The Thermochemistry of the Ionization Reactions of Alkyl Halides in Solution

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The study of substitution reactions of alkyl halides and related compounds in solution has provided a wealth of kinetic and mechanistic data. Although many refinements have been made, the entire range of mechanisms, S₈N₂ to pure S₈I, can be accommodated by the manifold of reactants in the Winstein ion-pair scheme [eqn. (1)].

\[ R-X \rightarrow R^+X^- \rightarrow R^+(\text{solvent})X^- \rightarrow R^+ + X^- \]  (1)

The \( S_81 \) mechanism is believed to occur with tertiary, and some suitably substituted secondary, substrates. Although these mechanisms have been studied intensively over the past sixty years, there are no data available for the free energy of ionization of simple alkyl halides in neutral solution. Data for the ionization of tert-buty1 and benzyl halides, obtained using thermochemical cycles, are reported here.

The free energy change in a reaction, or that for the sum or difference of two reactions, can often be equated to an electrode potential difference. The procedure is illustrated in Scheme 1 for the difference in heterolytic (\( \Delta G_{\text{ion}} \)) and homolytic (\( \Delta G_{\text{hom}} \)) bond dissociations of alkyl halides

\[ \text{Free energy} \]

\[ \begin{align*}
R^-X & \rightarrow R^+ + X^- & \Delta G_{\text{ion}}^0 \\
R^+ + X^- & \rightarrow R^-X & -\Delta G_{\text{hom}}^0
\end{align*} \]  (2)

\[ R^+ + X^- \rightarrow R^+ + X^- - F\Delta E' \]  (4)

\text{Scheme 1.}

(R-X) in solution. The sum of the free energies above is equal to that below the double line, completing the thermochemical cycle, giving rise to eqn. (5). Eqn. (5) is of limited value since \( \Delta G_{\text{hom}} \) are not generally available. Applying the common assumption that the entropies of formation of R-X and R' are expected to be very nearly

\[ \Delta G_{\text{ion}} = \Delta G_{\text{hom}} - F\Delta E^m \]  (5)

\[ \Delta G_{\text{hom}} = E_{\text{f}} - T[S^0(X')] + \Delta G_{\text{solv}}(X') \]  (6)

\[ \Delta G_{\text{ion}} = E_{\text{f}} - T[S^0(X')] - F\Delta E^m + \Delta G_{\text{solv}}(X') \]  (7)

equal, leads to eqn. (6) which allows \( \Delta G_{\text{ion}} \) to be evaluated from the corresponding enthalpic bond dissociation energy \( (E_{\text{f}}) \). Pertinent C-X \( E_{\text{f}} \) and standard entropies of formation \( [S^0(X')] \) data of the halogen atoms are available.

The electrode potential data necessary to determine \( \Delta G_{\text{ion}} \) are for the reductions of \( R^+ \) and \( X^- \). Pertinent data for the ionization reactions of benzyl halides, tert-buty1 halides and tropyl halides in acetonitrile (AN) are summarized in Table 1. Notice that two values of the reduction potentials of the halogen atoms are listed. The first values listed are from Eberstein's tabulation and are derived from thermochemical estimates. The second set of values are from Pearson's compilation which have been adjusted using the free energy of transfer of halide ions from water to AN. The latter values are probably more reliable (uncertainty ±0.15 V) since they are based on more recent thermochemical data. The reduction potentials of benzyI and tert-butyI, as well as tropyl, cations have been reported.

The remaining quantities required to use eqn. (7) to estimate \( \Delta G_{\text{ion}} \), are the free energies of solvation of the halogen atoms in AN, \( \Delta G_{\text{solv}}(X') \). Related work has shown a value of \( \Delta G_{\text{sol}}(H_2) \) of 5 kcal mol⁻¹ for the free energy of solvation of the hydrogen atom in AN is apparently a good approximation. The solubility of O₂ in AN can be estimated to be of the order of 0.008 M which corresponds to \( \Delta G_{\text{sol}}(O_2) \) equal to about 3 kcal mol⁻¹. Free energies of solvation of a number of gases including He,

\begin{tabular}{|c|c|}
\hline
Reduced form & \( E^\circ/V \text{ vs. NHE} \) \\
\hline
Cl⁻ & 2.1 ± 0.15 \( ^\circ \) \\
Br⁻ & 1.7 ± 0.15 \( ^\circ \) \\
I⁻ & 1.2 ± 1.0 \( ^\circ \) \\
PhCH₃⁻ & 0.97 \( ^\circ \) \\
(CH₃)₂C⁻ & 0.33 \( ^\circ \) \\
C₂H₅⁻ & -0.08 \( ^\circ \) \\
\hline
\end{tabular}

\( ^\circ \) Data from Ref. 7. \( ^\circ \) Data from Ref. 9. \( ^\circ \) Data from Ref. 10. \( ^\circ \) Data from Ref. 11.

Table 2. Ionization free energies of alkyl halides from electrode potential and thermochemical data for alkyl radicals and halogen atoms.

<table>
<thead>
<tr>
<th>Ionization</th>
<th>$E_{\text{red}}$</th>
<th>$-\frac{1}{2}(S^*(X^-))$</th>
<th>$-\text{FAE}^*$</th>
<th>$\Delta G_{\text{ion}}(\text{AN})$</th>
<th>$\Delta G_{\text{ion}}(\text{H}_2\text{O})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH$_2$Cl</td>
<td>72.2$^a$</td>
<td>-11.7</td>
<td>-19</td>
<td>41</td>
<td>29</td>
</tr>
<tr>
<td>PhCH$_2$Br</td>
<td>57.6$^a$</td>
<td>-12.5</td>
<td>-12</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>PhCH$_3$I</td>
<td>48.2$^a$</td>
<td>-12.9</td>
<td>-1</td>
<td>34</td>
<td>29</td>
</tr>
<tr>
<td>tert-ButylCl</td>
<td>80$^a$</td>
<td>-11.7</td>
<td>-34</td>
<td>34</td>
<td>22</td>
</tr>
<tr>
<td>tert-ButylBr</td>
<td>64$^a$</td>
<td>-12.6</td>
<td>-27</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>tert-Butyl</td>
<td>51$^c$</td>
<td>-12.9</td>
<td>-16</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>C$_2$H$_5$Cl</td>
<td>72$^d$</td>
<td>-11.7</td>
<td>-43</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>C$_2$H$_5$Br</td>
<td>58$^d$</td>
<td>-12.5</td>
<td>-36</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>C$_2$H$_5$I</td>
<td>48$^d$</td>
<td>-12.9</td>
<td>-26</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$Data from Ref. 6. $^b$Data from Ref. 5. $^c$Tabulated in Simoes, J. A. and Beauchamp, J. L. Chem. Rev. 90 (1990) 629. $^d$Assumed to be the same as the corresponding value for the benzyl halide.

N$_2$, Ar, and ethane in N-methylacetamide have been reported to be equal to 6.0, 5.1, 4.7 and 3.4 kcal mol$^{-1}$ respectively. From these solubility trends it appears to be highly unlikely that $\Delta G_{\text{ion}}(X^-)$ for any of the gaseous halogen atoms will be less than 0 (solubility of 1 M). Furthermore, it appears reasonable to suggest that the most likely range of $\Delta G_{\text{ion}}(X^-)$ is from about +3 to 0 kcal mol$^{-1}$. Thus, $\Delta G_{\text{ion}}(X^-)$ can be neglected acknowledging that the $\Delta G_{\text{ion}}$ obtained using eqn. (7) may be minimum values with a small error due to this omission.

Free energies of ionization of benzyl, tert-butyl and tropyli halides in AN and water are summarized in Table 2. The AN values were obtained using eqn. (7) while those in water were estimated by adding the free energies of transfer of the halide ions$^{12}$ to the AN values. The C-X $E_{\text{red}}$ for benzyl and tert-butyl halides are from the literature and those for tropyli halides are assumed to be equal to the corresponding benzyl values.$^{13}$ Consequently, the $\Delta G_{\text{ion}}$ data for the tropyli halides are subject to a greater uncertainty than those of the other two series of halides and are included for the purpose of comparison.

The features of most interest in the data are: (i) that $\Delta G_{\text{ion}}$ of both benzyl and tert-butyl halides are large and positive in AN and that (ii) ionization is considerably less favorable for benzyl than for tert-butyl halides in both solvents. These data suggest that the formation of the free ions in non-aqueous solvents is unfavorable and is not expected to be an important reaction pathway. The stabilization of the halide ions by hydrogen bonding is the dominant factor in the lowering of $\Delta G_{\text{ion}}$ on going from AN to water solvents.

The preliminary data reported here show that application of Scheme 1 and eqn. (7) can be expected to provide $\Delta G_{\text{ion}}$ for a variety of S$_8$I reactions. These data are of fundamental importance for one of the most basic reactions in organic chemistry. Further work is in progress on the alkyl halides and related systems in both protic and aprotic solvents.$^{17}$

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References

3. Richie$^{14}$ derived an equation similar to (5) for the ionization of R-X leading to stable carbenium ions but concluded that it could only be applied to obtain relative values because of the unavailability of $\Delta G_{\text{ion}}$ values. More recently, Arnett$^{15}$ and coworkers have derived a similar equation which applies to enthalpies of heterolysis and homolysis of C-C bonds in solution.
12. Free energies of transfer of halide salts from acetoniitrile to water are expected to be dominated by the contribution from the halide ions.$^{16}$
13. Homolytic $E_{\text{red}}$ of similar bonds are relatively insensitive to structural changes as can be seen in data reported in Ref. 5.

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