Oxidative Polymerization Studies of 8-Hydroxyquinoline in Different Media

by S.M. Ahmed* and S.A. Ahmed**

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt
*e-mail: sm_ahmed@yahoo.com
**saleh_63@hotmail.com

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Oxidative polymerization reaction of 8-hydroxyquinoline (HQ) in different media has been studied experimentally by spectrophotometric technique and confirmed computationally by molecular mechanics (MM+) calculations. MM+ calculations showed that the PE of the optimum molecular geometric (OMG) of the anionic HQ (HQ-NaOH) form is about two (1.985) times greater than the PE in the protonated (HQ-HCl) form. PE of the OMG structure of the PHQ was computed (~30.651 kJ mol$^{-1}$). These calculations indicate that the matrix is highly stable. The oxidation constant ($K_{ox}$) of the anionic form (HQ-NaOH) is about twice (2.02) greater than that of the protonated (HQ-H$_2$SO$_4$) form. The proposed procedure was successfully applied for the oxidation of diiodohydroxyquinoline in streptoquin (SQ) (anti-diarrhea, tablets). The $K_{ox}$ of HQ in SQ was also found to be lower than the $K_{ox}$ in synthetic (HQ) solution. Kinetic parameters of the oxidative polymerization of the anionic form of HQ (HQ-NaOH) were deduced on the basis of absorbance variations. The results of computer-oriented kinetic analysis indicate that the rate-controlling step of the HQ polymerization is governed by Ginstling-Brostein equation representing the three-dimensional diffusion (D4). Activation parameters of the oxidative polymerization of the anionic form of HQ (HQ-NaOH) were computed and discussed.

Key words: 8-hydroxyquinoline, streptoquin, polymerization, MM+ calculations

The significance of polyhydroxyquinoline (PHQ) in biological systems is widely recognized. It has been reported that the polymers bearing 8-quinolinol have potential applications as antimicrobial surgical materials and ointments for medicinal purposes [1,2]. Moreover, oxidation of some phenols by metal complexes leading to the production of quinones has generated great interest recently [3–11].

Several authors reviewed the permanganate oxidation of organic compounds and the synthetic applications of permanganate to organic chemistry [12–15].

Recently, we have reported that the electrochemical activity of poly(8-hydroxyquinoline) (PHQ) and its copper ion chelates in different solutions by use of differential pulse polarographic techniques [16]. We also characterized the coordination polymers based on PHQ complexed with some metal ions, using several spectroscopic techniques [17]. Moreover, we studied the oxidative polymerization of aniline hydrochloride in different media [18].

In the present study, mechanism of the oxidative polymerization process of the cationic and anionic forms of 8-hydroxyquinoline (HQ) in synthetic solution and
streptokin tablets was investigated. Activation parameters as well as molecular mechanics (MM+) calculations support the proposed reaction mechanism.

**EXPERIMENTAL**

**Chemicals and solutions.** 8-Hydroxyquinoline (HQ) was obtained from Aldrich Chemicals Co. and used as received. Streptokin (anti-diarrhea) tablets were purchased from Medical Union Pharmacy (MUP), Egypt. All other used reagents were of analytical grade or of chemical-pure grade, and double-distilled water was used throughout.

Potassium permanganate solution (KMnO₄, BDH) was prepared by dissolving the appropriate amount sample in double distilled water. This solution was standardized against oxalic acid [19].

Stock solution of HQ was prepared by dissolving the appropriate amount (10 mmol) in sodium or potassium hydroxide solutions (10 mmol). The final product [poly(8-hydroxyquinoline) (PHQ)] obtained from the oxidative polymerization of HQ was verified experimentally and supported computationally using molecular mechanics (MM+) calculations in our previous work [16,17].

Streptokin (anti-diarrhea, SQ) tablets used for the oxidative polymerization of diiodohydroxyquinoline in SQ were prepared in the following way. The contents of five tablets of SQ were weighed and powdered. The resulting mass was then dissolved in NaOH (100 mmol). The solution was filtered and diluted to 100 ml in a volumetric flask with double distilled water.

**Instrumentation.** A Perkin-Elmer Lambda35 spectrophotometer with 1.0 cm quartz cell (scan speed, 8.0 nm s⁻¹) was used for normal (zero- or first derivative, Δʎ = 5 nm) spectrophotometric measurements. The pH measurements were carried out using a Fisher Scientific Accument, Digital pH meter model 810. A Heto thermostat (type HMT 200) was used for the accelerated kinetic studies.

**Procedure.** Ten milliliters of 0.5 mmol L⁻¹ solution of KMnO₄ (oxidant) in strong acid (pH 1.0, adjusted by H₂SO₄) or strong alkaline medium (adjusted by standard NaOH; 100 mmol L⁻¹) was put into a calibrated flask. The background spectrogram of this solution was recorded. Then, different amounts of HQ or SQ were added into individual flasks by means of a micropipette (Voaco, UK). All presented absorption spectra are corrected for the blank reagent, which was prepared in a similar manner as the samples, however, not containing analyte. All measurements were carried out at room temperature (297 ± 1 K), except for those used to assess the influence of temperature on the reaction rate of the oxidative polymerization of HQ.

**Molecular mechanics calculations.** MM+ calculations including MM2 and MMP2 force field [20–26] were carried out assuming the investigated molecule in the gas phase. The values of potential and geometrical energies as well as the dipole moment were obtained considering dPE = 0.42 J and the normal method [20–26]. The search for a minimum energy of the molecule geometry resulted in a 3D structure. MM+ calculations iteratively change the position of atoms towards the structure characterized by lower energy until the molecule internal energy has been minimized.

The energy of a molecule is influenced by the atomic coordinates and could be calculated according to the equation [21–26]

\[
E(x) = E_{\text{str}} + E_{\text{ang}} + E_{\text{stb}} + E_{\text{oop}} + E_{\text{tol}} + E_{\text{ele}} + E_{\text{sol}} + E_{\text{res}}
\]

where \(E_{\text{str}}\) is the bond stretch; \(E_{\text{ang}}\) – the bond angle bend; \(E_{\text{stb}}\) – the stretch-bend; \(E_{\text{oop}}\) – the out-of-plane; \(E_{\text{tol}}\) – the torsion; \(E_{\text{ele}}\) – the van der Waals; \(E_{\text{ele}}\) – electrostatic; \(E_{\text{sol}}\) – the implicit solvation and \(E_{\text{res}}\) – restraint energy.

**RESULTS AND DISCUSSION**

**UV-visible absorption spectra of the oxidative polymerization of HQ.** Absorption spectra of the oxidant in strong acidic medium (pH 1.0, adjusted by H₂SO₄) is shown in Fig. 1. The absorbance at ~525 nm decreased with an increasing of the HQ
concentration at constant oxidant (KMnO₄, 0.5 mmol L⁻¹). The data were analyzed using linear regression program [20], according to the following equation:

\[ A = a + bC \]  

(2)

where \( A \), and \( C \) are the absorbance and concentration of the analyte (8-HQ), \( a \) and \( b \) are the intercept and slope of the straight line, respectively. Statistical data, regression coefficient and relative standard deviation are given in Table 1. The slope of this straight line corresponds to the oxidation constant \( K_{ox} \) as shown in Table 1. The lower value of \( K_{ox} \) was recorded in neutral medium (Table 1), while the higher value of \( K_{ox} \) in H₂SO₄ medium. These observations indicate that the \( K_{ox} \) is highly dependent on the strength of the acidity of the medium. The intercept (Table 1) of the straight line \( (a) \) is attributed to the initial absorbance of the oxidant (KMnO₄) alone (without addition of HQ). This value is consisting well with the corresponding experimental value.

![Figure 1. Absorption spectra of the oxidant (KMnO₄, 0.5 mmol L⁻¹) in strong acidic medium (pH 1.0, adjusted by H₂SO₄) after addition of HQ (a–f): 0.0, 30, 50, 100, 150, and 200 μmol L⁻¹, respectively.](image)

**Table 1.** The calibration data of the absorbance (\( \lambda \), 525 nm) vs. HQ concentration.

<table>
<thead>
<tr>
<th>System</th>
<th>( K_{ox} \times 10^3 )</th>
<th>( a )</th>
<th>( r )</th>
<th>RSD ( \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQ (Neutral)</td>
<td>1.94</td>
<td>1.445</td>
<td>0.979</td>
<td>5.04</td>
</tr>
<tr>
<td>HQ-HCl</td>
<td>3.44</td>
<td>1.46</td>
<td>0.996</td>
<td>2.91</td>
</tr>
<tr>
<td>HQ-HClO₄</td>
<td>4.16</td>
<td>1.37</td>
<td>0.993</td>
<td>2.38</td>
</tr>
<tr>
<td>HQ-HNO₃</td>
<td>5.32</td>
<td>1.37</td>
<td>0.988</td>
<td>1.85</td>
</tr>
<tr>
<td>HQ-H₃PO₄</td>
<td>5.00</td>
<td>1.32</td>
<td>0.994</td>
<td>1.98</td>
</tr>
<tr>
<td>HQ-CH₃COOH</td>
<td>2.84</td>
<td>1.45</td>
<td>0.991</td>
<td>3.94</td>
</tr>
<tr>
<td>HQ-CSA</td>
<td>4.82</td>
<td>1.25</td>
<td>0.994</td>
<td>2.06</td>
</tr>
<tr>
<td>HQ-H₂SO₄</td>
<td>6.537</td>
<td>1.16</td>
<td>0.984</td>
<td>1.48</td>
</tr>
<tr>
<td>HQ-NaOH</td>
<td>13.21</td>
<td>1.5</td>
<td>0.982</td>
<td>0.742</td>
</tr>
</tbody>
</table>

CSA – camphor sulfonic acid. \( K_{ox} \) – oxidation constant.
The limit of detection can be as low as 4.32 ppm (mg L$^{-1}$) of HQ, suggesting the possible application of this procedure for the determination of HQ in real samples. Reproducibility (99–100.4%) of the oxidative polymerization reaction of HQ was calculated for five independent measurements [27,28].

The complete discoloration ($\lambda$ of about 525 nm) of the oxidant (Mn(VII)), in strong acidic medium (H$_2$SO$_4$, 100 mmol L$^{-1}$) was recorded at the ratio of 2:5 (oxidant (KMnO$_4$):monomer (HQ)). These observations could be attributed to $\sim$2 electrons for the ratio of oxidant to monomer and could be explained (Scheme 1) by the following equation:

$$n(\text{HQ}) \xrightarrow{-2n\text{e}^-} \text{HQ} \xrightarrow{-2n\text{H}^+} \text{PHQ} \text{ (poly(8-hydroxyquinoline))}$$ (3)

The oxidation/reduction of KMnO$_4$/HQ to form a polymer (PHQ) is given by:

$$n(5\text{HQ}) + 2\text{KMnO}_4 + 5\text{H}_2\text{SO}_4 \rightarrow \text{PHQ}_- + \text{K}_2\text{SO}_4 + 3\text{MnSO}_4 + 8\text{H}_2\text{O}$$ (4)

**Scheme 1.** The OMG possible structures formed during oxidative polymerization of the anionic form of HQ (HQ-NaOH), using MM$^+$ calculations.
A similar behavior was obtained for the oxidation of HQ in several acids (Table 1).

The electronic absorption spectra of oxidant (KMnO$_4$, 0.5 mmol L$^{-1}$) were scanned (Fig. 2) in strong alkaline solution (KOH, 100 mmol L$^{-1}$). It was found also, that the absorbance at ~525 nm decreases rapidly with increasing of the concentration of the monomer (HQ). The $K_{ox}$ for the anionic form (HQ-NaOH) was found to be two (2.02) times greater than the $K_{ox}$ of the cationic form of HQ (HQ-H$_2$SO$_4$) (Table 1).

**Molecular mechanics calculations.** Molecular mechanics (MM+) calculations (Table 2) showed that the potential energy PE / (kJ mol$^{-1}$) of the optimum geometric structure (OMG) of the HQ in example NaOH is about two (1.985) times greater than the PE in acidic (HQ-HCl) solution. From these calculations we can conclude that the anionic form of HQ is highly reactive for the polymerization than the cationic form. Optimization is necessary for understanding the stability of the investigated molecules (Scheme 2). For additional information, the PE of the OMG of the cationic HQ (HQ-HCl) structure is about five times (5.078) stable than that of the MG structure of the same matrix (Table 2).

The absorbance of the band at ~608 nm (green coloration), due to Mn(VI) was increased with increasing the concentration of 8-HQ (Fig. 2). This absorption is due to the transformation of permanganate (MnO$_4^{-}$) to manganate (MnO$_4^{2-}$) [27] through a one-electron reduction according to the mechanism illustrated in equation (5):

\[
n(2\text{HQ}) + 2\text{KMnO}_4 + 2\text{KOH} \rightarrow \text{PHQ} + 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} \quad (5)
\]
Table 2. The OMG and PE of the HQ in different forms, using MM+ calculations.

<table>
<thead>
<tr>
<th>Structure</th>
<th>OMG/(kJ mol(^{-1}))</th>
<th>PE/(kJ mol(^{-1}))</th>
<th>(\mu/(\text{D}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQ-HCl (MG)</td>
<td>–</td>
<td>58.724</td>
<td>6.50</td>
</tr>
<tr>
<td>HQ-HCl (OMG)</td>
<td>–7.022</td>
<td>–9.120</td>
<td>7.02</td>
</tr>
<tr>
<td>HQ (OMG)</td>
<td>–2.796</td>
<td>–5.927</td>
<td>5.85</td>
</tr>
<tr>
<td>HQ-NaOH (OMG)</td>
<td>–8.857</td>
<td>–18.107</td>
<td>7.53</td>
</tr>
</tbody>
</table>

MG – molecular geometric, OMG – optimum molecular geometric structure.

The oxidative polymerization mechanism of HQ in strong alkaline (NaOH or KOH, 100 mmol L\(^{-1}\)) medium was also supported by MM+ calculations (Table 3). It is noticeable from the data presented in Table 3 that the lower energy value of PE substantiated our proposed mechanism (Scheme 1).

Table 3. The OMG and PE energies and \(\mu\) of the possible configuration structures formed during polymerization of HQ, using MM+ calculations.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMG/(kJ mol(^{-1}))</td>
<td>–2.842</td>
<td>–4.263</td>
<td>0.250</td>
<td>–4.890</td>
<td>–5.057</td>
<td>–0.627</td>
</tr>
<tr>
<td>(\mu/(\text{D}))</td>
<td>5.78</td>
<td>10.47</td>
<td>7.56</td>
<td>6.59</td>
<td>8.70</td>
<td>8.11</td>
</tr>
</tbody>
</table>

The electronic absorption spectra of the oxidant (KMnO\(_4\), 0.5 mmol L\(^{-1}\)) were recorded (Fig. 1, curve \(a\)). A pronounced decrease of the absorbance at around ~525 nm by increasing of the concentration of streptoquin (SQ) in strong acid or alkaline medium was observed (Table 4). The oxidation constant (\(K_{ox}\)) was found to be strongly dependent on the pH of the medium. Higher value of the \(K_{ox}\) was obtained in strong H\(_2\)SO\(_4\) medium for a series of the acids used (Table 4). The \(K_{ox}\) value in strong alkaline is about twice (2.01) greater than the \(K_{ox}\) in acidic medium (Table 4), revealing again that the anionic form of HQ in SQ is also profitable form for polymerization process (Table 4). The value of \(K_{ox}\) of the oxidative polymerization of HQ in real sample (SQ, Table 4) is lower than the \(K_{ox}\) in synthetic medium (Table 1). This may be attributed to the presence of many additives in the SQ tablets.
### Table 4. The calibration data of absorbance ($\lambda$, 525 nm) vs. concentration of SQ.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$K_{av}/10^3$</th>
<th>$a$</th>
<th>$r$</th>
<th>RSD $\times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ (Neutral)</td>
<td>0.397</td>
<td>1.44</td>
<td>0.943</td>
<td>0.23</td>
</tr>
<tr>
<td>SQ-HCl</td>
<td>2.96</td>
<td>1.38</td>
<td>0.994</td>
<td>3.35</td>
</tr>
<tr>
<td>SQ-HClO₄</td>
<td>3.70</td>
<td>1.39</td>
<td>0.984</td>
<td>3.17</td>
</tr>
<tr>
<td>SQ-HNO₃</td>
<td>3.18</td>
<td>1.41</td>
<td>0.993</td>
<td>2.99</td>
</tr>
<tr>
<td>SQ-CSA</td>
<td>1.25</td>
<td>1.37</td>
<td>0.994</td>
<td>7.79</td>
</tr>
<tr>
<td>SQ-H₂SO₄</td>
<td>3.89</td>
<td>1.34</td>
<td>0.998</td>
<td>2.95</td>
</tr>
<tr>
<td>SQ-NaOH (λ, 525 nm)</td>
<td>7.82</td>
<td>1.31</td>
<td>0.963</td>
<td>3.41</td>
</tr>
<tr>
<td>SQ-NaOH (λ, 608 nm)</td>
<td>10.95</td>
<td>0.16</td>
<td>0.989</td>
<td>5.06</td>
</tr>
</tbody>
</table>

**Kinetic study.** Figure 3 presents the variation of the absorbance ($\lambda$ ~ 608 nm) of the oxidant (KMnO₄, 100 μmol L⁻¹) with time at different initial concentration of HQ in strong alkaline medium (NaOH, 100 mmol L⁻¹) by keeping other parameters constant. Computer-oriented kinetic analysis was carried out for each set of absorbance vs. time data assuming variant kinetic equations [18,20]. It was found that the Ginstling-Bronstein equation (D4) gives the best fit of the experimental data with the correlation coefficient ($r$) close to unity and low relative standard deviation. The Ginstling-Bronstein equation (D4) can be expressed as:

$$\left(1 - \frac{2}{3} A\right) - (1 - A)^{2/3} = kt$$  \hspace{1cm} (6)

where $A$ is the absorbance, $k$ is the rate constant, and $t$ time of oxidation.

Based on the fitting of experimental data obtained, e.g. when oxidative polymerization of HQ (30 μmol L⁻¹) by KMnO₄ (100 μmol L⁻¹) was carried out in the presence

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**Figure 3.** Variation of absorbance of the oxidant (KMnO₄, 100 μmol L⁻¹) at λ of about 608 nm with time during oxidative polymerization of HQ. The concentration of HQ (a–e) was: 40, 45, 50, 55, and 60 μmol L⁻¹, respectively.
of NaOH (100 mmol L\(^{-1}\)), reaction rate constant \(k = 2.039 \times 10^{-5} \text{ s}^{-1}\) was computed while the values of statistical parameters: \(r = 0.987\); and RSD = \(2.13 \times 10^{-5}\) were obtained. It is interesting to note that the \(k\) value calculated using the D4 model is about eleven, twenty four, and one hundred five times lower than the \(k\) values obtained by applying first- (F\(_1\)), second- (F\(_2\)), and third-order (F\(_3\)) kinetics under the same conditions.

**Activation parameters.** The rate constant of the oxidative polymerization of HQ in strong alkaline medium (NaOH, 100 mmol L\(^{-1}\)) were determined within the temperature range of 283–323 K by keeping all the other experimental conditions unaltered. The corresponding activation parameters (Table 5) were computed using Arrhenius and Eyring [18,20]. Both Arrhenius and Eyring plots showed a close fit of experimental data (Fig. 4). The values of activation parameters calculated for experimental runs with different concentrations of HQ are summarized in Table 5. These moderate values of activation energy supported the proposed mechanism of the oxidative polymerization of the HQ (Scheme 1).

**Table 5.** The activation parameters of the oxidative polymerization of HQ in strong alkaline medium (NaOH, 100 mmol L\(^{-1}\)).

<table>
<thead>
<tr>
<th>HQ (μmol L(^{-1}))</th>
<th>(E_a^*/(\text{kJ mol}^{-1}))</th>
<th>(\Delta H^*/(\text{kJ mol}^{-1}))</th>
<th>(\Delta S^*/(\text{JK}^{-1}\text{mol}^{-1}))</th>
<th>(\Delta G^*/(\text{kJ mol}^{-1}))</th>
<th>(r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>44.56</td>
<td>60.301</td>
<td>186.70</td>
<td>105.94</td>
<td>0.973</td>
</tr>
<tr>
<td>40</td>
<td>38.57</td>
<td>46.72</td>
<td>190.72</td>
<td>108.55</td>
<td>0.995</td>
</tr>
<tr>
<td>50</td>
<td>32.59</td>
<td>39.13</td>
<td>216.75</td>
<td>79.72</td>
<td>0.981</td>
</tr>
<tr>
<td>60</td>
<td>28.61</td>
<td>27.55</td>
<td>240.77</td>
<td>99.28</td>
<td>0.977</td>
</tr>
<tr>
<td>70</td>
<td>23.62</td>
<td>24.56</td>
<td>250.79</td>
<td>99.29</td>
<td>0.991</td>
</tr>
<tr>
<td>80</td>
<td>20.03</td>
<td>20.97</td>
<td>261.62</td>
<td>98.93</td>
<td>0.982</td>
</tr>
</tbody>
</table>

**Figure 4.** Plot of \(-\ln k\) (Arrhenius, solid line) and \(-\ln k'\) (Eyring, dashed line) vs. \(1/T\) (K) of the oxidative polymerization of HQ.
Variation of $\Delta H^\circ$ with $\Delta S^\circ$ for the series of experiments represented by a straight line (r about 0.991) are shown in Fig. 5, suggesting that the compensation or isokinetic effects occur. Several authors suspect the presence of isokinetic phenomena [30–33]. The most important application of the compensation and/or isokinetic effect that such behaviors constitute evidence for a dominant mechanism throughout the correlated series chemical catalysis, cooperative relaxation kinetics in thermally simulated process, the sorption and browning of garlic [31–34] etc. A higher positive value of $\Delta G^\circ$ indicates that the transition state is highly solvated. Negative value of $\Delta S^\circ$ within the range of radical reactions has been ascribed to the nature of electron pairing and electron unpairing processes and to the loss of degree of freedom, formerly available to the reactions on the formation of rigid transition state. Also, this is consistent with an SN$_2$ or associative mechanism the transition state.

![Figure 5](image)

**Figure 5.** Plot of $\Delta S^\circ$ vs. $\Delta H^\circ$ of the oxidative polymerization of HQ at different concentrations of HQ.

On plotting $\Delta H^\circ$ and $\Delta S^\circ$ against monomer (HQ) concentration (Fig. 6) and extrapolating to $C = 0.0$, $\Delta H^{00}$ and $\Delta S^{00}$ values were obtained and hence $\Delta G^{00}$ was computed at any given temperature. The values seem to be almost independent of the HQ concentration. These values are $108.16 \pm 0.1$ at $25^\circ$C and $68.352 \pm 0.3$ kJ mol$^{-1}$ for $\Delta H^{00}$ and $\Delta G^{00}$ respectively. The value of $\Delta S^{00}$ is equal to $-133.69 \pm 0.5$ J mol$^{-1}$.

**CONCLUSIONS**

Mechanistic investigation of the oxidative polymerization process of 8-hydroxyquinoline (HQ) was studied both experimentally using spectrophotometric technique and computationally using molecular mechanics (MM+) calculations. The proposed procedure was successfully applied for the oxidation of diiodohydroxyquinoline in streptokinase (SQ) tablets. The proposed mechanism was proved both experimentally and theoretically. It was observed that the method proposed was simple, precise, inexpensive, and unique and requires neither sophisticated instrumentation such as
spectroelectrochemical equipment nor transparent electrodes such as metal oxide anodes of the type indium-doped tin oxide coated glass-working electrode. The results obtained encourage the applicability of the proposed method for oxidation of some other organic compounds in different fields such as wastewater treatment than the Fenton or electro-Fenton processes [34,35]. Both of these methods require the addition of ferric chloride (FeCl₃) to the solution, which, in turn, invokes consecutive separation steps.

REFERENCES