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Stoichiometric and catalytic oxidation by a dinuclear copper(I) dioxygen complex and a dinuclear copper(II) complex of a macrocyclic ligand derived from the 2:2 condensation of pyridine-2,6-dicarboxaldehyde and 1,4,7-triazaheptane

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Abstract

The ligand 3,6,9,17,20,23,28,29-octaazatricyclo[23.3.1.1^{11,15}]tridecanedeca-1(28),2,9,11,13,15(30),16,23,25(29),26-ene $(PD)_2(DIEN)_2$, **1**, was used together with $Cu(CH_3CN)_4PF_6$ to prepare a dinuclear copper(I) complex (**2**) which, when oxygenated at 25.0°C produced a copper(II)–dioxygen adduct (**3**) as an initial species, which decomposed to a copper(II) complex (**4**). The complex cation of **4** was formed by the reaction of **1** with $CuCl_2$. It is shown that both **3** and **4**, in the presence of excess dioxygen, catalytically convert hydroquinone, *t*-butylhydroquinone, 2,6-di-*t*-butylphenol, 2,6-dimethoxyphenol and 3,5-di-*t*-butylcatechol to their respective oxidation products benzoquinone, *t*-butylbenzoquinone, 3,3′5,5′-tetra-*t*-butyldiphenoquinone, 3,3′,5,5′-tetramethoxydiphenoquinone and 3,5-di-*t*-butyl-1,2-benzoquinone. Under the same conditions **3** converts 2,4-di-*t*-butylphenol to 3,3′,5,5′-tetra-*t*-butyl-2-2′-dihydroxybiphenyl, 4-*t*-butylcatechol to the γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester, and 3,4-dimethylaniline to 3,3′4,4′-tetramethylazobenzene whereas **4** is inactive for these substrates. The complex **4** is found to oxidize 4-methylcatechol; however, for this substrate **3** is inactive. The oxidation of 3,5-di-*t*-butylcatechol is first order in **3** and zero order in substrate, having a pseudo first order rate constant of 1.3×10^{-3} s^{-1}. Under pseudo first order conditions the reaction between 3,5-di-*t*-butylcatechol and **4** is first order in **4**. The rates of stoichiometric reactions are determined to be greater for reactions with **3** than for those with **4** by factors which range between 5 and 100.

Keywords: Catechols; Copper; Dinuclear Cu(I) dioxygen complex; Dinuclear Cu(II) macrocyclic complex; Dioxygen complexes; Macrocyclic complex; Octaaza macrocycle; Oxidation; Phenols; Schiff base macrocycle

1. Introduction

Hemocyanin and tyrosinase are structurally related [1–3] enzymatic proteins. Hemocyanin is concerned with reversible oxygen transport while tyrosinase catalyzes the hydroxylation of phenols with subsequent oxidation of the resulting catechols to quinones. Tyrosinase is a monooxygenase possessing a dinuclear copper(I) active site [1,4] capable of forming a peroxo adduct which is similar to that formed by oxygen absorption in hemocyanin. The monooxygenase enzyme is considered to have a Cu···Cu separation of 3.6 Å when in the oxygenated form, by analogy with hemocyanin [5]. Although the literature contains a wealth of information on structural elucidation of tyrosinase, there is incomplete understanding

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of the nature of reactions which the enzyme undergoes. Several low molecular weight dinuclear copper(I) functional models have been prepared [6–30] and these compounds were found to be good spectroscopic analogs of the active site of tyrosinase. However, there is a dearth of information on the intermolecular reaction characteristics of such complexes. Reglier et al. [31] synthesized a dinuclear copper(I) complex based on biphenyl-2,2′-dicarboxaldehyde and 2-(2-pyridyl)ethylamine and were able to perform both α-hydroxylation of 2,6-di-*t*-butylphenol and also oxidation of the resulting catechol to the corresponding quinone, in excess dioxygen. Similar reactions were performed with a dinuclear copper(I) complex derived from a polybenzimidazole ligand system [32]. Karlin et al. [33] prepared several model complexes which were shown to perform coupling of phenols. Kitajima et al. [34] synthesized a dinuclear complex based on a hydroxotris(3,5-dimethyl-1-pyrazolyl)borate ligand system and was successful in performing oxidation reactions as well as coupling of phenols and 3,5-di-*t*-butylcatechol. A recent investigation [35] demonstrated that a copper(I)–dioxygen macrocyclic complex $[Cu_2(FD)_2(DIEN)_2O_2]^{2+}$ (whose ligand was prepared by the 2:2 condensation of furandicarboxaldehyde and diethylenetriamine), which is a spectroscopic analog of tyrosinase [17], catalytically converts phenols, hydroquinones and ascorbic acid to diphenoquinones, benzoquinones and dehydroascorbic acid respectively. Catechols and 3,4-dimethylaniline were also oxidized by this system but not catalytically.

To date the mechanisms of oxidation for the tyrosinase models are not well understood. Recent studies [36] suggest that there is not a catechol intermediate in the oxidation of methyl-4-hydroxybenzoate by Cu(I) and dioxygen. It is evident that more information needs to be provided in this regard.

In order to examine the effectiveness of macrocyclic complexes of copper(I) as models for the catecholase activity of tyrosinase, a ligand, $(PD)_2(DIEN)_2$, **1**, based on the 2:2 condensation of pyridine-2,6-dicarboxaldehyde and 1,4,7-triazaheptane was used to prepare a dinuclear copper(I) complex, **2** [37]. A dioxygen adduct **3** with a half-life of 7 min for oxygen absorption was generated. The dioxygen adduct was found to be thermally unstable, degrading to a copper(II) complex **4** of **1** with a half-life of 100 min at 25°C. A dinuclear copper(II) complex cation, **4**, of **1** was prepared directly from $(PD)_2(DIEN)_2$ and $CuCl_2$. The characterization of **2**, **4** and the dioxygen adduct **3** have been described [37]. In this research, the properties of **3** and the copper(II) dinuclear complex **4** as oxidants are investigated in the presence of substrates such as hydroquinones, phenols, catechols and 3,4-dimethylaniline, at room temperature.

2. Experimental

2.1. Instrumentation

The products of oxidation reactions were identified by ^1H and ^{13}C NMR spectroscopy and melting point determination. Proton and carbon-13 NMR spectra were measured in $CDCl_3$ on a Varian XL 200 FT spectrometer. Chemical shifts are reported relative to tetramethylsilane (TMS) as an internal standard. Melting point determinations were performed with a Fisher–Johns melting point apparatus. Mass spectral data were obtained by a direct probe electron impact method on a VG Analytical VG-705 spectrometer. Infrared spectra were obtained on an IBM IR/44 Version 1.0 FT spectrophotometer. Electronic spectra were recorded on a Perkin Elmer Model 553 fast scan spectrophotometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Oxygen uptake was measured as previously described [38].

2.2. Materials

The preparation of copper(I) complexes and all stoichiometric reactions were carried out under argon unless otherwise stated. Argon (99.98%

AIRCO) was prescrubbed with a 3% solution of pyrogallol in 0.8 M NaOH and dried by passage through H_2SO_4 and Drierite ($CaSO_4$). Solvents were deoxygenated by sonicating them prior to purging with argon for approximately 30 min. Deoxygenated solvents were used in experiments on the stoichiometric and catalytic oxidation of substrates. Solid reagents and solvents employed were reagent-grade commercially available chemicals supplied by Aldrich Chemical Co. Anhydrous methanol and anhydrous acetonitrile were dispensed under argon from Sure Seal® bottles for the storage of air-sensitive reagents. The reagent *t*-butylhydroquinone was recrystallized from a methanol/chloroform mixture and 2,6-di-*t*-butylphenol and 2,6-dimethoxyphenol were recrystallized from methanol.

2.3. Preparation of pyridine-2,6-dicarboxaldehyde

This compound was prepared by the method of Alcock et al. [39]. The crude product was recrystallized from a chloroform/petroleum ether mixture. ^{1}H NMR ($CDCl_3$) δ 8.00–8.25 (m), 10.18 (s).

2.4. 3,6,9,17,20,23,28,29-Octaazatricyclo[23.3.1.1^{11,15}]tridecanedeca-1(28),2,9,11,13,15(30),16,23,25(29),26-ene $(PD)_2(DIEN)_2$, 1

The ligand was prepared as previously described [40]. The crude product was recrystallized from a methanol/acetonitrile mixture. *m/e* 405 $(M+H)^+$. Mp: 279–281°C (dec).

2.5. Catalytic oxidation reactions

Catalytic reactions were performed in an atmosphere of oxygen whereas stoichiometric reactions were carried out under an atmosphere of argon. The reaction flask which was thermostated at 25°C was equipped with an inlet and outlet adapters for argon and oxygen purging and evacuation. A manometer was used to maintain the pressure of oxygen over the reaction solution at 1.0 atm. For catalytic reactions with the dioxygen complex of $[Cu_2(PD)_2(DIEN)_2]^{2+}$, **3**, the reaction solution was prepared by oxygenation of a total of 40 ml of a 3:1 methanol/acetonitrile solution comprising of 0.20 mmol of **1**, 0.40 mmol of $Cu(CH_3CN)_4PF_6$ and 4.0 mmol of substrate. The reaction was allowed to take place until oxygen absorption had ceased. The procedure for catalytic oxidations with the copper(II) complex **4** was identical to that described above except that the complex was generated in 30 ml of methanol with 0.40 mmol of $CuCl_2$ and 0.20 mmol of **1**. The product was isolated by evaporation of the solvent followed by chromatography on silica gel (grade 62 special).

2.6. Reactions with the Cu(I)–$(PD)_2(DIEN)_2$–dioxygen complex

2.6.1. Oxidation of hydroquinones

Hydroquinone (HQ): To a solution of complex **2** (prepared from 93.0 mg of **1** and 171 mg of $Cu(CH_3CN)_4PF_6$) was added 338 mg of hydroquinone. The reaction system was purged with oxygen, and on termination of the reaction, the solvent was removed on a rotary evaporator. The product was then extracted with CH_2Cl_2 and chromatographed on silica gel. Benzoquinone was eluted from the column with $CHCl_3$. ^{1}H NMR ($CDCl_3$) (benzoquinone) δ 5.30(s). ^{13}C NMR ($CDCl_3$) δ 136.50 (CC), 187.2 (CO); mp 111–114°C, lit. 115°C.

t-Butylhydroquinone (TBHQ): The substrate (419 mg) was added to a solution of **2**, which was prepared from 101 mg of **1** and 186 mg of $Cu(CH_3CN)_4PF_6$, and the system was purged with dioxygen according to the procedure stated above. When the reaction ceased, the solvent was removed on a rotary evaporator, the product was extracted with CH_2Cl_2 and chromatographed on silica gel. Elution with *n*-hexane produced *t*-butylbenzoquinone. ^{1}H NMR ($CDCl_3$) δ 1.29(s,9H) 6.68(d,1H) 6.60(t,2H). ^{13}C NMR ($CDCl_3$) δ 29.05 (CH_3), 35.25 ($C(CH_3)_3$), 131.48 ($CCC(CH_3)_3$), 134.88 (*C*CO), 138.63

(*C*CCO), 156.02 (C*C*C(CH$_3$)$_3$), 187.50 (CO), 188.30 (CO); mp 58–60°C, lit. 56–57°C.

2.6.2. Oxidation of phenols

2,6-*Di-t-butylphenol* (2,6-*DTBP*): The disubstituted phenol (526 mg) was allowed to react with **2** (101 mg of **1** and 187 mg of Cu(CH$_3$CN)$_4$PF$_6$) in an atmosphere of dioxygen. The precipitate which formed during the reaction was filtered, dried and identified as 3,3′,5,5′-tetra-*t*-butyldiphenoquinone. ^{1}H NMR (CDCl$_3$) δ 1.37(s,36H) 7.71 (s,4H), ^{13}C NMR (CDCl$_3$) δ 29.58 (CH$_3$), 36.02 (*C*(CH$_3$)$_3$), 126.00 (*C*CC(CH$_3$)$_3$), 136.12 (C*C*C(CH$_3$)$_3$), 150.43 (CC), 186.46 (CO); mp 245°C, lit. 243°C.

2,6-*Dimethoxyphenol* (2,6-*DMP*): The oxidation of this disubstituted phenol was accomplished with 272 mg of substrate and **2** (prepared from 67.6 mg of **1** and 125 mg of Cu(CH$_3$CN)$_4$PF$_6$) in the presence of excess dioxygen. The precipitate, which formed during the reaction, was filtered, dried and identified as 3,3′,5,5′-tetramethoxydiphenoquinone. ^{1}H NMR (CDCl$_3$) δ3.83 (s,12H) δ7.35 (s,4H), mp 287°C (dec.) lit. 290°C (dec.).

2,4-*Di-t-butylphenol* (2,4-*DTBP*): The phenol (491 mg) was added to a solution of **2** (94.7 mg of **1** and 174 mg of Cu(CH$_3$CN)$_4$PF$_6$) and the reaction was carried out under an atmosphere of dioxygen. When oxygen uptake ceased, the solvent was reduced to approximately 3 ml on a rotary evaporator and chromatographed on silica gel. Eluting with CHCl$_3$ gave a mixture of 2,4-DTBP and a small amount of 3,3′,5,5′-tetra-*t*-butyl-2-2′-dihydroxybiphenyl. ^{1}H NMR (CDCl$_3$) δ1.3 (s,9H), 1.44 (s,9H), 4.64 (s,1H), 7.24 (d, overlaps with solvent peak). ^{13}C NMR (CDCl$_3$) δ 30.3 (*C*H$_3$), 35.0 (*C*(CH$_3$)$_3$), 36.0 (*C*(CH$_3$)$_3$), 123.5 (CC), 129.5 (CC), 137.0 (*C*C(CH$_3$)$_3$), 144.0 (*C*C(CH$_3$)$_3$), 150.5 (COH).

2.6.3. Oxidation of catechols

3,5-*Di-t-butylcatechol* (3,5-*DTBC*): The substrate 3,5-DTBC (482 mg) was reacted with **2** (93.2 mg of **1** and 172 mg of Cu(CH$_3$CN)$_4$PF$_6$) in excess dioxygen. At the end of the reaction the solvent was removed on a rotary evaporator, extracted with CH$_2$Cl$_2$ and chromatographed on silica gel. Eluting with CHCl$_3$ gave 3,5-di-*t*-butyl-1,2-benzoquinone. ^{1}H NMR (CDCl$_3$) δ 1.21 (s,9H), 1.26 (s,9H), 6.20 (d,1H), 6.92 (d,1H). ^{13}C NMR δ 27.87 (CH$_3$), 29.20 (CH$_3$), 35.47 (*C*(CH$_3$)$_3$), 36.02 (*C*(CH$_3$)$_3$), 122.08 (CH), 133.46 (CH), 149.93 (*C*C(CH$_3$)$_3$), 163.32 (*C*C(CH$_3$)$_3$), 180.03 (CO), 181.12 (CO).

4-*t-Butylcatechol* (4-*TBC*): Oxidation of 4-TBC (416 mg) was performed with **2** (99.8 mg of **1** and 184 mg of Cu(CH$_3$CN)$_4$PF$_6$) in excess dioxygen. On termination of the reaction the solvent was reduced to 3 ml on a rotary evaporator and chromatographed on silica gel. The second fraction obtained on eluting with CHCl$_3$ was found to be the γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester. Only a small amount of the lactone was obtained. ^{1}H NMR (CDCl$_3$) δ 1.32 (s,9H) 3.90 (s,3H), 5.79 (s,1H), 6.30 (s,1H).

4-*Methylcatechol* (4-*MC*): The substrate 4-MC (335 mg) was reacted with **2** (90.5 mg of **1** and 167 mg of Cu(CH$_3$CN)$_4$PF$_6$) under an atmosphere of dioxygen. At the end of the reaction the product solution was reduced to approximately 3 ml on a rotary evaporator and chromatographed on silica gel. Elution with CHCl$_3$ gave, as the first fraction, the γ-lactone of 3-hydroxy-4-methylmuconic acid ester. Only a trace amount of the product was obtained. ^{1}H NMR (CDCl$_3$) δ 2.20 (s,3H), 3.82 (s,3H), 5.72 (s,1H), 6.24 (s,1H).

2.6.4. Oxidation of 3,4-dimethylaniline (3,4-DMA)

The complex **2** was generated with 88.9 mg of **1** and 164 mg of Cu(CH$_3$CN)$_4$PF$_6$ for the oxidation of 295 mg of 3,4-DMA in excess dioxygen. At the end of the reaction the solvent was removed on a rotary evaporator and the product was extracted with CH$_2$Cl$_2$ and chromatographed on silica gel. Eluting with CHCl$_3$ gave 3,3′4,4′-tetramethylazobenzene as the second fraction. ^{1}H NMR (CDCl$_3$) δ 2.34 (s,3H), 2.36 (s,3H), 7.25 (d, overlaps with solvent peak), 7.68 (m,2H). ^{13}C NMR (CDCl$_3$) δ 19.9 (CH$_3$), 120.7 (CC), 123.3

Table 1
Oxidations with $[Cu_2(PD)_2(DIEN)_2]^{2+}$ and dioxygen

Substrate	Conversion (%)	Turnover	Product
2,6-dimethoxyphenol	46	3	3,3′,5,5′-tetramethoxydiphenoquinone
2,6-di-*t*-butylphenol	56	3	3,3′,5,5′-tetra-*t*-butyldiphenoquinone
2,4-di-*t*-butylphenol	< 1	< 1	3,3′,5,5′-tetra-*t*-butyl-2,2′-dihydroxybiphenyl
hydroquinone	43	5	benzoquinone
t-butylhydroquinone	38	4	*t*-butylbenzoquinone
3,5-di-*t*-butylcatechol	43	4	3,5-di-*t*-butyl-1,2-benzoquinone
4-*t*-butylcatechol	< 1	< 1	γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester
4-methylcatechol	< 1	< 1	γ-lactone of 3-hydroxy-4-methylmuconic acid ester
3,4-dimethylaniline	6	< 1	3,3′,4,4′-tetramethylazobenzene

(CC), 130.2 (CC), 137.3 (*C*CH3) 139.8 (*C*CH3), 151.2 (CN). *m/e* 238.

2.7. Reactions with the Cu(II)–$(PD)_2(DIEN_2$ complex

The hydroquinones, phenols, catechols and 3,4-DMA were oxidized in excess dioxygen in the presence of **4**. Except for 4-TBC and 3,4-DMA, in which case no product was detected, the products obtained were identical to those for oxidations with **2** in excess dioxygen.

2.8. Stoichiometric oxidation reactions

The reaction vessel used in stoichiometric oxidations was identical to that used for catalytic oxidations. Typically, 0.010 mmol of the substrate in 10 ml of methanol was added to 0.020 mmol of the complex **4** in 60 ml of methanol. The reaction was conducted under argon and the appearance of products was followed spectrophotometrically. The general procedure for reactions with the dioxygen complex **3** involved generating the complex in 60 ml of a 5:1 methanol/acetonitrile mixture with approximately 0.010 mmol of **1** and 0.020 mmol of $Cu(CH_3CN)_4PF_6$. The system was then purged with oxygen for 20 min, then oxygen was removed by purging with argon. The reaction was allowed to take place under an atmosphere of argon. Product formation was followed by observing the absorbance of the reaction solution at wavelengths characteristic of the product. Stoichiometric reactions were performed in order to examine any difference in rate, for a particular substrate, for oxidations with **3** and **4**. The product obtained with a particular substrate was the same whether the reaction was performed with **3** or **4**.

2.9. Kinetic studies

Reactions of hydroquinones, phenols and catechols with the dioxygen complex, **3**, and with the copper(II) complex, **4**, under argon were performed in a reaction vessel which was connected to a quartz 1.00 cm flow cell. The reaction vessel and cell holder were thermostated at 25.0 ± 0.2°C and the formation of product was followed by the time dependence of the absorbance of a characteristic band for the particular product. Except initially, the concentration of the dioxygen complex **3** is believed to be a constant fraction of the dinuclear Cu(I) complex **2** at constant pressure of dioxygen, so that kinetic measurements of the order of the oxidation reaction rate dependence on **2** also applies to **3**. The identical procedure was used to investigate the reaction kinetics between 3,5-DTBC and both **3** and **4** in the presence of triethylamine.

3. Results and discussion

3.1. Reactions of the Cu(I)–$(PD)_2(DIEN)_2$–dioxygen complex, 3, and the Cu(II)–$(PD)_2(DIEN)_2$ complex, 4

Table 1 gives a summary of the oxidation reactions carried out with **2** and dioxygen and the

Table 2
Oxidations with the $Cu^{II}_2(PD)_2(DIEN)^{4+}_2$ complex

	Conversion (%)	Turnover	Product
2,6-dimethoxyphenol	46	2	3,3′,5,5′-tetramethoxydiphenoquinone
2,6-di-*t*-butylphenol	39	3	3,3′,5,5′-tetra-*t*-butyldiphenoquinone
t-butylhydroquinone	64	6	*t*-butylbenzoquinone
2,4-di-*t*-butylphenol	0	0	–
hydroquinone	35	3	benzoquinone
3,5-di-*t*-butylcatechol	73	5	3,5-di-*t*-butyl-1,2-benzoquinone
4-*t*-butylcatechol	0	0	–
4-methylcatechol	<1	<1	γ-lactone of 3-hydroxy-4-methylmuconic acid ester
3,4-dimethylaniline	0	0	–

respective oxidation products obtained. A summary of the oxidation reactions performed by **4** is given in Table 2.

A previous investigation [37] has demonstrated that the complex cation of the copper(II) thermal degradation product of **3** may be prepared from **1** and $CuCl_2$. These two compounds showed parallel physical characteristics. For the following oxidation reactions the complex cation **4** was prepared directly from **1** and $CuCl_2$.

3.1.1. Oxidation of hydroquinones

When a solution of hydroquinone (HQ) or *t*-butylhydroquinone (TBHQ) was purged with oxygen in the absence of the complex no oxidation product was detected in the solution within a period of 2 h. However, in the presence of **3** the solution gradually changed color from brown purple to yellow green and a brown precipitate formed. When the reaction was performed under argon, HQ was converted to benzoquinone and TBHQ was converted to *t*-butylbenzoquinone. The identical products were obtained when reactions occurred in excess oxygen in which case the conversions were catalytic in nature. For both stoichiometric and catalytic oxidations the final copper(II) product was dark brown in color. The electronic absorption spectrum showed a band with a maximum ca. 600 nm.

For oxidations with **4** under conditions of excess dioxygen the color change was from green to brown purple and ultimately oxidation products benzoquinone and *t*-butylbenzoquinone were obtained, respectively, when HQ and TBHQ were substrates. In addition to the oxidation product in each case, a brown residue was also obtained. When dissolved in $CDCl_3$, no ^1H NMR signals were observed, probably because of the presence of paramagnetic copper(II) centers. The same observation was made when the reactions were allowed to take place in an argon atmosphere, in which case the final copper(II) product was brown in color.

3.1.2. Oxidation of phenols

Both 2,6-DTBP and 2,6-DMP were oxidized by **3** giving the respective diphenoquinones as the oxidation products (Table 1). When 2,6-DTBP was added to a solution containing **3** and excess dioxygen there was a color change from dark purple to dark brown and a precipitate (identified as 3,3′,5,5′-tetra-*t*-butyldiphenoquinone) was formed. Addition of 2,6-DMP to **3** in the presence of excess dioxygen resulted in a similar color change and the solid precipitate was identified as 3,3′,5,5′-tetramethoxydiphenoquinone. Reactions in excess dioxygen gave the same products as those which occurred under argon. The substrate 2,4-DTBP was oxidized to 3,3′,5,5′-tetra-*t*-butyl-2,2′-dihydroxybiphenyl with **3** but only under conditions of excess dioxygen.

While oxygenation of a solution of 2,6-DTBP or 2,6-DMP did not result in oxidation products, in the presence of **4** and dioxygen, both 2,6-DTBP and 2,6-DMP were transformed to the respective diphenoquinones which precipitated out of solution. The solution color changes were from green to dark brown for 2,6-DTBP and green to purple

brown for 2,6-DMP. In both conditions of excess dioxygen and argon atmosphere the final copper(II) complex was brown in color and did not give an ^{1}H NMR spectrum. The electronic absorption spectrum of the brown complex showed an absorption maximum at approximately 600 nm indicating the presence of a copper(II) species. When 2,4-DTBP was the substrate no oxidation product was detected.

3.1.3. Oxidation of catechols

Addition of 3,5-DTBC and triethylamine to a solution of **3** in excess dioxygen resulted in a color change from grey purple to green. When 4-TBC was the substrate the color change was from grey purple to red brown. Under an atmosphere of argon, 3,5-di-*t*-butyl-1,2-benzoquinone was obtained as the oxidation product of 3,5-DTBC whereas the γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester resulted from the oxidation of 4-TBC. In contrast to 4-TBC where oxidation in excess dioxygen occurred to an extent of less than one turnover (Table 1) 3,5-DTBC was catalytically converted to the corresponding quinone. The final copper complexes for oxidation with **3** in excess dioxygen were dark brown in color and did not give a ^{1}H NMR spectrum. This suggests that copper(II) complexes are formed. The results obtained with 4-MC as a substrate were similar to those obtained with 4-TBC.

Oxidation of catechols did not proceed in the absence of triethylamine and/or the Cu(II) complex **4**. When a 2:1 mole ratio of triethylamine to catechol was introduced into the reaction mixture containing **4** in excess oxygen, 3,5-DTBC was converted to the corresponding quinone whereas 4-MC was converted to the corresponding γ-lactone. No product was obtained with 4-TBC. Among the three catechols investigated only 3,5-DTBC gave an oxidation product under an argon atmosphere and this substrate was also found to be catalytically converted to the corresponding quinone. The final copper(II) complex (implied by the lack of an ^{1}H NMR spectrum) was green in color for 3,5-DTBC and brown for both 4-MC and 4-TBC.

3.1.4. Oxidation of 3,4-DMA

Under conditions of excess dioxygen, 3,4-DMA was converted to 3,3′,4,4′-tetramethylazobenzene in the presence of **3** with low yield. The addition of triethylamine did not improve the yield of product. Attempted oxidation under argon gave no measurable amount of product after 48 h.

No product was obtained on the attempted oxidation of 3,4-DMA with **4**, both under conditions of excess dioxygen and under an argon atmosphere within a time period of 48 h.

3.2. Kinetic measurements on stoichiometric reactions

In order to establish the relative importance of copper(I) and copper(II) species in the catalytic process, a kinetic study on the stoichiometric reactions of substrates with **3** and **4** was undertaken. For each substrate the course of the reaction was monitored by observing the time-dependent changes in absorption at a particular wavelength characteristic of the product. Where there is oxidation by both **3** and **4**, the curve for copper(I)–dioxygen oxidation lies above that for copper(II) oxidation indicating that copper(I) oxidations generally occur at more rapid rates than copper(II) oxidations. The initial rates for oxidations with **3** and **4** were calculated from the rate curves described above. Initial rates were recorded in order to avoid the complications arising from oxidation of substrate by the degradation product of **3** and the copper(II) complex produced as a consequence of oxidation by the copper(I)–dioxygen complex. Such interferences were not factors for anaerobic copper(II) oxidations since the resulting copper(I) is inactive in the absence of dioxygen. The reactions were performed under conditions of thirty-fold excess substrate in order to establish pseudo first order conditions and obtain rates which were convenient to measure. Moreover, under the conditions described above, any contribution to the retardation in rate arising from degradation of **3** is considered to be negligible. The initial rates obtained for phenols, hydroquinones, catechols, and 3,4-DMA in this

investigation are reported in Table 3. The salient feature here is the higher initial pseudo first order rate for oxidations with **3** than for oxidations with **4**. In addition, it is noted that only those substrates which are oxidized by **3** and **4** are catalytically transformed to their products (Tables 1 and 2).

3.3. Reaction of 3,5-DTBC with 3 and 4

The spectral characteristics of a 3:1 methanol/acetonitrile solution of the dinuclear copper(I) complex **2** and its oxygen adduct have been previously described [37]. The complex **2** exhibits charge transfer absorptions at 275, 430 and 575 nm. Spectral changes accompanying addition of 3,5-DTBC to **3**, under argon, in a 3:1 solution of CH_3OH to CH_3CN show that the maximum at 575 nm is maintained (not shown in Fig. 1) and that at 275 nm slowly decreases with time (Fig. 1). The predominance of copper(I) features means that there is significant oxidation by the copper(II) species produced as a result of oxidation by the copper(I)–dioxygen complex. The appearance of product is signalled by the absorption maximum at 400 nm. At the point where the appearance of product is first observed the solution has an orange brown color. On the other hand, spectral changes of **4** in a methanolic solution of 3,5-DTBC under argon show the growth of absorptions at 275 and 580 nm and disappearance of the d–d absorption at 720 nm, which is characteristic of **4**, indicating that the complex is

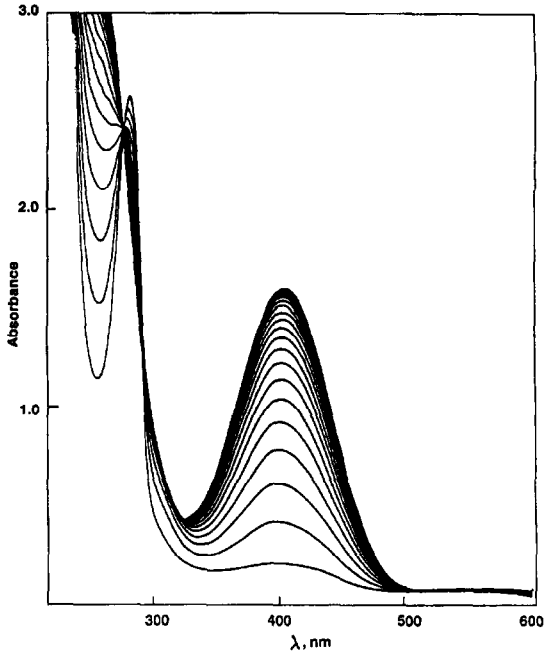


Fig. 1. Spectral changes accompanying the oxidation of 3,5-DTBC with $[Cu(I)_2(PD)_2(DIEN)_2] + O_2$ under argon (concentration of complex is 2.86×10^{-4} M).

reduced by 3,5-DTBC to give a copper(I) complex. The reaction between **4** and 3,5-DTBC was also monitored spectrophotometrically at 400 nm in the presence of an excess of dioxygen. The results (Fig. 2) indicate, from the two slopes, that there are at least two processes occurring consecutively. The initial gradient is considered to arise from the slow oxidation with Cu(II). Since the reaction occurs in the presence of excess dioxygen any Cu(I) formed as a consequence of this oxidation is capable of absorbing dioxygen and form-

Table 3
Initial rates for Cu(I)–dioxygen and Cu(II) oxidations of various substrates

Substrate	Product	Initial pseudo first order rates, $M\ s^{-1}$	
		$Cu(I) + O_2$	Cu(II)
2,6-dimethoxyphenol	3,3′,5,5′-tetramethoxydiphenoquinone	7.7×10^{-5}	1.5×10^{-5}
2,6-di-*t*-butylphenol	3,3′,5,5′-tetra-*t*-butyldiphenoquinone	6.7×10^{-5}	1.2×10^{-5}
2,4-di-*t*-butylphenol	3,3′,5,5′-tetra-*t*-butyl-2,2′-dihydroxybiphenyl	$< 1.4 \times 10^{-10}$	0
hydroquinone	benzoquinone	8.3×10^{-4}	8.9×10^{-5}
t-butylhydroquinone	*t*-butylbenzoquinone	9.3×10^{-4}	1.9×10^{-4}
3,5-di-*t*-butylcatechol	3,5-di-*t*-butyl-1,2-quinone	3.8×10^{-4}	3.8×10^{-5}
4-*t*-butylcatechol	γ-lactone of 3-hydroxy-4-*t*-butylmuconic acid ester	5.6×10^{-7}	≈ 0
4-methylcatechol	γ-lactone of 3-hydroxy-4-methylmuconic acid ester	≈ 0	5.5×10^{-9}
3,4-dimethylaniline	3,3′,4,4′-tetramethylazobenzene	2.0×10^{-5}	≈ 0

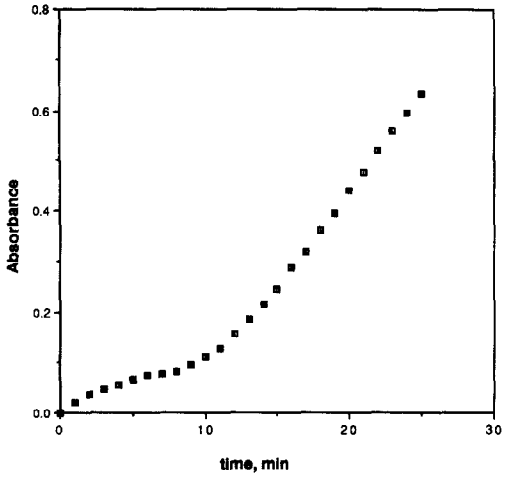


Fig. 2. Time dependence of the catalytic formation of 3,5-di-*t*-butyl-1,2-benzoquinone in the presence of **4** (1.76×10^{-4} M) and excess dioxygen ($P_{O_2}=1$ atm) monitored at 400 nm.

ing a Cu(I)–dioxygen complex. It is this species, in combination with Cu(II), which now performs oxidations on substrates. Once the Cu(I)–dioxygen complex is produced the reaction occurs according to a catalytic cycle which will be discussed presently. Therefore the second gradient of Fig. 2 corresponds to the catalytic rate of oxidation of 3,5-DTBC.

3.3.1. Kinetics of the reaction between 3 and 3,5-DTBC

In order to further understand the reaction between **3** and 3,5-DTBC the kinetics of this reaction was investigated. In the presence of a large excess of 3,5-DTBC any contribution to the initial rate of oxidation from the thermal decomposition of **3** is negligible. Under these conditions the formation of 3,5-di-*t*-butyl-1,2-benzoquinone (DTBQ) was followed by the increase in absorption at 400 nm (Fig. 3). The rates of formation of the benzoquinone were determined from the maximum slopes of Fig. 3 and were plotted against initial concentration of complex (Fig. 4) and initial concentration of catechol (not shown). The rate was found to be first order with respect to **3** and zero order with respect to substrate. The rate expression therefore has the form

$$(d[\mathrm{DTBQ}]/dt)_{max}=k_1[\text{complex }\mathbf{2}]_i \qquad (1)$$

where [complex **2**]$_i$ is the initial concentration of complex. The value of k_1 is calculated as $1.3\times10^{-3}\ s^{-1}$.

The rate of formation of the 1,2-benzoquinone in the presence of **4** and triethylamine was also investigated. A typical time dependence of the absorption at 400 nm shows that the shape of the curve may be represented by the sum of two expo-

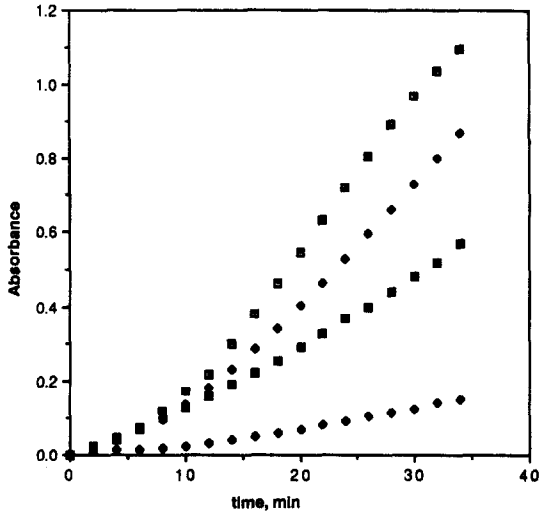


Fig. 3. Time course for the formation of 3,5-di-*t*-butyl-1,2-quinone in the presence of the dioxygen, complex **2**. The absorbance was measured at 400 nm under stoichiometric conditions. The molar concentration of substrate was □, 5.13×10^{-4} ♦, 3.81×10^{-4} ■, 2.50×10^{-4}; ◇, 1.34×10^{-4}.

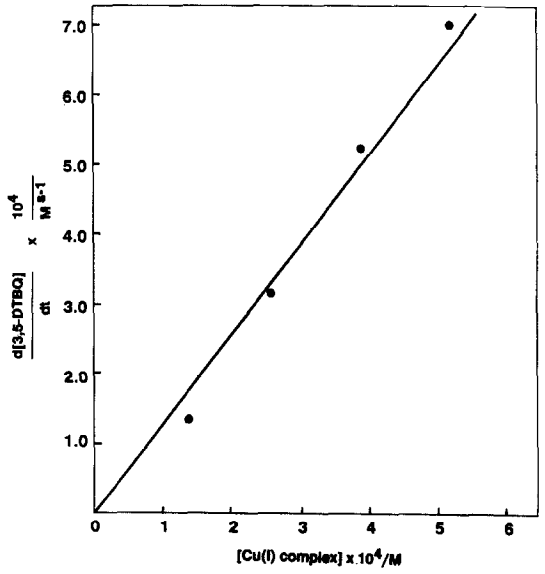


Fig. 4. Initial rate of formation of 3,5-DTBQ as a function of [Cu(I) complex].

nential terms of the form ae^{-mt}, where a is a pre-exponential constant, m is a constant which is derived from the root of the integrated first order rate equation and t represents time. The plot of ln$A$ vs. t (Fig. 5) shows that there is considerable curvature in the region for small values of t. The bimodal nature of the reaction course may be explained by considering that there are two consecutive reactions occurring and that there is some measure of overlap between the first and second reactions. The first reaction is very fast (estimated rate constant $> 1 \times 10^2\ s^{-1}$) and is followed by a much slower process. Since the difference in rates is greater than 10^2, the reactions were considered to be separable kinetically [41] and were treated as such. A plausible conclusion is that the first segment pertains to the formation of a substrate-bound copper complex, which is a precursor to electron transfer, since the absorption spectrum of the reaction solution initially showed a slight change over that of the complex alone when no product was yet detected. The subsequent reaction, which is observed spectrophotometrically, is associated with formation of the 1,2-benzoquinone. Under pseudo first order conditions the reaction rate was found to be a linear function of both [complex **4**] and [3,5-DTBC].

3.3.2. *Oxidation of hydroquinones and phenols*

The oxidation of hydroquinones and phenols was found to proceed under both conditions of excess dioxygen and in an argon atmosphere with **3** and **4**. For the reactions of phenols, only oxidatively coupled products were obtained with both **3** and **5** whereas hydroquinones were converted to the respective 1,4-benzoquinones. Reactions of phenols and hydroquinones with copper(I) are likely to proceed in the same manner as that described for catechols; the initial step is formation of a redox unstable copper–substrate precursor. These reactions were also found to be expedited in the presence of triethylamine suggesting that substrate deprotonation is an important process for formation of the precursor. The kinetic assistance given to the reaction by the base also implies that hydrogen abstraction by the per-

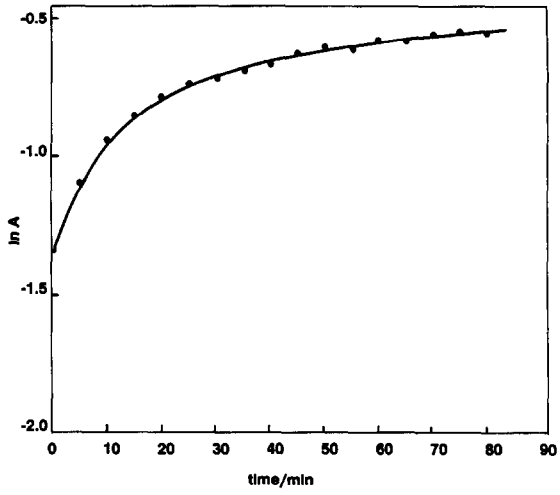
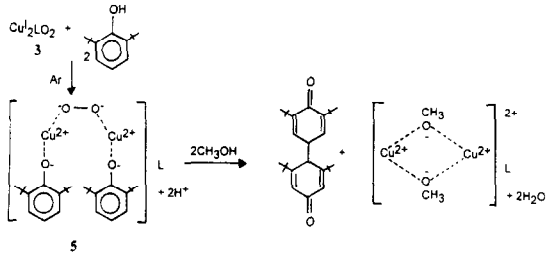


Fig. 5. Plot of ln$A$ vs. time for the formation of 3,5-di-*t*-butyl-1,2-benzoquinone in the presence of the Cu(II)–$(PD)_2(DIEN)_2$ complex, **4**, under argon, where A is absorbance at 400 nm.

oxo complex in oxidations with **3** may be a slow process. Such assistance was found to be unnecessary when oxidations were performed with the Cu(I)–$(FD)_2(DIEN)_2$ complex [35], in which case the peroxo derivative must be a stronger base. Oxidations initiated by **2** in the presence of excess dioxygen are expected to proceed through the dinuclear Cu(I)–$(PD)_2(DIEN)_2$–O_2 complex **3**, which is formed by absorption of O_2 by **2**. The phenol or hydroquinone then rapidly binds with the peroxo complex **3** forming a precursor to electron transfer shown below as **5**. If the ultimate fate of the dioxygen, which initially binds to **2**, is reduction to water, then the substrate must provide two electrons to the redox system. In view of the fact that phenols are 1e transfer reagents, the requirement here is for having two phenolate units presented to the peroxo complex in order that two additional electrons may be provided for the reduction of peroxide to water. The species formed is presumably the peroxo complex with one phenolate moiety bonded to each copper center (Scheme 1).

Another possibility is the formation of a di-μ-phenolate copper(II) complex of the type proposed by Kitajima et al. [34], in which there is replacement of peroxide by a second phenolate anion and production of H_2O_2. Since there is no evidence of the presence of H_2O_2 from the thermal



Scheme 1.

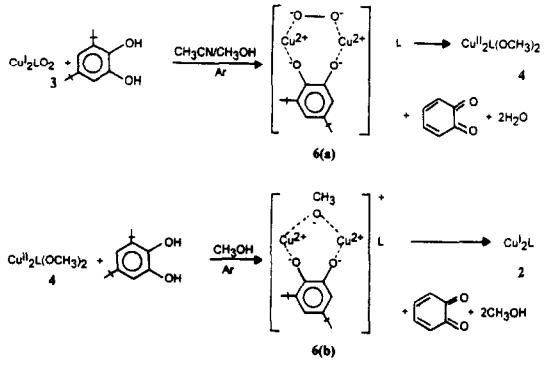
degradation of **3** [37] it is suggested that the precursor does not contain bridging phenolate units. In addition, the use of CPK models has demonstrated that the existence of a di-bridged species is very unlikely from a steric point of view. This complex–substrate entity subsequently dissociates after electron transfer to give a copper(II) complex and the oxidation product. The initial product is thought to be the phenoxide radical, two of which couple to produce the diphenoquinone.

This type of reaction sequence is also likely for oxidation of 2,6-disubstituted phenols with **3**. The compound 1,4-benzoquinone has been reported as a minor oxidation product in the reaction of 2,6-DTBP and 2,6-DMP when the catalyst was the $Cu(I)–(FD)_2(DIEN)_2–O_2$ complex [35], however, it was not detected when **3** was used as the active oxidant. In contrast, when 2,4-di-*t*-butylphenol was used as substrate the product was the coupled 3,3′,5,5′-tetra-*t*-butyl-2,2′-dihydroxybiphenyl in which case the reaction mechanism is also expected to involve initial production of a phenoxide radical which dimerizes to give the dihydroxybiphenyl. Since the 4-position is blocked there is no pathway for production of the diphenoquinone. This reaction was not found to be catalytic under an atmosphere of oxygen.

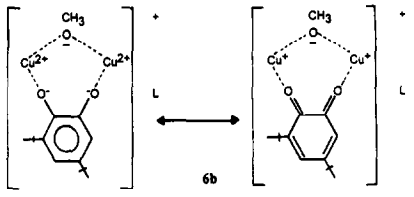
3.3.3. Oxidation of catechols

There is spectroscopic and kinetic evidence that the aerobic oxidation of 3,5-DTBC with **3** proceeds through a substrate bound precursor to electron transfer. The substrate bound peroxo intermediate (shown below as **6**) is proposed by analogy with the reactions with phenols. In this case it is reasonable to suggest that only one substrate unit will bind to the complex since catechol is a 2e reductant and contains two binding positions. Subsequent to electron transfer there is release of the product to give initially a copper(II) dinuclear complex represented by **4**. The rate determining step is considered to be the formation of the dicopper(II)–peroxo-catecholate complex (Scheme 2).

Oxidations may also be initiated with **4** in the absence of dioxygen. Spectral changes indicate that, on addition of 3,5-DTBC to the solution, there is a rapid reduction to **2** which persists until all the substrate is consumed. Similar to oxidations with **3** the precursor to electron transfer most likely consists of the 3,5-DTBC substrate bonded to the copper(II) complex which is formed from the displacement of a methoxo ligand by a catecholate moiety. Intermediates of this type have been proposed [42–46] and semiquinone [46] and catecholate [47] complexes have actually been isolated. In the study of oxidation of catechols with the $Cu(I)_2–(FD)_2(DIEN)_2$ complex [35] there is NMR evidence (paramagnetic broadening of proton resonances related to the catechol moiety) of formation of a complex–catecholate intermediate. The stabilities of intermediates resembling **6** were found to depend on the redox potential of the corresponding quinone; the higher the reduction potential of the quinone, the more stable is the copper–catecholate complex [42,43]. The intermediates described act as precursors to the electron transfer reaction. Subsequent to electron transfer there is release of the product to give initially a copper(II) dinuclear complex repre-



Scheme 2.



Scheme 3.

sented by **6**, two resonance forms of which are depicted in Scheme 3: **6b**. There are also intermediate forms in which the organic ligand is written as a semiquinone. It is reasonable to expect that dissociation of the product is the rate determining step in stoichiometric oxidations involving **4** since formation of the precursor is considered to be a rapid process and electron transfer is generally extremely rapid compared with bond making and bond breaking processes.

In the study of oxidation of catechols with the $Cu(I)_2$–$FD)_2(DIEN)_2$ complex [35] there was NMR evidence of formation of a complex–catecholate intermediate. When 3,5-DTBC was oxidized with the Cu^{II}_2–$(PD)_2(DIEN)_2$ complex, in excess dioxygen, at the end of the reaction a green Cu(II) complex was obtained. On the other hand, oxidation of 4-MC and 4-TBC with **4** produced brown colored compounds which are not ^{1}H NMR active. The implication here is that a type of complex–substrate entity may be formed since the green color of **4** is not regenerated.

The most striking feature of these oxidations is the fact that ring cleavage does not occur with the di-substituted catechols, in which case the oxidation reaction terminates at the production of a corresponding 1,2-benzoquinone. The reaction pathway is thought to be a function of the stability of the intermediate **6**, the monosubstituted catechols forming more redox unstable complexes than the disubstituted catechol. This finding is consistent with the fact that there is only one electron-releasing *t*-butyl group on each substrate. In support of the redox instability of the proposed intermediates with monosubstituted catechols is the fact that oxidations with 3,5-DTBC yield a green copper(II) complex ultimately whereas with 4-MC and 4-TBC as substrates a copper–substrate complex is indicated.

Recent results [48–50] point toward a relationship between the structure and reactivity of copper(II) mononuclear and dinuclear complexes. Generally, it has been observed that planar copper(II) complexes do not catalyze oxidation of catechols, whereas copper(II) complexes with a square pyramidal or trigonal bipyramidal arrangement of bonds are active. There is evidence [51] suggesting that tyrosinase is five coordinate with respect to copper when the catecholate intermediate is attached to the copper centers. X-ray analysis [17] has revealed that the copper(II) ions of the Cu^{II}–$(FD)_2(DIEN)_2$ complex are four-coordinate, the geometry being described as distorted square planar. An investigation of the solution structure of **4** suggests that the bond configuration about the central atom is distorted square pyramidal [37]. Complex **4** is also expected to contain methoxy ligands which are easily displaced in order to accommodate the oxygen atoms of the catechol moiety. In view of the relationship between structure and reactivity as suggested by Malachowski et al. [48,50], in which the effectiveness of a catalyst increases as the geometry approaches trigonal bipyramidal, it is proposed that there is a more highly distorted geometry in **4** than in the Cu^{II}–$(FD)_2(DIEN)_2$ complex. In addition to structural requirements, the effectiveness of catalysts for the oxidation of catechols was found to be a function of the Cu–Cu separation in dinuclear complexes [52]. The most efficient catalysts are usually those with a Cu–Cu separation within the range 3–5 Å. The Cu–Cu distance in the Cu^{II}–$(FD)_2(DIEN)_2$ complex was determined as 2.96 Å [17]. The improved catalytic action displayed by **4** implies that the 'steric match' criterion of Oishi et al. [52] may be better satisfied in this case.

3.4. The catalytic cycle

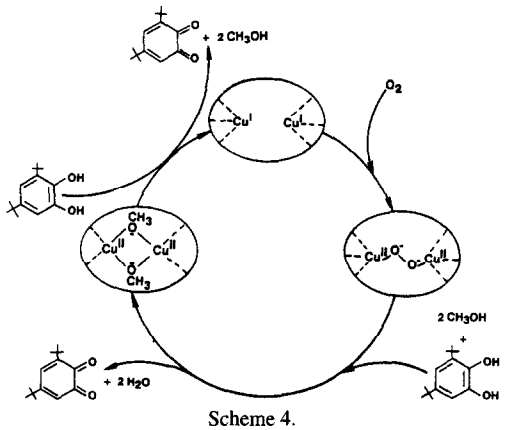
Examination of Tables 1, 2 and 3 shows that catalytic conversions were obtained only for those substrates which were oxidized by both **3** and **4**. A distinction between the oxidation processes involving **3** and **4** has been established through

the determination of initial rates of conversion of substrate in the presence of each complex. The data contained in Table 3 show that initial rates of copper(I)–dioxygen complex oxidations are generally more rapid than oxidations with copper(II). These observations led to the proposal of the involvement of both copper(I) and copper(II) in the catalytic cycle. Scheme 4 depicts a suggested catalytic cycle for the oxidation of 3,5-DTBC in the presence of excess dioxygen. The process proposed here is essentially the same as that suggested for oxidation of phenols and hydroquinones by a $Cu(I)-(FD)_2(DIEN)_2$–dioxygen complex in a previous investigation [35]. When the initiator is the copper(I) complex, the essential steps involve (i) oxygen uptake by **2** to form the peroxo complex, (ii) binding of the catechol to the peroxo complex and its oxidation to produce the quinone and a copper(II) complex and (iii) the oxidation of 3,5-DTBC by the copper(II) complex to give the quinone and the copper(I) complex. Then the copper(I) complex formed as a consequence of oxidation by copper(II) absorbs oxygen to form the peroxo complex; hence the cyclic process is continued. The water produced in step (ii) is expected to inhibit oxidation of the catechol since it competes with the substrate for the macrocyclic complex hence there is a gradual retardation of the catalytic process. It is noted that the cycle may be initiated with either **3** or **4**.

4. Summary

Macrocyclic copper(I) and copper(II) complexes based on $(PD)_2(DIEN)_2$ have been prepared and used in the oxidation of hydroquinones, phenols, catechols and 2,4-DMA. It was discovered that oxidations were catalytic only when both copper(I) and copper(II) complexes are active oxidants. Hydroquinones were oxidized to benzoquinones, 2,6-DTBP and 2,6-DMP were oxidized to the corresponding diphenoquinone and 3,5-DTBC was oxidized to the related 1,2-benzoquinone, the reactions being catalytic in nature. On the other hand oxidations of 2,4-DTBP, 4-MC, 4-TBC and 3,4-DMA with **3** and **4** were not found to be catalytic.

Kinetic studies on the oxidation of 3,5-DTBC with **2** and dioxygen have shown that the reaction occurs via a copper(I)–dioxygen complex **3**. Reactions of 3,5-DTBC with **4** have been found to be second order, the rate determining step proposed being the dissociation of the product from the complex.



Scheme 4.

Acknowledgements

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