Pulse Radiolysis of Monohalogenated Biphenyls. Correlation of Absorption Spectra of the Radical Cations with Photoelectron Spectroscopic Data

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Radical cations from monohalogenated biphenyls have been investigated by means of pulse radiolysis, and their optical and kinetic properties are compared with corresponding data for the biphenyl radical cation itself. While fluoro substitution does not exert a strong effect on the optical absorption characteristics and decay kinetics of the radical cations, *para*-substitution by chlorine, bromine, or iodine leads to a substantial red shift in the absorption maxima and an increase in the half-life. The maxima of the transient near i.r. absorption bands can be linearly correlated to ionization potentials from photoelectron spectroscopy. The data suggest that the investigated monohalogenated biphenyls undergo at least partial planarization upon radical-cation formation.

The radical cation of biphenyl in solution exhibits two absorption bands, one with a maximum around 380 nm and the other in the near i.r. at *ca.* 690 nm [1,2] which is in agreement with its absorption in glassy matrices.[3,4] A significant number of investigations have been concerned with the photoelectron spectra of biphenyls.[5-13] Some of these studies have compared PES data with the absorption spectra of radical cations obtained by pulse radiolysis of various compounds.[11,12] Another investigation has revealed that the absorption spectra in the red region correlate with the photoelectron spectra for $\pi_3 \longrightarrow \pi_6$ transition.[13] Maier and Turner found an empirical correlation between the separation of the first and fourth photoelectron bands and the dihedral angle (θ) of a group of substituted biphenyls.[5] They demonstrated that the $\pi_3 \longrightarrow \pi_6$ energy separation decreases from a maximum at $\theta = 0°$ to a minimum (zero) at $\theta = 90°$. The resulting ΔE-values are considered to be a measure of the degree of planarity. For the biphenyl radical cation which is planar in its excited state [14,15] ΔE is equal to 1.48 eV.[5,13] The measured values of ΔE suggest that some of the substituted biphenyls undergo a substantial structural change in the dihedral angle upon ionization resulting in partial planarization.[13]

Recently we reported a pulse radiolysis study of some polychlorinated biphenyls (PCBs) [16] and polyfluorinated biphenyls.[17] The biphenyl radical cation itself has also been investigated in great detail, but no systematic comparison has been made as yet between the absorption spectra of the radical cations of halogenated biphenyls and their respective photoelectron spectra. In order to study the influence of the halogen atom and the substitution sites on the positions of the absorption bands and the kinetic characteristics of halogenated radical cations, we have now conducted a pulse radiolysis investigation of monohalogenated biphenyls. The present work compares, in particular, the photoionization potentials (obtained from the literature [5,13]) with the absorption bands of the radical cations in the near i.r.

Experimental

The monohalogenated biphenyls are named by listing the substitution site and the halogen atom; the word biphenyl is usually omitted (*e.g.* 2-chlorobiphenyl: 2-Cl). 2-F, 4-F, 4-Cl, 2-Br, 3-Br, and 4-Br were purchased from Aldrich, 2-Cl was obtained from Ventron. The other compounds were synthesized by a Cadogan reaction of the corresponding halogenated anilines with benzene.[18] The compounds were redistilled under vacuum or recrystallized from methanol before use.

The pulse radiolysis set up and procedures for optical detection and data analysis have been described in the literature.[19] The solutions were generally exposed to short pulses of high-energy electrons (3.8 MeV). The pulse width was *ca.* 1 µs. Due to the low solubility of the compounds in water the monohalogenated biphenyls were dissolved in freshly distilled 1,2-dichloroethane (DCE) which is an ideal solvent for radiation chemical studies.[16,20,21] The solute concentration was generally 10^{-3} mol dm^{-3}. The samples were de-aerated by bubbling with nitrogen for *ca.* 1 h per dm^3. 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 are calculated on the basis of an aqueous thiocyanate dosimeter [22] 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}). The applied doses were generally 3.8 and 15 Gy pulse^{-1} (1 Gy = 1 J kg^{-1}) in DCE.

Results and Discussion

Absorption Spectra.—Pulse radiolysis of biphenyl and monohalogenated biphenyls in deoxygenated DCE yields characteristic transient absorption spectra. The absorption maxima, radiation chemical yields (in terms of $G\varepsilon$), and half-lives are summarized in Table 1.

All radical cations exhibit one or two absorption bands in the u.v. region (370–410 nm) and one weaker visible/near i.r. band at *ca.* 700 nm. The obtained absorption spectrum of the biphenyl radical cation correlates well with that described in the literature,[4] and the average of the two absorption bands at 370 and 392 nm fits well with the reported band at 380 nm.[4] Recording of the spectra occurred in 2 nm steps. The assignment of the transient spectra to the respective radical cations of the halogenated biphenyls (Hal-BP) is made on the same grounds as in previous publications on this subject.[4,16] The underlying chemistry of the radical-cation formation is as follows:

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

Compound	λ_1/nm	λ_2/nm	λ_3/nm	$G\varepsilon_1$	$G\varepsilon_2$	$G\varepsilon_3$	$\tau_{\frac{1}{2}}/\mu s$[b]	$\tau_{\frac{1}{2}}/\mu s$[c]
Biphenyl	370	392	690	9 400	9 800	5 600	22	10
2-F[d]	368	390	705	8 800	8 500	5 000	15	10
3-F[d]	370	391	700	8 600	8 500	4 500	13	8
4-F[d]	370	394	685	10 000	12 500	6 100	30	16
2-Cl	380		740	5 200		3 300	13	7
3-Cl[e]	372	392	710	7 800	7 300	4 300	11	7
4-Cl[e]	380	412	720	11 500	11 200	7 000	28	14
2-Br	377		770	5 600		2 800	12	6
3-Br	373	390	720	9 200	8 800	5 200	10	8
4-Br	388	412	760	10 000	9 600	8 000	26	12
2-I	380		695	6 400		3 600	20	18
3-I	374	392	690	10 800	13 900	5 400	15	9
4-I	376	405	750	8 600	13 700	3 400	32	16

[a] In mol^{-1} dm^3 cm^{-1}. [b] 3.8 Gy. [c] 15 Gy. [d] See also ref. 17. [e] See also ref. 16.

$$\text{1,2-DCE} \longrightarrow (\text{1,2-DCE})^{+\bullet} + e^- \qquad (1)$$

$$e^- + \text{1,2-DCE} \longrightarrow Cl^- + {}^{\bullet}CH_2CH_2Cl \qquad (2)$$

$$(\text{1,2-DCE})^{+\bullet} + e^-, Cl^- \longrightarrow \text{products} \qquad (3)$$

$$(\text{1,2-DCE})^{+\bullet} + \text{Hal-BP} \longrightarrow \text{1,2-DCE} + (\text{Hal-BP})^{+\bullet} \qquad (4)$$

This scheme includes a competition between the neutralization (mostly by a geminate recombination process) of the solvent radical cation by the electron or chloride ion [formed by reaction (1) and (2)] in reaction (3)[20,21] and the ionization of the halogenated biphenyl by reaction (4). Accordingly, the yield of $(\text{Hal-BP})^{+\bullet}$ radical cations is dependent on the solute concentration, and can be suppressed by any third competitor which also reacts with the oxidizing solvent radical cations. This latter aspect has, in principle, been investigated in an earlier study[16] and will not be elaborated on any further in this paper.

As can be seen in the Table, fluoro substitution does not exert any significant effect on the optical absorption spectra of the radical cations by comparison with that of the biphenyl radical cation itself. The transient absorption spectra of the *ortho*-substituted species, *i.e.* 2-Cl, 2-Br, and 2-I show only one absorption band in the u.v., a phenomenon which may be related to steric effects. It is, of course, also possible that the single band may actually be two unresolved bands. A comparison of the average values for the transient absorption bands in the u.v. region shows that *ortho*- and *meta*-halogen substitution hardly alters the position or intensities of the absorption bands but a substantial red shift is observed for the *para*-substituted analogues.

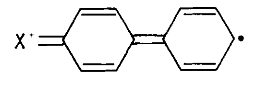
Except for 2-I and 3-I the radical cations of all other halogenated biphenyls show a significant red shift of the near i.r. band relative to that obtained from biphenyl itself. Similar red shift results have been observed for the absorption bands of a number of other substituted biphenyls in the vapour phase.[13]

The radiation chemical yields ($G\varepsilon$) are similar to those obtained for the biphenyl radical cation, except those of 2-Cl, 2-Br, and 2-I, *i.e.* the *ortho*-substituted species. Since lower extinction coefficients have also been observed in u.v. investigations of halogenated benzenes,[23] it would seem that the measured differences in $G\varepsilon$ primarily reflect the differences in ε rather than G. Alternatively, the lower $G\varepsilon$ values for the *ortho*-substituted species could be explained in terms of the slower scavenging reaction (4).

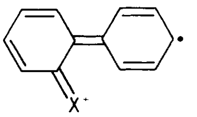
Decay Kinetics.—The decay of the radical cations was analysed at their respective absorption maxima. In all cases, all observable absorption bands show similar decay kinetics which were found to be neither clean first- nor second-order. The results rather show that all transients decay in a mixed-order manner, a decay mode which has also been described for the biphenyl radical cation in the literature.[4] The first half-lives measured at two doses (3.8 Gy and 15 Gy) of the radical cations of biphenyl and the monohalogenated biphenyls are listed in Table 1. Generally the radical cations of the *para*-substituted biphenyls are more stable than that of biphenyl itself while *ortho*- and *meta*-substitution leads to a decrease in the half-life.

The mixed-order decay makes an interpretation of these effects difficult; both the first- and second-order reactions are competitive. The first-order process, *i.e.* the exponential part of the decay, could be explained by a deprotonation of the radical cations—as has previously been assumed for radical cations of biphenyl itself[1,24]—and of polychlorinated biphenyls (PCBs).[16] Dimerization of the radical cations, or their reaction with chloride ions by reaction (3) could be responsible for the second-order decay. Evidence for dimerization of radical cations has, in fact, been described in the radiolysis of bromobenzene.[25] It is suggested that dimerization occurs preferentially from a planar state. Although experimental and theoretical investigations of biphenyl indicate that biphenyl can exist both in a twisted[26–29] and in a planar configuration[30,31] in the ground state, it is generally accepted that biphenyl in its excited state (triplet) as well as in its ionic state (radical cation, radical anion) has a planar conformation.[32–34] It has also been shown that planarization is assisted by substitution.[5,13] Assuming a planar state also for the radical cations of the monohalogenated biphenyls investigated in this study,[35] the *para*-substituents should particularly stabilize the transient radical cation by their $+M$-effect (Scheme 1).

This consideration thus provides a reasonable rationale for the comparatively long life-times of the *para*-substituted biphenyl radical cations. A similar stabilization effect is expected by the *ortho*-substituents (Scheme 2). Kinetically, however, this does not show up to the same extent. The corresponding radical cations of the *ortho*-substituted biphenyls are clearly longer



Scheme 1.



Scheme 2.

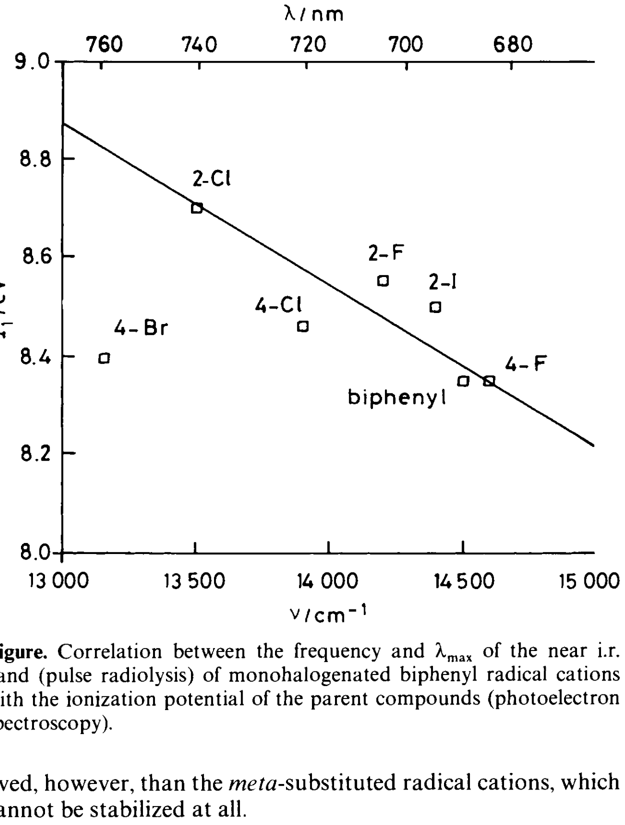


Figure. Correlation between the frequency and λ_{max} of the near i.r. band (pulse radiolysis) of monohalogenated biphenyl radical cations with the ionization potential of the parent compounds (photoelectron spectroscopy).

lived, however, than the *meta*-substituted radical cations, which cannot be stabilized at all.

The decrease in life-time of the *ortho*-substituted biphenyl radical cations (except 2-F) relative to the *para*-substituted species may be correlated with the conclusions obtained by photoelectron spectroscopy of some substituted biphenyls. The $\pi_3 \longrightarrow \pi_6$ energy separation (ΔE-value) is smaller for *ortho*-substituted biphenyls[5] which correlates with a bigger dihedral angle and less planarization upon formation of their radical cations. This, in turn, implies less resonance stabilization and consequently a higher reactivity. Similar effects have, in fact, been observed upon photolysis of polychlorinated and polybrominated biphenyls (PCBs and PBBs).[36–40] In this case *ortho*-substitution leads to an increase in dehalogenation rates.[36–40] These findings were also confirmed by the mass spectroscopic behaviour of PCBs.[41,42]

The radical cation of 2-I is longer lived than those of the corresponding F-, Cl-, and Br-analogues and, at higher doses, even than that of biphenyl itself. A similar kinetic stabilization effect by iodine has also been observed during photolysis of monoiodinated biphenyls where deiodination of the *para*-substituted compound occurred much faster than that of the 2-I.[43] An explanation for this particular behaviour of the iodo substituent cannot be given.

Since the rates of the possible first- and second-order reactions, and other possibly important parameters such as acidity and the exact conformation of the investigated radical cations (steric and mesomeric effects) are unknown or cannot be determined with sufficient accuracy, it is difficult to interpret the kinetic results satisfactorily.

Comparison with Results from Photoelectron Spectroscopy.— As has been mentioned already, it has been demonstrated that the ΔE-values ($\pi_3 \longrightarrow \pi_6$ separation energies) obtained by photoelectron spectroscopy[5] can be taken as a direct measure of the planarity of radical cations. Broad photoelectron bands in the near i.r. indicate substantial structural relaxation upon ionization.[13] Some ionization potential data I_1 (π_6) for monohalogenated biphenyls are available in the literature.[5] These are correlated with our experimental λ_{max} values in the Figure. Except for 4-Br all our λ_{max} values in the i.r. absorption bands of the radical cations fit well into a linear relationship with the observed ionization energies.

These results suggest that the monohalogenated biphenyls investigated undergo at least partial planarization upon formation of their respective radical cations.

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