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A kinetic study of the copper-catalysed oxidative coupling of 2,6-dimethylphenol. The role of copper, base and phenol concentrations

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Abstract

The influence of varying concentrations and ratios of phenol, base and copper on the copper/N-methylimidazole catalysed oxidative coupling of 2,6-dimethylphenol (DMP) has been studied. The reaction obeys simple Michaelis–Menten kinetics with respect to the phenol. The amount of DPQ formed during the reaction increases linearly with the increasing initial amount of DMP. At higher base-to-copper ratios an oxidative coupling experiment takes longer to complete, despite higher initial rates, which is probably due to the formation of inactive copper hydroxide species in the later stages of the reaction. The phenol oxidation step is most likely the rate-determining step, and the fractional reaction orders in copper are determined by the position of the equilibrium between mono- and dinuclear copper species, the latter being the active one. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Reaction mechanism; Kinetics; Dioxygen uptake; Phenol oxidation; Homogeneous copper catalysis; N-Methylimidazole; Michaelis–Menten

1. Introduction

1.1. General

The oxidative coupling of 2,6-dimethylphenol (DMP) as catalysed by copper–amine complexes was discovered in 1959 by Hay et al. [1]. This reaction, schematically depicted in Fig. 1, takes place under ambient conditions, and yields either a polymer, poly(1,4-phenylene ether) (PPE), or a diphenoquinone (DPQ [1]). The polymer is formed from C–O-coupling of phenol moieties. This polymer has excellent mechanical properties and chemical resistance at elevated temperatures, which makes it an important engineering plastic. It is produced by GE Plastics, who markets it, blended with polystyrene, under the name Noryl™ [2]. The other main product of this reaction is formed by C–C-coupling of two monomeric phenol moieties to give a bisphenol that is oxidised, under

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[1] Systematic name: 4-(3,5-dimethyl-4-*oxo*-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone.
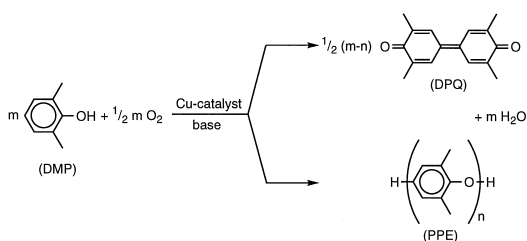
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Fig. 1. Overall reaction scheme for the oxidative coupling of DMP to PPE and DPQ.

the reaction conditions employed, to afford DPQ, a very intensely coloured, side-product. Formation of DPQ is not desired, because it not only reduces the yield of polymer, but also degrades the polymer upon further processing at higher temperatures [3].

Because of the importance of PPE as an engineering plastic and the surmised relationship between the mechanism of this reaction and the one catalysed by tyrosinase, a mono-oxygenase that catalyses the conversion of phenol into catechol, this reaction has been investigated extensively over the last three decades [3–17]. However, no mechanism could be formulated as yet that was able to explain all experimental findings. Initially, the mechanism was thought to involve phenoxyl radicals, generated by mononuclear copper-phenoxo species [4,8,18]. Phenoxy radicals, however, have a strong tendency to afford mainly DPQ [19–23]. In the case of the copper-catalysed reactions, less than 5% of DPQ is formed under optimal conditions. Subsequently, more sophisticated models were developed involving dinuclear phenolate-bridged copper(II) complexes, which can afford phenoxonium cations as the key species after a, supposedly rate-determining, 2-electron transfer [3,9,11,24]. Although these proposals were a major improvement with respect to the 1-electron (radical) mechanisms, they also failed to explain certain experimental findings.

This prompted us to study the mechanism of this reaction in more detail, especially with respect to the first steps in the mechanism. Our model catalytic system consisted of copper(II)

nitrate, to prevent interference from a strongly coordinating anion, *N*-methylimidazole (Nmiz) as the *N*-donor ligand, sodium methoxide as the base co-catalyst and DMP as the substrate. Part of the kinetic and spectroscopic research performed with this system has been published before [25]. As the results presented in this paper are a continuation and extension of this research, a short summary of earlier findings will be given first.

1.2. Overview of earlier results [25]

A very important factor influencing both the rate and selectivity of the reaction is the ligand-to-copper (abbr. N/Cu) ratio [25]. Increasing this ratio resulted in a drastic increase in reaction rate and a decrease of the amount of DPQ formed, which levelled off at an N/Cu ratio of 30. On the other hand, from EPR measurements, it was found that all copper was already converted into a catalyst precursor complex at an N/Cu ratio of 4. The need for an excess of the ligand has been explained in terms of a hampering of the formation of inactive (dinuclear) complexes by shifting a number of pre-equilibria [25]. The catalyst precursor was shown to be $[Cu^{II}(Nmiz)_4(NO_3)_2]$, both in solution (EPR) and in the solid state (X-ray diffraction).

Further kinetic investigations revealed that the order in copper of this reaction was fractional and dependent on the N/Cu ratio, as shown in Table 1, which was thought to indicate that in this system two competing rate-determining steps are operative. These steps were

Table 1

Order in Cu at different Nmiz/Cu ratios at base/Cu = 1 (redrawn from Ref. [25])

Nmiz/Cu	Order in Cu[a]	k (s^{-1})[b]
10.0	1.22	0.18
20.0	1.29	0.42
37.5	1.42	1.31
75.0	1.70	9.82

[a]An uncertainty interval of $\pm 5\%$ must be taken into account.
[b]The unit of k is strictly speaking not s^{-1}, but (mol/l)^x s^{-1}, where $x = 1 -$ (order in Cu).

thought to be the phenol oxidation step, which up till now has always been considered as being the sole rate-determining step, and the formation of an active dinuclear copper species. At higher N/Cu ratios, a higher order in copper is observed, probably because the formation of the dinuclear intermediate is hampered by an excess of the ligand.

Experiments where dioxygen and/or water were excluded showed that dioxygen is not needed for the phenol oxidation step to occur. Dioxygen seems only needed as a terminal oxidant for the reoxidation of the copper catalyst, and to regenerate the base co-catalyst. Water, however, was found to be essential for the oxidation step to take place. The need for water in combination with the occurrence of dinuclear copper complexes was explained in terms of the nature of the catalytically active intermediate, which is not a bis-μ-phenoxo bridged dinuclear copper complex, as proposed in the earlier mechanisms [9], but rather a (μ-phenoxo)(μ-hydroxo)dicopper(II) species. The water is needed to form an initial (catalytic) amount of hydroxide by reaction with the base co-catalyst (NaOMe).

These novel insights have resulted in a modified mechanistic proposal [25]. However, some aspects of the reaction still needed clarification. One of these aspects is the Michaelis–Menten, or saturation, kinetics that is commonly observed for this reaction [12,26–29], which has not been studied in full detail for this particular catalytic system. Another one is the role of the base co-catalyst that is not fully understood yet, as are the observed fractional orders in copper. In this paper, we address these aspects with additional experiments and a detailed discussion.

2. Experimental

2.1. General

Solvents (toluene and methanol) were obtained from Baker as analytical grades. Methanol

was dried on molecular sieves (3 Å) prior to use, toluene was used as received. $Cu(NO_3)_2 \cdot 3H_2O$ (analytical grade) was obtained from Merck and was used without further treatment. 2,6-dimethylphenol (reagent grade) was purchased from Baker and was purified by repeated crystallisation from *n*-hexane prior to use. *N*-methylimidazole (Nmiz; 99% pure) was used as obtained from Janssen. Sodium methoxide (NaOMe) was synthesised by treating methanol with sodium metal under a dinitrogen atmosphere. Subsequent removal of the remaining methanol under reduced dinitrogen pressure afforded $NaOCH_3$ as a white, fluffy powder.

Dioxygen-uptake experiments were performed using in-house designed equipment [25,30]. ^{1}H-NMR spectra were obtained on a Jeol JNM-FX (200 MHz) FT-NMR spectrometer in $CDCl_3$ solvent. UV/Vis/NIR spectroscopy was performed using a Camspec M302 single-beam spectrophotometer.

2.2. Catalyst and substrate solutions

The catalyst solution was prepared by mixing, in a 100-ml volumetric flask, 20 ml of a 0.05 M $Cu(NO_3)_2 \cdot 3H_2O$ solution in methanol, 30 ml of a 1.0 M Nmiz solution in toluene, and filling it up to 100 ml with toluene, which resulted in a 0.01 M $Cu(NO_3)_2$ and 0.3 M Nmiz (thus, N/Cu = 30) solution in toluene/methanol (4/1 v/v).

The substrate solution was prepared by mixing, in a 10-ml volumetric flask, the required amount of a 0.66 M DMP solution in toluene/methanol (13/2 v/v), 0.5 ml of a 0.11 M or 0.198 M NaOMe (for a base-to-copper ratio of 1 to 1 or 1.8 to 1, respectively) solution in methanol as a co-catalyst, and filling it up to 10 ml with toluene/methanol (13/2). To this solution was added another 1.0 ml of toluene/methanol (13/2 v/v) which resulted in 11 ml of a DMP/DMPO$^-$ solution in toluene/methanol (about 5/1 v/v). A basic DMP solution has only limited stability, as the phenol(ate) is slowly oxidised under air. There-

fore, this solution was made fresh each day when measurements were performed.

2.3. Dioxygen-uptake measurements

In a typical quantitative, time-resolved dioxygen-uptake experiment, one compartment of a special reaction vessel was filled with 5 ml of the catalyst solution, and the other compartment with 10 ml of the DMP/base solution. Thus, the resulting reaction mixture was 3.33 mM in copper and 3.33 mM or 5.99 mM in NaOMe, so that the base-to-copper (abbr. base/Cu) ratio was 1 to 1 or 1.8 to 1, respectively. DMP-to-copper (abbr. DMP/Cu) ratios were varied between 6 to 1 and 96 to 1. All reactions were performed at 25°C under 100% dioxygen at atmospheric pressure. The amount of DPQ formed during the reaction was determined spectrophotometrically by measuring the absorbance of the diluted reaction mixture at 421 nm. A more detailed description of a dioxygen-uptake experiment and the processing of the experimental data have been given in previous publications [25,30,38].

3. Results

3.1. Variation of the DMP-to-copper ratio

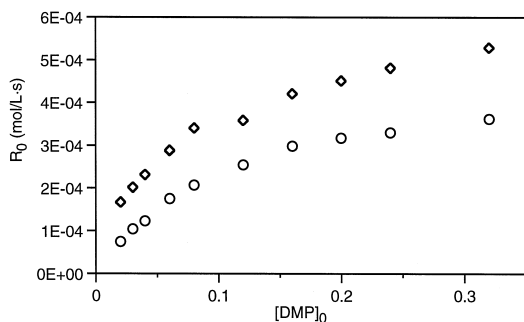Tsuchida et al. [12], Viersen et al. [28] and Chen and Challa [29] found that their respective

Fig. 2. Initial dioxygen-uptake rate as a function of the initial DMP concentration at base/Cu = 1 (○) and 1.8 (◇). [Cu] = 3.33 mM, N/Cu = 30 and T = 298 K.

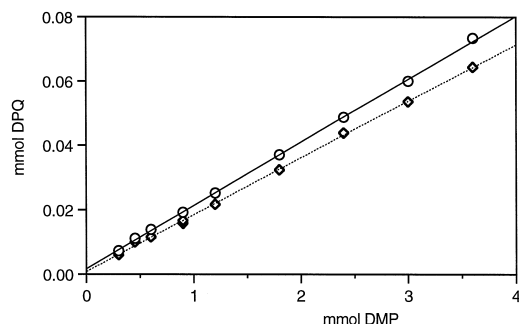Fig. 3. Amount of DPQ formed vs. the initial amount of DMP, at base/Cu = 1 (○) and 1.8 (◇). [Cu] = 3.33 mM, N/Cu = 30 and T = 298 K. The lines are least-squares fits of the experimental data.

catalytic systems obey Michaelis–Menten kinetics [31], also known as saturation kinetics, with respect to the substrate. To investigate whether this behaviour is also valid for our catalytic system, the initial amount of DMP has been varied at base/Cu ratios of 1 to 1 and 1.8 to 1, at [Cu] = 3.33 mM and N/Cu = 30. The results of these measurements with respect to the reaction rate are shown in Fig. 2. The curves level off at higher concentrations of DMP, which is characteristic for saturation kinetics. At initial DMP concentrations higher than 0.32 M (not shown) the reaction rates start to drop, which may be related to a too large change in the reaction medium, because of the high concentration of DMP.

Increasing DMP concentrations result in slightly lower percentages of DPQ, which are otherwise comparable to those normally observed under the reaction conditions applied, i.e., ca. 4% for base/Cu = 1 and ca. 3.6% for base/Cu = 1.8. A plot of the total amount of DPQ formed during the reaction vs. the initial amount of DMP, shows straight lines for both base/Cu ratios, as shown in Fig. 3; this implies that a constant percentage of the initial amount of DMP is always converted into DPQ. Furthermore, the non-zero intercepts with the y-axis suggest that a small, constant amount of DPQ is always formed, independent of the initial amount of DMP.
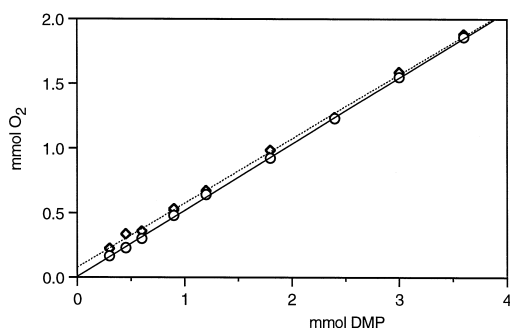
Fig. 4. Amount of dioxygen absorbed vs. the initial amount of DMP, at base/Cu = 1 ($\bigcirc$) and 1.8 ($\diamondsuit$). [Cu] = 3.33 mM, N/Cu = 30 and T = 298 K. The lines are least-squares fits of the experimental data.

The amount of dioxygen absorbed at low DMP concentrations appeared to be more than stoichiometrically expected, especially at a base/Cu ratio of 1.8 to 1. With increasing initial amounts of DMP these amounts levelled off to stoichiometric quantities. A plot of the amount of dioxygen absorbed during the reaction vs. the initial amount of DMP, as shown in Fig. 4, results in straight lines with slopes of ca. 0.5, as would be expected for a reaction stoichiometry of DMP: O_2 = 2:1. However, the intercept with the y-axis is positive. So, an additional, constant amount of dioxygen is absorbed independent of the initial amount of DMP. This additional uptake may be caused by oxidation of methanol [32], (oxidative) incorporation of the ligand into the polymer chain [33], or simple dissolution of dioxygen into the reaction mixture. Analysis of reaction mixtures by NMR and HPLC showed that oxidation of methanol and/or ligand are less likely, leaving dissolution of dioxygen into the mixture as the most likely possibility. Apparently, the dissolved amount of dioxygen is dependent on the base/Cu ratio.

4. Discussion

4.1. Variation of the DMP-to-copper ratio

The form of the curves shown in Fig. 2 is characteristic of Michaelis–Menten (MM) kinetics, which is commonly observed for enzyme-catalysed reactions. The main feature of MM kinetics is the reversible formation of a catalyst–substrate complex, prior tot the rate-determining step (see Scheme 1).

In the first step, the catalyst (C) binds DMP reversibly with rate constants k_1 and k_{-1}. Then follows the rate-determining step, which is presumably the oxidation of the phenolate, with a rate constant k_2. The reduced catalyst (C∗), a copper(I) species, is reoxidised by dioxygen with rate constant k_{reox}, which can be taken as much larger than k_2. The initial rate equation for this scheme is given by:

$$R_0 = \frac{k_2[C]_0[DMP]_0}{K_m + [DMP]_0} \qquad (1)$$

where $[C]_0$ = initial catalyst concentration (= initial copper concentration) (mol/l), $[DMP]_0$ = initial DMP concentration (mol/l), K_m = Michaelis constant = $(k_{-1} + k_2)/k_1$ (mol/l).

Eq. (1) rearranges into:

$$\frac{1}{R_0} = \frac{1}{k_2[C]_0} + \frac{K_m}{k_2[C]_0[DMP]_0} \qquad (2)$$

So, if true Michaelis–Menten kinetics is applicable, a plot of $1/R_0$ vs. $1/[DMP]_0$ should result in a straight line, from which k_2 may be derived from the intercept with the y-axis when $[C]_0$ is known. K_m, the reciprocal of which is a measure for the accessibility of the catalytically active site, is equal to the slope of the line divided by the intercept. Such double-reciprocal, or Lineweaver–Burk, plots have been made of the resulting reaction rates as a function of the initial DMP concentration for both base/Cu
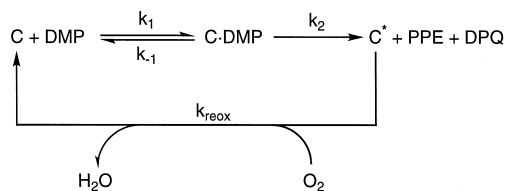
Scheme 1.

ratios employed (see Fig. 5). Straight lines are observed, and so the Michaelis–Menten kinetic scheme seems applicable, although the curve for the base/Cu ratio of 1.8 is not truly linear at $[DMP]_0^{-1} < 10$. The values for k_2 and K_m derived from the plot in Fig. 5 are listed in Table 2, together with the values found by Chen [9] and Chen and Challa [29] for a system in which copper(II) chloride was used.

As can be seen from Table 2, the experimental values of k_2 and K_m at a base/Cu ratio of 1.0 and the literature values [9,29] are in excellent agreement. It appears that the anion used (nitrate or chloride) does not play a significant role in the reaction mechanism under these conditions, implying that phenolate is the coordinated anion in the actual catalyst. The value for k_2 obtained at a base/Cu ratio of 1.8 is, within experimental error, also in agreement with the other values. This is to be expected, as k_2 is the rate constant of the oxidation of the phenolate, which should not be affected by the amount of base present. The value for K_m, however, is clearly lower than those observed at lower base/Cu ratios. Apparently, a higher amount of base facilitates the formation of a complex between the substrate and the catalyst. It should be noted that the phenol itself is needed to form the Michaelis–Menten complex, not the phenolate anion.
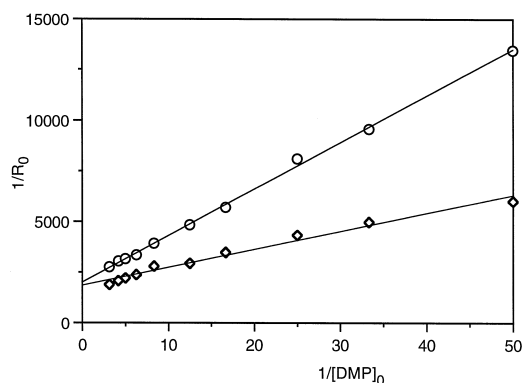
Table 2
Values obtained for the rate constant of the oxidation of DMP (k_2) and the Michaelis constant (K_m). Literature values [9,29] have been added for comparison

	Base/Cu ratio	k_2 (s^{-1})	K_m (mol/l)
Experimental	1.0	0.149	0.114
Experimental	1.8	0.161	0.048
Literature [9,29]	1.0	0.15	0.11

The Michaelis–Menten scheme as described above is in fact a major simplification of the actual mechanism of this reaction. For a catalytic system of copper bromide with a mixture of aliphatic amines, Mobley [34] made some adjustments to this scheme by taking into account a first-order inactivation of the copper catalyst and the different reactivities of monomer DMP on the one hand and dimer and higher oligomers on the other. In this way, the anomalous behaviour of the reaction rate at high DMP concentrations (> 0.35 M), when the rates start to drop, could be explained. It is not clear if and to what degree these effects play a role in our catalytic system, but because in the current study the DMP concentrations did not exceed this limit, the simple Michaelis–Menten scheme is always obeyed.

The amount of DPQ formed shows a linear dependency on the initial amount of DMP (see Fig. 3), implying that a constant percentage of DMP is always converted into DPQ. Also, both lines have positive intercepts with the y-axis, suggesting that a constant, small amount of DPQ is always formed, independent of the initial amount of DMP. However, it is not clear whether this positive intercept is due to a non-zero UV/Vis-absorption at 421 nm because of an experimental factor, or because of some minor side reaction affording DPQ. The bulk of the DPQ is formed during the copper-catalysed reaction itself, either by a radical path due to one-electron oxidation of the phenolate by mononuclear copper complexes, or by an ionic pathway after a two-electron oxidation, as there is always a (small) possibility [3] that a (mono-

Fig. 5. Plot of $1/R_0$ vs. $1/[DMP]_0$ at base/Cu = 1 (○) and 1.8 (◇). [Cu] = 3.33 mM, N/Cu = 30 and T = 298 K. The lines are least-squares fits of the experimental data, for the parameters given in Table 2.

mer) phenoxonium cation may undergo C–C coupling with a monomeric DMP moiety.

4.2. Effect of the base-to-copper ratio

From previous investigations [25] with copper(II) nitrate, it was found that the optimal base/Cu ratio with regard to the reaction rate is 1.8 to 1. The selectivity of the reaction was found to improve slightly with increasing base/Cu ratio. Apparently an increase in the amount of phenolate anions present in solution favours the C–O coupling reaction. Furthermore, the reaction order in copper at a base/Cu ratio of 2 was found to be somewhat lower than at a base/Cu ratio of 1, indicating that the formation of a dinuclear catalytic intermediate is facilitated at this higher ratio. This finding is further substantiated by the lower value for K_m observed at higher base/Cu ratios (see Section 4.1). Such behaviour is to be expected, since at a higher base concentration, more (potentially) bridging ligands (hydroxide, methoxide, phenoxide) are available. These observations clearly indicate that dinuclear complexes are indeed responsible for the C–O coupling reaction.

Other effects were also observed. At higher base/Cu ratios (≥ 2 to 1) no PPE precipitate was formed when the reaction was nearing completion, which is indicative of a lower degree of polymerisation. A precipitate only formed after a relatively long reaction time, during which only little additional dioxygen was consumed. It is known [35] that in this particular polymerisation reaction, high-molecular weight PPE is only formed when the reaction is nearing completion, because only then the coupling of entire low-molecular weight PPE chains becomes predominant, resulting in a rapid increase in the average molecular weight [35]. Furthermore, although initial dioxygen-uptake rates were higher at higher base/Cu ratios (> 1 to 1), the reaction took longer to complete. Both effects are quite likely caused by the higher initial amount of phenolate end groups as a consequence of the higher amount of base, and, since the starting amount of DMP was the same in all these reactions, there will be more, short PPE chains towards the end of the reaction.

Furthermore, during the oxidative coupling reaction, the number of phenolic groups gradually decreases. Near the end of the process, the amount of phenolic groups becomes smaller than the amount of added base. From this point on, the coordinated, reduced dioxygen, formed from the reoxidation of the copper catalyst, as shown in Scheme 1, needs an alternative, additional source to abstract protons from. The only other sources of protons are the methanol co-solvent and the water formed during the reaction, which have pK_a values of 15.2 and 14.2 at 20°C, respectively [36,37]. Deprotonation of these species will result in the formation of methoxide and/or hydroxide anions. However, an increase in the amount of hydroxide or methoxide will inhibit the reaction, as gradually more inactive copper hydroxide or methoxide species will be formed.

So, when the reaction is nearing completion, the oxidative coupling of phenol(ates) becomes increasingly difficult because of increasing inhibition of the copper catalyst. This effect is more pronounced at higher base/Cu ratios, explaining why the reaction takes longer to complete, and, hence, takes longer to form high-molecular weight PPE, at these higher ratios.

4.3. The order in copper

As stated in Section 1.2, a distinct effect of the N/Cu ratio was observed on the order in copper of the reaction. Fractional orders in copper were observed for all N/Cu ratios tested. These orders increase with increasing N/Cu ratios (see Table 1). The observation of fractional orders between 1 and 2, clearly indicates that the formation of a dinuclear copper complex must play a significant role in this reaction. Previously, these fractional orders have been explained by assuming that in this system two

competing rate-determining steps are operative [25], those steps being the formation of a dinuclear copper(II)-phenoxo species and the oxidation of the phenolate. However, a more reasonable explanation can be found in the analysis of the equilibrium between mono- and dinuclear copper species, while assuming that only a dinuclear copper species is catalytically active in this reaction, and mononuclear species are not active, at least not in the desired reaction. The equilibrium between mono- and dinuclear species can be written as (Eq. (3)):

$$(L)_3Cu^{II}(X^-) + (L)_3Cu^{II}(Y^-) \rightleftharpoons (L)_2$$
$$\times Cu^{II}(\mu - X^-)(\mu - Y^-)Cu^{II}(L)_2 + 2L \tag{3}$$
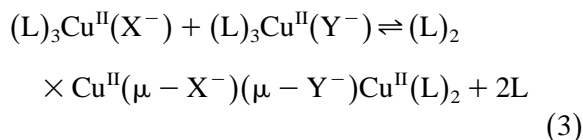
Where: $L = Nmiz$, X^-, $Y^- =$ phenolate, hydroxide, methoxide or the original anion (Cl^-, NO_3^-, etc.). The equilibrium constant K for this reaction is:

$$K = \frac{[Cu_2] \cdot [L]^2}{[Cu_1]_2} \tag{4a}$$

With: $[Cu_1] =$ concentration of mononuclear copper species, $[Cu_2] =$ concentration of dinuclear copper species. For constant $[L]$, Eq. (4a) reduces to:

$$K' = \frac{[Cu_2]}{[Cu_1]^2} = \frac{K}{[L]^2} \tag{4b}$$

This K' has a constant value for a given temperature and ligand concentration, and is not dependent on the initial concentration of (mononuclear) copper ($[Cu]_0$). The ratio of $[Cu_2]/[Cu_1]$ is, however, dependent on $[Cu]_0$, as follows from (Eq. (5)):

$$[Cu]_0 = [Cu_1] + 2[Cu_2] \tag{5}$$

Combination of Eqs. (4b) and (5) results in:

$$\frac{[Cu]_0 - [Cu_1]}{2} = [Cu_1]^2 \cdot K' \tag{6}$$

which rearranges into:

$$2[Cu_1]^2 \cdot K' + [Cu_1] - [Cu]_0 = 0 \tag{7}$$

This equation can be solved for $[Cu_1]$ according to (Eq. (8)):

$$[Cu_1] = \frac{-1 \pm \sqrt{8K'[Cu]_0 + 1}}{4K'} \tag{8}$$

This equation only affords rational solutions for the $-1 + \sqrt{\ldots}$ variant, because the discriminant is always larger than or equal to 1. Thus, the following dependencies of $[Cu_1]$ and $[Cu_2]$ on $[Cu]_0$ are obtained:

$$[Cu_1] = \frac{\sqrt{8K'[Cu]_0 + 1} - 1}{4K'} \tag{9a}$$

$$[Cu_2] = \frac{[Cu]_0}{2} - \frac{\sqrt{8K'[Cu]_0 + 1} - 1}{8K'} \tag{9b}$$

So, when the value of K' and the initial concentration of copper(II) ($[Cu]_0$) are known, the amounts of mono- and dinuclear species can be calculated. A reasonable estimate for K' was made from an EPR experiment, where reaction mixtures of catalyst and substrate/base were immersed in liquid dinitrogen shortly after mixing of the reactant solutions [25]. A rapid decrease in the amount of EPR-detectable, mononuclear copper(II) species till 40% of the initial amount was observed. This experiment was performed at an N/Cu ratio of 30, a base/Cu ratio of 1, and a $[Cu]_0$ of 5.0 mM. Assuming that this rapid decrease of the EPR signal is solely caused by the formation of an EPR-silent, dinuclear copper complex, then it follows that: $[Cu_1] \approx 2.0$ mM and $[Cu_2] \approx 1.5$ mM, and thus $K' = 375$ M^{-1}. This value for K' was used to calculate values for $[Cu_2]$ with Eq. (9b), using the same values for $[Cu]_0$ as in the original dioxygen uptake experiments [25]. The outcome of these calculations is listed in Table 3.

Assuming that the reaction rate of the oxidative phenol coupling reaction is proportional to

Table 3

Theoretical concentrations of dinuclear copper species calculated from the initial concentrations of copper and Eq. (9b) for $K' = 375$ M^{-1}

$[Cu]_0$ (mM)	$[Cu_2]$ (mM)
0.3333	0.02858
0.6667	0.08933
1.000	0.1667
1.667	0.3503
2.667	0.6667
3.333	0.8943

Table 4

Calculated values for the order in copper of the oxidative coupling reaction as a function of K', based on Eq. (9b) and Table 3.

K' (M^{-1})	Order in Cu (calc.)
1	2.00
100	1.72
375	1.49
1000	1.33
10000	1.11

the concentration of dinuclear copper(II) species, a theoretical order in copper of the reaction can be determined by plotting the logarithm of $[Cu_2]$ vs. the logarithm of $[Cu]_0$, as shown in Fig. 6. A straight line is obtained, from the slope of which a theoretical order in copper of 1.49 was derived. So, a fractional order is theoretically predicted, just as experimentally found.

The dependence of the experimentally found reaction orders on the N/Cu ratio can now also be explained. The actual equilibrium constant, K, will be unaffected by a change in the concentration of the ligand. However, it is clear from Eq. (4b) that an increase in the ligand concentration will result in a lower value for K', i.e., equilibrium (Eq. (3)) is shifted to the left (mononuclear) side. A different value for K' results in a different theoretical order in copper of the reaction, as is shown in Table 4. The same range of initial copper concentrations as
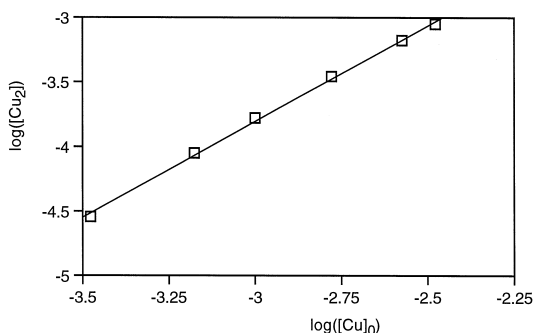
taken in Table 3, is used in the calculation of these orders.

So, at lower values for K', which are observed at higher N/Cu ratios, higher theoretical orders in copper are found; [2] this agrees very nicely with the experimental findings listed in Table 1. It is noted that, although the formation of a dinuclear intermediate is obviously hindered by an increase in the N/Cu ratio, the rate of the reaction (and the selectivity for PPE) increases upon increasing the N/Cu ratio, which is expressed in the higher values for the rate constant k obtained at these higher ratios (see Table 1). It is clear that besides hampering the formation of the active species, the excess ligand must have some other, beneficial, influence on the reaction, as has been detailed in a previous paper [25].

It can be concluded that the rate-determining step is most probably the phenol oxidation step, which in previous studies has already been proposed as the sole rate-determining step [9,15]. The order in copper observed for this reaction is controlled by the position of the equilibrium between mono- and dinuclear copper species. These results and the above analysis provide further evidence that the key catalytic intermediate in this reaction is indeed a dinuclear copper complex.

Fig. 6. Calculated values of $\log([Cu_2])$ vs. $\log([Cu]_0)$ for $K' = 375$ M^{-1}. The line represents the linear least-squares fit of the datapoints.

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[2] Apart from the N/Cu ratio, the theoretical order in copper is also dependent on the range of initial copper concentrations chosen. If for example a concentration range between 1–10 mM is chosen with a K' of 375 M^{-1}, a theoretical order in copper of 1.31 is calculated.

5. Conclusions

The results of kinetic measurements, in which the initial amount of DMP was varied, have been described with a simple Michaelis–Menten kinetic scheme. It has been observed that the amount of DPQ formed is linearly proportional to the initial amount of DMP, showing that regardless of the starting amount of DMP, a constant fraction is always converted into DPQ. No significant differences were observed with experiments in which copper(II) chloride [29] was used instead of copper(II) nitrate. So, the original anion does not appear to have a serious impact on the reaction mechanism, which clearly indicates that a phenolate ion is actually coordinated to the active copper catalyst.

Although initial reaction rates were found to be higher at higher base/Cu ratios, the reaction takes longer to complete, because the higher amount of base present hampers the reaction in the final stages by inhibition of the copper catalyst through formation of inactive copper hydroxide species.

It has been shown that the phenol oxidation step is most likely the rate-determining step, and that the fractional order in copper is linked to the position of the equilibrium between mononuclear and dinuclear copper species, the latter one being the active catalyst. So, it has been demonstrated unequivocally that a dinuclear copper species is the key intermediate in the oxidative coupling reaction.

Acknowledgements

References

[1] A.S. Hay, H.S. Stafford, G.F. Endres, J.W. Eustance, J. Am. Chem. Soc. 81 (1959) 6335.
[2] D. Aycock, V. Abolins, D.M. White, in: H.F. Mark (Ed.), Encycl. Polym. Eng. Sci., Vol. 13, Wiley, New York, 1988, p. 1.
[3] F.J. Viersen, PhD Thesis, Groningen University, 1988.
[4] A.S. Hay, P. Shenian, A.C. Gowan, P.F. Erhardt, W.R. Haaf, J.E. Theberge, in: N.M. Bikales (Ed.), Encyclopedia of Polymer Science and Technology, Vol. 10, Wiley, New York, 1969, p. 92.
[5] P.D. McDonald, G.A. Hamilton, in: W.S. Trahanovsky (Ed.), Oxidation in Organic Chemistry, Vol. 5B, Academic Press, New York, 1973, p. 97.
[6] G. Coudurier, H. Praliaud, M.V. Mathie, Spectrochim. Acta A 30 (1974) 1399.
[7] H. Praliaud, Y. Kodratoff, G. Coudurier, M.V. Mathieu, Spectrochim. Acta A 30 (1974) 1389.
[8] H.L. Finkbeiner, A.S. Hay, D.M. White, in: C.E. Schildknecht (Ed.), Polymerization Processes, Vol. XXIV, Wiley, New York, 1977, p. 537.
[9] W. Chen, PhD Thesis, Groningen University, 1991.
[10] C.E. Koning, F.J. Viersen, G. Challa, J. Reedijk, J. Mol. Catal. 44 (1988) 245.
[11] J. Kresta, A. Tkác, R. Prikryl, L. Malik, Makromol. Chem. 176 (1975) 157.
[12] E. Tsuchida, M. Kaneko, H. Nishide, Makromol. Chem. 151 (1972) 221.
[13] E. Tsuchida, H. Nishide, H. Nishikawa, J. Polym. Sci. 47 (1974) 47.
[14] M.A. El-Sayed, A. Abu-Raqabah, G. Davies, A. El-Toukhy, Inorg. Chem. 28 (1989) 1909.
[15] F.J. Viersen, G. Challa, J. Reedijk, Polymer 31 (1990) 1368.
[16] E.P. Talsi, N.I. Shaikhutdinova, A.A. Shibin, V.D. Chinakov, B.M. Khlebnikov, B.I. Yudkin, V.M. Nekipelov, K.I. Zamaraev, J. Mol. Catal. 57 (1990) 325.
[17] K.-T. Li, J. Appl. Polym. Sci. 54 (1994) 1339.
[18] A.S. Hay, J. Polym. Sci. 58 (1962) 581.
[19] K. Auwers, T. Markovits, Chem. Ber. 38 (1905) 226.
[20] C.G. Haynes, A.H. Turner, W.A. Waters, J. Chem. Soc. (1956) 2823.
[21] E. McNelis, J. Org. Chem. 31 (1966) 1255.
[22] B.O. Lindgren, Acta Chem. Scand. 14 (1960) 1203.
[23] S.L. Cosgrove, W.A. Waters, J. Chem. Soc. (1951) 388.
[24] J. Kresta, A. Tkác, R. Prikryl, L. Malik, J. Elastoplast. 5 (1973) 20.
[25] P.J. Baesjou, W.L. Driessen, G. Challa, J. Reedijk, J. Mol. Catal. A 110 (1996) 195.
[26] H. Nishide, T. Minakata, E. Tsuchida, Makromol. Chem. 183 (1982) 1889.
[27] A.H.J. Tullemans, E. Bouwman, R.A.G. de Graaff, W.L. Driessen, J. Reedijk, Recl. Trav. Chim. Pays-Bas 109 (1990) 70.

[28] F.J. Viersen, G. Challa, J. Reedijk, Polymer 31 (1990) 1361.

[29] W. Chen, G. Challa, Eur. Polym. J. 26 (1990) 1211.

[30] P.J. Baesjou, PhD Thesis, Leiden University, 1997.

[31] L. Michaelis, M.L. Menten, Biochem. Z. 49 (1913) 333.

[32] L.I. Simándi, Catalytic Activation of Dioxygen by Metal Complexes (Catalysis by Metal Complexes, Vol. 13), Kluwer Academic Publishers, Dordrecht, 1992, p. 396.

[33] D.M. White, S.A. Nye, Macromolecules 23 (1990) 1318.

[34] D.M. Mobley, J. Polym. Sci. Polym. Chem. 22 (1984) 3203.

[35] G.F. Endres, J. Kwiatek, J. Polym. Sci. 58 (1962) 593.

[36] J. March, Advanced Organic Chemistry, 3rd edn., Wiley, New York, 1985, p. 1346.

[37] R.C. Weast, M.J. Astle (Eds.), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 1981.

[38] P.J. Baesjou, W.L. Driessen, G. Challa, J. Reedijk, J. Am. Chem. Soc. 119 (1997) 18590.