Molecular complexes of paraquat with sodium phenolates

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Molecular complexes of paraquat with sodium phenolates have been studied spectrophotometrically in aqueous medium at different temperatures. All the complexes exhibit charge transfer bands in the visible region where neither of the components have any absorption. The stoichiometry of each of the complex is found to be 1:1 and is unaffected by the variation of temperature. The stabilities and thermodynamic parameters of the complexes have been determined from the absorption studies on the CT bands. Both positions of CT bands and the stabilities of the complexes are affected by the substituents but in different order.

1,1'-Dimethyl-4,4'-bipyridinium dichloride (paraquat, PQ) was shown to form charge transfer complexes with inorganic anions\(^\text{1-4}\) as well as with neutral organic donors\(^\text{5-9}\) owing to its strong electron acceptor property. However, the reports on the charge transfer complexes of PQ with organic anions are sporadic. Barnett et al.\(^\text{6}\) reported the formation of CT complex between PQ and benzilate anion. Prasad and Hoffman\(^\text{7}\) showed that PQ forms CT complex with cysteine and exhibits CT band only at higher pH at which sulfhydryl group is deprotonated to produce its anion. Lack of extensive studies on the CT complexes of PQ with organic anions prompted us to carry out a systematic study of such complexes. To accomplish this, a series of sodium phenolates have been prepared and the charge transfer spectra, stabilities and thermodynamic parameters of their molecular complexes with PQ have been investigated and reported.

\[
\text{H}_3\text{C} - \begin{array}{c} \text{N} \\ \text{CH}_3 \end{array} \text{N} - \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} , 2 \text{Cl}^-
\]

Paraquat, PQ

Materials and Methods

Paraquat was prepared by the dimerisation of pyridine to 4,4'-bipyridyl, followed by quaternization with methyl chloride and isolation as the dihydrate. Commercial phenols (BDH Analar) were purified by the methods available in the literature till TLC pure. All the phenols were converted to the phenolates by adding calculated amounts of NaOH (BDH Analar). The UV-Vis absorption spectra (Fig. 1) of the complexes were recorded on Shimadzu-240 double beam spectrophotometer in the temperature range 10-50°C at 10°C intervals with an accuracy of ±0.1°C using a matched pair of quartz stoppered cells of 10 mm path length. The studies at different temperatures were made in a thermostated sample compartment. Temperatures above 25°C were attained by electrical heating of the sample compartment while lower temperatures by circulating cold water. Stock solutions of donors and acceptors were prepared and maintained under nitrogen atmosphere and the solutions were mixed just before recording the spectra. Each sample was allowed to equilibrate at least for 5 min before measuring the absorbance. The concentration of PQ was held constant at 2 \times 10^{-3} \text{ M}, while that of phenolates varied between 0.01 and 0.05 M. The absorption bands due to acceptor or donor individually have fallen to the base much before the wavelength of CT absorption. However, the lower wavelength side of the CT band is complicated by other absorption probably due to the complexed donor\(^\text{18}\). The complicated CT bands are analysed using the relation by Briegleb and Czekalla\(^\text{11}\).

\[
\frac{(v_h-v_l)\times 2}{(v_m-v_l)}=1.2
\]

where \(v_h\) and \(v_l\) refer to the frequency at the half the maximum intensity to the high and low frequency side of the peak located at \(v_m\). The formation constants of the complexes were determined using Rose-Drago equation\(^\text{12}\) viz.,

\[
K'=A/e-([A_0]+[D_0])+[A_0][D_0]e/A
\]

where 'K' is stability constant, 'A' is absorbance and 'e' is molar extinction coefficient of the complex. [A\(_0\)] and [D\(_0\)] are initial concentrations of acceptor
Table 1—Charge transfer spectra and stabilities of PQ complexes with phenolates

<table>
<thead>
<tr>
<th>Donor</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(e) (lit.mol(^{-1}) cm(^{-1}))</th>
<th>K (lit.mol(^{-1})) at 10(^0)C</th>
<th>20(^0)C</th>
<th>30(^0)C</th>
<th>40(^0)C</th>
<th>50(^0)C</th>
<th>(-\Delta H) (k.cal. mol(^{-1}))</th>
<th>(-\Delta S) (cal. mol(^{-1}) deg(^{-1}))</th>
<th>(-\Delta G) (k.cal. mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-naphtholate</td>
<td>552</td>
<td>560</td>
<td>23.88</td>
<td>14.42</td>
<td>9.00</td>
<td>5.75</td>
<td>3.81</td>
<td>8.35</td>
<td>23.2</td>
<td>1.44</td>
</tr>
<tr>
<td>(\beta)-naphtholate (phenolates)</td>
<td>523</td>
<td>560</td>
<td>23.21</td>
<td>14.1</td>
<td>8.82</td>
<td>5.68</td>
<td>3.78</td>
<td>8.25</td>
<td>22.9</td>
<td>1.43</td>
</tr>
<tr>
<td>(p)-OCH(_3)</td>
<td>510</td>
<td>300</td>
<td>15.91</td>
<td>10.52</td>
<td>7.14</td>
<td>5</td>
<td>3.54</td>
<td>6.82</td>
<td>18.6</td>
<td>1.28</td>
</tr>
<tr>
<td>(p)-CH(_3)</td>
<td>476</td>
<td>240</td>
<td>13.7</td>
<td>9.52</td>
<td>6.78</td>
<td>4.93</td>
<td>3.65</td>
<td>6</td>
<td>16</td>
<td>1.23</td>
</tr>
<tr>
<td>(o)-CH(_3)</td>
<td>469</td>
<td>230</td>
<td>13.2</td>
<td>9.52</td>
<td>6.55</td>
<td>4.77</td>
<td>3.54</td>
<td>5.98</td>
<td>16</td>
<td>1.21</td>
</tr>
<tr>
<td>(m)-CH(_3)</td>
<td>464</td>
<td>220</td>
<td>11.84</td>
<td>8.37</td>
<td>6.05</td>
<td>4.77</td>
<td>3.36</td>
<td>5.77</td>
<td>15.3</td>
<td>1.16</td>
</tr>
<tr>
<td>(p)-H</td>
<td>452</td>
<td>215</td>
<td>10.6</td>
<td>7.53</td>
<td>5.48</td>
<td>4.07</td>
<td>3.08</td>
<td>5.6</td>
<td>15.1</td>
<td>1.1</td>
</tr>
<tr>
<td>(o)-Cl</td>
<td>449</td>
<td>200</td>
<td>8.01</td>
<td>5.88</td>
<td>4.36</td>
<td>3.33</td>
<td>2.55</td>
<td>5.22</td>
<td>14.3</td>
<td>0.96</td>
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<tr>
<td>(p)-Cl</td>
<td>455</td>
<td>200</td>
<td>7.68</td>
<td>5.64</td>
<td>4.23</td>
<td>3.23</td>
<td>2.5</td>
<td>5.08</td>
<td>13.9</td>
<td>0.94</td>
</tr>
</tbody>
</table>

and donor respectively. The formation constants and molar extinction coefficients are evaluated from the intersection points of Rose-Drago plots. Thermodynamic parameters viz., \(\Delta H\) and \(\Delta S\) have been determined from the temperature variation of formation constants using van't Hoff method and are reported in Table 1 together with \(\Delta G\) at 25\(^0\)C. The stoichiometry of the complexes was determined by the Job’s continuous variation method (Fig. 2).

**Results and Discussion**

The colourless solutions of paraquat and sodium phenolate turned reddish orange immediately after mixing. Substituted phenolate anions also produced characteristic colours with paraquat indicating the formation of charge transfer complexes. The complex of sodium phenolate-PQ exhibit a new absorption band at 452 nm, the wave length region where individual components do not have any absorption. Substituted phenolates also exhibited CT bands in the region between 400-600 nm (Table 1).

Phenolates with two donor sites viz., the \(n\)-electrons of oxygen and the \(\pi\)-electrons of benzene ring, can form \(n-\pi\) or \(\pi-\pi\) complexes with PQ. If the phenolates act as \(n\)-donors, a correlation between \(v_{CT}\) of the complexes and ionization constants of the phenolates \((K_a)\) or Hammett \(\sigma\) constants is reasonably expected since the ionization constants and the Hammett \(\sigma\) constants are the measure of donor strengths of the phenolate oxygen towards \(H^+\) ion or an electron acceptor. The absence of such correlation between \(v_{CT}\) and \(K_a\) or \(\sigma\) rules out the possibility of \(n\)-donation.

On the other hand, the plots of \(v_{CT}\) of PQ complexes are found to bear linear relation with \(v_{CT}\) of phenols or anisole complexes of TCNE. In the latter two types of complexes, \(\pi-\pi\) interaction was suggested with \(\psi\), M.O. acting as the donor level. This suggests that in PQ complexes, the nature of interaction is the same as that in phenols/anisole-
TCNE complexes with ψ, M.O. acting as donor level leading to the formation π-π complexes.

Effect of substituents on CT bands

The CT band of PQ-phenolate at 452 nm is shifted to longer wavelengths by all the substituents in the benzene ring and the shifts are in the order: α-naphtholate > β-naphtholate > phenolates (p-OCH₃ > p-CH₃ > o-CH₃ > m-CH₃ > p-Cl > p-H > o-Cl). The shifts in the CT bands are explicable in terms of conjugative, mesomorphic or inductive effects of substituents. The conjugative interaction in naphthalene, the mesomorphic effect of methoxy and the inductive effect of methyl groups perturb the resonance in the benzene ring and boost up the energy of the donor level and bring it closer to the LUMO of PQ and thus cause a bathochromic shift in the CT band.

Ionization potentials of the donors

The energies (Eₐ) of the CT bands of molecular complexes of structurally similar donors, with a common acceptor were shown to vary linearly with ionization potentials (I₀) of the donors as given by the equation Eₐ = I₀ + b where ‘a’ and ‘b’ are constants. This relation is used for the determination of ionization potentials of donors from the positions of the CT bands. Since the values of constants ‘a’ and ‘b’ for PQ complexes in aqueous medium are not available in literature, they were determined by us from the energies of CT bands of PQ with donors of known ionization potentials. For this purpose, a few anilines, phenols and naphthylamines were used as donors. The energies of CT bands were plotted against ionization potentials of donors. The slope and intercept of the plot are found to be 0.976 and -4.50 eV respectively. Using these constants, the ionization potentials of phenolates have been determined and are found to be much lower than those of phenols (Table 2).

The formation constants of the complexes were determined by Rose-Drago method and are reported with an accuracy of ± 0.1 lit.mol⁻¹ (Table 1).

The formation constants of the complexes and molar extinction coefficients are in the order: α-naphtholate > β-naphtholate > phenolates (p-OCH₃ > p-CH₃ > o-CH₃ > m-CH₃ > p-Cl > p-H > o-Cl). Within the series of phenolates, the logarithmic functions of the formation constants are linearly related to the Hammett σ constants. This relation, however, was not observed in case of vCT. The energy of CT band depends on the difference in the energy of highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor, which in turn is governed by the extent to which the energy of HOMO is boosted up by the substituent. The stability of the complex, on the other hand depends on the forces holding the components. In phenolate-PQ complexes, the ion-ion attractions play a significant role in the stabilization of the complexes. The charge on the benzene ring is enhanced by electron releasing groups viz., OCH₃ and CH₃ but decreases by Cl group and hence the stabilities of the complexes are altered by the substituents in the same order as the charge on the benzene ring. The thermodynamic parameters viz., ΔH and ΔS were determined from the slope and intercept of the plot of log K vs 1/T. The ΔG values were calculated using the relation, ΔG = ΔH + TΔS.

The enthalpies of formation are below 10 kcal.mol⁻¹, a characteristic feature of weak CT complexes. The ΔH, ΔS and ΔG values increase with increasing electron releasing ability of the donors and follows the same trend as the stabilities of the complexes. A linear relationship obtained between ΔH and ΔS for all the complexes indicating that formation of complex is not hindered by substituents. The negative values of ΔG indicates the spontaneity of complex formation while negative enthalpy and entropy suggest that the complexes are very stable and undergo strong restraint.
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References