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Polychlorobiphenyls: problems of the pollution of the environment and technological neutralisation methods

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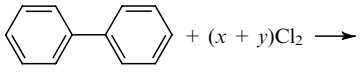
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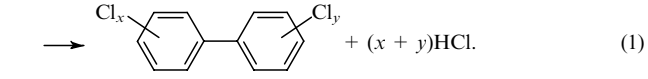
Abstract. The principal sources of the pollution of the environment by polychlorobiphenyls are indicated and their ecological danger is estimated; the output in the manufacture and applications of polychlorobiphenyls are quoted. The known methods for the neutralisation of polychlorobiphenyls are examined. The methods considered are analysed and their practical significance for industry is estimated. The bibliography includes 277 references.

I. Introduction

Polychlorobiphenyls (PCB) possess a series of unique physical and chemical properties: exceptional thermophysical and electrical insulating characteristics, thermal stability, inertness to acids and bases, fire resistance, satisfactory solubility in fats, oils, and organic solvents, high compatibillty with resins, plasticity, resistance to corrosion, and an excellent capacity for adhesion.[1–9] All these features are responsible for their wide-scale employment as dielectrics in transformers and capacitors,[1,3,7,10–18] as hydraulic liquids,[10,13,16–20] as heat exchangers and refrigerants,[1,3,6,9,10,12–14,16–18,20] as lubricating oils,[3,6,16,17,20] as components of varnishes, paints, and adhesive compositions,[6,10,14,15–17,20–24] as plasticisers and fillers in plastics and elastomers,[1,3,6,16,17,20,24] as antipyrenes,[1,9,15,20,25] and as solvents.[1,6,16,22]

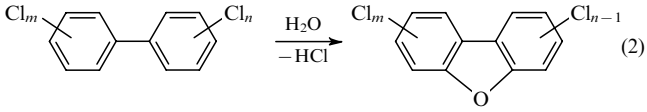
The industrial synthesis of PCB is based on the substitutional chlorination of biphenyl in the presence of electrophilic substitution catalysts:[7,26]





(1)

Polychlorodibenzofurans: (PCDF) are formed as side products:[7]



(2)

There are 209 individual PCB differing in the number and positions of chlorine atoms in the molecule. Depending on the content of chlorine atoms, PCB have different numbers of isomers (Table 1).

Table 1. The number of possible PCB isomers for different contents of chlorine atoms in the molecules.[27]

Name of PCB	Molecular formula of PCB	No. of isomers
Monochlorobiphenyl	$C_{12}H_9Cl$	3
Dichlorobiphenyl	$C_{12}H_8Cl_2$	12
Trichlorobiphenyl	$C_{12}H_7Cl_3$	24
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	42
Pentachlorobiphenyl	$C_{12}H_5Cl_5$	46
Hexachlorobiphenyl	$C_{12}H_4Cl_6$	42
Heptachlorobiphenyl	$C_{12}H_3Cl_7$	24
Octachlorobiphenyl	$C_{12}H_2Cl_8$	12
Nonachlorobiphenyl	$C_{12}HCl_9$	3
Decachlorobiphenyl	$C_{12}Cl_{10}$	1

Technical PCB mixtures produced by industry consist of 50 – 70 individual compounds. Most of them contain between 3 and 8 chlorine atoms, although there are small amounts of both more and less chlorinated PCB. These mixtures are known under different names: Arochlor (USA), Phenochlor (France), Chlophen (Federal Republic of Germany), Kanechlor (Japan), Fenchlor (Italy), and Sovol (Russia). The proportions of PCB in the Arochlors are presented in Table 2.

The world manufacture of PCB has increased successively from 1929 to 1970 when these compounds were recognised as

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Table 2. Approximate composition of various Arochlors (%).

PCB	[Cl] (mass %)	Brand of Arochlor			
		1242	1248	1254	1260
$C_{12}H_9Cl$	18.8	3	–	–	–
$C_{12}H_8Cl_2$	31.8	13	2	–	–
$C_{12}H_7Cl_3$	41.3	28	18	–	–
$C_{12}H_6Cl_4$	48.6	30	40	11	–
$C_{12}H_5Cl_5$	54.4	22	36	49	12
$C_{12}H_4Cl_6$	59.0	4	4	34	38
$C_{12}H_3Cl_7$	62.8	–	–	6	41
$C_{12}H_2Cl_8$	66.0	–	–	–	8
$C_{12}HCl_9$	68.8	–	–	–	1

pollutants of the environment.[16] Towards the end of the 1980s, the total amount of PCB produced was estimated as 1 million tonnes.[16,17] Analysis of the pattern of the consumption of PCB in various countries showed that about 40% of this amount, *i.e.* 400 000 tonnes enter the environment, while the remaining 600 000 tonnes, at the time when the estimate was made, was still being used or was stored in settling tanks.[17] According to later estimates, even after the prohibition of the manufacture of these products in the USA, Japan, and a number of European countries, the content of PCB in the environment hardly changed.

The nature and dynamics of the distribution of PCB in the environment is in many respects determined by their physical properties such as persistence, chemical inertness, fairly high vapour pressure, and capacity for diffusion.[1–9,26–33] The persistence of PCB makes it possible to include them among typical xenobiotics which are not very susceptible to the action of a wide variety of microorganisms and animal enzyme systems.[34] Persistence combined with lipophilicity promotes the bioaccumulation of PCB in the fatty tissues of man and animals in amounts dangerous for vital activity.[9,10,16,17,35–37] Chemical inertness is responsible for the resistance of PCB to the action of environmental abiotic factors, the relatively high vapour pressure facilitates their spreading in the atmosphere, while their capacity for diffusion favours their migration in the soil and in subterranean and surface waters.

Despite the gradual reduction of the applications of PCB in the economy, they continue to pollute the environment[4,10] and nowadays these toxic products, which have spread virtually throughout the entire terrestrial globe, are present in the organism of each of us.[10,16] As PCB are incorporated in the biological chains, the weakly chlorinated components are progressively lost by virtue of their selective biotransformation.[8,9,28,37,38] The most dangerous highly chlorinated PCB therefore accumulate in the human and animal organisms.

According to data of the World Health Organisation,[28] the principal ways in which PCB enter the environment are as follows: vaporisation from plasticisers; evolution on combustion of industrial and domestic waste and also when transformers, capacitors, and other industrial equipment in which PCB are used are switched on; leakage together with other industrial waste; the removal of PCB to rubbish dumps and aeration fields; other unmonitored pathways.

The environment is polluted mainly *via* the first three pathways. The typical PCB concentrations in various objects in the environment[27] are as follows: in the air of agricultural regions 0.05 ng m^{-3}, in the air of cities 1–5 ng m^{-3}; on the surface of soil 2–50 μg kg^{-1}; in plants 10 μg kg^{-1}; in water 2 ng $litre^{-1}$; in fatty tissues 1 ng kg^{-1}; in human breast milk 10 μg kg^{-1}; in the organisms of marine animals 5–50 ng kg^{-1}; in the fat of the otter 5–200 ng kg^{-1}.

The potential danger of PCB is associated with their use in open systems, with possible spillage, with leakage and vaporisation from capacitors, transformers, and other elements of equipment in the course of their cleaning, emptying, and filling, with the breakdown of hermetic seals in equipment, and with the occurrence of fires in plant where PCB are employed as dielectric liquids or heat exchangers.[7,8,16,17,36–42] An example of mass poisoning of people by PCB as a consequence of the breakdown of hermetic seals in heat-exchange apparatus in the course of the refining of rice oil is known. This incident, which has entered history as the 'Yusho incident', occurred in Japan in 1968. The symptoms of poisoning were an increase in the size and hypersecretion by mammary glands, nausea, vomiting, enlargement and porphyria of the liver, pathological changes in the peripheral nervous system and in the composition of blood, and disturbance of the functioning of adrenal glands.

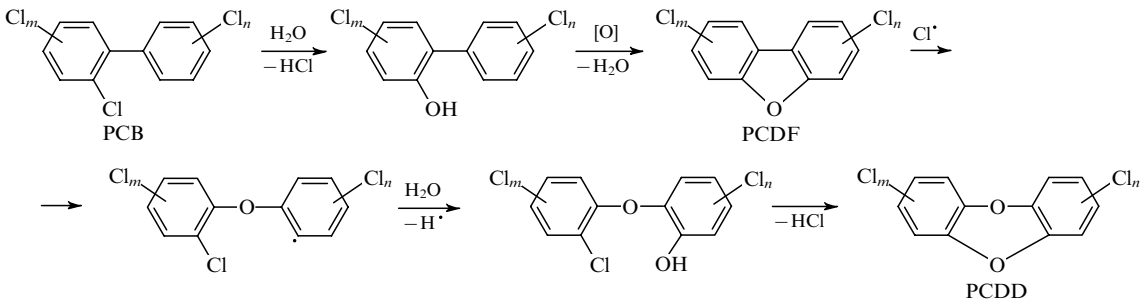
Thermal overloading or fires in plant (transformers, capacitors) in which PCB-containing materials were employed as dielectrics or refrigerants constitutes a major hazard to the environment, because uncontrolled combustion of PCB results in the formation of the highly toxic polychlorodibenzodioxins (PCDD) and polychlorodibenzofurans (PCDF).[7–9,39,40,42–45] According to certain ideas,[7,46,47] such transformations may occur in accordance with processes (3).

The combination of persistence, chemical stability, and lipophilicity of PCB creates the possibility of their bioaccumulation in lipid-rich liver, kidney, adrenal gland, lung, and brain tissues of man and animals.[1,4,8,15,28] The concentration of PCB in human blood and milk has been noted.[1,7,16,28]

Until recently, the toxicity of PCB remained controversial. Some investigators denied the existence of a connection between various diseases and the presence of PCB in human and animal organisms, others attributed a number of serious toxicological effects, causing chronic illnesses, to the action of PCB.[1,5,7,9,15,16,24,35,48,49]

More rigorous studies carried out recently made it possible to discover a whole spectrum of the toxic effects of PCB on man and laboratory animals, including lethal effects, harmful influence on reproduction and development, liver porphyria, weight loss, dermatological effects, suppression of the immune system, disturbance of the functioning of the kidneys, atrophy of the thymus, carcinogenesis, disorganisation of the homeostasis of the steroid hormones, and a mutagenic effect.[37,45,50]

The massive effect of PCB on ecosystems as a whole and on man in particular is intensified by constantly operating factors such as the increase in the content of PCB in water and aqueous ecosystems as a result of the entry of surfactants into the latter,[2] the biotransformation of PCB in the environment into still more



(3)

toxic products,[51] and the accumulation of PCB in human and animal organisms as a consequence of their accumulation in the food chains.[37] The increase in the level of PCB in living organisms and the destruction of animals induced by this, sometimes on a mass scale, noted in a number of regions of the planet (particularly in the aquatic systems of the Pacific Ocean), indicates the potential danger of the bioaccumulation of PCB to populations of living organisms and whole ecosystems.[7, 18, 37] It has to be borne in mind that, by virtue of their chemical and thermal stability and exceptional operating properties, the PCB-containing materials produced earlier by industry will continue in use for a long time yet (more than 20 years) in active closed systems.[52]

Thus the danger of the accumulation of PCB in living organisms and the threat of the destruction of populations and whole ecosystems, as well as the potential possibility of leakages or a series of discharges from settling tanks and active plant have raised the problem of the pollution of the environment by these compounds to the class of global environmental problems.

Bearing in mind the very serious level of environmental danger, Canada, the USA, Japan, the countries of the EEC, and other states have developed measures regulating the manufacture, use, processing, and destruction of PCB.[8, 18, 35, 53–63] These measures include the following: complete prohibition of the manufacture of PCB, gradual replacement of PCB by alternative materials with less toxic properties, the monitoring of materials containing PCB in the course of their employment, storage, transport, and distribution, the development of effective ecologically safe technologies for the processing and neutralisation of PCB-containing materials, the monitoring of the neutralisation and processing of waste, and the development of new rules for the operation of plant in which PCB is employed taking into account more stringent requirements for the ecological safety of industries.

The possibility of the gradual removal of PCB-containing materials from the sphere of man's economic activity and of a universal ban on their manufacture depends on the solution of the problem of the replacement of PCB by new materials with similar operating characteristics but with a significantly lower toxicity. The question of the search for substitutes of PCB-based dielectric materials is most acute.

New compositions and individual compounds have been obtained and tested in recent years. They have been recommended as substitutes for PCB in transformers and capacitors. For example, these are mineral and silicone oils,[9, 17, 64–66] high-molecular paraffins,[9, 65] alkylated biphenyls and terphenyls,[9, 17] esters of phosphoric, phthalic, and other carboxylic acids,[9, 17] and esters of polyhydric alcohols.[65] While less toxic, these substances approach PCB as regards their dielectric properties but are inferior to them in chemical inertness and resistance to combustion.

Less toxic polychlorotoluenes [67] and chloromethylbenzenes [68] have been proposed for the replacement of PCB in hydraulic systems.[68] The report of the promising application of absolutely nontoxic and chemically stable perfluorinated organic compounds as components of lubricating oils merits attention.[41]

However, overall the search for new materials to be used as substitutes for PCB for various purposes has been fragmentary.

In the system of measures designed to lower the degree of pollution of the environment, the conservation of PCB removed from the sphere of economic activity in settling tanks or storage sites occupies a definite place.[5, 35, 69–77] In practice, various storage methods are employed, but the safest is the method involving enclosure in glass.[71] However, there is no information about the ecological risk when this operation is performed. Thus enclosure in glass may entail the formation of toxic PCDD and PCDF and their subsequent diffusion together with PCB into the environment. The hardening method is widely used in the storage of PCB, but it cannot guarantee their complete isolation from the environment.[70, 76, 77] The main disadvantages of the method involving the storage of hardened PCB are as follows: as a consequence of the appreciable volatility and diffusibility as well as the leaching of PCB, one cannot rule out the possibility of their entry into soil, underground and surface waters, and the atmosphere; the need to search for storage sites remote from populated areas, definite requirements for geological structures at the storage sites, and the continually rising cost of this operation;[69, 72, 74] One should also take into account the negative attitude of the population to the possibility of storage of any waste on adjacent territories.

The storage of undecomposed PCB in settling tanks is a less reliable method of their conservation. The inevitability of the diffusion of PCB from the settling tanks is aggravated by the probability of accidents at the storage sites.

The most promising procedure for lowering the amount of PCB in the environment involves their conversion into environmentally safe products. One may identify the following methods for the processing of PCB: chemical and electrochemical dechlorination, thermal, photochemical, and radiation-chemical and biotechnological methods, oxidation, and hydrogenolysis. These methods may include operations involving the concentration of PCB before treatment. Such operations include extraction, adsorption, dialysis, vaporisation, distillation, and filtration.[5, 18, 25, 63, 50, 77–88] Operations of this kind acquire particular importance when the removal of residual PCB from transformers and capacitors is required. By virtue of the application of extraction by liquids at the critical temperature and pressure, the effectiveness of the extraction of PCB from plant to be cleaned has increased in recent years.[80, 85, 87]

II. Reagent-based neutralisation methods

Diverse reagents, reaction conditions, catalytic systems, and apparatus are used in the chemical methods for the neutralisation of PCB. The reagents are usually alkali metals (Na, K, Li),[9, 52, 80, 89–97] with the aid of which a version of the Wurtz reaction takes place:[98]

$$2ArCl + 2Na \longrightarrow Ar-Ar + 2NaCl. \quad (4)$$

In this method, use is made of the dechlorinating effect of the alkali metal (in particular, sodium). The organic dechlorination products are high-molecular polynuclear compounds.

According to the ideas developed by Oku *et al.*,[99] the mechanism of reaction (4) includes the following stages:

$$ArCl + Na \longrightarrow Ar^{\bullet} + NaCl, \quad (5)$$

$$2Ar^{\bullet} \longrightarrow Ar-Ar. \quad (6)$$

In the presence of compounds containing relatively mobile hydrogen (hexane, cyclohexane, other hydrocarbons), the aryl radicals are involved in a chain of new reactions:

$$Ar^{\bullet} + RH \longrightarrow R^{\bullet} + ArH, \quad (7)$$

$$R^{\bullet} + Ar^{\bullet} \longrightarrow Ar-R, \quad (8)$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R. \quad (9)$$

The main result is the substitution of the chlorine atoms in PCB by hydrogen *via* reaction (7). Thus hydrocarbons with fairly reactive C–H bonds regulate the average molecular mass of the dechlorination products, but are themselves decomposed in this process. The regulating function of hydrocarbons is important because it permits the retention of the possibility of further dechlorination of PCB at advanced stages of the reaction with respect to chlorine, whereupon contact between the sodium atoms and the chlorine atoms still present in the polynuclear chlorination products becomes sterically hindered.

In order to decompose PCB, the alkali metal is usually dispersed in the bulk of the material being treated or a hydrocarbon solvent is used as the reaction medium. A version of the process in a flow system using the alkali metal (Na or K) deposited on an inert material as the reagent has also been described.[89] This method is characterised by a high degree of decomposition of

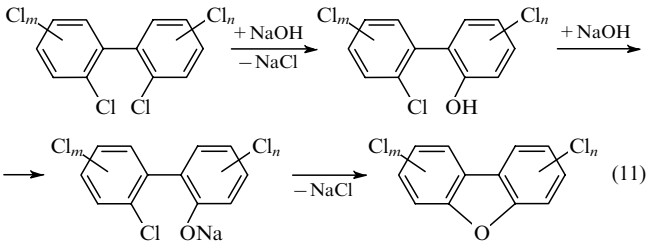
PCB, but its application is held back by a series of limitations and deficiencies — the high cost of the neutralisation process, increased danger of the process, and conversion of the treated compounds into high-molecular products which lower the quality of the materials being purified. Furthermore, alkali metals may interact with valuable components of the materials being purified, exerting a negative effect on their operating characteristics.[100]

There are data concerning the use of alkaline earth and other metals, such as Mg, Ca, Fe, Sb, Zn, and Pb [101, 102] in a molten salt and in the vapour phase [101, 103] for the dechlorination of PCB. As regards safety and dechlorination efficiency alkali metal naphthalides and anthracides have a definite advantage over alkali metals.[18, 77, 104–107] The higher efficiency of the dechlorination by the naphthalides and anthracides is due to the possibility of increasing the degree of dispersion of the reagent down to the molecular level. On the other hand, the metals in the compounds specified are chemically bound and this makes them more inert to oxygen and water, which increases the safety of the process in its turn. Compounds between alkali metals and carbon are a variety of reagents of this type.[108] The main disadvantages of the dechlorinating agents listed is the difficulty of isolating them from the reaction mass and the fact that high-molecular products, exerting a negative influence on the quality of the neutralised material, are formed with participation of the given reagents.

Strong bases — alkali and alkaline earth metals and oxides and hydroxides,[77, 80, 101, 102, 109–115] alkoxides, glycolates, and polyglycolates [18, 77, 80, 85, 95, 116–123] — constitute a large group of reagents. Alkali metal carbonates or hydrogen carbonates make up yet another group.[124, 125] Their dechlorinating activity is based on the nucleophilic substitution of the chlorine in PCB. Thus, when aqueous solutions of alkalies are used, the main reaction proceeds in accordance with the equation

$$\mathrm{ArCl + NaOH \longrightarrow ArOH + NaCl.} \qquad (10)$$

Aqueous solutions of alkalies are insufficiently effective and are quite expensive. Furthermore, the presence of chlorine in the 2- and 2′-positions in the PCB being neutralised creates structural preconditions for the formation of PCDF:



(11)

Alkali metal glycolates, polyglycolates, carbonates, and hydrogen carbonates are more effective dechlorinating agents, since the polarisability of their anions is greater:[110, 126]

$$\mathrm{ArCl + (CH_2CH_2O)_nHO^- \longrightarrow ArO(CH_2CH_2O)_nH + Cl^-,} \qquad (12)$$

$$\mathrm{ArCl + CO_3^{2-} \xrightarrow[-Cl^-]{} ArOCO_2^- \xrightarrow[-OH^-]{H_2O} ArOCO_2H \xrightarrow[-CO_2^-]{} ArOH.} \qquad (13)$$

In contrast to alkali metals, as well as compounds of alkali metals with naphthalene, anthracene, and carbon, these reagents do not require the use of special safety measures, the processes involving them can be readily controlled, and the products obtained after dechlorination can be readily separated from the purified material. In most cases, the methods for the employment of such reagents are universal in relation to the object being treated: they can be applied in the detoxification of soils, sludges, sewage, and simply PCB-containing materials. The disadvantages of these methods are as follows: the need to neutralise the excess alkaline agent with formation of salt waste, the possibility of the impairment of the operating quality of the materials being neutralised as a consequence of the formation of hydrolysis and alcoholysis products, the rapid wear of the equipment working in corrosive media at high temperatures.

In view of the existence of the last problem, the process involving the detoxification of PCB-containing materials by alkaline agents, initiated with ultrasound under milder conditions, merits attention.[115] The influence of alkaline reagents on the quality of the processed materials imposes certain limitations on their content of PCB: it should not exceed 1 mass %.[100]

The oxidation–reduction processes with participation of a wide variety of oxidants and reductants constitute a separate group of methods for the chemical detoxification of PCB-containing materials. The oxidants include hydrogen peroxide, sodium iodate,[125, 127] permanganates, persulfates and perborates,[49] and peracetic acid,[128] while the reductants comprise the hydrides of alkyl derivatives of alkaline metals,[95] alkali and alkaline earth metal hydroborates,[49, 129] and alcohols.[130, 131] When alcohols are used as the reducing agents, the attainment of the necessary rate of the process requires either more severe conditions (170–200 atm, 150–350 °C) or the radical reduction reaction must be carried out in the presence of alkali metal hydroxides and chemical initiators.

The methods indicated require the application of expensive reagents and can hardly be recommended for industrial application.

Methods for the processing of PCB involving their interaction with elemental sulfur in the vapour phase at high temperatures are of undoubted practical interest.[59, 130, 132] An environmentally safe polymeric product is obtained and can be used as an additive to asphalt, a binder for concrete, a vulcanising agent for raw rubber, and as a material for the preparation of resistors. The products SCl_2 and CS_2 formed together with the polymer can be readily separated from the latter together with the unreacted elemental sulfur, which is returned to the process. This method is suitable exclusively for the treatment of concentrated PCB, but the possibilities for its wide-scale application are restricted by the available elemental sulfur resources.

III. Electrochemical methods

The majority of the known methods for the electrochemical oxidation and reduction of PCB are used within the framework of laboratory research.[77, 133–141] Certain results are promising as regards energy expenditure [134] and apparent yields,[142] but overall the prospects for the application of these methods in industry are at the present time small owing to the insufficiently high degree of conversion of PCB [137, 141] and the high requirements which must be met by the purity of the initial PCB. However, the interest in the electrochemical methods has persisted for several reasons. Firstly, it is possible to organise the process under the conditions of cathodic reduction:

$$\mathrm{C_{12}Cl_nH_{10-n} + nH_2O + 2ne^- \longrightarrow C_{12}H_{10} + nCl^- + nOH^-,} \qquad (14)$$

which imparts to it resource-saving qualities. Secondly, electrochemical devices are suitable for the creation of mobile systems for the processing of waste at the site of their formation and accumulation. Thirdly, such devices have an advantage in the conversion of dielectric liquids, lubricating oils, and other spent PCB-containing materials into a valuable hydrocarbon fuel.

IV. Pyrolytic methods

Among the pyrolytic methods for the decomposition of PCB, the process in which a hollow tube heated from the outside by electrodes or other electrically heated elements merits attention.[16, 122, 142–144] Porous graphite may be used for the preparation of the tube. In order to avoid the breakdown of the material of the reactor, a stream of nitrogen or other inert gas is passed from the outside into the porous surface.

The PCB decomposition products are a solid carbon residue and gases, mainly HCl and Cl_2, as well as a certain amount of organochlorine compounds. The gases are trapped in series-connected absorbers irrigated with water and an alkaline solution and also in an adsorber with activated charcoal. In order to ensure the effective destruction of the PCB and a decrease in process temperature, it is recommended that a small amount of oxygen be added to the initial mixture.[122]

In order to attain the quantitative decomposition of PCB, in certain cases the pyrolytic processes are carried out on solid catalysts, activated charcoal, metallic Zn, Ni, Cu, Fe, Al, Pb, Pt, Rh, and Cr or the oxides, carbonates, and silicates of these metals.[145–147]

One of the difficulties in the application of pyrolytic methods is the difficulty of achieving an effective supply of heat to ensure the specified temperature. This problem can be solved successfully if the process is carried out in salt melts.[87, 148] Nevertheless pyrolysis in melts has hardly come to be widely used, since equipment wears rapidly in a salt medium and the high temperatures needed to apply these methods render industries of this kind dangerous.

The plasma pyrolysis occurring at temperatures from 5000 to 25 000 °C involves the complete decomposition of PCB; H_2, CO, CO_2, HCl, CH_4, H_2O, and elemental carbon being formed as the products.[87, 149–151] The presence of oxygen-containing compounds in the products is associated with the use of alcohols as solvents for the preparation of the initial mixtures.[151]

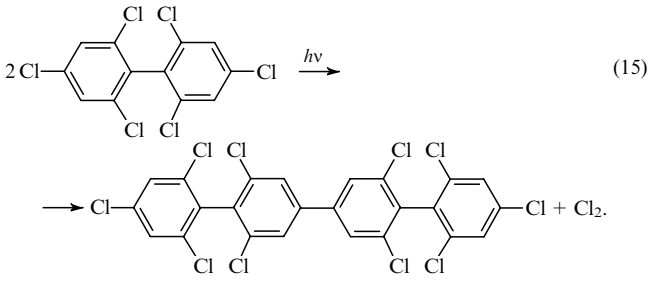
A novel method for the pyrolysis of PCB has been put forward in France.[152] The process is carried out at 1500 °C in the presence of water vapour. The main reaction products are chlorine and C_1–C_2 hydrocarbons. The chlorine is absorbed by a solution of alkali while the hydrocarbons are used as a fuel.

In the communications quoted above, devoted to pyrolytic decomposition methods, the degree of decomposition of PCB is quoted as the sole criterion of the effectiveness of the processes and this parameter is in all cases close to 100%. The lack of any kind of data on the composition of the products with different degrees of conversion hinders even a preliminary interpretation of the process mechanisms. Certain conclusions about the initial period of the pyrolytic decomposition of PCB can be made on the basis of the results of a detailed study of the pyrolysis of chlorobenzenes in the region of relatively low temperatures.[153, 154] The principal pyrolysis products under these conditions are chlorobiphenyl and dichlorobiphenyl and the reactions responsible for their formation are reversible. Adopting the principle of microreversibility as a guide,[155] the proposed mechanism of the pyrolysis of chlorobenzenes can be extended also to the pyrolysis of polychlorobiphenyls.

An important advantage of the pyrolytic methods compared with the widely used combustion is the absence of the highly toxic PCDF and PCDD from the products. However, the large energy consumption in these processes increases their cost and impairs their ecological parameters. Furthermore, the pyrolytic process is relatively unselective and is therefore unsuitable for the dechlorination of materials with a low PCB content. To a certain extent, these disadvantages are overcome by employing catalytic pyrolysis, but the formation of pyrolytic carbon leads to rapid deactivation of the catalyst.

V. Radiation and photochemical dechlorination methods

The radiation and photochemical dechlorination methods are being rigorously investigated.[2, 77, 156–181] Their successful application does not require additional chemical reagents.[77, 156–165] The processes can be described by the following stoichiometric equation in relation to the dechlorination of 2,2′,4,4′,6,6′-hexachlorobiphenyl:[182]



(15)

Thermokinetic analysis[155, 183] made it possible to put forward the following mechanism of the photochemical dechlorination:

$$ArCl \xrightarrow{h\nu} Ar^{\bullet} + Cl^{\bullet}, \quad (16)$$

$$Ar^{\bullet} + ArCl \longrightarrow [Ar...Ar...Cl]^{\#} \longrightarrow Ar{-}Ar + Cl^{\bullet}, \quad (17)$$

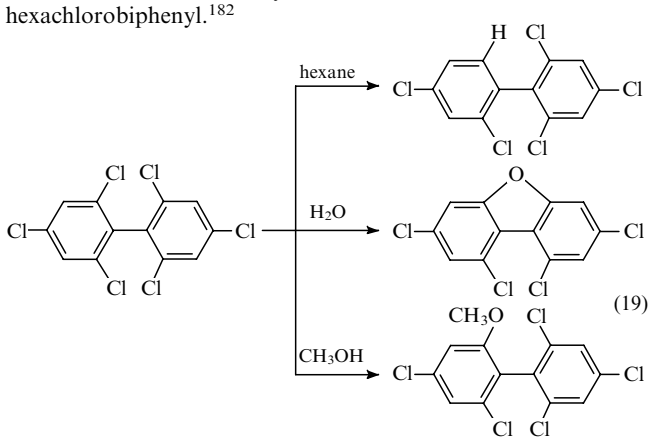
$$Ar^{\bullet} + Ar^{\bullet} \longrightarrow Ar{-}Ar. \quad (18)$$

Evidently in the dechlorination initiated by γ-quanta the reactions involving the homolysis of the C–Cl bond are accompanied by competing reactions in which the C–H and C–C bonds are homolysed.

An advantage of the radiation and photochemical methods compared with the reagent-based dechlorination methods is simpler composition of the products and the absence of salt waste. However, the very low quantum or radiation-chemical yields of these processes lead to large energy expenditures and hence an impairment of the economic parameters of the industrial processes. In this connection, the search for photocatalytic systems and methods whereby the reagent concentration fields can be altered in the initiation stage in order to achieve the selective absorption of energy quanta and their effective utilisation for the generation of the necessary intermediates are of definite interest.[156, 157, 159, 160, 163–167, 173, 184] On the other hand, the possibility of economising on the energy by increasing the quantum and radiation-chemical yield is limited because the rate constants for reaction (17) are low at the low temperatures characteristic of these processes[153] and conditions for the occurrence of chain processes are not therefore realised.

Radiation and photochemical dechlorination may find a practical application for the neutralisation of industrial and domestic sewage, provided that more effective and selective methods are developed for the application of energy to PCB-containing materials. In this sense, the report on the detoxification of waste waters in the presence of titanium dioxide on treatment with ultrasound under normal conditions merits attention.[185]

The nature of the products of the photochemical and radiation-chemical dechlorination changes in the presence of compounds containing comparatively mobile hydrogen (cyclohexane, other hydrocarbons, alcohols, water, sodium tetrahydroborate, *etc.*)[169, 172, 173, 175, 176, 179–184, 186] Some of the reactions occurring are indicated schematically below in relation to 2,2′,4,4′,6,6′-hexachlorobiphenyl.[182]



(19)

As can be seen, in the presence of hydrocarbons chlorine is replaced by hydrogen, which in fact gives rise to the neutralisation effect. On the other hand, when water and alcohols are used, there is a risk of the formation of the highly toxic PCDF. Evidently this risk exists also under the conditions of the photochemical and radiation-chemical dechlorination of PCB in an oxidising medium.[46, 166] From the standpoint of the protection of nature, it is therefore useful to employ only hydrocarbons as the reagents. Nevertheless, despite the high reactivity of hydrocarbons in radical reactions, the quantum and radiation-chemical yields remain low and this prevents the introduction of such processes into industry.

When caustic alkali is added to the PCB–alcohol reaction system, the radiation or photochemical dechlorination of PCB by the alcohol proceeds *via* a radical-chain mechanism:[170, 177–181, 186, 187]

$$(CH_3)_2CHOH + C_{12}H_nCl_{10-n} + OH^- \longrightarrow (CH_3)_2C{=}O + H_2O + C_{12}H_{n+1}Cl_{9-n} + Cl^- \quad (20)$$

Here the quantum yield increases by two–three orders of magnitude.[179] This effect can be accounted for by the operation of the following mechanism (in relation to the radiation-chemical dechlorination of PCB by the 2-propanol–NaOH system):

$$(CH_3)_2CHOH \longrightarrow R^{\bullet}, e^-_{solv}, \text{ other products}, \quad (21)$$

$$R^{\bullet} + (CH_3)_2CHOH \longrightarrow (CH_3)_2C^{\bullet}OH + RH, \quad (22)$$

$$ArCl + e^-_{solv} \longrightarrow Ar^{\bullet} + Cl^-, \quad (23)$$

$$Ar^{\bullet} + (CH_3)_2CHOH \longrightarrow ArH + (CH_3)_2C^{\bullet}OH, \quad (24)$$

$$(CH_3)_2C^{\bullet}OH + OH^- \rightleftharpoons (CH_3)_2CO^- + H_2O, \quad (25)$$

$$ArCl + (CH_3)_2CO^- \longrightarrow (CH_3)_2C{=}O + Ar^{\bullet} + Cl^-. \quad (26)$$

It is seen from the scheme presented that the function of alkali is associated with the production of the anion $(CH_3)_2CO^-$, which effectively dechlorinates the PCB molecule and regenerates the initial $Ar^{\bullet}$ radical by means of electron transfer *via* reaction (26). A significant economy in energy is achieved in this dechlorination method,[188, 189] but the additional consumption of expensive reagents limits its application.

One should bear in mind that the use of visible and ultraviolet light to initiate the reactions is relatively ineffective owing to the lack of transparency of the majority of the reaction media to waves in this range, while the technique of radiation-chemical initiation is too expensive and the effect obtained does not compensate for the expenditure. When chemical reagents are used as initiators, the caustic alkali–alcohol system may be recommended for the detoxification of sewage and materials with a low PCB content.

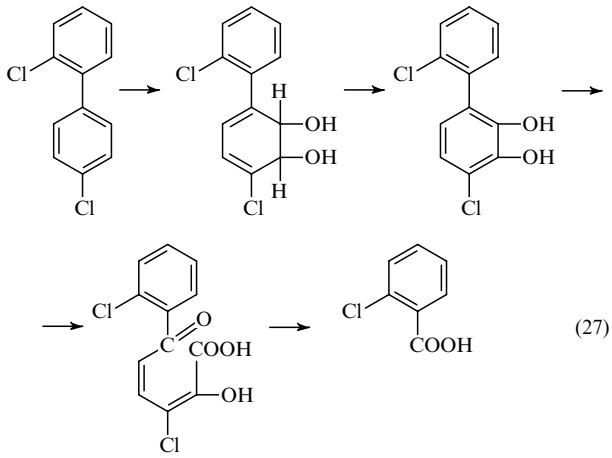
In conclusion of the consideration of dechlorination processes initiated by photochemical reactions, we may mention the method for the decomposition of PCB in the plasma of a radiofrequency glow discharge developed in Japan.[190] The nature of the products formed under these conditions is determined by the nature of the dechlorinating agent. In an oxygen plasma, PCB decomposes to CO_2, CO, $C1O_2$, Cl_2, and HCl, while in the presence of water vapour CO_2 and HCl are formed. The use of a hydrogen plasma leads to the formation of C_2–C_7 hydrocarbons (alkanes, alkenes) and HCl. The application of these processes ensures the quantitative binding of PCB without risk of the formation of PCDD and PCDF. Dechlorination in a plasma is most attractive because the hydrocarbons obtained may be used as a fuel. The prospects for this method are associated exclusively with the processing of concentrated PCB. There are so far no data on its industrial tests, which is apparently due to the low productivity of the process and the large energy expenditures.

VI. Biotechnological methods

During the last two decades, investigators have shown a steady interest in the problem of the search for effective PCB biodecomposition methods. This can be accounted for, firstly, by the high resistance of PCB and, secondly, by the fact that biological purification is the concluding stage in many detoxification processes, including the purification of sewage. The object neutralised usually consists of complex mixtures of toxicants and the decomposition of the PCB present in them limits the entire process as a whole.

A series of investigations have been devoted to the problem of the biodegradation of PCB.[3, 9, 37, 38, 51, 77, 85, 191–202] It has been shown that both pure cultures of micro organisms and their mixtures can be used for the detoxification of PCB-containing materials. The microflora from the bottom deposits in rivers, lakes, and soils and the active sludge from the purification equipment in the cellulose-paper industry and undertakings of the food industry are used as mixtures of microorganism cultures.[77, 192–198, 200–202] None of the natural strains isolated is capable of fully decomposing PCB, the highly chlorinated PCB being the most resistant to biodegradation.[100, 200]

The difficulty of the study of the biodegradation mechanism is associated with the complexity of the processes investigated, which constitute a chain of consecutive-parallel reactions, each of which is catalysed by its own enzyme. Nevertheless, many groups of investigators who have studied the aerobic decomposition of PCB by microorganisms maintain a single view on the sequence of reactions leading to the decomposition of these compounds.[203–214] This sequence includes the following stages: the interaction of an oxygen molecule with one of the aromatic rings of PCB with formation of the corresponding dihydrodiol; the transformation of the dihydrodiol into a dihydric phenol; the cleavage of the aromatic ring and the formation of the chlorinated 2-hydroxy-6-oxo-6-phenylpenta-2,4-dienecarboxylic acid; the formation of chlorobenzoic acid:



(27)

The above scheme has been confirmed by mass-spectrometric studies of the intermediate and final biodecomposition products, as well as by chemical tests on the latter.[203] At the same time, on the basis of this scheme one cannot answer the fundamental question concerning the possibility of the intensification of biodecomposition processes.

An increase in the effectiveness of the decomposition of PCB may be promoted by the application of substrates such as sodium acetate[200] or inorganic nitrogen and phosphorus compounds[215] as nutrients for the microorganisms, as well as by the use of mixtures of different cultures[200, 201] and by the combination of PCB biodegradation processes with other biotechnological processes, for example composting.[216]

The biodegradation methods are very convenient for the dechlorination of PCB dispersed in the environment, for example in soils and water sources, and also for the detoxification of

subterranean waters, sewage, sludge, and domestic waste with a low PCB content.[3, 9, 51, 77, 85, 192, 194, 195, 200, 216]

The rate of biotechnological purification of sewage can be increased by employing emulsifying agents, which increase the solubility of PCB and PCB-containing oils in water.[77] The creation of highly productive biotechnological PCB degradation methods is possible if more active strains of microorganisms are cultured. For the productivity achieved at the present time, the biotechnological method for the decomposition of PCB is most reasonably employed at the end of the dechlorination process in combination with other methods, for example chemical and photochemical.[77, 123, 130, 202] This is favoured also by the high degree of decomposition of PCB molecules containing fewer chlorine atoms in the concluding stage.

Another problem arising when biodegradation methods are employed consists in the preservation of the vitality of the PCB-decomposing microorganisms in the soil, where they should compete effectively with soil microorganisms.

Finally, certain difficulties arise owing to the interaction of PCB molecules with compounds in the bottom deposits and the soil. Such interaction prevents the microbiological decomposition of PCB.

VII. Oxidative methods

Among the methods for the neutralisation of PCB-containing materials, the oxidative procedures predominate. They can be divided into combustion proper and special oxidation methods. The latter include catalytic oxidation, plasma methods, ozonisation, and oxidation under hypercritical conditions.

Combustion predominates not only among the oxidative methods but in general among the methods for the detoxification of PCB and PCB-containing materials. This is due to the universality of this procedure as regards the types of materials processed, the ease of controlling the process, and its suitability for various technological versions and conditions of the neutralisation process, which facilitates the creation of mobile apparatus and ensures the possibility of employing the heat of the combustion process, complete decomposition of the PCB in the cycle, *etc*.

The processes involving the combustion of PCB and polychlorobiphenyl-containing mixtures have been the object of numerous investigations[5, 6, 9, 16, 18, 42, 48, 50, 55, 56, 74, 77, 85, 87, 143, 217–232] in the course of the last three decades, the aim of which consisted in the search for conditions ensuring the most complete oxidation. The requirements which must be met by the PCB combustion processes are fairly rigorous. Thus, according to the standards established by the Environmental Protection Agency in the USA the degree of destruction of PCB in these processes should not be less than 99.9999%.[233] This is achieved by selecting the optimum ratios of PCB , the oxidants, and the additional fuel as well as the temperature and residence time of the mixture in the combustion chamber.[234] We shall examine the principles governing this choice.

The ratios of the components of the initial mixture are determined primarily by stoichiometric considerations.[234] Thus exhaustive oxidation of the $C_{12}H_xCl_{10-x}$ molecule to CO_2, H_2O, and HCl should be described by the equation

$$C_{12}H_xCl_{10-x} + \frac{12 + (2x - 10)}{4}O_2 = \quad (28)$$
$$= 12CO_2 + (10 - x)HCl + \frac{(2x - 10)}{2}H_2O.$$

This equation has a physical significance only for $x > 5$. When $x = 5$, water is not formed. For $x < 5$, the combustion process proceeds in the direction of the formation of molecular chlorine[235] in accordance with the equation

$$C_{12}H_xCl_{10-x} + 12O_2 = 12CO_2 + xHCl + \frac{(10 - 2x)}{2}Cl_2. \quad (29)$$

The formation of molecular chlorine is undesirable for two reasons. Firstly, it has a highly corrosive effect on the material of the apparatus used in the combustion processes. Secondly, its quantitative extraction from effluent gases is a difficult problem and requires the use of expensive alkaline agents. Direct combustion of the majority of the commercial PCB mixtures should lead irreversibly to the formation of appreciable amounts of molecular chlorine. The virtually complete suppression of the formation of molecular chlorine in the combustion of highly chlorinated PCB can be achieved by introducing into the initial mixture of PCB and the oxidant an additional hydrocarbon fuel, which is an external source of the hydrogen atoms lacking in the PCB molecules.[235, 236] If methane is used as such a fuel, the PCB combustion process can be described by the equation

$$C_{12}H_xCl_{10-x} + \beta CH_4 + \left(12 + 2\beta + \frac{2x - 10}{4}\right)O_2 = \quad (30)$$
$$= (12 + \beta)CO_2 + (10 - x)HCl + \left(2\beta + \frac{2x - 10}{2}\right)H_2O$$

The introduction of a fuel, the amount of which is expressed by the stoichiometric coefficient β, should not only make good the deficiency of the hydrogen in PCB but should also ensure the required temperature of the flame and its stability.

In its turn, the combustion temperature is determined from the condition for the complete suppression of the formation of PCDD and PCDF. The Environmental Protection Agency in the USA recommends that this requirement be satisfied by ensuring a temperature in excess of 1200 °C and a residence time in the combustion chamber longer than 2 s.[46, 233, 237] A definite excess of the fuel relative to PCB and an excess of the oxidant relative to the fuel are necessary for this purpose.[235, 236] There is no need to go far beyond the limit of 1200 °C, because this leads to an excess consumption of fuel and rapid wear of the equipment. A certain excess of the oxidant (oxygen, air) is needed for the exhaustive degradation of PCB and the suppression of soot formation.[235, 236] However, this excess should not be enormous, because, in accordance with the Deacon equilibrium

$$Cl_2 + H_2O \rightleftharpoons 2HCl + \tfrac{1}{2}O_2 \quad (31)$$

the undesirable formation of chlorine is possible at a high oxygen concentration.

There have been few studies devoted to the quantitative aspects and mechanisms of the combustion processes of halohydrocarbons and they are concerned mainly with halomethanes.[235, 236, 238–240] We suggest that the ideas developed in these investigations cannot be extended to haloarenes, because the chemical properties of the latter differ too much from those of halomethanes. On the other hand, two phenomena observed in the study of the combustion of halohydrocarbons may have a bearing also on the combustion of PCB.

The first concerns the inhibiting effect of halohydrocarbons. By extending the ideas developed in a series of investigations,[236, 241–244] it is possible to put forward the following mechanism of the inhibition of the combustion of the PCB–fuel mixture,

$$H^{\bullet} + HCl \rightleftharpoons H_2 + Cl^{\bullet}, \quad (32)$$

$$OH^{\bullet} + HCl \rightleftharpoons H_2O + Cl^{\bullet}, \quad (33)$$

$$Cl^{\bullet} + Cl^{\bullet} \rightleftharpoons Cl_2, \quad (34)$$

$$Cl^{\bullet} + Ar \longrightarrow ArCl. \quad (35)$$

Reactions (32) and (33) reflect the role of HCl (the product of the combustion of any chlorohydrocarbon) as a trapping agent for the $H^{\bullet}$ and $OH^{\bullet}$ free radical species responsible for the combustion process. Reactions (34) and (35) describe the involvement of chlorine atoms in chain termination and hence also in the inhibition of the combustion process.

The second observed phenomenon is the acceleration of the combustion of chlorohydrocarbons by water vapour:

$$Cl^{\bullet} + H_2O \rightleftharpoons HCl + OH^{\bullet}, \quad (36)$$

$$OH^{\bullet} + CO \longrightarrow CO_2 + H^{\bullet}, \quad (37)$$

$$H^{\bullet} + O_2 \longrightarrow \ddot{O} + OH, \quad (38)$$

$$\text{fuel} + (H^{\bullet}, \ddot{O}, OH^{\bullet}) \longrightarrow \text{combustion products}. \quad (39)$$

Water vapour initiates the formation of the $H^{\bullet}$, $O^{\bullet\bullet}$, and $OH^{\bullet}$ radicals which are responsible for the oxidation process. The mechanism examined explains the suppression of the formation of chlorine in the chlorohydrocarbon combustion process.[245,246] Firstly, by virtue of the occurrence of reaction (36), the concentration of chlorine radicals falls and hence their recombination [reaction (34)] with formation of Cl_2 diminishes. Secondly, water vapour behaves as a donor of hydrogen atoms [reactions (36) and (37)] and hence it makes good the deficiency of hydrogen in PCB.

The technological formulation of the process depends in many respects on the state of aggregation of the material being neutralised. The simplest apparatus consists of a hollow combustion chamber fitted with a special burner with attachments for the supply of the PCB-containing material, the fuel (when this is necessary), and air (oxygen).[217,231] It is used to neutralise PCB-containing liquid waste and sewage. The joint combustion of concentrated sewage and liquid PCB-containing waste makes it possible to avoid the formation of PCDD and PCDF.[231] A two-chamber apparatus, consisting of a rotary furnace and a final combustion chamber,[6,18,42,77,179,183] in which a temperature higher by 200 °C than in the first chamber is maintained to ensure the completion of the process and the suppression of the PCDD and PCDF formation reactions, is used in certain cases. The two-chamber apparatus proved to be the most effective device for the combustion of liquid waste and its universal application has been recommended by the Environmental Protection Agency in the USA.[183]

The most widely used procedure for the destruction of PCB-containing solid and liquid waste is combustion in cyclone and cement furnaces and incinerators. By virtue of the high temperature and a fairly long contact time, the complete decomposition of PCB and the intermediate PCDD and PCDF is achieved in rotating cement furnaces,[54,77,174,176] while the limestone present in the initial charge binds quantitatively the acid gases formed on combustion (Cl_2, HCl, *etc.*). The addition of PCB-containing materials to the initial charge improves the quality of the cement obtained.[77] The materials combusted served as an additional source of heat and this makes it possible to economise on the main fuel.[174]

An interesting method involving the combination of the combustion of PCB-containing materials with a blast furnace process has been proposed.[174] As in the cement furnaces, here the problem of the recovery of the heat is solved successfully and the acid gases formed are bound by the limestone used as the flux.

The highest efficiency of the combustion of solid PCB-containing waste is achieved in special furnaces consisting of three series-connected reaction units: a rotating furnace, a final combustion furnace, and a chamber for the combustion of gaseous products.[18,183] Such devices are suitable for the combustion of materials. In the version described, they are used for the combustion of domestic rubbish, whilst liquid PCB-containing waste can be supplied directly into the final combustion chamber. Gas, petroleum products, or coal can be used as the fuel for the combustion of any PCB-containing waste.[18] In most cases, the effluent acid gases are absorbed in two series-connected scrubbers irrigated with water and an aqueous solution of alkali.[184,242] Limestone is sometimes added to the initial mixture to bind the acid gases.[77,171] A fluidised bed regime may be established to intensify the process in the combustion chamber,[77] but the melting point of the inert material used in this case imposes certain limitations on the combustion conditions. For example, the melting point of sand is 1100 °C.

The combustion furnaces can be combined into a single aggregate with any heat consuming unit. Thus examples of the combustion of PCB-containing oils in boiler aggregates,[216] for heating aluminium furnaces,[223] and for the generation of the additional heat in the lime preparation process [77] are known. The combustion methods are very convenient to use in devising mobile systems designed for the processing of local sources of pollution by PCB on trailers and in ocean-going vessels.[77,219]

The main deficiency of the combustion method is the risk of the formation of the highly toxic PCDD and PCDF during the oxidative degradation of PCB.[18,218,235,247] In a number of instances, the absence of PCDD and PCDF among the combustion products was noted [54,217,221] and these data have been confirmed by kinetic and thermodynamic calculations, according to which these compounds should not be formed at temperatures above 1200 °C and for contact times longer than 2 s.[237] Nevertheless, in the highly productive plant which actually exists it is difficult to ensure the ideal functioning of the combustion reactors, *i.e.* a uniform temperature throughout the volume of the chamber and an identical residence time in the reaction zone for all the particles in the reaction stream. For this reason, there is always a probability of the formation of the highly toxic PCDD and PCDF. A greater uniformity of the temperature field in the combustion chamber can apparently be ensured by employing a fluidised bed technique or by carrying out the process in the melt of an inert material, for example glass.[77]

The complete suppression of the formation of PCDD and PCDF is achieved when PCB are combusted in an oxygen and water vapour atmosphere.[220]

One of the deficiencies of the combustion processes is a low selectivity, so that their use for the destruction of PCB is fully justified only for a fairly high content of the latter in the materials being neutralised.[87] The Environmental Protection Agency in the USA determined the lower limit of the PCB content in spent materials at the level of 500 mg of PCB per kilogram of the material.[224]

Among other deficiencies of the combustion processes, one may note the high cost, the additional consumption of fuel, the rapid wear of equipment in corrosive media (Cl_2 and HCl) and at high temperatures, and also the irreversible loss of the hydrocarbon component.[68,230] The last deficiency is of a fundamental character, because the aim of the overall strategy in the development of the world technology is the creation of resource-saving industries.

Only a few scattered studies have been devoted to the field of the catalytic oxidation of PCB.[12,232,237,248–252] The application of catalysts makes it possible to lower appreciably the process temperature and hence to reduce the capital and energy expenditure. It is remarkable that PCDD and PCDF are not formed under catalytic conditions, and the emission of nitrogen oxides is appreciably reduced. RuO_2, Cr_2O_3/Al_2O_3, CuO/Al_2O_3, Co_3O_4, the mixed catalysts $CuCr_2O_4$, Pt–Pd, and metal chlorides on an inert porous support, which are capable of being converted into the corresponding oxides on heating in air, are used as catalysts. Despite promising results, systematic studies on the characteristic features of the catalytic PCB oxidation processes are lacking and this hinders an assessment of the prospects for their application.

The methods for the oxidative decomposition of PCB in plasma or electric arc discharges are of undoubted interest.[11,151,252,253] The complete conversion of PCB into gaseous products (CO, CO_2, H_2O, HCl, Cl_2 ClO_2) without risk of the formation of PCDD and PCDF is ensured under these conditions. However, such processes are characterised by low selectivity and high energy expenditures, so that their application is justified only if it is necessary to detoxify concentrated PCB-containing materials.

The neutralisation of PCB by the ozonisation method has been tested in relation to aqueous solutions of these toxicants.[77,254,255] At the usual temperatures, the degree of decomposition of PCB reaches 97.0%–99.4%. The acceleration of this process is promoted by UV irradiation and by the addition of potassium hydroxide to the solution. This method is of interest for the detoxification of sewage, since simultaneous ozonisation ensures its disinfection.

PCB can also be oxidised by employing a mixture of oxygen (air) with water as the reagent under conditions ensuring the attainment of hypercritical parameters of the latter.[77] In this state, the hydrogen bonds are significantly weakened and the dielectric constant diminishes to 3–10. As a result, water becomes a good solvent for the organic mass and the oxygen supplied to such a system rapidly oxidises the substrate. The exothermicity of the process makes it possible to maintain the temperature at a level of ~ 550 °C. When this method is used, the formation of PCDD and PCDF is ruled out and the complete decomposition of PCB is ensured. However, additional studies are needed in order to analyse the material and energy balances and to elucidate the economic desirability of the development of the method.

VIII. Hydrogenolysis of polychlorobiphenyls

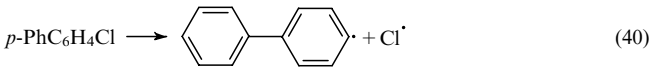
The interest in detoxification of organochlorine waste by the dechlorination method has increased in recent years.[255] This has been induced by a series of evident advantages of this process compared with other procedures for the conversion of organochlorine compounds, including PCB. Firstly, hydrogenolysis proceeds fairly 'smoothly' under comparatively mild conditions up to the complete conversion of the initial organic reagent. Secondly, the reaction is selective in relation to the object processed, which makes it possible to achieve successfully the dechlorination of organochlorine compounds within any range of their concentrations. If other undesirable organoelement compounds are present in the reaction mixture, then they can be readily converted into the corresponding hydrocarbons by hydrogenolysis. Thus there is a possibility of the regeneration of the spent lubricating oils and other PCB-containing materials. Thirdly, in the hydrogenolysis the formation of PCDD and PCDF is ruled out. Fourthly, this method has an evident resource-saving character.

Processes involving the hydrogenolysis of organohalogen compounds have been the objects of numerous investigations. Nevertheless, the number of studies in which the chemical behaviour of PCB in these reactions has been considered is limited.[49, 80, 129, 256–271] The aim of the majority of studies was to solve applied problems in the detoxification of PCB-containing materials.

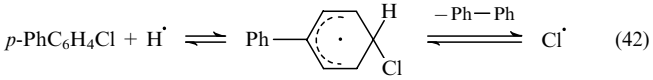
The hydrogenolysis of PCB can be achieved by the thermal, catalytic, and the usual chemical methods. In the last case, expensive alkali and alkaline earth metal hydrides and hydroborates[49, 100, 186, 267] as well as silanes and polymethylsiloxanes[129, 268] are used as the dechlorinating agents. These methods are more in the nature of preparative procedures and cannot be considered as a basis for industrial application.

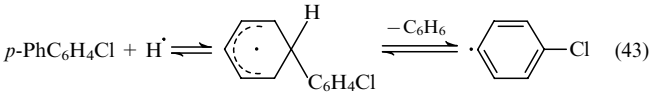
There have been several studies devoted to quantitative aspects of the thermal hydrogenolysis of chloroarenes, including chlorobiphenyls.[259, 272–274] The results of the investigation of the pyrolytic decomposition of arenes and chloroarenes should be regarded as a component of these studies.[152, 275] The gas-phase thermal hydrogenolysis of PCB by hydrogen at 700–925 °C leads to the formation of benzene and hydrogen chloride as the final products with insignificant soot formation.[259]

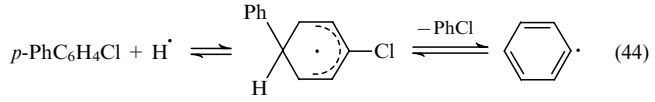
Analysis of the results obtained in the studies quoted above and of the thermal kinetic data presented in some of them makes it possible to postulate the following mechanism of the thermal hydrogenolysis (in relation to 4-chlorobiphenyl):

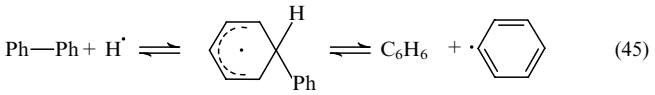

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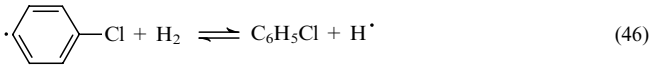

(41)

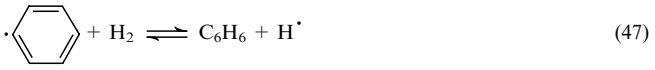

(42)


(43)

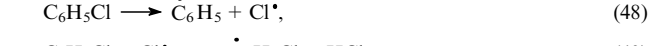

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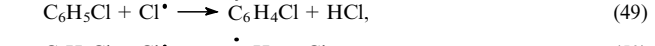

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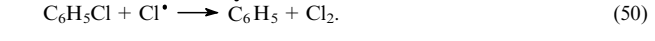

(46)


(47)

Detailed investigation of the behaviour of PCB at different hydrogen concentrations[153, 259, 275] has shown that reactions (43)–(45) are reversible. The processes which are the reverse of the above reactions may be regarded as stages in the thermolysis of chlorobenzenes. The pyrolysis of chlorobenzenes should then be supplemented by stages involving initiation and the formation of HCl:


(48)


(49)


(50)

Under the pyrolysis conditions, the concentration of molecular hydrogen is extremely low and equilibrium (41) is significantly displaced to the left, which leads to high $[Cl^{\bullet}]/[H^{\bullet}]$ ratios. This induces in its turn the displacement of equilibrium (43)–(45) also to the left, *i.e.* in the direction of the products of the thermolysis of chlorobiphenyls.

The main difficulty in the occurrence of thermal hydrogenolysis is the supply of heat for the creation of the required temperature regime. However, at the current level of the technology of high-temperature processes, this difficulty has been overcome. There have been promising communications concerning the possibility of replacing hydrogen in the thermal hydrogenolysis of PCB by the cheaper methane and other alkanes.[257, 263, 275] A tubular furnace, in the intertubular space of which it is possible to combust the methane employed, is entirely suitable for the organisation of such a process.

Numerous versions of the catalytic hydrogenolysis of organochlorine compounds have been described in the literature.[256, 271] The processes are carried out both in the liquid and gas phases, usually on metals such as Pt, Pd, Rh, Ru, Ir, Os, Ni, Co, Fe, Re, Mn, Mo, W, Cr, V, Cu, Ag, and Au. The properties of the catalysts can be varied widely by fusing them with other metals, by adding promoting agents, and by selecting supports.

A detailed analysis of the characteristic features of the catalytic hydrogenolysis of various aromatic chloro-compounds, including PCB, has been carried out in mutually complementing reviews[256, 271] and we shall therefore confine ourselves here to a brief description of the existing ideas.

The kinetics of the catalytic hydrogenolysis of a series of chloroalkanes, chloroalkenes, and chloroarenes indicate that the majority of the process proceed *via* the Langmuir–Hinshelwood mechanism with dissociative adsorption of hydrogen on the catalyst surface. The extensive experimental data accumulated provide guidelines in the search for more effective catalysts and for the extension of the ideas developed to new objects.

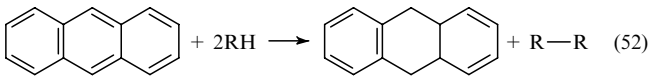
Many experimental data have been obtained in recent years on the catalytic hydrogenolysis of polychlorobiphenyls.[258, 260–262, 264, 265, 270, 276] The reactions take place in the gas and liquid phases and in the latter case alkalis may be added to the reaction mass in

order to bind the hydrogen chloride formed. Supported Group VIB and Group VIII metals, Raney nickel, and the nickel–molybdenum alloy catalyst have been used successfully as catalysts. The hydrogenolysis of PCB on nickel, deposited on kieselguhr, in the gas and liquid phases has been studied in detail.[276]

The possibility of the quantitative dechlorination of certain PCB to biphenyl under mild conditions indicates major prospects for catalytic hydrogenolysis. The heat of reaction is sufficient to maintain the necessary, comparatively low, temperature in the reaction zone. In connection with the problem of increasing the useful life of the catalyst and of the restoration of its activity in the regeneration cycle, attention has been drawn to a study [277] of the hydrogenolysis of PCB with the aid of a combined reagent comprising alkali and a hydrogen-transferring agent. The authors regard this process as an alternative to the usual catalytic hydrogenolysis. Hydrocarbons incorporating highly mobile hydrogen atoms (alkanes containing tertiary C–H bonds or alkylarenes with benzyl C–H bonds) are used as the hydrogen donor. The role of the hydrogen-transferring agent is performed by anthracene, phenanthrene, alkylnaphthalenes, and also graphite, soot, or transition metals (in the first place iron). The overall process can be described by the equation

$$C_{12}H_xCl_{10-x} + (10-x)NaOH + 2(10-x)H^* \longrightarrow C_{12}H_{10} + (10-x)NaCl + (10-x)H_2O, \quad (51)$$

where H* are active hydrogen atoms evolved by the hydrogenating form of the transferring agent, for example the dihydroanthracene formed on interaction with the hydrogen donor, *i.e.*



(52)

or the adsorbent (carbon, transition metals). In the latter case, the version proposed by the authors differs little from the usual heterogeneous-catalytic hydrogenolysis, because transition metals (the classical catalysts for these processes) promote the dissociative adsorption of H_2 and the formation of atomic hydrogen as the active surface intermediate. The idea of hydrogen transfer with the aid of polycyclic aromatic compounds is attractive, but the prospects for the technological application of this process are obscure, because problems arise associated with the application of expensive alkali and the difficulties in the separation of the reaction mass and the utilisation of the products of the conversion of the hydrogen donors.

* * *

The examination of the problem of the pollution of the environment by PCB and of the known methods for their neutralisation has shown that, in the practical solution of this ecological problem, it is possible to apply both individual methods for the processing of PCB and their various combinations. The use of two and more methods is most rational, for example, in the utilisation of articles containing high PCB concentrations. Such methods may be combustion and biological purification, dechlorination, oxidation, *etc*. A concrete technology for the neutralisation of PCB, determined by the state of aggregation of the material, the concentration of PCB in it, the specified degree of purification, and other technological and ecological factors, must be selected in each case.

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