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Citation for published version (APA):

Koning, C. E., Viersen, F. J., Challa, G., & Reedijk, J. A. (1988). A mechanistic study on the oxidation of 2,6-dimethylphenol by DMAP- and polystyrene-bound DMAP-based copper catalysts. *Journal of Molecular Catalysis*, 44(2), 245-257. [https://doi.org/10.1016/0304-5102\(88\)80035-X](https://doi.org/10.1016/0304-5102(88)80035-X)

DOI:

[10.1016/0304-5102\(88\)80035-X](https://doi.org/10.1016/0304-5102(88)80035-X)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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A MECHANISTIC STUDY ON THE OXIDATION OF 2,6-DIMETHYLPHENOL BY DMAP*- AND POLYSTYRENE-BOUND DMAP**-BASED COPPER CATALYSTS

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(Received February 16, 1987; accepted September 29, 1987)

Summary

A possible mechanism for the oxidation of 2,6-dimethylphenol by soluble- and polystyrene-bound Cu(II)-DMAP catalysts is described. From our earlier work it is known that, under our standard reaction conditions, the only Cu(II)-DMAP complexes that are initially present in significant amounts in the catalyst solution are mononuclear. From the difference in reaction order in copper for the phenol oxidation and the Cu(I) reoxidation, *viz.* 1 and 2 respectively, it had been concluded that dimerization of Cu(I) complexes is needed to allow the reoxidation step. For this dimerization, a small amount of copper-coordinating counter-ions proved to be required. The present study shows that under standard conditions for the low molar mass catalyst the dimerization reaction is rate-limiting. For the polymeric catalyst, however, the local copper concentration within the polymer coils is relatively high, the dimerization is accelerated and now the phenol oxidation becomes rate-limiting.

The present work further shows that the phenol oxidation obeys Michaelis-Menten kinetics. For the Cu(I) reoxidation, an equilibrium is suggested in which molecular O₂ is reversibly bound to mononuclear Cu(I)-DMAP complexes, prior to Cu(I) dimerization and electron transfers.

Combination of the present results with generally accepted steps in the oxidation of phenols allowed the construction of a possible reaction mechanism for our particular system.

*4-(*N,N*-dimethylamino)pyridine.

**Poly[styrene-co-4(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine]

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Introduction

In previous papers the oxidative coupling of 2,6-dimethylphenol (DMP) by copper(II) complexes of 4-(*N,N*-dimethylamino)pyridine (DMAP, (1)) [1] and poly[styrene-co-4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine] (PS-DMAP, (2)) [2] has been described.

Scheme 1.

Provided that reaction conditions are properly chosen, both ligand (1)- and (2)-based catalysts are able to transform 96 - 97% of the substrate DMP into the engineering plastic polyphenyleneoxide (PPO), and only a minor amount of the undesired byproduct diphenoquinone (DPQ) is formed. A detailed spectroscopic study revealed [1, 2] that under these particular conditions the only species present in solution in significant amounts, prior to the addition of DMP, is the mononuclear species $\text{Cu}^{\text{II}}(\text{DMAP})_4(\text{OH})\text{Cl}$, again for both ligand (1) and the polymeric ligand (2).

The general reaction scheme for the oxidative coupling of phenols with basic copper amine complexes as catalysts is given below (Scheme 2). In the present case E represents the $\text{Cu}(\text{II})$ complex of DMAP or PS-DMAP, S stands for the substrate DMP, E^* the $\text{Cu}(\text{I})$ complex of DMAP or PS-DMAP and P the products PPO and DPQ.

Scheme 2.

Scheme 2 is in agreement with earlier reports on the copper-catalyzed oxidative coupling of phenols, from which it is known that dioxygen may only serve to reoxidize the $\text{Cu}(\text{I})$ species, which is formed after each oxidation step [3, 4].

It is clear from previous work [2, 41] that for PS-DMAP (2) k_2 is the rate-limiting step in Scheme 2, at least under our standard conditions (see Experimental). So, in that case Michaelis-Menten kinetics in terms of

substrate DMP are obeyed, and plots of R^{-1} versus $[DMP]^{-1}$ yield straight lines intersecting the y-axis according to:

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_M}{k_2[E]_0[S]_0}$$

in which $K_M = (k_{-1} + k_2)/k_1$ is the Michaelis constant. However, for ligand (1) the reoxidation of Cu(I) to Cu(II) is rate limiting (again, at our standard conditions). Verlaan *et al.* [5] performed dioxygen-pressure-dependent measurements for this system, and they concluded that a Michaelis-Menten mechanism for the Cu(I) reoxidation might be valid. Our work on the Cu(I) reoxidation for the low molar mass Cu(II)-DMAP catalyst [1] showed a second-order rate dependence on $[Cu(II)]_0$. It was concluded that for the reoxidation step, dimerization of mononuclear Cu(I) complexes is required. To allow this dimerization, copper-coordinating counter-ions should be present. In fact, the Cu(I) reoxidation rate has a maximum for $Cl/Cu = 1$ [1].

Moreover, it was found that a high initial concentration of the species $Cu^{(II)}(DMAP)_4(OH)Cl$ leads to a highly active catalyst solution, no matter whether the DMP oxidation or the Cu(I) reoxidation is rate-limiting. Obviously, under our standard conditions, E in Scheme 2 is mononuclear. E^* , however, forms dimers in order to reoxidize to E.

For the interpretation of our results, the following is of great importance. In biochemistry several mechanisms are known for copper-containing enzymes involving complex formation between copper, dioxygen and in some cases also the substrates [6-10]. When the enzyme contains a dinuclear copper pair, the end product of the dioxygen reduction always appears to be H_2O , whereas H_2O_2 is usually formed when the enzyme contains mononuclear copper [11]. To our knowledge this correlation between the end product of the dioxygen reduction and the character of the copper complex is generally valid.

Having obtained a variety of experimental data on the oxidation of DMP by Cu(II)-DMAP catalysts [1, 2], of which the most important have been summarized above, it is the intention of the present paper to deduce a reaction mechanism for our particular system which is in line with all available data.

Experimental

Materials

1,2-Dichlorobenzene, $CuCl_2 \cdot 2H_2O$ and KOH were obtained from Merck as analytically pure grades. The copper salt and the hydroxide were used as methanolic solutions in which the methanol was of Uvasol quality from Merck. 2,6-Dimethylphenol was from Aldrich and was purified by recrystallization from n-hexane. 4-(*N,N*-dimethylamino)pyridine (1) was from Janssen and used without further purification. Polystyrene-bound DMAP

(2) was synthesized by high conversion copolymerization as described previously [2]. The degree of functionalization α of the polymers was determined by elemental analysis. The number-average molar mass, $\bar{M}_n$, was determined in chloroform with a Knauer membrane osmometer.

For PS-DMAP with $\alpha = 0.251$, $\bar{M}_n = 6.4 \times 10^4 \text{ g mol}^{-1}$ and for PS-DMAP with $\alpha = 0.283$, $\bar{M}_n = 5.6 \times 10^4 \text{ g mol}^{-1}$.

Oxidative coupling

The rate R of the oxidative coupling reaction was calculated from the dioxygen consumption, which was recorded at constant pressure using an automatic gas burette with pure dioxygen. The procedure was as described previously [1, 2] and the standard reaction conditions were: $T = 298.2 \text{ K}$, $[\text{DMP}] = 0.06 \text{ mol dm}^{-3}$, $[\text{Cu(II)}] = 8.3 \times 10^{-4} \text{ mol dm}^{-3}$, $\text{DMAP/Cu} = 4$ (for both ligands (1) and (2)), $(\text{OH/Cu})_0 = 1$, $P_{\text{O}_2} = 101.3 \text{ kPa}$, total reaction volume = 0.015 dm^3 and solvent mixture 1,2-dichlorobenzene/methanol = 13/2 (v/v).

Results and discussion

The reaction order in copper

In Fig. 1. $\log R$ has been plotted *versus* $\log [\text{Cu(II)}]_0$ for ligands (1) ($\square$) and (2) ($\bullet$ and $\circ$). Reaction conditions, which are mentioned in the legend, are such that initially only mononuclear species $\text{Cu}^{\text{(II)}}(\text{DMAP})_4(\text{OH})\text{Cl}$ are present in solution [1, 2]. It is striking that for both types of catalyst the reaction order in copper changes from 1 to 2 upon lowering $[\text{Cu(II)}]_0$. Experiments in which P_{O_2} was varied exhibited DMP oxidation rates in the first-order regions, for both ligands (1) and (2). On the other hand, in the second-order regions Cu(I) reoxidation rates were observed, again for both ligands (1) and (2). In fact, when the order in copper is 2, roughly a first-order dependence on P_{O_2} is found.

In studying Fig. 1 one should realize that in our dilute catalyst solutions the polymer coils can be regarded as separate micro-reactors. Thus, a proportional reduction in the amount of such micro-reactors with the amount of copper ions, of course, results in a first-order rate dependence on $[\text{Cu(II)}]_0$. In order to obtain further valuable information, the reaction order in $[\text{Cu(II)}]_0$ had to be determined within each of the micro-reactors. Thus, R was determined at standard conditions as a function of the added amount of copper, while the number of polymer coils, *i.e.* the number of DMAP ligands, was kept constant. However, note that DMAP/Cu cannot remain constant for such experiments ($\bullet$). It was checked that an enhancement of DMAP/Cu from 12 to 20 with constant $[\text{Cu(II)}]_0$ did not alter the reaction rate. On the other hand, a reduction of DMAP/Cu from 50 to 20 (again, with $[\text{Cu(II)}]_0$ constant) by offering a smaller amount of polymer coils lead to a significant increase of R . (Note that in this case the number of copper ions per polymer coil is enhanced.) This is illustrated in Fig. 1 by the

Fig. 1. $\log R$ versus $\log [\text{Cu(II)}]_0$ for DMAP (1, $\square$) and PS-DMAP (2, $\alpha = 0.251$, $\bullet$ and $\circ$). For DMAP standard conditions with $P_{\text{O}_2} = 162.1$ kPa and $[\text{DMP}] = 0.05$ mol dm^{-3} . For PS-DMAP standard conditions with 1.245×10^{-2} mol ligands dm^{-3} . For ($\bullet$) ligand/Cu values are indicated at the top of the Figure. For ($\circ$) ligand/Cu = 20 (see text). SC = standard conditions.

filled symbol furthest left ($\bullet$, DMAP/Cu = 50) and the open symbol ($\circ$, DMAP/Cu = 20). This open symbol fits the rates very well for PS-DMAP obeying a first-order dependence on $[\text{Cu(II)}]_0$.

By combining all results on the reaction order in copper, the following conclusion can be drawn, assuming a random distribution of copper ions over all polymer coils. When the overall or local copper concentration is low (for DMAP and PS-DMAP respectively), *i.e.* for low values of $[\text{Cu(II)}]_0$ in the case of DMAP and for high values of DMAP/Cu in the case of PS-DMAP, respectively, then the dimerization of mononuclear Cu(I) complexes — necessary to reoxidize Cu(I) to Cu(II) — becomes rate-limiting and R is second order in $[\text{Cu(II)}]_0$. However, when the overall or local copper concentration is high, *i.e.* for high values of $[\text{Cu(II)}]_0$ in the case of DMAP and for DMAP/Cu ≤ 20 for PS-DMAP, respectively, then the Cu(I) dimerization is facilitated, and now the DMP oxidation becomes rate-limiting, with R being first order in $[\text{Cu(II)}]_0$.

Finally it must be mentioned that the second-order dependence is already observed for $[\text{Cu(II)}]_0 \leq 1.70 \times 10^{-3}$ mol dm^{-3} ($\log [\text{Cu(II)}]_0 \leq -2.8$) in case of the ligand DMAP (1), whereas for PS-DMAP (2) the reaction is still first order in $[\text{Cu(II)}]_0$ for $[\text{Cu(II)}]_0 = 6.20 \times 10^{-4}$ mol dm^{-3} ($\log [\text{Cu(II)}]_0 = -3.2$). This can be explained by the high local copper

concentration within the polymer coils with regard to the overall copper concentration. Thus, the polymer plays an active promoting role in the dimerization process, which already was evident from our earlier work [2].

On the Cu(I) reoxidation

Measurements with varying dioxygen pressures were carried out with DMAP (1) and with PS-DMAP (2, $\alpha = 0.283$) under standard conditions (see Experimental). The results are given in Fig. 2, which shows a perfect first-order rate dependence on P_{O_2} for the low molar mass DMAP-based catalyst up to $P_{O_2} = 162.1$ kPa. This indicates that for DMAP in this region of P_{O_2} for $[Cu(II)]_0 = 0.83$ mM, Cu(I) reoxidation rates are measured. This is consistent with the observed second-order rate dependence on $[Cu(II)]_0$ around $[Cu(II)]_0 = 0.83$ mM, both for $P_{O_2} = 162.1$ kPa (See Fig. 1) and for $P_{O_2} = 101.3$ kPa [2]. In the case of PS-DMAP-based catalyst, some kind of saturation kinetics seems to occur (see Fig. 2). However, one should realize that for PS-DMAP the levelling off in Fig. 2 around $P_{O_2} = 101.3$ kPa is caused by the fact that the DMP oxidation becomes rate limiting in this region of P_{O_2} . In fact, Fig. 1 clearly demonstrates that in the case of the polymer ligand, for $P_{O_2} = 101.3$ kPa, a first-order rate dependence on $[Cu(II)]_0$ applies around $[Cu(II)]_0 = 0.83$ mM (SC in Fig. 1). This means that DMP oxidation rates are indeed measured under these reaction conditions. Thus, the levelling off in Fig. 2 for PS-DMAP is not brought about by a saturation in P_{O_2} and Michaelis-Menten kinetics in terms of dioxygen is not valid; we therefore have to look for another Cu(I) reoxidation scheme. Before doing this, it should be noted that it cannot be unambiguously concluded from the present data whether the Cu(I) dimerization, which obviously is the rate-limiting step in the reoxidation process, takes place before or after the coordination of dioxygen, although chemical intuition would prefer O_2 addition as the first step. Rainoni and Zuberbühler [12] have already mentioned the possibility of the following reaction scheme for the autoxidation of Cu(I) with non-coordinating counter-ions such as ClO_4^- and BF_4^- in DMSO, including a dimeric reaction intermediate:

For this process a second-order reoxidation rate dependence on $[Cu(I)]$ was found [12]. For copper complexes with substituted imidazole ligands, a second-order reoxidation rate dependence on $[Cu(I)]$ has also been observed [13, 14], which agrees with the proposed reoxidation scheme. Such a scheme could serve to explain our experimental data if the equilibrium in which CuO_2^+ adduct is formed is far from complete, indeed.

It is known that the autoxidation rates of Cu(I) complexes can be quite high [15], although the low redox potential of -0.33 V for the $O_2/\cdot O_2^-$ couple [16, 17] would be very unfavourable. This problem can

Fig. 2. R versus P_{O_2} for DMAP (1, ●) and PS-DMAP (2, $\alpha = 0.283$, ○). Standard conditions.

be bypassed by two-electron reduction of O_2 in a dimeric transition state $[\text{Cu}^+(\text{O}_2)\text{Cu}^+]$, avoiding the formation of free $\cdot\text{O}_2^-$ [15]. Therefore the existence of such an intermediate, which has already been suggested by *e.g.* Bettelheim *et al.* [18], might be possible. In analogy, in hemocyanin two Cu(I) ions are known to reversibly bind one dioxygen molecule in a dinuclear complex [19]. In this dimeric species $[\text{Cu}^+(\text{O}_2)\text{Cu}^+]$ the molecular dioxygen is thought to form a bridge between the two Cu(I) ions. Initially two electrons are transferred to the O_2 to produce a peroxo-bridged bis[copper(II)] species [9, 20]. This type of species has been proposed in the autoxidation mechanism of other Cu(I) complexes [10, 21 - 24]. In fact the dimeric intermediate $[\text{Cu}^{2+}(\text{O}_2^{2-})\text{Cu}^{2+}]$ has also been suggested by Schouten *et al.* [25] in the copper-catalyzed oxidative coupling of DMP. In view of this dimeric intermediate, it is not unexpected that for the copper-bridging Cl anions an optimum value of $\text{Cl}/\text{Cu} = 1$ has been found for the Cu(I) reoxidation [1].

As stated above, the existence of such an intermediate is advantageous for the electron transfer. However, for the formation of $[\text{Cu}^{2+}(\text{O}_2)^{2-}\text{Cu}^{2+}]$ only two electrons have been transferred. As O_2 is reduced to H_2O in our DMP oxidation reactions with copper catalysts based on ligands (1) and (2), it is clear that an overall transfer of four electrons to O_2 must take place. Fallab [26] has reported three possible routes for this process:

- (a) four one-electron transfer steps, of which the first electron transfer is highly unfavourable (see above);
- (b) two two-electron transfer steps, which are much faster than (a);
- (c) one four-electron transfer step, which is faster than (b). However, this would require a reduction of Cu(II) to Cu(0) in our dimeric intermediate, and up to now no evidence for the existence of Cu(0) in the oxidative coupling of phenols has been reported in the literature [27].

Thus, as was assumed by *e.g.* Kaneko and Manecke [28] and Schouten *et al.* [25], route (b), *i.e.* two 2-electron-transfer steps, seems the most probable, and the coordinated O_2^{2-} must accept two more electrons simultaneously. This second two-electron transfer is much more favourable than the first, as made clear by Fallab [26], and consequently much faster. Below, it

is indicated in which way the second two-electron transfer is thought to take place.

For the oxidative coupling of DMP, several authors have given experimental evidence that the reoxidation of Cu(I) could occur in a ternary complex (copper, O₂, substrate) [29 - 31]. This point will also be discussed in the next section.

A possible mechanism for the DMP oxidation

For convenience, a possible reaction mechanism for the oxidation of DMP is already presented at this stage of the paper (Scheme 3). This Scheme is in agreement with all experimental data mentioned here, and with results of related work by Viersen *et al.* [32] in our laboratories. Moreover, Scheme 3 which is discussed below, is consistent with some generally accepted steps in the oxidation of phenols.

As oxidative coupling is strictly limited to substrates with labile acidic hydrogen atoms, it has been suggested that the first steps in the oxidation reaction might be deprotonation followed by coordination [30, 33, 34]. The findings of Viersen *et al.* [32] clearly confirm this. The role of OH⁻ proved to be merely that of extracting a proton from DMP, thereby allowing the actively coordinating phenolate anion to form a complex with the Cu(II)-amine complex. In such a reaction, according to the fast equilibrium in Scheme 2, H₂O would be produced. Verlaan *et al.* [35] reported for the

Michaelis-Menten in Phenol (For PS-DMAp k₂ is rate-limiting at standard cond.)

O₂-coordination; dimerization (For DMAp k_{dim} is rate-limiting at standard cond.)

Non rate-limiting consecutive steps (electron-transfers, dissociation)

Scheme 3.

system poly[styrene-co-4-vinylpyridine]/CuCl₂ that addition of small amounts of water does not affect k_2 (Scheme 2), but significantly decreases the substrate complexation constant K_1 .

The coordination of the phenolate to the active complex is followed by the first important, and now generally accepted step, in the phenol oxidation, namely the formation of a phenoxy radical via a one-electron transfer from the phenolate to the Cu(II) [25, 30, 36, 37]. The produced Cu(I) species must be reoxidized to Cu(II) by dioxygen (see above).

Measurements were carried out with PS-DMAP (2, $\alpha = 0.283$) with varying DMP concentration under our standard conditions. In Fig. 3 a Lineweaver-Burk plot of R^{-1} versus $[\text{DMP}]^{-1}$ has been drawn. The linear relationship points to a Michaelis-Menten mechanism for the DMP oxidation as shown in Scheme 2. To ensure that a Michaelis-Menten mechanism for the oxidation of DMP is indeed valid, and to exclude the possibility that at high concentrations of DMP the reoxidation of Cu(I) becomes rate limiting, without actually 'saturating' Cu(II) with DMP, the influence of increasing P_{O_2} on R was investigated for the upper DMP concentration in Fig. 3. Within experimental error such influence proved to be absent.

The three findings mentioned above allow the construction of the first line in Scheme 3. Since, according to the previous section, dimerization takes place only during the Cu(I) reoxidation process, it is clear that during the deprotonation, the coordination of PhO^- and the first one-electron transfer, the copper-DMAP complexes are mononuclear.

At the end of the first line in Scheme 3, several possibilities for reaction of the phenoxy radical seem to occur. It might either stay coordinated during the Cu(I) reoxidation [31], or leave the Cu(I) complex before the

Fig. 3. Lineweaver-Burk plot of R^{-1} versus $[\text{DMP}]^{-1}$ for PS-DMAP (2, $\alpha = 0.283$). Standard conditions.

reoxidation takes place [37]. In the previous section it was mentioned that in the present oxidation reactions one dioxygen molecule accepts four electrons during the process and that two 2-electron transfers seem to be most likely. In view of the dimerization during the reoxidation process of Cu(I), it is now possible to distinguish between these several possibilities. After the dimerization has taken place the first two electrons can be transferred from both Cu(I) ions to the dioxygen molecule, yielding the dimer $[\text{Cu}^{2+}(\text{O}_2^{2-})\text{Cu}^{2+}]$. If phenoxy radicals are still present in this complex, a fast second 2-electron transfer from the two phenoxy radicals via the Cu(II) ions to O_2^{2-} can take place, yielding phenoxonium ions as reported by *e.g.* Kresta *et al.* [37]. The existence of phenoxonium ions as intermediates in the oxidative coupling of 2,6-disubstituted phenols has also been suggested by Roubaty *et al* [38] and Waters [39].

According to Kresta [37], the generated phenoxonium ions react with a phenol molecule and a basic amine to yield C—O coupling and a protonated amine. In fact, Kresta suggests that the phenoxy radicals dissociate from the Cu(I) complex. These dissociated phenoxy radicals may combine to yield DPQ, or they may enter an available Cu(II) complex to release a second electron (see above). In this way an ionic mechanism for PPO formation and a radical mechanism for DPQ formation would apply. As dissociated phenoxy radicals would have an electron density about two times higher in the *para*-carbon position ($\rho = 0.45$) than at the oxygen ($\rho = 0.23$) [37], these free radicals would predominantly yield C—C coupling (DPQ formation). As under optimum conditions only 3 - 4% of the substrate DMP is transformed into DPQ by our catalyst systems [1, 2], it seems unlikely that the phenoxy radicals would dissociate from the complex. Another indication that the phenoxy radicals remain in the complex stems from observations by Price and Nakaoka [31]. They mention that the dissociation of phenoxy radicals from the complex would occur more readily when the basic ligand/Cu ratio is enhanced. For our system, it was found that up to $\text{DMP}/\text{Cu} \leq 6$ an increasing DMAP/Cu ratio leads to a decreasing amount of produced DPQ. For $\text{DMP}/\text{Cu} > 6$, the amount of DPQ levels off [1, 2]. In view of the high electron density of the free phenoxy radical at the *para* position and the ideas of Price and Nakaoka, however, an increasing amount of DPQ with increasing DMAP/Cu values would be expected. Thus, it seems likely that in our case the phenoxy radicals remain coordinated in the complex. This conclusion has also been drawn by Stern [40]. In view of the high specificity for PPO formation, which proved to be a function of the catalyst composition for pyridine-based Cu(II) complexes, Stern feels that it is unlikely that phenoxy radicals are formed and coupled in an independent step. Further, Gampp and Zuberbühler [27] prefer the idea that the radicals formed in the coordination sphere of Cu(II) react further in a complex. Moreover, if the re-entrance of phenoxy radicals in Cu(II) complexes can occur rapidly, then Kresta's proposal would still be valid (see above). However, at this point a radical mechanism for both C—O and C—C coupling — although unlikely — cannot be completely ruled out.

According to related work [32], a formed phenoxonium ion is released from the dimeric $[\text{Cu}^{\text{II}}(\text{O}_2^{4-})\text{Cu}^{\text{II}}]$ structure, and the coupling reactions take place in solution yielding predominantly PPO and a small amount of DPQ. In principle, phenoxonium ions might also react with water and methanol molecules which are present in the reaction medium. The corresponding reaction products, however, are not found to any appreciable extent in most copper/amine catalyst systems. It is likely that the reaction of phenoxonium ions with phenol molecules activated by amines is much faster than with neutral water and methanol molecules. Experimental results, supporting the idea that coupling takes place in solution and not in the copper-amine complex, are the following. The selectivities of our DMAP- and PS-DMAP-based copper catalysts for PPO formation are absolutely identical under comparable reaction conditions [2]. Furthermore, the optimum selectivity (only 3 - 5% of DPQ) for our catalyst systems is the same as that obtained by Viersen *et al.* [32] for copper complexes based on TMED (= *N, N, N', N'*-tetramethylethane-1,2-diamine) under the same conditions. Moreover, the specificity of the PS-DMAP-based catalysts was not affected by the chain loading α of the polymer catalyst [41]. Thus, the nature of the catalyst only affects the activity and not the selectivity.

The above considerations, together with our experimental data, allow the construction of the second and third lines in Scheme 3. It should be noted that Scheme 3 is valid only for experimental conditions under which initially only mononuclear complexes $\text{Cu}^{\text{II}}(\text{DMAP})_4(\text{OH})\text{Cl}$ appear to be present, *i.e.* under our standard conditions.

Some final remarks on Scheme 3 are given below. For DMAP at our standard conditions, the dimerization (second line) is relatively slow, but for PS-DMAP it is promoted due to the higher local $[\text{Cu}^{\text{II}}]$ in the polymer coil, and k_2 becomes rate-limiting. Thus, possible steric hindrance for the formation of the complicated polymeric intermediate complex I in Scheme 3 seems to be of minor importance. In addition, the polymer is expected to have another accelerating effect on the Cu^{I} reoxidation. According to Tsuchida *et al.* [42], k_{reox} is accelerated by the 'non-polar field' created by the polymer backbone. In our case, however, promotion of the dimerization seems to be of major importance. Moreover, it should be emphasized that the redox potential for the second 2-electron transfer is much higher than that for the first 2-electron transfer. This implies that the transformation of the phenoxy radicals into phenoxonium ions occurs rapidly. It should be noted that all dimeric structures in Scheme 3 (structures I, II and to some extent III) are merely resonance structures. In structure I the bridging ions are Cl^- , which is consistent with the optimum reoxidation activity for $\text{Cl}/\text{Cu} = 1$ [1]. Recently, Karlin *et al.* [10] reported three-dimensional structures of dimeric phenoxo-bridged Cu^{I} and Cu^{II} complexes. Although no DMP was used, it is clear that in principle phenolate anions may act as bridging ions. It might be possible that phenoxy radicals can yield similar dimeric structures, but at this point we prefer Cl^- to phenoxy radicals as bridging ligands in the structures I, II and III.

Acknowledgements

The authors are indebted to Prof. Dr. A. D. Zuberbühler, University of Basle (Switzerland), for his constructive suggestions.

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