Solvation models in the reaction between benzyl bromide and diphenyl amine

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The effect of different protic and dipolar aprotic solvents on the rate of the reaction between benzyl bromide and diphenyl amine has been studied. Correlation of the rate constants with different solvent parameters indicates that the polarity, nucleophilicity and hydrogen bond donor ability of the solvent simultaneously influence the rate and the solvation of the reactants and the transition state is due to these properties of the solvent.

According to Reichardt\(^1\) the polarity of a solvent is determined by its solvation ability due to intermolecular interactions with the solute molecules. According to Koppel and Palm\(^2\), the solvation of any reagent is due to polarity, polarizability, electron exchange or hydrogen bond formation with the solvent. Therefore any solvent dependent physicochemical property, \(A\), can be expressed as:

\[
A = A_0 + yY + pP + eE + bB + \ldots \quad \ldots \quad (1)
\]

where \(A_0\) is the property in an inert solvent which doesn’t solvate the solute molecule at all, \(Y, P, E, B\) etc. are measures of different solvation properties of the solvent, \(y, p, e, b\) etc. describe susceptibility of ‘A’ towards the respective solvation properties. Since the rate constant is also a solvent dependent property, we have studied the effect of 13 different solvents on the reaction rate between benzyl bromide and diphenyl amine and correlated the rate constant with different solvent parameters. From the results of this correlation analysis, a solvation model is proposed.

**Experimental**

Benzylbromide (RIEDELM) and diphenyl amine (BDH, AnalaR) were used as such. The solvents, methanol, \(n\)-propanol, \(n\)-butanol, \(t\)-propanol, \(t\)-butanol benzyl alcohol, acetonitrile, benzonitrile (Qualigens, ExcelaR) dimethyl sulphoxide, dimethyl formamide, acetone, ethyl methyl ketone and formamide (SD Fine, AR Grade) were distilled following literature methods before use. The solutions of diphenylamine (DPA) were prepared by dissolving the required weighed quantity in these solvents. Solutions of benzyl bromide (BzBr) were prepared by dissolving a known volume in the appropriate solvent. The reactions were initiated by mixing the thermally equilibrated solutions of BzBr and DPA at appropriate temperatures. The progress of the reaction was followed by measuring the conductance of the reaction mixture at different time intervals using a digital conductivity bridge (CENTURY make). The reactions were conducted in different solvents in the temperature range 293-313K. The reaction rates at different concentrations of BzBr and DPA indicated that the reaction is overall second order with first order dependence each on [BzBr] and [DPA]. The reactions were conducted at \([\text{BzBr}] = [\text{DPA}] = 0.02\) mol dm\(^{-3}\) and the second order rate constants \((k)\) were determined from the slopes of the linear plots obtained when \((C_i - C_0)/(C_\infty - C_0)\) was plotted against time, where \(C_0, C_i\) and \(C_\infty\) are the conductance of the reaction mixture at 0, \(t\) and infinite time intervals.\(^3\) The validity of the corresponding multiparametric equations obtained was tested applying the statistical F-test and Student t-test.

**Results and discussion**

The second order rate constants, \(k\), determined in 13 different protic and aprotic solvents are presented in Table 1. Correlation of these log \(k\) values with different solvent parameters, namely, polarity \((Y)^{1}\), polarisability \((P)^{2}\), solvent electrophilicity \((E)^{3}\), solvent nucleophilicity \((B)^{4}\), hydrogen bond donor acidity \((\alpha)^{5}\), hydrogen bond acceptor basicity \((B)^{6}\) and specific polarisation \((\pi^*)^{6}\) indicated that there is poor correlation when a single parameter is used.

Addition of a second parameter to the single parameteric equations improved the strength of the correlation, and some of these relationships are:

\[
\log k = -16.991 + 32.019 Y - 0.094 \alpha; \quad R = 0.7920 \\
SE = \begin{pmatrix} 5.291 \end{pmatrix} \begin{pmatrix} 11.200 \end{pmatrix} \begin{pmatrix} 0.450 \end{pmatrix} \\
t = \begin{pmatrix} -3.217 \end{pmatrix} \begin{pmatrix} 2.858 \end{pmatrix} \begin{pmatrix} -2.688 \end{pmatrix}
\]
The rate of the reaction is strongly influenced by non-specific solvent parameter 'Y' which is a measure of the polarity of the solvent. A positive value of the coefficient of Y in Eq. 5 suggests that the transition state is more solvated than the reactants due to long range interaction with the solvent.

The reaction rate is also influenced by nucleophilicity of the solvent, B, (due to electron donation). The negative sign of this coefficient in the above equation suggests that the reactant is more solvated than the transition state.

α is another parameter which successfully enters into the above equation. This parameter, 'α', is a measure of hydrogen bond donor ability of the solvent. The coefficient of this solvent parameter is also negative indicating that the reactants are more solvated than the transition state due to hydrogen bond donation.

Based on the above, the mode of solvation of the reactants and the transition state is represented as shown in Scheme I.

Since there is extensive charge separation in the transition state, it is more solvated than the neutral nucleophile and the substrate BzBr. This is indicated by a large positive coefficient of Y in Eq. 6. The negative value of 'B' coefficient indicates that 'H' is more solvated due to specific electron donation by the solvent. The negative coefficient of 'α' suggests that the reactants, especially 'N' of DPA and 'Br' of BzBr.

### Table 1—Second order rate constants and activation parameters in the reaction between benzyl bromide and diphenyl amine in different solvents. [[BzBr] = [DPA] = 0.02 mol dm⁻³

<table>
<thead>
<tr>
<th>Solvent</th>
<th>k × 10⁴, dm³ mol⁻¹ s⁻¹ at temp/K</th>
<th>ΔH°</th>
<th>ΔS°</th>
<th>ΔG°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>293</td>
<td>298</td>
<td>303</td>
<td>313</td>
</tr>
<tr>
<td>n-propanol</td>
<td>7.77</td>
<td>13.25</td>
<td>22.83</td>
<td>45.32</td>
</tr>
<tr>
<td>i-propanol</td>
<td>6.84</td>
<td>15.51</td>
<td>23.14</td>
<td>37.87</td>
</tr>
<tr>
<td>Butanol</td>
<td>6.94</td>
<td>8.33</td>
<td>11.11</td>
<td>15.15</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>3.46</td>
<td>4.17</td>
<td>5.83</td>
<td>6.94</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>16.66</td>
<td>23.41</td>
<td>46.29</td>
<td>59.52</td>
</tr>
<tr>
<td>Acetone</td>
<td>10.71</td>
<td>11.66</td>
<td>13.33</td>
<td>16.66</td>
</tr>
<tr>
<td>Butan-2-one</td>
<td>648.11</td>
<td>763.81</td>
<td>925.92</td>
<td>--</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>--</td>
<td>41.65</td>
<td>72.9</td>
<td>62.58</td>
</tr>
<tr>
<td>Formamide</td>
<td>104.13</td>
<td>166.66</td>
<td>277.72</td>
<td>509.11</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>17.01</td>
<td>238.11</td>
<td>3286</td>
<td>44.90</td>
</tr>
</tbody>
</table>

\[
\log k = -0.351 - 0.012 B + 1.047 \alpha; \quad R = 0.689 \tag{3}
\]

\[
SE = (0.893) \quad (0.007) \quad (0.529) \quad (0.003) \quad (0.28)
\]

\[
\log k = -18.368 + 38.285 Y - 0.015 B; \quad R = 0.863 \tag{4}
\]

\[
SE = (4.289) \quad (9.134) \quad (0.005) \quad (0.003) \quad (0.28)
\]

\[
\log k = -16.532 + 34.759 Y - 0.014 B - 0.797 \alpha \quad \ldots \ldots \ldots \ldots (5)
\]

\[
SE = (3.268) \quad (6.947) \quad (0.003) \quad (0.28) \quad (0.003)
\]

\[
t = -5.059 \quad 5.003 \quad 3.953 \quad -2.841 \\
\]

\[
R = 0.934, SE = 0.321, F = 18.324
\]
are more solvated due to hydrogen bond donation by the solvent.

The product separated in this reaction, diphenyl benzyl amine, has a m.p. of 142°C. The IR spectrum recorded doesn’t show any absorption due to N-H bond (around 3140 cm\(^{-1}\)). Therefore the overall reaction is represented as Eq. 6:

\[
\text{N-H} + \text{H-Br} \rightarrow \text{N-C} \quad (6)
\]

The temperature effect on these reactions has been studied by determining \(k\) values in the temperature range 293-313 K (Table 1) in each solvent. The activation parameters \(\Delta H^\ddagger\), \(\Delta S^\ddagger\) and \(\Delta G^\ddagger\) are computed from this data and presented in Table 1.

\(\Delta S^\ddagger\) values are all negative, indicating that the relative overall solvation of the transition state due to all the above factors is more than that of the reactants. Since the leaving group is negative and the nucleophile is neutral, the two ends in the transition state have different solvation energies\(^6\). The free energy of activation, \(\Delta G^\ddagger\), in all the solvents is nearly constant at 89.22±4.61 kJmol\(^{-1}\), indicating that the process under investigation follows a similar mechanism in all the solvents, which is a necessary condition for the applicability of linear solvation energy relationship (LSER).

References