A kinetic and spectroscopic study on the copper catalyzed oxidative coupling polymerization of 2,6-dimethylphenol. X-ray structure of the catalyst precursor tetrakis(N-methylimidazole) bis(nitrato) copper(II)

Patrick J. Baesjou [a], Willem L. Driessen [a], Ger Challa [b], Jan Reedijk [a,*]

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, Netherlands
[b] Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

Abstract

The complex of copper(II) nitrate with N-methylimidazole (Nmiz) ligand has been studied as a catalyst for the oxidative coupling of 2,6-dimethylphenol by means of kinetic and spectroscopic measurements. The order of the reaction in copper is fractional and depends on the N/Cu ratio and the base/Cu ratio, indicating that there are at least two possible rate-determining steps, i.e. the formation of a dinuclear copper species and the phenol oxidation. EPR spectroscopy performed on frozen solutions with varying ligand to copper ratios shows that all Cu(II) is converted into the precursor complex at a ratio of 4 to 1, whereas in kinetic experiments, maximum activity and selectivity are reached only at a ratio of at least 30 to 1. Base is needed as a co-catalyst, and the maximum reaction rate is reached at a base to copper ratio of 1.8 to 1. The solid-state X-ray structure of the catalyst precursor complex has been determined to be [Cu(Nmiz)$_4$(NO$_3$)$_2$], monoclinic, space group $P2_1/n$, $a = 8.452(1)$ Å, $b = 10.376(2)$Å, $c = 12.821(2)$ Å, $\beta = 94.88(2)°$, $Z = 1$, $R = 0.049$ for 3525 reflections. This structure consists of an axially elongated octahedral CuN$_4$O$_2$ chromophore, which is in agreement with frozen-solution EPR spectra. Investigations under conditions where water and dioxygen were carefully excluded, have shown that for the phenol oxidation step the presence of dioxygen is not required. However, the reaction does require a trace of water (or hydroxide) to form the reactive intermediate. A modified reaction mechanism for the oxidative coupling is presented with special attention to the first steps of the reaction and the equilibrium species present in solution. The role of dioxygen appears to be only to reoxidize the formed Cu(I) species and to regenerate base.

Keywords: Reaction mechanism; Kinetics; Dioxygen uptake; Phenol; Oxidation; Copper; Imidazole derivatives

1. Introduction

In 1959 Hay and co-workers discovered that a copper(I)–pyridine complex in the presence of dioxygen was able to catalyze the oxidative coupling polymerization of 2,6-dimethylphenol (DMP), as shown schematically in Fig. 1 [1]. Since then a number of copper compounds with nitrogen-donor ligands have been investigated and proven to be successful as a catalyst in this system [2–11]. This reaction occurs under ambient conditions (room temperature and atmospheric dioxygen pressure) and yields straight-
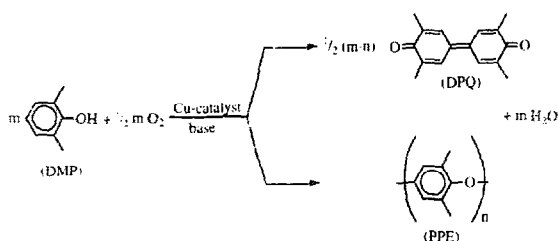
* Corresponding author.

Fig. 1. Overall reaction scheme for the oxidative coupling of DMP to PPE and DPQ.

chain polyphenylene ether (PPE) by C–O coupling of DMP in high yield and of high molecular mass. The non-catalyzed reaction takes place only at 300°C and yields a crosslinked polymer with inferior mechanical properties.

Polyphenylene ether is an important engineering plastic, because of its outstanding mechanical properties at elevated temperatures and its good weathering resistance. It has for instance applications in filter stacks, filter discs, valve seats, hot water tanks, automotive fixtures and computer housings [12,13]. It is sold by General Electric blended with polystyrene under the name Noryl™.

The other main product of the reaction, resulting from C–C coupling of two phenols, is an intensely coloured diphenoquinone (DPQ [1]). The formation of DPQ not only decreases the yield of polymer, but also degrades the polymer upon further processing at high temperatures. Therefore extensive, and thus expensive, purification is often needed. It is therefore important to suppress the formation of this side product as much as possible [14].

The selectivity of the reaction (i.e. PPE vs. DPQ formation) is governed by a number of factors, the most important one being the presence and size of the phenol *ortho* substituents. When no (or only one) substituent is present, a complex mixture of worthless branched products will result. Small *ortho* substituents favour polymer formation, whereas large ones will lead

to formation of diphenoquinones [1,12,15]. Therefore 2,6-dimethylphenol is the most commonly used substrate. Another factor is the nature of the amine ligands coordinated to the copper catalyst. Small and strongly basic ligands favour polymer formation [8,16]. Temperature and solvent polarity also influence the ratio of C–C to C–O coupling. An increase in either of these reaction parameters will result in more diphenoquinone [14].

Because of the importance of the PPE as an engineering plastic, many aspects of the reaction and its mechanism have been studied in detail [4,12,17–28]. However, so far the exact mechanism is not yet clear. Historically, the reaction mechanism was thought to employ mononuclear copper–phenoxo complexes affording phenoxy radicals as the key species. Other, more recent proposals [14,21,23,29] are more inclined towards a two-electron transfer mechanism, with formation of phenoxonium cations as intermediates. The most recent proposals by Challa and co-workers [14,21], as shown schematically in Fig. 2, involve the formation of a dinuclear phenolate-bridged copper(II) complex, after initial deprotonation of the phenol by the base that is used as co-catalyst.

This dinuclear phenolato-bridged complex will then undergo, in what is believed to be the rate-limiting step, two one-electron transfers from one bridging phenolate to the copper ions, resulting in a, possibly, dinuclear copper(I) species and a phenoxonium cation. This cation may then react with a (possibly coordinated) phenol, which will result in C–O coupling. This will afford the dimeric phenol (after deprotonation and tautomerization). After reoxidation of the copper(I) species by dioxygen the dimer phenol can react further and will ultimately afford the polymer. The reduced dioxygen will eventually form water. Hence, the reaction is more accurately called a dehydrogenation than an oxidation as no dioxygen is incorporated into the products. Also possible is the C–C coupling of a phenoxonium cation and a phenol, resulting

[1] Systematic name: 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone.

L Cu^{II} L / L / L ——— [PhO-H-OPh]⁻ ———→ L Cu^{II} L / L / L ,,,H-OPh / ⁻OPh ——————→

L Cu^{II} / Cu^{II} L with Ph–O bridge, O, HOPh, Ph ——— rate-limiting ———→ L Cu^{I} / Cu^{I} L, Ph–O, ⁺O, HOPh, Ph ——— (– 2H⁺) ———→

L Cu^{I} / Cu^{I} L, Ph–O, O, PhOPh ——— + O₂ / + PhOH ———→ L Cu^{II} / Cu^{II} L, Ph–O, PhOH, O, PhOPh + H₂O ——→ ——→ PPE
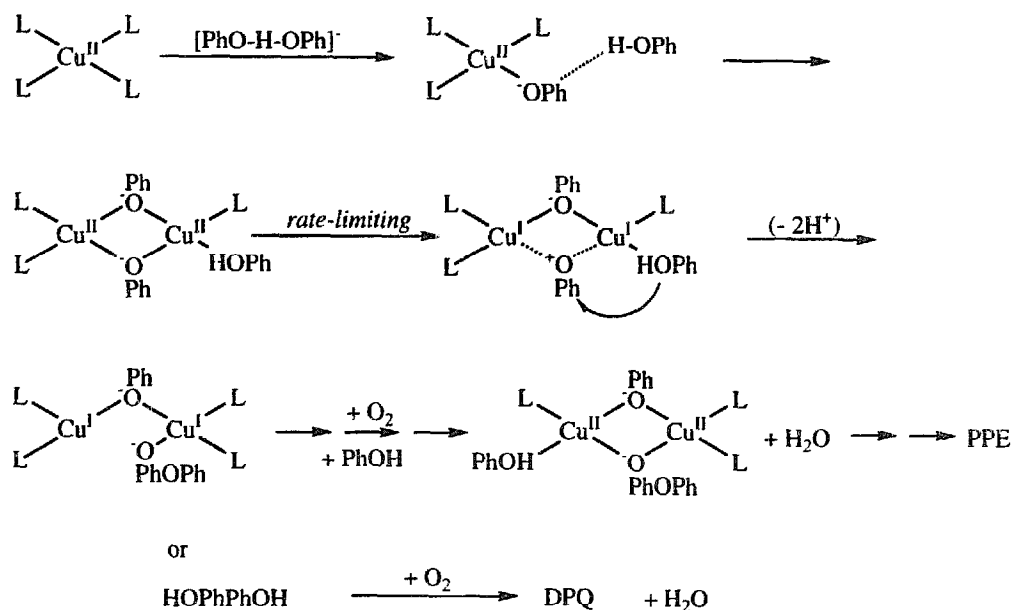
or

HOPhPhOH ——— + O₂ ———→ DPQ + H₂O

Fig. 2. Schematic catalytic cycle for the oxidative coupling of DMP [14,21].

in the formation of a bisphenol that will be oxidized to afford DPQ.

The fact that the mechanism of formation of this important polymer is still not elucidated satisfactorily is the main origin for an ongoing study to the understanding of the first steps in this reaction. Furthermore, the catalytic system bears some resemblance to the mechanism of action of copper proteins with a type 3 active site, e.g. tyrosinase, which also justifies a detailed mechanistic study. The ultimate goal is, of course, to obtain a detailed understanding of the reaction mechanism, with respect to the copper geometry, possible formation of clusters, structures of intermediates and the mode of action of the actual phenol coupling step. Therefore, insight is required into the following subjects: (i) the role of the amine ligand; (ii) the role of the base co-catalyst; (iii) a possible additional role of dioxygen, apart from reoxidizing copper(I) [30]; (iv) the nature and structure of the copper intermediate species.

In order to achieve these goals, kinetic (quantitative dioxygen uptake), spectroscopic (EPR, UV/Vis/NIR) and X-ray measurements have been performed. N-methylimidazole (Nmiz) has been chosen as a model ligand,

because it forms very active and rather selective catalysts [2] and for its resemblance to biological systems where the copper atoms are commonly surrounded by histidine amino acids, which contain imidazole residues. As a copper salt copper(II) nitrate was used, to prevent interference from a strongly coordinating anion. The first important results of these experiments are presented in this paper, including a molecular structure determination for the copper(II)–N-methylimidazole catalyst precursor.

2. Experimental

2.1. General

Solvents (toluene, methanol and diethyl ether) were obtained from Baker as analytically pure grades. THF was obtained from Janssen as chemically pure grade. Methanol was dried on molecular sieves (3 Å) prior to use, toluene was used as received. Diethyl ether and THF were distilled from sodium sand under a dinitrogen atmosphere. $Cu(NO_3)_2 \cdot 3H_2O$ (analytically pure) was obtained from Merck and was used without further treatment. $CuCl_2 \cdot 2H_2O$ (ana-

lytically pure) was also obtained from Merck, and was dehydrated by heating it under reduced dinitrogen pressure. 2,6-dimethylphenol (technical grade) was purchased from Baker and was purified by repeated crystallization from n-hexane prior to use. N-Methylimidazole (99% pure) was used as obtained from Janssen. Sodium methoxide ($NaOCH_3$) was synthesized by treating methanol (vide supra) 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 (vide infra) were performed using apparatus designed in-house, described in detail in an earlier publication [9]. Experiments conducted under a dry dinitrogen atmosphere were performed using standard Schlenk techniques. EPR spectra were recorded on a JEOL JES-RE2X ESR spectrometer (X-band) equipped with a JEOL Esprit 330 ESR data system. UV/Vis/NIR spectroscopy was performed using a Perkin Elmer 330 double beam spectrophotometer or a Camspec M302 single beam spectrophotometer.

2.2. Catalyst and substrate solutions

A typical catalyst solution was prepared by mixing, in a 10 ml volumetric flask, 2 ml of a 0.05 M $Cu(NO_3)_2 \cdot 3H_2O$ solution in methanol, the appropriate amount of a 0.5 M Nmiz solution in toluene, and filling it up to 10 ml with toluene, which resulted in a 0.01 M $Cu(Nmiz)_x(NO_3)_2$ solution in toluene/methanol (4/1 v/v).

The substrate solution was prepared by mixing, in a 25 ml volumetric flask, 10 ml of a 0.75 M DMP solution in toluene/methanol (13/2 v/v), the calculated amount of a 0.125 M $NaOCH_3$ solution in methanol as a co-catalyst, and filling it up with toluene/methanol (13/2), which resulted in a 0.3 M DMP/DMPO⁻ solution in toluene/methanol (about 5/1 v/v).

The solvent composition varies slightly as the amount of methanol in the solution is dependent on the amount of base used. However, the effect on the rate and the selectivity of the reaction due to this variation in solvent composition was found to be negligible.

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 a catalyst solution, and the other with 10 ml of a substrate/base solution. Thus, the resulting reaction mixture was 0.00333 molar in copper and 0.20 molar in DMP, hence the DMP to copper ratio was 60 to 1 for all kinetic measurements. The reaction vessel was connected to a shaking device and placed in a thermostated bath of 298 K. After flushing the entire system with dioxygen the measurement was started by turning on the shaking device and after a 30 s period for equilibration reliable measurements were obtained. The shaking frequency is ca. 15–20 Hz, which not only ensures thorough, immediate mixing of the reactants, but also prevents dioxygen diffusion limitation. During mixing, dioxygen is being consumed by the reaction system. The decrease in pressure in the system is equalized by pushing water into a gas burette filled with dioxygen, thereby pushing dioxygen into the reaction vessel. The rise of the water level in the burette, which is proportional to the amount of dioxygen consumed by the reaction system, is optically monitored and directly recorded by a computer as a function of time. From the resulting dioxygen uptake curve, the initial dioxygen uptake rate can be derived, as it is proportional to the initial slope of the dioxygen uptake curve, as given in Eq. (1):

$$R_0 = (\Delta pO_2')/(M_w V_r) \qquad (1)$$

where

R_0 = initial dioxygen uptake rate (mol/l · s)
Δ = maximum (initial) slope (l O_2/s)
M_w = molecular weight dioxygen (= 32 g/mol)

V_r = reaction volume (typically 15 ml)

$\rho O_2'$ = dioxygen density (g/l) at $t°C$, according to Eq. (2):

$$\rho O_2' = (\rho O_2^0 p)/(760\{1 + \alpha t\}) \qquad (2)$$

with

ρO_2^0 = dioxygen density at 0°C (= 1.429 g/l)

α = temperature factor (= 0.00367 K^{-1})

p = atmospheric pressure (mmHg)

The amount of dioxygen absorbed is proportional to the amount of reacted phenolic ROH groups (monomer and oligomers alike).

After completion of the dioxygen uptake measurement the amount of DPQ can be determined spectrophotometrically. The resulting reaction mixture is diluted to 100 ml with toluene/methanol (13/2 v/v). This solution is diluted further (usually 50 or 100 times), so that the final absorption will be within the spectrophotometer range. The absorption maximum of DPQ is observed at 421 nm with a molar extinction coefficient ϵ of 58500 l/mol·cm in toluene/methanol (13/2 v/v). The extinction coefficient was established using solutions of pure DPQ, synthesized using a literature procedure [31]. Beer's law is obeyed at this wavelength, so that the amount of DPQ can easily be determined. Since PPE and DPQ are practically the sole products of this reaction [32], the amount of C–O coupled product can be calculated from the amount of DPQ and the conversion of DMP.

2.4. Rapid-freeze EPR measurements

The rapid-freeze EPR experiments were performed by deoxygenating 25 ml of a 0.01 M copper(II) nitrate solution with 30 equivalents of Nmiz and 25 ml of a 0.02 M DMP + 0.01 M base solution. These solutions were mixed under a dinitrogen atmosphere. At several time intervals samples were taken while carefully excluding dioxygen, and put in EPR tubes, which were immediately immersed in liquid dinitrogen to prevent further reaction, after which EPR spectra were measured.

2.5. Role of water

The role of water (and dioxygen) was investigated by preparing a suspension of dehydrated $CuCl_2$ (2.54 g; 18.9 mmol) and Nmiz (3.05 ml; 3.14 g; 38.3 mmol; distilled from NaOH pellets under a dinitrogen atmosphere prior to use) in diethyl ether (25 ml). To this suspension was added a THF solution of DMP/NaODMP, prepared by adding sodium sand (0.865 g; 37.6 mmol) to a stirred solution of DMP (6.98 g; 57.1 mmol) in THF (125 ml). After stirring for 6 days under a dinitrogen atmosphere, NaCl was filtered off. The resulting, intensely red/brown coloured filtrate was evaporated to dryness under reduced dinitrogen pressure. Yield: 10.67 g of a highly viscous, intensely red/brown coloured oil. No solid could be obtained, as the resulting oil could not be brought to crystallization.

2.6. X-ray data collection and structure determination

Crystals of the compound, $[Cu(Nmiz)_4(NO_3)_2]$, were obtained by preparing a solution with an Nmiz to copper ratio of 10 to 1, as described in Section 2.2, but using a solvent composition of toluene/methanol of 13/2 (v/v) instead of 4/1 (v/v). After two weeks, dark blue single crystals suitable for X-ray diffraction were isolated. Data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The cell dimensions were determined by 24 independent reflections. Corrections for Lorentz and polarization effects were applied. Atomic scattering factors and anomalous dispersion constants were taken from Ref [33]. For further details see Table 1. The position of the copper atom was determined from a Patterson map. The remainder of the

Table 1
Crystallographic data for [Cu(Nmiz)₄(NO₃)₂]

Chemical formula	$C_{16}H_{24}CuN_8O_6$	Crystal system	monoclinic
a, Å	8.452 (1)	Space group	$P2_1/n$
b, Å	10.376 (2)	T, K	293
c, Å	12.821 (2)	ρ_{calcd}, g/cm³	1.5295 (4)
β, °	94.88 (2)	μ, cm⁻¹	10.26
V, Å³	1120.3 (3)	$F(000)$	534
Z	1	R	0.049
F_w (g/mol)	515.97	R_w	0.042
Reflections measured	4894	scan range (°)	$2 < \Theta < 35$
Reflections observed ($I > 2\sigma(I)$)	3525	h, k, l range	$-13/13, 0/16, 0/20$
No. of parameters	200	min. max residual density	$-1.40, 0.56$

atoms was found in subsequent difference Fourier syntheses. Full-matrix least squares refinement on F of the positional and the anisotropic thermal parameters of the non-hydrogen atoms, and of the positional and isotropic thermal parameters of the hydrogen atoms was applied. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$ using the XTAL set of programs [34]. Fractional coordinates of the non-hydrogen atoms are collected in Table 2. Tables of bond distances and bond angles, anisotropic thermal parameters of the non-hy-

drogen atoms and fractional coordinates of the hydrogen atoms are available from the authors as supplementary material.

3. Results

3.1. Dioxygen uptake experiments

3.1.1. Effect of the Nmiz to copper ratio

A very important experimental factor influencing the rate and selectivity of the DMP coupling reaction in the case of simple uni- and bidentate ligands has been proven to be the ratio of ligand to copper [8,10,16,35,36]. This effect has been observed before for the copper(II)–Nmiz system, where a coordinating anion (chloride) was used [2]. In the present study the nitrate anion is used, which has a lesser tendency to coordinate, in order to minimize interference. For this system the Nmiz-to-copper (N/Cu) ratio was also varied. The effects on the activity (initial dioxygen uptake rate) and selectivity (PPE vs. DPQ formation) of the coupling reaction are shown in Fig. 3a and b, respectively. For all N/Cu ratios 100% conversion of DMP was observed, except for N/Cu is 1 to 1 where only about 30% conversion was reached after 1.5 h. The amounts of DPQ as shown in Fig. 3b are not corrected for the DMP conversions, since Viersen et al. have shown that most DPQ is formed during the beginning of the reaction [36].

Table 2
Fractional atomic coordinates and isotropic temperature parameters for non-hydrogen atoms for [Cu(Nmiz)₄(NO₃)₂], with estimated standard deviations in parentheses

	x/a	y/b	z/c	U (Å²)
Cu1	0.5(–)	0.5(–)	0.5(–)	0.02866(8)
N11	0.7746(2)	0.5192(1)	0.2444(1)	0.0359(4)
C12	0.7424(2)	0.4812(2)	0.3404(1)	0.0352(5)
N13	0.6099(2)	0.5351(1)	0.3679(1)	0.0321(4)
C14	0.5562(2)	0.6099(2)	0.2835(1)	0.0388(5)
C15	0.6564(2)	0.6005(2)	0.2073(1)	0.0416(6)
C16	0.9088(3)	0.4739(3)	0.1886(2)	0.0549(8)
N21	0.1522(2)	0.7577(1)	0.3912(1)	0.0367(4)
C22	0.2101(2)	0.6399(2)	0.4119(1)	0.0364(5)
N23	0.3519(1)	0.6458(1)	0.4630(1)	0.0309(4)
C24	0.3852(2)	0.7747(2)	0.4756(1)	0.0360(5)
C25	0.2621(2)	0.8444(2)	0.4315(2)	0.0398(5)
C26	−0.0038(3)	0.7883(3)	0.3375(3)	0.0602(9)
N30	0.2965(2)	0.7805(1)	0.0850(1)	0.0439(5)
O31	0.1860(2)	0.8478(1)	0.1146(1)	0.0582(5)
O32	0.4285(2)	0.8297(2)	0.0788(2)	0.0730(6)
O33	0.2722(2)	0.6667(1)	0.0609(2)	0.0856(8)

$U_{eq} = 1/3(\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j)$.

Fig. 4. Plot of $^{10}\log(R_0)$ vs. $^{10}\log([Cu])$ at $N/Cu = 37.5$, base$/Cu = 1$. $[DMP]_0 = 0.2$ M and $T = 298$ K.
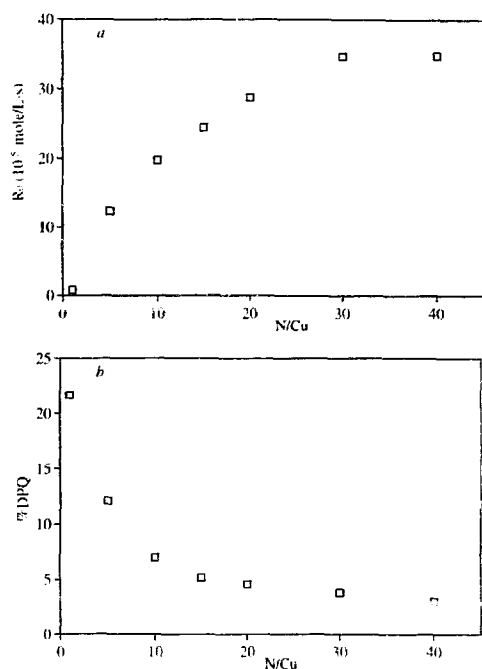

Fig. 3. Effect of the N/Cu ratio on the initial dioxygen uptake rate (R_0) (a) and on the formation of DPQ (b) at $[Cu] = 3.33$ mM. $[DMP]_0 = 0.20$ M, base$/Cu = 1$ and $T = 298$ K.

It is clear from Fig. 3a and b that maximum activity and selectivity are reached only when at least a 30-fold excess of the ligand Nmiz is used. This agrees with the results found by Chen et al. for copper(II) chloride [2]. Viersen et al. found maximum activity and selectivity with copper(II) chloride and the bidentate ligand N,N,N',N'-tetramethylethylenediamine at a ligand to copper ratio of at least 5 to 1 (i.e. nitrogen-to-Cu = 10 to 1) [10].

3.1.2. Determination of the order in Cu

To determine whether the rate-limiting step of the reaction is indeed the electron-transfer (phenol oxidation) step, the order in copper was determined, at different N/Cu ratios. The base (methoxide) to copper ratio was chosen as 1 to 1 during all measurements. At each N/Cu ratio the plot of the logarithm ($^{10}\log$) of the initial dioxygen uptake rate vs. the logarithm of the copper concentration afforded a straight line, as shown for N/Cu = 37.5 in Fig. 4. The slope of this line is equal to the order in copper of the reaction. The rate constant (k) was obtained
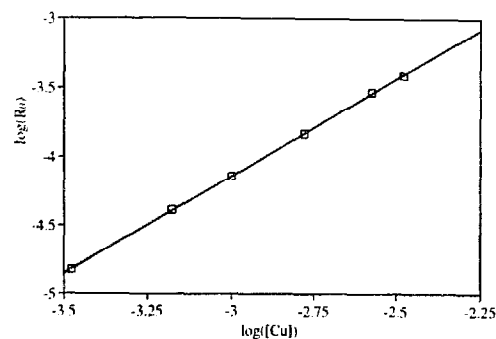
from the intercept with the y axis. The values obtained at different N/Cu ratios are listed in Table 3. Two facts are obvious from these data: (i). The order in copper is fractional and (ii). there is a distinct dependence of the order in copper on the N/Cu ratio. DMP conversions were 100% for all measurements, except for the lowest copper concentration at N/Cu = 10 to 1 and 20 to 1, where only ca. 80% conversion was achieved. DPQ percentages have not been corrected for the conversion. In all cases the amount of DPQ formed during the reaction was inversely proportional to the copper concentration, resulting in a dramatic increase of selectivity with increasing copper concentration. DPQ formation was less at higher N/Cu and base/Cu ratios.

At an N/Cu ratio of 37.5 to 1 the order in copper was also determined at a base-to-copper (base/Cu) ratio of 2 to 1. Also at this higher base/Cu ratio the order proved to be fractional, 1.30, slightly lower than at a base/Cu ratio of 1 to 1, where it was 1.42. The rate constant k was also somewhat lower: 0.78 's^{-1}' vs. 1.31 's^{-1}'.

Table 3
Order in Cu at different Nmiz/Cu ratios at base/Cu = 1

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

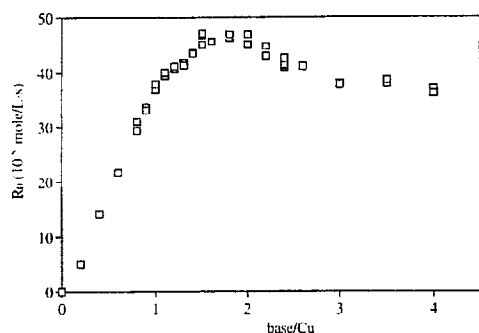[a] The unit of k is strictly speaking not s^{-1}, but (mol/l)^x·s^{-1}, where $x = 1 - $(order in Cu).

Fig. 5. Effect of the base/Cu ratio on the initial dioxygen uptake rate (R_0) at [Cu] = 3.33 mM, N/Cu = 30, [DMP]$_0$ = 0.2 M and T = 298 K.

3.1.3. Variation of the base to copper ratio

Variation of the base/Cu ratio has been reported [2] to influence the activity and selectivity of the coupling reaction. This study has now been expanded for our system. The activity results at an N/Cu ratio of 30 to 1 are shown in Fig. 5. At all base/Cu ratios 100% conversion of DMP was achieved, except when no base was added, because then no reaction takes place.

The maximum activity is reached at a base/Cu ratio of 1.8 to 1. There is a small, approximately linear decrease in DPQ formation with increasing base/Cu ratio, from 4% DPQ formation at a base/Cu ratio of 0.2, to 2.5% DPQ at a base/Cu ratio of 4. Another effect of increasing the base/Cu ratio is found in the total reaction time. At larger base/Cu ratios (≥ 2 to 1) the initial reaction rate is larger than or equal to the rate at lower ratios (≈ 1 to 1), but the reaction takes longer to complete, i.e. to reach 100% conversion of DMP. Furthermore, at low base/Cu ratios a PPE precipitate is formed [2] when the reaction is completed, but not at the higher ratios (≥ 2 to 1).

---

[2] The number average molecular weight of the resulting polymer in these experiments is known to be in the order of 10^4 g/mol [21]. The actual molecular weight is controlled by the solvent composition. The more methanol is present, the lower the molecular weight. In fact this so-called precipitation polymerization has been used as a method to prepare PPE of a well-defined molecular mass [37].

3.2. Spectroscopic measurements

3.2.1. Variation of the Nmiz to copper ratio

The effect of the N/Cu ratio on the composition of the catalyst precursor solution was investigated by performing EPR spectrometry on frozen (77 K) solutions of copper(II) nitrate with increasing amounts of Nmiz. The resulting spectra are shown in Fig. 6.

Obviously, there is a gradual transformation from $Cu^{II}(NO_3)_2$ into a mononuclear $Cu^{II}(Nmiz)_4$ species with increasing N/Cu ratio. After a ratio of 4 to 1 is reached, any extra addition of ligand does not result in further changes in the EPR spectrum. The final spectrum is very nicely resolved, showing even superhyperfine splitting on the lowfield $A_{\parallel}$ signal, and affords the following spectral parameters: $g_{\parallel}$ = 2.27 with $A_{\parallel}$ = 182 G, $a_{\parallel}$ = 11.0 G and $g_{\perp}$ = 2.04 with $a_{\perp}$ = 15.2 G. These figures are typical of an axial spectrum, as $g_{\parallel} \gg g_{\perp} > 2.0$ [38], and are indicative of a CuN_4 chromophore.

3.2.2. Crystal structure of the catalyst precursor complex

The molecular structure of the crystals obtained from a solution of copper(II) nitrate with Nmiz, $[Cu^{II}(Nmiz)_4(NO_3)_2]$, is shown as a PLUTON [39] projection in Fig. 7. Relevant bond distances and angles are listed in Table 4.
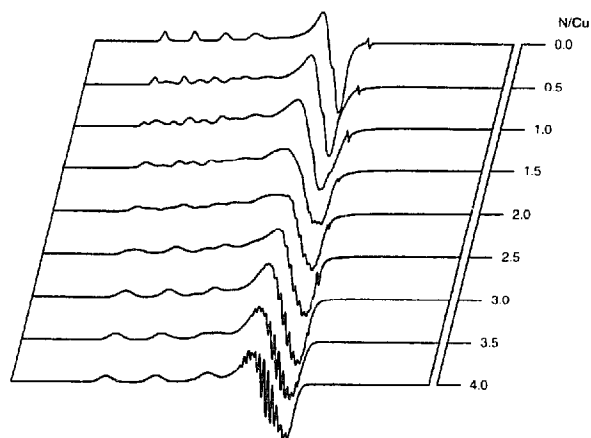

Fig. 6. Effect of varying the Nmiz to copper ratio on the frozen solution catalyst precursor EPR spectrum (77 K). [Cu] = 10 mM. scan range: 225–375 mT.
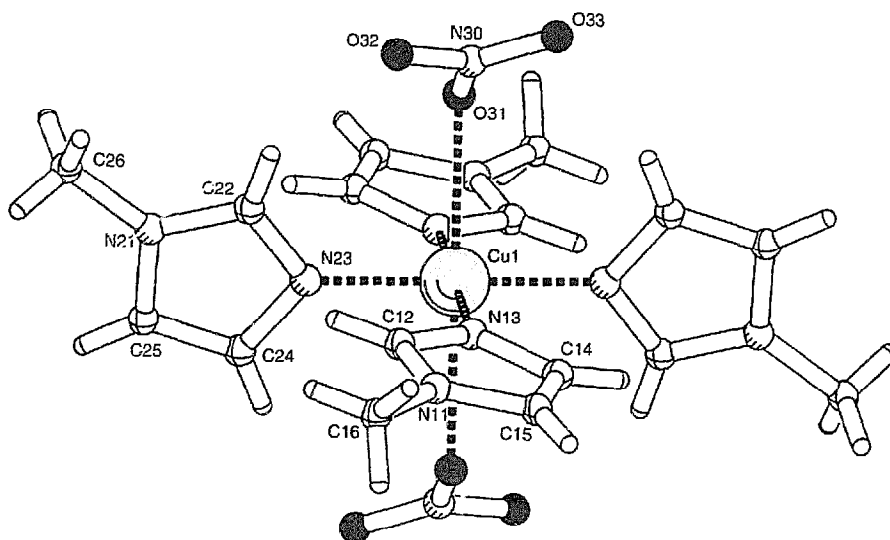
Fig. 7. Molecular structure. PLUTON [39] projection. of the catalyst precursor complex: [Cu(Nmiz)₄(NO₃)₂], together with the numbering scheme adopted.

The copper atom is positioned at a center of inversion and is coordinated by four imidazole nitrogens in a slightly distorted square planar arrangement. Two of the imidazole rings lie roughly in the CuN_4 plane, while the other two are more or less perpendicular to this plane. The nitrates are coordinated axially at rather long distances. The N_4O_2 chromophore around the Cu(II) ion is best characterized as elongated octahedral. The structure of the $[Cu(Nmiz)_4]^{2+}$ cation is almost identical to those found by Clegg et al. [40] for these subunits in a number of other copper complexes. This solid-state structure is consistent with the frozen solution EPR spectrum of a mixture of copper(II) nitrate with at least 4 equivalents of Nmiz (vide supra).

3.2.3. Role of dioxygen and water

To study the role of dioxygen in the reaction and to obtain information about reaction intermediates, an experiment was conducted in which

solutions of the catalyst and DMP/base were mixed while carefully excluding dioxygen. EPR spectra of frozen samples (77 K), taken at different time intervals under rigorous exclusion of dioxygen, were all identical to the spectrum of the catalyst solution. So, unfortunately, possible intermediate species could not be detected in this way. However, integration of the EPR signals clearly shows a decrease in intensity in time, as depicted in Fig. 8. Moreover, the copper(II) d–d absorption band in the visible region had disappeared after prolonged stirring of the catalyst and DMP/base solution in a dinitrogen atmosphere.

In the freeze EPR experiment dioxygen was excluded, but water was still present. To study whether water may be essential for the reaction, an experiment was performed in which anhydrous copper(II) chloride, Nmiz, DMP and DMPONa were mixed while carefully excluding both dioxygen and water, from which a very

Table 4
Bond distances (Å) and angles (°) around Cu for [Cu(Nmiz)₄(NO₃)₂], with estimated standard deviations in parentheses

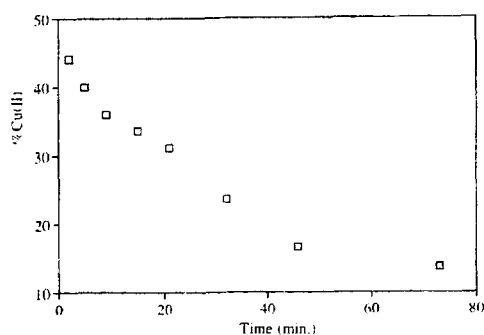|			
Cu1–N13	2.0326 (15)	O31–Cu1–N13	86.27 (5)
Cu1–N23	1.9949 (11)	O31–Cu1–N23	89.38 (5)
Cu1–O31	2.5945 (14)	N23–Cu1–N13–C12	172.16 (14)
N13–Cu1–N23	89.31 (5)	N13–Cu1–N23- C22	94.50 (13)
N13–Cu1–N13a	180.0 (5)		

Fig. 8. Intensity of the catalyst precursor EPR signal (77 K) after anaerobic reaction vs. time. %Cu^{II} = 100% at $t = 0$ min. [Cu] = 5 mM, N/Cu = 30, base/Cu = 1 and [DMP]$_0$ = 10 mM.

the formation of phenolate anions, which will not be formed when starting with copper(II) alone. Starting with copper(II) and externally added base results in the formation of very active catalysts, especially when the base is added to the DMP solution instead of to the catalyst solution [10,44]. Also, shorter initiation times have been observed. Furthermore, the amount of base used can be controlled better when using copper(II). Therefore, in the present study copper(II) complexes were used.

intensely coloured, viscous oil resulted. UV/Vis performed on a THF solution of this oil showed the presence of a d–d transition and a very broad, intense charge transfer band. The charge transfer band is attributed to the copper(II)–phenolate MLCT [41]. This solution is stable for prolonged periods of time when stored under a dry dinitrogen atmosphere. Addition of a few drops of water to this solution resulted in an almost immediate disappearance of the intense charge transfer colour, and eventually in the complete decolourization of the solution, proving that some water is required for the oxidation step. After some more minutes a yellow colour indicative of DPQ appeared.

4. Discussion

4.1. General

Originally, because copper(II) salts were found to form rather inactive catalysts, mostly copper(I) salts were used [1]. However, these catalysts were not really copper(I) species, as their solutions were 'pre-oxygenated' by stirring these in a dioxygen atmosphere [42,43], which resulted in the oxidation of copper(I) to copper(II) and also in the in situ formation of a basic species as the product of the dioxygen reduction. This latter effect has long been overlooked. The implicit base formation results in

4.2. Effect of the Nmiz to copper ratio

It is clear from the kinetic experiments that the maximum activity and selectivity are reached only when an N/Cu ratio of at least 30 to 1 is employed. The EPR measurements on the other hand show that already at a ratio of 4 to 1 virtually all copper(II) is converted into [Cu(Nmiz)$_4$(NO$_3$)$_2$], which, therefore, must be the catalyst precursor species. Obviously, the excess ligand must play some other, significant role during the reaction. This role could be related to shifting some (pre-)equilibrium (or equilibria) to a more favourable position, and thereby influencing the reaction rate and PPE formation.

Furthermore, there is a distinct effect of the N/Cu ratio on the order in copper of the reaction. A fractional order in copper is observed for all N/Cu ratios, which indicates that at least two competing rate-limiting steps are operative, the rates of which are of the same order of magnitude. One of these steps is probably the actual phenol oxidation, up till now seen as the only rate-limiting step, which has an order in (dinuclear) copper of one. The other rate-determining step must therefore be the formation of a dinuclear copper(II) species, since this is the only step in the mechanism that would result in an order in copper of 2 if it were the sole rate-determining step. As neither step is completely rate-determining, a fractional order is observed and it would be expected that chang-

ing any factor favouring (or disfavouring) either one of these steps will result in a change in the order in copper of the reaction. This appears to be the case for the N/Cu ratio, as at higher ratios a higher order in copper is observed, indicating that the formation of dinuclear copper species becomes the slower step. This observation nicely correlates with the effect that increasing the N/Cu ratio has on reaction (3), where it shifts this equilibrium to the side of the mononuclear species. Therefore the dinuclearization step is hampered, resulting in a higher order in copper, as was indeed found with higher N/Cu ratios (see Table 3). Increasing the base/Cu ratio at a constant N/Cu ratio resulted in a lower order in copper, which is easily explained because increasing the amount of base will increase the amount of potentially bridging anions in solution, thereby making the formation of dinuclear species easier.

$$(L)_3Cu^{II}(X^-) + (L)_3Cu^{II}(Y^-)$$

$$\rightleftharpoons (L)_2Cu^{II}(\mu\text{-}X^-)(\mu\text{-}Y^-)Cu^{II}(L)_2 + 2L$$
$$(3)$$
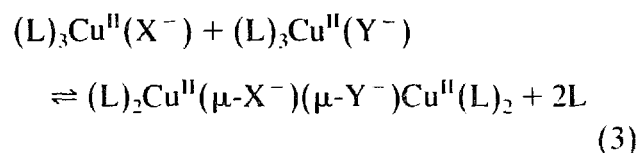
where

L $\quad$ = Nmiz (or another ligand)
X^-, Y^- = phenolate, hydroxide or the original copper counter ion.

The observed fractional order in copper, implies the formation of a dinuclear copper(II) species during a 'rate – limiting' step. This is in fact the first direct evidence for the more recent mechanistic proposals, which incorporate such dinuclear complexes [22,26,45].

The dramatic increase in selectivity of the reaction with increasing copper concentration is a trend which is observed for all N/Cu ratios, and also for other catalytic systems [36]. This may be explained as follows: the equilibrium constant for reaction (3) is defined as: $K = [Cu_2]/[Cu]^2$. This value is constant for any given copper concentration. This means that the ratio $[Cu_2]/[Cu]$ is *not* constant. With increas-

ing copper concentration, the amount of dinuclear species will be increased relative to the amount of mononuclear species. Since mononuclear species will yield preferentially DPQ by a 1-electron transfer mechanism [36], increasing the copper concentration gives rise to less DPQ formation.

4.3. Effect of the base to copper ratio

It appears that the optimal base/Cu ratio for a maximum initial reaction rate is about 1.8 to 1. Also, at higher ratios a slightly improved selectivity is found. Moreover, some other effects on the reaction are observed. At higher base/Cu ratios (≥ 2 to 1) no PPE precipitate has been formed when the reaction is completed, which is indicative of a lower degree of polymerization. This is due to the higher number of phenolate end groups in correspondence to the higher amount of base. Since the starting amount of DMP was the same in all these reactions, it is evident that with increasing base concentration, the polymerization degree will be lower as there will be more, shorter chains at the end of the experiment.

Even though the initial dioxygen uptake rate may be higher at higher base/Cu ratios, it takes longer for the reaction to complete. No clear explanation can be given yet for this effect, but it may be envisioned that at higher base/Cu ratios the (slower) coupling of PPE chains will begin earlier in the reaction, since there will be more, shorter chains as compared to the situation at lower ratios. Another possibility is poisoning of the copper catalyst by hydroxide due to the combination of excess base and the formation of water during the reaction, resulting in inactive copper hydroxide species.

4.4. Role of dioxygen and water

Rapid-freeze EPR measurements were performed in order to gain insight into the nature of intermediate copper species. Only the signal of

[Cu(Nmiz)$_4$(NO$_3$)$_2$], the catalyst precursor complex, is observed in the EPR spectra. Under anaerobic conditions a significant decrease in the intensity of the signal of this precursor complex is observed, as shown in Fig. 8. This decrease may be due either to the formation of an EPR-silent dinuclear copper(II) complex, or to the reduction of copper(II) to copper(I). EPR cannot distinguish between these possibilities, but visible spectroscopy can, because if a dinuclear copper(II) species would be formed, a d–d transition band should still be observed in the visible spectrum. The spectrum of the resulting solution after several hours of stirring under a dinitrogen atmosphere does not show such a peak. However, shaking the solution with air results in a complete return of the d–d band in the visible spectrum, as compared to the spectrum of the initial copper solution. Therefore, it is concluded that all copper(II) present at the beginning of the experiment has been reduced to copper(I). This implies that even in the absence of dioxygen, the first reaction steps, including the phenol oxidation step, still occur. The reaction stops of course when all copper has been reduced to copper(I). It is clear that dioxygen is only required as a terminal oxidant for the reoxidation of the copper(I) species, so that the catalytic cycle can be closed.

The role of water in the reaction was studied by performing an experiment in which all reactants were mixed in THF while rigorously excluding both dioxygen and water. The resulting intensely coloured solution was stable for prolonged periods of time when stored under a dry dinitrogen atmosphere. UV/Vis spectroscopy confirmed the presence of copper(II) and showed the presence of an intense charge transfer band, identified as a copper(II)–phenolate MLCT [41], indicating that a copper(II)–phenoxo species was present in solution. Addition of water to this solution resulted an immediate decolourization and formation of DPQ. Apparently some water is essential for the actual phenol oxidation step to take place, most probably by forming the reactive intermediate.

4.5. Mechanistic implications

Up till now, even the most recent mechanistic proposals in literature [22,26,45], as discussed in the introduction (vide supra), are still not completely satisfactory. The evident need for an excess of the ligand is not explained, and neither is the necessity of some water in the beginning of the reaction. In view of the results presented in this paper, a more realistic mechanism will be discussed.

In the present study it has been shown that dinuclear copper species play a key role in the catalytic process, as concluded from the fractional order in copper and the dependence of this order on the N/Cu ratio. Furthermore it has been shown that a little water is needed at the start of the reaction to make the actual phenol oxidation possible. This indicates that it is very unlikely that the dinuclear bis-phenoxo bridged copper(II), as proposed in earlier literature mechanisms, is the catalytically active intermediate, but rather is either unreactive or slowly decomposes to form DPQ. In fact the possibility of such a reaction has been suggested from experiments performed by Kitajima et al. with copper pyrazole complexes [46]. It is highly unlikely that in such a bis-phenoxo bridged complex a two-electron transfer with only one of the phenolates will occur. If one of the phenolates has been oxidized to the corresponding radical, for reasons of symmetry it would seem much more likely that the other phenolate is also oxidized than to oxidize the radical once again to form a phenoxonium cation, even if one of the phenolate ions is a monomer and the other an oligomer, which is more easily oxidized because of the presence of an electron donating para-phenoxy substituent. Therefore, the most likely candidate for the actual catalytically active species is an asymmetric dinuclear copper(II) species containing one bridging phenolate and another bridging ligand, such as hydroxide or chloride. Since the experiment where water was excluded was performed with copper(II) chloride resulted in a stable complex,

hydroxide is the most probable activating species. This would explain why some water is required to start the reaction: i.e. to form the catalytically active species. Hydroxide may be formed if a little water is present because of the Lewis acidic properties of the copper(II) ion or in the presence of base, according to reaction (4):

$$DMPO^- + H_2O \rightleftharpoons DMPOH + OH^- \qquad (4)$$

Since hydroxide is the stronger base, equilibrium (4) lies to the left, but nevertheless a small (catalytic) amount of hydroxide will be present. Note that during a normal dioxygen uptake experiment sodium methoxide was used as a base (see the Experimental section). The

methoxide anion might also be a candidate for a bridging anion in the catalytically active species. However, since methoxide is a very strong base it will be completely protonated in the presence of excess water and phenol, therefore methoxide is not considered here.

An excess of the ligand will influence the nature of the mononuclear copper species, as shown in equilibria (5), that will be shifted to the left upon increasing the N/Cu ratio.

$$Cu(L)_4 + X^- \rightleftharpoons (L)_3Cu(X^-) + L \qquad (5a)$$

$$(L)_3Cu(X^-) + Y^- \rightleftharpoons (L)_2Cu(X^-)(Y^-) + L \qquad (5b)$$
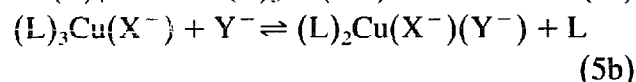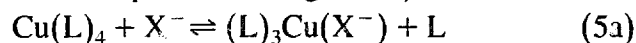
where X^-, Y^- = phenolate, hydroxide or the original copper counter ion.
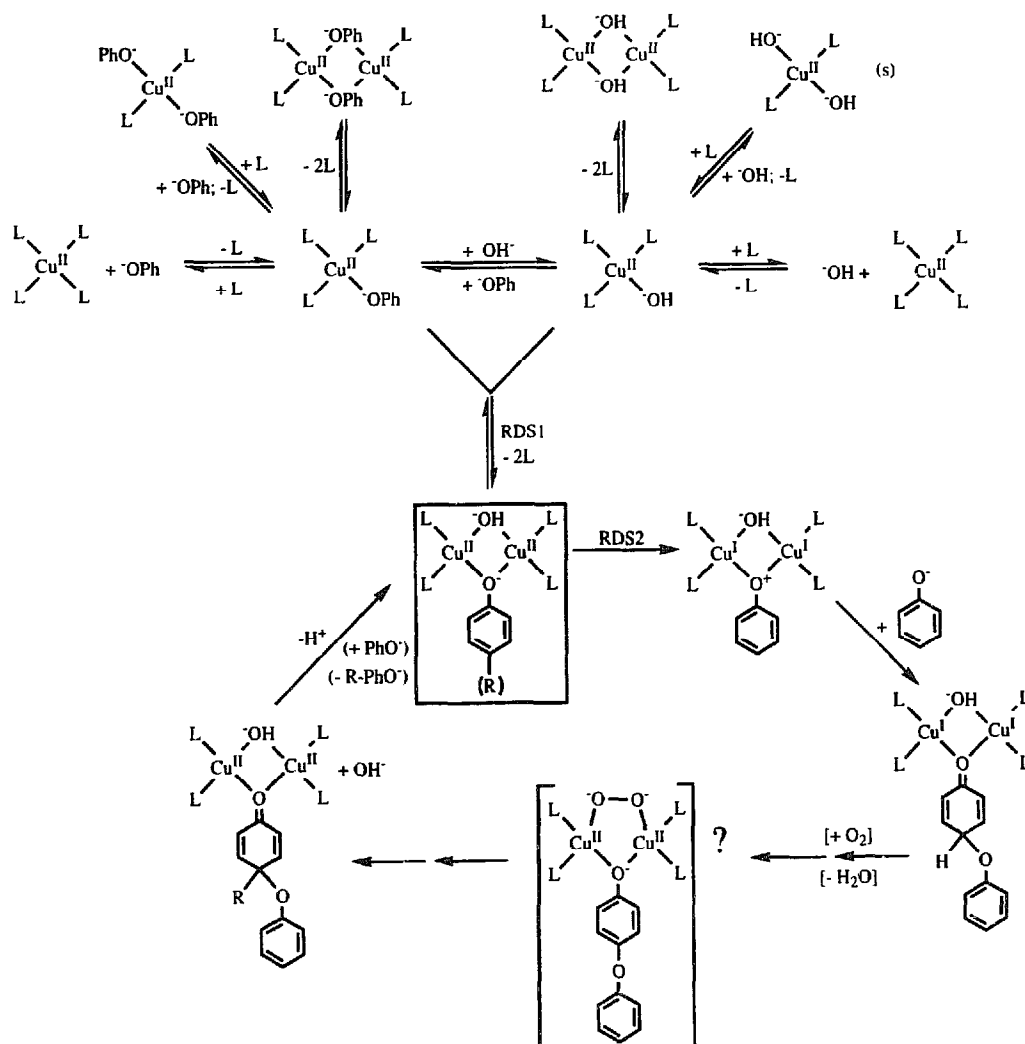

Fig. 9. New mechanistic proposal for the oxidative coupling of DMP. The DMP methyl groups have been omitted for clarity.

Two effects of increasing the N/Cu ratio can now be distinguished: (i) the amount of mononuclear copper(II) phenoxo or hydroxo species will decrease; (ii) the amount of non-coordinated (free) hydroxide and especially phenolate in solution will increase. However, as phenolate and hydroxide are both strongly coordinating anions, one can still expect coordination to copper, even at a high N/Cu ratio.

The first effect will hinder the formation of dinuclear hydroxo or phenoxo bridged copper species by decreasing the amount of monomeric copper compounds suitable for forming dinuclear species. Furthermore, the actual dinuclearization itself is also hampered, according to equilibrium (3), which is shifted to the left (mononuclear species) upon increasing the N/Cu ratio. Thus, the formation of any dinuclear copper species will be severely hampered by an increasing N/Cu ratio. However, if the catalytically active dinuclear copper species, supposedly the (μ-hydroxo)(μ-phenoxo)-bridged one, is formed, the irreversible double one-electron transfer will occur, and the equilibria will be driven to the right for this species. Other species, like the supposedly unreactive bis-phenoxo bridged or the bis-hydroxo bridged one, will hardly be formed at a high N/Cu ratio. Thus, the net effect of a high N/Cu ratio is positive as far as reaction rate and selectivity are concerned, because more copper ions are available for the catalytic process as they are not bound in inactive or DPQ-forming species (vide infra). It is noted that bis-hydroxo bridged dinuclear copper species may be formed especially near the end of the reaction, as the increasing amount of water will shift equilibrium (4) to the right thereby forming hydroxide ions. Indeed it was observed that at a low N/Cu ratio (1 to 1) complete conversion of DMP could not be reached.

The second effect, the occurrence of free basic species in solution, especially phenolate, may also play a positive role. In the catalytic cycle a phenoxonium cation is formed after the phenol oxidation step. This cation may be at-

tacked by either a phenol or a phenolate. Because of the negative charge, a free phenolate is the most active species for this coupling step. Since phenolate will be liberated from the copper complexes in the case of an excess of the ligand the reaction will be accelerated. After attack of the phenolate on the cation a neutral molecule is formed that will give the dimer phenol after tautomerization.

These novel mechanistic insights have been summarized in Fig. 9, where a new reaction mechanism is proposed employing all (pre-)equilibria discussed above.

In this modified mechanism, the supposedly catalytically active intermediate (μ-hydroxo)(μ-phenoxo)–dicopper(II) is formed eventually in one of the rate-determining steps (rds1). This species may then undergo a second rate-determining step (rds2) as the bridging phenolate is oxidized to the corresponding phenoxonium cation. This new species may then be attacked by a free phenolate. Two possibilities exist, the probabilities of which are dependent on the charge distribution on the phenolate. Formation of a bisphenol may occur by C–C coupling if both the anion and cation are monomers. The bisphenol can than be oxidized to DPQ. C–O coupling of the anion and cation, which has a much higher probability and which can also occur between oligomeric species, will afford a, possibly coordinated, quinone ether. After tautomerization the dimer phenol may be replaced by a monomeric phenolate, or may remain coordinated after deprotonation. Reoxidation of the copper(I) ions may proceed via a peroxo-bridged dicopper(II) complex [47]. Such reactions are known to be extremely fast. At this point the growing phenolic chain may be displaced by a monomeric phenolate, or remain coordinated to the copper and undergo another cycle.

Two aspects of the reaction need to be studied in more detail. Firstly it must become clear why maximal activity is found at a base/Cu ratio of about 1.8 to 1. Possibly the equilibria discussed above are shifted somewhat to a more

favourable position, in terms of reaction rate and selectivity. Two effects might be distinguished: (i) the formation of the undesired bis-μ-phenoxo bridged dinuclear copper species will be stimulated, but (ii) more free phenolate is present in solution which is positive for the actual phenol coupling step. Apparently at a base/Cu ratio of about 1.8 to 1 an optimum is found between these two opposed effects, as far as reaction rate is concerned.

Secondly, the Michaelis–Menten kinetics observed for the copper(II) chloride–Nmiz system [2] needs further attention. It is possible that a phenol will be hydrogen bonded to the (bridging) phenolate prior to the rate-limiting step, or that a DMP molecule is coordinated terminally to one or both copper ions. It is even possible that for this copper(II) nitrate system Michaelis–Menten kinetics does not apply. This is subject of a further investigation.

5. Conclusions

A detailed study of the copper(II) nitrate/N-methylimidazole catalyst in the oxidative coupling of 2,6-dimethylphenol, by means of kinetic and spectroscopic measurements, has provided important new insights into the reaction mechanism. The order of the reaction in copper was found to be fractional and dependent on the N/Cu ratio, indicative that in this system at least two competing rate-limiting steps are operative. One of these is likely to be the actual phenol oxidation step, that has up till now always been seen as the sole rate-limiting step. Because of the observed fractional order in copper the other rate-limiting step must be the formation of a dinuclear copper(II) species. The formation of these dinuclear complexes are hampered by an excess of the ligand Nmiz, and indeed an increase in the order in copper was observed with increasing N/Cu ratio. Also the importance of a dinuclear copper species as a key intermediate in the oxidative coupling reaction has been demonstrated.

Variation of base/Cu ratio showed that maximum activity was reached at a ratio of about 1.8 to 1. The selectivity (PPE vs. DPQ formation) was found to increase slightly with increasing base/Cu ratio.

The solid-state structure of the catalyst precursor complex has been determined and proved to be $[Cu^{II}(Nmiz)_4(NO_3)_2]$, an axially elongated octahedron where the Nmiz molecules are coordinated equatorially and the nitrates axially. This structure was found to be consistent with the (frozen) solution structure of the compound as determined by EPR spectroscopy.

It has been conclusively shown that dioxygen is not essential for the phenol oxidation step to occur. Dioxygen is only needed for the reoxidation of copper(I) to copper(II), and the regeneration of base by formation of hydroxide. On the other hand water was found to be essential for the oxidation step to take place. In the new proposal for a reaction mechanism the need for water is explained in terms of the nature of the key catalytic intermediate: this is not a bis-μ-phenoxo bridged dinuclear copper species which is thought to be either unreactive, or forming DPQ, but rather a (μ-phenoxo)(μ-hydroxo)dicopper(II) species. Water is then needed to form a (catalytic) amount of hydroxide according to reaction (4).

The maximum reaction rate and maximum selectivity for polymer formation are reached at an N/Cu ratio of at least 30 to 1. On the other hand all copper nitrate is converted into the catalyst precursor species already at an N/Cu ratio of 4 to 1. The necessity for the excess ligand is explained in terms of the effects it has on the nature of the copper species by influencing a number of pre-equilibria, as shown in the new mechanistic proposal in Fig. 9.

Acknowledgements

port by the European Union, allowing regular exchange of preliminary results with several European colleagues, under contract ER-BCHRXCT920014 is gratefully acknowledged. This study was supported by the Foundation for Chemical Research in the Netherlands (SON) with financial aid from the Dutch Organization for Scientific Research (NWO).

References

[1] A.S. Hay, H.S. Stafford, G.F. Endres and J.W. Eustance, J. Am. Chem. Soc., 81 (1959) 6335.

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

[3] S.S. Mahajan, B.B. Idage, B.D. Sarawade, N.N. Chavan and S. Sivaram, Macromol. Rep., A28 (Suppl. 1) (1991) 7.

[4] E. Tsuchida, M. Kaneko and H. Nishide, Makromol. Chem., 151 (1972) 221.

[5] E. Tsuchida, H. Nishide and T. Nishiyama, Makromol. Chem., 176 (1975) 1349.

[6] S. Tsuruya, Y. Kishikawa, R. Tanaka and T. Kuse, J. Catal., 49 (1977) 254.

[7] C.E. Koning, G. Challa, F.B. Hulsbergen and J. Reedijk, J. Mol. Catal., 34 (1986) 355.

[8] S. Tsuruya, K. Nakagawa and M. Masai, J. Polym. Sci. A, 25 (1987) 995.

[9] A.H.J. Tullemans, E. Bouwman, R.A.G. de Graaff, W.L. Driessen and J. Reedijk, Recl. Trav. Chim. Pays-Bas, 109 (1990) 70.

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

[11] K.-T. Li, Polym. Bull., 34 (1995) 419.

[12] A.S. Hay, P. Shenian, A.C. Gowan, P.F. Erhardt, W.R. Haaf and J.E. Theberge, in N.M. Bikales (Ed.), Encyclopedia of Polymer Science and Technology, Vol. 10, John Wiley & Sons, New York, 1969, p. 92.

[13] D. Aycock, V. Abolins and D.M. White, in H.F. Mark (Ed.), Encycl. Polym. Eng. Sci., Vol. 13, John Wiley and Sons, New York, 1988, p. 1.

[14] F.J. Viersen, Ph.D. Thesis, Groningen University, 1988.

[15] A.S. Hay, J. Polym. Sci., 58 (1962) 581.

[16] G.F. Endres, A.S. Hay and J.W. Eustance, J. Org. Chem., 28 (1963) 1300.

[17] P.D. McDonald and G.A. Hamilton, in W.S. Trahanovsky (Ed.), Oxidation in Organic Chemistry, Vol. 5B, Academic Press, New York, 1973, p. 97.

[18] G. Coudurier, H. Praliaud and M.V. Mathie, Spectrochim. Acta, 30A (1974) 1399.

[19] H. Praliaud, Y. Kodratoff, G. Coudurier and M.V. Mathieu, Spectrochim. Acta, 30A (1974) 1389.

[20] H.L. Finkbeiner, A.S. Hay and D.M. White, in C.E. Schild-knecht (Ed.), Polymerization Processes, Vol. XXIV, Wiley, New York, 1977, p. 537.

[21] W. Chen, Ph.D. Thesis, Groningen University, 1991.

[22] C.E. Koning, F.J. Viersen, G. Challa and J. Reedijk, J. Mol. Catal., 44 (1988) 245.

[23] J. Kresta, A. Tkac, R. Prikryl and L. Malik, Makromol. Chem., 176 (1975) 157.

[24] E. Tsuchida, H. Nishide and H. Nishikawa, J. Polym. Sci., 47 (1974) 47.

[25] M.A. El-Sayed, A. Abu-Raqabah, G. Davies and A. El-Toukhy, Inorg. Chem., 28 (1989) 1909.

[26] F.J. Viersen, G. Challa and J. Reedijk, Polymer, 31 (1990) 1368.

[27] E.P. Talsi, N.I. Shaikhutdinova, A.A. Shibin, V.D. Chinakov, B.M. Khlebnikov, B.I. Yudkin, V.M. Nekipelov and K.I. Zamaraev, J. Mol. Catal., 57 (1990) 325.

[28] K.-T. Li, J. Appl. Polym. Sci., 54 (1994) 1339.

[29] J. Kresta, A. Tkac, R. Prikryl and L. Malik, J. Elastoplast., 5 (1973) 20.

[30] E. Tsuchida, M. Kaneko and H. Nishide, Makromol. Chem., 151 (1972) 235.

[31] C. Walling and R.B. Jr. Hodgon, J. Am. Chem. Soc., 80 (1958) 228.

[32] W.J. Mijs, J.H. van Dijk, W.G.B. Huysmans and J.G. Westra, Tetrahedron, 25 (1969) 4233.

[33] A.J.C. Wilson (Ed.), International Tables for X-ray Crystallography, Kluwer, Dordrecht, 1992.

[34] S.R. Hall, H.D. Flack and J.M. Stewart, XTAL3.2 User's Manual, Universities of Western Australia and Maryland, 1992.

[35] G.F. Endres, A.S. Hay, J.W. Eustance and J. Kwiatek, Am. Chem. Soc., Div. Polymer Chem., Prepr., 2 (1961) 325.

[36] F.J. Viersen, G. Challa and J. Reedijk, Recl. Trav. Chim. Pays-Bas 109 (1990) 97.

[37] H.A.M. van Aert, R.W. Venderbosch, M.H.P. van Genderen, P.J. Lemstra and E.W. Meijer, J. Macromol. Sci., Pure Appl. Chem., A32 (1995) 515.

[38] B.J. Hathaway, in G. Wilkinson, R.D. Gillard and J.A. McLeverty (Ed.), Comprehensive Coordination Chemistry, Vol. 5, Pergamon Press, Oxford, 1987, p. 594.

[39] A.L. Spek, PLUTON-92: Interactive Molecular Graphics Program, Utrecht University, 1992.

[40] W. Clegg, J.R. Nicholson, D. Collison and C.D. Garner, Acta Crystallogr., C44 (1988) 453.

[41] J.F. Harrod, Can. J. Chem., 47 (1969) 637.

[42] H.S. Blanchard, H.L. Finkbeiner and G.F. Endres, Am. Chem. Soc., Div. Polym. Chem., Prepr., 2 (1961) 331.

[43] H. Finkbeiner, A.S. Hay, H.S. Blanchard and G.F. Endres, J. Org. Chem., 31 (1966) 549.

[44] F.J. Viersen, G. Challa and J. Reedijk, Recl. Trav. Chim. Pays-Bas, 108 (1989) 247.

[45] G. Challa, W. Chen and J. Reedijk, Makromol. Chem., Macromol. Symp., 59 (1992) 59.

[46] N. Kitajima, T. Koda, Y. Iwata and Y. Moro-oka, J. Am. Chem. Soc., 112 (1990) 8833.

[47] D.A. Rockcliffe and A.E. Martell, Inorg. Chem., 32 (1993) 3143.