Kinetics of Oxidation of 2,6-Dimethylphenol (DMP) Using Novel μ-Carbonato \[(\text{Pip})_{4n}\text{Cu}_{4}X_{4}(\text{CO}_{3})_{2}\] Complexes

Mohamed A. El-Sayed\(^1\), Hoda A. Elwakeil\(^1\), Ahmed H. Abdel Salam\(^{1,2*}\), Hemmat A. Elbadawy\(^1\)

\(^1\)Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
\(^2\)Chemistry Department, Faculty of Science, University of Jeddah, Jeddah, KSA

Received 29 February 2016; accepted 19 July 2016; published 22 July 2016

Copyright © 2016 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
http://creativecommons.org/licenses/by/4.0/

Abstract

This paper reports the kinetics of the oxidation of 2,6-dimethylphenol (DMP) to get 3,3’,5,5’-tetramethyl-4,4’-diphenoquinone (DPQ) using novel oxidative coupling complexes \[(\text{Pip})_{4n}\text{Cu}_{4}X_{4}(\text{CO}_{3})_{2}\] \((n = 1 \text{ or } 2, \text{X} = \text{Cl or Br, Pip = piperidine})\). The new prepared tetranuclear complexes were characterized using cryoscopic measurements, electronic spectra, FTIR, EPR and cyclic voltammetry techniques. These complexes are catalytically active. The proposed mechanism of the catalytic oxidative coupling can be illustrated as a pre-equilibrium, \(K\), between the catalyst and DMP to form a complex intermediate which is converted to activated complex through the rate determining step, \(k_2\), to form the final product. The inverse of the observed rate constants \(k_{\text{obsd}}\) versus \(1/\lfloor\text{DMP}\rfloor^2\) gives a straight line with intercept. From the slope and the intercept, both \(K\) and \(k_2\) are obtained. At different temperatures, thermodynamic and kinetic parameters are evaluated. It is worth to mention that, the dependence of \(k_{\text{obsd}}\) on \([\text{DMP}]^2\) indicates that the coordination number for every copper center in both \(n = 1 \text{ or } 2\) in \[(\text{Pip})_{4n}\text{Cu}_{4}X_{4}(\text{CO}_{3})_{2}\]\ is equal to six. Therefore, carbonate bridging centers in \(n = 1\) acts as a tridentate ligand, while for \(n = 2\) acts as a bidentate ligand.

Keywords

Catalysts, Kinetics, Thermodynamic, Copper Complexes

1. Introduction

The study of homogenous oxidative coupling of DMP using copper catalysts has attracted scientists for several

*Corresponding author.

years from the catalytic industry point of view as well as a model for tyrosinase enzyme. These copper catalysts showed activity towards phenol oxidation like tyrosinase [1]-[13]. In previous work it was reported that the oxo copper complexes showed a catalytic activity towards phenol oxidation [14]-[18]. The full 3D-molecular structure of tetranuclear copper (I) complex of [(Pip)CuI]4 was studied by Volker Schramm [19] and also the crystal structure of the copper (I) iodide-pyridine was previously reported [20].

The aim of this work is to study the kinetics of oxidation of DMP to DPQ (Scheme 1) using the prepared [(Pip)4nCu4X4(CO3)2] complexes and the strategy is:

1) The use of well investigated tetranuclear carbonato-copper (II) complexes, [(Pip)4nCu4X4(CO3)2] as catalysts for oxidation of (DMP) to (DPQ).
2) To evaluate those initiators [(Pip)4nCu4X4(CO3)2] with [(Pip)4nCu4X4O2], the mechanism will deal with the first cycle under dinitrogen and the reaction followed by reduction of copper (II) to copper (I) at 740 nm or by DPQ formation at 431 nm.
3) The efficiency of the [(Pip)4nCu4X4(CO3)2] relative to the oxo analogues for oxidative coupling of (DMP) to (DPQ).
4) The impact of structural change in [(Pip)4nCu4X4(CO3)2] when n changes from 1 to 2, since the maximum coordination number of copper (II) is six.

2. Experimental
2.1. Reagents
Piperidine, Pip (Aldrich) was used as received. 10 cm column of Drierite was utilized to dry CO2 gas. The copper (I) halides as well as C6H5NO2, CH2Cl2, DMP and N2 gas were prepared for this work according to the procedures described in the literature [21].

2.2. Instrumentation
The rates of oxidation of (DMP) by copper complexes [(Pip)4nCu4X4(CO3)2]; in C6H5NO2 were measured by 160 A uv-visible recording spectrophotometer Shimadzu in matched quartz cells. The monitoring wavelength was 740 nm. Activation parameters were elucidated by repeating the reactions at different temperatures (20˚C - 50˚C). All reactions and measurements are carried out at least three times under fixed conditions to give maximum error of ±4% in each reported rate constant.

2.3. Kinetic Measurements
The mechanism and kinetics of the catalytic oxidation of DMP (2.0 - 16.0) × 10^-2 M using the copper [(Pip)4n- Cu4X4(CO3)2] complexes (1.0 × 10^-3 M) in C6H5NO2 were investigated by uv-vis spectrophotometer at 740 nm. Activation parameters were elucidated by repeating the reactions at different temperatures (20°C - 50°C). All reactions and measurements are carried out at least three times under fixed conditions to give maximum error of ±4% in each reported rate constant.

3. Results and Discussion
3.1. Stoichiometry and Products of Oxidation of Copper (I) Complexes by O2 and CO2
The formation of tetranuclear complexes [(Pip)4nCu4X4]; n = 1 or 2, X = Cl, Br or I under N2 in C6H5NO2 or CH2Cl2 as aprotic solvents were carried out as described in Equation (1) and Equation (2).

Scheme 1. Proposed catalytical cycle for homogenous oxidative coupling of phenols.
The preparation of the new μ-carbonato complexes [(Pip)$_{4n}$Cu$_4$X$_4$(CO$_3$)$_2$] was performed under N$_2$ by the reaction of [(Pip)$_{4n}$Cu$_4$X$_4$] (n = 1 or 2) with O$_2$ followed by fast reaction with CO$_2$ as described in Equation (3) and Equation (4) and Scheme 1 [22]-[28].

\[
\begin{align*}
4\text{Pip} + 4\text{CuX} & \rightarrow \left[ (\text{Pip})_4 \text{Cu}_4 \text{X}_4 \right] \quad (1) \\
8\text{Pip} + 4\text{CuX} & \rightarrow \left[ (\text{Pip})_8 \text{Cu}_4 \text{X}_4 \right] \quad (2)
\end{align*}
\]

The μ-carbonato [(Pip)$_{4n}$Cu$_4$X$_4$(CO$_3$)$_2$] complexes are easily soluble in C$_6$H$_5$NO$_2$ and CH$_2$Cl$_2$. The molar mass determination, analytical data, FTIR and electronic spectra (Figure 1) indicate that the formed complexes, [(Pip)$_{4n}$Cu$_4$X$_4$(CO$_3$)$_2$] are stable tetranuclear, similar to their copper (I) precursors (Scheme 2) [22]-[28].

![Figure 1. Electronic spectra of (a) [(Pip)$_2$Cu$_4$Cl$_4$(CO$_3$)$_2$], (b) [(Pip)$_2$Cu$_4$Br$_4$(CO$_3$)$_2$], (c) [(Pip)$_2$Cu$_4$Cl$_4$(CO$_3$)$_2$], (d) [(Pip)$_2$Cu$_4$Br$_4$(CO$_3$)$_2$].](image)

![Scheme 2. Proposed molecular structures for [(Pip)$_{4n}$Cu$_4$X$_4$(CO$_3$)$_2$].](image)
3.2. Kinetics of Oxidation of DMP to DPQ Using Novel [(Pip)₄ₙCu₄X₄(CO₃)₂] Complexes

The kinetics of homogeneous oxidative coupling of DMP to DPQ, Equation (5) are investigated at λₘₐₓ = 740 nm under pseudo 1st order conditions, where the concentration of [(Pip)₄ₙCu₄X₄(CO₃)₂] complex is 1.0 × 10⁻³ M while the excess DMP concentration changes from 2 × 10⁻² to 16 × 10⁻² M in C₆H₅NO₂ under N₂ atmosphere to insure one cycle only, Figures 2-5. The first-order plots of \( \ln \frac{A_\infty - A_t}{A_\infty - A_\infty} \) with time t, where \( A_t \) is the absorbance of [(Pip)₄ₙCu₄X₄(CO₃)₂] at time t, were linear for at least 4 half-lives, Figures 6-9. A plot of the reciprocal of the observed pseudo first-order rate constant \( 1/k_{\text{obsd}} \) vs. \( 1/([\text{DMP}]^2) \) at constant temperature gives a straight line, Figures 10-13, suggesting that 2 molecules of (DMP) are included in the rate determining step with 1 molecule of [(Pip)₄ₙCu₄X₄(CO₃)₂]. Such results suggest a mechanism similar to that reported for oxo complexes [(Pip)₄⁻Cu₄X₄O₂] (Scheme 1), Equations (6)-(10) [29] [30]. From the relation of \( 1/k_{\text{obsd}} \) vs. \( 1/[\text{DMP}]^2 \), K and \( k_2 \) are collected in Table 1. Thermodynamic and activation parameters associated with K and \( k_2 \) respectively are shown in Figures 10-13, Table 1.

\[
\text{[pip]}_n \text{Cu}_4 \text{X}_4 \text{(CO}_3\text{)}_2 + 2 \mu-\text{carbonato copper(II) complex} \quad \text{(5)}
\]

\[
\left[ \text{(Pip)}_n \text{Cu}_4 \text{X}_4 \left( \text{CO}_3\right)_2 \right] + 2 \text{DMP} \xrightarrow{k_2} \text{(Activated complex)}^* \quad \text{(7)}
\]

\[
\text{(Activated complex)}^* \xrightarrow{\text{Fast}} \text{Products} \quad \text{(8)}
\]

\[
k_{\text{obsd}} = \frac{k_2 [\text{DMP}]^2}{1 + K[\text{DMP}]} \quad \text{(9)}
\]

\[
\frac{1}{k_{\text{obsd}}} = \frac{1}{k_2} + \frac{1}{KK_2[\text{DMP}]^2} \quad \text{(10)}
\]

3.3. Thermodynamics of the Oxidation of DMP to DPQ

On changing X from Cl to Br in [(Pip)_₄Cu₄X₄(CO₃)₂]; n = 1 or 2, \( k_2 \) and K are increased and both \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) are directed to a more favourable reaction (Table 1) indicating that reduction of copper (II) is involved in the
Figure 3. Absorbance-time data for the reaction of $[(\text{Pip})_4\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, $1.0 \times 10^{-3}$ M with 2,6-dimethylphenol; (a, ×) $2.0 \times 10^{-2}$ M, (b, ●) $3.8 \times 10^{-2}$ M, (c, ▲) $5.2 \times 10^{-2}$ M, (d, ♦) $8.0 \times 10^{-2}$ M, (e, -) $10.8 \times 10^{-2}$ M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 22°C. Monitoring wavelength is 740 nm.

Figure 4. Absorbance-time data for the reaction of $[(\text{Pip})_8\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, $1.0 \times 10^{-3}$ M with 2,6-dimethylphenol; (a, ×) $5.0 \times 10^{-2}$ M, (b, ●) $6.4 \times 10^{-2}$ M, (c, ▲) $9.6 \times 10^{-2}$ M, (d, ♦) $16.0 \times 10^{-2}$ M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C. Monitoring wavelength is 740 nm.

Figure 5. Absorbance-time data for the reaction of $[(\text{Pip})_8\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, $1.0 \times 10^{-3}$ M with 2,6-dimethylphenol; (a, ×) $2.5 \times 10^{-2}$ M, (b, ●) $5.4 \times 10^{-2}$ M, (c, ▲) $6.9 \times 10^{-2}$ M, (d, ♦) $9.4 \times 10^{-2}$ M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C. Monitoring wavelength is 740 nm.
Figure 6. First order plots for the reaction of [(Pip)₄Cu₄Cl₄(CO₃)₂], 1.0 × 10⁻³ M, with 2,6-dimethylphenol, 9.0 × 10⁻² M, in C₆H₅NO₂ at 24°C (a, ♦), 32°C (b, ▲), 38°C (c, △) and 50°C (d, ×). Monitoring wavelength is 740 nm.

Figure 7. First order plots for the reaction of [(Pip)₄Cu₄Br₄(CO₃)₂], 1.0 × 10⁻³ M, with 2,6-dimethylphenol, 7.8 × 10⁻² M, in C₆H₅NO₂ at 22°C (a, ♦), 28°C (b, ▲), 36°C (c, △) and 45°C (d, ×). Monitoring wavelength is 740 nm.
Figure 8. First order plots for the reaction of [(Pip)$_8$Cu$_4$Cl$_4$(CO$_3$)$_2$], $1.0 \times 10^{-3}$ M, with 2,6-dimethylphenol, $9.6 \times 10^{-2}$ M, in C$_6$H$_5$NO$_2$ at 25°C (a, ♦), 38°C (b, ■), 45°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.

Figure 9. First order plots for the reaction of [(Pip)$_8$Cu$_4$Br$_4$(CO$_3$)$_2$], $1.0 \times 10^{-3}$ M, with 2,6-dimethylphenol, $9.4 \times 10^{-2}$ M, in C$_6$H$_5$NO$_2$ at 20°C (a, ♦), 25°C (b, ■), 40°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.
Figure 10. Dependence of the observed pseudo-first order rate constant (1/k_{obsd}) on the \{1/[DMP]^2\} for the reaction with [(Pip)_4-Cu_4Cl_4(CO_3)_2], 1.0 \times 10^{-3} M, in C_6H_5NO_2 at 25°C (a, •), 32°C (b, ■), 38°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.

Figure 11. Dependence of the observed pseudo-first order rate constant (1/k_{obsd}) on the \{1/[DMP]^2\} for the reaction with [(Pip)_4-Cu_4Br_4(CO_3)_2], 1.0 \times 10^{-3} M, in C_6H_5NO_2 at 22°C (a, •), 28°C (b, ■), 36°C (c, ▲) and 45°C (d, ×). Monitoring wavelength is 740 nm.
Figure 12. Dependence of the observed pseudo-first order rate constant \((1/k_{\text{obsd}})\) on the \(\{1/[\text{DMP}]\}^2\) for the reaction with \([\{(\text{Pip})_8\text{Cu}_4\text{Cl}_4\text{(CO}_3\text{)}_2\}], \ 1.0 \times 10^{-3} \text{ M}, \) in \(\text{C}_6\text{H}_5\text{NO}_2\) at 25°C (a, •), 38°C (b, ■), 45°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.

Figure 13. Dependence of the observed pseudo-first order rate constant \((1/k_{\text{obsd}})\) on the \(\{1/[\text{DMP}]\}^2\) for the reaction with \([\{(\text{Pip})_8\text{Cu}_4\text{Br}_4\text{(CO}_3\text{)}_2\}], \ 1.0 \times 10^{-3} \text{ M}, \) in \(\text{C}_6\text{H}_5\text{NO}_2\) at 20°C (a, •), 25°C (b, ■), 40°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.
Table 1. Kinetic and thermodynamic parameters for oxidation of DMP by \( [(\text{Pip})_4n\text{Cu}_4\text{X}_4\text{Y}_2] \); \( n = 1 \) or \( 2 \), \( \text{X} = \text{Cl} \) or \( \text{Br} \) and \( \text{Y} = \text{O}^2^- \) or \( \text{CO}_3^- \), in \( \text{C}_6\text{H}_5\text{NO}_2 \) at 740 nm.

<table>
<thead>
<tr>
<th>([\text{Pip}]_n\text{Cu}_4\text{X}_4\text{Y}_2)</th>
<th>Temp. °C</th>
<th>( k_2^{ab} )</th>
<th>( \Delta H^{bc} )</th>
<th>( \Delta S^{cd} )</th>
<th>( K^e )</th>
<th>( \Delta H^{ce} )</th>
<th>( \Delta S^{de} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, Cl, O(^-)</td>
<td>18</td>
<td>0.170</td>
<td>16.5 ± 0.5</td>
<td>−116 ± 3</td>
<td>3440</td>
<td>13.4 ± 0.5</td>
<td>−86 ± 3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.260</td>
<td></td>
<td></td>
<td>3800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>0.440</td>
<td></td>
<td></td>
<td>8760</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>0.770</td>
<td></td>
<td></td>
<td>9100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, Cl, CO(_3)</td>
<td>25</td>
<td>0.015</td>
<td>11.2 ± 0.5</td>
<td>−30 ± 3</td>
<td>62</td>
<td>12.0 ± 0.5</td>
<td>−10 ± 3</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>0.018</td>
<td></td>
<td></td>
<td>78</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>0.040</td>
<td></td>
<td></td>
<td>104</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.062</td>
<td></td>
<td></td>
<td>380</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, Br, CO(_3)</td>
<td>22</td>
<td>0.192</td>
<td>11.0 ± 0.5</td>
<td>−26 ± 3</td>
<td>430</td>
<td>4.0 ± 0.5</td>
<td>−32 ± 3</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.263</td>
<td></td>
<td></td>
<td>540</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>0.510</td>
<td></td>
<td></td>
<td>560</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.770</td>
<td></td>
<td></td>
<td>1040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2, Cl, CO(_3)</td>
<td>25</td>
<td>0.067</td>
<td>12.0 ± 0.5</td>
<td>−23 ± 3</td>
<td>120</td>
<td>3.0 ± 0.5</td>
<td>−39 ± 3</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>0.167</td>
<td></td>
<td></td>
<td>176</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.213</td>
<td></td>
<td></td>
<td>196</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.263</td>
<td></td>
<td></td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2, Br, CO(_3)</td>
<td>20</td>
<td>0.210</td>
<td>12.0 ± 0.5</td>
<td>−22 ± 3</td>
<td>323</td>
<td>0.4 ± 0.5</td>
<td>−46 ± 3</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.310</td>
<td></td>
<td></td>
<td>333</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.870</td>
<td></td>
<td></td>
<td>357</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.72</td>
<td></td>
<td></td>
<td>375</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Previously published data [29] [30].

*Units are sec\(^{-1}\). †Uncertainties for \( k_2 \) ca. ± 5% sec\(^{-1}\). ‡Units are Kcal\( \cdot \)mol\(^{-1}\). §Units are cal deg\(^{-1}\)\( \cdot \)mol\(^{-1}\). ‡Uncertainties for \( K \) ca. ± 5%.

rate determining step as observed before for the oxo analogues [29] [30]. When the number of piperidine per each Cu changes from one to two, (i.e. for \( [(\text{Pip})_n\text{Cu}_4\text{X}_4\text{CO}_3]_2 \)), the mode of coordination of the carbonato-moiety changes from structure \( a \) to structure \( b \) (scheme 2), such a change let \( \Delta H^o \) to decrease from 12 to 3 Kcal\( \cdot \)mol\(^{-1}\), when \( \text{X} = \text{Cl} \) and from 4.40 to 0.36 Kcal\( \cdot \)mol\(^{-1}\), when \( \text{X} = \text{Br} \), while \( \Delta S^o \) are directed to more negative values for both halo ligands. Therefore, the efficiency of structure \( b \) (bidentate carbonato), as an initiator is higher than structure \( a \) (tridentate carbonato). On comparing the data for \( [(\text{Pip})_n\text{Cu}_4\text{Cl}_4\text{CO}_3]_2 \); \( n = 1 \) or \( 2 \), with \( [(\text{Pip})_n\text{Cu}_4\text{Cl}_4\text{CO}_3]_2 \) (Table 1) where copper (II) centres in all of them are six coordinate, therefore the only difference is oxo versus carbonato, either structure \( a \) or \( b \), (scheme 2). In case of oxo, \( k_2 \) is at least higher by about factor of 10 and \( K \) is higher by a factor of ~50, while \( \Delta H^o \) and \( \Delta H^r \) are more endothermic and also \( \Delta S^o \) and \( \Delta S^r \) are getting more negative. This indicate that the oxo bridging centre let the catalyst, \( [(\text{Pip})_n\text{Cu}_4\text{Cl}_4\text{CO}_3]_2 \), more efficient to initiate the cycle than the less basic, more steric carbonato initiators \( [(\text{Pip})_n\text{Cu}_4\text{Cl}_4\text{CO}_3]_2 \) in either structure \( a \) (\( n = 1 \)) or \( b \) (\( n = 2 \)).

4. Conclusion

Novel complexes of \( [(\text{Pip})_n\text{Cu}_4\text{X}_4\text{CO}_3]_2 \) can be used as initiators for the oxidation of DMP to DPQ, Equation (5). Formation of \( [(\text{Pip})_n\text{Cu}_4\text{X}_4\text{CO}_3]_2 \) complexes suggested that, the Cu-O-Cu angle in \( [(\text{Pip})_n\text{Cu}_4\text{X}_4\text{O}_2]_2 \) is sharp to an extent enough to let oxo centre be sufficiently basic for catalytic activity and to ease CO\(_2\) insertion to give the carbonato complexes. On the basis of \( k_2 \), \( K \) and their kinetic and thermodynamic parameters for the first catalytic cycle, the \( [(\text{Pip})_n\text{Cu}_4\text{X}_4\text{CO}_3]_2 \) are less powerful initiators for oxidative coupling reactions when
compared to [(Pip)₄nCu₄X₄O₂]. The above result was attributed to less basic, more steric carbonato moiety relative to the oxo analogue. However, the final yield of the overall catalytic cycles was about the same.

References


Submit or recommend next manuscript to SCIRP and we will provide best service for you:

- Accepting pre-submission inquiries through Email, Facebook, LinkedIn, Twitter, etc.
- A wide selection of journals (inclusive of 9 subjects, more than 200 journals)
- Providing 24-hour high-quality service
- User-friendly online submission system
- Fair and swift peer-review system
- Efficient typesetting and proofreading procedure
- Display of the result of downloads and visits, as well as the number of cited articles
- Maximum dissemination of your research work

Submit your manuscript at: [http://papersubmission.scirp.org/](http://papersubmission.scirp.org/)