**Abstract:** Determinations of the specific rates of solvolysis of 1-adamantyl bromide and 1-adamantyl iodide in 1,1,1,3,3,3-hexafluoro-2-propanol-water mixtures, in conjunction with earlier reported values in 80% ethanol, have led to additional YBr and YI solvent ionizing power values. These new values will be especially important in avoiding multicollinearity when the extended Grunwald-Winstein equation (extended by addition of a term involving solvent nucleophilicity) is used to correlate solvent-induced changes in the specific rates of solvolyses involving a bromide or iodide ion leaving group.

**Keywords:** 1-adamantyl bromide, 1-adamantyl iodide, 1,1,1,3,3,3-hexafluoro-2-propanol, Grunwald-Winstein equation, solvent ionizing power.

**1. Introduction**

The one-term Grunwald-Winstein equation (eqn 1) [1] was developed to correlate the specific rates of solvolytic displacements proceeding by a unimolecular ionization pathway ($S_N1 + E1$ reactions).

$$\log(k/k_0) = mY + c$$  \hspace{1cm} (1)

In eqn 1, $k$ and $k_0$ represent the specific rates of solvolysis of a substrate in a given solvent and in the standard solvent (80% ethanol-20% water v/v), $Y$ is a scale of solvent ionizing power, $m$ is the
sensitivity towards changes in the solvent ionizing power value and \( c \) is a (usually small) constant (residual) term. The original \( Y \) scale was developed using \( \text{tert-butyl chloride} \) as the standard substrate \((m\ \text{value set at unity})\).

For the correlation of bimolecular solvolytic displacements, where the solvent also functions as a nucleophile in the rate-determining step; it was proposed that a second variable should be added (eqn 2) \([2]\), where \( N \) is a measure of solvent nucleophilicity and \( l \) is the sensitivity towards changes in its value.

\[
\log(\frac{k}{k_0}) = lN + mY + c \tag{2}
\]

Only in 1976 did an extensive listing of \( N \) values (the \( N_{OTS} \) scale) become available \([3]\), based on the specific rates of solvolysis of methyl p-toluene sulfonate (tosylate). More recently, an \( N_T \) scale based on the solvolyses of the \( S\)-methyl dibenzothiophenium ion has been developed \([4, 5]\).

A further development as regards solvent ionizing power scales involved the recognition that the \( Y \) scale based on \( \text{tert-butyl chloride} \) solvolyses included a nucleophilic component \([6-9]\), which could be avoided by the use of the bridgehead \( 1\)-adamantyl chloride \([6]\) as the standard substrate. Further, the solvent ionizing power scale was found to be leaving-group dependent and scales have been independently determined for several leaving-groups\((X)\) and termed, in general, \( Y_X \) scales \([10]\). These have been determined, for relatively poor leaving groups using \( 1\)-adamantyl derivatives \((I)\) and for relatively good leaving groups using \( 2\)-adamantyl derivatives \((2)\).

\[
X \quad (1) \quad X \quad (2)
\]

The application of eqn 2 is usually with the incorporation of the \( N_T \) scale of solvent nucleophilicity and the appropriate \( Y_X \) scale for the leaving group \( X \).

An important aspect of the use of eqn. 2 is that, for the majority of the binary solvent mixtures used as the solvents, as the \( Y_X \)-value increases on increasing the water content, the \( N_T \) value decreases approximately linearly and multicollinearity can be a major problem. Indeed, if, as historically was often the case, a study of the solvolyses of a substrate is restricted to ethanol-water, methanol-water, acetone-water, and dioxane-water mixtures, multicollinearity is unavoidable \([11, 12]\). Fortunately multicollinearity problems can be avoided by the incorporation of fluoroalcohol-containing solvents and \( 2,2,2\)-trifluoroethanol (TFE)-water and \( 1,1,1,3,3,3\)-hexafluoro-2-propanol (HFIP)-water mixtures are strongly recommended systems for incorporation into any study involving the application of eqn. 2 \([5, 10]\). TFE-ethanol mixtures are also frequently used \([13]\). The fluoroalcohol-containing binary systems make an essential contribution because of the quite different relationships between \( N_T \) and \( Y_X \) values relative to those for the other four mixed solvent systems mentioned above. For example, in TFE-H\(_2\)O mixtures, as \( N_T \) increases the \( Y_X \) values show a modest increase \([5,10]\).

Fewer \( Y_X \) values are available for HFIP-H\(_2\)O mixtures and the review by Bentley and Llewellyn lists a \( Y_X \) value for the important chloride, bromide, and iodide leaving groups only for a 97% HFIP (w/w)
A subsequent extension of the previous [6,10] kinetic study of 1-adamantyl chloride solvolyses has led to the availability of $Y_{\text{Cl}}$ values for more aqueous HFIP-H$_2$O mixtures [8]. In the present study, we determine the specific rates of solvolysis of 1-adamantyl bromide and 1-adamantyl iodide in these more aqueous mixtures, which allows the determination of the corresponding $Y_{\text{Br}}$ and $Y_{\text{I}}$ values.

2. Results and Discussion

The specific rates of solvolyses were determined, at 25.0°C, for 1-adamantyl bromide and 1-adamantyl iodide in 97%, 90%, 70%, and 50% HFIP (weight-weight basis, with other component water). The values (Table 1) for 97% HFIP are in very good agreement with earlier determinations [14,15]. The specific rates are the averages from at least four independent kinetic runs. The specific rates are reported within Table 1, together with the calculated $Y_{\text{Br}}$ and $Y_{\text{I}}$ values and, for comparison, previously reported [6, 8] $Y_{\text{Cl}}$ values.

<table>
<thead>
<tr>
<th>solvent</th>
<th>1-AdBr</th>
<th>1-AdI</th>
<th>1-AdCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate constant, s$^{-1}$</td>
<td>rate constant, s$^{-1}$</td>
<td>rate constant, s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$80\text{EtOH}$</td>
<td>$2.8\times10^{-7}$</td>
<td>0.00</td>
<td>$5.8\times10^{-7}$</td>
</tr>
<tr>
<td>$97\text{HFIP}$</td>
<td>$(9.1\pm0.2)\times10^{-3}$</td>
<td>4.51$^g$</td>
<td>$(4.00\pm0.02)\times10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$(9.68\pm0.01)\times10^{-3}$</td>
<td>4.54</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$(9.37\pm0.06)\times10^{-3}$</td>
<td>4</td>
<td>4.52</td>
</tr>
<tr>
<td>$90\text{HFIP}$</td>
<td>$(2.29\pm0.05)\times10^{-3}$</td>
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<td>3.91</td>
</tr>
<tr>
<td>$70\text{HFIP}$</td>
<td>$(1.09\pm0.04)\times10^{-3}$</td>
<td>4</td>
<td>3.59</td>
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<tr>
<td>$50\text{HFIP}$</td>
<td>$(1.06\pm0.04)\times10^{-3}$</td>
<td>4</td>
<td>3.58</td>
</tr>
</tbody>
</table>

$^a$ With associated standard errors. $^b$ 80EtOH on volume-volume basis and HFIP-containing solvents on weight-weight basis, other component is H$_2$O. $^c$ Concentration of $8.1\times10^{-4}M$. $^d$ Concentration of $6.6\times10^{-4}M$. $^e$ Number of determinations. $^f$ From ref. 8. $^g$ Data from ref. 6. $^h$ Data from ref. 14. $^i$ Data from ref. 15.

Differences in $Y_X$ values for a given solvent are believed to be primarily due to differences in electrophilic solvent assistance [6] and the halide series, showing a reduction in electrophilicity as one moves down the periodic table, is a useful one for assessing the significance of the specific anion solvation [14].

It was found [14] that, while 1-adamantyl iodide reacts in most solvents faster than 1-adamantyl bromide, the rates become essentially identical in 97% TFE and the order was reversed in the most acidic solvents studied: 97% HFIP, acetic acid, and formic acid. In the present study (Table 1), we find the bromide to be the more reactive in both 97% HFIP and 90% HFIP. The rates would become equal at about 77% HFIP and the iodide is 14% and 18% more reactive in 70% and 50% HFIP. Clearly, there is a balance between the resistance of the carbon-halogen bond towards heterolysis and the magnitude of the superimposed electrophilic assistance from the solvent.
When the comparison is made in terms of $Y_x$ values, it is important to realize that, for a given solvent, the $Y_x$ values are relative to the behavior of that particular 1-AdX substrate in 80% ethanol. Variations in $Y_x$ values for different leaving groups will have components both from differences in interactions in the solvent under consideration and from differences in interactions in the 80% ethanol. However, the observation that the 1-AdI/1-AdBr specific rate ratio varies only from 2.3 in 90% EtOH to 1.9 in 60% EtOH [14] suggests that interactions in ethanol-rich ethanol-water mixtures are similar for different halides. In contrast, appreciably larger variation (0.46 to 1.14) is observed over the similar concentration range of 97% HFIP to 70% HFIP, consistent with the dominant influence of differences in the interactions of the various 1-adamantyl halides with a more electrophilic fluoroalcohol-rich solvent.

In addition to the obvious utility in correlations using eqn 1, the presently reported $Y_{Br}$ and $Y_I$ values for HFIP-H$_2$O mixtures will be especially useful in extended Grunwald-Winstein equation (eqn 2) treatments of solvolyses involving displacement of bromide or iodide ion. In conjunction with available $N_T$ values for the solvents [4,5], they will assist in promoting a good mix of solvent types. This will avoid the high degree of multicollinearity present when only specific rates determined in binary mixtures of water with acetone, dioxane, ethanol, and methanol are available.

3. Experimental

The 1-adamantyl bromide (Aldrich, 99%) and 1-adamantyl iodide (Aldrich, 98%) were used as received. The 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich, 99+%) was purified as previously described [15]. The apparatus, allowing rapid response to changes in conductivity [16], has been previously described [17]. Typically, the determinations of the specific rates were made after the injection of 4.0 µl of a 10% (weight-weight) solution of the substrate in dry acetonitrile into the conductivity cell containing 2.00mL of the solvent mixture.

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References and Notes


