

The oxidative coupling polymerization of 2,6-dimethylphenol catalyzed by a μ -OCH₃-bridged dicopper(II) complex catalyst

Jian Gao^{a,b,*}, Shun He Zhong^a, Ralph A. Zingaro^b

^a College of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

^b Department of Chemistry, Texas A & M University, College Station, TX 77843-3255, USA

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Abstract

An oxidative coupling reaction intermediate, a μ -OCH₃-bridged dinuclear(II) complex [Cu₂(μ -OCH₃)(μ -OAC)(μ -CH₃OH)(ClO₄)₂Bipy₂](ClO₄) has been synthesized and characterized crystallographically and spectroscopically. This complex crystallizes in the monoclinic space group *P*2₁/*n*, with cell constants *a* = 7.914(2) Å, *b* = 11.434(3) Å, *c* = 34.336(10) Å, α = 90, β = 92.035(5), γ = 90, *V* = 3105.3(14) Å³ and *Z* = 4. The dicopper(II) complex was investigated in the oxidative coupling reaction of 2,6-dimethylphenol (DMP) to polyphenylene ether (PPE) and shown to function as an effective catalyst. The product yield of 70% and PPE selectivity near 99% were achieved.

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1. Introduction

Polyphenylene ether (PPE) is a valuable plastic material due to its properties of chemical stability, high glass transition temperature and self-extinguishing properties [1,2]. A copper(I)-pyridine complex was first found to catalyze the oxidative coupling polymerization of 2,6-dimethylphenol (DMP) by Hay et al. [3]. Since then many investigations have been reported on this O₂ related coupling reaction [4–13]. Our recent work has suggested that a μ -alkoxo bridged dicopper(II) structure serves as the real catalytic center for this oxidative coupling reaction [14]. However, no such an intermediate species has been successfully separated and the formation of the by-product 3,3',5,5'-tetra-methyl-4,4'-diphenoquinone (DPQ) is inevitable in the catalytic reaction. To develop our work towards practical application, it was first found that a μ -alkoxo bridged dicopper(II) complex serves as an effective catalyst in the polymerization of DMP in the presence of NaOMe and imidazole.

The overall oxidative coupling process of DMP to PPE is shown in Scheme 1. The only by-product of this reaction is

DPQ [15]. Thus, the entire reaction process can be monitored by absorption spectra experiments. Three different reaction pathways including the radical, anion and the phenoxonium have been thus far proposed [16]. Our experimental results suggest an alternate reaction mechanism.

2. Experimental

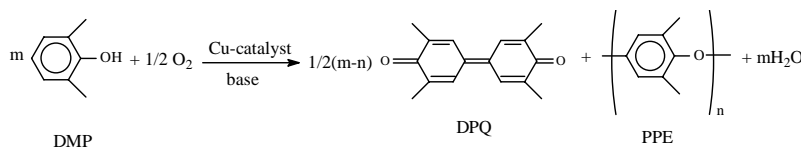
2.1. Materials and measurements

All solvents were purchased from the Sigma–Aldrich Chemical Company and were of analytical grade or better. Methanol was dried over molecular sieves (3 Å) prior to use. DMF was distilled before use. Sodium methoxide (NaOMe) was synthesized by treating methanol with sodium metal under a nitrogen atmosphere and its concentration was determined by titration to be 0.1 mol/l. Dioxygen up-take experiments were performed using in-house designed equipment. Analyses for C, H, and N were carried out on a Perkin-Elmer analyzer, Model 240 and metal contents were determined by EDTA titration. Infrared spectra were recorded on a Perkin-Elmer IR spectrophotometer, FTIR 5300, using KBr-disks. Electronic spectra (in methanol) were measured on a Shimadzu UV-240 spectrophotometer. Solution electrical conductivity measurements were made

* Corresponding author. Tel.: +1-979-845-2732;

fax: +1-979-845-4719.

E-mail address: gao@mail.chem.tamu.edu (J. Gao).



Scheme 1.

with a DKK AD-10 conductometer in DMF solution at room temperature. Variable-temperature magnetic susceptibilities were measured on a SQUID susceptometer (sensitivity $m = 10^{-6}$ emu), over the temperature range of 4–300 K. The applied magnetic field is 1000 Gs and calibrations were made with $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ for the SQUID susceptometer. Diamagnetic corrections were made using Pascal's constants for all of the constituent atoms, and the magnetic moment were calculated using $\mu_{\text{eff}} = 2.828(X_{\text{M}}T)^{1/2}$.

2.2. Preparation of the reaction solution and kinetic study

The catalyst solution was prepared by mixing, in a 50 ml volumetric flask, 0.05×10^{-3} mol of the complex in 10 ml of DMF with 10 ml substrate solution. The substrate solution was prepared by adding 2.5×10^{-3} mol DMP to 10 ml DMF. The basic solution of NaOMe was added accordingly and the total reaction solution was taken to 25 ml.

2.3. Dioxygen up-take experiment

In a typical dioxygen up-take experiment, the solution containing the complex was placed in the reaction flask and the substrate solution, stored in a syringe, was injected in order to initiate the reaction. The concentration of the resulting mixture was 2.0×10^{-3} M for the complex and 1.0×10^{-1} M for DMP, respectively. All reactions were performed at 25 °C at atmospheric pressure under an atmosphere of dioxygen.

The reaction system was stirred magnetically and thermostated at 298 K. After flushing the entire system with oxygen and mixing of the reactants, the measurements were started. When dioxygen was being consumed by the reaction, the decrease in pressure was equalized by injecting water into a gas burette filled with dioxygen, which, in turn, forced O_2 into the reaction vessel. The rise in the water level in the burette is directly proportional to the amount of dioxygen consumed by the reaction system and this change was recorded as a function of time. The initial dioxygen up-take rate can be derived from the resulting oxygen up-take curve from Eq. (1):

$$R_0 = \frac{k\rho_{\text{O}_2}^t}{M_{\text{O}_2}V_r} \quad (1)$$

where k is the initial maximum slope (O_2 l/s); $M_{\text{O}_2} = 32$ g/mol; $V_r = 25$ ml reaction volume; $\rho_{\text{O}_2}^t = \text{O}_2$ density (g/l) at t °C corrected by Eq. (2).

$$\rho_{\text{O}_2}^t = \rho_{\text{O}_2}^{273} \frac{p}{760(1 + \alpha t)} \quad (2)$$

where p is the atmospheric pressure (mmHg); α the temperature factor, 0.00367 K^{-1} ; $\rho_{\text{O}_2}^{273} = \text{O}_2$ density at 0 °C (1.429 g/l).

Since the amount of dioxygen absorbed is proportional to the amount of reacted substrate, the conversion of DMP can also be derived from these data. The amount of DPQ formed during the reaction was determined by UV-Vis spectra by measuring the absorbance at 420 nm. The value of the extinction coefficient was determined by using a solution of pure DPQ synthesized using a literature procedure [17]. As PPE and DPQ are the sole products of this reaction, the amount of C–O coupled product can be calculated from the amount of DPQ and the degree of conversion of DMP.

2.4. Crystal structure determination of the complex

Crystallographic measurements were carried out using a CCD diffractometer with graphite-monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å) and a 12 kW rotating generator. The data were collected at 25 ± 1 °C. Pertinent crystallographic parameters are summarized in Table 1. The structure was solved by direct method and expanded using full matrix least-squares on F^2 .

2.5. Synthesis of the complex catalyst

2.5.1. $[\text{Cu}_2(\mu\text{-OCH}_3)(\mu\text{-OAC})(\mu\text{-CH}_3\text{OH})(\text{ClO}_4)\text{bipy}_2](\text{ClO}_4)$

To a solution containing 0.1 mmol of bipy in 15 ml of MeOH, was added 0.1 mmol $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.05 mmol solid NaOAc. After 5 min, 0.05 mmol of NaOEt in methanol was added to the system and the solution attained a deep green color. After stirring for another 2 h the final solid products was separated, washed with absolute ethanol and diethyl ether for three times and dried in vacuum. The yield was 85%. Calcd. for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{Cl}_2\text{O}_{12} \cdot \text{Cu}_2 \cdot \text{CH}_3\text{OH}$, formula weight 760.47: C, 37.9; H, 3.7; N, 7.4; Cu, 16.7; found: C, 37.8; H, 3.7; N, 7.5; Cu, 17.0%.

IR (KBr, cm^{-1} , selected peaks): 1600, 1480, 1100, 750 and 620. Conductivity (CH_3OH , 10^{-3} M solution at 298 K): $\Lambda_{\text{M}} = 105 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Absorption spectrum (λ_{max} , nm; ϵ , $\text{M}^{-1} \text{ cm}^{-1}$): in CH_3OH , 600 (110), 210 (8200).

3. Results

3.1. Structural characterization of the complex

Satisfactory elemental analyses were obtained for the complex. Molar conductance values fell into the expected

Table 1
Crystallographic data for the complex

Molecular formula	C ₂₄ H ₂₆ Cl ₂ Cu ₂ N ₄ O ₁₂
Formula weight	760.47
Crystal color; habit	Blue
Crystal dimensions	0.3 × 0.25 × 0.2
Crystal system	Monoclinic
<i>a</i> (Å)	7.914(2)
<i>b</i> (Å)	11.434(14)
<i>c</i> (Å)	34.336(15)
α (°)	90
β (°)	92.035(5)
γ (°)	90
<i>V</i> (Å ³)	3105.3(14)
Space group	<i>P</i> 2 ₁
<i>Z</i>	4
ρ (calcd.) (c/g cm ⁻³)	1.627
<i>F</i> (000)	1544
θ range (°)	1.78–26.37
Absorption correction	None
<i>T</i>	298(2)
λ (Å)	0.71073
Absorption coefficient (mm ⁻¹)	1.607
Independent reflections	6344 (<i>R</i> _{int} = 0.0665)
Number of observations	6344 (<i>I</i> > 2.0 σ (<i>I</i>))
<i>R</i> ^a	0.0475
<i>Rw</i> ^b	0.0981
GOF on <i>F</i> ²	0.896
Peak, hole in final difference map (e Å ⁻³)	0.652; -0.451

$$^a R = \sum ||F_o| - |F_c|| / \sum F_o.$$

$$^b Rw = \left\{ \left[\sum (F_o^2 - F_c^2)^2 / \sum w (F_o^2) \right] \right\}^{1/2}.$$

range for a 1:1 electrolyte. The IR spectrum shows characteristic bands at 1600 and 1480 cm⁻¹ which can be assigned to the symmetric and asymmetric vibration of the bridged- μ -carboxyl ligand. A strong band at 750 cm⁻¹ for this complex was diagnostic for the presence of bridged- μ -alkoxo structure. The split ClO₄ vibrations at 1090 and 630 cm⁻¹ indicates the coordinated feature of one of these groups, which is consistent with molar conductance measurement. The electronic spectrum of the complex shows a broad band at ca. 600 nm characteristic of five coordinated Cu(II) ions.

A good single-crystal of suitable quality for X-ray crystallographic analysis was obtained from methanol solution. A view of the X-ray structure is shown in Fig. 1. The bond lengths of O(4)–Cu(2) and O(4)–Cu(1) are 2.351 and 2.350 Å, respectively. They are much longer than those of O(3)–Cu(2) and O(3)–Cu(1) bonds of 1.930 and 1.929 Å (Table 2). This indicates that μ -HOME is a weak bridging ligand compared with μ -OCH₃. One perchlorate anion sits inside the coordination sphere by way of an intramolecular hydrogen bond with the bridged methanol molecule. The hydrogen bond length (H₄–O₇) and bond angle (O–H \cdots O₇) are 2.004 Å and 147.4°, respectively. The other perchlorate functions as a counter ion and is located in the lattice.

3.2. Catalytic intermediates

Previous investigations suggested that the bis-alkoxo bridged dicopper(II) complexes are insoluble in common organic solvents. Therefore, we designed the mixed ligand

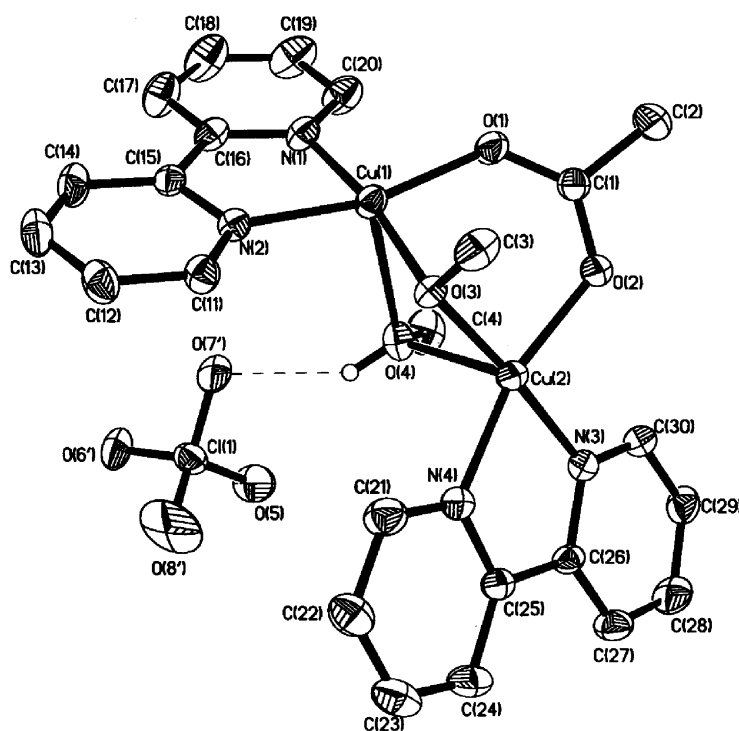


Fig. 1. Crystal structure of the complex.

Table 2
Selected bond lengths and bond angles for the complex

Bond lengths (Å)					
Cu(1)–O(3)	1.930(3)	Cu(2)–O(3)	1.929(3)	C(1)–O(1)	1.255(6)
Cu(1)–O(1)	1.944(3)	Cu(2)–O(2)	1.953(3)	C(2)–O(2)	1.269(6)
Cu(1)–N(2)	2.005(4)	Cu(2)–N(3)	1.989(4)	C(3)–O(3)	1.421(6)
Cu(1)–N(1)	2.009(4)	Cu(2)–N(4)	2.000(4)	C(4)–O(4)	1.426(6)
Cu(1)–O(4)	2.350(4)	Cu(2)–O(4)	2.351(4)	N(1)–C(16)	1.335(5)
Bond angles (°)					
O(3)–Cu(1)–O(1)	94.78(14)	O(2)–Cu(2)–N(3)	91.03(16)		
O(3)–Cu(1)–N(2)	94.12(15)	O(3)–Cu(2)–N(4)	94.06(16)		
O(1)–Cu(1)–N(2)	166.48(15)	O(2)–Cu(2)–N(4)	164.71(16)		
O(3)–Cu(1)–N(1)	170.37(16)	N(3)–Cu(2)–N(4)	80.79(16)		
O(1)–Cu(1)–N(1)	91.70(17)	O(3)–Cu(2)–O(4)	84.13(13)		
N(2)–Cu(1)–N(1)	80.86(18)	O(2)–Cu(2)–O(4)	93.95(15)		
O(3)–Cu(1)–O(2)	94.29(14)	N(3)–Cu(2)–O(4)	95.38(15)		
O(3)–Cu(1)–N(3)	174.68(16)	N(4)–Cu(2)–O(4)	99.63(16)		

bridged Cu^{II} complex for the purpose of increasing its solubility in organic solvents, and subsequently facilitating the homogeneous reaction. During the initial stages of the catalytic reaction (under an atmosphere of argon), when an equivalent amount of DMP was added to the catalytic system, the peak of the absorption maximum shifted from 600 to 650 nm (Fig. 2). The band at 420 nm is ascribed to a PhO^- –Cu(II) ligand to metal charge transfer (LMCT). On introducing O_2 into the system, the coupling reaction quickly began as indicated by the O_2 up-take. These observations suggest that the bridged-phenolate is readily oxidized in the catalytic system (Scheme 2).

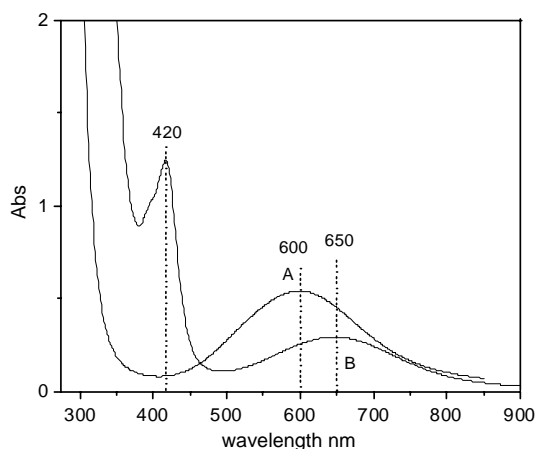
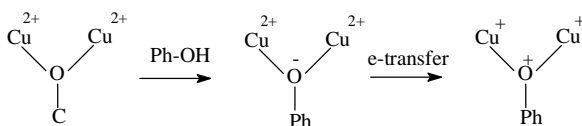


Fig. 2. UV-Vis spectra for before and after introduction of the substrate DMP; (A) Cu(II) complex only; (B) complex + DMP under argon.



Scheme 2.

3.3. Magnetic properties and magnetic mechanisms

Variable-temperature magnetic susceptibility measurements for the complex were made over the range of 4.2–300 K. The magnetic moments decrease with decreasing temperature (Fig. 3). This implies the existence of antiferromagnetic coupling of Cu(II)–Cu(II) pairs. Quantitative magnetic analyses was based on the Heisenberg spin-exchange operator $H = -JS_1S_2$. The molar susceptibility of the Cu–Cu ($S_1 = S_2 = 1/2$) system was calculated from the Bleaney–Bowers equation:

$$\chi_M = \frac{2Ng^2\beta^2}{kT} \left[3 + \exp\left(-\frac{2J}{kT}\right) \right]^{-1} (1 - \rho) + \frac{Ng^2\beta^2}{2kT} \rho + N_\alpha$$

where χ_M is the susceptibility per binuclear complex, N_α the temperature-independent paramagnetism ($90 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$), ρ the fraction of mononuclear paramagnetic impurity, and other symbols have their usual meanings. The magnetic parameters thus obtained are $J = -239 \text{ cm}^{-1}$, $g = 1.95$ and $\rho = 0.005$. This result indicates

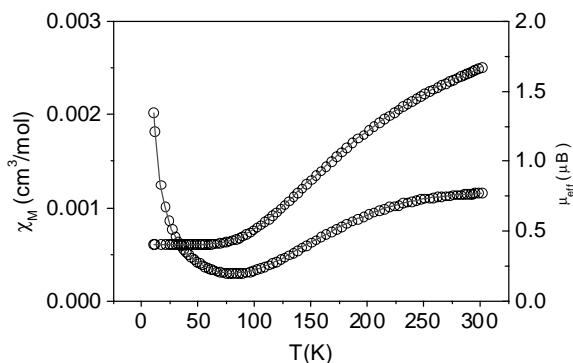
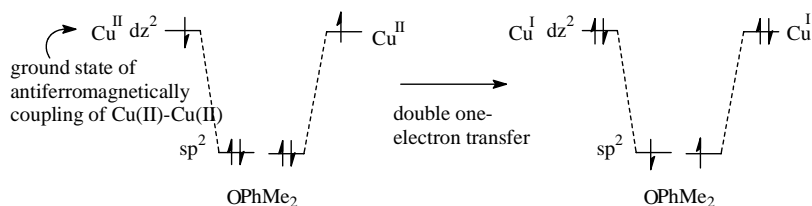


Fig. 3. Temperature variation of magnetic moment of the complex.



Scheme 3.

the existence of strong antiferromagnetic interaction between the metal ions [14].

This magnetic behavior means that the unpaired electrons on copper(II) ions occupy a singlet ground state with opposite spins. This indicates that in the reduction to Cu(I)-Cu(I), twin-electron oxidation of the bridged phenol is needed (Scheme 3). The transferred electrons form electron pairs with the unpaired electrons in copper(II) ions. Thus, the overall spin state of the bridged phenolate ($S = 0$) is not changed when oxidized to the cation.

3.4. Catalytic activity of the complexes

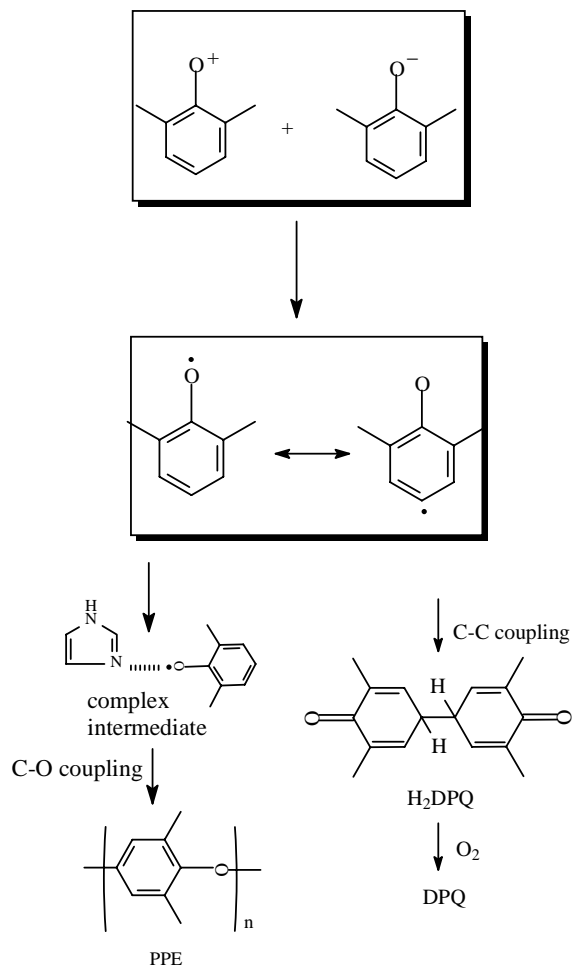
The O_2 up-take rates and yields of these complexes are shown in Table 3. With increase in the methoxide to complex ratio, the reaction rate and the product yields increased dramatically, but following a ratio of 4–1, the PPE yields are only slightly improved. This suggests that the strong base, MeO^- , promotes oxidative coupling and the by-product DPQ is always involved. If the bridged phenolate were oxidized to the corresponding phenoxonium cation and existed freely in the catalytic solution, it would be attacked by the phenolic anion created by the reaction of DPM with the excess amount of MeO^- . H_2DPQ is formed by C–C coupling of a resonance form of the phenoxy radicals, and phenoxy radicals may form in the one electron transfer between the corresponding cation and anion. To verify this hypothesis, the effect of the radical scavenger DMS was tested and this shows that the reaction rate is reduced significantly. However, in the presence of imidazole, the selectivity of PPE increased significantly to nearly 99% (also Table 3).

3.5. Mechanistic discussion

Although several possible mechanisms have been proposed in the literature [16], none is considered to be completely satisfactory. One reason may lie in the lack of structural information about the catalytic intermediate, the lack of understanding about the initial step and the intermediate forms of the substrate during the catalytic cycle. This study shows that the μ -alkoxo dicopper(II) complex may represent a real catalytic center, and it transfers into the μ -phenolate-bridged structure upon interaction with the substrate. Once a bridged phenolate is oxidized to phenoxonium cation, the active center is ready to undergo electron transfer process in the presence of O_2 . To complete the cat-

alytic cycle, a dicopper-dioxygen adduct must be formed to oxidize the dicopper(II) centers.

It should be noted that during the dioxygen up-take experiment, NaOMe was used as the basic co-catalyst. It serves to remove protons from the phenol substrate, and thus facilitate the oxidation of the phenol. This suggests that the μ -alkoxo dicopper(II) structure is critical in the coupling reaction. The presence of DPQ is due to the C–C coupling between the phenoxy radicals formed. The role of imidazole is to stabilize the phenoxy radicals by forming an intermediate complex and thus facilitate the C–O coupling process (Scheme 4). Indeed, further mechanistic investigation is needed in order to firmly establish the mechanism of this reaction.



Scheme 4.

Table 3
Oxidation rates and yields of PPE under different conditions

Ratio of Cu(II):MeO ⁻	Reaction rate (O ₂ mmol min ⁻¹)	Conversion of PPE ^a (wt.% after 24 h)	Conversion of PPE ^b (wt.% after 24 h)
1	1.78×10^{-3}	50.2	92.5
2	3.66×10^{-3}	60.4	93.9
4	4.78×10^{-3}	70.3	95.5
6	4.91×10^{-3}	74.6	98.0
8	5.09×10^{-3}	75.9	98.3
10	5.18×10^{-3}	77.2	99.1

^a With NaOMe only.

^b With NaOMe and 1 ml imidazole.

Acknowledgements

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