Mechanistic studies of the oxidative coupling polymerization of 2,6-dimethylphenol: 1. Kinetics of polymerization catalysed by a copper(II)–tmed complex*

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A kinetic study of the oxidative coupling polymerization of 2,6-dimethylphenol, catalysed by Cu(II)–tmed§ complexes, is described. The species detected in solution, before the reaction, appeared to be a dinuclear chloro-bridged complex containing one bidentate tmed ligand per copper(II) ion. Kinetic experiments in combination with vis spectra suggest that at least a fivefold excess of tmed is needed to obtain a maximum amount of the highly active catalyst. The rate of oxidative coupling is significantly enhanced by the addition of OH$^-$, resulting in a maximum rate at an OH/Cu ratio of ≈ 1. The role of hydroxide was determined to be that of a 'co-catalyst', required for the formation of 2,6-dimethylphenolate anions, allowing these to substitute the chloro-bridges in the dinuclear precursor complex. Under all the experimental conditions used the reaction rates were independent of the dioxygen concentration. A first-order rate dependence on catalyst concentration was found. When varying the 2,6-dimethylphenol (DMP) concentration, Michaelis–Menten behaviour was observed.

(Keywords: oxidative coupling; reaction order; induction time; Michaelis–Menten kinetics; polyphenylene oxide)

INTRODUCTION

Synthesis of aromatic ethers, using metallic copper as a catalyst, was discovered in 1904 by Ullman[1]. Metallic copper strongly facilitated the substitution of a halogen atom in an aromatic ring by a phenolic residue. Since 1904 many aromatic ethers have been prepared using, besides metallic copper, copper salts such as $CuCl_2$, CuCl, CuBr, $CuSO_4$ and Cu_2O (Reference 2). This method has become known as Ullmann condensation. It has been applied in attempts to synthesize poly-(phenylene oxide), starting from 4-bromo- (or 4-chloro-) substituted phenols. However, high catalyst concentrations (due to catalyst contamination by the halide acid eliminated from the phenol) and high reaction temperatures (required for the halogen displacement) generally resulted in low molar mass polymer and considerable amounts of by-products[3–7].

Polymerization of 4-bromo-substituted phenols by oxidizing catalysts in the presence of dioxygen, using two-phase solvent systems, resulted in high molar mass polymer at a very high reaction rate under mild conditions[8,9]. In these systems low catalyst concentrations could be used since the halides eliminated from the phenol were dissolved in the water layer. Copper–amine complexes were found to polymerize 4-halo-2,6-disubstituted phenols in the presence of dioxygen, though they required no less than stoichiometric quantities of the copper catalyst[10,11]. Again, catalyst contamination by the large amount of eliminated halide acid was the main problem.

The reaction of 2,6-dimethylphenol (DMP) in benzene using oxidants like $K_3Fe(CN)_6$[12,13], activated silver oxide[13,14] and manganese dioxide[14] yields poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of low molar mass and a considerable amount of the by-product diphenoquinone (DPQ)*.

However, in 1959 Hay described the use of catalytic amounts of a copper–pyridine complex in the presence of dioxygen for the polymerization of 2,6-disubstituted phenols[15]. Under mild reaction conditions (room temperature, for $<\frac{1}{2}$ h) poly(phenylene oxide) was formed in high yield and of high molar mass. By using 2,6-dimethylphenol the engineering plastic PPO results[16]. Because of its excellent properties and good weathering resistance, its synthesis and the mechanism of oxidative coupling have been extensively studied[16–27].
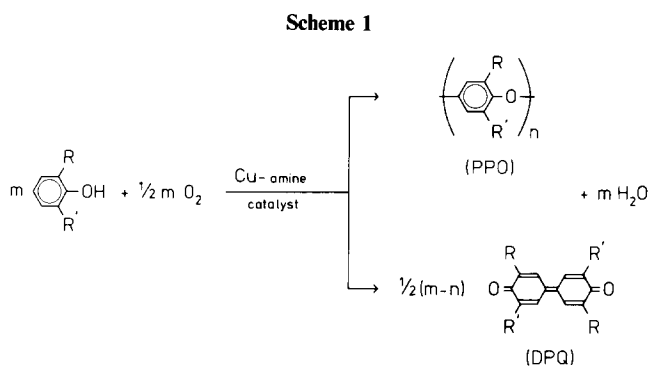
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* 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-2,6-dimethyl-2,5-cyclohexadiene-1-one

Scheme 1

As shown in *Scheme 1*, the synthesis of PPO (C–O coupling) is always accompanied by the formation of DPQ (C–C coupling). The highly conjugated structure of the diphenoquinone means that it has an intense (red) colour.

The most important factor determining the relative amount of diphenoquinone formed appears to be the size of the substituents on the 2 and 6 positions of the aromatic ring. Increasing the size of these substituents will, for steric reasons, subsequently give rise to increasing amounts of C–C coupling product[11,15,17].

Electron-withdrawing substituents also affect the reaction rate due to the increasing oxidation potentials of phenols[17]. With 2-chloro- or 2,6-dichloro-substituted phenols, highly branched polymers with inferior physical properties are formed[11]. No reaction appears to occur with 2,6-dinitrophenol[11].

In Challa's research group copper catalysed oxidative coupling has been studied using a variety of polymer-bound copper complexes[28–31]. In the present paper N,N,N',N'-tetramethylethylenediamine (tmed) is selected as a model amine in the copper–amine catalysed oxidative coupling polymerization of 2,6-dimethylphenol. It is known that bidentate amines, such as tmed, are very good ligands for the catalyst[16,32–34]. Moreover, data on crystal structures of chloro-bridged[35] and hydroxo-bridged[34] dinuclear copper(II)–tmed complexes are already known.

EXPERIMENTAL

Materials

$CuCl_2 \cdot 2H_2O$ was obtained analytically pure from Merck. The exact copper concentration of this salt was determined by ethylenediamine tetraacetic acid (e.d.t.a.) titration. Methanol was of Uvasol quality from Merck. 1,2-Dichlorobenzene (Merck) was distilled under reduced nitrogen pressure from CaH_2. 2,6-Dimethylphenol (DMP) was from Aldrich and was purified by repeated recrystallizations from n-hexane. Purity was checked by ultraviolet analysis and showed less than 5×10^{-4} wt% of diphenoquinone (DPQ). N,N,N',N'-tetramethylethylenediamine (tmed) from Aldrich was distilled from KOH under reduced nitrogen atmosphere. KOH and LiOH (Merck) were used without purification.

Sodium 2,6-dimethylphenolate was prepared by the reaction of sodium with DMP in 1,2-dichlorobenzene under nitrogen atmosphere. After filtration the light green solid was dissolved in methanol. The 2,6-dimethyl-phenolate concentration was determined by titration with 0.1 N HCl using phenolphthalein as indicator in a solvent mixture of water–methanol.

Oxidative coupling: general procedure

The catalyst was prepared by dissolving tmed in 1,2-dichlorobenzene. To this solution a methanolic solution of $CuCl_2 \cdot 2H_2O$ was added. The base was added as a methanolic solution of KOH or LiOH. The solutions of catalyst and of DMP were saturated with dioxygen before addition to the cylindrical reaction vessel. The reaction vessel was connected with an automated gas burette containing pure dioxygen[28]. As our batch-type reaction vessel contained one or two partitions separating the reactor into, respectively, two or three sections, the reactant and catalyst components could be added to separate sections, allowing the dioxygen pressure and the reaction temperature to be adjusted to the desired values. A constant reaction temperature was further assured by using a thermostated bath. Upon starting the shaking machine the catalyst and DMP solutions from the different sections were mixed, yielding homogeneous conditions within 5 s. The dioxygen consumption was recorded at constant pressure as a function of reaction time. The initial reaction rate, R_0, was calculated from the initial slope of this dioxygen consumption curve. *Figure 1* shows a schematic curve.

Oxidative coupling: reaction conditions

The following standard reaction conditions were used: $T = 298.2 \pm 0.1$ K, $[CuCl_2] = 3.32 \times 10^{-3}$ mol dm^{-3}, $[DMP] = 0.06$ mol dm^{-3}, total reaction volume = 0.015 dm^3, solvent mixture 1,2-dichlorobenzene/methanol = 13/2 (v/v). The dioxygen pressure could be varied between 50 and 165 kPa. The shaking speed of the reaction vessel of 15–20 Hz proved to be high enough to prevent diffusion limitation of dioxygen into the reaction medium. Since oxidation rates are to be determined instead of reoxidation or diffusion, experiments were generally carried out in duplicate under at least two different dioxygen pressures. The reaction rates shown further are independent of dioxygen pressure. In *Figure 2* an example is given of the dependence of initial reaction rate on applied dioxygen pressure. In this example dioxygen pressures exceeding 115 kPa were sufficient to make sure that oxidation rates were measured.

RESULTS AND DISCUSSION

Effect of ligand/copper ratio

In *Figure 3* the dioxygen consumption rate is shown *versus* the N/Cu ratio. In the absence of mineral base
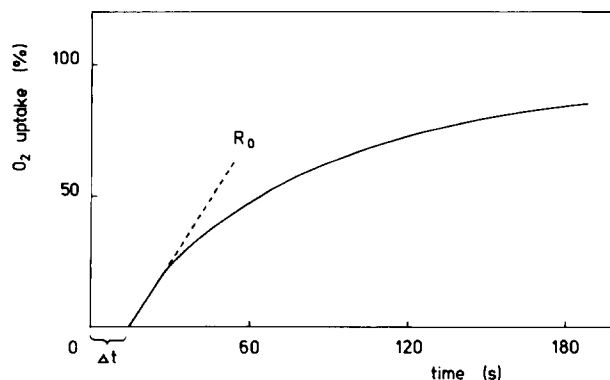

Figure 1 Schematic dioxygen consumption curve *versus* reaction time under standard conditions (see text; 100% uptake of dioxygen is usually reached after 45–60 min)
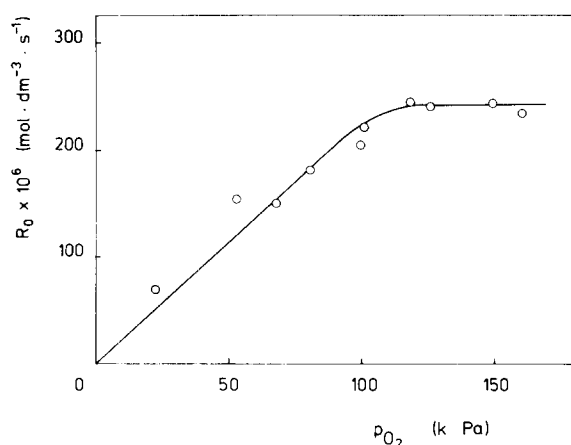
Figure 2 Initial dioxygen consumption rate in the oxidative coupling polymerization of DMP *versus* applied dioxygen pressure for standard conditions with $N/Cu = 10$ and $OH/Cu = 1$
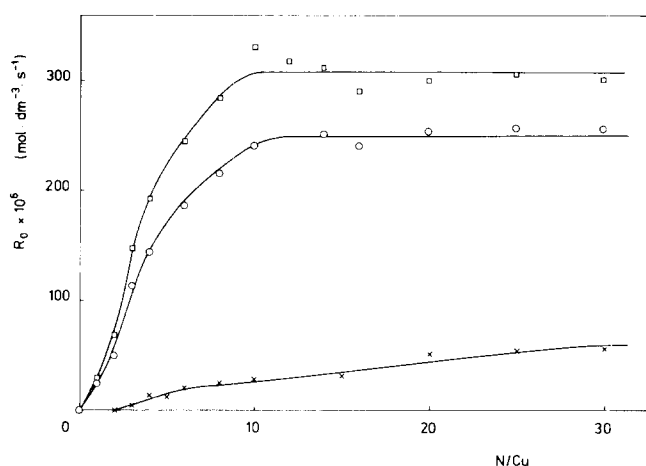

Figure 3 Effect of N/Cu ratio on initial dioxygen consumption rate for standard conditions: ×, $OH/Cu = 0$; ○, $OH/Cu = 1$; □, $OH/Cu = 1$, KOH added to DMP

the reaction rate continuously increases with N/Cu. In the presence of base $(OH/Cu = 1)$, a much higher activity is observed; however, above $N/Cu = 10$ the catalytic activity ceases to be affected. As is supported by spectroscopic results in another publication[36], the increase in reaction rate up to an N/Cu ratio of 10 is the result of a gradual change in the composition of copper complexes in solution. A fivefold excess of tmed $(N/Cu = 10)$ is required to obtain the maximum amount of the highly active Cu(II) complex.

The effect of hydroxide to copper ratio

The effect of changing the way of adding the hydroxide is also shown in *Figure 3*. The hydroxide was added either to the copper–tmed solution or to the solution of DMP. The latter method showed $\approx 20\%$ higher activity. If the base is added directly to the copper–tmed complex the reduction of activity is likely to be caused by strong-base-induced formation of an inactive copper complex, resulting in a smaller amount of active catalyst. If the hydroxide is added to the DMP solution, it will react with DMP to form 2,6-dimethylphenolate. This anion will then react with the copper complex, in agreement with the observations of Gampp and Zuber-bühler, who assumed that deprotonation of the substrate is a logical first step[37].

The effect of hydroxide concentration on the activity of the catalyst was investigated at different N/Cu ratios. Results are shown in *Figures 4* and *5* for N/Cu ratios of 4 and 30, respectively. Using LiOH, rather than KOH, had no effect on catalytic activity.

In *Figure 4*, at $N/Cu = 4$, for both methods of hydroxide addition a maximum activity is found at $OH/Cu = 1$. When a large excess of amine is used, as in *Figure 5*, and the hydroxide is added to the copper–amine solution, a maximum is found again at exactly

Figure 4 Initial dioxygen consumption rate *versus* OH/Cu ratio for $N/Cu = 4$ and standard conditions. KOH added to: ○, $CuCl_2$; □, DMP; ×, separately; ■, as sodium salt of DMP
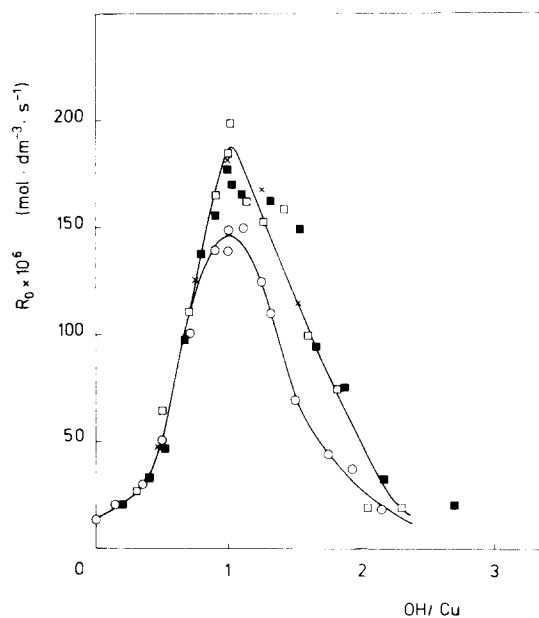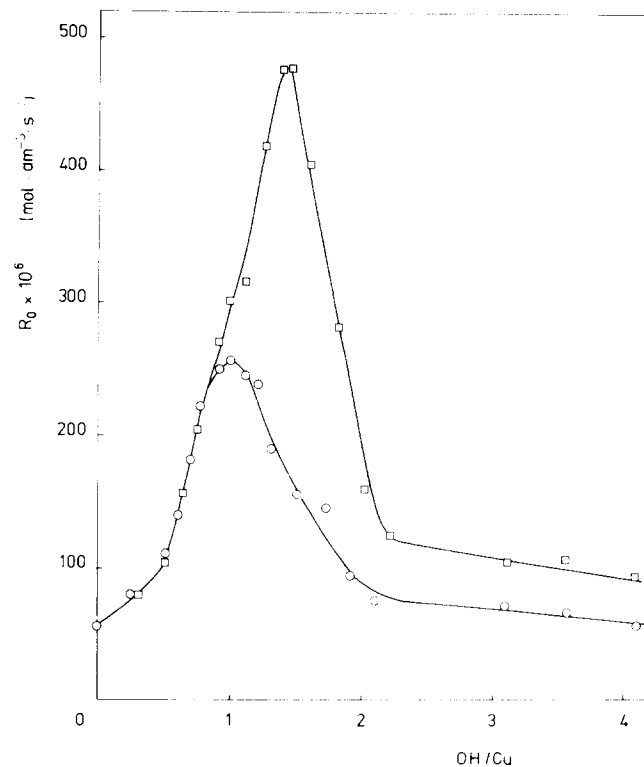

Figure 5 Initial dioxygen consumption rate *versus* OH/Cu ratio for $N/Cu = 30$ and standard conditions. KOH added to: ○, $CuCl_2$; □, DMP

OH/Cu = 1. Addition of the hydroxide to the DMP solution allows the use of a small excess of hydroxide to reach an extremely high dioxygen consumption rate, probably due to the stabilizing effect of the large amount of tmed on the catalyst.

Increasing OH/Cu from 0 to 0.5 yields, independent of N/Cu, only a moderate increase in reaction rate. A further increase to 1.0, however, strongly accelerates the reaction.

From the literature it is known that in the synthesis of hydroxy-bridged complexes side products can be formed, identified as $Cu_2(OH)_3Cl$ [38] and $Cu_2(OH)_3Br$ [39], depending on the copper salt used. Such complexes are likely to be present in any system of copper–amine complexes containing a strong base[40]. Low ligand/copper ratios yield even more of such unwanted copper complexes. The declining activities as the hydroxide/copper ratio is increased further above stoichiometric amounts is probably caused by conversion of active copper complexes into inactive ones. Elemental analyses of the precipitate formed upon the addition of hydroxide ($Cu = 24–31$, $Cl = 24$, $K = 26\%$; mole ratio $Cl/K = 1.02$) indicated no more chloride than expected for KCl. Therefore, $Cu_2(OH)_3Cl$ either is formed in only small quantities or remains soluble in the reaction medium. The precipitates found have a variable composition and consist mainly of a copper–hydroxide complex of polymeric nature.

The role of hydroxide

Since hydroxide apparently plays a very important role in the oxidative coupling polymerization of phenols its function was studied in more detail. Its role may be to convert the weakly coordinating phenol to a strongly coordinating phenolate anion[37]. In *Figure 4*, for N/Cu = 4, two curves are shown resulting from different ways of adding the hydroxide. If the hydroxide was only required to produce 2,6-dimethylphenolate anion, addition of its sodium salt should give exactly the same reaction rates. In such experiments the amount of DMP added was 'corrected' for the amount of 2,6-dimethylphenolate used ($[DMP] + [Na^+PhO^-] = 0.06$ M). *Figure 4* shows the reaction rates found, indicating that the base is used to produce phenolate anion.

In another series of experiments a reaction vessel consisting of three sections was used, allowing the reaction to start with separate solutions of copper–amine, DMP and hydroxide. In this way it was studied whether hydroxide, once present in the reaction mixture, will coordinate to copper or react with DMP to give phenolate anion. The measured reaction rates coincide with the rates found using 2,6-dimethylphenolate to start the reaction. This points to a mechanism wherein the initial catalyst is a chloro-bridged dinuclear complex and hydroxide is primarily needed for the formation of phenolate anion (see also References 37 and 41–44).

The induction period, Δt

The induction time, Δt, (see *Figure 1*) is defined as the time between mixing the solutions of DMP and catalyst and the moment the first dioxygen consumption is recorded. As the N/Cu ratio increases the induction time shortens from 55 to 15 s (for OH/Cu = 1). A similar result has been reported by others for related systems[45–47]. For N/Cu ratios $\gtrsim 6$ a further increase does not reduce the
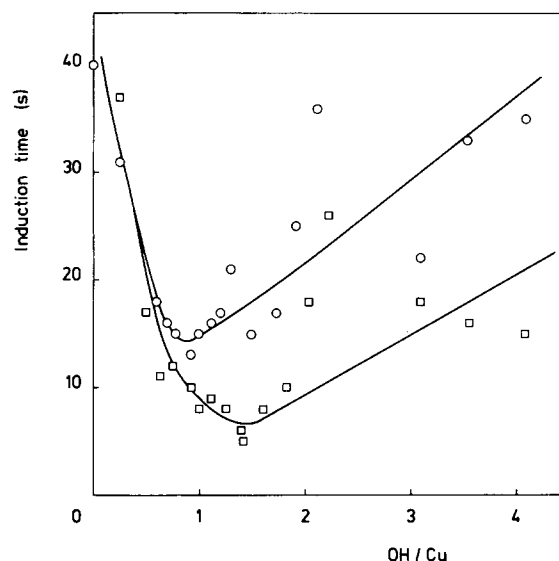

Figure 6 Induction time *versus* OH/Cu ratio for N/Cu = 30 and standard conditions. KOH added to: O, $CuCl_2$; □, DMP

induction time further. With such high ligand/copper ratios, addition of the hydroxide to the copper–amine solution gives $\Delta t = 15$ s, whereas starting the reaction with phenolate anions, i.e. adding OH^- to DMP, reduces the induction period to only 5 s.

A more complete picture of the difference between adding the hydroxide to copper–amine solution and to DMP solution is shown in *Figure 6* as a function of the ratio OH/Cu for N/Cu = 30. The shortest induction times are found at OH/Cu ≈ 1. For higher or lower ratios the induction time increases.

The observed shorter induction times when starting the reaction with phenolate anions confirm that free hydroxide is needed for the reaction with DMP to form 2,6-dimethylphenolate anion.

Reaction rate dependence on $[CuCl_2]$ and $[DMP]$ at $N/Cu = 10$

In *Figure 7* the reaction rate is shown as a function of the catalyst concentration. Under these conditions further addition of tmed did not affect the complex composition. The reaction shows first-order kinetics in catalyst concentration, indicating that all copper must be present as active dinuclear complex[36].

At low concentrations of catalyst the activity drops. Vis spectroscopy[36] shows that, when the copper(II) chloride concentration is $< 1 \times 10^{-3}$ mol dm^{-3}, a change in complex composition takes place as shown in *Figure 8*. A shift to lower wavenumber in this system suggests that dinuclear complexes are converted into other, probably mononuclear, species. A similar observation was made by Speier *et al.* using copper–pyridine complexes as catalysts for catalytic oxidations[48,49].

For catalyst concentrations of 1.5×10^{-3} and 3.32×10^{-3} mol dm^{-3} reaction rates were measured at different DMP concentrations. As shown in *Figure 9*, an apparent first-order rate dependence is only observed for very low DMP concentrations. At higher concentrations the reaction rate levels off. This behaviour is known as saturation kinetics, and is generally found in kinetics for reactions catalysed by enzymes[50].

Figure 7 Initial dioxygen consumption rate *versus* catalyst concentration for N/Cu = 10 and OH/Cu = 1 (KOH added to catalyst)

When deriving a Michaelis–Menten type kinetic scheme, it has to be taken into account that hydroxide is required for deprotonation of phenol. Hydroxide (or methoxide, CH_3O-) and DMP react to give phenolate anion and water[51], as shown below:

$$[OH^-] + [DMP] \to [PhO^-] + [H_2O] \qquad (1)$$

Dioxygen consumption plots show that after the induction time a constant reaction rate is achieved almost instantaneously; see *Figure 1*. Before the rate-determining step an equilibrium complex between DMP and copper catalyst is formed according to Michaelis–Menten kinetic behaviour. A schematic presentation of such a catalytic cycle is given in *Scheme 2*. A more detailed description, also considering other experimental results, will be given in a subsequent paper[52].

Coordination of a phenolate anion to the initial dinuclear copper complex is schematically given by (roman numerals refer to copper complexes in *Scheme 2*)

$$[I] + [PhO^-] \rightleftharpoons [II] + [Cl^-] \qquad (2)$$

The phenolate anion coordinates in the bridge of the copper(II) complex. Considering the Michaelis–Menten type kinetic behaviour, DMP coordinates are given by

$$[II] + [DMP] \rightleftharpoons [III]; \qquad K_{III} = \frac{[III]}{[II][DMP]} \qquad (3)$$

Figure 8 Absorption (●) and wavenumber (○) of absorption band *versus* copper(II) chloride concentration (relative absorption with respect to 0.382 for $[CuCl_2] = 3.32 \times 10^{-3}$ mol dm^{-3}) for N/Cu = 10 and OH/Cu = 1 (no DMP added)

Figure 9 Initial dioxygen consumption rate *versus* 2,6-dimethylphenol concentration for N/Cu = 10 and OH/Cu = 1 (KOH added to catalyst): ●, $[CuCl_2] = 1.5 \times 10^{-3}$ M; ○, $[CuCl_2] = 3.32 \times 10^{-3}$ M

Kinetic scheme and mechanism

If the results from *Figure 9* are arranged as R_0^{-1} *versus* $[DMP]^{-1}$ in a so-called Lineweaver–Burk plot, straight lines are found, intersecting the y-axis as shown in *Figure 10*. This means that a Michaelis–Menten type behaviour, as known from enzyme kinetics, indeed applies to this system.

Scheme 2

In the following rate-determining reaction step, a two-electron transfer takes place, yielding a dinuclear copper(I) complex, V, and oxidation products:

$$[III] \xrightarrow[-H^+]{k_{rd}} [V] + \text{products} \qquad R = k_{rd}[III] \qquad (4)$$

Reaction of V with O_2 is very rapid under the applied O_2 pressures:

$$[V] + [O_2] \xrightarrow{k_{reox}} [VI] \rightarrow [I] \qquad (5)$$

Coordination of PhO^- (2) has to be practically complete under these reaction conditions $(N/Cu = 10, OH/Cu = 1)$ and thus $[I] \approx 0$. This has already been indicated by the observed increase in rate dependence on hydroxide concentration around $OH/Cu = 0.5$, as discussed above. Assuming that all reaction steps after the rate determining step (4) are very fast, the total amount of dinuclear copper complexes is given by

$$[II] + [III] \approx \tfrac{1}{2}[CuCl_2]_0 \qquad (6)$$

Substitution of (6) into (3) gives:

$$[III] = \frac{K_{III}\tfrac{1}{2}[CuCl_2]_0[DMP]}{1 + K_{III}[DMP]} \qquad (7)$$

After substitution of [III], from (7) into (4) the following initial rate equation results:

$$R_0 = k_{rd}[III] = \frac{k_{rd}K_{III}\tfrac{1}{2}[CuCl_2]_0[DMP]_0}{1 + K_{III}[DMP]_0} \qquad (8)$$

or

$$\frac{1}{R_0} = \frac{1}{k_{rd}\tfrac{1}{2}[CuCl_2]_0} + \frac{1}{k_{rd}\tfrac{1}{2}[CuCl_2]_0 K_{III}[DMP]_0} \qquad (9)$$
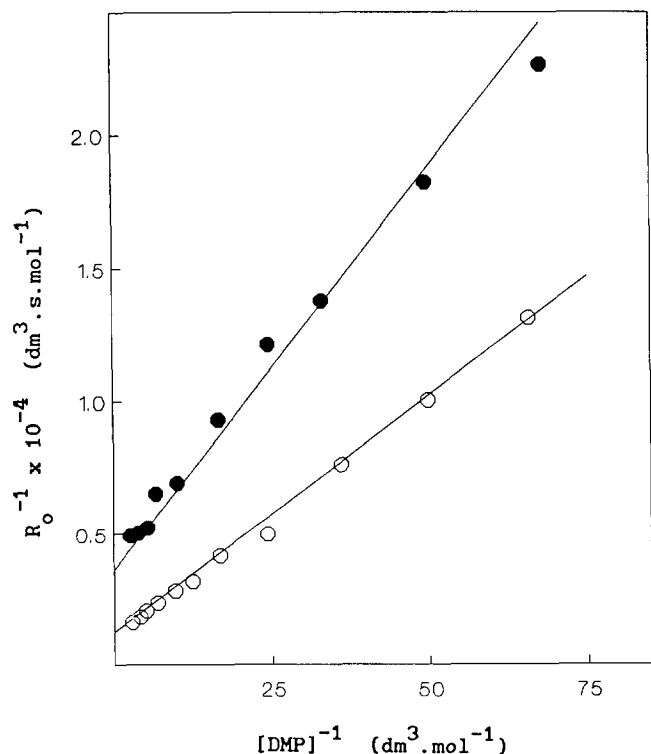
Michaelis–Menten type kinetics are depicted in *Figure*

Figure 10 Lineweaver–Burk plot of data from *Figure 9*: ●, $[CuCl_2] = 1.5 \times 10^{-3}$ M; ○, $[CuCl_2] = 3.32 \times 10^{-3}$ M

10. A straight line is found in the so-called Lineweaver–Burk plot of R_0^{-1} *versus* $[DMP]_0^{-1}$. If the equilibrium (2) were not shifted strongly to the right, this would result in an additional dependence of R_0^{-1} on $[DMP]_0^{-2}$, requiring an upward turn in the Lineweaver–Burk plot for low $[DMP]_0$, as was indicated by Meinders[28]. However, no such behaviour is observed, implying that $[I] \approx 0$. The first-order rate dependence on catalyst concentration, shown in *Figure 7*, is also in agreement with formula (8). This kinetic analysis together with spectroscopic results in other papers[38,53] will allow us to propose a reaction mechanism in a subsequent paper[52].

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