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Carbon-Halogen Bond Cleavage Energies of Polyhaloalkyl Radical Anions in Solution

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Abstract: The solution heterolytic bond dissociation energies of seven polyhaloalkyl radical anions $\Delta H_{het}(R\text{-}X^{\cdot -})$ were derived from a cycle using homolytic bond energy (BDE) and electrochemical data. A brief quantitative discussion on the structural influence on $\Delta H_{het}(R\text{-}X^{\cdot -})$ and on the effect of one-electron reduction on weakening the C-X bonds are presented.

Radical anions formed upon addition of an electron to neutral species are commonly encountered transient intermediate in reaction and are usually found to decay via a variety of possible pathways depending on substrate structure and reaction environment.[1] The most characteristic property for the radical anions derived from organic halides, in particular, has been known to be the severe weakening of the carbon-halogen bond and consequently the ease of its dissociative cleavage to form halide ion and radical (eq 1) as seen in the key step of the $S_{RN}1$ mechanism.[2]

$$RX^{\cdot -} \longrightarrow R^{\cdot} + X^{-} \qquad (1)$$

Although studies on kinetic characteristics and on effects of substrate structure on the associated electron transfers and product distributions for such process were extensively made, the thermodynamic parameters regarding the driving force for eq (1) are, however, extremely limited. Up to now the $C\text{-}X^{\cdot -}$ bond energies were estimated only in three cases where only simple aromatic halides were considered.[3] In this paper we report the heats of $C\text{-}X^{\cdot -}$ bond heterolysis for a group of aliphatic halides. To our knowledge no precedent data of this kind for this general category of compounds appeared to be available in literature.

Since direct measurements of equilibrium concentrations for the transient species involved in eq (1) are either impossible or extremely difficult, the heats of heterolysis for the radical anions studied in the present work were evaluated alternatively by combining homolytic bond dissociation energy (*BDE*) of the parent compound with relevant electrochemical data as shown in Scheme 1.

Scheme 1

$$\begin{array}{lcll}
RX^{\bar{\cdot}} - e^- & \rightleftharpoons & RX & FE_{red}(RX) \\
R\text{-}X & \longrightarrow & R^{\cdot} + X^{\cdot} & BDE(R\text{-}X) \\
X^{\cdot} + e^- & \rightleftharpoons & X^- & -FE_{red}(X^{\cdot}) \\
\hline
R\text{-}X^{\bar{\cdot}} & \longrightarrow & R^{\cdot} + X^- & \Delta H_{het}(R\text{-}X^{\bar{\cdot}})
\end{array}$$

$$\Delta H_{het}(R\text{-}X^{\bar{\cdot}}) = BDE(R\text{-}X) + F[E_{red}(RX) - E_{red}(X^{\cdot})] \qquad (2)$$

This general approach, *i.e.* using the electrode potential data in a cycle with the measurable quantities (*e.g. BDE*, pK_a, *etc.*) to derive experimentally inaccessible thermodynamic parameters, has recently been applied to solve many important problems such as the pK_a of radical cations,[4,5] the hydride affinity of carbenium ions and radicals,[6] the *BDE* of the R-H bonds and R-R' bonds in solution,[7,8] and so on. In fact equation (2) is basically an analog of the method of Parker[3] where the cleavage free energies were estimated instead on the basis of an isodesmic reaction relationship.[7c] The bond energy values of seven polyhaloalkane radical anions derived using eq (2) together with the necessary data used in the evaluation are summarized in Table 1.

Table 1. Enthalpies of C-X bond heterolysis of polyhaloalkane radical anions and the pertinent data

R −X	$BDE(C\text{-}X)^a$	$E_{red}(RX)^b$	$E_{red}(X^{\cdot})^c$	$\Delta H_{het}(RX^{\bar{\cdot}})^d$
CCl_4	73.1	-2.06	1.57	-14
$CHCl_3$	77.6	-2.64	1.57	-22
CBr_4	56.2	-1.25	1.17	-3
$CHBr_3$	62 [e]	-1.93	1.17	-12
CH_2Br_2	64 [e]	-2.71	1.17	-28
CHI_3	45.7 [e]	-1.29	0.67	-2
CH_2I_2	51.3 [e]	-2.11	0.67	-16

[a] Bond dissociation energies in kcal/mol from literature (McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493) unless otherwise noted. [b] Irreversible reduction potentials in volts (*vs.* ferrocenium/ferrocene redox couple) measured in acetonitrile under the conditions as described in reference 9(a). [c] Reduction potentials of halogen atoms in acetonitrile (in volts, *vs.* Fc^+/Fc), quoted from literature (Eberson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag: New York, 1987). [d] Enthalpies of heterolysis of radical anions in kcal/mol derived from eq. (2) and corrected for kinetic shift (see text). [e] From literature (Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta*, **1973**, *56*, 1516).

The reduction potentials of the halides listed (E_{red}(RX)) were measured in acetonitrile on a BAS-100B electrochemical analyzer.[9] Since irreversible data were obtained for all the cases due to the extremely rapid follow-up dissociation of the incipient radical anions,[10] corrections reflecting the effect of kinetic shift on the reversible potentials need to be considered. While many rate data up to $10^8 M^{-1}s^{-1}$ were reported for the unimolecular cleavage of the $C\text{-}X^{-\cdot}$ bonds in aromatic halides,[12] no corresponding values for aliphatic halides seem to have ever been exactly determined. In this work, the diffusion-controlled rate constant of $1\times10^{10} M^{-1}s^{-1}$ was assumed for the $C\text{-}X^{-\cdot}$ dissociation of all the multihaloalkanes in Table 1, which corresponds to a 126mV kinetic shift[13] to the observed E_{red}(RX)s or 2.9 kcal/mol to the end bond energy data. It is worth pointing out here that since the actual rate of $C\text{-}X^{-\cdot}$ cleavage may very well be falling into the range of $1\times10^8\sim1\times10^{10} M^{-1}s^{-1}$, the corrected $\Delta H_{het}(RX^{-\cdot})$ data derived according to the assumed rate may be in error by 0.9 kcal/mol (*i.e.* 39mV[13]) and thus indicate a minimum estimate for the $C\text{-}X^{-\cdot}$ cleavage energy if the other two terms in eq (2) are both reliable.

The C-X *BDE*s listed in Table 1 are gas phase values. A practical problem associated with directly using them as the analogous solution values in Eq (2) involves the assumption that the solvation energies of RX and $R^{\cdot}$ cancel. While this requirement is yet a matter of further confirmation for the group of compounds in Table 1, it is indeed commonly observed that homolytic *BDE*s in solution do match the corresponding gas-phase values very well within experimental errors for almost all the compounds whose *BDE*s are known in both phases.[8b] This should be understandable since that only neutral species are involved in the homolytic cleavage of a neutral molecule and thus no significant variation of solvation energies are expected. Therefore in the present work the gas phase *BDE*s were treated similarly without invoking further corrections.

The mingling of enthalpic BDE value with free energy redox potentials in eq (2) requires neglecting the entropy contributions for the two electron transfer processes in Scheme 1. This problem was encountered by others too[7,15] in estimating various bond cleavage enthalpies utilizing the electrochemical redox potentials similar to those included in Scheme 1. It was either commonly assumed[7a~d,15] or found[7e] that the entropy changes for electron transfer were negligible. In our case (Scheme 1), the alkyl halide radical anion and the halogen atom were converted respectively to the neutral halide and halide ion at the electrodes. It is therefore conceivable that the entropy loss as solvent molecules are restricted to a charged species in process $X^{\cdot} + e^{-} \rightarrow X^{-}$ may be largely compensated by an entropy gain as solvent molecules are released from electrostriction in process $RX^{-\cdot} \rightarrow RX + e^{-}$, thus making no significant overall change in entropy for electron transfers. For this reason, the electron transfer free energies were similarly treated in this work as the equivalence of the electron transfer enthalpies.

A comparison of the *BDE*(C-X) and $\Delta H_{het}(RX^{-\cdot})$ data in Table 1 reveals that introducing an electron to haloalkane indeed causes a severe weakening to the C-X bond as it is evident from the $\Delta\Delta H$(C-X) of 48 kcal/mol for CHI_3 as the minimum bond energy decrease and 100 kcal/mol for $CHCl_3$ as the maximum. There seems to be a general trend that the effect of one electron reduction on weakening the C-X bond is enhanced with an increase of the C-X bond strength as shown by the satisfactory linearity (r = 0.98) of the plot of $\Delta\Delta H$(C-X) vs. *BDE*(C-X). It is also obvious from the data in Table 1 that all the $R\text{-}X^{-\cdot}$ bond cleavage processes are exergonic and that the more energy released, the less substitution of the halogen atoms of the same kind. Further work on estimating the heats of heterolysis of the $R\text{-}X^{-\cdot}$ bonds is in progress.

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9. Experimental conditions for electrochemical measurements were the same as previously described in reference 8(a).
10. There is ESR evidence[11] showing that simple alkyl halides of the type RCH_2X undergo concerted dissociative one-electron reduction and therefore $E_{RX/R^{\cdot}+X^{-}}$ is actually measured, instead of $E^{\circ}_{RX/RX^{\cdot-}}$.[12] In this work, however, it is better to assume that the measured quantity is, much like the case for aromatic halides, $E_{RX/RX^{\cdot-}}$, due to an increase in stability of the radical anions by multi-halogen substitution. We thank one referee for pointing out this difference.
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