Charge transfer complexes of anilines-DDQ: A kinetic study

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The kinetics of transformation of charge transfer complexes of anilines-DDQ has been studied spectrophotometrically by stabilising the complexes in CCl₄, a low polar solvent, at low temperatures and under low donor concentrations. The decay of CT complexes has been followed by decrease in the absorbance of CT band and it has been found to follow pseudo first order kinetics. The stability constants of the complexes have been determined from kinetic studies, using the method described by Rappoport. A linear relationship is observed between logarithmic functions of stability constants and Hammett σ constants. Thermodynamic parameters of the complexes have been evaluated from temperature variation of stability constant.

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., UV-vis spectrophotometry¹, IR spectroscopy², kinetic³ and conductivity⁴. Dwivedi et al.⁵ observed 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 monosubstituted derivative of DDQ and the yellow colour (λ_max 350 nm) to the final product which was identified as a disubstituted derivative of DDQ. The authors studied the kinetics of formation of disubstituted DDQ from monosubstituted one. However, they were unsuccessful in studying the CT spectra and the stabilities of the CT complexes of anilines-DDQ due to fast transformation into products. Issa et al.⁶ too, were unsuccessful in stabilising the complexes and studying their IR spectra. From the conductance measurements, Dwivedi et al.⁷ observed that CT complexes soon decompose into ions in solvents of sufficient polarity and exhibit appreciable conductivity. From this they demonstrated that the stoichiometry of anilines-DDQ complexes is 1:1. Srivastava and Verma reported the stability constant of CT complex between o-toluidine and DDQ⁸. However, they 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 in low polar solvents, under low temperature, and under low donor concentrations⁹,¹⁰. This prompted us to investigate the CT spectra and kinetics of transformation of CT complexes of anilines – DDQ in a low polar solvent, viz., CCl₄, at low temperatures and under low donor concentrations. The cumulative effect of these factors is expected to stabilise the complexes for sufficient time, enabling the detection of λ_max of CT band and study of kinetics of the decay CT band with time. The results of the investigation are reported in this note.

Experimental

The commercial sample of DDQ obtained from Aldrich was repeatedly recrystallized from benzene-chloroform (2:1) mixture (m.p. 213-214°C). Anilines (BDH-Analar) were purified by the methods available in literature⁷. Spectrograde CCl₄ (BDH) was used without further purification.

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 instrument was fitted with temperature variable cell compartment. The experimental temperatures were maintained by circulating thermostated water of required temperature around the cuvettes. The λ_max of CT band was determined by measuring the optical density of solution between 250-900 nm at an interval of 5 nm using fresh solution each time. The decay of the CT band was followed at λ_max by noting the optical density of complex at an interval of 30 s. The decay was found to follow pseudo first order kinetics and the decay constants (k) were determined from
Table 1—Charge Transfer spectra, stability constants (K) and thermodynamic parameters of anilines-DDQ complexes

<table>
<thead>
<tr>
<th>Substituent</th>
<th>(\lambda_{\text{max}}) CT (nm)</th>
<th>(\varepsilon) (l mol(^{-1}) cm(^{-1}))</th>
<th>(K) (l mol(^{-1}))</th>
<th>(-\Delta H) kcal mol(^{-1})</th>
<th>(\Delta S) cal deg(^{-1}) mol(^{-1})</th>
<th>(-\Delta G) kcal mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10^\circ C)</td>
<td>(15^\circ C)</td>
<td>(20^\circ C)</td>
<td>(25^\circ C)</td>
<td>(30^\circ C)</td>
<td>(35^\circ C)</td>
</tr>
<tr>
<td>N-phenyl</td>
<td>947</td>
<td>5200</td>
<td>77.24</td>
<td>56.82</td>
<td>42.23</td>
<td>31.70</td>
</tr>
<tr>
<td>N,N-dimethyl</td>
<td>806</td>
<td>8850</td>
<td>67.84</td>
<td>50.03</td>
<td>37.30</td>
<td>28.07</td>
</tr>
<tr>
<td>p-CH(_3)</td>
<td>800</td>
<td>10100</td>
<td>63.01</td>
<td>47.00</td>
<td>35.38</td>
<td>26.90</td>
</tr>
<tr>
<td>p-CH(_3)</td>
<td>746</td>
<td>7050</td>
<td>42.20</td>
<td>32.55</td>
<td>25.32</td>
<td>19.88</td>
</tr>
<tr>
<td>o-CH(_3)</td>
<td>735</td>
<td>7370</td>
<td>39.52</td>
<td>30.75</td>
<td>24.16</td>
<td>19.12</td>
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<tr>
<td>N-methyl</td>
<td>725</td>
<td>8900</td>
<td>33.32</td>
<td>26.40</td>
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<tr>
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<td>7450</td>
<td>28.85</td>
<td>23.10</td>
<td>18.63</td>
<td>15.14</td>
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<tr>
<td>p-H</td>
<td>689</td>
<td>6720</td>
<td>22.35</td>
<td>18.18</td>
<td>14.90</td>
<td>12.30</td>
</tr>
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</table>

Fig. 1—Plots of log \(D_0 / D_t\) versus time for the CT complex of DDQ-aniline at various concentrations of aniline (at \(10^\circ C\)). \([\text{DDQ}] = 1.25 \times 10^{-4}\) M; \([\text{Aniline}] = 1, 3.2 \times 10^{-3}\) M; 2, 6.4 \times 10^{-3}\) M; 3, 9.6 \times 10^{-3}\) M; 4, 12.8 \times 10^{-3}\) M; 5, 16 \times 10^{-3}\) M].

\[ k = 2.303 \ln \frac{D_0}{D_t} \]

where \(D_0\) and \(D_t\) are absorbances measured immediately after mixing aniline with DDQ and after a time \(t\), respectively.

The pseudo-first rate constants were determined using various concentrations of donors with a fixed concentration of acceptor. The stability constants of the CT complexes were determined from these kinetic runs by adopting the method proposed by Rappoport. The thermodynamic parameters viz., \(\Delta H\) and \(\Delta S\) were determined from van't Hoff's method. A plot of log \(K\) versus \(\ln T\) gave linear graphs, from the slope and intercept of which \(\Delta H\) and \(\Delta S\) respectively, have been calculated. The thermodynamic characters are reported in Table 1.

Results and discussion

All the anilines (0.002 to 0.016 M) produced blue coloured solutions upon mixing with DDQ (1.25 \times 10^{-4} M) in CCl\(_4\) but faded slowly. The decay of the CT complexes of DDQ-anilines was found to follow pseudo first order kinetics under the conditions \([\text{donor}] > [\text{acceptor}]\). A plot of log \(D_0 / D_t\) versus time gave a straight line, from the slope of which the decay constant \(k\) was determined (Fig. 1). The decay constant, however, was found to increase with increase in donor concentration. The \(k_{\text{exp}}\) or second order rate constants \(k_{\text{exp}} = k / [\text{donor}]\) have been calculated and are found to decrease with increase in the concentration of donor. The reaction may be represented as

\[ A + D \rightarrow AD \rightarrow \text{Products} \]

Rappoport and Horowitz proposed six possible mechanisms for the reactions proceeding through the formation of CT complexes, each of which gives a relationship between the \(k_{\text{exp}}\) and stability constant of the complex, \(K\).

For the mechanism \((a)\) in which the product is formed with equal rate coefficients from all the acceptor present \((A_0)\) in a bimolecular reaction, viz.,
A free + D $\xrightarrow{k_1} \text{Products}$

$A_{\pi \text{complex}} + D \xrightarrow{k_2} \text{Products}$

The relationship derived is

$$k_{\text{exp}} = k_1$$

and implies that the $k_{\text{exp}}$ is independent of donor concentration.

For mechanism (b), the product is formed only by a bimolecular reaction of the $\pi$-complexed acceptor with a second molecule of donor, viz.,

$$A_{\pi \text{complex}} + D \xrightarrow{k} \text{Products}$$

$$k_{\text{exp}} = (k_1K[D_D]) / (1 + K[D_D])$$

For (c), the product is formed by two bimolecular reactions of donor with the complexed and uncomplexed acceptor, each having a different rate constant.

$$A_{\text{free}} + D \xrightarrow{k_1} \text{Products}$$

$$A_{\text{free}} + D \xrightarrow{k_2} \text{Products}$$

$$k_{\text{exp}} = (k_1K[D_D] + k_2) / (1 + K[D_D])$$

The relationship derived for paths (b) and (c) imply that $k_{\text{exp}}$ should increase with increase in the concentration of donor. For (d) the product is formed by unimolecular transformation of the CT complex.

$$\text{CT}_{\pi \text{complex}} \xrightarrow{k} \text{Products}$$

$$k_{\text{exp}} = k_1K / (1 + K[D_D])$$

while for (e) the product is formed by bimolecular reaction of the uncomplexed acceptor with donor.

$$A_{\text{free}} + D \xrightarrow{k_1} \text{Products}$$

$$k_{\text{exp}} = k_1 / (1 + K[D_D])$$

For (f), the products is formed in two concurrent reactions, in a monomolecular one from the CT complex, and in a bimolecular one with the free acceptor.

$$\text{CT}_{\pi \text{complex}} \xrightarrow{k} \text{Products}$$

$$A_{\text{free}} + D \xrightarrow{k_2} \text{Products}$$

$$k_{\text{exp}} = (k_1 + k_2) K^2 / (1 + K[D_D])$$

The relationship derived for paths (d), (e) and (f) imply that the $k_{\text{exp}}$ should decrease with increase in donor concentration.

Our experimental data in conformity with any of the three paths, (d), (e) and (f). For any of those, stability constant $K$ can be evaluated from the intercept and slopes of the plots of $1/k_{\text{exp}}$ versus [donor] (Fig. 2). The stability constants ($K$) obtained from such plots are reported along with thermodynamic parameters in Table 1. However, with a view to distinguish amongst the three possibilities, the rate of decay of DDQ band (360 nm) with time was also investigated. The rate of decay of this band

![Fig. 2-Plots of $\frac{1}{k_{\text{exp}}}$ versus [donor] of DDQ-anilines complexes.](image)

**Fig. 2**—Plots of $\frac{1}{k_{\text{exp}}}$ versus [donor] of DDQ-anilines complexes. [1, N-phenyl aniline; 2, N,N-dimethyl aniline; 3, p-methoxy aniline; 4, p-toluidine; 5, o-toluidine; 6, N-methyl aniline; 7, m-toluidine; 8, aniline; [DDQ] = $1.25 \times 10^{-4} M$, [donor] = $2.0 \times 10^{-3}$-$1.6 \times 10^{-3} M]$. 
was found to be faster than that of the CT band of any complex. The rate constants for the decay of DDQ band in the presence of different anilines are in the range of 1.5×10⁻³ to 15×10⁻³ s⁻¹ while those of the decay of CT band in the range of 3×10⁻³ to 21×10⁻³ s⁻¹.

If the reaction proceeds through path 'd', the absorbance of CT band should increase with time because the decay of CT complex is slower than its formation. If the reaction follows path 'e' then the rates of decay of CT band and DDQ band should be equal because any decrease in the concentration of free DDQ should be compensated by backward shift of equilibrium, i.e., decomposition of CT complex into components. In the light of the above observations it may be agreed that the reaction proceeding through path 'f' is more likely.

The stability constants are found to increase with increase in electron releasing ability of the substituents present in the benzene ring or on nitrogen atom of aniline. The logarithmic functions of stability constants are found to bear a linear relationship with Hammett σ constants, A plot of ΔH versus ΔS is linear indicating that the complexation is unhindered by the substituent present in the ring or on the N-atom and the interaction is of π-π* in nature.

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References