Radical Cations of Polychlorinated and Polybrominated Biphenyls in 1,2-Dichlorethane: A Pulse Radiolysis Study

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The pulse radiolysis of polychlorinated (PCBs) and polybrominated biphenyls (PBBs) in 1,2-dichloroethane has been investigated. The radical cations exhibit specific absorption spectra with one or two bands in the u.v., and one weak transition in the near i.r. region. The latter are red shifted relative to the corresponding absorption band of the plain biphenyl radical cation. *ortho*-Substitution leads to a blue shift while *meta*-substitution exerts only a weak effect on the absorptions in the u.v. The life-times of both *meta*- and *ortho*-substituted biphenyl radical cations are decreased relative to that of the unsubstituted biphenyl species. Radical cations of *ortho*-substituted PCBs and PBBs, as well as those containing many vicinal halogen atoms, decay by approximately first-order kinetics. The underlying reaction is assumed to be deprotonation. Radical cations of biphenyls with *para*-substituents show a red shift in the u.v. absorption and an increase in life-time relative to the corresponding properties of the unsubstituted biphenyl species. Their decay occurs mostly by second-order kinetics. On the basis of these physico-chemical characteristics a probable structure is suggested for the radical cations of halogenated biphenyls.

Polyhalogenated biphenyls, *e.g.* polychlorinated (PCBs) and polybrominated (PBBs) have been widely used as plasticizers, transformator oils, organic dilutents, and flame retardants. Although their use has now been limited in many countries, they can still be found in animal fat and human adipose tissue. Investigation of the toxicity of polyhalogenated biphenyls has shown that they induce a specific spectrum of biologic and toxic effects. The brominated analogues seem to be more toxic than the corresponding chlorinated derivatives.[1] The most toxic polyhalogenated biphenyls are those which can assume a coplanar structure but the underlying mechanism is incompletely understood.[1] Recently we reported a pulse radiolysis study which described the optical and kinetic characteristics of radical cations of PCBs.[2] Two types of radical cations were identified. Either planar or twisted structures were proposed for these intermediates. Our recent study on the pulse radiolysis behaviour of monohalogenated biphenyls showed that the radical cations of these compounds have similar absorption and decay characteristics to those of biphenyl itself.[3] A correlation of the frequencies of the absorption bands in the near i.r. to ionization potentials from photoelectron spectra provided evidence that monohalogenated biphenyls may undergo at least partial planarization upon radical cation formation. In contrast to the reported results on PCB radical cations, only one transient type was observed. In order to clarify these differences and to gain more information about the absorption and decay characteristics of such radical cations, a more systematic pulse radiolysis study of several PCBs and PBBs has now been undertaken and the results are presented and discussed in this paper.

Experimental

The mono- and polyhalogenated biphenyls are named by listing the substitution site and the halogen atom; the word biphenyl is omitted (*e.g.* 2-chlorobiphenyl: 2-Cl). 4-Cl, 2-Br,

3-Br, and 4-Br were purchased from Aldrich; 2,2′-Cl and 3,3′,4,4′-Cl from Riedel-de Häen, 4,4′-Br from Kodak, 2-Cl from Ventron and 3,4-Cl from Promochem. The others were synthesized as described.[4–6] The compounds were redistilled under oil vacuum or recrystallized from methanol before use.

The PCBs and PBBs were dissolved in freshly distilled 1,2-dichloroethane (DCE), which is an ideal solvent for radiation chemical studies on radical cations, particularly from water-insoluble compounds.[7–8] The solutions (10^{-3} mol dm^{-3}) were de-aerated by bubbling with nitrogen. All experiments were carried out at room temperature. Due to the lack of a specific dosimeter in DCE the radiation chemical yields are given in terms of $G\varepsilon$ and calculated on the basis of an aqueous thiocyanate dosimeter[9] taking into account the differences in density of water (1.0) and DCE (1.256). G is defined as the number of species produced or destroyed per 100 eV absorbed radiation dose ($G = 1$ corresponds to 0.104 μmol J^{-1}). Typical doses per pulse were 3.8 and 15 Gy (1 Gy = 1 J kg^{-1}) in DCE. The pulse radiolysis set up and procedures for optical detection and data analysis have been described.[10]

Results and Discussion

Absorption Spectra.—Upon pulse radiolysis of PCBs and PBBs in DCE solution, radical cations are produced which display transient absorptions in the u.v. region (one or two bands, 370–420 nm) and in the near i.r. region (usually one weaker band). The radical cation formation *via* the general reaction:

$$(1,2\text{-DCE})^{+\bullet} + \text{PCB} \longrightarrow (\text{PCB})^{+\bullet} + 1,2\text{-DCE} \quad (1)$$
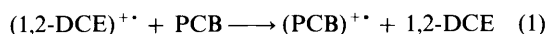
and their identification has been elaborated in detail in our previous publications.[2,3] Absorption maxima, radiation chemical yields, and half-lives of the various radical cations from PCBs and PBBs are summarized in Table 1 and Table 2, respectively.

Table 1. Absorption maxima, radiation chemical yields (expressed in terms of $G\varepsilon^a$) and first half-lives determined in pulse-irradiated 10^{-3} mol dm^{-3} N_2-saturated DCE solutions of mono- and poly-chlorinated biphenyls.

Compound	λ_1/nm	λ_2/nm	λ_3/nm	$G\varepsilon_1$	$G\varepsilon_2$	$G\varepsilon_3$	$\tau_{\frac{1}{2}}$/μs[b]	$\tau_{\frac{1}{2}}$/μs[c]
Biphenyl	370	392	690	9 400		9 800	5 600	22	10
2-Cl[d]		380	740		5 200		3 300	13	7
3-Cl[d]	372[e]	398[e]	710	7 800		7 300	4 300	11	7
4-Cl[d]	380[e]	412[e]	720	11 500		11 200	7 000	30	14
2,4-Cl	380	394 sh[f]	790	4 900		4 500	2 900	12	7
2,5-Cl		378	730		4 000		2 100	9	5
2,6-Cl		382	700		6 800		3 200	16	15
3,4-Cl	382[e]	410[e]	745	11 500		13 600	7 000	18	10
3,5-Cl	380	397 sh	720	7 600		8 000	5 000	4	3
2,2'-Cl		372	830		4 200		2 400	4	4
4,4'-Cl	392[e]	422[e]	805	11 200		17 600	7 000	32	15
2,3,4-Cl	382.	395 sh	835	9 300		8 000	6 500	14	10
2,4,5-Cl	382	404	810	7 600		6 400	4 600	8	7
2,4,6-Cl		385	>850		4 300		ca. 2 200	7	6
3,4,5-Cl	385	412	800	8 400		8 000	5 700	7	5
2,3,4,5-Cl	390	400 sh	830	7 000		6 600	3 600	6	5
2,3,4,6-Cl		388	>850		3 600		ca. 800	4	4
2,3,5,6-Cl		378	—		3 200		—	5	5
2,2',4,4'-Cl		390	840		7 000		3 300	12	8
3,3',4,4'-Cl	400[e]	430[e]	810	12 800		15 200	8 000	17	10
2,2',4,4',5,5'-Cl		398[e]	—		5 100		—	7	6

[a] In mol^{-1} dm^3 cm^{-1}. [b] 3.8 Gy. [c] 15 Gy. [d] See also ref. 3. [e] See also ref. 2. [f] sh = shoulder.

Table 2. Absorption maxima, radiation chemical yields (expressed in terms of $G\varepsilon^a$) and first half-lives determined in pulse-irradiated 10^{-3} mol dm^{-3} N_2-saturated DCE solutions of mono- and poly-chlorinated biphenyls.

Compound	λ_1/nm	λ_2/nm	λ_3/nm	$G\varepsilon_1$	$G\varepsilon_2$	$G\varepsilon_3$	$\tau_{\frac{1}{2}}$/μs[b]	$\tau_{\frac{1}{2}}$/μs[c]
Biphenyl	370	392	690	9 400		9 800	5 600	22	10
2-Br[d]		377	770		5 600		2 800	12	6
3-Br[d]	373	390	720	9 200		8 800	5 200	10	8
4-Br[d]	388	412	760	10 400		9 600	8 000	26	12
2,4-Br		390	820		6 400		5 200	16	8
2,5-Br		385	780		4 400		2 500	15	10
2,6-Br		388	700		3 500		1 600	10	9
3,4-Br	390	410	790	12 000		12 000	8 800	15	10
3,5-Br		380	820	10 400			5 400	7	5
4,4'-Br	400	430	820	14 400		15 000	8 800	22	9
2,4,5-Br		390	820		6 200		3 200	6	5
2,4,6-Br		390	690		4 200		1 800	12	8
3,4,5-Br		396	820	10 000			3 500	5	5
2,3,4,5-Br		396	840		5 600		2 200	5	4
3,3',4,4'-Br	406	432	820	11 000		11 500	4 900	12	8
3,3',5,5'-Br		380	800	8 800			1 100	6	4
3,3',4,4',5,5'-Br	412	438	—	10 200		10 000	—	5	3

[a]−[d] See footnotes Table 1.

As can be seen, *para*-substitution leads to a red shift in absorption maxima of the u.v. bands compared with that of the unsubstituted biphenyl radical cation (*e.g.* 4-X, 4,4'-X), while *meta*-substituents do not exert a strong effect on the position of these bands (*e.g.* 3-X, 3,5-X, 3,3'5,5'-X). A characteristic feature of *ortho*-substituted radical cations is that only one band can be

recognized in the u.v. spectrum. Its maximum is slightly blue shifted with respect to the centre of the two biphenyl radical cation u.v. bands (*e.g.* 2-X, 2,2'-X). A single u.v. band only is also detected for radical cations of highly *meta*-substituted PBBs, *e.g.* 3,5-Br and 3,3',5,5'-Br. On the basis of our experiments we cannot provide a rationale for this. It is possible that the two

bands are just too close to each other to be resolved under the experimental conditions. The observation that in some cases the u.v. spectrum contains a shoulder may support this interpretation. The fact that the radical cation of unsubstituted biphenyl shows two absorption bands in the u.v. has been discussed already in the study on pulse radiolysis of mono-halogenated biphenyls.[3] The single band described in an earlier publication[14] is probably born from a much lower spectral resolution of the experimental set up. Similar effects with respect to *ortho*-substitution have been observed in u.v. spectra of PCBs, PBBs, and 2-fluorobenzidine.[11-13] The blue shift had been explained by a slight steric influence of the *ortho*-substituents on the coplanarity of the molecules and it is suggested that this also pertains to our radical cations. Looking at our present results these hypso- and batho-chromic shifts of the absorption maxima appear to be additive.

The i.r. bands of all radical cations of PCBs and PBBs investigated are red-shifted relative to that of biphenyl, as is apparent from Tables 1 and 2. Higher halogen substitution induces an additive effect; the i.r. bands are widely shifted (100–150 nm).

By comparing the transient absorption bands of the PCB and PBB radical cations, it can be recognized that *ortho*-substitution leads to a decrease and *para*-substitution to an increase in intensity relative to the biphenyl radical cation itself. A similar effect has been observed in the u.v. spectra of halogenated benzenes.[15] Any further quantification of these observations is not justified, however, since our absorption measurements can only be given in terms of $G\varepsilon$. Our assumption that the actual yield (*i.e. G*) does not differ very much for the various species at any given solute concentration is probably valid. But a relatively high error limit (possibly $\pm 50\%$) must be allowed, owing to the fact that radical cation formation according to reaction (1) is imbedded into a rather complex kinetic scheme.[2,3]

In most cases the i.r. bands have a lower intensity than the u.v. bands (*ca.* 1:2). Comparatively still much weaker i.r. absorptions are observed for the radical cations of 3,3',5,5'-Br (*ca.* 1:8), and 2,3,4,6-Cl (*ca.* 1:4), and two of the investigated PCB- (2,3,5,6-Cl and 2,2',4,4',5,5'-Cl) and one of the PBB-radical cations (3,3',4,4',5,5'-Br) exhibit no visible i.r. band at all. From photoelectron spectra of some substituted biphenyls it is known that the i.r. bands are related to the planarity of the radical cations. In particular, it has been shown that the $\pi_3 \longrightarrow \pi_6$ energy separation is a measure of the dihedral angle.[16,17] Therefore, one may conclude that the lower intensities in the i.r. bands are due to steric factors which oppose planarization. The absorption in the i.r. may be related to an association of the radical cations with a ground-state molecule or the solvent (A) in equilibrium [reaction (2)].

$$X\text{-}BP^{+\bullet} + A \rightleftharpoons [X\text{-}BP \cdots A]^{+\bullet} \qquad (2)$$

In the case of polysubstituted bulky biphenyls the interaction of the radical cations with A can be hindered, resulting in a shift of the equilibrium to the left, and consequently in a lower intensity of the i.r. band.

Bromo- instead of chloro-substitution does not result in any significant changes. The corresponding λ_{max} are just slightly red-shifted for the PBB radical cations, while the absorption intensities are practically the same.

In a previous paper we postulated that two different radical cations are formed upon oxidation of various PCBs.[2] The distinction was based in different decay kinetics for the respective species. It was further postulated that the species which absorbs in the i.r. was responsible for the low-energy band of the u.v. absorptions and that this species should have a

high degree of planarity. The remaining u.v. band was related to a second, more twisted radical cation. The present work does not provide further support for this postulate. In several cases, where two u.v. bands were observed, no i.r. band was observed (3,3',4,4',5-Br, 2,2',4,4',5,5'-Cl) which is, however, not a conclusive argument against two different populations of transients. A more serious concern is based on the fact that absorption spectra of twisted cations of substituted benzenes were found to exhibit sharp bands between 500 and 600 nm.[18] No such absorption bands could be detected upon pulse radiolysis of PCBs and PBBs. Furthermore, photoelectron spectra of some substituted biphenyls[16] and pulse radiolysis of monohalogen-ated biphenyls[3] have demonstrated that all compounds investigated undergo at least partial planarization during the generation of the radical cations. Therefore one may conclude that the radical cations of PCBs and PBBs are generally more or less planar[19] and only one population of transients is observed, which exhibits one or two absorptions in the u.v. region and possibly another weaker absorption in the near i.r.

Decay Kinetics.—The first half-lives of the PCB- and PBB-radical cations were determined from the decay of their optical absorptions at the respective maxima. In all cases, all observable absorption bands show similar decay kinetics indicating that the observed spectrum can be attributed to a single transient species. This is consistent with the results obtained for the unsubstituted biphenyl radical cation described in the litera-ture[14,20,21] but in contrast to the decay kinetics described for some PCB radical cations in our previous paper.[2] The present results show that the radical cations of most of the PCBs and PBBs and of biphenyl itself decay by mixed-order kinetics. A mixed-order decay for the biphenyl radical cation has, in fact, also been described[14] in the literature; other authors have, however, observed a monomolecular decay.[20,21] The first half-life of the biphenyl radical cation in DCE has been found to be 1.3 μs (mixed order)[14] and 4 μs (first order);[21] exact doses have not been described in both cases. The present results show a first half-life of 22 μs at 15 Gy and 10 μs at 3.8 Gy (*cf.* Tables 1 and 2) for the unsubstituted biphenyl radical cation. These different observations are probably indicative of a general difficulty in establishing clean decay kinetics for ionic species in irradiated low-polarity solvents. Particularly the contribution of the geminate ion recombination kinetics (which include coulombic parameters and the spatial distributions of the ions) may be difficult to assess and could be influenced by small con-centrations of impurity in the solvent.

The first half-lives of the investigated radical cations at two different doses (3.8 Gy and 15 Gy) are summarized in Tables 1 and 2. Radical cations of the purely *para*-substituted com-pounds show a greater contribution of second-order decay (the half-lives are clearly dependent on the dose), while those with *ortho*-substituents, especially 2,2'-Cl, but also 2,3,4,5-Cl, 2,3,4,6-Cl, 2,2',4,4',5,5'-Cl, 2,4,5-Br, 3,4,5-Br, and 2,3,4,5-Br, decay preferentially by first-order kinetics.

As discussed for the pulse radiolytic investigations of mono-halogenated biphenyls[3] and other PCBs,[2] the first-order decay can be explained by deprotonation of the radical cations or reactions with molecules in the ground state, while dimerization of the PCB- and PBB-radical cations or reaction with free Cl⁻-ions (generated upon irradiation in DCE[7,8]) leads to the second-order decay. The pronounced tendency of purely *para*-substituted radical cations of biphenyls to decay *via* second-order kinetics can be explained by the electronic stabilization of the radical cation relative to that of the unsubstituted species.

Possible dimerization is suggested to occur preferentially from a planar state. This process would thus be favoured by *para*-substitution which stabilizes this conformation through a $+M$-effect, as has been discussed for radical cations of

monohalogenated biphenyls.[3] A similar stabilization would be expected by the *ortho*-substituents. The experimental results, however, reveal decreased life-times of the radical cations from *ortho*-substituted PCBs and PBBs and furthermore more or less pure first-order decay kinetics. This can be explained by the fact that such PCBs and PBBs do not undergo planarization upon formation of the corresponding radical cations to a degree which is necessary for dimerization. For these species deprotonation will probably be favoured and thus account for the exponential decay.

By comparing the life-times (Tables 1 and 2) it can be seen that all species decaying predominantly *via* first-order kinetics exhibit a similar life-time of about 3–6 μs which corresponds to a rate constant of $k = 1.1$–2.3×10^5 s^{-1}. This is of the same magnitude as the value of 2.4×10^5 s^{-1} derived by Ueda for the deprotonation of the biphenyl radical cation in DCE.[21] Another approach to the determination of the first-order rate constant was performed by deconvolution of the mixed-order decay. With this procedure a half-life of 2 μs was evaluated which corresponds to $k = 3.5 \times 10^5$ s^{-1}. It has to be considered that the presence of Cl$^-$-ions (from irradiation of DCE) possibly enhances the deprotonation. Second-order rate constants could not be extracted within reasonable limits from the mixed-order decay kinetics. Nor could our present kinetic measurements provide any support for our previous assumption of two distinguishable radical cations (planar and twisted, respectively[2]).

By comparing the life-times of the chloro- and bromo-analogues it can be seen that the first-order as well as the mixed-order reactions are not very much affected by the nature of the halogen.

In conclusion, radical cations from polyhalogenated biphenyls are readily formed in irradiated 1,2-DCE solutions. They exhibit distinct optical absorptions in the u.v. and i.r. which are indicative of planarization of the radical cations relative to the parent compounds. This possibly corroborates the observed dependence of planarity and toxicity of the PCBs and PBBs.[1] The decay kinetics of the radical cations are difficult to analyse and allow only limited quantitative conclusions.

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