Molecular complexes of anilines with DDQ

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Molecular complexes of DDQ with anilines have been studied spectrophotometrically by stabilising the complexes in a low polar solvent (CCl₄), at low temperatures and under low donor concentrations. All the complexes exhibit well resolved charge transfer bands in the visible region where neither of the components has any absorption. The stoichiometry of each of the complex is found to be 1:1 and is unaffected by the variation of temperature. A linear relationship is observed between the v_CT of DDQ-anilines and the v_CT of TCNE-anilines indicating a π-π interaction between the DDQ and the donors. The stabilities and thermodynamic parameters have been determined from the absorption studies on the CT bands. A linear relationship has been observed between logarithmic functions of stability constants and Hammett ρ constants. Both ring and N-substituents affect the position of CT band and the stabilities of the complexes.

The molecular interaction between 2,3-dichloro-5, 6-dicyano-p-benzoquinone (DDQ) and anilines has been a subject of considerable interest and has been investigated by many workers using different methods, viz., kinetic, IR spectroscopy, and conductivity. Dwivedi et al.² found that DDQ forms blue coloured solutions with anilines, which soon turn into green and finally become yellow. The blue colour was attributed to the formation of CT complexes. The green colour (λ_max 540 nm) was attributed to the formation of a mono substituted derivative of DDQ while the yellow colour (λ_max 350 nm) to the final product which was identified as a disubstituted derivative of DDQ. They studied the kinetics of formation of disubstituted derivative of DDQ from the monosubstituted one. However, the authors were unsuccessful in studying the CT spectra and stabilities of the complexes due to their fast transformation into products. Issa et al.² too, were unsuccessful in stabilising the complexes and studying their IR spectra. From the conductance measurements, Dwivedi et al.⁴ demonstrated that CT complexes of DDQ anilines soon decompose into ions in solvents of sufficient polarity and exhibit appreciable conductivity. From this they pointed out that the stoichiometry of anilines-DDQ complexes is 1:1.

From a study of kinetics of decay of CT band, Srivastava and Verma have reported the stability constant of CT complex of o-toluidine-DDQ¹. But the authors have neither reported the CT spectra nor the method of stabilising the CT complex to accomplish their study.

Literature survey revealed that the CT complexes can be stabilised for longer time (a) in low polar solvents (b) at low temperatures and (c) under low donor concentrations. This prompted us to investigate the CT spectra stabilities and thermodynamic parameters of CT complexes of anilines-DDQ in low polar solvent, viz., CCl₄, at low temperatures and under low donor concentrations. The combined effect of these factors is expected to stabilise the complexes for considerable time enabling the detection of λ_max of CT band and carry out necessary equilibrium studies.

Experimental

The commercial sample of DDQ (Aldrich) was repeatedly re-crystallized from benzene-chloroform (2:1) mixture (m.p. 213-214 °C). Anilines (BDH-Analar) were purified by the methods available in literature. CCl₄ (BDH, Spectrograde) was used without further purification.

The optical measurements were carried out on a Shimadzu-240 double beam spectrophotometer using a matched pair of quartz cells of 10 mm path length. The λ_max of the CT band was determined by measuring the optical densities of the solution between 250–900 nm at an interval of 5 nm using fresh solution each time (Fig. 1). The instrument was fitted with a temperature variable cell compartment and the optical densities at λ_max of CT band were noted in the temperature range of 10–30°C at 5°C intervals with an accuracy of ±0.1°C. The experimental temperatures were maintained by circulating thermostated water at required temperature around the cuvettes. The concentration of DDQ was held constant at 1.5×10⁻⁴M while that of the anilines were varied between 2×10⁻³M and 1.6×10⁻²M to determine the stability constants and molar extinction coefficients of CT complexes by using the Rose-Drago equation, viz.,

\[ K^{-1} = \frac{A}{[D]} - ([A] + [D]) + [A] [D] \epsilon / \lambda \]
where $K$ is stability constant, $A$ is absorbance, $\varepsilon$ the molar extinction coefficient of the complex and $[A_0]$ and $[D_0]$ the initial concentrations of acceptor and donor respectively. Thermodynamic parameters were determined from the temperature variation of formation constants using van’t Hoff method. The stoichiometry of the complexes was determined by the Job’s continuous variation method.

**Results and discussion**

All the anilines produced blue colored solutions on mixing with DDQ indicating the formation of CT complexes. Each of the solutions exhibited a CT band in the 645-950 nm wavelength region, which is attributed to the excitation of an electron from the HOMO of the donor to the LUMO of the acceptor. Anilines have two sites of donation, viz., $n$-electrons on N atom and the $\pi$ electrons of benzene ring and hence can form $n-\pi$ or $\pi-\pi$ complexes with DDQ. To distinguish between the two possibilities, the $\nu_{CT}$ of DDQ-anilines were plotted against the $\nu_{CT}$ of TCNE-anilines ($\pi-\pi$ complexes$^9$) and I$_2$-anilines ($n-\pi$ complexes$^{10}$). A linear relationship was observed between $\nu_{CT}$ of DDQ-anilines and TCNE-anilines, while that of I$_2$-anilines exhibited a scatter indicating that the anilines act as $\pi$ donors towards DDQ$^{11}$.

The ionization potentials of the donors were determined from the following equation$^{12}$:

$$h\nu_{CT} = 0.77 I_p - 4.19$$

The IP of aniline of present study is close to the IP of $\pi$ - HOMO (8.02 eV) and is far lower than that of $n$-electrons (10.78 eV) as obtained from the photoelectron spectra$^{13}$. These data support the assumption that the anilines act as $\pi$ - donors. The ionization potentials of all donors are comparable to those determined from CT bands of TCNE anilines$^9$.

**Effect of substituents on the CT bands**

The CT band of the DDQ-aniline complex (690 nm) is significantly affected by both ring and N-substituents. The band is shifted to longer wavelengths by electron-releasing ring substituents, viz., $p$-$\text{OCH}_3$, $p$-$\text{CH}_3$, $m$-$\text{CH}_3$, $o$-$\text{CH}_3$ and N-substituents, viz., N-methyl and N, N-dimethyl. The electron-attracting $p$-Cl causes hypsochromic shift in the order, N,N-dimethyl$>p$-$\text{OCH}_3$p-$\text{CH}_3$o$-$\text{CH}_3>N$-$\text{CH}_3> m$-$\text{CH}_3>p$-$\text{H}>p$-$\text{Cl}$ (Table 1).
Table 1—Charge transfer spectra, stability constants ($K$) and thermodynamic parameters of DDQ-aniline complexes

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$\lambda_{CT}$ (nm)</th>
<th>$\varepsilon_{CT}$ (1 mol$^{-1}$ cm$^{-1}$)</th>
<th>IP (eV)</th>
<th>$K^\circ$ (1 mol$^{-1}$)</th>
<th>$-\Delta H$ (kcal mol$^{-1}$)</th>
<th>$-\Delta S$ (kcal deg$^{-1}$ mol$^{-1}$)</th>
<th>$-\Delta G$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-phenyl</td>
<td>947</td>
<td>8,850</td>
<td>7.14</td>
<td>71.27</td>
<td>59.90</td>
<td>39.90</td>
<td>30.19</td>
</tr>
<tr>
<td>N,N-(CH$_2$)$_2$</td>
<td>806</td>
<td>8,500</td>
<td>7.44</td>
<td>63.50</td>
<td>43.90</td>
<td>33.38</td>
<td>25.72</td>
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<tr>
<td>p-OCH$_3$</td>
<td>746</td>
<td>7,500</td>
<td>7.60</td>
<td>38.40</td>
<td>29.87</td>
<td>23.51</td>
<td>18.65</td>
</tr>
<tr>
<td>p-CH$_3$</td>
<td>735</td>
<td>7,100</td>
<td>7.64</td>
<td>36.35</td>
<td>28.41</td>
<td>22.41</td>
<td>17.81</td>
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<tr>
<td>N-CH$_3$</td>
<td>725</td>
<td>6,900</td>
<td>7.66</td>
<td>30.52</td>
<td>24.13</td>
<td>19.26</td>
<td>15.47</td>
</tr>
<tr>
<td>m-CH$_3$</td>
<td>697</td>
<td>6,600</td>
<td>7.75</td>
<td>25.60</td>
<td>20.52</td>
<td>16.57</td>
<td>13.48</td>
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<tr>
<td>p-H</td>
<td>689</td>
<td>6,400</td>
<td>7.78</td>
<td>19.63</td>
<td>16.07</td>
<td>13.24</td>
<td>10.96</td>
</tr>
<tr>
<td>p-Cl</td>
<td>649</td>
<td>5,800</td>
<td>7.92</td>
<td>10.03</td>
<td>8.62</td>
<td>7.44</td>
<td>6.45</td>
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</tbody>
</table>

* Accurate up to ± 0.25

The shifts in the CT bands are explicable in terms of mesomeric and inductive interactions of the substituents. The +M effect of p-OCH$_3$ and the +I effect of p-CH$_3$, m-CH$_3$, N-methyl and N,N-dimethyl boost up the energy of the HOMO of the donor bringing it closer to the LUMO of the DDQ, thus lowering the energy gap between the two orbitals and therefore the CT band is shifted to longer wavelengths. The -I effect of chloro substituent stabilises the donor level and produces hypsochromic shift.

**Stability constants and thermodynamic parameters**

The stability constants of the complexes are found to increase with increasing electron-releasing ability of the substituent present in the benzene ring or on the N-atom and are in the order: N-phenyl N,N-dimethyl > p-OCH$_3$ > p-CH$_3$ > o-CH$_3$ > N-CH$_3$ > m-CH$_3$ > p-H > p-Cl (Table 1). It is interesting to note that the stabilities of anilines –DDQ complexes are greater than those of correspondingly substituted benzenes. The greater stability may be due to increase in the basicity of benzene ring rendered electron dense by the lone pair of electron on N-atom. The interaction not only increases the $\pi$-electron density of benzene ring but also produces a dipole in the molecule. The dipolar donor strongly interacts with the dipolar acceptor (DDQ). The possibility of hydrogen bonding between the N-H of aniline and C=O of quinone ring increasing the stability of complex can be ruled out because Issa et al. demonstrated by IR spectroscopy that there is no evidence of such hydrogen bonding.

Linear plots were obtained when log $K$ was plotted against $1/T$. The $\Delta H$ and $\Delta S$ have been evaluated from the slope and intercept of these plots and are presented in Table 1. The $\Delta H$ values are below 10 kcal mol$^{-1}$ a feature characteristic of weak CT complexes. The negative enthalpies show that the complex formation is spontaneous, while negative entropy indicates a decrease in the degree of freedom of the components upon complexation. A linear relationship is obtained between $\Delta H$ and $\Delta S$ for all CT complexes. It is interesting to note that the N-methyl, N,N-dimethyl anilines too, fit into the linear relation showing that complex formation is not sterically hindered. If the complex formation is due to donation, a steric hindrance by N-methyl, N,N-dimethyl groups to the approach of acceptor towards the N-atom is reasonably expected. Sterically unhindered complex formation too, indicates that the interaction is of the $\pi-\pi$ type and favours a sandwich structure of complex in which the interacting orbitals have greatest possible overlap.

**Acknowledgement**

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**References**