Interaction of Anilines with 2,3-Dichloro-5,6-dicyano-p-benzoquinone: Spectroscopic & Kinetic Studies

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Interaction of aniline, and o-, m- and p-toluidines with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) has been studied spectrophotometrically. The blue coloured solutions obtained by mixing anilines and DDQ solution instantaneously change into green (\( \lambda_{\text{max}} \), 540 nm) and finally become yellow (\( \lambda_{\text{max}} \), 350 nm) in all the solvents studied. Pseudo-first order rate constants have been evaluated at both 540 nm and 350 nm. Possible participation of electron donor-acceptor complexes between anilines and DDQ in the reaction is indicated.

Aromatic amines are known to act as electron donors and form electron donor-acceptor (EDA) complexes with a number of electron acceptors. Some aromatic amines are reported to undergo chemical reaction with strong electron acceptors through EDA complexes. Nagakura and coworkers studied the interaction of aniline with chloranil (CA) and the formation of product was rationalised via EDA and \( \sigma \)-complexes as intermediates. 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) is a much stronger electron acceptor than structurally similar CA. The electron acceptor strength of DDQ is comparable to that of tetracyanoethylene (TCNE). Therefore, it is expected to undergo chemical reactions with a variety of electron donors. Murlikrishna and coworkers studied EDA interaction between piperidines and DDQ and reported the formation of mono- and disubstituted products via a substitution reaction. We have recently investigated the interaction of aza-aromatics with DDQ wherein the occurrence of a reaction through EDA complex was proposed. However, systematic studies on the interaction of anilines with DDQ have not been reported so far. It was, therefore, worthwhile to undertake spectroscopic and kinetic investigations on the interaction of aniline and o-, m- and p-toluidines with DDQ.

Materials and Methods

All the anilines were commercial products and were purified before use. Chloroform (BDH, AR) and dichloromethane (E. Merck, LR) were dried and distilled before use. DDQ was purified by recrystallising several times from chloroform.

Electronic absorption spectra were measured on a Beckman-DU spectrophotometer fitted with variable temperature cell compartment using matched silica cells of 1 cm pathlength. Freshly prepared stock solutions were used for measurements. Pseudo-first order rate constants \( k \) (in the presence of a large excess of donor) at 540 nm and 350 nm were evaluated employing Eqs (1) and (2), respectively.

\[
k = \frac{2.303}{t} \log \frac{D_0}{D_t} \quad \ldots (1)
\]

\[
k = \frac{2.303}{t} \log \frac{D_\infty - D_0}{D_\infty - D_t} \quad \ldots (2)
\]

Here \( D_0 \), \( D_t \) and \( D_\infty \) are the absorbances measured immediately after mixing aniline with DDQ, after time \( t \) and at the end of the reaction, respectively. Some typical plots employed for these calculations are shown in Fig. 1. The energies of activation were evaluated by measuring the temperature dependence of \( k \) in the range 288-310 K.

![Fig. 1—Pseudo-first order rate plots for the aniline+DDQ system in CHCl₃ solution at 298 K [(1) at 540 nm and (2) at 350 nm]
Results and Discussion

Absorption spectra

Anilines on mixing with DDQ produce blue coloured solutions which instantaneously change into green ($\lambda_{\text{max}}$ 540 nm) and finally become yellow ($\lambda_{\text{max}}$ 350 nm) in all the solvents studied. As the blue solution turned green before spectral measurements, its absorption could not be measured. The blue colour may be attributed to the formation of EDA complexes between anilines and DDQ which are unstable under the experimental conditions. It may be mentioned here that aniline forms a stable EDA complex with CA below 200 K but on raising temperature aniline reacts with CA to give 2,5-dichloro-3,6-dianilino-$p$-benzoquinone as the reaction product. It is, thus, possible that the EDA complexes formed between anilines and DDQ (which is more reactive than CA) are unstable in the temperature range 288-310 K. The intensity of the 540 nm band decreases with time whereas that of the 350 nm band continues to increase until the end of the reaction as evidenced by Fig. 2. This shows that the 350 nm band is due to the final reaction product. On analogy with the reaction of CA with aniline, we may expect the final product to be 2-chloro-5-cyano-3,6-dianilino-$p$-benzoquinone. This is supported by the elemental analyses of the product. The 540 nm band may be assigned to a monosubstituted product (either 2,3-dichloro-5-cyano-6-anilino-$p$-benzoquinone or 2-chloro-5,6-dicyano-3-anilino-$p$-benzoquinone). The monosubstituted product, however, could not be isolated.

Kinetic data

To explore the possibility of the EDA complexes as the reaction intermediates in the reactions of DDQ with anilines, we have carried out the kinetic measurements on these systems. Pseudo-first order rate constants ($k$) were obtained spectrophotometrically at 540 and 350 nm. The $k$ values increase with increase in donor strength of anilines and follow the order: p-toluidine > o-toluidine > m-toluidine > aniline. The donor strength of these compounds, as judged from their ionization potentials (Table 1) also follows the same order. The $E_a$ values (Table 1) decrease as $k$ increases. These $k$ and $E_a$ values seem to suggest

Table 1—Kinetic Data on the Interaction of Anilines with DDQ at 298 K

<table>
<thead>
<tr>
<th>Electron donor</th>
<th>$I_p$ (ev)</th>
<th>Solvent</th>
<th>Dielectric constant</th>
<th>$k^a$ (min$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\dagger$ (JK$^{-1}$ mol$^{-1}$)</th>
<th>$k^a$ (min$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\dagger$ (JK$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>7.70</td>
<td>CHCl$_3$</td>
<td>4.5</td>
<td>0.414</td>
<td>13</td>
<td>-242</td>
<td>0.184</td>
<td>34</td>
<td>-180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHCl$_3$+$CH_2Cl_2$ (1:1)</td>
<td>6.6</td>
<td>0.438</td>
<td>10</td>
<td>-251</td>
<td>0.218</td>
<td>23</td>
<td>-215</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_2Cl_2$</td>
<td>9.1</td>
<td>0.484</td>
<td>8</td>
<td>-258</td>
<td>0.253</td>
<td>17</td>
<td>-234</td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>7.66</td>
<td>CHCl$_3$</td>
<td>4.5</td>
<td>0.495</td>
<td>10</td>
<td>-251</td>
<td>0.219</td>
<td>25</td>
<td>-188</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHCl$_3$+$CH_2Cl_2$ (1:1)</td>
<td>6.6</td>
<td>0.529</td>
<td>8</td>
<td>-258</td>
<td>0.242</td>
<td>18</td>
<td>-229</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>7.62</td>
<td>CHCl$_3$</td>
<td>4.5</td>
<td>0.576</td>
<td>6</td>
<td>-264</td>
<td>0.276</td>
<td>13</td>
<td>-247</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHCl$_3$+$CH_2Cl_2$ (1:1)</td>
<td>6.6</td>
<td>0.541</td>
<td>8</td>
<td>-252</td>
<td>0.253</td>
<td>19</td>
<td>-226</td>
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<tr>
<td>p-Toluidine</td>
<td>7.48</td>
<td>CHCl$_3$</td>
<td>4.5</td>
<td>0.587</td>
<td>6</td>
<td>-262</td>
<td>0.276</td>
<td>14</td>
<td>-242</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHCl$_3$+$CH_2Cl_2$ (1:1)</td>
<td>6.6</td>
<td>0.633</td>
<td>5</td>
<td>-267</td>
<td>0.311</td>
<td>10</td>
<td>-254</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_2Cl_2$</td>
<td>9.1</td>
<td>0.587</td>
<td>7</td>
<td>-256</td>
<td>0.299</td>
<td>14</td>
<td>-241</td>
</tr>
</tbody>
</table>
| (a) Uncertainty in $k$ values is less than ± 1%
that the reactions proceed through the initial formation of EDA complexes in all the systems investigated.

Further, the $k$ values increase and $E_a$ values decrease with increase in solvent polarity. The rate constants at 540 nm are larger (and $E_a$ smaller) than those at the 350 nm, indicating the existence of an intermediate in the transformation of the monosubstituted product to the disubstituted product of the reaction. In the absence of an intermediate, the two rate constants are found to be equal in the reactions of the EDA complexes$^{11,12}$. Nagakura and coworkers$^6$ considered reactions (3) and (4) in the interaction of aniline with CA:

$\text{D} + \text{A} \rightarrow \text{EDA complex} \rightarrow \text{Product}$ \hspace{1cm} (3)

$\text{D} + \text{A} \rightarrow \text{EDA complex} \rightarrow \text{Intermediate} \rightarrow \text{Product}$ \hspace{1cm} (4)

The plots of concentration of the product ([P]) (calculated by solving the rate equations) versus time ($t$) in the initial stage of reaction (4) were quadratic in nature and closely resembled the experimental [P] versus $t$ plots. This was taken as an evidence for the existence of an intermediate in the reaction of aniline with CA. In the present investigation, the plots of experimental [P] (measured in terms of the absorbance of the product) versus $t$ exhibit initial quadratic behaviour (see Fig. 3). This observation provides further support to the existence of the intermediate in the transformation of the monosubstituted product to the disubstituted product.

The reaction of DDQ with anilines may, therefore, be rationalised as shown in Scheme 1:

Aniline + DDQ $\rightarrow$ EDA complex $\rightarrow$ monosubstituted-product (blue solution)

substituted-product $\rightarrow$ Intermediate (green solution, $\lambda_{\text{max}}$, 540 nm)

$\rightarrow$ (step II) Fast disubstituted product (yellow solution, $\lambda_{\text{max}}$, 350 nm)

Scheme 1

The $\Delta S' \text{ values for the transformation of the monosubstituted product to the intermediate (step-I)}$ are larger and negative than those for the transformation of the intermediate to the final disubstituted product (step-II), the magnitude being higher in more polar solvents. This indicates that the transition state in step-I is more polar than the initial state (which is likely to be the monosubstituted product) and also that the transition state in step-II differs in polarity from the initial state (the intermediate).

Fig. 3—Time versus absorbance plots for product formation at 288K in CHCl$_3$ ([Amine]=2.0 x $10^{-2}$ mol dm$^{-3}$ and [DDQ]=1.0 x $10^{-4}$ mol dm$^{-3}$; curves a, b, c and d for aniline, m-toluidine, o-toluidine and p-toluidine, respectively)

References