Effect of Dielectric Constant & Temperature on Hammett Reaction Constants in Substitution Reactions of cis-[Coen₂(H₂O)₂]³⁺ Ion with Benzoic Acids

Chhaya Chaudhury & S K Siddhanta*
Department of Chemistry, University of Burdwan, Burdwan 713104
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The reactions of cis-[Coen₂(H₂O)₂]³⁺ with benzoic and substituted benzoic acids have been studied: (a) in solvents of different dielectric constants, at constant temperature (30°C); and (b) in the same solvent [15° (v/v) ethanol-water mixture] at different temperatures. It has been conclusively established that the reactions proceed only by S₉² mechanisms. Hammett reaction constants (p) have been determined in all the cases. The linear plot of p versus 1/O provides support to the S₉² mechanism. The linear plot of p versus 1/T establishes the dependence of the activation parameters on Hammett substituent constant (σ).

In our previous paper¹, we have shown that the Hammett relationship is applicable to the reactions of cis-[Coen₂(H₂O)₂]³⁺ with benzoic and substituted benzoic acids. Presently we have studied the effect of varying dielectric constant and temperature on Hammett reaction constants (p) of the reactions of cis-[Coen₂(H₂O)₂]³⁺ ion with benzoic acids.

Materials and Methods
cis-[Coen₂(H₂O)₂]³⁺[NO₃⁻] was prepared and characterised as described earlier¹. The ligands used were the ammonium salts of benzoic and substituted benzoic acids. The reaction products cis-[Coen₂(H₂O)₂]³⁺ (where L = benzoate or substituted benzoate) were isolated and characterised as given in our earlier paper¹.

Ethanol-water mixtures containing 15, 22, 30, 35 and 40° (v/v) ethanol were prepared using doubly distilled water and ethanol obtained by distilling absolute alcohol over quick lime. The dielectric constants of ethanol-water mixtures containing 15, 22, 30, 35 and 40° (v/v) ethanol were collected from the data given by Gosta Akerlof². The pK₀ values of benzoic and substituted benzoic acids at 30°C in 30° ethanol-water mixture have been taken from our earlier publication⁴, but the pK₀ values at 30°C in other ethanol-water mixtures used were determined afresh analogously.

In the present study, kₜₚ values were determined under pseudo conditions ([NH₄L] in 10-fold excess, [L⁻] low and constant due to buffer action of NH₄L) at constant pH (4.4) and ionic strength (0.08 mol dm⁻³) in every case: (a) in solvents of different dielectric constants at constant temperature (30°C); and (b) at different temperatures 30°, 35°, 40° and 45°C in the same solvent, i.e. 15° (v/v) ethanol-water mixture. In the case of p-methoxybenzoate, however the reaction was studied at pH 5.9 for reasons stated in our earlier paper¹. This ligand was not used for studies at higher temperatures since base hydrolysis of the complex interfered with the reaction of the complex with the ligand.

Results and Discussion
In our previous paper¹, we showed that equilibria (1) and (2) contributed to the reaction of cis-[Coen₂(H₂O)₂]³⁺ with NH₄L

\[ \text{HL} = \text{H}^+ + \text{L}^- \]  \hspace{1cm} (1)

\[ \text{cis-[Coen₂(H₂O)₂]}^{2+} + \text{L}^- \rightarrow [A] \]

\[ \text{cis-[Coen₂(H₂O)₂]}^{2+} + \text{H}_2\text{O} \rightarrow [B] \]  \hspace{1cm} (2)

To decide whether the reaction between A and L⁻ proceeds by an S₉₂ or an ion-pair (IP) path, we considered the general case, where the complex (A) reacted with the benzoate ion [L⁻] in two parallel paths: S₉₂ path with a second order rate constant k₂; and IP path with a first order rate constant k₁ to produce complex (B) as the end product of each path. Since ion pairing equilibrium (association constant = Kᵢ) is very fast, we have

\[ \text{Rate} = kₙ[A][L^-] + k₀[I] \]

or \( (k₂ + kᵢ)Kᵢ[A][L^-] \)

since \[ [I] = Kᵢ[A][L^-] \]

Now if [A]₀ is the initial concentration of complex
(A) and [A]un is the concentration of the unreacted complex (A) not converted into complex (B),

\[ [A]_{un} = [A]_0 - [B] = [A] + [I] \]

From Eqs (3) and (4), we have

\[ \text{Rate} = \frac{(k_2 + k_i K_i) [A]_{un} [L^-]}{1 + K_i [L^-]} \]

But, \( k_{obs} = k_{obs} [A]_{un} \)

Therefore, \( k_{obs} = \frac{k_2 + k_i K_i}{1 + K_i [L^-]} \) \( [L^-] \)

Eq. (6) indicates that a plot of \( k_{obs} \) versus \( [L^-] \) will be non-linear starting from the origin \(( [L^-] = 0, k_{obs} = 0 \) and becoming parallel to the abscissa \(( k_{obs} = \text{constant} \) at large \( [L^-] \) where \( K_i [L^-] > 1 \). However, such a plot is linear passing through the origin (values of \( k_{obs} \) at varying concentrations of \( I^- \) are given in Table 1).

This anomalous behaviour can be regarded as consistent with Eq. (6) only if \( K_i [L^-] \) in the denominator is \( \ll 1 \), i.e. if \( K_i \) is of the order of 1 or less, since \( [L^-] \) is of the order of 0.05 (Table 1). To decide as to what might be the actual magnitude of the ion-association constant \( K_i \), the following procedure was adopted. Eq. (6) can easily be transformed into Eq. (7).

\[ \frac{1}{k_{obs}} = \frac{1}{K_i} + \frac{1}{(k_2 + K_i k_i)} \]

Eq. (7) indicates that a plot \( 1/k_{obs} \) versus \( 1/[L^-] \) should be linear with slope \( = 1/(k_2 + K_i k_i) \) and intercept \( = K_i/(k_2 + K_i k_i) \). Though such a plot is linear it passes practically through the origin (Fig. 1) indicating that the intercept \( K_i/(k_2 + K_i k_i) \approx 0 \), i.e. the numerator \( K_i \approx 0 \). This means that stable ion-pairs are not formed in the present systems and there is no IP mechanism operative here.

If we put \( K_i = 0 \) in Eq. (7) we get

\[ k_{obs} = k_2 [L^-] \]

Rate = \( k_2 [A] [L^-] \) where \( k'' = k_2 \) \( [L^-] \)

in which \( k'' \) is a pure second order rate constant. The Hammett relation is straightforward applicable to S2 reactions.

Table 1: Effect of Varying \([L^-]\) on \( k_{obs} \)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>[Complex] (mol dm(^{-3}))</th>
<th>( k_{obs} \times 10^5 ) (s(^{-1}))</th>
<th>( [L^-] ) (mol dm(^{-3}))</th>
<th>( 1/k_{obs} \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>NH(_4)L (mol dm(^{-3}))</td>
<td>pH</td>
<td>( [L^-] )</td>
<td>( k_{obs} \times 10^5 )</td>
</tr>
<tr>
<td>0.05</td>
<td>4.4</td>
<td>0.016</td>
<td>1.15</td>
<td>62.5</td>
</tr>
<tr>
<td>0.05</td>
<td>4.7</td>
<td>0.024</td>
<td>1.90</td>
<td>41.0</td>
</tr>
<tr>
<td>0.05</td>
<td>5.0</td>
<td>0.033</td>
<td>2.62</td>
<td>30.3</td>
</tr>
<tr>
<td>0.10</td>
<td>4.7</td>
<td>0.049</td>
<td>3.84</td>
<td>20.5</td>
</tr>
</tbody>
</table>

In the title system \( L^- \) is the only reacting species; the entity HL, though present does not take any significant part in the reaction. This is proved by two facts: (a) \( k_{obs} \) versus \( [L^-] \) plot is linear passing through the origin showing that \( k_{obs} \) is directly proportional to \( [L^-] \). This would not have been the case if HL was also participating in the reaction; (b) When the experiment was conducted with the reaction mixture having the recipe \([A] = 0.005 \text{ mol dm}^{-3}; [NH}_4\text{Bz} = \text{0.05 mol dm}^{-3}; \text{pH} 3.0; \text{and temp.-30 C (under which conditions, [Bz-] = 0.0009 mol dm}^{-3}; \text{and [HBz] = 0.0491 mol dm}^{-3}) \) it was found that there was no change in absorbance even after 10 hr. This conclusively proved that HBz did not react to any measurable extent. Thus,

\[ k_{obs} = k'' [L^-] = k'' K_i [HL][H^+] \]

where \( K_i \) = dissociation constant of the acid HL.

The Hammett equation for the reaction of benzoate and substituted benzoate ions with complex (A) for any one solvent mixture can be written as

\[ \log k'' = \log k''_0 + \sigma \rho \]

where \( k'' \) is the second order rate constant for any substituted benzoate with the substituent constant \( \sigma \), \( k''_0 \) that for the parent benzoate ion and \( \rho \) the reaction constant for a particular solvent mixture. From the slopes of the linear plots of \( \log k'' \) versus \( \sigma \) for each reaction mixture, the \( \rho \)-values at 30 C in the reaction medium of varying dielectric constants were calculated using the least squares method (Table 2). The plot of \( \rho \) against 1 \( D \) was also found to be linear.

Similarly, the different \( \rho \)-values for the same reactions at different temperatures using the same solvent (15% ethanol-water) were determined. These reaction constants (Table 3) are linearly related to the reciprocal of the corresponding temperatures (Fig. 2).

The activation parameters \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) have been calculated for the reaction (2) and the values are given in Table 4.
### Table 2—Effect of Varying Dielectric Constant on $pK_a$, $k_{obs}$, and $k''$

(Temp = 30°C; pH = 4.4; [Complex] = 0.005 mol dm$^{-3}$; [NH$_4$L] = 0.05 mol dm$^{-3}$; $\mu \approx 0.08$ mol dm$^{-3}$)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$pK_a$</th>
<th>$k_{obs}$ ($10^3$ s$^{-1}$) and $k''$ (mol$^{-1}$ dm$^3$ s$^{-1}$)</th>
<th>Unsubstituted</th>
<th>p-Hydroxy</th>
<th>m-Hydroxy</th>
<th>m-Nitro</th>
<th>m-Methyl</th>
<th>$p$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 71</td>
<td>4.34 1.60 0.60</td>
<td>4.83 3.20 2.36</td>
<td>4.12 1.10 0.34</td>
<td>3.64 0.22 0.03</td>
<td>4.40 2.74 1.09</td>
<td>4.62 3.10 1.65</td>
<td>-1.58</td>
<td></td>
</tr>
<tr>
<td>22 68</td>
<td>4.60 1.23 0.65</td>
<td>5.03 3.00 1.16</td>
<td>4.35 1.68 0.64</td>
<td>3.89 0.38 0.10</td>
<td>4.68 2.01 1.17</td>
<td>4.90 2.88 2.40</td>
<td>-1.39</td>
<td></td>
</tr>
<tr>
<td>30 63</td>
<td>4.72 1.15 0.71</td>
<td>5.23 2.11 1.92</td>
<td>4.57 0.95 0.18</td>
<td>4.01 0.69 0.12</td>
<td>4.80 1.82 1.27</td>
<td>5.09 2.27 2.68</td>
<td>-1.15</td>
<td></td>
</tr>
<tr>
<td>35 60</td>
<td>4.94 1.82 0.71</td>
<td>5.43 2.04 1.20</td>
<td>4.78 1.92 1.23</td>
<td>4.23 0.69 0.40</td>
<td>5.01 1.81 1.27</td>
<td>5.21 2.18 2.95</td>
<td>-0.92</td>
<td></td>
</tr>
<tr>
<td>40 57</td>
<td>5.12 2.93 2.91</td>
<td>5.66 2.33 1.90</td>
<td>5.02 2.29 2.37</td>
<td>4.39 2.11 0.83</td>
<td>5.18 2.66 3.74</td>
<td>5.40 1.66 3.66</td>
<td>-0.79</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3—Variation of $k_{obs}$ and $k''$ with Temperature

(Solvent = 15% (v/v) ethanol; pH = 4.4; [Complex] = 0.005 mol dm$^{-3}$; [NH$_4$L] = 0.05 mol dm$^{-3}$; $\mu \approx 0.08$ mol dm$^{-3}$)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$k_{obs}$ ($10^3$ s$^{-1}$) and $k''$ (mol$^{-1}$ dm$^3$ s$^{-1}$)</th>
<th>Benzoic acid</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 35 40 45</td>
<td>10$^3$k$_{obs}$ 10$^3$k''</td>
<td>unsaturated</td>
<td>p-hydroxy</td>
</tr>
<tr>
<td>30</td>
<td>1.60 0.60</td>
<td>3.20 1.91</td>
<td>1.10 1.18</td>
</tr>
<tr>
<td>35</td>
<td>5.00 1.00</td>
<td>5.91 1.87</td>
<td>3.67 2.36</td>
</tr>
<tr>
<td>40</td>
<td>8.02 1.82</td>
<td>8.55 3.00</td>
<td>5.12 1.56</td>
</tr>
<tr>
<td>45</td>
<td>14.34 3.00</td>
<td>13.48 3.00</td>
<td>10.90 1.56</td>
</tr>
</tbody>
</table>

### Table 4—Relationship between Activation Parameters and Substituent Constants

<table>
<thead>
<tr>
<th>Benzoic acid</th>
<th>Substituent</th>
<th>$\Delta H^\ddagger$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J deg$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta H_0^\ddagger - \Delta H^\ddagger$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_0^\ddagger - \Delta S^\ddagger$ (J deg$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Nitro</td>
<td>+0.71</td>
<td>168.28</td>
<td>225.58</td>
<td>-8.24 x 10$^4$</td>
<td>-239.5</td>
</tr>
<tr>
<td>m-Hydroxy</td>
<td>+0.12</td>
<td>120.35</td>
<td>84.05</td>
<td>-8.79 x 10$^4$</td>
<td>-237.5</td>
</tr>
<tr>
<td>Unsubstituted</td>
<td>0.00</td>
<td>109.80</td>
<td>55.55</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>m-Methyl</td>
<td>-0.08</td>
<td>102.81</td>
<td>35.66</td>
<td>-8.74 x 10$^4$</td>
<td>-248.6</td>
</tr>
<tr>
<td>p-Hydroxy</td>
<td>-0.37</td>
<td>79.07</td>
<td>-36.71</td>
<td>-8.31 x 10$^4$</td>
<td>-249.4</td>
</tr>
</tbody>
</table>

\[
\Delta H_0^\ddagger - \Delta H^\ddagger = \frac{-0.44 \times 10^4}{2.303 R} \text{ whence } \frac{\Delta H_0^\ddagger - \Delta H^\ddagger}{\sigma} = -8.5 \times 10^4 J \text{ mol}^{-1}
\]

\[
\Delta S_0^\ddagger - \Delta S^\ddagger = \frac{-12.92}{2.303 R} \text{ whence } \frac{\Delta S_0^\ddagger - \Delta S^\ddagger}{\sigma} = -249.1 J \text{ deg}^{-2} \text{ mol}^{-1}
\]
In an $S_n2$ reaction between two oppositely charged ions, the transition state is more easily attained in media of lower dielectric constants resulting in a relatively low values of the activation energy; in otherwords the reaction rate increases as the dielectric constant of the reaction medium decreases in an $S_n2$ reaction between oppositely charged ions. The slope of $\rho$ versus $1/D$ plot is positive showing that $\rho$ increases as $1/D$ increases i.e. as $D$ decreases, this providing strong evidence for the reaction to proceed by an $S_n2$ path.

A comparison of the reaction constant values ($\rho$) at different temperatures (Table 3) shows that the negative value of $\rho$ decreases with rise in temperature and $\rho$ varies linearly with $1/T$ (Fig. 2). This is also to be anticipated since at high temperature, the selectivity of the reagent becomes less due to thermal randomisation and therefore the sensitivity of the reaction towards the electron density changes at the reaction site decreases.

A comparison of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values (Table 4) for different ligands shows that the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ follow the order: $p$-hydroxybenzoic acid $< m$-methylbenzoic acid $< \text{benzoic acid} < m$-hydroxy benzoic acid $< m$-nitro benzoic acid. An explanation for this trend has been provided in an earlier publication.$^3$

It has been presumed that the stronger the association, the more ordered is the activated complex and the less will be the magnitude of the positive $\Delta S^\ddagger$. As has been argued earlier, the strength of the association in the seven coordinated activated complex $[\text{Coen}_3(H_2O)_2L^-]^2+$ decreases as the ligand $L^-$ is varied in the order of their decreasing basicities namely, $p$-hydroxybenzoate $> m$-methyl benzoate $> \text{benzoate} > m$-hydroxy benzoate $> m$-nitrobenzoate, and hence the positive values of $\Delta S^\ddagger$ increase in the same order. In the case of $p$-hydroxybenzoate, however, $\Delta S^\ddagger$ has a low negative value perhaps showing that the decrease in activation entropy resulting from the strong association in the activated complex has more than compensated for the increase in the same due to desolvation effects. It may be remarked that in the case of the activated complex $[\text{Coen}_3(H_2O)Cl^-L^-]^+$ formed in the reaction between cis-$[\text{Coen}_3(H_2O)Cl]^2+$ and $L^-$ studied by Ghoshal and Siddhanta,$^3$ the entropy of activation value was $+18.8$ e.u. when $L^- = p$-hydroxybenzoate; presumably, the strength of association in the seven membered activated complex $[\text{Coen}_3(H_2O)_2(p-$ (Bz $)^-)]^2+$ is greater than that in $[\text{Coen}_3(H_2O)Cl\cdot p$-Bz $]_+^+$ in which some instability is caused by the proximity of two negatively charged ions in the complex.

A plausible explanation for the $\rho$ versus $1/T$ linear relationship has been provided in an earlier publication.$^3$ It was pointed out that if $(\Delta H_0^\ddagger - \Delta H_0^\ddagger)/\sigma$ and $(\Delta S_0^\ddagger - \Delta S_0^\ddagger)/\sigma$ are constants then $\rho$ versus $1/T$ plot becomes linear with slope $(\Delta H_0^\ddagger - \Delta H_0^\ddagger)/2.303R$ and intercept $(\Delta S_0^\ddagger - \Delta S_0^\ddagger)/2.303R$ respectively. $\Delta H_0^\ddagger, \Delta H_0^\ddagger, \Delta S_0^\ddagger, \Delta S_0^\ddagger$ are respectively the enthalpies and entropies of activation corresponding to the rate constants $k_0$ and $k^\ddagger$. In Table 4 we have tabulated the values of $(\Delta H_0^\ddagger - \Delta H_0^\ddagger)/\sigma$ and $(\Delta S_0^\ddagger - \Delta S_0^\ddagger)/\sigma$ for the pairs benzoic-$p$-hydroxybenzoic, benzoic-$m$-hydroxybenzoic, benzoic-$m$-methylbenzoic and benzoic-$m$-nitrobenzoic acids. The values are found to be approximately constant. The experimental values of slope and intercept of the plot of $\rho$ versus $1/T$ have been found to be approximately equal to $-0.44 \times 10^4$ and $-12.92$ respectively.

The near constancy in $(\Delta H_0^\ddagger - \Delta H_0^\ddagger)/\sigma$ and $(\Delta S_0^\ddagger - \Delta S_0^\ddagger)/\sigma$ values (Table 4) indicates that the difference between enthalpies/entropies of activation in the two reactions, viz. the reaction of $A$ with unsubstituted $L^-$ and the reaction of $A$ with any substituted $L^-$ is proportional to the substituent constant $\sigma$, which is again a measure of electron density difference between the $-\text{COO}$ reaction sites of the unsubstituted and substituted $L^-$.

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References