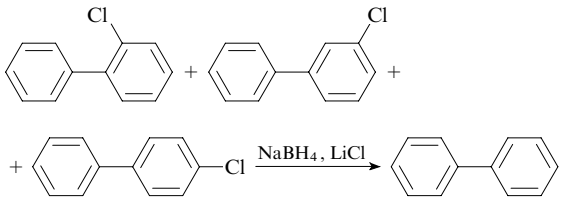
complete hydrodechlorination

$$C_{12}Cl_{10} + 10\,H^- \longrightarrow C_{12}H_{10} + 10\,Cl^-.$$

Conversion of technical PCB mixtures (Aroclor 1221, Aroclor 1232 and Aroclor 1254) under the reaction conditions is at most 75% after 6 h and the yield of biphenyl ranges from 25% to 50%.[34]

High degree of conversion of conventional PCB under hydrodechlorination conditions in the presence of boron hydrides is also favoured by an increase in the catalyst surface area owing to its support on porous inert substrates. Treatment of a solution of the 'Sovtol-10' technical mixture in ethanol/toluene mixture with sodium borohydride ($NaBH_4$) in hydrogen atmosphere (20–40 °C, 3 h) in the presence of a Ni/C (or Ni–Pd/C) catalyst led to 95% conversion of the starting PCB.[35] The yield of biphenyl was not specified.

Good results were obtained using the $LiCl/NaBH_4$ system for hydrodechlorination of the Aroclor 1016 mixture.[29] A 99% conversion of the technical PCB in tetraglyme at 130 °C is attained after 4 h. Monochlorobiphenyls PCB 2, PCB 3 and PCB 4 undergo a complete hydrodechlorination to biphenyl in diglyme.



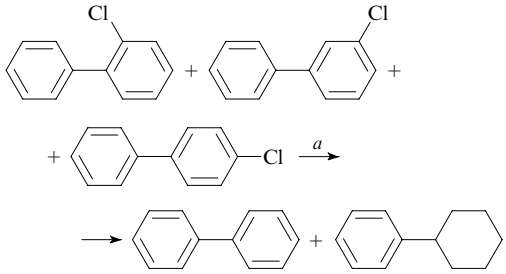
It was established [29] that the degree of reductive dechlorination of PCB using the catalytic system $LiCl-NaBH_4$ depends on the solvent nature and decreases in the order

tetraglyme > triglyme > diglyme.

These examples demonstrate that hydrodechlorination of PCB with hydrides or boron hydrides in the presence of metal salts is an efficient, but labour-consuming and expensive technology, which makes it of limited use in detoxication of chloroaromatic compounds, well recognized persistent organic pollutants.

This Section looks incomplete without information on the use of Raney nickel which includes nickel hydride as a component.[36] In this catalyst, hydrogen is present not only in the form of an anion, H^-. Taking into account the fact that Raney nickel is cheaper than the hydrides and borohydrides mentioned above and that reductive dechlorination in the presence of Raney nickel can be carried out in aqueous media, one can assume that this material is promising as a reagent for hydrodechlorination of PCB. Unfortunately, studies of this type of reactions have almost ceased recently, probably because of incomplete isolation of reaction products from the reaction mass.

The effect of Raney nickel prepared using two different methods on the degree of conversion of PCB 1, PCB 2 and PCB 3 was studied.[37] Following the first method (method *A*), a Ni–Al alloy was added to a mixture of a PCB congener in alkali solution. In the second case (method *B*), an alkali solution was added to a mixture of PCB, Ni–Al alloy and water. It was established that the result of reduction of PCB 1, PCB 2 and PCB 3 depends on the concentration of alkali in solution, the type of the alkali metal in the hydroxide composition, the amount of Raney nickel and the reaction temperature.[37] A general scheme of hydrodechlorination of three PCB congeners is shown below.



(*a*) Ni-Ra, HO^-, H_2O.

According to GC analysis, reactions using 5% and 10% NaOH solutions at 90 °C (method *A*) and 0.2% NaOH solution at 60 °C (method *B*) result in biphenyl as the sole product. Using method *B* and 1% KOH and CsOH solutions at 90 °C, one can obtain phenylcyclohexane (conversion 100%). In other experiments, a 100% conversion of the starting PCB 1, PCB 2 and PCB 3 was attained and the hydrodechlorination reactions resulted in biphenyl/phenylcyclohexane mixtures with different product ratios. Summing up, attempts to isolate biphenyl and phenylcyclohexane from the reaction mixtures have failed.

5. Reactions under the action of electromagnetic radiation

Most studies on the effect of electromagnetic radiation are devoted to investigations of the behaviour of particular PCB congeners. Technical PCB and PCB-containing materials are much less studied. The reasons are the initially complex PCB mixtures, which require elaboration of specific methods for detoxication of each PCB congener owing to different reactivities, large energy expenditures for the processes under the action of electromagnetic radiation, low rates of chemical reactions, low quantum yields and, often, incomplete conversion of PCB. Note that the most rapidly

developing studies include photochemical and radiation-chemical dechlorination in the presence of compounds with mobile protons, which excludes the formation of polymers using new C—C bonds. Exposure of PCB to electromagnetic radiation results in biphenyl and less chlorinated PCB as major products. This type of reactions can be treated as a kind of reductive dechlorination.

The method is based on the generation of $Ar^{\bullet}$ radical from molecules of the reaction medium under the action of electromagnetic radiation. Conventional reaction media for hydrodechlorination of PCB under the action of electromagnetic radiation are an aqueous alcohol solution (usually, $Pr^{i}OH$) and an alkali. In this case, alcohol (sometimes, a hydrocarbon) acts as the source of both radicals and hydrogen, and the hydrodechlorination of PCB proceeds by the radical-chain mechanism (for detailed scheme, see a review [1]).

In a continuation of their studies, Yao *et al.* [38] extended the range of PCB congeners to investigate their reductive dechlorination in a NaOH solution in $Pr^{i}OH$ under the action of 254-nm UV radiation emitted by a mercury lamp. Dechlorination of 3,3′,4,5,5′-pentachlorobiphenyl (PCB 127) under similar conditions was studied earlier [39] and demonstrated that replacement of chlorine atoms by hydrogen atoms occurs successively and involves the formation of tetrachloro-, trichloro-, dichloro-, monochlorobiphenyls and biphenyl. A mixture of these compounds was detected upon completion of the reaction.

The dechlorination study [38] of non-*ortho*-substituted PCB 12, PCB 14, 3,3′,5-trichlorobiphenyl (PCB 36), 3,4,5-trichlorobiphenyl (PCB 38), 3,3′,4,5-tetrachlorobiphenyl (PCB 78) and 3,4,4′,5-tetrachlorobiphenyl (PCB 81) revealed changes in the compositions of the starting compounds upon 10-min exposure of the reaction mass to light of the mercury lamp. Mixtures isolated contained the starting PCB, lower-chlorinated PCB and biphenyl. No biphenyl formation (yield 0%) was observed in the case of PCB 78; UV-irradiation led to a mixture of the starting PCB 78, two trichloro-substituted PCB, three dichloro-substituted PCB and two monochloro-substituted PCB. The highest yield of biphenyl (3.2%) and the highest conversion of the starting PCB (95.8%) were attained for PCB 38.

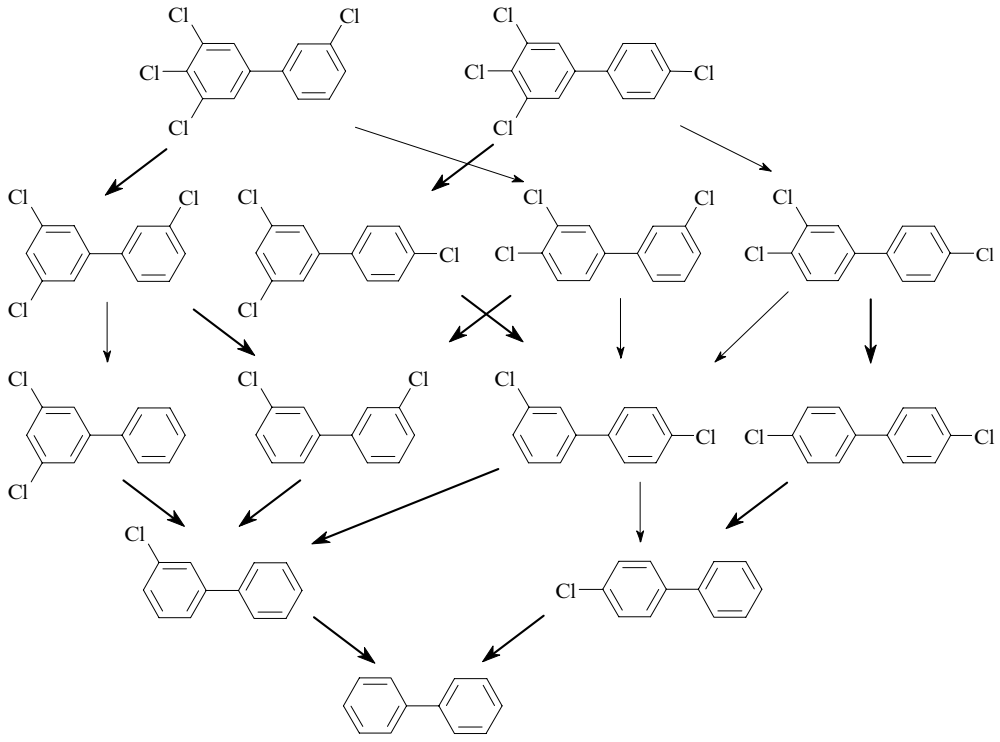
It was established [38, 39] that high-chlorinated aryl fragments are the first to undergo reductive dechlorination under these conditions. Asymmetrical congeners undergo dehydrohalogenation faster than symmetrical ones and replacement of chlorine atoms by hydrogen atoms leads to thermodynamically more stable symmetrical structures. Non-*ortho*-substituted PCB are highly reactive under photo-initiation conditions due to redistribution of the π-electron density of the aromatic ring over the chlorine atoms in *para*- and *meta*-positions (Scheme 4).

Similar conclusions were made in studies of photochemical hydrodechlorination of PCB 5, 2,4′,5-trichlorobiphenyl (PCB 31), 2,2′,5,5′-tetrachlorobiphenyl (PCB 52), PCB 77, 2,2′,3,4,5′-pentachlorobiphenyl (PCB 87), PCB 126, PCB 138 and PCB 169 in hexane on exposure to light of a mercury lamp.[40] Symmetrical and coplanar (planar non-*ortho*-substituted) PCB are low reactive; the chlorine atoms in the higher-substituted aryl fragments are more sensitive to reductive dechlorination; hydrodechlorination can result in coplanar PCB, which make the resulting mixture of reaction products more toxic. Investigations of mixed *ortho*-, *para*- and *meta*-substituted PCB led to the following order of reactivity:

ortho > *meta* > *para*,

which is the reverse of the reactivity order established for the reductive dehalogenation of PCB in the presence of Pd-catalysts. High reactivity of *ortho*-chlorine atoms under similar conditions (reaction time 1 h) was confirmed.[41] It

Scheme 4



The darker arrows in the Scheme show the pathways to major products of photolysis, and the lighter arrows show the pathways to minor products.

should also be noted that none of the PCB congeners is transformed to biphenyl,[40] as was determined by highly sensitive GC–MS method.

A small amount of biphenyl (< 0.1%) was detected after photolysis of PCB 169 in aqueous Pr^iOH solution.[42] Conclusions about the reactivities of particular PCB congeners used in Ref. 42 are in excellent agreement with the conclusions drawn in other studies.[38–41] To be correct, it should be noted that the fastest hydrodechlornation under conditions of a photochemical reaction concerns not only the *ortho*-substituted PCB, but also the congeners containing three neighbouring chlorine atoms in the same aromatic fragment. It is believed [42] that natural reductive dechlorination of technical PCB under the action of sunlight favours the formation of coplanar PCB with enhanced toxicity, which can lead to even greater environmental pollution.

To increase the quantum yields of photocatalytic reactions, not only organic compounds containing OH groups, but also inorganic compounds capable of generating highly reactive intermediates from substrates immobilized on the surface of solid catalysts through adhesion are widely used. An example of such a catalyst is provided by TiO_2, which was used for detoxication of waste water by sonication.[1] The activity of the TiO_2 surface to a great extent depends on the catalyst preparation procedure, in particular, on the type of etching solution. Successful photochemical hydrodechlorination of PCB 138 using TiO_2 was reported.[43] TiO_2 is pretreated with a mineral acid (HF), using a xenon lamp (150–900 nm) as source of electromagnetic radiation. Analysis of reaction products revealed that reductive dechlorination of PCB 138 under irradiaton with the xenon lamp proceeds 1.3–1.6 times faster because this lamp is more powerful than the mercury lamp. The reaction results in a mixture of less chlorinated penta-, tetra-, tri- and dichlorobiphenyls including 2,2′,4,4′5-pentachlorobiphenyl (PCB 99); PCB 87; 2,3′,4,4′-tetrachlorobiphenyl (PCB 66); PCB 49; 2,4,4′-trichlorobiphenyl (PCB 28); PCB 17 and dichlorobiphenyls PCB 9 and PCB 7. A specific feature of PCB 138 is preferred dechlorination at the *meta*-position under the photochemical reaction conditions.[43]

The reactivity of PCB 138 under different photochemical reaction conditions is somewhat different. For instance, the reaction mass in aqueous acetone solution in the presence of Et_2NH as electron donor was irradiated by a xenon lamp (210–310 nm) over a period of 0.5 to 8 h.[44] It was established that the degree of hydrodechlorination of PCB 138 depends on the exposure time and that the photochemical reaction results in a mixture of less chlorinated PCB, namely, 2′,3,4,4′,5-pentachlorobiphenyl (PCB 123) and 2,2′,3′,4,5-pentachlorobiphenyl (PCB 97) were detected after 0.5 h; 2,3′,4′,5-tetrachlorobiphenyl (PCB 70) and 2,3′,4,5-tetrachlorobiphenyl (PCB 67) were detected after 1 h; 2′,3,4-trichlorobiphenyl (PCB 33), PCB 29 and PCB 17 were detected after 2 h and dichlorobiphenyls PCB 12 and PCB 9 were detected after 3 h. The hydrodechlorination of PCB 138 under these conditions begins with homolysis of the C–*p*-Cl bond.[44] Similar conclusions were drawn for technical PCB present in transformer oil.

Almost all published data mentioned above are in essence similar (the action of electromagnetic radiation on different PCB leads to less chlorinated congeners as reaction products), being different in details (compositions of products of photochemical and radiation-chemical hydrodechlorination depend on the type of the source of electromagnetic radiation, its power, wavelength, gradient of applied electromagnetic field, exposure time, reaction medium, *etc.*).

The effect of the solvent type on the conversion of technical PCB present in a liquid dielectric was studied.[45] Photolysis at 254 nm in acetone led to a PCB conversion of 34%, but no biphenyl was detected among the products of reductive dechlorination. The same reaction in a NaOH solution in Pr^iOH is characterized by a conversion of 92% after 60 min and the formation of a mixture of biphenyl, quaterphenyl and condensation products of biphenyl with Pr^iOH.

It was shown [46] that the conversion of PCB present in transformer oil in Pr^iOH and Et_3N under the action of γ- or UV radiation is 90% after 120 h. When KOH was used instead of Et_3N, the yield of dechlorination products increased. Compared to NaOH and NH_4OH, KOH favours the hydrodechlorination of technical PCB mixtures (Aroclor 1254 and Aroclor 1016) under the action of γ-radiation in Pr^iOH; convincing proofs of this effect are available.[47]

Detoxication of PCB present in contaminated water under the action of γ- or UV radiation in the presence of Et_3N and alcohols is characterized by a 83% and 60% conversion of the technical PCB, respectively; thus, γ-radiation is more efficient.[48] The action of γ-radiation on PCB 54 (low-reactive symmetrical congener present in transformer oil) led to a 99% conversion.[49]

A trend in recent studies on the reductive dechlorination of PCB under the action of electromagnetic radiation is the search for and design of new types of reactors for more efficient dechlorination of natural matrices.[50–52] Examples are provided by reactors made of plastics [50] and porous solids.[51, 52]

For instance, a novel type of a photochemical reactor which utilizes a plastic torus instead of a conventional quartz tube was reported.[50] Five UV lamps are arranged along the outer perimeter of the torus and one source of UV radiation is located within the torus. Taking detoxication of Aroclor 1254 as an example, it was shown that its hydrodechlorination in Pr^iOH and alkali begins prior to adding water necessary for the process to occur.

Granulated activated carbon is used as solid porous material added to soil contaminated with technical PCB to activate the detoxication.[51, 52] There are two reasons for using this kind of carbon. First, porous carbon is heated when absorbs microwave radiation and thus its activity as reducing agent enhances. Second, adsorption of PCB from alkaline aqueous alcohol solution into preheated carbon pores affects the acceleration of hydrodechlorination of these pollutants. When the process is completed, granulated activated carbon is purified and reduced for re-use. First data on the use of porous carbon as microreactor for reductive dechlorination of PCB indicate the possibility of removal of chlorine atoms from PCB 29. The reaction results in a mixture of trichloro- and dichloro-substituted PCB.

The use of microwave radiation for neutralization of soil is explained by facilitation of desorption of technical PCB from porous surfaces of natural matrices, which improves the efficiency of subsequent processing operations.[53, 54] In the case of detoxication of transformer oils, microwave radiation is necessary for fast removal of PCB reaction products using their volatility (evaporation).

6. Reactions under subcritical conditions

The notion 'subcritical conditions' implies that the system is in the temperature range between the boiling point and the critical point at a pressure that is no lower than the equilibrium vapour pressure. Creation of subcritical conditions for carrying out chemical reactions is energy-consuming and requires complex and expensive equipment. Therefore, the prime cost of technologies used for operation under subcritical conditions can be reduced by cheapening the reagents.

The use of subcritical water for reductive dechlorination of chloroaromatic compounds is promising from both cost/efficiency and environmental safety viewpoints. In addition, utilization of subcritical water for detoxication of PCB and PCB-containing materials is a rather 'young' method.

Reductive dechlorination of PCB in subcritical water is based on removal of chlorine atoms from chloroaromatic compounds by a metal (usually, Fe) in aqueous solutions [55]

$$Fe^0 + 2H_2O \rightleftharpoons Fe^{2+} + H_2 + 2OH^-,$$

$$H_2 + RX \longrightarrow RH + H^+ + X^-$$

X = Hal.

The efficiency of this technique is low due to a short time of contact between hydrogen produced *in situ* with PCB and rapid corrosion of the iron surface followed by the formation of a surface oxide layer, which makes the uncorroded metal inaccessible to the reaction with water.

Using deaerated subcritical water, one can carry out reductive dechlorination of PCB including technical PCB with high conversion of the starting substrates [55]

$$Fe^0 + 2H_2O \longrightarrow Fe^{2+} + H_2 + 2OH^-,$$

$$3Fe(OH)_2 \longrightarrow Fe_3O_4 + H_2 + 2H_2O,$$

$$H_2 + RX + H_2O \longrightarrow RH + H_3O^+ + H^-$$

X = Hal.

Hydrodechlorination of PCB 3 by activated iron in subcritical water (supercritical conditions were created using a 260D Syringe Pump, the temperature was 250 °C, no pressure was specified) was reported.[56] The authors proved that the efficiency of dechlorination of PCB 3 depends on the nature of activator and on the particle size of the reducing agent. Pretreatment of iron with hydrochloric acid enables the preparation of a highly active reagent with a particle size of about 10^{-6} m. The surface area of iron increases by a factor of 170 compared to that of the starting reagent, with some contribution from the metal nanoparticles. Other mineral acids do not exhibit this effect. Using iron thus activated, the conversion of PCB 3 can be as high as 86% (GC–MS data). No other reaction products were reported in Ref. 56.

High-chlorinated PCB congeners undergo a complete transformation to low-chlorinated aromatic compounds in the presence of subcritical water and iron. For instance, 2,2′,3,3′,4,4′,5,6,6′-nonachlorobiphenyl (PCB 207) is transformed to a mixture of PCB containing mono- to heptachlorobiphenyls with the major proportion of tetrachlorinated congeners after 90-min treatment (250 °C, 100 atm).[55] Similar results were obtained taking Aroclor 1260 (250 °C, 10 MPa, 8 h) as an example.[57, 58]

Iron is not the best reagent for hydrodechlorination of PCB in subcritical water; Pb, Cu, Al and Zn are much more active.[59] Reductive dechlorination of Aroclor 1254 can be carried out in the presence of copper (350 °C, pressure not specified, 1 h, conversion 99%) or aluminium (250 °C, pressure not specified, 18 h, conversion 95%). In all cases, the resulting mixtures contained a number of low-chlorinated PCB congeners, while the metal reactivity decreased as follows:

$$Pb \approx Cu > Al > Zn > Fe.$$

Other reaction routes were considered in the studies [60, 61] carried out using H_2O_2/MeOH mixtures or oxygen-containing and oxygen-free co-solvents instead of metals. Of course, reactions under subcritical conditions may result in both hydrodehalogenation products (due to the hydrogen atoms of water and solvent molecules) and oxidation products. For instance, the conversion of PCB 77 in subcritical water containing MeOH and H_2O_2 (500 °C, 25.3 MPa, 20.7 s) is 99.5% and the reaction products include 3,3′,4-trichlorobiphenyl (PCB 35), 3,4,4′-trichlorobiphenyl (PCB 37), PCB 11, PCB 12, PCB 13, PCB 15, PCB 2, PCB 3, biphenyl, CO and CO_2.[60] The degree of conversion of PCB 77 is comparable with that of tetrachlorobiphenyls present in Aroclor 1248.

The degree of conversion of monochlorinated congeners (PCB 1, PCB 2 and PCB 3) under subcritical conditions (500 °C, 25 MPa) in the presence of an oxygen-free co-solvent is only 30%.[61] In the presence of MeOH, it increases to 97% and the reaction results in a mixture of biphenyl, acetophenone and benzaldehyde (both are products of aromatic ring opening followed by oxidation), CO, CO_2, HCl. It is believed [61] that the reactivity of monochlorinated congeners enhances in the order

$$PCB\ 1 < PCB\ 2 < PCB\ 3.$$

The possibility of PCB transformations under the action of K_2CO_3 in subcritical water (500 °C, 3 h) was demonstrated taking PCB 52 and PCB 153 as examples.[62] Under the reaction conditions, both congeners undergo high-temperature destruction with the formation of methane (major product), propylbenzene, toluene, ethylbenzene, acetone and hydrocarbons $\geqslant C_3$. The concentrated fractions of mixtures thus obtained (except for gaseous products) contained less than 4% of unconverted PCB. For comparison, we will also consider soil cleaning from PCB impurities using $NaHCO_3$ and water (335 °C, 1 h, the reaction was carried out in an autoclave).[63] In this case, the major reaction products include low-chlorinated PCB; the degree of conversion of the starting contaminants is 99.79%. In both cases, chlorine liberated in all forms is bound to form inorganic chlorides.

Technical PCB mixtures (Aroclor 1242, Aroclor 1248) can be efficiently (but not quantitatively!) dechlorinated using supercritical CO_2, which carries chloroaromatic substrates through a column filled with a zero-valent metal or an alloy of two neutral metals.[64] The degree of conversion of PCB depends on the type of the metal, the temperature and the pressure. The activities of metals in the course of reductive dechlorination of PCB in supercritical CO_2 decrease as follows:

$$Fe > Ni > Zn > Cu,$$

while the highest conversion of chloroaromatic substrates is attained at 400 °C and a pressure of $\ll 300$ atm. The efficiency of this type of hydrodechlorination also depends on the nature of solvents, *viz.*, the results obtained using a diglyme/water mixture are poorer than those obtained with

a diglyme/acetone mixture. According to GC–MS data, an Ag/Fe bimetallic pair is suitable for dechlorination of Aroclor 1242 (degree of conversion is higher than 99.5%) and the reaction products include PCB 1, PCB 7 and/or PCB 10, methylbiphenyls, dimethylbiphenyls, toluene and phthalic acid esters.

A similar procedure for reductive dechlorination of PCB 209 in subcritical CO_2 under relatively mild conditions (H_2, 70 °C, 0.5 h, 0.69 MPa) uses $Pd(5\%)/Al_2O_3$ as catalyst.[65] The starting product undergoes dearomatization and the reaction results in dicyclohexyl in a quantitative yield (96.9%).

Reductive dechlorination and oxidation of PCB under subcritical conditions is a labour- and energy-consuming technology. However, the results presented above demonstrate the potential of further research in this field. Of particular promise is that detoxication of PCB-containing materials under subcritical conditions allows products of their transformaton to be separated from the contaminated matrix without loss.

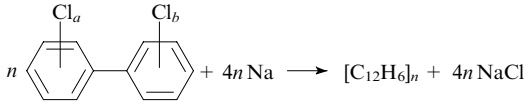
III. Substitutive dechlorination

1. Dechlorination under the action of alkali and alkaline-earth metals and their oxides

In the preceding Section we considered methods of chemical transformations of PCB resulting in the formation of new C–H bonds instead of C–Cl bonds in the aromatic structure of substrate. The target product was unsubstituted biphenyl. In this Section we will dwell on the methods for generation of new non-C–H bonds to give products of deeper reduction of PCB.

Among industrial methods for detoxication of PCB, it is interesting to carry out the main reaction on the surface of a dispersed alkali metal (Na).[66,67] Dechlorination is accompanied by some concurrent processes, *e.g.*, polymerization proceeding in the reaction mass. In the absence of solvents with labile C–H bond (hydrogen donors) dechlorination of PCB under the action of sodium also obeys the pattern of a Würtz reaction. In the presence of such solvents, aryl radicals produced are involved in the chain of new transformations.[1]

The available results obtained by this technique are concerned with detoxication of PCB-containing oils and particular congeners. For instance, a study of dechlorination of capacitor oils with PCB content from 10% to 30% showed that an increase in the PCB concentration requires that the temperature of their reaction with sodium be raised from 60 to 120 °C.[66] In this case, the role of solvent is played by the capacitor oil itself. The reaction proceeds in inert atmosphere and results in a chlorine-free polymer.



$a + b = 4$.

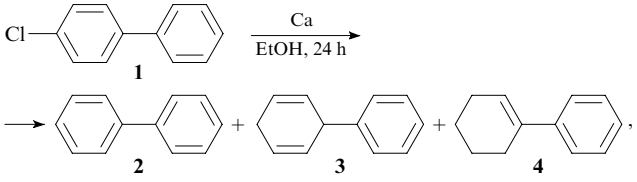
Having studied the reaction routes of particular congeners, possible pathways of obtaining polymeric products were revised.[67] A study of the reactions of nine congeners with dispersed sodium in hexadecane in nitrogen atmosphere revealed the formation in all cases of binary mixtures containing $C_{40}H_{54}$ and $C_{56}H_{86}$. It is believed that these empirical formulas may belong to products obtained by coupling of one or two hexadecane-based radicals with two radicals produced from phenylcyclohexylhexadiene. In any case, the degree of conversion of reagents was 100% and no chlorinated products (except for NaCl) were detected. It was also shown that dechlorination of congeners at 60 °C proceeds much slower than at 160 °C. It is also noteworthy that dechlorination of each PCB congener occurs in specific fashion. The larger the number of chlorine substituents in the phenyl fragment of a PCB molecule the more prone this fragment to dechlorination under given conditions. The chlorine atom having neighbouring chlorine atoms on both sides is most reactive owing to the overall electronic effect of the neighbouring chlorine atoms. For instance, in the case of 2,3′,4,4′,5-pentachlorobiphenyl (PCB 118), PCB 153, PCB 209, *etc.* the order of dechlorination is as follows: *para* > *ortho* > *meta*-position.

The conclusion about preferred involvement of the *para*-chlorine atoms in the reaction was also drawn in a study[68] of the reaction of PCB 153 with a K–Na alloy in benzene or cyclohexane in inert atmosphere. The highest reactivity of *para*-chlorine atoms was explained by the steric factor, *viz.*, these atoms are more accessible to dechlorination by the K–Na alloy. The reaction results in a mixture of biphenyl, cyclohexylbenzene and dicyclohexyl whose content depends on the initial temperature of the dechlorination of PCB 153. The concentration, in the mixture, of residual PCB formed as a result of stepwise dechlorination is of the order of 10^{-4}%.

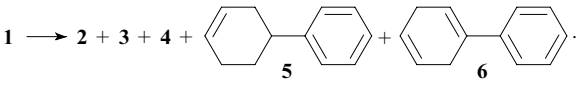
As in the case of alkali metals, the result of PCB dechlorination under the action of alkaline-earth metal (Ca) mainly depends on the reaction temperature and on the type of solvent. In particular, purification of capacitor oil from PCB (40 % by mass) by a threefold excess of calcium in tetraglyme (inert atmosphere, 600 °C) leads to complete destruction of PCB (conversion 99.95%).[69] The major products of dechlorination are $CaCl_2$ and atomic carbon.

PCB dechlorination under the action of calcium under mild (normal) conditions in EtOH makes it possible not only to efficiently remove chlorine atoms, but also to obtain a number of chemical compounds.[70,71] In this case, the solvent (EtOH) plays a dual role of the source of hydrogen and a reactant for removal of $CaCO_3$ coating formed under the action of carbon dioxide present in atmospheric air from the surface of calcium;[70] dechlorination of PCB continues after removal of the coating, as indicated by GC–MS data: the degree of conversion of PCB present in oils and individual PCB congeners varies from 99.45% (Ref. 70) to 99.96%.[71]

Based on the results of identification of products of the reaction with calcium, the following scheme of transformations of PCB 3 was proposed:[71]



This scheme was revised:[70]



The variety of chemical compounds formed in the dechlorination of PCB can be explained by a large number

of channels of formation of aryl radical ions, which tend to be stabilized through fast dissociation of C–Cl bonds.[70] Owing to relatively strong electron-withdrawig effect of chlorine atoms, PCB containing a large number of Cl atoms are the first to undergo dechlorination.

Successful dechlorination of technical PCB is attained using mixtures of active metals with inert components. To this end, columns or filters filled with ash containing Al (5.96%), C (8.24%), Ca (3.5–5.3%), Fe (9.7–9.8%), Mg (0.38%), Si (33.96%), Zn (0.2%), Cr (0.2–0.22%), Ni (0.36%), Cu (0.29%), Pb (8.6%) and water (2.41%) were used.[72] Passage through this column of a mixture of extracted PCB (Delor 103) or solvent-free PCB at 260 or 340 °C leads to efficient dechlorination of conventional mixtures (conversion of 87.6% and 99.9%, respectively) with the formation of biphenyl as the major product. Other reaction products include mixtures of mono-, di-, trichlorobiphenyls and biphenylene formed in the Ullmann reaction from *o*-dichloro-substituted biphenyls.

By and large, progress in methods of PCB dechlorination under the action of alkali and alkaline-earth metals is not concerned with impact on reaction procedures and results obtained. Dechlorination under the action of sodium, potassium or calcium remains an expensive and hazardous technology. When purifying oils contaminated with PCB, one should not only dechlorinate chloroaromatic products, but also completely isolate reaction products while the oils should be inert towards the alkali and alkaline-earth metals. Otherwise, further operation of materials cleaned from PCB becomes impossible owing to reduction of their quality.[1]

Summing up, note that alkali and alkaline-earth metal oxides are also active reagents for dechlorination of PCB. They are relatively cheap compared to pure metals, which makes it possible to use such oxides for detoxication of technical PCB. Among them, the most available are CaO and MgO.[73, 74]

A promising method of detoxication of technical PCB ('Sovtol-10') was patented.[73] The initial step involves the reaction of the technical PCB with a threefold excess of CaO or with water-soluble calcium (or magnesium) salts of sulfonic acids. Exothermic reactions result in hydrophobic powder-like products, *viz*., calcium (or magnesium) diphenyl hypochlorite or diphenyl sulfochlorite. For stronger binding, the compounds formed are treated with bitumen from [150–200 g per kilogramme of calcium (or magnesium) diphenyl hypochlorite (diphenyl sulfochloride)]. Products thus blocked are ready for disposal. Inspection after 8 months showed no re-transformation of PCB from the final compounds.[73]

About 10% conversion of technical PCB is observed upon their interaction with CaO, SiO_2, TiO_2, Fe_2O_3 or mixtures of these oxides under anaerobic conditions at 800–1000 °C in the presence of graphite or coal.[74] This results in complete mineralization of PCB and the major components of the final mixtures are H_2, CH_4 and $CaCl_2$.

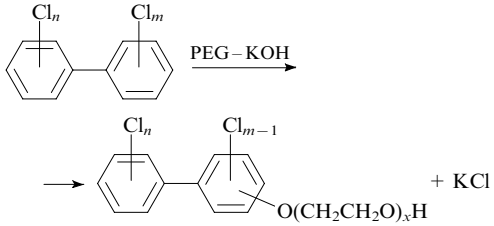
2. Nucleophilic substitution for aromatically bound chlorine atom

a. Reactions of polychlorobiphenyls with alkoxides

Nucleophilic substitution reactions are useful for only partial dechlorination of substrate molecules. Reactions of PCB with alkali metal alkoxides proceed by the mechanism of nucleophilic substitution of alkoxy groups for aromatically bound chlorine atoms and belong to non-destructive methods preserving the biphenyl structure. The advantages of this technique include simplicity of replacement of chlorine atoms by alkoxy substituents and versatility (method is widely used for neutralization of soils, slurries, waste water and for cleaning of PCB-containing equipment). The drawbacks are fast wear of equipment (corrosive reaction media) and the need for neutralization of alkali waste. Nevertheless, the return of researchers to problems of PCB detoxication with alkali metal alkoxides shows that the method is promising for reduction of toxicity of conventional PCB by reducing the number of chlorine atoms in the PCB molecules and pretreatment of technical PCB for possible biodegradation.

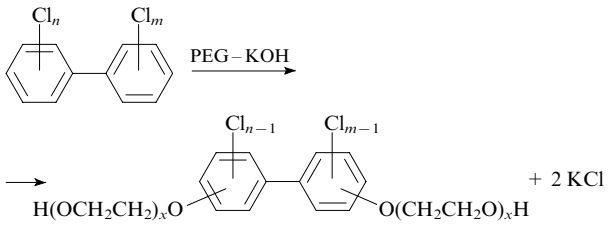
A convenient method[75] of cleaning the surface of transformers from PCB residues was developed in more recent studies.[76–85] Essentially, the technique involves treatment of the residues of technical PCB present inside a transformer by a mixture of KOH and higher poly(ethylene glycols) (PEG) at 100 °C for 2 h. This results in the formation of substituted products containing PEG groups instead of some Cl atoms. Subsequent removal of solid wax-like compounds from transformer walls presents no difficulties. Taking into account the fact that final mixtures are well-soluble in water, trace amounts of such mixtures can be removed with water. The reactivities of technical PCB were left out of consideration.[75]

In a more recent study[76] on removal of traces of technical PCB from dielectric oils under the action of KOH and PEG-400 at 110 °C, it was established that the congeners containing 5–7 chlorine atoms in their molecules are much more reactive than tri- and tetrachlorinated PCB congeners. The effect of the KOH : PEG and PEG : dielectric oil ratios on the conversion of PCB was also reported.[76] Optimum conditions for replacement of chlorine atoms in PCB by alkoxy groups are as follows: KOH : PEG ratio is 2.0, PEG : dielectric oil ratio is 0.2 anf the reaction time is 5 h. This allows one to attain a 99.8% conversion of PCB.

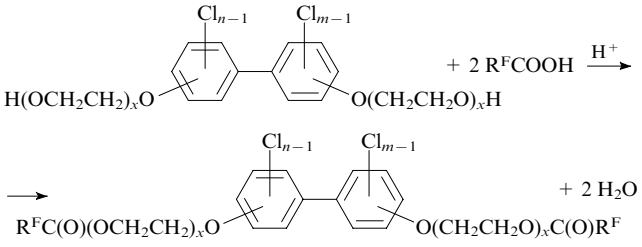


One should take into account that this scheme ignores the reactivities of particular PCB congeners in substitution reactions and that analytical procedures are carried out after completion of the reaction of PCB with KOH and PEG-400 using extracted mixtures of unreacted congeners. Based on the analysis of chromatograms, it was concluded[76] that one chlorine atom was replaced by a PEG group. The kinetics of this process was also investigated.[77]

Replacement of two chlorine atoms in the 'Sovol' technical PCB mixture by PEG groups was substantiated by elemental analysis data.[78–80]

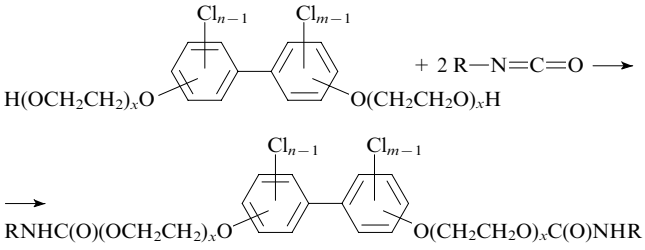


When using PEG as reactant and solvent, one assumes a deeper dechlorination of PCB due to the catalytic action of PEG, which facilitates replacement of halogens atoms by alkoxy groups.[86] Methods used for preparation of products of chemical transformations of the 'Sovol' technical PCB mixture under the action of various PEG and alkalis (120–140 °C, 3–5 h) and fields of application of these products as intermediates for production of lubricating oils, antiadhesive and anti-friction compositions were patented.[81,82] The patented [82] compounds are shown below.



$R^F = CF_3(CF_2CF_2O)_4CF_2$.

To attain a complete detoxication of technological waste, products of modification of technical PCB are exposed to subsequent chemical transformations. A patented [83] method of chemical processing of a capacitor dielectric ('Trichlorobiphenyl') and transformer liquid ('Sovol' or 'Sovtol-10') involves treatment of the technical PCB with a mixture of hydroxyl-containing compounds (PEG, glycerol, saccharose, triethanolamine, polyesters, polyols) and RN=C=O at 25–50 °C. As the reaction mass is cooled to room temperature, it is poured into moulds to set solid and a solid organic hydrophobic product, biphenylaminoisocyanate chloride, is formed. Additional information on the structure of the compounds prepared is unavailable. However, one can assume that initially PCB react with polyhydroxy derivatives and then free OH groups are involved in the reaction with isocyanates.



R = Alk.

The advantage of this technique consists in solidification of liquid technological waste. A complete dechlorination of PCB was additionally substantiated by studying the possibility of re-transformation of the PCB from biphenylaminoisocyanate chloride after a long time (8 months). It was established that the amount of PCB detected after completion of the reaction remains unchanged after 8 months and agrees with specification requirements (at most 50 mg per kilogramme of dry product). The conversion of the starting PCB is 99.999%.

Studies on the chemical transformations of PCB under the action of PEG and alkalis showed that the technique can be modified. To accelerate the dechlorination, a non-alkali metal (*e.g.*, Al) is added to the reaction mixture.[84,85] This method is used for processing of objects contaminated with technical PCB.

In a detoxication study of a transformer oil containing Aroclor 1242, Aroclor 1254 and Aroclor 1260 by a mixture of Al, KOH and PEG-600 (100 °C, 2 h) it was established that the degree of dechlorination reaches 78% with complete conversion of the congeners containing 7–9 chlorine atoms in their molecules.[84] As the temperature and reaction time increases (to 150 °C, 4 h), the degree of dechlorination is as high as 99.99%. Small amounts of dichlorobiphenyls are not involved in the nucleophilic substitution reaction.

Similar results were obtained in the cleaning of transformer oil from PCB impurities (Aroclor 1242 and Aroclor 1254 mixtures) using PEG with a molecular mass of $\geqslant$6000 (100 °C, 2 h).[85] After completion of the reaction, analysis of the extracts containing unreacted PCB revealed trace amounts of di-, tri- and tetrachlorobiphenyls.

Incomplete conversion of PCB in the nucleophilic substitution of alkoxy groups for aromatically bound chlorine atoms is due to different reactivities of congeners. Reactivity studies require identification of all components present in the starting mixture of technical PCB and the final composition of the alkoxylation products.

A reactivity study of PCB congeners was carried out using a State reference sample (GSO 7821–2000) designed based on a 'Sovol' mixture of technical PCB.[87,88] It was established that 'Sovol' contains more than 30 components, *viz.*, tetrachlorobiphenyls (overall content about 20%), pentachlorobiphenyls (overall content more than 50%), hexachlorobiphenyls (overall content about 20%), 1,2,4-trichlorobenzenes (overall content about 10%); the lowest proportion (trace amounts) of trichloro- and heptachlorobiphenyls. PCB congeners containing in the 'Sovol' technical mixture are listed in Table 1.

To determine the reactivity of the PCB congeners in the alkoxylation reactions, the reactions of 'Sovol' with MeONa under anhydrous conditions [89] and with a mixture of KOH and EtOH were studied.[90,91] Both reactions were carried out in DMSO. It is important that these studies [89,90]

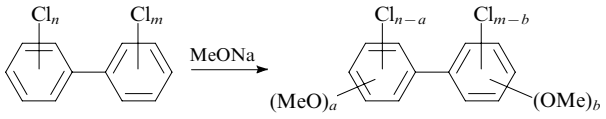
Table 1. Main congeners of the 'Sovol' technical mixture of polychlorinated biphenyls.[87,88]

PCB number [a]	Positions of chlorine atoms	PCB number [a]	Positions of chlorine 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

Note. PCB congeners containing in the 'Sovol' mixture are listed in order of their elution from an HP-5 column of low polarity.
[a] In accordance with IUPAC nomenclature.

allowed GC–MS analysis of the entire final mixture of products compared to PEG derivatives.[76–80]

Processing of chromatographic data obtained for the mixtures isolated after the reaction



$n + m = 3–6$; $a + b = 1–3$,

showed that the reactivity of the PCB congeners in the 'Sovol' mixture enhances as the chlorine content in them increases.[89]

Hexachlorobiphenyls (PCB 149, PCB 153, PCB 138, PCB 128) react with MeONa at a relatively low temperature (60°C) to give monomethoxy derivatives (empirical formula $C_{12}H_4Cl_5OMe$) as major products. As the temperature increases, the conversion becomes deeper and, starting with a temperature of 150 °C, no $C_{12}H_4Cl_5OMe$ is detected, the reactions resulting in di- and trimethoxy derivatives [$C_{12}H_4Cl_4(OMe)_2$ and $C_{12}H_4Cl_3(OMe)_3$, respectively], the former being the major product. In addition, no starting hexachlorobiphenyls are detected.

Enhancement of the reactivity with the temperature is also observed in the reactions of pentachlorobiphenyls (see Table 1), which mainly result in the monomethoxy ($C_{12}H_5Cl_4OMe$) and dimethoxy [$C_{12}H_5Cl_3(OMe)_2$] derivatives and small amounts of trimethoxydichlorobiphenyls [$C_{12}H_5Cl_2(OMe)_3$]. PCB 85, PCB 99, PCB 105 and PCB 118 whose molecules contain chlorine atoms in both *para*-positions are more reactive.

Tetrachlorobiphenyls are relatively low-reactive in this reaction, which affords $C_{12}H_6Cl_3OMe$ as the major product; small amounts of $C_{12}H_6Cl_2(OMe)_2$ were also detected. PCB 47, PCB 60, PCB 66 and PCB 74 containing two *para*-chlorine atoms are highly reactive, while PCB 41, PCB 49, PCB 64 and PCB 70 containing one *para*-chlorine atom are less reactive. Tetrachlorobiphenyls PCB 52 and PCB 44 containing no *para*-chlorine atoms did not react. Trichlorobiphenyls PCB 28 and PCB 33 containing one *para*-chlorine atom undergo only partial dechlorination to monomethoxy derivatives ($C_{12}H_7Cl_2OMe$).

Thus, the reaction of the 'Sovol' mixture with MeONa in DMSO under anhydrous conditions (170 °C, 25–120 min, PCB : MeONa = 1 : 4) is characterized by only partial conversion of conventional technogenic pollutants (PCB). This conclusion also holds for other aprotic solvents (DMF, sulfolane and *N*-methyl-2-pyrrolidone). Similar results were reported by other authors[90,91] who showed that the reaction of the 'Sovol' mixture with KOH in aqueous EtOH proceeds in two stages involving the formation of ethoxy derivatives of PCB followed by their transformation to hydroxy derivatives. According to GC–MS data, trichlorobiphenyls undergo transformation only to ethoxydichlorobiphenyls, while tetrachlorobiphenyls form ethoxytrichloro-, diethoxydichloro- and hydroxytrichlorobiphenyls under the reaction conditions. Pentachlorobiphenyls react to give monoethoxy, diethoxy, triethoxy, monohydroxy, hydroxyethoxy and hydroxydiethoxy derivatives. Hexachlorobiphenyls are mainly transformed to the hydroxyethoxy, diethoxy and hydroxydiethoxy derivatives. As in Ref. 89, it was established[90,91] that some tri- and tetrachloro-substituted congeners remain unchanged under the reaction conditions.

Chain elongation and branching of alkoxy groups also affect the reactivity of PCB congeners, thus reducing their functionalization.[92,93] For instance, the degree of conversion of the 'Sovol' mixture in the reaction with a mixture of PrOH with KOH in the presence of water is lower than in the case of EtOH but higher than for Pr^{i}OH. On going from Bu^{n}OH to Bu^{s}OH and Bu^{t}OH the degree of conversion of PCB congeners in the 'Sovol' mixture also decreases and no PCB transformation products were detected in the case of the reaction with Bu^{t}OH.

The regularities established in studies of replacement of aromatically bound chlorine atoms in PCB congeners by alkoxy groups by the nucleophilic substitution mechanism exactly confirm the conclusions drawn in the other Sections of this review, *viz*., the most reactive are those compounds whose molecules contain the largest number of chlorine atoms, while the lowest reactivities (in all cases) are exhibited by the congeners bearing the smallest number of electron-withdrawing substituents.

b. Hydrolysis

The results obtained in a study[94] of hydrolysis of the 'Sovol' mixture are similar to those mentioned above. PCB congeners contained in this mixture were hydrolyzed by a solution of KOH in DMSO and water. Analysis of reaction products revealed that a number of tetrachlorobiphenyls (PCB 52, PCB 47, PCB 44) do not undergo hydrolysis while PCB 49 and PCB 70 undergo partial hydrolysis. No signals of the starting penta- and hexachlorobiphenyls were detected in the chromatograms. The reaction results in monohydroxypolychlorobiphenyls as major products. Generally, the reactivities of PCB congeners containing in the 'Sovol' mixture are reduced on going from hexa- to tetrachlorobiphenyls.

The hydroxy derivatives of PCB thus obtained can be transformed to glycidyl ethers and titanates, which can be used to obtain practically valuable materials, *e.g*., components of epoxy compositions:[95–97]

$C_{12}H_{4.09}Cl_{4.74}(OH)_{0.46}(OCH_2CH_2OH)_{0.07}(OCH_2—CH_2)_{0.64}$,
O

$C_{12}H_{4.69}Cl_{3.61}(OH)_{0.75}(OCH_2CH_2OCH_2CH_2OH)_{0.64}(OCH_2—CH_2)_{0.31}$,
O

$Ti[(O)_{0.8}C_{12}H_{5.4}Cl_{3.62}(OCH_2CH_2O)_{0.18}]_{3.24}(OBu^n)_{0.76}$,

$Ti[(O)_{1.06}C_{12}H_{4.69}Cl_{3.61}(OCH_2CH_2OCH_2CH_2OH)_{0.64}]_{2.86}(Bu^n)_{1.14}$ –
$-4.4\,(HO)_{1.06}C_{12}H_{4.69}Cl_{3.61}(OCH_2CH_2OCH_2CH_2OH)_{0.64}$.

Glycidyl derivatives and titanates are used as active diluting agents and curing agents of epoxy compositions, respectively.

Thermomechanical studies of cured epoxy compositions were carried out and data on their thermo-oxidative destruction were obtained, as well as the specific impact viscosity and the adhesion strength of steel were determined. Based on the results obtained, it was concluded that the glycidyl and titanium-containing PCB derivatives can be used for the synthesis of epoxy polymers, namely, insoluble, cross-linked glassy polymers possessing rubbery properties in the temperature range 40–250 °C. Such polymers also exhibit a rather high thermal stability and good mechanical properties. No toxicological studies of the polymeric products obtained were carried out.

c. Replacement of chlorine atoms by fluorine atoms

Theoretically, the best method of PCB detoxication by the nucleophilic substitution mechanism consists in complete replacement of chlorine atoms by fluorine atoms. The toxicity of the final products is thus potentially minimized while their dielectric properties can compete with those of PCB. However, studies on transformation of technical PCB to organofluorine derivatives under conditions of nucleophilic substitution of fluorine atoms for chlorine atoms have almost ceased due to low conversion of the starting substrates. A method of fluorination of trichlorobiphenyl ('Sovol' plasticizer) and 'Sovol' under the action of rubidium, caesium, potassium and sodium fluorides was patented.[98] The process can be conducted in both open systems using aprotic bipolar solvents (diglyme, DMF, DMSO, tetramethyl sulfone) and in autoclaves in the temperature range from 100 to 400 °C. The maximum conversion (75%) was attained using 'Sovol' and KF (no solvent, 10 atm, 380–400 °C); the final mixture contained a wide range of chlorofluoro derivatives of PCB.

d. Carbonylation

Chemical reactions involving PCB and various nucleophilic compounds listed in this Section confirm the fact that non-activated aryl chlorides are low reactive in nucleophilic substitution reactions. Carbonylation of PCB can also be treated as partial rather than complete dechlorination.

Recently, catalytic systems based on modified cobalt carbonyl were designed to carry out transformations of PCB under relatively mild conditions (~60 °C, 0.1 MPa).[99] The true catalysts of the carbonylation reaction are alkylcobalt carbonyl complexes formed *in situ* from the cobalt tetracarbonyl anion and an activator.

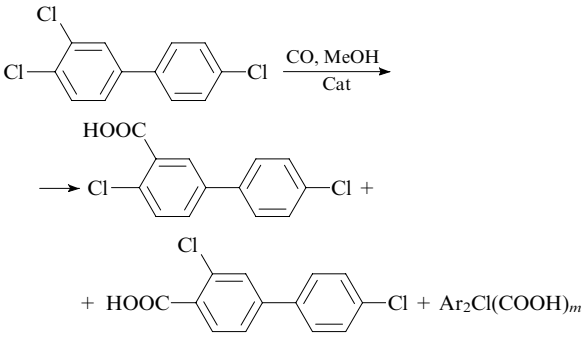
$$RX + Co(CO)_4^- \longrightarrow RCo(CO)_4 + X^-$$

R = Alk, X = Hal.

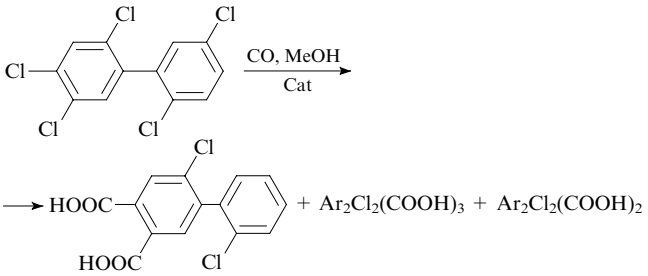
$$ArHal + CO + RCo(CO)_4 \longrightarrow ArCOOH + Hal^-$$

Hal = Cl, Br.

Activators include alkyl halides, benzyl halides, halohydrins and epoxides. The highest activity in the carbonylation of aryl halides was found for the catalytic systems based on cobalt carbonyl modified by epoxy derivatives. Carbonylation of individual PCB congeners using propylene oxide as modifier can be carried out in CO and MeOH (60 °C, 1 atm).[100]



m = 1, 2.



Cat = $Co(CO)_4$ + MeCH—CH_2 + K_2CO_3.

A method of detoxication of technical PCB ('Sovol' and 'Sovtol') using a catalytic system based on cobalt carbonyl and activator was described in a patent.[101] Carbonylation of PCB is carried out in CO atmosphere (55–70 °C, 1–3 atm) in lower aliphatic alcohols, mainly MeOH, using alkali or alkaline-earth metal carbonates, hydroxides and alkoxides. The catalytic system contains cobalt carbonyl or an alkali (or alkaline-earth) metal salt of cobalt carbonyl [*e.g.*, $NaCo(CO)_4$ or $KCo(CO)_4$] and an activator (co-catalyst), *viz.*, epoxy derivatives. The necessary amount of catalyst is 0.2 mol.%–5.0 mol.% per mole of PCB while that of cocatalyst is 10–80 mol per mole of cobalt carbonyl. It was established that under the carbonylation conditions the technical PCB mixture is transformed to nontoxic low-chlorinated carboxyl compounds (acids or esters) at a maximum conversion of the starting PCB of about 99% (in some cases). Unfortunately, no proofs of non-toxic character of the new chemical compounds was reported.[101]

IV. Oxidation methods

1. Oxidation by Fenton's reagent

Oxidation of organic products proceeds most efficiently using reagents with high oxidation potentials, *e.g.*, a Fenton's reagent representing a mixture of $FeSO_4$ with H_2O_2 and capable of generating $HO^{\bullet}$ radicals. Since hydroxyl radicals are highly reactive, they oxidize even very stable organic compounds including chloroaromatic products with ease at room temperature.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{\cdot} + HO^-,$$

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet},$$

$$HO_2^{\bullet} + Fe^{3+} \longrightarrow Fe^{2+} + O_2 + H^+,$$

$$H^+ + HO^- \longrightarrow H_2O,$$

$$HO^{\bullet} + RH \longrightarrow H_2O + R^{\bullet},$$

RH is organic substrate,

$$R^{\bullet} + O_2 \longrightarrow ROO^{\cdot} \longrightarrow \text{oxidation products.}$$

Despite the fact that Fenton's reagent is well known, it is of limited use for oxidative degradation of PCB for many reasons and was not reported in the review [1].

It is believed that the oxidation of PCB by Fenton's reagent cannot be used for complete dechlorination of chloroaromatic structures;[102, 103] the best systems for treatment with the mixture of $FeSO_4$ and H_2O_2 are PCB-contaminated materials (mainly soil). Partial dechlorination of PCB under the action of Fenton's reagent can be treated as preprocessing of chloroaromatic structures for subsequent biodegradation, because reduction of the chlorine content leads to higher solubilization of low-chlorinated

PCB in water, which favours enhancement of the activity of microorganisms present in the environment towards newly formed congeners.

The efficiency of Fenton's reagent mainly depends on the correct choice of the $FeSO_4/H_2O_2$ ratio and on the pH value of the reaction medium.[102] An oxidation study of technical PCB taking Delor 103 (equivalent of Aroclor 1248) as an example showed that a Fenton's reagent prepared from 1 mmol of $FeSO_4$ and 1 mol of H_2O_2, at pH 3.0 has the most pronounced effect on the chloroaromatic substrate. Oxidation products were determined after five days shaking of Delor 103 with Fenton's reagent at 28 °C; the total concentration of 41 congeners (components of Delor 103) decreased; all congeners underwent only partial transformation; and the oxidation rate was higher for the less chlorinated PCB. Similar conclusions were drawn in a study on the oxidation of the Aroclor 1242 mixture present in soil.[104]

It is believed [102] that the oxidation by Fenton's reagent depends on the PCB structure, whereas subsequent biodegradation of less-chlorinated products depends only on the number of halogen atoms in the chloroaromatic structures.

It was reported [105] that the action of Fenton's reagent on PCB in the presence of MeOH (90 °C) causes two successive reactions, *viz*., dechlorination followed by oxidation of the dechlorinated product to CO_2. The reaction of PCB with Fenton's reagent is accelerated on UV-irradiation and results in complete mineralization of PCB 3 and PCB 15 to HCl, CO_2 and H_2O.[106]

Thus, one can assume that initially low-chlorinated PCB congeners undergo a complete dechlorination under the action of Fenton's reagent to give HCl and hydrocarbons, which are then oxidized to CO_2 and H_2O. High-chlorinated congeners undergo only the first stage of chain oxidation reaction resulting in less chlorinated congeners.

2. Other oxidation methods

This Section is devoted to a number of oxidation methods that are at present of limited use in organic synthesis.

TiO_2 treated with a mineral acid is efficient for hydrodechlorination of PCB 138.[43] The reaction proceeds in an aqueous medium under irradiation at 338 nm (xenon lamp).

Reactions of PCB congeners with nanosized TiO_2 in water provide examples of oxidative degradation of PCB.[107] Irradiation of a mixture of tri- and tetrachlorobiphenyls in water without catalysts over a period of 4 h leads to only 10% conversion of the starting PCB.[107] Using TiO_2 nanoparticles, other reaction parameters being equal, a PCB conversion of about 90% can be attained after 3 h. The major reaction products include hydroxy derivatives of PCB, namely, 2,3,3′,4′-tetrachlorobiphenyl (PCB 56) forms 4-hydroxy-2′,3,3′-trichlorobiphenyl and 2-hydroxy-3,3′,4′-trichlorobiphenyl while PCB 70 forms 4-hydroxy-2′,3,5′-trichlorobiphenyl and 2-hydroxy-3′,4′,5′-trichlorobiphenyl.

Noteworthy is a study [108] which involves sonication of PCB 1, PCB 3 and PCB 29 in water resulting in a mixture of products including ethylbenzene, diethylbenzene, dibutylbiphenyl, phenol, propylphenol and di-*tert*-butylphenol (GC–MS data). This method requires further investigations and optimization of reaction conditions because the conversion of PCB congeners is low, *viz*., 77% for PCB 1, 79% for PCB 3 and 70% for PCB 29.

V. Electrochemical methods

Electrochemical processes of PCB dechlorination are of very limited use in the detoxication of PCB and PCB-containing materials. Main trends in recent development of electrochemical methods for processing of chloroaromatic products include the search for electrode materials, electrochemical media and mediators for enhancement of the yield with respect to current.

The electrochemical reaction conditions allow one to carry out both the oxidation and reductive dechlorination of PCB.

The amount of information on electrochemical oxidation of chloroaromatic compounds accumulated to date is small.[109] The major oxidation products are phenols. Deeper electrochemical oxidation (at high anodic potential) of chloroaromatic compounds results in CO_2 and Cl_2, *e.g*.,

$$C_{12}Cl_{10} + 24\,H_2O \longrightarrow 5\,Cl_2 + 12\,CO_2 + 48\,H^+ + 48\,e^-.$$

However, the process is characterized by a low yield with respect to current and large energy expenditure.

Electrochemical oxidation of chlorine-containing aromatic compounds including PCB requires high positive potentials. Therefore, the anode material should exhibit a rather high electrochemical corrosion resistance. The search for such materials is topical. The design of novel types of electrodes is mainly aimed at modifying the surface of conventional electrodes by coating thin layers of metals including Ti, Zr, Ta and Nb.

To date, the mechanism of electrochemical oxidation of PCB is still poorly studied.

Practically, it is more promising to use electrochemical reduction of PCB, which involves transfer of two electrons per chlorine atom to an organic substrate and subsequent liberation of Cl^- ions. The cathode, which is usually made of Pb, should have a high potential. Electrochemical reduction can proceed in aprotic media (DMF, DMSO, MeCN, *etc*.). The role of the reducing agent in nonaqueous media is played by hydrogen liberated from the solvent under the action of aromatic radical ($Ar^{\bullet}$); transfer of this radical to the chloroaromatic compound competes with electron transfer.

It was also reported [109] that high-chlorinated PCB are more prone to reduction under conditions of electrochemical reaction resulting in low-chlorinated aromatic and nonaromatic compounds. Reactions of monochlorobiphenyls (PCB 1, PCB 2 and PCB 3) afford mixtures of phenylcyclohexane, phenylcyclohexene and phenylcyclohexa-1,4-diene.

Recently, mediators (Med) have been used to facilitate the electrochemical reduction of PCB at the cathode;[109, 110] these are derivatives of polycyclic aromatic hydrocarbons (anthracene, phenanthrene, *etc*.). They are introduced into the electrochemical reaction to activate transfer of electrons to the chloroaromatic substrate.

$$Med + e \longrightarrow Med^{-\bullet},$$

$$Med^{-\bullet} + ArCl \longrightarrow Med + ArCl^{-\bullet},$$

$$ArCl^{-\bullet} \longrightarrow Ar^{\bullet} + Cl^-,$$

$$Med^{-\bullet} + Ar^{\bullet} \longrightarrow Med + Ar^-,$$

$$Ar^- + H^+ \longrightarrow 2ArH.$$

A great contribution to progress in electrochemical methods for detoxication of PCB is the choice of surfactants for enhancement of solubilization of lipophilic substrates in nonaqueous media and protection of electrode surface, which eventually improves transfer of electrons. Note also that carrying out electrochemical reactions involving PCB in aqueous media is always accompanied by a competing reaction, *viz*., electrolysis of water, which requires a large energy expenditure. In this connection, the yields with respect to current are low (40% – 50%). The use of surfactants hampers electrolysis of water and increases the yields of the target compounds with respect to current.

Successful dechlorination of PCB 29 was carried out [111, 112] using a porous palladium cathode modified with titanium (see Ref. 111) or nickel (see Ref. 112). Electrochemical reduction was conducted in aqueous MeOH solution in the presence of quaternary ammonium salts. The total conversion of PCB 29 after 9 h was 96.2% including the conversion to biphenyl of 89.6% (GC – MS data).[111]

The results of studies [113, 114] on electrochemical hydrodechlorination of PCB 1 deserve attention due to a specific procedure for preparation of a graphite electrode to the operation under electrochemical reaction conditions. The electrode is coated with palladium formed *in situ* and then aqueous MeOH solution, PCB 1 and quaternary ammonium salts are added. The conversion of PCB 1 after 4 h was 66.4%.[113]

Electrochemical reaction using steel electrodes in H_2SO_4 solution can be treated as modification of the PCB oxidation by Fenton's reagent.[115] In this case, the oxidizing agent is formed in the electrochemical reaction, no H_2O_2 addition is required and the steel electrodes act as the source of cations. Low pH values of the reaction medium are maintained by adding H_2SO_4 to the electrolyte.

Concurrent processes, oxidation and reduction, enable transformation of the Aroclor 1248 mixture of PCB to biphenyl (3.5%) and low-chlorinated PCB congeners with preferred dechlorination at *meta*- and *para*-positions.

Our attempts to find some other significant studies on the electrochemical oxidation and reduction of PCB reported in the last decade have failed. The lack of interest in this research avenue can be explained by the relatively low conversion and yield with respect to current, high corrosion of electrodes, the use of highly diluted PCB solutions, competing reactions, incomplete oxidation and reduction of PCB and, as a result, complex mixtures of products of electrochemical reactions.

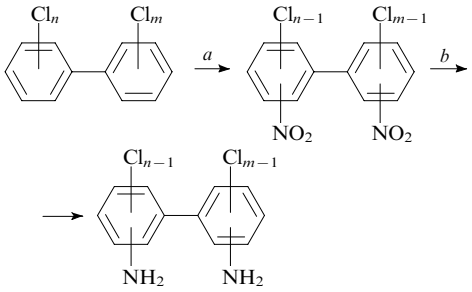
VI. Electrophilic aromatic substitution

Investigations of electrophilic substitution of PCB occupy a special position because chlorine is not removed from substrates and reduction of its content is due to an increase in the molecular mass of reaction products. Nevertheless, these processes can be treated as intermediate stages in the involvement of PCB derivatives in subsequent transformations. In this connection, studies on sulfuration [116, 117] and nitration [79, 118, 119] of technical PCB are noteworthy.

Sulfuration of technical PCB mixtures ('Sovtol-10' or 'Sovol') is performed with oleum or H_2SO_4 (conc.) at 100 – 210 °C for 18 h.[116] More recently, the sulfuration procedure was modified, namely, it is carried out with oleum only at 105 – 125 °C for 15 – 150 min in the presence of a catalyst (liquid glass).[117] The sulfo derivatives of PCB are treated with a salt-forming agent [$N(C_2H_4OH)_3$] to give pasty products, which are completely dissolved in water, being antiseptic, non-flammable, nonvolatile and low-toxic (IVth class of hazard) compounds. No PCB were detected in the target products at a PCB : oleum : catalyst : $N(C_2H_4OH)_3$ molar ratio of 1 : 2.0 : 0.01 : 4.0.[116]

A similar scheme was proposed [120] for cleaning a transformer from the 'Sovtol-10' technical PCB mixture (a dielectric liquid). The procedure involves preheating of equipment, removal of PCB, cleaning of the transformer from trace amounts of PCB by washing with toluene, collection of all PCB fractions and their successive treatment with oleum and $N(C_2H_4OH)_3$. In other words, a wasteless method of cleaning of transformers to meet the environmental safety requirements and a procedure for obtaining a product with antiseptic properties were proposed. Information on the structures of the reaction products thus obtained [116, 117, 120] is unavailable.

Nitration of the technical mixture 'Sovol' is better described in the scientific literature.[79, 118] Nitro groups are introduced into the aromatic nuclei of PCB using a nitrating mixture (HNO_3 + oleum). Qualitative monitoring of the course of nitration (Janowski reaction) showed that the reaction goes to completion after 22 – 24 h (100 °C); the yield of nitro derivatives was about 100%.



(*a*) HNO_3 + H_2SO_4 (20% SO_3), 100 °C, 22 – 24 h;
(*b*) $SnCl_2$ + HCl, 100 °C, 2 h.

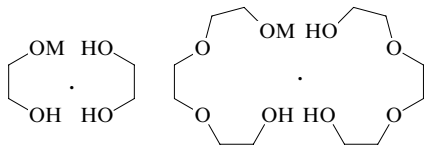
The reaction product is a solid yellow amorphous mass. According to elemental analysis data, there are on the average two nitro groups per PCB molecule, which in no case characterizes the individual reactivities of the congeners containing in the 'Sovol' mixture.

Studies of subsequent reduction of nitro groups by various reagents showed that the highest conversion of the nitro derivatives of PCB is attained using $SnCl_2$ + HCl, the yield of amino derivatives is 86% (see the last equation).[79, 118, 119] The use of iron and zinc in various media leads to much lower yields of the amino derivatives of PCB.

Methods for nitration of PCB derivatives and reduction of nitro groups are elaborated to obtain monomeric products capable of undergoing polycondensation. However, a single amino group surrounded by several chlorine atoms is a weak reaction centre for polycondensation. Our attempts to find in the literature any encouraging results on the involvement of amino derivatives of PCB in the synthesis of polymers have failed.

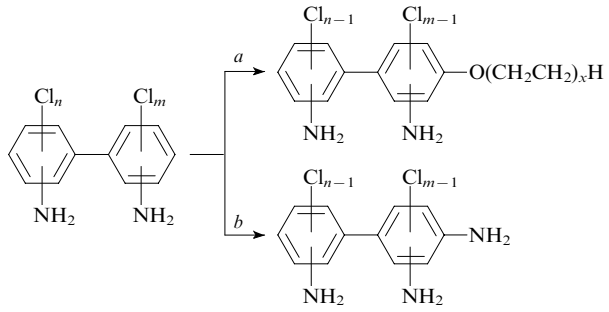
Nevertheless, nitro derivatives of PCB are interesting from theoretical viewpoint. Attempts to replace aromatically bound chlorine atoms in PCB by alkoxy fragments obtained from lower PEG (ethylene glycol and diethylene glycol) and alkali by the mechanism of nucleophilic substitution have failed. This can be explained by the formation of structurally stable monoethylene glycolates (in the case of ethylene glycol) and monodiethylene glycolates (in the

case of diethylene glycol) of alkali metals, with are tightly bound to the diol molecules and have too low reactivities for the nucleophilic attack to occur.[121]



M = Na, K.

At the same time, if aromatic compounds contain two second-kind substituents (*e.g.*, nitro groups) in *ortho*- and *para*-positions relative to halogen atoms, replacement of the halogen atom by alkoxy group (or other nucleophile) becomes much easier.[122]



(*a*) KF, $H(OCH_2CH_2)_xOH$ [x = 1 (yield 73%), 2 (yield 79%)]; (*b*) NH_4F (yield 81%).

Thus, in this Section we demonstrated that products of electrophilic aromatic substitution in technical PCB can be derivatized and then used for the synthesis of useful materials and highly reactive compounds. However, toxicological expertise of industrially used PCB derivatives is still required and the potential avenues of chemical transformations involving products of electrophilic aromatic substitution should be specified.

VII. Conclusion

Chemical methods of processing of PCB developed in the last decade, reaction products and potential fields of their application are shown in Fig. 1.

The most promising group of methods includes reductive dechlorination, which allows one to obtain biphenyl as well as aromatic and non-aromatic hydrocarbons. Biphenyls and hydrocarbons can find applications in chemical industry.

Renewal methods also include electrochemical reactions at cathode and dechlorination in the presence of alkali and alkaline-earth metals and their oxides. The reactions result in biphenyl in the former and in various hydrocarbons in the latter case. In addition, dechlorination allows one to obtain polymers and solid higher hydrocarbons which can be buried.

Oxidation methods and anodic electrochemical reactions have a destructive character. They result in low-molecular-mass mineral substances as major products. Complete destruction of PCB under conditions of the oxidation methods and electrochemical reactions requires strong oxidation systems and efficient electrodes for the first and second group of methods, respectively, and efficient traps for the destruction products.

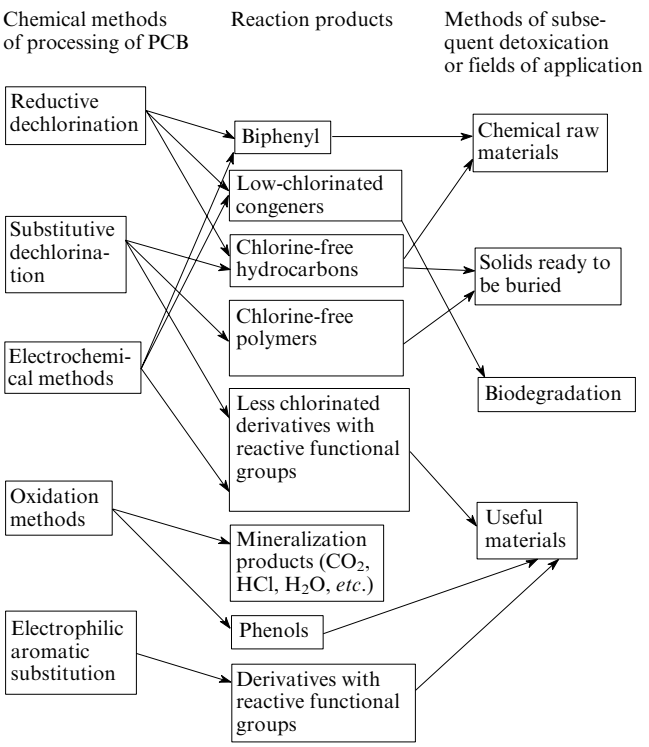


Figure 1. Methods of detoxication of polychlorobiphenyls, the final products and hypothetical fields of their application.

Methods based on electrophilic substitution in the aromatic nucleus do not belong to conventional methods for detoxication of PCB; however, products obtained using this mechanism can serve as intermediates for subsequent detoxication. This also to the full extent holds for products of nucleophilic substitution of alkoxy and other groups for aromatically bound chlorine atom in PCB structures.

Summing up, note that most products obtained in various types of reactions of PCB with chemicals still contain some amount of chlorine, which makes these methods inappropriate for wide use in production related to removal of toxic waste. At the same time, a large proportion of chlorine can be removed and the products thus obtained can be subsequently processed. Thus, there is a demand for either closed cyclic processes for multiple treatment of PCB and their derivatives until complete dechlorination or a combination of methods aimed at the same goal. In this respect, the authors of this review agree with the authors of the reviews cited above.[1, 123]

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