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Heterolytic Alkyl Hydroperoxide O–O Bond Cleavage by Copper(I) Complexes

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The reaction of copper(I) complexes and cumene hydroperoxides was examined to demonstrate that heterolytic O–O bond cleavage of the peroxides proceeds predominantly to give the corresponding alcohols (cumyl alcohols) as the major product, when the stoichiometry of Cu^{I} /peroxide is 2:1. The

Introduction

Alkyl peroxide complexes (M–OOR) of transition metal ions have been long-standing research objectives because of their strong relevance to biological and catalytic oxidation reactions.^[1] Among them, non-heme iron complexes have been studied most extensively,^[2,3] to provide profound insights into the catalytic mechanism of iron-containing monooxygenases and iron-catalyzed hydrocarbon oxygenation reactions.^[4,5] Homolytic cleavage of the O-O bond of Fe^{III}-OOR provides Fe^{IV}=O, whereas O-O bond heterolysis gives Fe^V=O species, both of which have been invoked as key reactive intermediates in oxygenation reactions. However, little attention has been focused on alkyl peroxide complexes of copper.^[6] In this respect, we have recently investigated the reaction of cumene hydroperoxide (^HCmOOH) and a copper(II) complex supported by the N,N-di(2-pyridylmethyl)benzylamine tridentate ligand (L^a, Figure 1) to find that the generated (cumylperoxido)copper(II) complex L^aCu^{II}(OO^HCm) undergoes homolytic O-O bond cleavage, inducing C-H bond activation of an external substrate such as 1,4-cyclohexadiene.^[7] The results provided important insights into the mechanism of dioxygen activation by mononuclear copper complexes in biological and catalytic oxygenation reactions.^[8]

In this study, we investigate the reaction of copper(I) complexes of similar tridentate ligands (L^a and L^b) and cumene hydroperoxide derivatives (^xCmOOH; X = Et, Me, H, Br, F, and NO₂) to find that the copper(I) complexes

result is in sharp contrast to the 1:1 reaction between the copper(II) complexes and cumene hydroperoxide, which provides the ketone (acetophenone) as the major product through homolytic O–O bond cleavage.



Figure 1. Ligands (L^a and L^b) and cumene hydroperoxide derivatives (^XCmOOH).

induce *heterolytic* O–O bond breaking in the alkyl hydroperoxides in contrast to the case of the former copper(II)/ $^{\rm H}$ CmOOH system.

Results and Discussion

The reaction of $[Cu^{I}(L^{a})(CH_{3}CN)](PF_{6})$ (1a) (0.5 mM) and an equimolar amount of ^HCmOOH was first examined in acetonitrile. The HPLC analysis of the organic products derived from ^HCmOOH demonstrated that cumyl alcohol (^HCmOH) was formed in 43% yield together with a small amount of acetophenone (PhCOMe, 7%). In this case, however, almost 50% of the starting material, ^HCmOOH, was recovered (Figure S1). The result indicates that the stoichiometry of copper(I) complex 1a and ^HCmOOH was 2:1. In fact, the reaction of 1a (0.5 mm) with 0.5 equiv. of ^HCmOOH (0.25 mM) under otherwise the same experimental conditions consumed almost all of the substrate, (^HCmOOH), to give ^HCmOH and PhCOMe in 93% and 7% yield, respectively (Figure S2). The formation of ^HCmOH (alcohol) as the major product is in sharp contrast to the product distribution in the reaction of the copper(II) complex of the same ligand, L^a, and ^HCmOOH, where PhCOMe (ketone) is the major product, and the yields of PhCOMe and ^HCmOH are 76% and 15%, respectively.^[7]

It has been reported that the products obtained from a cumyl peroxide complex largely depend on the O–O bond

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cleavage pattern, as indicated in Scheme 1. Namely, if homolytic O–O bond cleavage occurs (path a), acetophenone (PhCOMe) is produced from the cumyloxyl radical by β -scission to release the methyl radical (CH₃⁻). On the other hand, heterolytic O–O bond cleavage (path b) gives cumyl alcohol (^HCmOH) after oxyanion protonation.^[9] Thus, formation of ^HCmOH as the major product (93%) in the present system suggests that the reaction of copper(I) complex **1a** and ^HCmOOH mainly involves O–O bond heterolysis (path b).



Scheme 1. Possible decomposition pathways of cumyl peroxide complex M-OO ^{H}Cm .

Since the stoichiometry of the reaction between mononuclear copper(I) complex 1a and ^HCmOOH was 2:1, we also examined the reaction of a dinuclear copper(I) complex and cumene hydroperoxide to get more insight into the reaction intermediate and products. Dicopper(I) complex **1b** was prepared by treating the dinucleating ligand L^b and 2 equiv. of $[Cu^{I}(CH_{3}CN)_{4}](PF_{6})$ in acetonitrile, the crystal structure of which is shown in Figure 2. Each copper(I) ion is ligated by three nitrogen atoms of one of the tridentate metal-binding moieties of L^b and one acetonitrile co-ligand, exhibiting a highly distorted tetrahedral geometry. The τ_4 values for Cu(1) and Cu(2) are 0.69 and 0.62, respectively; the τ_4 value is a simple geometry index for four-coordinate complexes proposed by Houser and co-workers defined as $\tau_4 = [360^\circ - (a + \beta)]/141$, where a and β are the two largest θ angles in the four-coordinate species.^[10] The τ_4 value will range from 1.0 for perfect tetrahedral geometry to zero for perfect square-planar geometry. Thus, the structure of the copper(I) center of 1b is similar to that of the reported mononuclear copper(I) complex [Cu^I(L^a)-(CH₃CN)]B(C₆F₅)₄, which exhibits a τ_4 value of 0.72.^[11]

The reaction of dicopper(I) complex **1b** with an equimolar amount of ^HCmOOH (molar ratio of Cu^{I/H}CmOOH = 2:1) was then examined. In this case as well, cumyl alcohol (^HCmOH) was obtained as the major product (95%) together with a small amount of acetophenone (5%) (Figure S3), indicating that the reaction also involves heterolytic O–O bond cleavage of ^HCmOOH. Figure 3 shows the UV/Vis spectral change for the reaction at –40 °C. Addition of an equimolar amount of ^HCmOOH to an acetonitrile solution of **1b** initially gave a spectrum having an intense absorption band at 363 nm ($\varepsilon = 2045 \text{ M}^{-1} \text{ cm}^{-1}$) together with a weak band at 560 nm ($\varepsilon = 168 \text{ M}^{-1} \text{ cm}^{-1}$) (solid line).^[12] This species, designated as **2b**, gradually decomposed even at lower temperature to provide another copper(II) species, **3b**. The same species, **3b**, was generated



Figure 2. ORTEP diagram of $[Cu^{I}_2(L^b)(CH_3CN)_2](PF_6)_2$ (1b) with 50% probability ellipsoids. The counteranions and the hydrogen atoms are omitted for clarity.

rapidly when a small amount of $H_2O(0.5 \,\mu L)$ was added to the solution of **2b**, suggesting that **3b** is produced by hydrolysis of 2b. ESI-MS analysis of the final reaction mixture exhibited a prominent ion peak cluster at m/z = 330.2, whose mass and isotope distribution pattern were consistent with the chemical formula of di(µ-hydroxido)dicopper(II) complex $[Cu^{II}_{2}(L^{b})(\mu-OH)_{2}]^{2+}$ (m/z = 330.1; Figure S4). In spite of our great efforts, a pure sample of 3b could not be isolated, but its di(μ -methoxido) variant 3b' was successfully obtained in 81% yield by recrystallization of **3b** from methanol. The crystal structure of 3b' is shown in Figure 4. Each copper(II) ion has a largely distorted square-pyramidal geometry consisting of two pyridine nitrogen atoms and two bridging methoxide oxygen atoms in a basal plane and the tertiary amine nitrogen atom in the apical position, where no ligand modification took place.



Figure 3. UV/Vis spectrum of **2b** (solid line) generated by the reaction of **1b** (0.5 mM, dotted line) with ^HCmOOH (0.5 mM) in CH₃CN at -40 °C under anaerobic conditions and its decomposition product **3b** (dashed line) generated by the addition of H₂O at -40 °C. Inset: Expanded UV/Vis spectra in the 500–900 nm region.

The similarity of the absorption spectrum of isolated 3b' to that of 3b also supports the di(μ -hydroxido)dicopper(II) core structure in the latter (see Supporting Information).



Figure 4. ORTEP diagram of $[Cu^{II}_2(L^b)(\mu$ -OCH₃)₂](PF₆)₂ (**3b**') with 50% probability ellipsoids. The counteranions and the hydrogen atoms are omitted for clarity.

A possible mechanism for the reaction of **1b** and cumene hydroperoxide to generate **3b** is shown in Scheme 2. As clearly demonstrated by the product analysis, heterolytic cleavage of the O–O bond takes place. The Cu^I/CmOOH stoichiometry of 2:1 suggests that formally two electrons are transferred from the copper(I) ions to the peroxide moiety to induce O–O bond heterolysis. This event may produce (μ -hydroxido)dicopper(II) intermediate **A** and cumyl alkoxide CmO[–], both of which quickly collapse to give (μ - hydroxido)(μ -alkoxido)dicopper(II) species **2b**. Finally, **3b** or **3b**' is produced by hydrolysis or methanolysis of **2b**.

Further evidence in support of the generation of the postulated intermediate 2b is the fact that essentially similar spectra but having slightly different λ_{max} values were obtained in the reactions of 1b with a series of cumene hydroperoxide derivatives ^XCmOOH (X = Et, Me, Br, F, and NO₂) under the same experimental conditions [Figure S5, $\lambda_{\text{max}} = 538-567$ nm; nearly quantitative (> 95%) formation of the corresponding alcohols ^XCmOH was also confirmed by HPLC analysis]. Such a difference in λ_{max} of the intermediates 2b generated by using ^xCmOOH may be due to the electronic effects of the *p*-substituents on the LMCT transition from the alkoxide ligand to Cu^{II}. As indicated in Figure S5B, there is a weak correlation between λ_{max} and Hammett σ_p values, where the λ_{max} shifts toward longer wavelengths as the electron-withdrawing nature of the psubstituent (X) increases.

Conclusions

In this study, we investigated the reaction of copper(I) complexes **1a** and **1b** with cumene hydroperoxide derivatives (^XCmOOH) to find that the reaction proceeds in 2:1 stoichiometry to induce *heterolytic* O–O bond breaking of the alkyl hydroperoxides. In this case, the corresponding alcohol was obtained as the major product. The result is in sharp contrast to the 1:1 reaction between the copper(II) complexes and CmOOH to produce the ketone [PhC(O) Me] as the major product by homolytic O–O bond cleavage.

Very recently, Hutchings and co-workers reported a significant result: in the oxidation of methane with H_2O_2 , catalyzed by Fe-loaded zeolite (ZSM-5), alcohol (methanol)



Scheme 2. Proposed mechanism of the reaction of 1b and ^xCmOOH.

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product selectivity is significantly improved by the addition of copper.^[13] In this reaction, the primary product is methyl hydroperoxide (MeOOH), which is produced by the direct reaction of methane with a generated dinuclear iron active oxygen species.^[13] Our present study suggests that the role of copper in the methane oxidation reaction of Hutchings is the enhancement of O–O bond heterolysis of the primary product MeOOH to give MeOH as the major product. Mechanistic details of the O–O bond cleavage process and application to catalytic oxidation reactions are now under investigation.

Experimental Section

Materials: The reagents and solvents used in this study, except *p*-substituted cumene hydroperoxide derivatives (^XCmOOH), were commercial products of the highest available purity that were further purified by standard methods if necessary.^[14] Ligands L^a [*N*,*N*-di(2-pyridylmethyl)benzylamine] and L^b [*N*,*N*,*N'*,*N'*-tetra(2-pyridylmethyl)-*m*-xylylenediamine] and the copper(I) complex of L^a, [Cu^I(L^a)(CH₃CN)](PF₆) (1a), were prepared according to reported procedures.^[11,15] Cumene hydroperoxide (^HCmOOH) and 8-hydroperoxy-*p*-cymene (^{Me}CmOOH) were prepared by reported procedures.^[16] Other cumene hydroperoxide derivatives, ^RCmOOH (R = Et, Br, F, and NO₂), were prepared in a similar manner, as described in the Supporting Information.

 $[{\rm Cu}_2({\rm L}^{\rm b})({\rm CH}_3{\rm CN})_2]({\rm PF}_6)_2 \text{ (1b): Ligand } {\rm L}^{\rm b} (30 \text{ mg, } 60 \text{ mmol}) \text{ was treated with 2 equiv. of } [{\rm Cu}^1({\rm CH}_3{\rm CN})_4]({\rm PF}_6) (45 \text{ mg, } 120 \text{ mmol}) \text{ in } {\rm CH}_2{\rm Cl}_2 (1 \text{ mL}) \text{ under a } {\rm N}_2 \text{ atmosphere in a glove box (Miwa MFG Co., Ltd. DB0–1KP). After stirring the mixture for 30 min at room temperature, the insoluble material was removed by filtration. Addition of ether (30 mL) to the filtrate gave a pale yellow powder that was precipitated by letting the mixture stand for 10 min. The supernatant was then removed by decantation, and the remaining pale yellow solid was washed with diethyl ether three times and dried to give complex 1b in 67%. Single crystals of 1b were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. FTIR (KBr): <math display="inline">\tilde{v} = 843 \text{ cm}^{-1} ({\rm PF}_6^{-}).$ ${\rm C}_{36}{\rm H}_{38}{\rm Cu}_2{\rm F}_{12}{\rm N}_8{\rm P}_2$

 $[{\rm Cu}^{\rm I}_2({\rm L}^{\rm b})({\rm CH}_3{\rm CN})_2]$ (PF_6)2: C 43.25, H 3.83, N 11.21; found C 43.31, H 4.04, N 11.45.

[Cu^{II}₂(L^b)(μ-OMe)₂](PF₆)₂(Et₂O) (3b'): An acetonitrile solution (1.0 mL) of **1b** (12 mg, 12 mmol) was prepared in a glove box at room temperature. The solution was cooled to -40 °C, and an acetonitrile solution (100 mL) of ^HCmOOH (240 mM) was added by using a microsyringe through the rubber septum cap. After stirring the mixture for 10 min, an excess amount of precooled ether was poured into the solution to give a blue powder that was precipitated by letting the mixture stand for several minutes. The supernatant was removed by filtration to give **3b**' as a blue powder in 81% yield. Single crystals of **3b**' were obtained by vapor diffusion of diethyl ether into CH₃CN/MeOH (v/v = 1:1) solution of the complex. FTIR (KBr): $\tilde{v} = 842 \text{ cm}^{-1}$ (PF₆⁻). C₃₈H₄₈Cu₂F₁₂N₆O₃P₂ (1053.9) [Cu^{II}₂(L^b)(μ-OMe)₂](PF₆)₂(Et₂O): C 42.31, H 4.59, N 7.97; found C 42.02, H 4.61, N 8.05.

CCDC-883133 (for **1b**) and -883134 (for **3b**') contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **Supporting Information** (see footnote on the first page of this article): Experimental details including physical measurements, product analysis, and synthetic procedures.

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O–O Bond Heterolysis

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Heterolytic Alkyl Hydroperoxide O–O Bond Cleavage by Copper(I) Complexes

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