Homolytic Bond Dissociation Energies of the Carbon–Halogen Bonds in the Benzyl Halide Radical Anion Intermediates Formed in Radical Nucleophilic Substitution Reactions

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A simple method has been devised for estimating the homolytic bond dissociation energies (E_{bd}) for cleavage of the C–X bonds in the radical anion intermediates formed in radical nucleophilic substitution reactions of benzyl chloride, benzyl bromide, and *m*- and *p*-substituted benzyl bromides. The method consists of combining values for: (*a*) the E_{bd} of the C–X bond in $PhCH_2X$; (*b*) the redox potential of $PhCH_2X$; and (*c*) the redox potential of the ionic fragment (X^-). Methods of obtaining these quantities are presented. The estimates indicate: (*a*) that the C–Cl bond in the $PhCH_2Cl^{•-}$ radical anion is thermodynamically unstable by about 6.5 kcal mol^{-1} toward cleavage to the $PhCH_2^•$ radical and Cl^- ion; and (*b*) that the C–Br bond in the $PhCH_2Br^{•-}$ radical anion is endoenergetic toward a comparable cleavage by only about 3 kcal mol^{-1}. On the other hand, the bond dissociation energies of the C–X bonds in these radical anions estimated for the cleavage to form a $PhCH_2^-$ ions and $X^•$ atoms are not much less than those for the corresponding homolytic cleavage in the neutral parent benzyl halides. These thermodynamic estimates are consistent with various kinetic and EPR experimental results which reveal that cleavage of the C—X bonds in benzyl chloride and bromide is concerted with the addition of an electron.

Since the discovery of aliphatic nucleophilic substitution reactions occurring by radical mechanisms,[1] a large literature concerning such reactions has accumulated.[2] The initial step in these reactions is addition of an electron from a nucleophile to an alkyl or benzyl halide to form a radical anion $RX^{•-}$ [eqn. (1)]. This is followed by cleavage of the C–X bond to form an alkyl or benzyl radical and a halide anion [eqn. (2)].

$$RX + e^- \longrightarrow RX^{•-} \qquad (1)$$

$$RX^{•-} \xrightarrow{k} R^• + X^- \qquad (2)$$

Although a considerable amount of information concerning the nature of these radical anions, and the kinetics and mechanisms of their dissociation reactions has appeared in the literature,[3] little or no quantitative information concerning the strength of the C–X bonds in $R–X^{•-}$ radical anions has been reported. Theoretical calculations by Baird suggest that the energies of three electron bonds in molecules will be about one-half of those in the corresponding parent bonds,[4a] and calculations by Clark indicate that addition of one electron to halogen molecules will give $X–X^{•-}$ radical anions with bonds that have only about 79, 50, 57 and 67% of the strength of the parent halogens, F_2, Cl_2, Br_2 and I_2, respectively.[4b] The driving force (ΔE, activation barrier) for halide radical anions is estimated to be one fourth of the bond dissociation energy.[3d–e] Recently, we have developed a simple method of estimating the homolytic bond dissociation energies (E_{bd}) of the acidic H–A bonds in $H–A^{•-}$ type radical anions by combining the equilibrium acidities (pK_{HA}s) and the reduction potentials of the weak acids, $E_{re}(HA)$, by eqn. (3).

$$E_{bd}(HA^{•-}) = 1.37\, pK_{HA} + 23.1\, E_{re}(HA) + C \qquad (3)$$

This method, which is based on the thermodynamic cycle shown in Scheme 1, has been applied to estimate the $E_{bd}(HA^{•-})$ values for the acidic H–A bonds in various radical anions derived from more than 60 weak acids.[5] The empirical constant *C*, which includes a term for the reduction potential of the proton, has a value of 73.3 kcal mol^{-1}† when the redox potentials are referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple.[6]

$$\begin{array}{ll} HA^{•-} \rightleftharpoons HA + e^- & E_{re}(HA) \\ HA \rightleftharpoons H^+ + A^- & pK_{HA} \\ H^+ + e^- \rightleftharpoons H^• & C \\ \hline HA^{•-} \rightleftharpoons A^- + H^• & E_{bd}(HA^{•-}) \end{array}$$

Scheme 1

Eqn. (3) can be further modified by addition and subtraction of the oxidation potential of the conjugate base A^-, $E_{ox}(A^-)$, to give eqn. (4). The first three terms on the right side of eqn. (4) are

$$E_{bd}(HA^{•-}) = 1.37\, pK_{HA} + 23.1\, E_{ox}(A^-) + C + 23.1\, [E_{re}(HA) - E_{ox}(A^-)] \qquad (4)$$

equal to the $E_{bd}(HA)$ value of the acidic H–A bond in neutral weak acids [eqn. (5)].[6] The $E_{bd}(HA)$ values of the acidic C–H, N–H, O–H and S–H bonds in several hundred weak acids estimated by eqn. (5) have been shown to agree to within

$$E_{bd}(HA) = 1.37\, pK_{HA} + 23.1\, E_{ox}(A^-) + 73.3 \qquad (5)$$

±2 kcal mol^{-1} of the best gas-phase literature values.[6] The availability of this method of estimating $E_{bd}(HA)$ values allows eqn. (3) to be simplified to eqn. (6). Eqn. (6) shows that the E_{bd} of

$$E_{bd}(HA^{•-}) = E_{bd}(HA) + 23.1\, [E_{re}(HA) - E_{ox}(A^-)] \qquad (6)$$

the H–A bond in a radical anion of the type $HA^{•-}$ can be estimated by combining: (*a*) the $E_{bd}(HA)$ value for the neutral parent, HA; (*b*) the reduction potential of HA; and (*c*) the oxidation potential of its conjugate base, $E_{ox}(A^-)$. These values can usually be determined readily.[5]

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† 1 cal = 4.18 J.

Table 1 Homolytic bond dissociation energies of the C–X bonds in benzyl halides and redox potentials of phenyl methide anions and benzyl radicals

Substrate	E_{bd}(C–X)[a]	E_{re}(RX)[e]	E_{re}($R^•$)[f]	E_{ox}(R^-)[e]
$C_6H_5CH_2Br$	59.4[b]	−2.051	−1.935	−1.94[g]
p-$MeC_6H_4CH_2Br$	59.7	−2.175	−2.13	
p-$FC_6H_4CH_2Br$	58.9	−2.029	−2.01	
p-$BrC_6H_4CH_2Br$	57.6	−1.940	−1.81	
m-$BrC_6H_4CH_2Br$	57.0[c]	−1.945		
p-$CNC_6H_4CH_2Br$	54.4	−1.788	−1.28	
p-$NO_2C_6H_4CH_2Br$	55.0[c]	−1.215		−0.644[h]
m-$NO_2C_6H_4CH_2Br$	53.9[c]	−1.412		
$C_6H_5CH_2Cl$	72.2[d]	−2.505	−1.935	−1.94[g]

[a] In kcal mol^{-1}, ref. 9 unless otherwise indicated. The E_{bd} values are given to three significant figures, but the accuracy is estimated to be about ±2 kcal mol^{-1}. [b] Ref. 7(*b*). [c] Estimated from the linear Hammett plot reported in ref. 9 [also see eqn. (9) in text]. [d] Ref. 8. [e] In volts; referenced to the Fc^+/Fc couple.[5] [f] In volts; from ref. 12 and converted to reference to the Fc^+/Fc couple by subtraction of −0.750 V.[5,6] [g] Ref. 17. [h] Ref. 5(*a*).

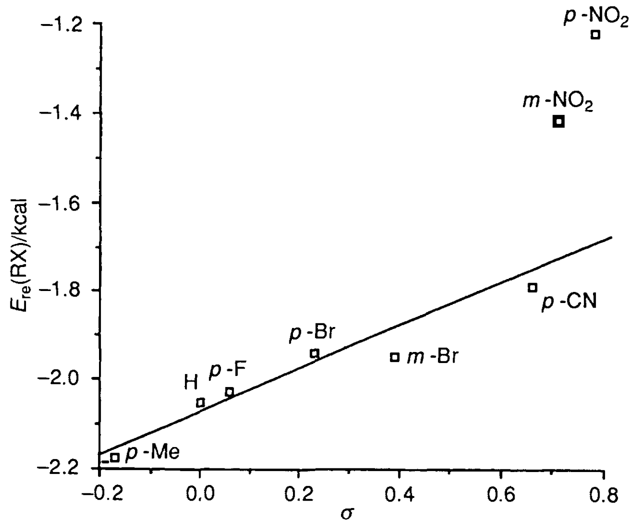
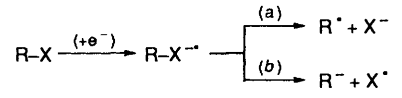


Fig. 1 Plot of the reduction potentials of the substituted benzyl bromides *vs.* Hammett σ constants (C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165); $E_{re}(RX) = -2.07 + 0.425\sigma$; $R = 0.974$

Our objective in the present paper is to extend this method to estimate the E_{bd}s of the C–X bonds in $R\text{–}X^{•-}$ type radical anions derived from benzyl chloride, benzyl bromide and a number of substituted benzyl bromides by both paths (*a*) and (*b*) as shown in Scheme 2.



Scheme 2

Results and Discussion

Pathways for Clearing the C–X Bonds in $R\text{–}X^{•-}$ Type Radical Anions.—It is conceivable that $R\text{–}X^{•-}$ radical anions could undergo cleavage of the C–X bond either by loss of a halide ion (X^-) and a carbon-centred radical ($R^•$) [path (*a*) in Scheme 2] or by loss of a carbanion (R^-) and a halogen atom ($X^•$) [path (*b*) in Scheme 2]. Product studies[2] leave no doubt that the radical anion intermediates formed by addition of an electron to an alkyl or benzyl halide cleave preferentially by path (*a*) [eqn. (2)], but the E_{bd} values of the C–X bonds in the corresponding radical anions do not appear to have been reported in the literature for either of these pathways.

The bond dissociation energies for cleavage of the C–X bonds in radical anions ($R\text{–}X^{•-}$) by paths (*a*) and (*b*) can be estimated by eqns. (7) and (8), respectively, which are based on two newly

$$E_{bd}(C\text{–}X^{•-})\,(a) = E_{bd}(C\text{–}X) + 23.1\,[E_{re}(RX) - E_{ox}(X^-)] \quad (7)$$

$$E_{bd}(C\text{–}X^{•-})\,(b) = E_{bd}(C\text{–}X) + 23.1\,[E_{re}(RX) - E_{ox}(R^-)] \quad (8)$$

designed thermodynamic cycles as shown in Schemes 3 and 4, respectively.

$$\begin{array}{ll} RX^{•-} \rightleftharpoons RX + e^- & E_{re}(RX) \\ RX \rightleftharpoons R^• + X^• & E_{bd}(C\text{–}X) \\ X^• + e^- \rightleftharpoons X^- & -E_{ox}(X^-) \\ \hline RX^{•-} \rightleftharpoons R^• + X^- & E_{bd}(C\text{–}X^{•-})\,(a) \end{array}$$

Scheme 3

$$\begin{array}{ll} RX^{•-} \rightleftharpoons RX + e^- & E_{re}(RX) \\ RX \rightleftharpoons R^• + X^• & E_{bd}(C\text{–}X) \\ R^• + e^- \rightleftharpoons R^- & -E_{ox}(R^-) \\ \hline RX^{•-} \rightleftharpoons R^- + X^• & E_{bd}(C\text{–}X^{•-})\,(b) \end{array}$$

Scheme 4

Examination of eqns. (7) and (8) shows that the values of E_{bd}(C–X) and E_{re}(RX) of the neutral alkyl halide are needed to estimate the $E_{bd}(C\text{–}X^{•-})$ values for both paths (*a*) and (*b*) in Scheme 2. In addition, $E_{ox}(X^-)$ is needed for path (*a*) and $E_{ox}(R^-)$ is needed for path (*b*). In the sections that follow, we will describe sources and methods used to obtain the required data values.

Homolytic Bond Dissociation Energies of the C–X Bonds in Neutral Benzyl Chloride and Benzyl Bromides.—The E_{bd}(C–X) values for benzyl chloride and benzyl bromide[7,8] have been known for some time, and Clark and Wayner have recently measured the relative E_{bd}s of the C–Br bonds in seven *para*-substituted benzyl bromides in triethylsilane–benzene solution by photoacoustic calorimetry.[9] They found that these E_{bd}(C–Br) values were linearly correlated by the Hammett equation ($\rho = -5.5$; $R = 0.958$). The negative slope of the Hammett correlation shows that electron-withdrawing groups weaken and electron donating groups strengthen the polar C–Br bonds in neutral substituted benzyl bromides.[9] The E_{bd}s of the C–Br bonds in three additional benzyl bromides (*m*-bromo, *m*-nitro, and *p*-nitro) were estimated by this linear correlation, eqn. (9). These E_{bd} values along with those for the other benzyl bromides and benzyl chloride, are summarized in column 2 of Table 1.

$$E_{bd}(\text{C–Br in } ArCH_2Br) = 59.4 - 5.5\,\sigma \quad (9)$$

Reduction Potentials of Substituted Benzyl Bromides.—The reduction potentials of eight substituted benzyl bromides were measured in acetonitrile solution by conventional cyclic voltammetry.[5] The results are summarized in column 3 of Table 1. The reduction potential values, $E_{re}(GC_6H_4CH_2Br)$, for six of these with G equal to *p*-Me, H, *p*-F, *p*-Br, *m*-Br, and *p*-CN were found to give a linear correlation with Hammett σ constants with $\rho = 0.425$ as shown in Fig. 1.[10]

Examination of the data in column 3 in Table 1 shows that

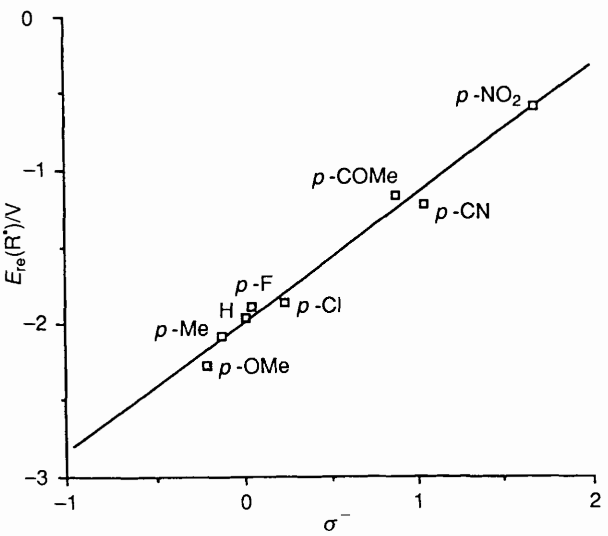


Fig. 2 Plot of the reduction potentials of *para*-substituted benzyl radicals and the oxidation potentials of the *para*-substituted phenylmethide anions *versus* Hammett σ^- constants (C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* 1991, **91**, 165); $E_{re}(R^•) = -2.018 + 0.838\sigma^-$; $R = 0.991$

the reduction potentials of these benzyl bromides are all at least 1.75 V (40 kcal mol^{-1}) more positive than that of toluene, $E_{re}(PhCH_3) = -3.93 \pm 0.05$ V *vs.* the Fc$^+$/Fc couple,*[11] which means that the extra electron is not adding to the benzene π* orbitals in these benzyl bromides but instead is probably adding to the σ* orbital of the C–Br bond. The points for *m*-NO$_2$- and *p*-NO$_2$–C$_6$H$_4$CH$_2$Br deviate sharply from the line in Fig. 1, the redox potentials being 0.376 (8.7) and 0.573 V (13.2 kcal mol^{-1}), more positive, respectively, than that for *p*-CNC$_6$H$_4$CH$_2$Br, which fits close to the line. This was expected since the nitro group is a powerful electron acceptor in its own right.[5] In earlier studies, evidence was presented to show that the reduction potentials for related nitro compounds are all the same regardless of the structure of the rest of the molecule because in each instance the electron was adding to a π* orbital of the nitro groups.[5]

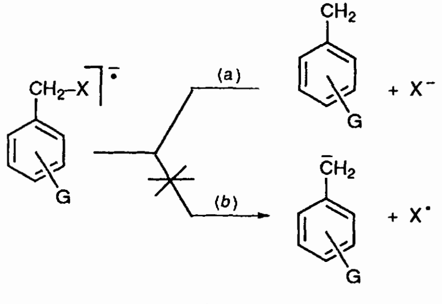
Reduction Potentials of Benzyl Radicals ($ArCH_2^•$) *and Oxidation Potentials of Arylmethide Anions* ($ArCH_2^-$).—The reduction potentials of GC$_6$H$_4$CH$_2^•$ radicals, where G is *p*-MeO, *p*-Me, *m*-Me, H, *p*-F and *p*-CN, have recently been measured by photomodulation voltammetry.[12] These values should be the same as the oxidation potentials of the corresponding ArCH$_2^-$ anions, but the latter are usually impossible to obtain in acetonitrile or DMSO solution because most of these anions are too basic to be generated in these solutions. For example, the pK_{HA} values of toluene is estimated to be 43 in DMSO[13] and 51 in acetonitrile.[14] This means that the acidities of toluene and some of the substituted toluenes are weaker than those of the corresponding solvents.† The oxidation potential of phenylmethide anion, $E_{ox}(PhCH_2^-)$, has been obtained in THF, however, by measurements on PhCH$_2$Li with HMPA added to dissociate the lithium aggregate.[16] The presence of the lithium cations are known to cause significant positive shifts in the oxidation potentials of organic anions subject to chelation,[17] but the good agreement of the $E_{ox}(PhCH_2^-)$ value with the reduction potential of benzyl radical, $E_{re}(PhCH_2^•)$,[12] indicates that both the E_{ox} and E_{re} values should be near the $E°_{\frac{1}{2}}$ value. This conclusion was supported further by the observation that the points for $E_{ox}(PhCH_2^-)$ and $E_{ox}(p\text{-}NO_2C_6H_4CH_2^-)$ fitted nicely on the linear Hammet σ^- correlation for the $E_{re}(GC_6H_4CH_2^•)$ values (Fig. 2). (The oxidation potential for the *p*-NO$_2$C$_6$H$_4$CH$_2^-$ anion was determined in DMSO by conventional cyclic voltammetry.[5a])

The ρ^- value (19.3 kcal mol^{-1}) of the Hammett σ^- correlation for the reduction potentials of benzyl radicals, $E_{re}(GC_6H_4CH_2^•)$ is somewhat larger, as expected, than that for the oxidation potentials of 10-G-9-anthrylmethide anions ($\rho^- = 14.2$ kcal).[5b] (These ρ^- values become 14.0 and 10.4, respectively when divided by 1.37 for comparison with the ρ^- values expressed in pK_{HA} units.[12a,13]) The related redox potentials for substituted benzyl radicals and arylmethide anions are summarized in columns 4 and 5 of Table 1.

The Oxidation Potentials of Bromide and Chloride Anions in Acetonitrile Solution.—The oxidation potentials of bromide and chloride ions in acetonitrile have been estimated to be 0.45 and 0.85 V, respectively, *vs.* the Fc$^+$/Fc couple by Eberson.‡[18] A measurement by conventional cyclic voltammetry in acetonitrile using tetrabutylammonium bromide [(CH$_3$-CH$_2$CH$_2$CH$_2$)$_4$N$^+$Br$^-$] gave $E_{ox}(Br^-) = 0.413$ V *vs.* the Fc$^+$/Fc couple in good agreement with Eberson's estimated oxidation potential of the bromide anion in acetonitrile solution.[18] Oxidation measurements in acetonitrile were made on three chloride salts, *P*-cyanomethyltriphenylphosphonium chloride (CNCH$_2^+$PPh$_3$ Cl$^-$) (0.874 V), *P*-phenacyltriphenylphosphonium chloride (PhCOCH$_2^+$PPh$_3$ Cl$^-$) (0.917 V) and *N*-benzyltrimethylammonium chloride (PhCH$_2^+$NMe$_3$ Cl$^-$) (0.921 V). (The numbers in parentheses are the oxidation potentials.) The average value (0.904 V) was also in good agreement with the Eberson's estimated oxidation potential of the chloride anion in acetonitrile.[18]

Bond Dissociation Energies of the C–X Bonds in the Radical Anions Derived from Benzyl Bromide, Substituted Benzyl Bromides and Benzyl Chloride.—Data presented in Table 1 allow estimates to be made of the E_{bd} of the C–Cl bond in the radical anion derived from benzyl chloride, and of the E_{bd}s of the C–Br bonds in the radical anions derived from benzyl bromide and some *meta*- and *para*- substituted benzyl bromides. The estimates for the $E_{bd}(C\text{–}X^{•-})$ values in these radical anions by both paths (*a*) and (*b*) are summarized in Table 2.

Examination of Table 2 shows that the $E_{bd}(C\text{–}X^{•-})$ values for reactions of benzyl chloride or bromide with an electron by path (*a*) to form a halide anion and a carbon-centred radical are about 24–65 kcal mol^{-1} smaller than those for reactions by path (*b*) to form a halogen atom and a carbanion (Scheme 5),



Scheme 5

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[*] The reduction potential of toluene in DMF referenced to the NHE[11a,b] was referred to the Fc$^+$/Fc couple by subtraction of 0.750 V.[5,6]

[†] The pK_{HA} values of acetonitrile and DMSO were 31.3 and 35 in DMSO solution, respectively.[13] The pK_{HA} of acetonitrile is estimated to be *ca.* 41 in acetonitrile solution since the pK_{HA} values in acetonitrile are usually *ca.* 10 pK_{HA} units higher than those in DMSO solution.[15]

[‡] The reported oxidation potentials[18] referenced to NHE was referred to the Fc$^+$/Fc couple by subtraction of 0.750 V.[5,6]

Table 2 Homolytic bond dissociation energies of the C–X bonds in benzyl bromides and chloride and the corresponding radical anions

Substrates	$E_{bd}(C–X)^a$	$E_{bd}(C–X^{•-})\ (a)^e$	$E_{bd}(C–X^{•-})\ (b)^f$
$C_6H_5CH_2Br$	59.4^b	2.5	56.6
p-$MeC_6H_4CH_2Br$	59.7	−0.1	58.7
p-$FC_6H_4CH_2Br$	58.9	2.5	58.5
p-$BrC_6H_4CH_2Br$	57.6	3.3	54.6
m-$BrC_6H_4CH_2Br$	57.0^c	2.6	
p-$CNC_6H_4CH_2Br$	54.4	3.2	42.7
p-$NO_2C_6H_4CH_2Br$	55.0^c	17.4	41.8
m-$NO_2C_6H_4CH_2Br$	53.9^c	11.7	
$C_6H_5CH_2Cl$	72.2^d	−6.5	58.9

[a] In kcal mol^{-1}, ref. 9 unless otherwise indicated. The E_{bd} values are given to three significant figures, but the accuracy is estimated to be about ±2 kcal mol^{-1}. [b] Ref. 7*b*. [c] Estimated from the linear Hammett plot reported in ref. 9 [also see eqn. (9) in text]. [d] Ref. 8. [e] In kcal mol^{-1}, estimated by using eqn. (7). [f] In kcal mol^{-1}, estimated by using eqn. (8).

indicating that the cleavage of the C–X bond in radical anions by path (*a*) is favourable. The striking preference for cleavage of the C–X bond in radical anions by path (*a*) rather than by path (*b*) is understandable since the electron affinity of a halogen atom is much greater than that of a carbon radical.[19]

Further examination of the data in Table 2 reveals that the strength of the C–Br bond in benzyl bromide is decreased from *ca.* 59 to *ca.* 3 kcal mol^{-1} with respect to the cleavage by path (*a*) when the $PhCH_2Br^{•-}$ radical anion is formed. In other words, the C–Br bond in $PhCH_2Br$ loses about 95% of its strength on the addition of one electron. This is to be compared with a calculated loss of 57% of the strength of the Br–Br bond on conversion to $Br–Br^{•-}$.[4b] On the other hand, the homolytic cleavage of the C–Br bond in the benzyl radical anion by path (*b*) is almost as endoenergetic for the radical anion as for the parent benzyl bromide (57 *vs.* 59 kcal mol^{-1}). The direct addition of an electron to the σ* orbital of the C–Br bonds in benzyl bromide[3f] and the low E_{bd} value of the C–Br bond cleaved by path (*a*) in the corresponding radical anions suggest that processes for the addition of one electron to the substrate and the dissociation of the C–Br bond in benzyl radical anions are concerted not stepwise. This is consistent with Bowman and Symons'[3a] observation that the *p*-methylbenzyl bromide radical anion is completely dissociated even at 77 K.[3a] Recently, the concern about the concerted and step-wise mechanisms for the halide radical anion dissociation reactions has received extensive attention.[3d,e]

The data for most of the substituted benzyl bromides reveal similar remarkable bond weakening effects on addition of an electron. For the most part the effects of substituents are small and show no obvious trend. It seems likely, however, that electrolytic reductive dissociation of the C–Br bonds in m-NO_2– and p-NO_2–$C_6H_4CH_2Br$ may follow a different mechanism than that for the other benzyl bromides since the electron appears to be transferred initially to the π* orbital of the nitro group instead of to the σ* orbital of the C–Br bonds (see Fig. 1).[5,20] Note that their $E_{bd}(C–X^{•-})$ (*a*) values are 8–14 kcal mol^{-1} larger than those for the other benzyl bromide radical anions cleaved by path (*a*). The mechanism may be similar to that for the dissociation of aryl halides, where theoretical calculations and EPR spectroscopy indicate that π* radicals may be formed, but that dissociation of the C–X bonds from the radical anions occurs only when the odd electron is located in the σ* orbital.[21] The electron in the π* orbital must then be transferred to the σ* orbital of the C–X bond before the bond dissociation reaction occurs.[20,21] EPR spectroscopy shows that m-NO_2– and p-NO_2–$C_6H_4CH_2Br^{•-}$ radical anions are stable for some time even at room temperature.[3a,20]

The results with benzyl chloride are even more striking. Here the C–Cl bond in neutral benzyl chloride is about 13 kcal mol^{-1} stronger than the C–Br bond in neutral benzyl bromide, but our estimate indicates that the C–Cl bond in benzyl chloride radical anion is thermodynamically unstable by 6.5 kcal mol^{-1}. Evidently, the bond cleavage of the C–Cl bond must be concerted with the addition of an electron. This is consistent with the conclusion from kinetic and EPR experimental results. For example, the lifetime of the $Ph_2CHCl^{•-}$ radical anion has been estimated to be less than 20 ps.[22] EPR studies at low temperature have shown that the species formed by reduction of Ph_2CHCl is not a descrete radical anion, but is in a state of a loose $Ph_2CH^{•}\ Cl^{-}$ complex.[23] These results show that the reductive cleavage of the C–X bonds in benzyl chloride, bromide and substituted benzyl bromides (except for the nitro substituent) proceeds *via* the concerted mechanism, but the reductive cleavage of the C–Br bonds in nitro benzyl bromides probably proceeds *via* the stepwise mechanism.

Experimental

Materials.—The benzyl halides were commercially available (Aldrich) and were used as received.

Electrochemistry.—The reduction potentials of the benzyl halides and the oxidation potentials of chloride anion and bromide anion were measured in acetonitrile solution (Aldrich; packaged under nitrogen in a Sure/Seal™ bottle) by cyclic voltammetry with tetraethylammonium tetrafluoroborate (0.1 mol dm^{-3}) as supporting electrolyte. The working electrode for the measurements of the reduction potentials was a glassy carbon electrode, and that for the measurements for the oxidation potentials was a platinum electrode. The auxiliary electrode was platinum and the reference electrode was Ag/AgI.[5] The sweep rate was 100 mV s^{-1} and the redox potentials reported were referenced to the ferrocene–ferrocenium couple ($E_{\frac{1}{2}}$ = 0.875).[6]

Acknowledgements

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