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Unimolecular Dissociation of Benzyl Halide Radical Anions Studied by Low-Temperature Pulse Radiolysis

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The one-electron reduction of benzyl halides (BzX; X=F, Cl, Br) by solvated electrons in 2-methyltetrahydrofuran has been investigated by using a pulse radiolysis technique at different temperatures above 77 K. The radical anions of BzX ($\lambda_{\max}=300$ nm) formed by the capture of an electron in the π^*-orbital of the benzene ring dissociate into Bz$^\bullet$ ($\lambda_{\max}=320$ nm) and X$^-$ via Bz$^\bullet$/X$^-$ complexes ($\lambda_{\max}=340$ nm for BzCl and 370 nm for BzBr). The corresponding species were observed with 4-phenylbenzyl halide at 85 K and below. A spectral change observed at 95 K has been attributed to a structural change of the biphenylyl group. The dissociation rate of the radical anions increased in the order BzF<BzCl<BzBr. On the basis of these results, the reaction mechanism is discussed.

A one-electron reduction of aromatic halides produces a frangible radical anion which decomposes to the corresponding aryl radical and the halide ion. Mechanistic and kinetic studies have been undertaken by using electrochemical[1—3] and pulse radiolysis[4—6] techniques. The dissociation rate of the radical anions largely depends on the kind of halides and the aromatic residue.

Radiation chemical studies concerning the one-electron reduction of benzyl halides (BzX) have been performed mainly in organic glassy matrices γ-irradiated at 4 or 77 K.[7—12] Yoshida and co-workers[11,12] have observed charge-transfer bands of Bz$^\bullet$/X$^-$ complexes and free benzyl radicals. A gas-phase study has shown that the electron is accommodated in the π^*-orbital of the benzene ring before dissociation.[13] However, in the liquid or solid phase, such a radical anion has not yet been detected.

The present study was undertaken in order to clarify the mechanism of the one-electron reduction of BzX based on a direct observation of the transient species generated immediately after irradiation in the solid phase. Pulse radiolyses of BzX (X=F, Cl, Br) and 4-phenylbenzyl halide (PBzX; X=Cl) were carried out in a 2-methyltetrahydrofuran (MTHF) solution at different temperatures above 77 K. The mechanism of the unimolecular dissociation of the radical anion is discussed.

Experimental

Benzyl halides (BzF, BzCl, BzBr) obtained commercially were distilled under reduced pressure. PBzCl (Aldrich) was recrystallized from ethanol. The MTHF used as a solvent was distilled over sodium metal after being freed from peroxides. The solutions were degassed in a vacuum line and sealed into Suprasil quartz cells (optical path length, 10 mm).

The sample solutions, which were held in quartz cells mounted in a variable-temperature liquid-nitrogen cryostat (Oxford DN1704), were irradiated with an 8-ns pulse of 28 MeV electrons. The apparatus used for the pulse radiolysis experiments were described in a previous paper.[14]

Results and Discussion

The MTHF solutions of BzX and PBzCl were irradiated at different temperatures above 77 K, and the transient absorption spectra were measured at various times after the pulse. The spectrum of the trapped electrons generated in γ-irradiated MTHF at 77 K shows a peak at 1250 nm and an absorption tail extending at least to 400 nm.[15,16]

BzX. At 85 K and below, the spectra observed immediately after the pulse showed a peak at around 300 nm. As typical examples, the transient absorption spectra observed with BzCl and BzBr at 85 K are presented in Fig. 1, together with that of neat MTHF measured as a control. The spectrum observed at 180 µs after the pulse shows the formation of a new band with a peak at 340 nm for BzCl and 370 nm for BzBr and a growth of the 300 nm bands. However, at 80 K the 300 nm band alone grew over the same time interval. These new bands are very similar to the charge-transfer bands of Bz$^\bullet$/X$^-$ complexes ($\lambda_{\max}=340$ and 370 nm for BzCl and BzBr,[12] respectively) observed from MTHF glasses containing BzCl and BzBr γ-irradiated at 4 K.

The absorption band with a peak at 300 nm is very similar to that of the toluene radical anion (a peak at 300 nm and a weak, broad absorption in the visible region)[17] observed in the MTHF matrix γ-irradiated at 77 K. The latter weak absorption in the visible region is superimposed on the electron absorption tail, as shown in Fig. 1. Thus, the absorption around 300 nm suggests the formation of radical anions of BzX involving an unpaired electron in the π^*-orbital of the benzene ring.

On the other hand, when MTHF solutions of BzX were irradiated at 95 K, the 320 nm bands due to the benzyl radicals appeared immediately after the pulse irradiation, together with those of the radical anions and the complexes, and the 320 nm bands grew along with the decay of these species, as shown in Fig. 2. These results suggest that at 95 K the medium is fairly softened, i.e., the MTHF solutions of BzX do not change

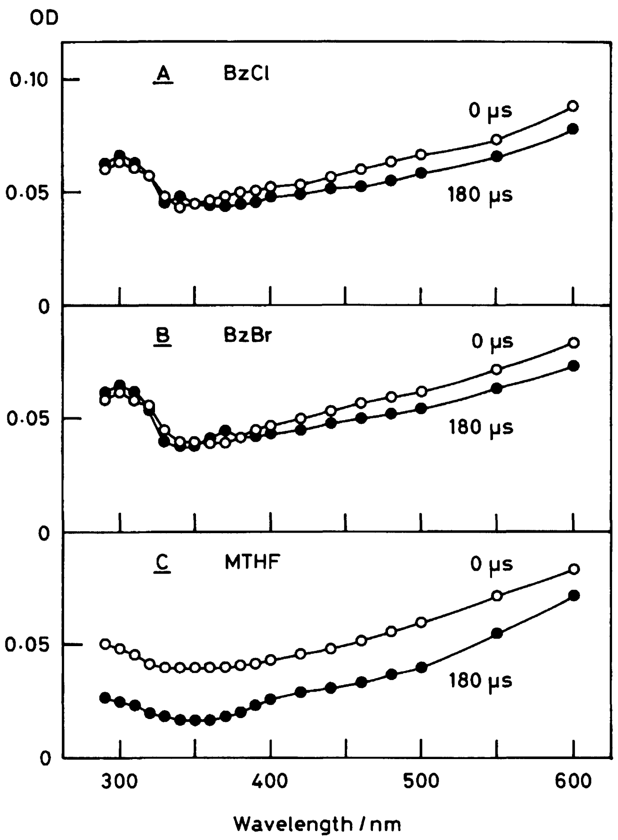


Fig. 1. Transient absorption spectra observed with benzylhalides (BzX; X=Cl, Br) in MTHF solutions (1×10^{-2} mol dm^{-3}) and neat MTHF at 85 K: (A) BzCl, (B) BzBr, and (C) neat MTHF; (○) end of the pulse, (●) 180 μs after the pulse. Absorption dose was 0.7 kGy/pulse.

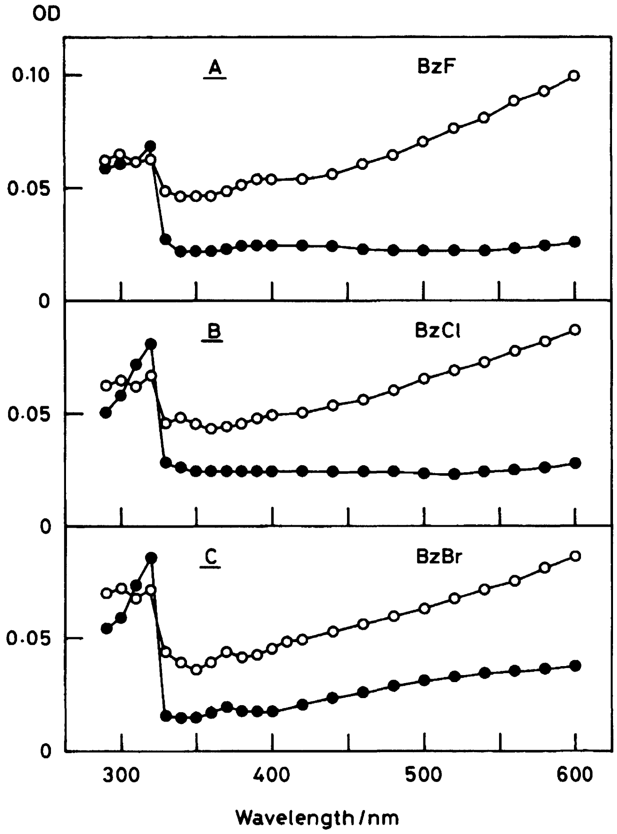
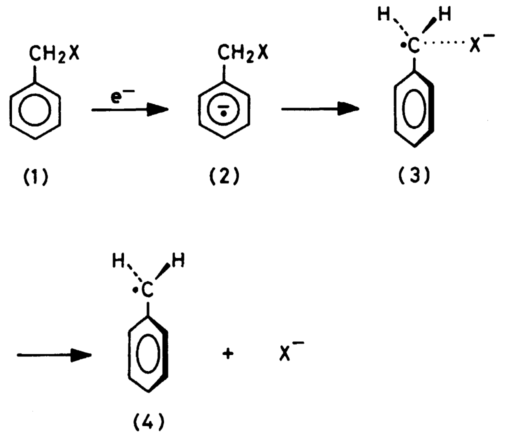


Fig. 2. Transient absorption spectra observed with benzyl halides (BzX; X=F, Cl, Br) in MTHF solutions (1×10^{-2} mol dm^{-3}) at 95 K: (A) BzF and (B) BzCl; (○) end of the pulse, (●) 180 μs after the pulse; (C) BzBr (○) end of the pulse, (●) 90 μs after the pulse. Absorption dose was 0.7 kGy/pulse.

to a glassy matrix. The growth rate of the 320 nm bands increased with an increase in the temperature. On the other hand, as the temperature increased, the 300 nm band of the radical anion (**2**) disappeared from the initial spectrum, successively, in the order BzBr> BzCl>BzF.

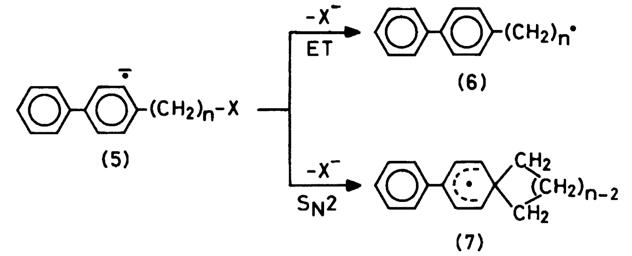
On the basis of these results, the sequence of events in the one-electron reduction of benzyl halide (**1**) can be depicted as shown in Scheme 1. That is, the reaction involves two successive distinct steps; the addition of an electron to give the radical anion (**2**), and then a cleavage of the C–X bond to form the benzyl radical (**4**) and the halide ion (X^-) via the complex (**3**). The latter reaction involves the shift of an electron from the benzene ring to the α-carbon atom (as described later).

Judging from the decay rate of the radical anion (**2**; $\lambda_{max}=300$ nm) in Fig. 2, it seems that the stability of the radical anions increases in the order BzBr<BzCl< BzF. This trend is consistent with those of the homopolar and heteropolar C–X bond dissociation energies in benzyl halides.[18] It can, therefore, be assumed that the dissociation of the C–X bond is the rate-determining step.



Scheme 1.

In a previous investigation concerning the intramolecular reaction of the radical anions of 1-(4-biphenylyl)-ω-haloalkane (**5**; $\lambda_{max}=410$ nm),[19] an electron transfer (ET) reaction yielding a terminal carbon radical (**6**) occurred competitively to an S_N2 reaction, leading to the production of a spirocyclic radical (**7**; $\lambda_{max}=330$ nm), as shown in Scheme 2. The ratio of the ET and S_N2 reactions changed as a function of the kind of halides,



Scheme 2.

the methylene chain length (n), and the polarity of the solvent.[20] However, a first-order kinetic plot of the decay of the 410 nm band showed a straight line in all cases; the rate constant measured from the decay of the 410 nm band showed good agreement with that observed from the formation of the 330 nm band. These results suggest that the ET and $\mathrm{S_N2}$ reactions proceed at the same time via a common intermediate, e.g., a loose association complex between a biphenyl radical anion and a terminal halide. Accordingly, it is clear that the ET and $\mathrm{S_N2}$ reactions involve a common mechanism, in which an electron is transferred from a biphenyl radical anion to a terminal carbon accompanied by a simultaneous release of the halide ion.

At the complex (**3**) formed as a transient intermediate during the course of the dissociation of the radical anion (**2**), planarity of the $\mathrm{PhCH_2}$ group ($\mathrm{sp^2}$) should be achieved, as illustrated in Scheme 1. However, this dissociation reaction is retarded in the rigid matrix formed at below 85 K (see, for example, Fig. 1). It thus seems that, in analogy with the cases of the ET and $\mathrm{S_N2}$ reactions (described above), the decay reaction of the radical anion (**2**) requires a deformation of the molecule, i.e., a stretching of the C–X bond and umbrella motion. Such a configurational change necessarily induces a vacant orbital in which an electron can be accepted at the backside of the stretched C–X bond (σ^*). It has consequently become feasible to form the transition state for loss of $\mathrm{X^-}$. The decay reaction of the radical anion (**2**) is considered to be an intramolecular ET reaction involving an electron shift from a benzene radical anion to an α-carbon accompanied by the simultaneous release of $\mathrm{X^-}$.

PBzCl. At 85 K the spectrum observed immediately after the pulse shows two main peaks at 300 and 320 nm and a weak absorption around 340 nm; these absorption bands grow with the decay of solvated electrons absorbing above 400 nm, as shown in Fig. 3(A). A similar spectrum was observed at 80 K. Although these absorption bands have not yet been reported for the spectra of the irradiated PBzX solutions, these absorption bands coincide with those of the radical anions of BzX (λ_{max}=300 nm), $\mathrm{Bz^\bullet}$ (λ_{max}=320 nm), and the $\mathrm{Bz^\bullet/Cl^-}$ complex (λ_{max}=340 nm), respectively. The similarity between both spectra (BzCl and PBzCl) suggests the formation of similar species, i.e., the radical anions of PBzCl involving an unpaired electron in the π^*-orbital of the main (**9a**) or 4-substituted (**9b**) benzene ring, $\mathrm{PBz^\bullet}$ (**11a**), and the $\mathrm{PBz^\bullet/Cl^-}$ complex (**10a**) (Scheme 3).

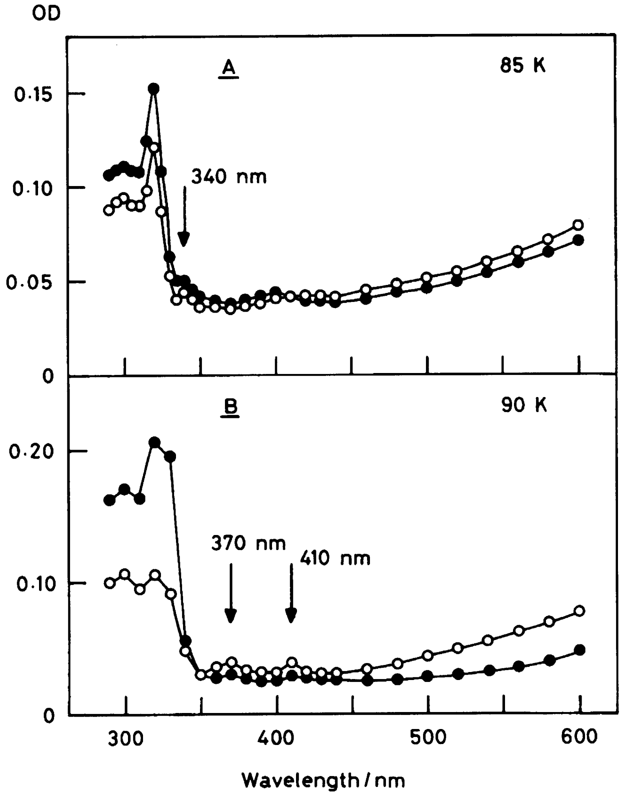
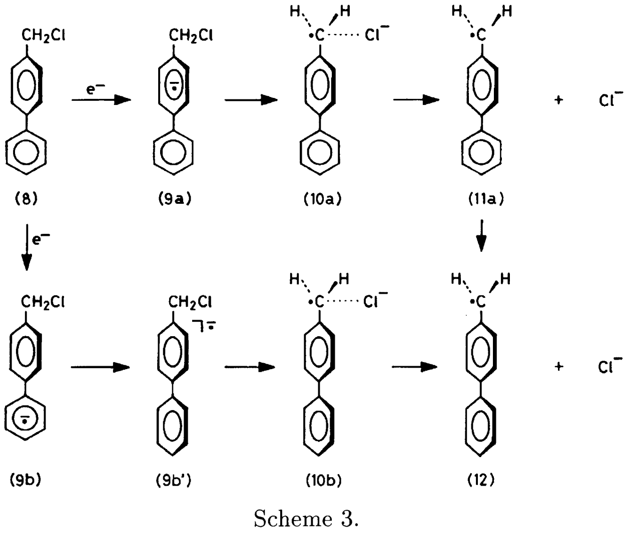


Fig. 3. Transient absorption spectra observed with 4-phenylbenzyl chloride (PBzCl) in MTHF solution (3×10^{-3} $\mathrm{mol\,dm^{-3}}$) at 85 K (A) and 90 K (B): (○) end of the pulse, (●) 180 μs after the pulse. Absorption dose was 0.7 kGy/pulse.

On the other hand, when the irradiation temperature is raised to 90 K, a shoulder (330 nm) at the longer wavelength side of the 320 nm band and two new absorption bands with a peak at 370 and 410 nm appear



Scheme 3.

immediately after the pulse, and the 330 nm absorption grows with the decay of the latter two bands, as shown in Fig. 3(B). However, at temperatures above 95 K, the 330 nm band due to the 4-phenylbenzyl radical (**12**) alone appeared immediately after the pulse.

In the same manner as in the case of PBzCl, a spectral change with temperature was observed with biphenyl itself. That is, at 85 K the spectrum observed immediately after the pulse irradiation shows a peak at 300 nm and a weak absorption at around 400 nm, which grow with the decay of solvated electrons, as shown in Fig. 4(A). The spectrum is very similar to that of the toluene radical anion (a peak at 300 nm and a weak, broad absorption in the visible region)[17] observed from the MTHF matrix containing toluene γ-irradiated at 77 K. On the other hand, when the irradiation temperature was raised to 95 K, two main peaks at 300 and 410 nm appeared immediately after the pulse, and the 410 and 650 nm bands due to the biphenyl radical anion grew along with the decay of the 300 nm band and solvated electrons, as shown in Fig. 4(B).

The gas-phase electron-diffraction studies suggest that the two rings of neutral biphenyl are oriented at an angle of ca. 40° to each other.[21] The fully optimized structures of biphenyl itself and the radical anion were calculated to be almost perpendicular and planar with a twist angle of 83° and 7°,[22] respectively. On the other hand, the absorption of biphenyl in the UV region occurs near to that of benzene, i.e., the absorption spectra of benzene and biphenyl are rather similar. These results indicate that the π-electron interaction between the two benzene rings of neutral biphenyl is small. However, the addition of an electron to give the radical anion reduces the dihedral angle; it absorbs light at 410 nm.

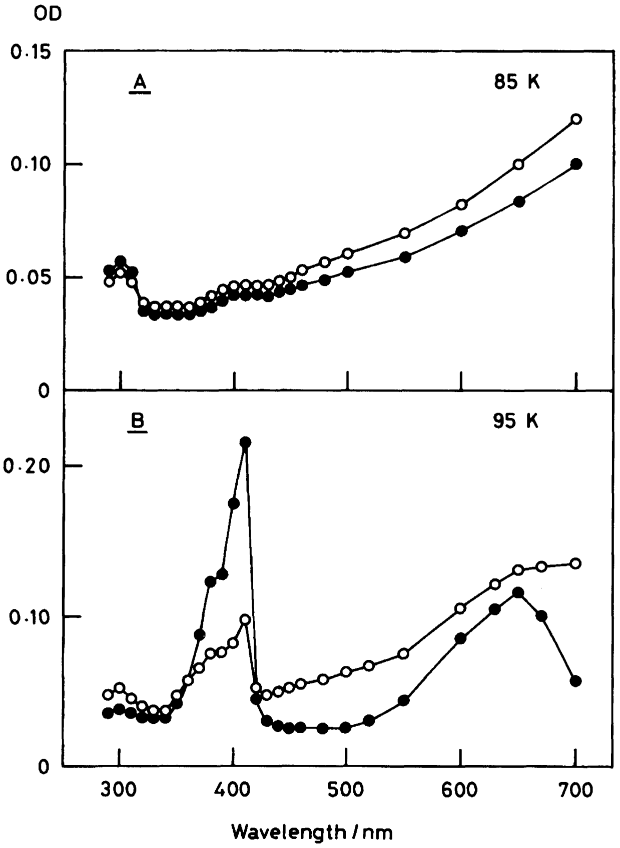


Fig. 4. Transient absorption spectra observed with biphenyl in MTHF solution (3×10^{-3} mol dm^{-3}) at 85 K (A) and 95 K (B); (○) end of the pulse, (●) 180 μs after the pulse. Absorption dose was 0.7 kGy/pulse.

As described in the preceding part of this section, the absorption bands with $\lambda_{\max}$ at 300, 320, and 340 nm assigned to the radical anions (**9a**) and (**9b**), the radical (**11a**), and the complex (**10a**) coincide with those of the radical anions of BzX, Bz$^{\bullet}$, and the Bz$^{\bullet}$/Cl^{-} complex, respectively. The agreement between both absorption bands indicates that the two benzene rings in these species observed at temperatures lower than 85 K are almost electronically independent of each other. Hence, the structure of the biphenylyl group in radical anions (**9a**) and (**9b**), complex (**10a**), and radical (**11a**) is almost the same to that of the neutral molecule (**8a**), i.e., the structure of the biphenylyl group is maintained during the course of the dissociation of the radical anion (**9a**), as illustrated in Scheme 3.

The initial spectrum observed at 90 K (Fig. 3(B)) shows the formation of two new absorption bands with peaks at 370 and 410 nm. The 410 nm band coincides in position with that of the biphenyl radical anion. Thus, the absorption with a peak at 410 nm suggests the formation of radical anion (**9b′**), in which the π-electron conjugation between the two benzene rings is achieved (Scheme 3). As described above, a structural change in the biphenylyl group is retarded in the rigid matrix formed at below 85 K. It therefore seems that the dissociation of radical anion (**9b**) is retarded in the rigid matrix. This is because the decay reaction of radical anion (**9b**) requires a reduction in the dihedral angle to form radical (**9b′**), which dissociates into radical (**12**) and Cl^{-} via complex (**10b**) (Scheme 3). However, the transient absorption spectra observed at 90 K showed a growth of the 330 nm band due to radical (**12**) with decays of the 370 and 410 nm bands (Fig. 3(B)). Accordingly, the 370 nm band can be attributed to complex (**10b**) formed as a precursor of radical (**12**). This dissociation reaction involves an electron transfer from the 4-phenyl group to an α-carbon through the main benzene ring.

In conclusion, the one-electron reduction of benzyl halides produces a radical anion (π^*) which decomposes to a benzyl radical and a halide ion via a benzyl radical-halide ion complex. The latter reaction involves an electron transfer from a benzene radical anion to an α-carbon accompanied by a simultaneous release of the halide ion. The similar results were observed with 4-phenylbenzyl chloride. Spectral change with temperature has been attributed to a structural change in the biphenylyl group.

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