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# Formation and decay of biphenyl at consecutive radiolytic dechlorination of pentachlorobiphenyl in aqueous solution

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**Step-by-step transformation of 3,3′,4,4′,5-pentachlorobiphenyl to biphenyl by dissociative capture of hydrated electrons and the recombination interactions of biphenyl radicals are studied in aqueous solutions upon electron beam irradiation.**

The detoxication of polychlorinated biphenyls (PCBs) presents a severe environmental problem.[1] Transportation of PCB with natural water and wastewater takes place mainly due to their concentrating in colloidal and ultra dispersible suspended matters[2] – individual solubility of PCB in water does not exceed 1 μmol dm$^{-3}$.

Radiolytic dechlorination is a promising process for PCB detoxication.[1,3,4] The process of dechlorination is most productive when PCB ($C_{12}H_{10-n}Cl_n$, where $n \leq 10$) interacts with reducing radiolytic intermediates, for the most part, the electrons:[1]

$$C_{12}H_{10-n}Cl_n + e^- \rightarrow {}^{\cdot}C_{12}H_{10-n}Cl_{n-1} + Cl^- \qquad (1)$$

Radiolysis of aqueous solutions was examined only with 2,6-dichlorobiphenyl, 2,2′,6,6′-tetrachlorobiphenyl and decachlorobiphenyl.[3,4] The radiolytic transformations of 3,3′,4,4′,5-pentachlorobiphenyl in an aqueous micellar solution are considered here.[†]

Figure 1 shows gradual formation and decay of polychlorobiphenyls with diminished chlorination degree upon electron-beam irradiation of deaerated aqueous solution of 3,3′,4,4′,5-pentachlorobiphenyl in the presence of Triton X-100. The dose dependence of the concentration of tetra-, tri, bi- and monochlorinated biphenyl derivatives displays a maximum, and the position of this maximum for products of deep dechlorination shifts to a high dose region. The initial yield of pentachlorobiphenyl degradation coincides with the yield of free Cl$^-$ ions, being equal to 0.038±0.003 μmol J$^{-1}$.

The rate constant of reaction (1) for pentachlorobiphenyl, measured by decay of optical absorption of $e^-_{aq}$ at 720 nm, is $3.1\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. It predetermines an opportunity of a higher yield of pentachlorobiphenyl degradation in individual aqueous solution. However, in a micellar solution the majority of hydrated electrons are scavenged by Triton X 100 ($k = 1.2\times10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$)[4] to result in a lower yield of PCB dechlorination by dissociative electron capture. The role of H and OH radicals in dechlorination is much less significant: among their transformations, the fast reactions with ethoxylated alkylphenols ($k \geq 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$)[5] appear to be dominating.

The presence of an excess of alkyl-substituted organics $RCH_2R'$ also promotes the preferential role of a reaction of H-atom abstraction by the ${}^{\cdot}C_{12}H_{10-n}Cl_{n-1}$ radical and, accordingly,

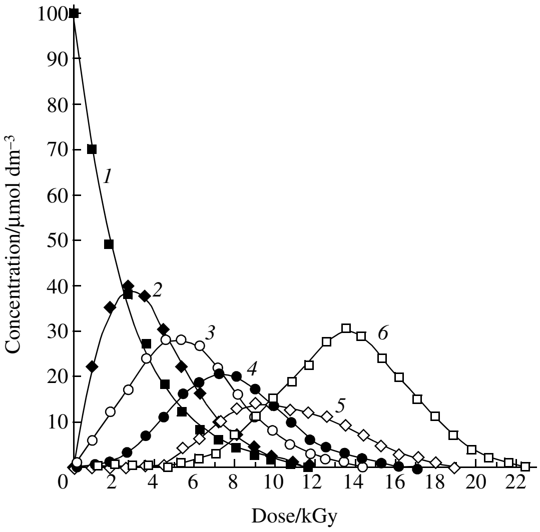

**Figure 1** Dose dependence of the concentration of polychlorinated biphenyls $C_{12}H_{10-n}Cl_n$ in a deaerated aqueous solution of 3,3′,4,4′,5-pentachlorobiphenyl (100 μmol dm$^{-3}$) and Triton X 100 (8.2 mmol dm$^{-3}$): (*1*) 3,3′,4,4′,5-pentachlorobiphenyl ($n = 5$), (*2*) $n = 4$, (*3*) $n = 3$, (*4*) $n = 2$, (*5*) $n = 1$, (*6*) biphenyl ($n = 0$).

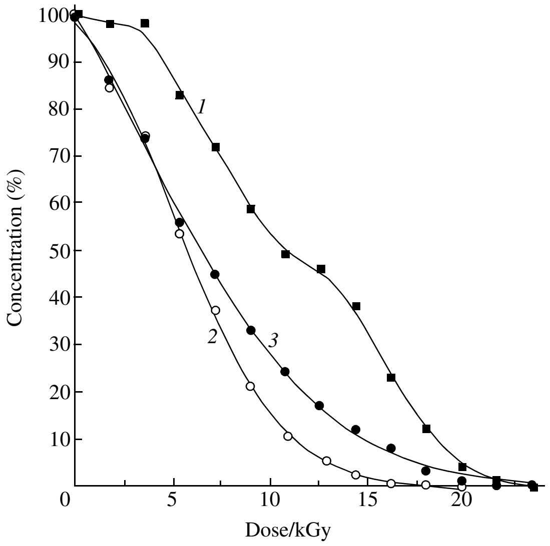

**Figure 2** Dose dependence in deaerated aqueous solution of 3,3′,4,4′,5-pentachlorobiphenyl (100 μmol dm$^{-3}$) and Triton X 100 (8.2 mmol dm$^{-3}$): (*1*) total concentration of polychlorinated biphenyls $C_{12}H_{10-n}Cl_n$ ($0 \leq n \leq 5$), (*2*) total content of Cl atoms inside polychlorobiphenyl molecules and (*3*) total content of Cl atoms in an organic phase.

formation of polychlorobiphenyl molecules with a diminished chlorination degree in consecutive reactions (1) and (2):

$$^{\cdot}C_{12}H_{10-n}Cl_{n-1} + RCH_2R' \rightarrow C_{12}H_{11-n}Cl_{n-1} + R^{\cdot}CHR' \qquad (2)$$

At a final stage, the dechlorination process results in biphenyl formation. At doses below 13–14 kGy, biphenyl is predominantly collected in solution, and a maximum yield of biphenyl formation is 0.005 μmol J$^{-1}$. At a higher dose and a low residual concentration of chlorinated biphenyls, there is a preferential decay of biphenyl: at 15–18 kGy, the average yield of biphenyl degradation is 0.004 μmol J$^{-1}$.

Figure 2 shows that reactions (1) and (2) are not the only significant processes of pentachlorobiphenyl transformation and low-chlorinated biphenyl formation. Thus, initially, the dose dependence of the content of chlorine atoms linked inside PCB molecules (curve *2*) practically coincides with the dose dependence of the total content of chlorine atoms in an organic phase (curve *3*). However, at a dose higher than 5 kGy, these two curves begin to ramify. In turn, curve *1* displays that at a dose lower 5 kGy the total concentration of polychlorinated biphenyls remains invariable, but at higher doses begins to reduce. These features seem to result from the fact that a part of $^{\cdot}C_{12}H_{10-n}Cl_{n-1}$ radicals, besides reaction (2), participate in radical recombination and are transformed to compounds other than PCBs. Among organic products, the high-molecular-weight compounds with a mass close to a mass of products of $^{\cdot}C_{12}H_{10-n}Cl_{n-1}$ radical dimerization and products of $^{\cdot}C_{12}H_{10-n}Cl_{n-1}$ radicals recombination with molecular radicals of surfactant were identified:

$$^{\cdot}C_{12}H_{10-n}Cl_{n-1} + {}^{\cdot}C_{12}H_{10-n}Cl_{n-1} \rightarrow (C_{12}H_{10-n}Cl_{n-1})_2 \qquad (3)$$

$$^{\cdot}C_{12}H_{10-n}Cl_{n-1} + R^{\cdot}CHR' \rightarrow R'RHC{-}C_{12}H_{10-n}Cl_{n-1} \qquad (4)$$

The probability of reactions (3) and (4) increases at high doses, when the content of initial (sterically accessible) surfactant molecules is essentially diminished.

While biphenyl accumulates, the probability of electron capture by PCB molecules becomes lower, since biphenyl is not less effective electron scavenger than PCB. The rate constant of reaction (5) measured in this work is $1.1\times10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$, which exceeds the rate constant of reaction (1).

$$C_{12}H_{10} + e^- \rightarrow C_{12}H_{10}^{\overline{\cdot}} \qquad (5)$$

Higher efficiency of electron capture by biphenyl was observed earlier. Thus, the experimental $k_5$ is $(7–12)\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$,[6,7] while $k_1$ is $2.6\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for decachlorobiphenyl[4] and $3.8\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for 2,6-dichlorobiphenyl.[3]

Biphenylide anions, produced in reaction (5), possess high reducing ability[8] and, apparently, take part in PCB dechlorination:

$$C_{12}H_{10}^{\overline{\cdot}} + C_{12}H_{10-n}Cl_n \rightarrow {}^{\cdot}C_{12}H_{10-n}Cl_{n-1} + Cl^- + C_{12}H_{10} \qquad (6)$$

The regeneration of biphenyl in consecutive processes (5) and (6) can be the basic reason of its accumulation at the end of

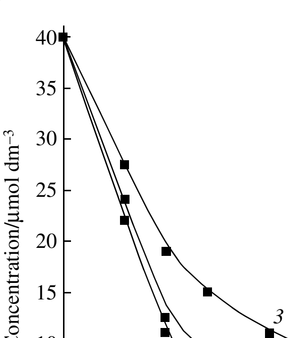

**Figure 3** Dose dependence of biphenyl concentration in aqueous solutions (40 μmol dm$^{-3}$) of $C_{12}H_{10}$: (*1*) deaerated solution, (*2*) deaerated solution in the presence of 400 μmol dm$^{-3}$ sulfite and (*3*) aerated solution.

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[†] Solutions were prepared in distilled water using 3,3′,4,4′,5-pentachlorobiphenyl (≥99%) and biphenyl of chemically pure grade. Biphenyl was additionally purified by sublimation. Micellar aqueous solutions of pentachlorobiphenyl (100 μmol dm$^{-3}$) contained 8.2 mmol dm$^{-3}$ ethoxylated alkylphenols (Triton X-100 from Carbide Chemicals and Plastics Co.). Aqueous micellar solutions of pentachlorobiphenyl were irradiated at pH 10 to prevent the reaction between $e^-_{aq}$ and excess hydrogen ions. The procedure for the preparation of micellar solutions was described previously.[4]

Pulse irradiation was performed using an ELU-6E Elektronika linear electron accelerator (electron energy, 6.5 MeV; pulse duration, 15 ns) equipped with an optical system of radiolytic intermediate registration. Stationary (quasi-continuous) irradiation of solutions was conducted using a U-12F linear electron accelerator (electron energy, 5 MeV; pulse repetition frequency, 400 Hz). Deaerated solutions were irradiated in sealed glass ampoules. Glass ampoules with aerated solutions were closed with ground-glass stoppers. The absorbance of solutions was measured on a Specord M-40 spectrophotometer. Composition of final products of radiolysis was analysed using a Perkin-Elmer Q-Mass 910 GC–MS system (glass capillary column, 60 m; carrier gas, helium; temperatures range, 40–365 °C) from hexane extracts.

the radiolytic dechlorination of pentachlorobiphenyl. As curve *1* in Figure 2 displays, during the accumulation of biphenyl, the dose dependence of the total concentration of chlorinated and non-chlorinated biphenyls in the irradiated solution changes the slope: PCB decay is retarded. While the residual PCB concentration decreases, reaction (6) loses the significance and biphenyl degradation begins to dominate.

A study of the kinetics and products of radiolysis of a deaerated aqueous biphenyl solution (40 μmol dm$^{-3}$, saturated solution) showed that biphenyl in the absence of other impurities was almost completely transformed into dimer products. The observed yield of biphenyl decay is 0.11 μmol J$^{-1}$. The processes of biphenyl degradation and dimer formation are accelerated in the presence of selective scavengers of OH radicals like sulfite (Figure 3, curve *2*) or formate. In the presence of 400 μmol dm$^{-3}$ sulfite, the observed yield of biphenyl decay is 0.13 μmol J$^{-1}$. In turn, the presence of oxygen gives an inhibiting effect on biphenyl degradation. The yield of biphenyl decay in aerated solution is reduced to 0.08 μmol J$^{-1}$.

One of the main products of biphenyl (or biphenylide anion) reduction is the H adduct.[8] It can be formed immediately as a result of H-atom addition

$$C_{12}H_{10} + {}^{\cdot}H \rightarrow {}^{\cdot}C_{12}H_{11}, \tag{7}$$

as well as by protonation of the biphenylide anion

$$C_{12}H_{10}^{-} + H^{+}(H_2O) \rightarrow {}^{\cdot}C_{12}H_{11}\ (+\ OH^{-}). \tag{8}$$

Similar processes with the participation of OH radicals, apparently, result in the formation of an OH adduct of biphenyl:

$$C_{12}H_{10} + {}^{\cdot}OH \rightarrow {}^{\cdot}C_{12}H_{10}OH \tag{9}$$

$$C_{12}H_{10} + {}^{\cdot}OH \rightarrow C_{12}H_{10}^{+} + OH^{-} \tag{10}$$

$$C_{12}H_{10}^{+} + OH^{-}(H_2O) \rightarrow {}^{\cdot}C_{12}H_{10}OH\ (+\ H^{+}) \tag{11}$$

In the absence of other organic radicals, almost the only reactions of H and OH adducts of biphenyls in water are recombination interactions with each other, which finally result in the formation of dimer derivatives of biphenyl:

$$C_{12}H_{10}^{-} + C_{12}H_{10}^{+} \rightarrow 2C_{12}H_{10} \tag{12}$$

$${}^{\cdot}C_{12}H_{11} + {}^{\cdot}C_{12}H_{11} \rightarrow H_{11}C_{12}{-}C_{12}H_{11} \tag{13}$$

$${}^{\cdot}C_{12}H_{11} + {}^{\cdot}C_{12}H_{11} \rightarrow C_{12}H_{10} + C_{12}H_{12} \tag{14}$$

$${}^{\cdot}C_{12}H_{11} + {}^{\cdot}C_{12}H_{10}OH \rightarrow H_{11}C_{12}{-}C_{12}H_{10}OH \tag{15}$$

$${}^{\cdot}C_{12}H_{11} + {}^{\cdot}C_{12}H_{10}OH \rightarrow C_{12}H_{10} + C_{12}H_{11}OH \tag{16}$$

$${}^{\cdot}C_{12}H_{10}OH + {}^{\cdot}C_{12}H_{10}OH \rightarrow HOH_{10}C_{12}{-}C_{12}H_{10}OH \tag{17}$$

$${}^{\cdot}C_{12}H_{10}OH + {}^{\cdot}C_{12}H_{10}OH \rightarrow C_{12}H_{10}O + C_{12}H_{11}OH \tag{18}$$

The optical absorption and light scattering spectra of the irradiated aqueous solutions additionally confirm the specified scheme of biphenyl degradation. Upon irradiation of deaerated solutions, the characteristic optical absorption spectrum of biphenyl in the UV range decays and an unstructured absorption in both UV and visible ranges, being characteristic of the process of light scattering by ultradispersed particles, appears. In the presence of sulfite, this absorption has a slightly higher intensity than in an individual deaerated solution of biphenyl. In aerated solution after irradiation the light scattering is almost twice lower than in deaerated one. Such an effect can result from a higher water solubility of the products of OH adduct recombination because of their higher hydrophilicity. Moreover, in the presence of oxygen, the initial dimerization of organic radicals is partially substituted for the formation of peroxide radicals and, accordingly, hydroperoxides. In turn, the products of H adduct dimerization conserve biphenyl's inherent hydrophobicity, and a double increase in the molecular mass due to dimerization results in a reduced solubility.

Effective radiolytic transformations of aromatic compounds to an insoluble state was observed previously.[1,8,9] In particular, Pikaev *et al.*[9] found that upon irradiation of aqueous solutions containing polychlorophenols, trichlorobiphenyls or hexachlorobiphenyls to a dose of 1.3 kGy practically complete sedimentation of these compounds takes place. Note that, while the products of transformations of chlorinated phenols (initially hydrophilic) fractionally (up to 30%) remain in the irradiated water, chlorinated biphenyls are completely converted to a sediment.

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