Studies on Immobilized polymer-bound imidazole copper(II) complexes as catalysts
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A Possible Mechanism of Oxidative Coupling Polymerization of 2,6-Dimethylphenol Catalyzed by Imidazole-Based Copper(II) Complexes

Abstract: Oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper-amine complexes is an important industrial process. Immobilization of homogeneous catalysts continues to receive increasing attention because of possible application in continuous processes. Therefore, both non-immobilized and immobilized imidazole-based copper(II) complexes have been investigated as catalysts for the oxidative coupling of DMP in a batch-type and continuous process, respectively. The present paper summarizes our experimental results and describes a possible mechanism, via a phenoxonium intermediate, of oxidative coupling of DMP catalyzed by imidazole-based copper(II) complexes.

7.1 Introduction

We have systematically investigated the oxidative coupling polymerization of DMP catalyzed by copper(II) complexes of N-methylimidazole (Cu(II)-NMIm) [1] or poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) [2] in toluene/methanol (13/2 v/v). In order to combine the advantages of both homogeneous and heterogeneous catalysts, some immobilized polymeric catalysts were also developed, e.g. Cu(II)-PS-Im immobilized on silica by quaternization or adsorption [3] and silica-grafted Cu(II)-PS-Im [4]. The goal of this paper is to summarize previous results and to present some additional observations, which support a possible mechanism of the oxidative coupling polymerization of DMP catalyzed by imidazole-based Cu(II) complexes.

7.2 Summary of Previous Experimental Results [1-4]

Under standard conditions without added DMP, EPR spectra of frozen solutions of immobilized or non-immobilized Cu(II) imidazole complexes indicate that the predominant species is a mononuclear [Cu(imidazole)]_{4}^{2+} complex, which is found to be a more favourable catalyst precursor for higher activity and better specificity for PPO formation than dinuclear complexes. In the absence of initial strong base no dioxygen consumption takes place. A catalytic amount of hydroxide, producing phenolate anions from DMP [5,6], appears to be essential for the start of the reaction. Particularly, with Cu(II)-NMIm or Cu(II)-PS-Im as catalysts, shorter induction times and higher
reaction rates are observed by adding the hydroxide to DMP. On the contrary, much longer induction times and very low reaction rates are obtained when the weaker base triethylamine is used instead of hydroxide (additional result).

When adding base to DMP or to Cu(II) complex, Michaelis-Menten kinetics for DMP are found. For very low [Cu(II)]0 at a constant concentration of polymeric imidazole ligands, a second-order rate dependence on [Cu(II)]0 indicates that dimerization of copper complexes is necessary prior to the re-oxidation of Cu(I) to Cu(II) [7]. The same reaction rates are obtained when either CuCl2 or Cu(ClO4)2 is used, which seems to confirm that the phenolate anions can also be the bridging ions in the dimerized copper complexes. This is in agreement with a dinuclear structure as proposed by Karlin et al. [8].

For continuous oxidative coupling catalyzed by immobilized Cu(II)-PS-Im, 2,6-di-tert-butylphenol (DTBP) was used as a substrate since it yields only DPQ, which could be continuously detected by UV/VIS spectrophotometry. From these measurements the stability of the catalysts could be derived. Successful application of immobilized polymeric catalysts in a continuous process confirms that phenolate anions, produced from initial hydroxide and DTBP, are regenerated during the oxidative coupling and do not escape from catalytic intermediates. This fact will be taken into account when considering the mechanism of oxidative coupling.

Finally, with Cu(II)-NMIm as catalysts and DMP as substrate, a control experiment carried out in a "stopped flow mixing cell" (0.5[DMP]= [CuCl2]= [KOH]= 3.32 mmol.dm-3; NMIm/Cu=30; toluene/methanol= 13/2 v/v; KOH was added to DMP) indicates that the amount of DPQ formed from totally added DMP is 1.8% (in situ measured by a UV/VIS spectrophotometer at 421 nm; ε=74000 dm3.mol-1.cm-1). This means that only about 3.6% of the dimer in structure VI of Scheme 1 consists of DPQ or biphenol, the C-C coupled precursor of DPQ, which is quickly oxidized to DPQ even under air atmosphere (Scheme 2) (additional result).

7.3 A Proposed Mechanism

For convenience a schematic representation of the catalytic cycle is given in Scheme 1. The following comments elucidate and support this mechanism (the roman and arabic numerals are corresponding to intermediate complexes and reaction steps in Scheme 1, respectively):

(I) Under standard conditions without added DMP strong EPR signals indicate that the predominant species is mononuclear [Cu(imidazole)4]2+, which
seems to be a favourable catalyst precursor.

(1) Without addition of catalytic amount of base, no dioxygen consumption takes place; adding base to DMP results in shorter induction time. Stable catalysis of immobilized catalysts in a continuous process confirms that phenolate anions are regenerated during the oxidative coupling and do not escape from the catalytic intermediates.

(2) Michaelis-Menten kinetics for DMP are found after adding base to Cu(II) or to DMP.

(3) Reaction rate is proportional to \([\text{Cu(II)}]^2\) at very low \([\text{Cu(II)}]\) for constant [ligand], which indicates that dimerization of copper complexes is necessary prior to re-oxidation [7].

\[
L_2^+\overset{(1)}{\rightarrow} L_2^+ + \text{PhO}^-\quad + \overset{(2)}{\rightarrow} L_2^+ + \text{PhO}^- + \overset{(3)}{\rightarrow} L_2^+ + \text{PhO}^- + \text{(III)}
\]

\[
L_2^+ + \text{PhO}^-\quad + \overset{(4)}{\rightarrow} L_2^+ + \text{PhO}^-\quad + \overset{(5)}{\rightarrow} L_2^+ + \text{PhO}^- + \text{Dimer}
\]

\[
L_2^+ + \overset{(6)}{\rightarrow} L_2^+ + \text{Dimer}\quad + \overset{(7)}{\rightarrow} L_2^+ + \text{Dimer}\quad + \overset{(8)}{\rightarrow} L_2^+ + \text{Dimer}
\]

\[
L_2^+ + \overset{(9)}{\rightarrow} \text{Trimer etc.}
\]

\[
L = \text{N-substituted imidazole ligands; }\quad \text{Dimer}^\text{-} = \text{Dimer phenolate anions; }\quad \text{PhOH} = \text{DMP.}
\]
Nearly the same reaction rates are found when either CuCl₂ or Cu(ClO₄)₂ is used. So, PhO⁻ can be the bridging ion (Cl⁻ is also a bridging anion, but ClO₄⁻ is not). Under standard conditions a first-order rate dependence on [Cu(II)]₀ is observed, which is correct when only dinuclear complex exists.

This is the rate-determining step: 2Cu(II) (square planar) + PhO⁻ → 2Cu(I) (tetrahedral) + PhO⁺.

Formation of PhO⁺ is preferred to formation of two phenol radicals since now one PhO⁻ can keep a bridge intact between two Cu(I).

The "side-on" coordinated phenoxonium cation, as described by Uechi et al. for a p-benzoquinone copper complex [9], prefers to attack the para position of a DMP molecule via electrophilic substitution [10] (Scheme 2).

Scheme 2

(a) PhO⁺ + PhOH  \[\text{C-O coupling}, \ -H^+ \] PhOPhOH (Dimer) (PhO⁺ in the triplet state [11]).

(b) PhO⁺ + PhOH  \[\text{C-C coupling}, \ -H^+ + [O] \] DPQ + H₂O (PhO⁺ in the singlet state [11]).

This is the re-oxidation step: 2Cu(I) + O₂ → 2Cu(II) + O₂²⁺.

This structure is in agreement with Karlin's model [8].

PhO⁻ + O₂²⁺ → PhO⁺ + 2O²⁺.

PhO⁺ + PhOH  \[\text{C-O coupling}, \ -H^+ \] Dimer (like (5)).
(9) $2(\text{O}^{2e}) + 2\text{H}^+ \rightarrow 2\text{OH}^-$.

(10) $2\text{PhOPhOH} + 2\text{OH}^- \rightarrow 2\text{PhOPhO}^- + 2\text{H}_2\text{O}$.

(11) Still Michaelis-Menten kinetics for DMP.

(12) In following oxidation cycles, dimer (or trimer, etc.) phenolate anions are preferentially oxidized to dimer (or trimer, etc.) phenoxonium cations, wherein some positive charge remains on the oxygen atom in the triplet state [11]. Then the reactions may take place as follows:

\[
\begin{array}{c}
\text{R} - \text{O}^- \text{O}^- \text{O}^+ \quad + \quad \text{H} - \text{O}^- \quad \text{OH} \\
\rightarrow \quad \text{R} - \text{O}^- \text{O}^- \text{O}^- \text{O}^- \text{OH}
\end{array}
\]

### 7.4 References


(4) Chen, W.; Boven, G. and Challa, G.; Macromolecules, accepted.


