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systems can be regarded as electronically independent at least when a large difference in nuclear coordinates accompanies the migration of energy *and* when the acceptor and donor state differ significantly in energy. Under these circumstances there is first vibrational equilibration among the donor excited states, followed by an equilibration of excitation energy between the donor and acceptor. In only one complex, $(bpy)_2(CN)Ru(CNRh(NH_3)_4I)$ in which the donor energy was greater than or equal to the acceptor energy, did we find spectroscopic characteristics which might suggest that the lowest energy excited state has mixed donor and acceptor character. At 77 K the lowest energy excited states of the cyanide bridged Ru-Cr complexes behave like typical (^2E)-Cr(III) excited states, presumably because the donor-acceptor energy difference is too great for appreciable mixing of their electronic configurations. One expects similar factors to contribute to donor-acceptor coupling in electron transfer and dipole forbidden energy-transfer systems. We have examined a few electron-transfer systems in which similar general features seem to be exhibited. This work will be reported elsewhere.[60] The cyano-bridged Ru-Rh complexes provide some unique insights into the "normal" relaxation pathways of (^3CT)Ru-polypyridyl excited states, since a tunable ^{3}dd relaxation pathway is introduced by the Rh(III) center. The observations are qualitatively in accord with the expectation that the $^3CT \rightarrow {}^3dd$ relaxation pathways will be characterized by large Arrhenius frequency factors ($A \cong 10^{13}$ s^{-1}) and activation energies that reflect both the donor-acceptor energy gap and the reorganizational energy for the relaxation of the ^{3}dd excited state.

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Supplementary Material Available: Table of elemental analyses for cyanide-bridged complexes (1 page). Ordering information is given on any current masthead page.

Reaction Aspects of a μ-Peroxo Binuclear Copper(II) Complex

Nobumasa Kitajima,* Takayuki Koda, Yusaku Iwata, and Yoshihiko Moro-oka*

Contribution from the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan. *Received September 25, 1989*

Abstract: The reactivity of a μ-peroxo binuclear copper(II) complex $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(O_2)$ (**1**) toward a variety of substrates is described. PPh_3 and CO are not oxidized by **1**; they generate mononuclear copper(I) complexes $Cu(L)(HB(3,5\text{-}Me_2pz)_3)$ (L = CO, PPh_3) via displacement reactions. Cyclohexene is oxidized to oxygenated products such as 2-cyclohexen-1-ol only under aerobic conditions, and labeling experiments established that the oxygen atoms incorporated into the products come from the exogeneous dioxygen, not from the peroxide ion in the μ-peroxo complex. Phenols and a catechol are oxidatively coupled under anaerobic conditions, while under a dioxygen atmosphere, both oxidatively coupling and oxygenation to give benzoquinones are observed. On the basis of kinetic results, a mechanism is proposed for the oxygenation reactions in which homolytic cleavage of the O-O bond in the μ-peroxo complex is followed by free radical chain reactions with dioxygen.

Introduction

Tyrosinase is a monooxygenase in which the active site contains a binuclear copper center that is known to bind dioxygen as a peroxide.[1] A similar binding mode is found in hemocyanin, a ubiquitous oxygen transport protein for invertebrates. Although tyrosinase was the first discovered monooxygenase,[2] few of its mechanistic details have been elucidated to date.[3] Currently increasing interest in the activation of dioxygen by monooxygenases prompted several groups to study oxidations using biomimetic copper complexes.[4] Valentine et al. reported catalytic epoxidations of olefines with iodosobenzene as an oxidant and suggested that a high-valent oxocopper species might be involved.[5] Recently, dioxygen was reported to effect the hydroxylation of certain CH bonds in the ligands of copper(I) complexes.[6] These oxidations are supposed to proceed via peroxocopper intermediates. However, there has been no stoichiometric oxidation of an externally added substrate by a well-characterized peroxo copper complex, except for the oxo-transfer reactions recently reported by Karlin et al. In these studies, three structurally distinctive types of μ-peroxo binuclear copper(II) complex were synthesized,[7] and two of these classes (one having an unsymmetric peroxo ligand and a μ-phenoxo group, and the other having a trans μ-1,2-peroxo) were demonstrated to be effective for oxo-transfer reaction to triphenylphosphine after protonation or acylation of the peroxo complexes.[8,9]

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The third type complex (μ-1,2 and possibly η^2:η^2) is ineffective for the oxo-transfer reaction,[8] whereas a structurally similar intermediate was suggested as the active species for an intramolecular arene hydroxylation.[10]

Recently we reported the synthesis of a μ-peroxo binuclear complex $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(O_2)$ (**1**) that shows many similarities to oxyhemocyanin and oxytyrosinase in its physicochemical properties.[11] The X-ray analysis of an analogous complex $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(O_2)$ established a remarkable coordination mode of the peroxide ion, μ-η^2:η^2.[12] The obvious question to be answered was whether the peroxo complex could incorporate an oxygen atom into a substrate such as phenol. We explored the anaerobic and aerobic oxidations of substrates including cyclohexene and phenols by **1** and found that oxygen incorporation occurs only when the reaction is carried out under aerobic conditions. The detailed kinetic–mechanistic reaction study is reported herein.

Experimental Section

Materials. All preparations and reactions were carried out under argon unless otherwise stated. $CHCl_3$ was the highest grade commercially available and was refluxed and distilled over P_2O_5 under argon prior to use. CH_2Cl_2 was stored with sulfuric acid in the dark and, after the acid layer was removed, washed several times with aqueous KOH/KCl and distilled water. Then the CH_2Cl_2 was dried over anhydrous $K_2CO_3/MgSO_4$ and finally refluxed and distilled in the presence of P_2O_5 under argon. $KHB(3,5\text{-}Me_2pz)_3$ was prepared by the literature method.[13] The phenols and a catechol were the highest grade commercially available and were purified by recrystallization. The other reagents were used without further purification. $^{18}O_2$ (96.5% atom ^{18}O) was obtained from MSD-Isotopes. $H_2{}^{18}O_2$ (ca. 95% atom ^{18}O) was prepared from the $^{18}O_2$ by a method using 2-ethylanthraquinone improved by Dr. Y. Tatsuno of Osaka University.[14]

$[Cu(HB(3,5\text{-}Me_2pz)_3)]_2O$ (**2**) was synthesized by the reaction of $Cu(PPh_3)(HB(3,5\text{-}Me_2pz)_3)$ (**3**) with an excess amount of PhIO in CH_2Cl_2.[15] $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(O_2)$ (**1**) was prepared by low-temperature treatment of **2** with H_2O_2 as described previously.[11] ^{18}O-labeled **1** was prepared in the same manner with $H_2{}^{18}O_2$. In order to avoid decomposition, the sample of **1** for the reaction study was prepared just prior to use. Because of the high reactivity of **1** and **2** toward CO_2, **1** used for the present study contained a slight amount of $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(CO_3)$ (**5**) (<5%). Further details of the syntheses of **1** and **2** will be provided elsewhere.[16]

Instrumentation. Electronic spectra were recorded on a Shimazu UV-260 spectrometer. ^1H NMR spectra were measured in $CDCl_3$ or CD_2Cl_2 on either a JEOL-GX-270 (270 MHz) or a JEOL-GX-500 (500 MHz) NMR spectrometer. Chemical shifts are reported as values relative to an internal standard of Me_4Si. Mass spectra measurements (FD-MS, GC-MS) were carried out on a Hitach M-80 instrument. ESR spectra were recorded on a Varian E-12 spectrometer equipped with a liquid nitrogen Dewar inset. IR spectra were measured in KBr on a Hitach 260-50 spectrometer.

Oxidation Reactions and Product Analyses. In a typical experiment, 10 mg of freshly prepared **1** and 100 mg of substrate were placed in a Schlenk flask. After the addition of 1.0 mL of $CHCl_3$, the mixture was stirred for 2 h at room temperature. An internal standard (such as toluene) was added to the solution and the products were analyzed by GC. Identification of the products was accomplished by GC-MS and comparison with authentic samples.

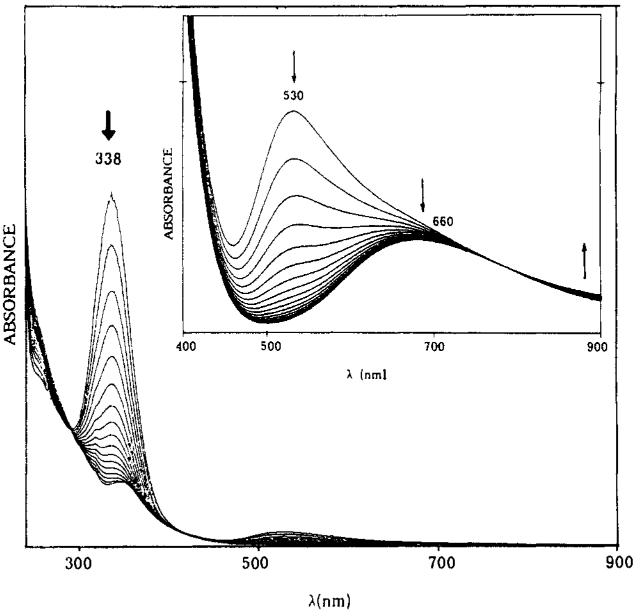

Figure 1. Electronic spectral change during the decomposition of **1** in $CHCl_3$ (the insert is an independent run to emphasize the change of the 530-nm band).

Reaction of 1 with PPh$_3$ To Give Cu(PPh$_3$)(HB(3,5-Me$_2$pz)$_3$) (3). Into a solution of **1** in $CHCl_3$ cooled at −20 °C was added 5 equiv of PPh_3. The deep purple color of the solution disappeared immediately. After being stirred for 10 min, the solution was warmed to room temperature and analyzed by GC. Only trace $OPPh_3$ was detectable. The solution was evacuated to dryness, and the solvent was replaced with $CDCl_3$. The ^1H NMR and ^{31}P NMR of the solution established the quantitative formation of $Cu(PPh_3)(HB(3,5\text{-}Me_2pz_3))$ (**3**).[15]

Reaction of 1 with CO To Give Cu(CO)(HB(3,5-Me$_2$pz)$_3$) (4). At −20 °C, CO was bubbled into the solution of **1** in $CHCl_3$. No striking color change was noted. The solution was allowed to warm up to room temperature, and after 1 h of stirring the purple color had completely disappeared. Evaporation of the solution gave a slightly greenish white solid, part of which was used for an IR measurement. The remaining solid was dissolved in $CDCl_3$, and its ^1H NMR was recorded. The IR and ^1H NMR spectra showed an almost quantitative formation of $Cu(CO)(HB(3,5\text{-}Me_2pz_3))$ (**4**);[15,17] a slight amount (~10%) of $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(CO_3)$ (**5**) was also found.[16,18]

Kinetic Studies. The spontaneous decomposition of **1** was followed by the intensity change of the characteristic 530 nm (ϵ = 840 M^{-1} cm^{-1}) band due to **1** at 25 °C. The spectra were recorded in a quartz cell of 1 cm thickness. The reaction of **1** and 2,6-dimethylphenol under an argon atmosphere was carried out in a reaction vessel connected to a quartz cell of 1 mm thickness, and the decomposition of **1** and formation of the diphenoquinone were followed by the time dependence of the absorbances at 338 nm (ϵ = 20 800 M^{-1} cm^{-1}) and 418 nm (ϵ = 90 000 M^{-1} cm^{-1}), respectively. The reaction method was essentially the same as that employed for the quantitative reaction of **1** as described above.

Labeling Experiments. Incorporation of ^{18}O into **2** from ^{18}O-labeled **1** was established by FD-MS of **2** prepared by thermal decomposition of ^{18}O-labeled **1** in $CHCl_3$ at room temperature under argon. Incorporations of ^{18}O into the products in oxidation reactions for cyclohexene and 2,6-dimethylphenol in the presence of $^{18}O_2$ and **1** were accomplished by GC-MS analyses. The reaction method is essentially the same as described above, except for the pressure of $^{18}O_2$ used, ca. 0.3 atm. In both experiments, the peak ratio of the parent ions due to ^{16}O and ^{18}O derivatives indicated a more than 90% atom ^{18}O incorporation into the products. For cyclohexene oxidation, the reaction was also carried out with ^{18}O-labeled **1** under 1 atm of $^{16}O_2$. In this case, no ^{18}O incorporation into the products was observed.

Results

Spontaneous Decomposition of 1. Solutions of μ-peroxo complex **1** are thermally unstable. For instance, at room temperature in $CHCl_3$, the intensely purple colored solution of **1** turns green within

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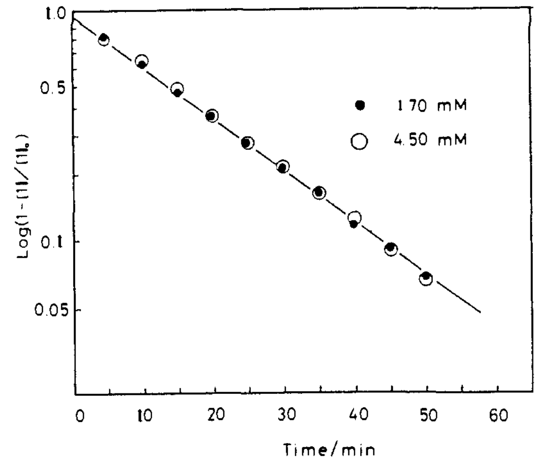
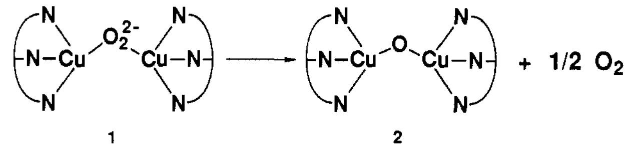


Figure 2. The first-order plots of the spontaneous decomposition of complex **1** in $CHCl_3$ at 25 °C: (●) 1.70 mM, (○) 4.50 mM.

Scheme I



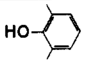
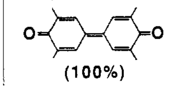
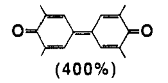
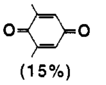
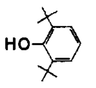
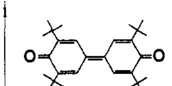
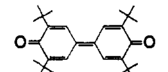
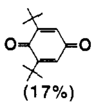
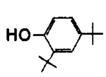
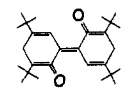
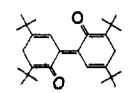
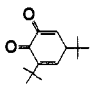
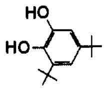
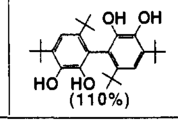
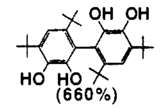
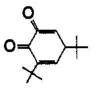
2 h, whereas below −20 °C it is reasonably stable. The evolution of the electronic spectrum during this decomposition at 25 °C under argon is presented in Figure 1. Complex **1** shows characteristic absorption bands at 338 and 530 nm. The intensities of these bands decrease gradually. The final spectrum is essentially identical with that of μ-oxo binuclear copper complex **2**,[15] whereas a weak shoulder band at 310 nm indicates formation of byproduct $Cu[(HB(3,5\text{-}Me_2pz)_3)]_2$ (**6**)[19] (<5%). The absorption maximum (ca. 345 nm) of the final spectrum in Figure 1 is slightly different from that of **2** (335 nm); this is due to the overlapping of the broad band of **6** and a strong band at 347 nm assignable to the $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(CO_3)$ (**5**) which is contaminated in **1** as an impurity (<5%).[20] The ^1H NMR spectrum of the resulting solution at room temperature (δ 12.6 (br s, 6 H), 2.45 (br s, 18 H), 1.86 (br s, 18 H)) also indicates essentially quantitative formation of **2** from **1**.[15] Thus, **1** decomposes to **2** according to Scheme I. The stoichiometry of the decomposition is confirmed by manometric measurements of O_2 evolution from the solid samples of **1**. ^{18}O-labeled **1** decomposes to ^{18}O-labeled **2** (>90% from FD-MS analysis of the product), so we infer that the oxo in **2** comes from the peroxide ion in **1**. When the spontaneous decomposition of **1** was carried out in a polar solvent such as methanol, the product was not **2** but **6**, the result of disproportionation.[19]

The kinetics of the decomposition were explored by following the time dependence of the absorbance at 530 nm due to **1**. A set of first-order plots for different initial concentrations of **1** is given in Figure 2. The plots show good linear relationships with identical slopes. Therefore, the spontaneous decomposition rate of **1** is first order with respect to the concentration of **1** as shown in eq 1, where k_{auto} denotes the spontaneous decomposition rate constant (1.83×10^{-3} s^{-1}).

$$-\frac{d[1]}{dt} = k_{auto}[1] \qquad (1)$$

Reactions of 1 with PPh₃ and CO. The addition of PPh_3 to the solution of **1** at −20 °C causes instantaneous displacement of dioxygen and quantitative formation of the copper(I) complex $Cu(PPh_3)(HB(3,5\text{-}Me_2pz)_3)$ (**3**). Only a trace amount of $OPPh_3$ in the resulting colorless solution is detectable by GC analysis. The CO treatment of **1** causes a similar displacement to afford $Cu(CO)(HB(3,5\text{-}Me_2pz)_3)$ (**4**), but this reaction requires a higher temperature than for the PPh_3 case. Both **3** and **4** are stable and are not reoxygenated to **1** with O_2.

Table I. Anaerobic and Aerobic Oxidations of Phenols and a Catechol by **1**

	Ar	O2	
	 (100%)	 (400%)	 (15%)
	 (100%)	 (230%)	 (17%)
	 (15%)	 (1700%)	 (18%)
	 (110%)	 (660%)	 (1080%)

The relatively higher reaction temperature (>−20 °C) for the CO-displacement reaction causes partial, but considerable, spontaneous decomposition of **1**, and the product solution is slightly green in color. The IR spectrum of the solids obtained by evaporation of the solution gives a characteristic band at 1592 cm^{-1} assignable to μ-carbonato binuclear copper complex **5**.[16] The formation of **5** is also supported by ^1H NMR, although the yield is low (~10%).

Oxidation of Cyclohexene. When a $CHCl_3$ solution of **1** is treated anaerobically in the presence of a 75-fold excess of cyclohexene for 2 h at 25 °C, a small amount of 2-cyclohexene chloride (ca. 10% yield based on **1**) is formed. Strikingly, under a dioxygen atmosphere (1 atm), the same treatment gives 2-cyclohexen-1-ol (212%), 2-cyclohexen-1-one (202%), and cyclohexene oxide (13%). The consumption rate of **1** in the presence of cyclohexene is consistent with that of spontaneous decomposition of **1**. The addition of proton source or $m\text{-}ClC_6H_4C(O)Cl$ only resulted in the decomposition of **1** and was not effective for the formation of oxygenated products such as cyclohexene oxide. Labeling experiments established that the oxygen atoms in the products come from the exogeneous dioxygen and not from the peroxide ion in **1**. Oxidations of other hydrocarbons including styrene, cyclooctene, cyclohexane, and adamantane were attempted, but no reactions were observed under either anaerobic or aerobic conditions.

Oxidations of Phenols and Catechol. The products obtained by anaerobic or aerobic reactions of **1** and phenols and a catechol are summarized in Table I. Under anaerobic conditions, only the oxidatively coupled products, diphenoquinones, are formed. On the other hand, in the presence of exogeneous dioxygen, benzoquinones are also formed, although the main products are still the oxidatively coupled products.

The reaction mechanism of the anaerobic reaction between **1** and 2,6-dimethylphenol was investigated. The first-order plots of the consumption of **1** in the presence of the phenol are given in Figure 3. The rate constants obtained from these plots are plotted against the initial concentration of 2,6-dimethylphenol as shown in Figure 4. A good linear relationship was found, and the intersection obtained by the least-squares fit is in excellent accord with the rate constant for the spontaneous decomposition of **1**. Accordingly, the consumption rate of **1** in the presence of the phenol is followed by eq 2, where $k_1 = 8.25 \times 10^{-1}$ s^{-1} M^{-1}. With 2,6-di-*tert*-butylphenol, the same rate expression was obtained, although the rate is considerably slower ($k_1 = 4.45 \times 10^{-2}$ s^{-1} M^{-1}).

$$-\frac{d[1]}{dt} = (k_{auto} + k_1[DMP])[1] \qquad (2)$$

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(20) λ_{max}, nm (ε, M^{-1} cm^{-1}): **2**, 335 (2560); **5**, 347 (9950); **6**, 310 (13400).

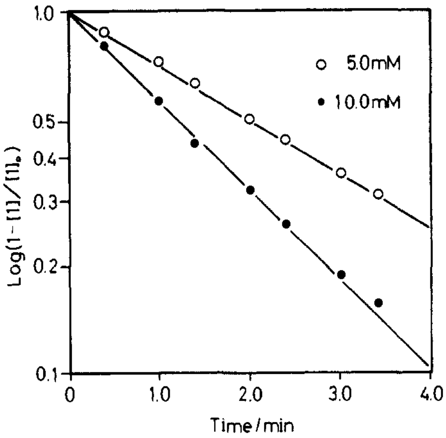

Figure 3. The first-order plots of the conversion of **1** in the presence of 2,6-dimethylphenol under nonaerobic conditions. The concentration of 2,6-dimethylphenol is (○) 5.0 mM and (●) 10.0 mM and the concentration of **1** was 4.65 mM.

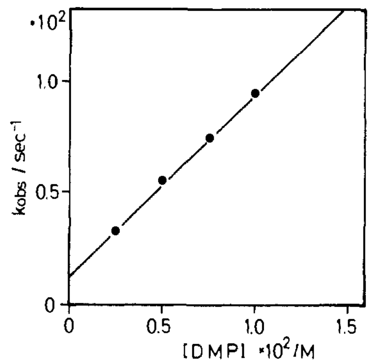

Figure 4. The dependence of the consumption rate constant k_{obs} on the initial concentration of 2,6-dimethlphenol; the concentration of **1** was 4.65 mM.

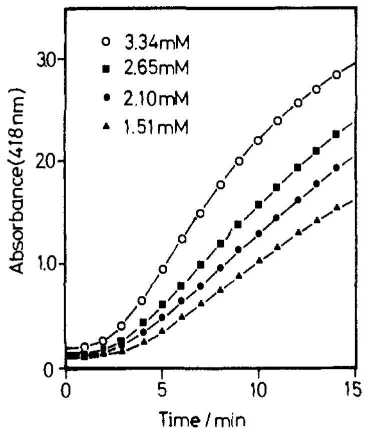

Figure 5. The time course plots of the formation of 3,3′,5,5′-tetramethyldiphenoquinone with various concentrations of **1**. The characteristic absorption band of the diphenoquinone at 418 nm was followed. The concentration of 2,6-dimethylphenol was 40 mM.

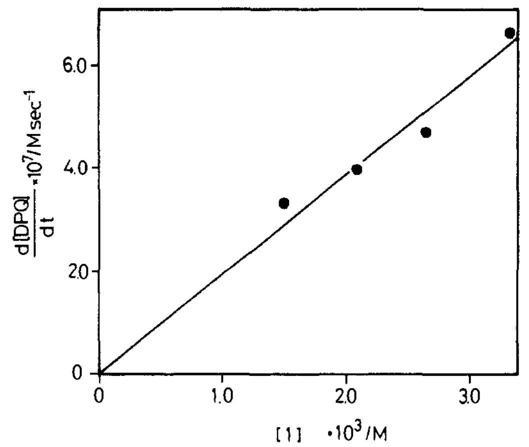

Figure 6. The dependence of the formation rate of the diphenoquinone on the initial concentration of **1**. The formation rate was determined from the maximum slope in Figure 5.

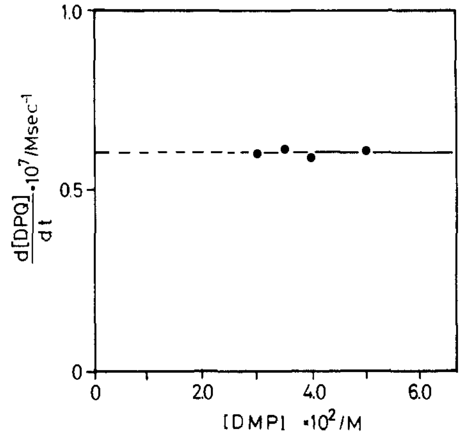

Figure 7. The dependence of the formation rate of the diphenoquinone on the initial concentration of 2,6-dimethylphenol.

With a high concentration of 2,6-dimethylphenol (>40 mM), the contribution of the spontaneous decomposition of **1** is negligible. Under such reaction conditions, the kinetics of the formation of 3,3′,5,5′-tetramethyldiphenoquinone was followed. Figure 5 shows the time dependence of the 418-nm band assignable to the diphenoquinone. An induction period, ca. 2 min, is noted. During the induction period, the color of the solution turns from purple to green and then, as the diphenoquinone forms, the color changes from green to yellowish brown. The green solution does not give any EPR signal but does give a characteristically shifted ^{1}H NMR signal (in $CDCl_3$ at -40 °C, δ 15.1) that can be assigned to a pyrazole ring proton of an antiferromagnetically coupled binuclear copper(II) complex. With the formation of the diphenoquinone, an EPR signal attributable to $Cu[HB(3,5\text{-}Me_2pz)_3]_2$ (**6**) develops; the time dependence of the signal intensity is almost identical with the time course of the diphenoquinone formation.

The rates of formation of the diphenoquinone (DPQ) were determined from the maximum slopes of the plots in Figure 5 and are plotted against the initial concentration of **1** and 2,6-dimethylphenol, as shown in Figures 6 and 7, respectively. The rate was found to be first order with respect to the initial concentration of **1** but zero order with respect to the concentration of the phenol, indicative of the overall rate equation as follows, where $k_2 = 2.22 \times 10^{-4}$ s^{-1} and $[\mathbf{1}]_0$ denotes the initial concentration of **1**,

$$(d[DPQ]/dt)_{max} = k_2[\mathbf{1}]_0 \qquad (3)$$

Discussion

Mechanism for Spontaneous Decomposition of 1. μ-Peroxo binuclear copper(II) complex **1** spontaneously decomposes to μ-oxo binuclear complex **2**. A similar decomposition is well-known for iron porphyrin complexes; iron(II) porphyrin complexes react readily with dioxygen to form μ-peroxo binuclear iron(III) complexes,[21] which are thermally unstable and decompose to μ-oxo binuclear iron(III) complexes. Mechanistic work on this reaction indicates that the rate-determining step is a homolytic cleavage of the O–O bond in the μ-peroxo intermediate.[22] In fact, the rate of consumption of the μ-peroxoiron complex is first order with respect to its concentration, which is consistent with this mechanism.[22] The decomposition rate in the present system is also first order with respect to **1**. This kinetic result is only explicable by

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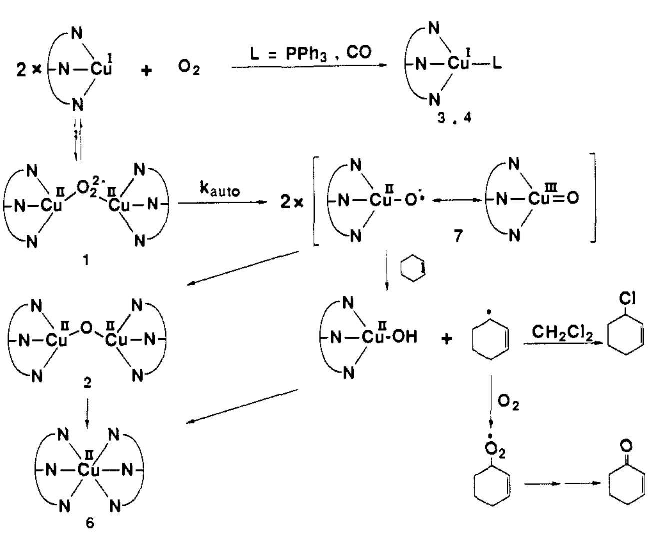

Figure 8. The mechanism for the spontaneous decomposition of **1** and its reactions with PPh_3, CO, and cyclohexene.

the spontaneous reaction of **1** as the rate-determining step, which is most reasonably ascribed to a homolytic cleavage of the O–O bond in **1** as shown in Figure 8. Homolytic cleavage is well established for the μ-peroxo binuclear iron complex,[22] but to our knowledge there was no prior experimental evidence for this process in copper systems. While an impurity such as water or a proton in the solvent could be responsible for the O–O bond cleavage, the careful purification of the solvent used for the present experiments and good reproducibility of the kinetic results exclude this possibility.

The structure of intermediate **7** formed by a homolytic cleavage of the O–O bond in **1** can be described as oxocopper(III) or copper(II)–oxygen atom anion radical in its canonical form. In the decomposition of the μ-peroxo iron(III) complex, the intermediate formed by a homolytic cleavage is suggested to be the oxoiron(IV) species. However, for late-transition-metal complexes, Mayer demonstrated that the metal–oxygen multiple bond is not possible because of the lack of d orbital of π-symmetry on the metal.[23] Thus, it may be more reasonable to identify the structure of **7** as the copper(II)–oxygen atom anion radical. Mayer also predicted the instability of such a species of a late-transition-metal ion (metal–oxygen single bond) because of the high basicity of the oxygen to favor μ-oxo complex. This may explain the facile formation of **2** via **7**. At the present stage, however, we do not draw this conclusion since **7** is very unstable and no spectroscopic data are available.

The addition of PPh_3 or CO results in release of O_2 to give the corresponding mononuclear copper(I) complex. Similar displacement reactions of μ-peroxo binuclear copper(II) complexes have been reported by Karlin et al.[7] The rate of the displacement is much higher than that of the spontaneous decomposition, indicative of the existence of an equilibrium between **1** and a coordinatively unsaturated copper(I) species which is readily trapped by PPh_3 or CO to form a stable copper(I) adduct as shown in Figure 8. In the absence of PPh_3 or CO, the copper(I) species reacts with intermediate **7** formed irreversibly by a homolytic cleavage of the O–O bond of **1** to afford μ-oxo binuclear complex **2**. If the rate-determining step is the homolytic O–O bond cleavage, the rate of the spontaneous decomposition should be first order with respect to the concentration of **1** as consistent with eq 1.

The strength for the displacement of the peroxide ion is $PPh_3 > CO$. This tendency is consistent with the observation that **3** is readily formed upon the treatment of **4** with PPh_3.[15] No oxygenated products are formed in either reaction, except that during CO displacement, a slight amount (~10%) of μ-carbonato binuclear copper(II) complex **5** is produced. The formation of **5** during the displacement reaction may be due to a partial oxidation of CO to CO_2 by **7** formed by the spontaneous decomposition of **1** because of the relatively high temperature (above −20 °C). CO_2 is known to react readily with **2** to afford **5**.[16,18] PPh_3 and CO are not oxidized by **1** at −20 °C, indicating the low reactivity of **1** for oxo-transfer reactions.

Cyclohexene Oxidations. The oxidation of cyclohexene seems to proceed via the same intermediate as the spontaneous decomposition of **1** because the disappearance of **1** in the presence of cyclohexene is consistent with that in the absence of cyclohexene. The oxidation of cyclohexene by **1** may be explained as follows: intermediate **7** formed during the spontaneous decomposition of **1** abstracts an allylic hydrogen atom from cyclohexene, generating a cyclohexenyl radical, which undergoes free radical chain oxidations in the presence of dioxygen. Under anaerobic conditions, the cyclohexenyl radical reacts with solvent $CHCl_3$ to give 2-cyclohexene chloride. The labeling experiment, which shows that the oxygen atoms in the products originate from the exogeneous dioxygen, supports this mechanism. Intermediate **7** works as a hydrogen acceptor rather than an oxo-transfer reagent. Accordingly, cyclohexene oxide is not the main product, whereas an electrophilic oxo-transfer reagent such as mCPBA or oxoiron(IV)-porphyrin π-cation radical[24] is known to epoxidize cyclohexene highly effectively. It is notable that the oxidizing capability of **1**, actually **7** formed by a homolytic O–O bond cleavage of **1**, is not very high and is ineffective for oxidation of hydrocarbons such as cyclohexane or adamantane.

On the basis of the parallelism between iron(II)/dioxygen chemistry and that of copper(I), the low reactivity of **7** (formally oxocopper(III)) may be analogous to that of oxoiron(IV) complex. Oxoiron(IV)-porphyrin is known to be prepared from the μ-peroxo binuclear iron(III) complex. Balch et al. showed that an oxoiron(IV) complex can oxygenate PPh_3 but does not epoxidize cyclohexene.[25] Therefore the reactivity of the oxoiron(IV) complex is apparently much less than that of the oxoiron(IV)–porphyrin π-cation radical (formally oxoiron(V)), which is extremely effective for epoxidations.[24] The limited oxidizing capability of **7** as well as the oxoiron(IV) complex may be ascribed to the formal valence of the metal center; copper(III) and iron(IV) are not high enough oxidation state, and they do not sufficiently enhance the electrophilicity of the oxo group to favor its incorporation into substrates.

Reaction Mechanism for Phenol Oxidations. In order to shed light on the reaction mechanism of tyrosinase, the phenols and a catechol, which are substrates for the enzymatic oxidations, were reacted with **1** under aerobic and anaerobic conditions. Only oxidatively coupled products of phenols and the catechol are formed under anaerobic reaction conditions, whereas some benzophenones are produced in the presence of dioxygen. These experimental results can be explained in terms of the mechanism proposed for oxidation of cyclohexene. Intermediate **7** formed by a homolytic O–O bond cleavage in **1** abstracts a hydrogen atom from phenols to initiate the free radical type reactions described for the cyclohexene oxidation. However, on the basis of the rate expression for the consumption of **1** (eq 2), it is evident that there is an alternative pathway for the consumption of **1** and formation of the diphenoquinone, at least in the anaeobic reaction with 2,6-dimethylphenol. A bimolecular reaction of **1** and 2,6-dimethylphenol is expected from the second term of eq 2. The suggested mechanism for this reaction is illustrated in Figure 9. Since most transition-metal-bound peroxo groups are basic,[26] **1** is anticipated to react with a phenol, an acid, to cause protonation and subsequent replacement of peroxide by phenoxide ion. We interpret the second term of eq 2 to indicate that the replacement

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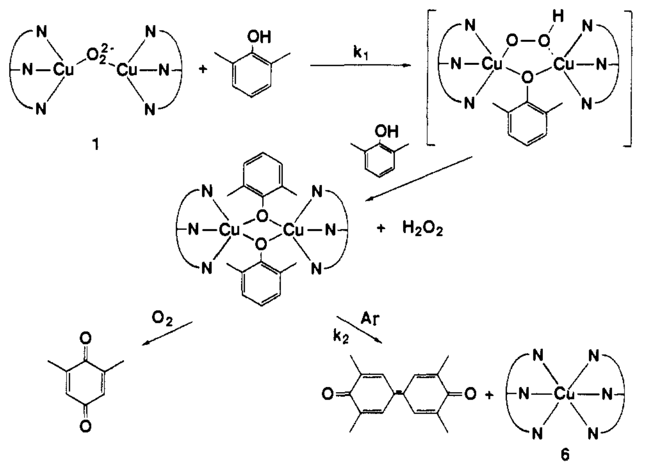

Figure 9. The proposed mechanism for the oxidation of 2,6-dimethylphenol by **1**.

of **1** with the first phenol is the rate-determining step for the consumption of **1**. The formed species, presumably μ-phenoxo-μ-hydroperoxo intermediate, immediately reacts with another phenol to give a binuclear di-μ-phenoxocopper(II) complex, which is relatively stable. The induction period observed in the reaction of **1** and the phenol is ascribed to this reaction. The spectroscopic properties of the resulting green solution indicate the formation of such a binuclear intermediate. The green solution is EPR silent and ^{1}H NMR active, from which we infer the existence of an antiferromagnetically coupled copper(II) complex. From our work on copper(II) complexes ligated by tris(pyrazolyl)borate ligands, we can reasonably make an assignment that the green color (ca. 700 nm) is due to a d–d band of a square-pyramidal copper(II) complex;[27] the binuclear structure is consistent with this assignment. Although the formation of H_2O_2 was not confirmed directly because of the experimental difficulty, the replacement of the peroxide ion with the phenoxide is highly likely. Karlin et al. have reported the replacement of the peroxide ion by a phenol in a μ-peroxo binuclear copper complex, with formation of H_2O_2.[8] Because of its instability, the isolation of the binuclear phenoxo intermediate was unsuccessful. However, we could isolate and determine the crystal structure of a mononuclear phenoxocopper(II) complex $Cu(OC_6H_4\text{-}p\text{-}F)(HB(3,5\text{-}iPr_2pz)_3)$ generated by the reaction of $[Cu(HB(3,5\text{-}iPr2pz)_3)]_2(O_2)$ with p-fluorophenol.[28] Although the steric hindrance of the ligand prevents the dimerization in this case, we believe that this experiment strongly supports the formation of the diphenoxo intermediate by the reaction of **1** and 2,6-dimethylphenol.

The diphenoxo intermediate decomposes spontaneously to give the phenoxy radical which couples with another radical to give the diphenoquinone. If this spontaneous decomposition of the diphenoxo intermediate is the rate-determining step for the formation of the diphenoquinone, the formation rate of the diphenoquinone will be first order with respect to the concentration of the diphenoxo intermediate, as indicated in eq 4 (DPC denotes the diphenoxo binuclear copper(II) intermediate). The consumption rate of **1** and formation rate of the diphenoxo complex are given in eqs 5 and 6, respectively. From these rate equations,

$$d[DPQ]/dt = k_2[DPC] \tag{4}$$

$$-d[\mathbf{1}]/dt = k_1[DMP][\mathbf{1}] \tag{5}$$

$$d[DPC]/dt = k_1[DMP][\mathbf{1}] - k_2[DPC] \tag{6}$$

$$\left(\frac{d[DPQ]}{dt}\right)_{max} = [\mathbf{1}]_0 \frac{k_1^* k_2}{k_2 - k_1^*}\left\{\left(\frac{k_1^*}{k_2}\right)^{-k_1^*/(k_1^*-k_2)} - \left(\frac{k_1^*}{k_2}\right)^{-k_2/(k_1^*-k_2)}\right\} \tag{7}$$

the maximum formation rate of the diphenoquinone is derived as eq 7, where $k_1^* = k_1[DMP]_0$. Under the reaction conditions, $k_1^* \gg k_2$ ($k_2 = 2.22 \times 10^{-4}$ s^{-1}, $k_1^* = (8.25 \times 10^{-1})(5.0 \times 10^{-2}) = 4.13 \times 10^{-2}$ s^{-1}). Hence, eq 7 is simplified to eq 8, which indicates that the rate of formation of the diphenoquinone is first order with respect to the initial concentration of **1** but zero order in initial concentration of 2,6-dimethylphenol, consistent with the experimental results (eq 3).

$$\left(\frac{d[DPQ]}{dt}\right)_{max} = k_2[\mathbf{1}]_0 \tag{8}$$

Under aerobic conditions, dioxygen reacts with the phenoxo radical or directly reacts with the diphenoxo intermediate to form the benzoquinone via free radical reactions. This is supported by the labeling experiment in which oxygen atom is incorporated into the benzoquinone from exogeneous dioxygen.

Biological Relevance. The present work clearly demonstrates that a μ-peroxo binuclear copper complex **1**, which has remarkable similarities to oxytyrosinase in its spectroscopic characteristics, is essentially ineffective for oxo-transfer reactions. There is no indication for a heterolytic O–O bond cleavage in **1** to generate an oxocopper(IV) intermediate, which we would expect to be very effective for electrophilic oxo-transfer reactions. These observations are consistent with the reported reactivity of a mononuclear acylperoxocopper(II) complex (which does not undergo heterolytic O–O bond cleavage).[29] In the present system, we suggest that intermediate **7** (possibly copper(II)–oxygen atom anion radical or oxocopper(III) complex), which is formed by homolytic cleavage of the O–O bond in **1**, is responsible for the observed oxidations. Intermediate **7** functions as a hydrogen acceptor, but it does not possess much reactivity for oxo-transfer reactions. The oxygenation by **1** of substrates such as cyclohexene and phenols does occur in the presence of dioxygen; it is a free radical chain reaction initiated by abstraction of hydrogen from the substrate. An oxygen atom is thus incorporated into the substrate from exogeneous dioxygen. For reactions of phenols with **1**, in addition to the direct hydrogen abstraction by **7** to give a phenoxo radical, an alternative reaction pathway to form a binuclear diphenoxocopper(II) complex is involved, and the spontaneous decomposition of the diphenoxo intermediate also results in generation of a phenoxo radical.

The oxygen incorporation reaction catalyzed by tyrosinase is, in general, believed to proceed via a high-valent oxocopper intermediate that is highly electrophilic and can incorporate oxo into the substrate[30] in a similar fashion to oxoiron(IV)–porphyrin π-cation radical,[24] the accepted active species in catalysis by cytochrome P-450. In this respect, the present result that **1** is not effective for oxo-transfer reactions is negative. Nevertheless, we believe that the low reactivity of **1** and the free radical mechanism for the oxygen incorporation reactions revealed in the present study sheds light on important aspects of copper oxidation chemistry relevant to tyrosinase. It is noteworthy that, even in our system, monooxygenase reactivity can be mimicked in the presence of dioxygen, the reaction conditions for the enzymatic oxidations. Therefore, one cannot easily exclude the possibility that the present reaction is a potentially good model for the oxidation reactions catalyzed by tyrosinase, although the mechanism is apparently of a classical free radical type. The oxygenation reaction catalyzed by tyrosinase is an effortless oxidation as compared with those catalyzed by cytochrome P-450. Therefore, it is not necessary that the oxidation catalyzed by tyrosinase proceeds via a highly reactive oxo-transfer intermediate. The high selectivity of the enzymatic reaction seems to be incompatible with a free radial type reaction mechanism. In fact, in the oxidations by **1**, the selectivity for oxygenation is not very

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high; however, the high selectivity of the enzymatic reaction may be due to the cooperative function of the substrate binding pocket in the active site of tyrosinase.

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Chemical Reduction of a Pentastanna[1.1.1]propellane Derivative and the Synthesis and Molecular Structure of a Bicyclo[1.1.1]pentastannane

Lawrence R. Sita*,[†] **and Isamu Kinoshita**

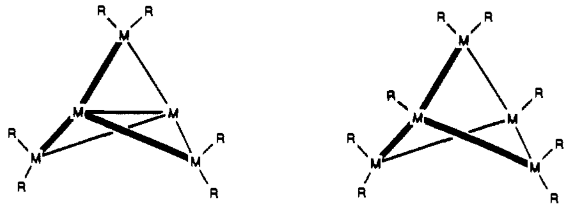
Contribution from the Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213. *Received March 21, 1990*

Abstract: Cyclic voltammetry of 2,2,4,4,5,5-hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (**3**) in THF shows two quasireversible one-electron reduction waves at $E_{1/2} = -1.41$ and -1.93 V (V vs NHE) which correspond to the $[\mathbf{3}]/[\mathbf{3}]^-$ and the $[\mathbf{3}]^-/[\mathbf{3}]^{2-}$ redox couples, respectively. Chemical reduction of **3** with 0.5% potassium amalgam can be achieved in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (abbreviated as crypt) to produce the radical anion complex $[\mathbf{3}]^-[\mathrm{K,crypt}]^+$. This radical anion has been characterized by ESR which shows $g_{iso} = 1.92$, $a(^{119/117}\mathrm{Sn}_{1,3}) = 15$ G, and $a(^{119/117}\mathrm{Sn}_{2,4,5}) = 57$ G for the isotropic spectrum at 410 K and $g_\parallel = 1.99$ and $g_\perp = 1.89$ for the anisotropic frozen spectrum at 130 K. Compound **3** quantitatively reacts with methyl iodide to produce 2,2,4,4,5,5-hexakis(2,6-diethylphenyl)-1-iodo-3-methylbicyclo[1.1.1]pentastannane (**4**), which can be isolated as deep-red crystals. Single crystals of **4** are, at 20 °C, monoclinic, space group $P2_1/c$–C_{2h}^5 (No. 14) with $a = 14.785$ (2) Å, $b = 20.319$ (3) Å, $c = 22.951$ (3) Å, $\beta = 97.63$ (1)°, $V = 6834$ (2) Å^3, and $Z = 4$. The tin–tin bond lengths between the bridging and bridgehead tin atoms of **4** are in the range of 2.825 (1) to 2.842 (1) Å, and the distance between the two bridgehead tin atoms is 3.361 (1) Å. The results of these investigations support the view that the central bridgehead–bridgehead bonding interaction of **3** contributes very little to the stability of this system.

Introduction

Investigations of "nonclassical" structures of the group IVA elements are of special interest since conclusive results can either support or challenge prevailing views concerning the nature of bonding in these molecules.[1] [1.1.1]Propellanes are a class of nonclassical structures since they possess bridgehead atoms having inverted tetrahedral geometries that force the four bonds from each of the bridgehead atoms to all lie within the same hemisphere as shown by **1** in Chart I. Given this configuration, theoretical investigations have long sought to determine the stability and reactivity of these molecular frameworks prior to the availability of representative synthetic derivatives.[2,3] Indeed, these investigations had previously led to the prediction that the simplest carbon [1.1.1]propellane derivative **1a** (M = C, R = H in **1**) should be a viable synthetic target, and this was later confirmed by its preparation.[2] Furthermore, Wiberg, Bader, and Lau[4] point out that by using total electronic charge density (ρ) as determined by all of the occupied orbitals in **1a**, there can be seen an appreciable accumulation of charge between the bridgehead nuclei which corresponds to a calculated bond order of four-fifths of a normal C–C bond. Thus, while generally accepted models of hybridized orbitals cannot adequately describe the bonding situation in [1.1.1]propellanes, as noted by these authors, an indepth theoretical analysis of nonclassical structures has led to the understanding "that the charge distribution of a carbon atom can be so arranged as to yield bond paths that correspond to an inverted structure for the atom".

Chart I



1a M = C and R = H 2a
1b M = Si and R = H 2b
1c M = Ge and R = H 2c

In contrast to the situation with carbon, recent theoretical investigations of the simple silicon and germanium [1.1.1]propellane analogues, **1b** and **1c** (M = Si, R = H and M = Ge, R = H, respectively), all agree that these structures should possess very small bond orders between the two bridgehead atoms with the effect being that the calculated bridgehead–bridgehead bond lengths are unusually long and quite similar to the corresponding calculated nonbonding distances between the bridgehead nuclei in the silicon and germanium bicyclo[1.1.1]pentane analogues, **2b** and **2c** (M = Si, R = H and M = Ge, R = H, respectively, in **2**, Chart I).[3] Interestingly, an outcome of the reduced central

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[†] Present address: Division of Chemistry and Chemical Engineering, Beckman Institute Materials Resource Center, California Institute of Technology, Pasadena, CA 91125.

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