Charge Separation in Transition States of Reactions Involving Neutral Molecules as Reactants

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Abstract
It is shown that the parameter \( m \) in the Grunwald-Winstein equation, \( \log(k/k_0) = mY \), can be equated to \( z/z_0 \) where \( z_0 \) is the charge separation in the transition state of solvolysis of t-butyl chloride in a given pair of solvents and \( z \) is the charge separation in the transition state of a reaction in which only neutral molecules are involved as reactants in the same pair of solvents.

Introduction
We have been interested in the interpretation and improvement of the various empirical linear free energy equations. In this paper we show that the Grunwald-Winstein equation (equation (1)) can be used to give a quantitative measure of the charge developed in transition states of reactions in which neutral molecules are involved as reactants.

Results and Discussion
In the Grunwald-Winstein equation

\[
\log(k/k_0) = mY
\]  

(1)

\( k \) and \( k_0 \) are the rate constants for a given reaction in a given solvent and in the reference solvent (80% ethanol) respectively, \( Y \) is calculated from \( \log(k/k_0) \) for the rate constants for solvolysis of t-butyl chloride for each solvent, and \( m \) is a constant characteristic of the nature of the reactants and the pair of solvents used in the reaction being studied.\(^{3–5}\) We find that the parameter \( m \) can be expressed as

\[
m = \frac{z}{z_0}
\]  

(2)

where \( z_0 \) refers to the charge developed in the transition state of solvolysis of t-butyl chloride in a given pair of solvents and \( z \) is the charge developed in the transition state of a reaction in which only neutral molecules are involved as reactants in the same pair of solvents. The solvents are divided into three groups, namely hydroxylic,

aprotic and non-polar. This classification takes account of the observation that the $z_0$ values for the solvolysis of t-butyl chloride in these three groups of solvents are different. The reported values are 0.85, 0.57 and 0.48, respectively. The $z$ values of various $S_N1$ and $S_N2$ reactions involving neutral molecules as reactants can be calculated from the reported $m$ values in the literature and the appropriate $z_0$ values by equation (2). The $m$ values for a large number of reactions have been reported and we only choose those reactions whose $z$ values have been calculated by other methods, so that a comparison can be made. Table 1 shows that our $z$ values calculated by equation (2) agree well with those obtained by Abraham. Thus, equation (2) provides a convenient method of calculating the charge developed in transition states of reactions in which only neutral molecules are involved as reactants.

Table 1. Comparison of $z$ values calculated by equation (2) with literature values

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactant Solvents</th>
<th>$m$</th>
<th>$z$ (this work)$^H$</th>
<th>$z$ (literature)$^I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me$_2$CBr</td>
<td>EtOH-H$_2$O</td>
<td>0.940$^A$</td>
<td>0.80</td>
</tr>
<tr>
<td>2</td>
<td>Me$_2$CHBr</td>
<td>EtOH-H$_2$O</td>
<td>0.544$^A$</td>
<td>0.46</td>
</tr>
<tr>
<td>3</td>
<td>PhCH$_2$Cl</td>
<td>EtOH-H$_2$O</td>
<td>0.425$^A$</td>
<td>0.36</td>
</tr>
<tr>
<td>4</td>
<td>EtBr</td>
<td>EtOH-H$_2$O</td>
<td>0.343$^A$</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>MeBr</td>
<td>EtOH-H$_2$O</td>
<td>0.258$^A$</td>
<td>0.22</td>
</tr>
<tr>
<td>6</td>
<td>Me(CH$_2$)$_3$Br</td>
<td>EtOH-H$_2$O</td>
<td>0.392$^A$</td>
<td>0.33</td>
</tr>
<tr>
<td>7</td>
<td>Ph(Me)CHCl</td>
<td>EtOH-H$_2$O</td>
<td>0.965$^F$</td>
<td>0.82</td>
</tr>
<tr>
<td>8</td>
<td>Me$_2$N+MeI</td>
<td>dioxan-Me$_2$CO</td>
<td>0.755$^F$</td>
<td>0.43</td>
</tr>
<tr>
<td>9</td>
<td>EtSn+HgCl$_2$</td>
<td>MeOH-H$_2$O</td>
<td>0.713$^F$</td>
<td>0.61</td>
</tr>
<tr>
<td>10</td>
<td>C$_2$H$_3$N+MeI</td>
<td>PhH-PhNO$_2$</td>
<td>0.582$^F$</td>
<td>0.28</td>
</tr>
<tr>
<td>11</td>
<td>PhNMe$_2$+MeI</td>
<td>aprotic solvents</td>
<td>0.549$^G$</td>
<td>0.31</td>
</tr>
</tbody>
</table>


Equation (2) has a theoretical basis since it can be derived from the sphere-in-continuum model of Born.$^7$ According to the Born model the electrostatic contribution to the medium effect on a reaction involving neutral molecules as reactants and in which charge is produced in the transition state is given by

$$\ln \Gamma = (ze)^2 (1/D_{S1} - 1/D_{S2})/r k_B T$$

(3)

where $\ln \Gamma$ is the medium effect due to electrostatic contribution, $e$ is the electronic charge, $z$ is the fraction of charge present in the reaction’s transition state, $D$ is the dielectric constant, $r$ is the radius of the charged transition state, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature; $S1$ and $S2$ denote two different solvents.

$^7$ Born, M., Z. Phys., 1920, 1, 45.
The two solvents should be closely related in order that the charges developed in the transition states in the two solvents are the same. Therefore, the medium effect on such a given reaction relative to that of the reference reaction, the solvolysis of t-butyl chloride, is given by

$$\ln \Gamma/\ln \Gamma_0 = (z^2/r)/(z_0^2/r_0)$$

where the subscript 0 denotes the reference reaction. Intuitively we expect the radius of the charged transition state to be proportional to the amount of charge present in the transition state because a larger \( r \) implies a greater extent of bond cleavage and, therefore, a larger amount of charge developed in the transition state. Therefore, equation (4) may be written as

$$\ln \Gamma/\ln \Gamma_0 = z/z_0$$

The term \( \ln \Gamma \) is related to the rate constants in the two solvents in the form of equation (6):

$$\ln \Gamma = \log(k_{s2}/k_{s1})$$

A combination of equations (5) and (6) gives equation (1) with \( m \) related to \( z \) in the form of equation (2), \( k_{s2} = k \), and \( k_{s1} = k_0 \).

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