Polychlorinated Biphenyl Radical Cations: a Pulse Radiolysis Investigation

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Pulse irradiation of polychlorinated biphenyls (PCBs) in 1,2-dichloroethane leads to the formation of transient radical cations PCB$^{+\bullet}$. The latter exhibit optical absorption spectra with maxima in the visible range (370—450 nm) and in the i.r. (at ≥800 nm). Investigations have been carried out with 3-chloro-, 4-chloro-, 3,4-dichloro-, 3,5-dichloro-, 4,4′-dichloro-, 3,3′,4,4′-tetrachloro-, 2,2′,5,5′-tetrachloro-, 2,3,4,4′,5-pentachloro-, and 2,2′,4,4′,5,5′-hexachloro-biphenyl. Two types of radical cations have been identified through their different optical and kinetic characteristics. Their structures are considered to be either planar or twisted with respect to the two aromatic rings. The relative yields are inversely related to the number of chlorine atoms *ortho* to the pivot bond, *i.e.* the 2-, 2′-, 6-, and 6′-positions. The PCB$^{+\bullet}$ radical cations have oxidizing properties and react readily with, for example, promethazine (PMZ) in the general reaction PCB$^{+\bullet}$ + PMZ $\longrightarrow$ PCB + PMZ$^{+\bullet}$ with bimolecular rate constants of the order of 10^9—10^{10} mol^{-1} dm^3 s^{-1}. On the basis of these reactions it was possible to calculate the yield of PCB$^{+\bullet}$ (which depends on the PCB concentration) and to estimate lower limits for the extinction coefficients of the PCB$^{+\bullet}$ radical cations.

The occurrence in the environment of certain polyhalogenated hydrocarbons of industrial origin has led to intensive investigations of the toxicity of these compounds in recent years.[1] Owing to their fat-soluble nature and persistence, the polychlorinated biphenyls (PCBs) in particular tend to accumulate to undesired levels in animals and man. Any risk assessment is difficult owing to an as yet incomplete understanding of their mechanism of toxicity.

In acute studies the toxic potency of congeneric PCBs appears to be receptor-mediated and highly structure-dependent. PCB isomers and congeners possessing *para-* and *meta-*halogen substituents are the most toxic, while increasing *ortho-*substitution diminishes toxicity.[2] Despite a comprehensive description of structure–activity relationships, the underlying toxic mechanism is completely unknown. Several studies indicate that commercial PCB mixtures enhance peroxidative degradation of lipid membranes.[3] Since the process of lipid peroxidation is usually initiated by free radicals,[4] the ability of PCBs to participate in such free-radical reactions warrants investigation.

Although the free-radical chemistry of PCBs has not been studied, the formation of radical cations from unsubstituted biphenyl in non-aqueous and acidic aqueous solutions has been demonstrated.[5–9] In both systems radical species display similar absorptions, with maxima at around 400 and 650 nm, which disappear on a microsecond time-scale.

We have now undertaken a detailed pulse radiolysis investigation into the optical and kinetic characteristics of radical cations derived from various PCBs. Owing to the limited water solubility of PCBs, these studies were carried out in 1,2-dichloroethane (DCE), a solvent which is ideally suited for radiation chemical studies.[9,10] Upon irradiation of DCE, radical cations and electrons are produced. The latter are irreversibly removed by immediate reaction with other solvent molecules [reactions (1) and (2)]. Reaction (2) is very important in the sense that it intercepts efficiently the geminate recombination [back reaction of (1)], a process which normally prevails in irradiated non-polar liquids. Therefore, a much higher yield of solvent radical cations is available, and these can be used for oxidation of solute molecules.

$$\mathrm{DCE} \dashrightarrow \mathrm{DCE}^{+\bullet} + e^- \qquad (1)$$

$$e^- + \mathrm{DCE} \longrightarrow \mathrm{Cl}^- + \mathrm{CH_2Cl\text{-}\dot{C}H_2} \qquad (2)$$

Experimental

The pulse radiolysis set-up and procedures for optical detection and data analysis have been described elsewhere.[11] In principle, short pulses of high-energy electrons (3.8 MeV) are introduced into solution. The pulse-width is typically around 1 μs, leading to an absorbed radiation dose of 5—80 Gy. The latter values have to be based on results from an aqueous thiocyanate dosimeter[12] owing to the lack of a specific dosimeter system in DCE. Since the electron densities of water and DCE are similar, the dosimetry was only corrected for the specific densities of the solvents (1.0 and 1.256 g cm^{-3} for water and DCE, respectively). The thiocyanate dosimeter is believed to yield values accurate to within 20%. Radiation chemical yields are expressed in terms of G, defined as the number of species produced or destroyed per 100 eV absorbed radiation dose (G = 1 corresponds to 0.1036 μmol J^{-1}). All experiments were carried out at room temperature.

Reagent grade DCE (Merck) was purified by distillation just prior to use. Nitrogen (Linde AG) was bubbled through all solutions to remove oxygen unless otherwise described. Promethazine free base was kindly provided by May & Baker Ltd. and used without further purification.

4-Chlorobiphenyl (4-CBP), purchased from Aldrich-Chemie GmbH, 3-chlorobiphenyl (3-CBP), 3,4-dichlorobiphenyl (3,4-DCBP), and 3,5-dichlorobiphenyl (3,5-DCBP), obtained from Riedel-de Haen AG, were used without further purification. 4,4′-Dichlorobiphenyl (4,4′-DCBP, Riedel-de-Haen AG) was highly coloured and therefore purified by passing in hexane (Merck) solution over a short column of Florisil (Macherey Nagel). 3,3′,-4,4′-Tetrachlorobiphenyl (3,3′,4,4′-TCBP) and 2,2′,4,4′,5,5′-hexachlorobiphenyl (2,2′,4,4′,5,5′-HCBP) were synthesized from 3,3′-dichloro- and 2,2′,5,5′-tetrachlorobenzidine, respectively, *via* a Sandmeyer-type reaction;[13] 2,2′,5,5′-tetrachlorobiphenyl (2,2′,5,5′-TCBP) was obtained by the reductive deamination of 2,2′,5,5′-tetrachlorobenzidine in an excess of hypophosphorous acid.[14] 4-Chloroaniline in a 10-fold excess of 1,2,3,4-tetrachlorobenzene (Aldrich-Chemie GmbH) was diazotized with n-pentyl nitrite[15] (Merck) and yielded the coupling product 2,3,4,4′,5-pentachlorobiphenyl (4′,2,3,4,5-PCBP). All synthetic PCBs were purified by Florisil or alumina (Aluminiumoxid 90, Merck AG) chromatography and recrystallization from methanol. Their purity was determined to be >99% by gas chromatography.[16] Structural assignments were confirmed by proton magnetic resonance and mass spectroscopy.

Results

(a) *Spectral Characteristics.*—Upon pulse irradiation of 3,3′,4,4′-TCBP (1×10^{-3} mol dm^{-3}) in N_2-saturated DCE solution a transient absorption spectrum was observed and recorded 5 μs after a *ca.* 1 μs pulse (Figure 1). Two distinct absorption maxima were seen at 400 and 430 nm. Another absorption band was indicated in the near-i.r. region. However, because of technical limitations, its actual maximum could not be determined. Pulse irradiation of N_2-saturated solutions of DCE alone yielded only a very weak absorption over the entire wavelength region. For comparison this spectrum is also included in Figure 1 (dotted line). The observed absorption in 3,3′,4,4′-TCBP solutions is attributed to radical cations from the PCB formed *via* the reactions (1), (2), and (3).

$$\mathrm{DCE}^{+\bullet} + 3,3',4,4'\text{-TCBP} \longrightarrow \mathrm{DCE} + 3,3',4,4'\text{-TCBP}^{+\bullet} \quad (3)$$

The assignment of the absorption is corroborated by experiments in the presence of oxygen. Since the spectrum does not change either in intensity or with respect to the observed maxima, contribution to the absorption from a negatively charged PCB radical anion can be ruled out. Anionic radical species and possible triplet states of aromatic hydrocarbons are selectively quenched by oxygen.[5,6,17,18] Similarly, any species resulting from $CH_2Cl\dot{C}H_2$ radicals [reaction (2)] cannot account for the optical absorption, since such carbon-centred radicals are also known to be effectively scavenged by oxygen.

The yields, measured in terms of $G\varepsilon$ (ε in dm^3 mol^{-1} cm^{-1}), of all absorption bands depend strongly on the concentration of 3,3′,4,4′-TCBP as shown in Figure 2. A similar dependence was reported previously[9] for other aromatic hydrocarbons irradiated in DCE solution and can be attributed to an increased probability of reaction (3) taking place at the expense of decay of the solvent radical cation [reaction (4)]. The

$$\mathrm{DCE}^{+\bullet} \longrightarrow \text{products} \quad (4)$$

observable yield of PCB radical cations at a given PCB concentration depends, therefore, strongly on k_5, the rate constant of the electron-transfer process (5) from the PCB to the solvent radical cation. Higher values of k_5 will result in larger

$$\mathrm{DCE}^{+\bullet} + \mathrm{PCB} \xrightarrow{k_5} \mathrm{DCE} + \mathrm{PCB}^{+\bullet} \quad (5)$$

yields of $\mathrm{PCB}^{+\bullet}$ radical cations.

Corresponding experiments have been undertaken with other PCB isomers and congeners. The spectral bands around 400 nm, which have been observed about 5 μs after the electron pulse in DCE solutions containing 2,2′,4,4′,5,5′-HCBP (1×10^{-3} mol dm^{-3}) or 3,5-DCBP (1×10^{-3} mol dm^{-3}), are shown in Figures 3a and b, respectively. These spectra show characteristics quite different from those found with 3,3′,4,4′-TCBP. In the case of 2,2′4,4′,5,5′-HCBP only a single, very broad absorption band at 400 nm was detected, whereas with 3,5-DCBP a broad maximum at 375 nm with an additional shallow shoulder at 397 nm is seen. All the spectra obtained from other PCBs fall into one of these three distinct spectral types. It appears that the number and position of chlorine substituents determine into which category the absorptions fall. In the following we will refer to the different absorption properties as types I (example: 3,3′,4,4′-TCBP), II (2,2′,4,4′,5,5′-HCBP), and III (3,5-DCBP). The results obtained from nine PCB isomers are summarized in the Table. The concentrations of the PCBs were 1×10^{-3} mol dm^{-3} except for 2,2′,5,5′-TCBP. For this last compound no transient was detected at this concentration; a 100-fold higher concentration was necessary to obtain a measurable spectrum of the $2,2',5,5'\text{-TCBP}^{+\bullet}$ radical

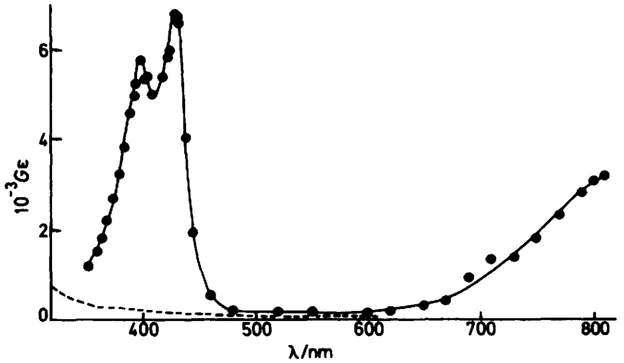


Figure 1. Absorption spectrum recorded 5 μs after pulse irradiation of a nitrogen-saturated 1,2-dichloroethane solution containing 3,3′,4,4′-TCBP (1×10^{-3} mol dm^{-3}) (dashed line: spectrum of a pulse-irradiated solution of 1,2-dichloroethane)

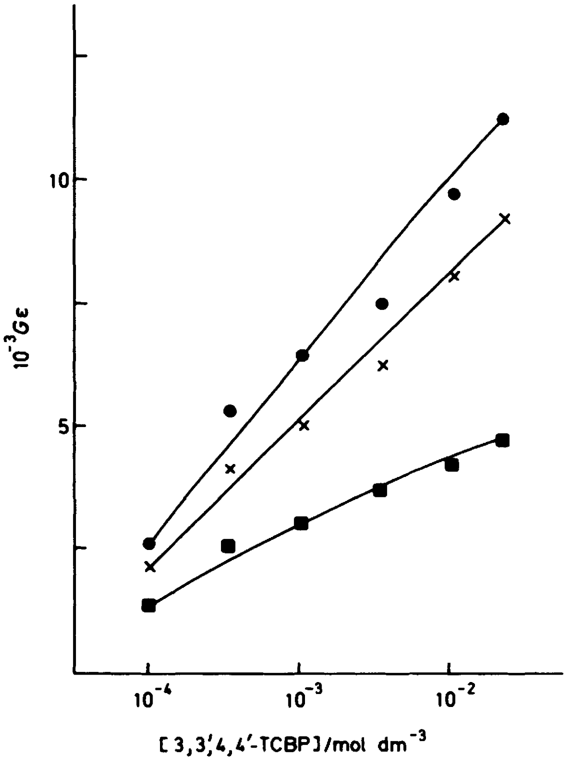


Figure 2. Radiation chemical yields in terms of $G\varepsilon$ *vs.* the concentration of 3,3′,4,4′-TCBP in DCE measured at 400 (×), 430 (●), and 800 nm (■)

Table. Absorption maxima and radiation chemical yields (expressed in terms of $G\varepsilon$) determined in pulse-irradiated N_2-saturated DCE solutions containing 1×10^{-3} mol dm^{-3} of PCB. The decay rate constants were measured in solutions containing 1×10^{-2} mol dm^{-3} of PCB; second-order rate constant defined by $-d[\times]/dt = 2k[\times]^2$

Compound	Spectral type	$\lambda_{max.}$/nm	$G\varepsilon$	Decay rate constant $(2k/G\varepsilon)^a$
3,3′,4,4′-TCBP	I	430	6 000	5.7×10^6
		400	4 900	3.4×10^6
3,4-DCBP	I	407	6 100	$1.1 \times 10^{5\,b}$
		379	5 300	$1.1 \times 10^{5\,b}$
4-CBP	I	414	10 500	4.0×10^6
		385	8 600	4.5×10^6
4,4′-DCBP	I	420	8 300	6.7×10^6
		388	5 600	5.6×10^6
2,2′,4,4′,5,5′-HCBP	II	400	3 200	1.3×10^7
2,2′,5,5′-TCBP	II	400	8 300^c	1.1×10^7
3,5-DCBP	III	397	5 900	$7.7 \times 10^{5\,b}$
		380	6 400	$7.7 \times 10^{5\,b}$
2,3,4,4′,5-PCBP	III	407	3 300	Not determined
		392	3 400	5.7×10^6
3-CBP	III	401	8 600	1.3×10^7
		373	8 600	6.9×10^6

^{a} In mol^{-1} dm^3 s^{-1} except where otherwise indicated. ^{b} First-order decay rate in s^{-1}. ^{c} Measured in solutions containing 2,2′,5,5′-TCBP (0.1 mol dm^{-3}).

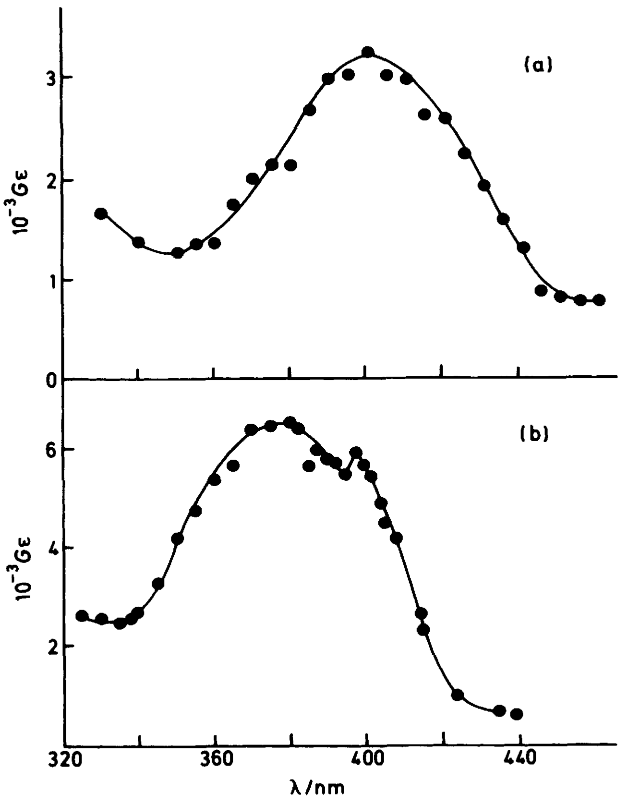


Figure 3. Absorption spectra of pulse-irradiated N_2-saturated solutions of (a) 2,2′,4,4′,5,5′-HCBP (1×10^{-3} mol dm^{-3}) in DCE, and (b) 3,5-DCBP (1×10^{-3} mol dm^{-3}) in DCE, respectively

cation. Besides the absorption(s) in the 400 nm wavelength region, each PCB$^{+\bullet}$ radical cation displayed an additional absorption band around 800 nm. The actual absorption maxima of these i.r. bands could not be determined, however; therefore reference to these absorbances has been omitted from the Table. In the case of 2,2′,4,4′,5,5′-HCBP also a slight shoulder around 550 nm was observed.

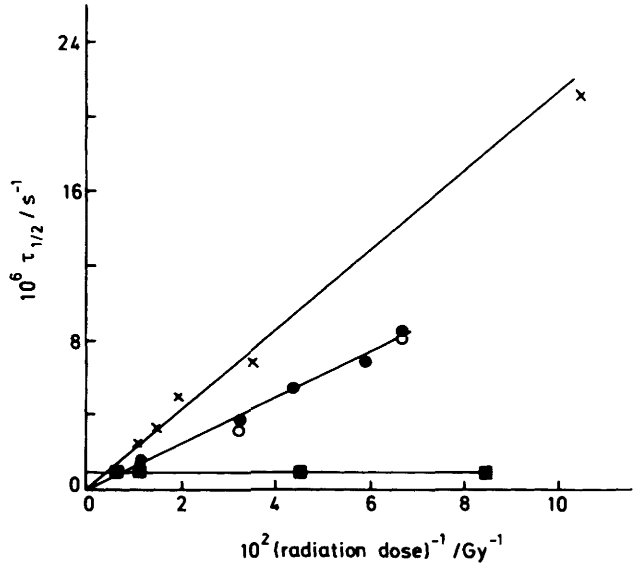


Figure 4. First half-lives *vs.* the inverse of the radiation dose for the disappearance of the radical cations derived from 3,3′,4,4′-TCBP [measured at 400 (×), 430 (●), and 800 nm (○)] and from 3,5-DCBP [measured at 380 nm (■)], respectively

(b) *Decay Kinetics.*—The decay kinetics of the various PCB$^{+\bullet}$ radical cations were determined at their respective absorption maxima. By measuring the first half-lives at different applied radiation doses (*i.e.* PCB$^{+\bullet}$ concentrations) a distinction between monomolecular decay pathways (first-order in radical concentration) and bimolecular pathways (second-order in radical concentration) was possible. The actual concentration of PCB$^{+\bullet}$ radical cations in our experiments is unknown. Only the product $G\varepsilon$ can be measured; hence one of the two parameters has to be determined independently. However, since the radical concentration is linearly correlated with the absorbed dose, a plot of $t_{\frac{1}{2}}$ *vs.* the inverse of the dose can be used to distinguish between first-order and second-order processes. This is illustrated in Figure 4 for two different PCBs.

The radical cations derived from 3,3′,4,4′-TCBP (type I) decay bimolecularly. Plots of $t_{\frac{1}{2}}$ *vs.* dose^{-1} yielded straight lines passing through the origin for all three absorption bands, implying that there is no contribution from any monomolecular decay. However, it is important that two different types of decay kinetics were found. The absorptions peaking at 430 nm and at around 800 nm (full circles and open circles in Figure 4, respectively) decay with the same rate within experimental error. The 400 nm absorption, on the other hand, decays more slowly (crosses). This finding strongly suggests that at least two different species result from the oxidation of 3,3′,4,4′-TCBP.

The radical cation of 3,5-DCBP (type III) decays monomolecularly. The half-life of the decay process was 0.9 μs, independent of the radiation dose (*i.e.* the concentration of 3,5-DCBP$^{+\bullet}$) (squares in Figure 4; in these experiments the pulse width was <0.5 μs).

The kinetic analysis was carried out for nine PCBs and the results are included in the Table. Most of the compounds tested were found to decay in pure second-order processes under the experimental conditions. In these cases the decay rate constants can only be given as $2k/G\varepsilon$, since the radical concentration c is unknown. It is interesting that the radical cations which

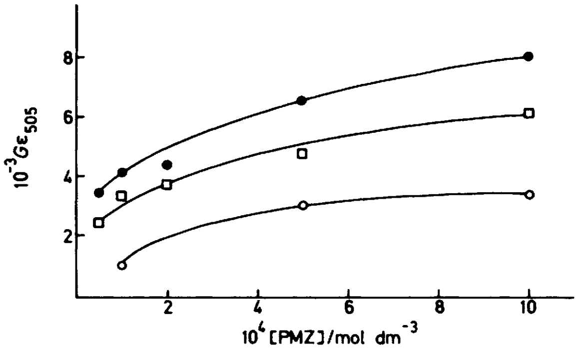


Figure 5. Yields of PMZ$^{+\bullet}$ radical cation (expressed as $G\varepsilon_{505}$) *vs.* the concentration of PMZ in N_2-saturated DCE solutions containing 1×10^{-2} mol dm^{-3} 4-CBP (●), 3,3′,4,4′-TCBP (□), and 2,2′,4,4′,5,5′-HCBP (○), respectively

exhibited type I spectral characteristics showed a different kinetic behaviour of the two absorption bands around 400 nm. The species absorbing at the shorter wavelength was always found to be longer lived. In those cases, where a kinetic analysis was possible, it was also found that the i.r. absorption band around 800 nm decayed with the same rate as the low-energy and shorter lived band around 400 nm.

3,5-DCBP$^{+\bullet}$ was the only radical cation which decayed purely monomolecularly. Mixed-order decay kinetics were observed for the radical cation derived from 3,4-DCBP. In this case the second-order process prevailed only at high radiation doses (>20 Gy), *i.e.* at high radical concentration. At low doses (around 5 Gy), however, hardly any change of $t_{\frac{1}{2}}$ with varying dose could be detected, indicating that the monomolecular decay is the main decay pathway under these conditions. For this species only the first-order decay rate at low doses has been included in the Table.

(c) *Estimation of the Radiation Chemical Yield.*—As already mentioned, the radiation chemical yield of PCB$^{+\bullet}$ formation, *i.e.* the *G* value, cannot be calculated as long as the extinction coefficients are unknown. Therefore, an indirect determination of the *G* value was attempted by adding a specific scavenger, which upon reaction with PCB$^{+\bullet}$ would yield a new species with known absorptivity. In principle, any solute with an ionization potential less than that of the PCBs should be able to reduce the PCB$^{+\bullet}$ radical cations to the neutral molecules. For example, in pulsed DCE solutions containing 3,3′,4,4′-TCBP (1×10^{-2} mol dm^{-3}) and varying small concentration of promethazine (PMZ), the natural decay of all absorption bands is accelerated with increasing PMZ concentration. Furthermore, the decay of the PCB$^{+\bullet}$ radical cations is accompanied by the formation of a new absorption with $\lambda_{max.}$ 505 nm. An identical absorption had previously been detected upon pulse radiolysis of aqueous solutions of promethazine hydrochloride (PMZH$^+$), and was assigned to the PMZH$^{2+\bullet}$ radical cation.[19] Therefore, it is suggested that the one-electron oxidation reaction (6) accounts

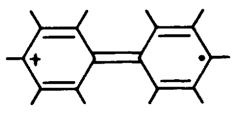
$$3,3',4,4'\text{-TCBP}^{+\bullet} + \text{PMZ} \xrightarrow{k_6} 3,3',4,4'\text{-TCBP} + \text{PMZ}^{+\bullet} \quad (6)$$

for our experimental observations in DCE solution. (The oxidation potential of PMZH$^+$ in aqueous solution is +0.865 V.[19]) As expected, the absorption of the 3,3′,4,4′-TCBP$^{+\bullet}$ radical cation decayed exponentially, with the rate inversely proportional to the concentration of PMZ. From the slope of the standard kinetic plot (ln $2/t_{\frac{1}{2}}$ *vs.* [PMZ]) the bimolecular rate constant $k_6 = 8.3 \times 10^9$ dm^3 mol^{-1} s^{-1} was derived for the PMZ oxidation. The yield of reaction (6) as determined by PMZ$^{+\bullet}$ formation depends strongly on the PMZ concentration used, since this reaction competes with the decay reaction of the radical cation.* This is illustrated in Figure 5 (squares). At very high PMZ concentrations $G\varepsilon_{505}$ levels off at an upper limit, suggesting that all PCB$^{+\bullet}$ radical cations have been scavenged by PMZ according to reaction (6). It can be assumed that the ε value of PMZ$^{+\bullet}$, which is known to be 9 500 dm^3 mol^{-1} cm^{-1} at 505 nm in aqueous solution,[19] is very similar in DCE, because the spectra of the unoxidized compounds (PMZ in DCE and PMZH$^+$ in water) are almost identical in the two solvents. Therefore, the *G* value for PMZ$^{+\bullet}$ formation, and hence for the formation of 3,3′,4,4′-TCBP$^{+\bullet}$, is found to be 0.65. Identical experiments have been carried out using 4-CBP and 2,2′,4,4′,5,5′-HCBP (full circles and open circles, respectively, in Figure 5). The *G* values for PMZ$^{+\bullet}$ formation, estimated again from the high PMZ concentration values, amounted to 0.86 for 4-CBP$^{+\bullet}$ and 0.36 for 2,2′,4,4′,5,5′-HCBP$^{+\bullet}$.

Discussion

This paper demonstrates for the first time that transient species are derived from various PCBs. These species, which have been obtained *via* pulse radiolysis in DCE, exhibit optical absorptions around 400 nm and in the near-i.r., and have been unambiguously shown to be the respective radical cations.

Several interesting trends emerge from the results. Both the spectra and the decay kinetics of PCB$^{+\bullet}$ are highly dependent on the chlorine substitution pattern. For example, type I spectra, with two distinct and well resolved absorption bands around 400 nm, were only observed for those PCBs which contained at least one chlorine atom in the *para*-position (at C-4) and which lacked *ortho*-chlorine substituents (at C-2, -2′, -6, or -6′). For the four compounds investigated which yielded type I spectra, the presence of at least two different transients is indicated. As already mentioned, the two low-energy bands always exhibited the same decay rate while the short-wavelength absorption band was significantly longer lived. However, all optically observable species are apparently PCB radical cations and have practically identical chemical properties. This conclusion is based on the observation that the absorption bands disappeared at the same rate in the presence of an oxidizable substrate such as promethazine. Therefore it is suggested that a one-electron oxidation of PCBs *via* reaction (5) yields two different radical cations with one and two electronic transitions, respectively, in the optical detection range from *ca.* 250—800 nm. In the light of the energy barriers to free rotation about the 1,1′-bond, various stable conformations of the PCB$^{+\bullet}$ radical cation may be envisaged. We postulate that the species which absorbs in the i.r. and is also responsible for the low-energy band in the 400 nm range is planar. This would ensure maximum π-orbital overlap and, consequently, should have a low-energy transition. The increased planar character of the possible mesomeric structure (1) is also in agreement with the


(1)

experimental finding that the 1,1′-rotational barrier is generally much larger in biphenyl radical cations than in their neutral counterparts.[20,21]

Normally, biphenyl and substituted biphenyls do not reside

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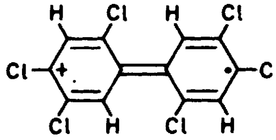
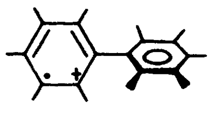
* As expected a strong dependence of PMZ$^{+\bullet}$ formation on the applied dose was observed. All experiments for the evaluation of ε were carried out at about 10 Gy.

in a planar conformation, even when free rotation about the 1,1′-bond is possible.[22–24] This rotation requires, however, sufficient energy to overcome the repulsive effects of the substituents at the 2-(2′-) and 6-(6′-) positions; the energy required depends on the size of the *ortho*-substituents. Also PCBs possessing two *ortho*-chlorine atoms would not normally assume a planar conformation. However, their radical cations may do just that, as is indicated by the near-i.r. absorbance. Apparently, the energy gain in establishing the expanded π-system is larger than that due to repulsion of the *ortho*-substituents. This may be possible because the two *ortho*-chlorine atoms (*e.g.* 2,2′,4,4′,5,5′-HCBP) may be opposite to each other [see (**2**)]. On the basis of these considerations it can be assumed that the yield of planar conformation and thus the intensity of the i.r. band is reduced with increasing chlorine substitution at the *ortho*-positions.*



(**2**)

The other, high-energy absorption bands are attributed to $PCB^{+\bullet}$ radical cations, where the two phenyl rings are twisted [see (**3**)]. The structure of such radical cations would largely resemble that of neutral PCBs, for which an average angle between the phenyl rings has been reported to be around 30°.[23–26]



(**3**)

The population of the two conformers is expected to depend on the substitution pattern. For PCBs without any *ortho*-chlorine atoms the largest energy gain would be expected for the planar conformation, and hence this conformation should be relatively more populated than for other PCBs. Type I spectra, which are typical for this situation, are accordingly observed only for PCBs without *ortho*-chlorine substituents. However, when the planar conformation becomes energetically less favourable, the high-energy absorption bands dominate and type II and type III spectra result from the overlap of the two bands at around 400 nm. Another feature which may contribute to the distribution of radical cations between the planar and twisted conformations is *para*-substitution. Radical cations from PCBs which possess only hydrogen atoms in the *ortho*-positions and lack *para*-chlorine substituents showed type III spectra, although type I spectra might have been expected. Apparently, the *para*-chlorine atoms afford an additional strong stabilization of the planar conformation and result in a corresponding higher population. This stabilization effect may be attributed to the $+M$ effect of chlorine atoms, most pronounced when Cl is aligned with the 1,1′-double bond.

Estimation of the extinction coefficients is difficult, since at least two different $PCB^{+\bullet}$ radical cations are formed and their respective *G* values cannot be determined independently. However, by using the total measured *G* for both bands, lower limits for ε can be derived. The values thus determined are: (a) 3,3′,4,4′-TCBP: $\varepsilon_{400} \geqslant 12\,400$, $\varepsilon_{430} \geqslant 14\,900$; (b) 2,2′,4,4′,5,5′-HCBP: $\varepsilon_{400} \geqslant 14\,400$; and (c) 4-CBP: $\varepsilon_{414} \geqslant 19\,500$, $\varepsilon_{385} \geqslant 16\,000$ dm^3 mol^{-1} cm^{-1}. The only other ε value reported[8] for biphenyl radical cations in acidic aqueous solution ($\varepsilon_{380} = 19\,000$ dm^3 mol^{-1} cm^{-1}) is in general agreement and on this basis it can be assumed that ε values of unsubstituted and chlorine-substituted biphenyl radical cations do not vary to any great extent.

Since the oxidation of PCBs [reaction (5)] is in competition with the self-decay of the solvent radical cation, the *G* value for $PCB^{+\bullet}$ formation depends on the concentration of PCB (see previously). At a given PCB concentration the *G* values are also indicative of the rate constants of oxidation of various PCBs. According to the theory of Marcus,[27] the rate constants for electron-transfer processes are correlated with the difference in oxidation potentials between donor molecule (in our case PCB) and acceptor molecule ($DCE^{+\bullet}$), *i.e.* the bigger the difference, the larger the rate constant for the process. From the present results we conclude that the ease of PCB oxidation decreases in the order 4,4 DCBP ~ 3,3′,4,4′-TCBP > 2,2′,4,4′,5,5′-HCBP ⩾ 2,2′,5,5′-TCBP.

For substrates displaying type I spectra the planar radical cations were always shorter lived than the twisted species. This finding appears surprising, since radical cations with the larger conjugated π system should be thermodynamically more stable. A satisfactory explanation is, however, provided by the following considerations on the generally bimolecular decay of these species. In principle, two processes, namely reaction (7) or

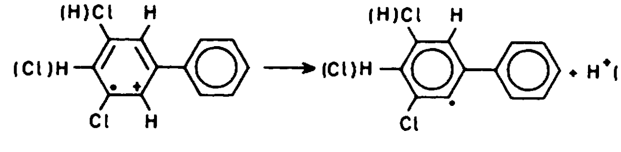
$$PCB^{+\bullet} + PCB^{+\bullet} \longrightarrow PCB + PCB^{2+} \quad (7)$$

a reaction (8) of a secondary species A, resulting from radiolysis

$$PCB^{+\bullet} + A \longrightarrow \text{products} \quad (8)$$

of DCE, with $PCB^{+\bullet}$ can be envisaged for the bimolecular decay. Reaction (7) requires sufficient π-orbital overlap of two $PCB^{+\bullet}$ radical cations. This would be more effective in the case of the planar radical cations, since steric restrictions are minimal and the two species can easily adopt a sandwich-like structure. On this basis, the experimental findings suggest that reaction (7) is the main decay pathway for $PCB^{+\bullet}$. Another plausible explanation is, of course, that the population of the two types of radical cation is significantly different.

Monomolecular decay pathways are also possible, as has been observed for $3,5\text{-}DCBP^{+\bullet}$ and $3,4\text{-}DCBP^{+\bullet}$. This can be explained by a deprotonation process, which may be accelerated by the *meta*-chlorine substituent [reaction (9)]. Such a reaction has, in fact, been proposed to account for the observed first-order decay of the biphenyl radical cation, which occurs with rate constants of 5×10^3 s^{-1} in acidic aqueous solution[8] and 2.4×10^5 s^{-1} in 1,1-dichloroethane.[28] In principle, deprotonation reactions are expected for all $PCB^{+\bullet}$ radical cations which still carry a hydrogen atom. Our experimental results imply that such processes have very low rate constants (possibly $\leqslant 5 \times 10^3$ s^{-1}) for most $PCB^{+\bullet}$ radical cations in DCE, and that they cannot compete with the bimolecular decay under pulse radiolysis conditions. In biochemical systems, however, a bimolecular radical–radical interaction would be rather unlikely, in view of the low steady-state radical concentrations. Therefore, $PCB^{+\bullet}$ radical cations, if formed, would be sufficiently long lived to reach vital cellular sites and inflict damage on biological targets.



(9)

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* Work is in progress for synthesis of such compounds in the required amounts.

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