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Superoxo, Peroxo, and Hydroperoxo Complexes Formed from Reactions of Rhodium Porphyrins with Dioxygen: Thermodynamics and Kinetics

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Dioxygen reactions with rhodium tetramesitylporphyrin (TMP)Rh^{II}• (**1**) and the hydride complex ((TMP)Rh−H (**2**)) result in formation of superoxo ((TMP)RhO_2• (**3**)) (eq 1), μ-peroxo ((TMP)Rh−OO−Rh(TMP) (**4**)) (eqs 2 and 3), and hydroperoxy ((TMP)Rh−OOH (**5**)) (eq 4) complexes in benzene at 300 K. The (TMP)Rh system provides an unusual opportunity to evaluate the equilibrium relationship between the superoxo and μ-peroxo complexes (eqs 1−3) and to observe the formation and reactions of the rhodium hydroperoxy species. The central role of these types of dioxygen reactions in hydrocarbon oxidations[1] and the transport and activation of oxygen in biological processes[2] motivates communicating these interim results.

$$(TMP)Rh^{\bullet} + O_2 \rightleftharpoons (TMP)RhO_2^{\bullet} \quad (1)$$

$$(TMP)Rh^{\bullet} + (TMP)RhO_2^{\bullet} \rightleftharpoons (TMP)Rh\text{-}OO\text{-}Rh(TMP) \quad (2)$$

$$2\,(TMP)Rh^{\bullet} + O_2 \rightleftharpoons (TMP)Rh\text{-}OO\text{-}Rh(TMP) \quad (3)$$

$$(TMP)Rh\text{-}H + O_2 \longrightarrow (TMP)Rh\text{-}OOH \quad (4)$$

Benzene solutions of (TMP)Rh^{II}• (**1**) in contact with dioxygen show ^{1}H NMR spectra that are interpreted in terms of mole fraction averaged positions resulting from limiting fast interchange of O_2 between **1** and a dioxygen complex, (TMP)RhO_2• (**3**) (eq 1) (Figure 1). Toluene solutions of **1** when exposed to dioxygen (P_{O_2} = 90 Torr) give EPR spectra in solution ($\langle g \rangle$ = 2.031; T = 253 K) and glass (g_1 = 2.099; g_2 = 2.013; g_3 = 1.988; T = 90 K) that are nearly indistinguishable from the values for L(CH_3CN)$RhOO^{2+}$ (L = *meso*-Me_6-[14]aneN_4), which has been structurally characterized as a coordinated superoxo species.[3]

Solutions of (TMP)Rh^{II}• (**1**) and O_2 in equilibrium with (TMP)RhO_2• (**3**) are meta-stable with respect to the very slow formation of a diamagnetic complex assigned as the μ-peroxo complex ((TMP)Rh−OO−Rh(TMP) (**4**)[4] (eqs 2 and 3). Rapid formation of the μ-peroxo complex of rhodium octaethylporphyrin ((OEP)Rh−OO−Rh(OEP))[5] from reaction of [(OEP)Rh]$_2$ and O_2 suggests that the steric demand of the tetramesitylporphyrin ligand leads to a kinetic barrier to produce the μ-peroxo derivative from reaction of **1** and **3**.

Changes in the ^{1}H NMR shifts for the pyrrole and *p*-methyl hydrogens ($\delta_{pyrrole}$ and δ_{p-CH_3}) as a function of the molar concentration of O_2 are accurately fitted to an expression derived for the 1:1 equilibrium (eq 1) (Figure 2). Excellent agreement between the equilibrium constants (K_1(300 K))[6] evaluated from two independent observables (K_1(pyrr) = 8.4(0.5) × 10^3, K_1(*p*-CH_3) = 8.5(0.4) × 10^3; T = 300 K)[6] provides confidence that the equilibrium between **1** and **3** is accurately described. Equilibrium constants for producing the μ-peroxo complex **4** from reaction of **1** and **3** (eq 2) (K_2 = 1.2(0.6) × 10^3)[6] and from the overall reaction (eq 3) (K_3 = 1.0(0.6) × 10^7)[6] are evaluated by integration of the ^{1}H NMR at equilibrium at 300 K.

Reaction of the hydride complex (TMP)Rh−H (**2**) in benzene with O_2 produces a transient diamagnetic species identified as the

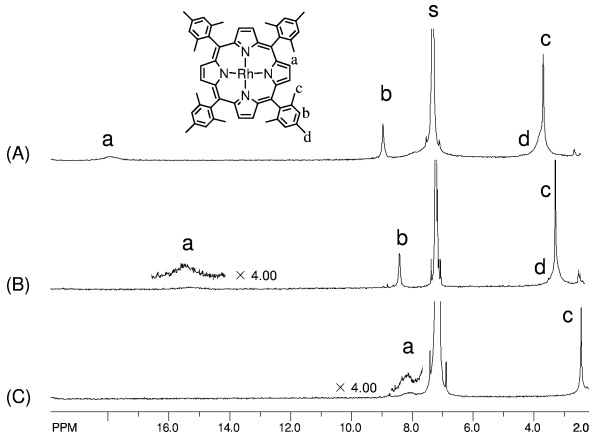

Figure 1. Proton NMR spectra for a benzene solution of (TMP)Rh• (1.0×10^{-3} M) at 300 K: (A) absence of O_2; (B) 6 Torr of O_2; (C) 760 Torr of O_2.

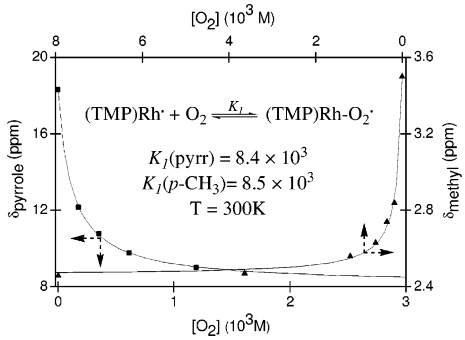

Figure 2. Fast exchange mole fraction averaged ^{1}H NMR chemical shifts for the pyrrole (■) and *p*-methyl (▲) hydrogens of (TMP)Rh• (**1**) and (TMP)Rh−O_2• (**3**) in C_6D_6 as a function of [O_2] at 300 K ([(TMP)Rh] = 1.0×10^{-3} M). The solid curves are the calculated nonlinear least-squares best fit lines for K_1, δ_1, and δ_3 fitted to the equation for 1:1 equilibrium: $\delta_{obs} = (\delta_1 + K_1[O_2]\delta_3)/(1 + K_1[O_2])$, in which δ_1 and δ_3 are the ^{1}H NMR shifts of for species **1** and **3**, respectively.

hydroperoxy complex (TMP)Rh−OOH (**5**).[7] The ^{1}H NMR resonance at −0.30 ppm that is absent in the deuterated derivative ((TMP)Rh−OOD) is assigned to the hydroperoxy hydrogen. A kinetic study for the reaction of **2** with O_2 is shown in Figure 3. Disappearance of the hydride **2** is accompanied by formation of the transient hydroperoxy complex **5**, which decays to an equilibrium distribution of **1** and **3**. The kinetic observations in Figure 3 are accurately fitted to a pathway where the hydroperoxy complex **5** is formed by direct reaction of O_2 with **2** followed by an apparent first-order decay of the hydroperoxy complex **5** to products (TMP)Rh^{II}•, H_2O, and O_2 (eqs 4 and 5).

$$(TMP)Rh\text{-}OOH \longrightarrow (TMP)Rh^{II}\bullet + 1/2H_2O + 3/4O_2 \quad (5)$$

The rate law for reaction 4 ($-d[Rh-H]/dt = k_4[Rh-H][O_2]$) is consistent with a direct reaction of (TMP)Rh−H with O_2. Hydrogen

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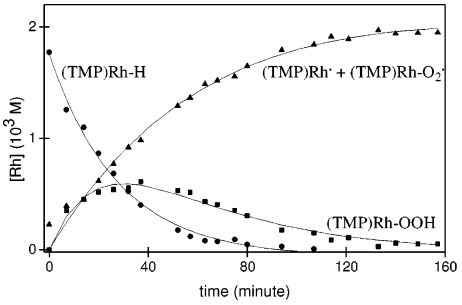


Figure 3. Change of concentrations of (TMP)Rh−H (●), (TMP)Rh−OOH (■), and the paramagnetic (TMP)Rh species (▲) with time in the reaction of (TMP)Rh−H with O_2 (680 Torr) in benzene at 300 K ([(TMP)Rh] = 1.0×10^{-3} M). The solid curves are the nonlinear least-squares best fit lines for the solution species, which provide rate constants of k_4 and k_5 as $7.1(1.0) \times 10^{-2}$ $M^{-1}s^{-1}$ and $4.7(1.4) \times 10^{-4}$ s^{-1}, respectively.

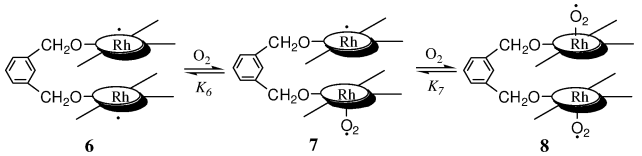
atom transfer from Rh−H to a superoxo oxygen (RhO_2•) was the anticipated route to form the hydroperoxy complex (Rh−OOH) because of several similar precedents,[8] but the kinetic study clearly indicates that an alternate pathway is operating in the (TMP)Rh system. The sterically demanding mesityl groups must inhibit (TMP)Rh−H and (TMP)RhO_2• from reaching the transition state for hydrogen transfer. A small deuterium isotope effect ($k_{4(H)}/k_{4(D)} = 1.5$) and the rate law observed for reaction 4 are most consistent with a near concerted addition of O_2 to the Rh−H unit through a low symmetry transition state.

The hydroperoxy complex (TMP)Rh−OOH is a transient that reacts on to form water and (TMP)Rh^{II}• (**1**), which contrasts with most transition metal hydroperoxy complexes that produce a hydroxide complex (MOOH → MOH + $^1/_2O_2$).[9] Reaction of H_2 and O_2 is catalyzed by **1** as evidenced by the growth of the broad ^{1}H NMR resonance for H_2O at 0.38 ppm, but formation of H_2O proceeds slowly because the reaction of **1** with H_2 is a rate-limiting termolecular process.[10] Tethered dirhodium(II) diporphyrin complexes with three mesityl groups per porphyrin unit have sterics similar to those of rhodium(II) tetramesitylporphyrin ((TMP)Rh^{II}•) and give fast bimolecular reactions with H_2,[11] which provides a better opportunity to illustrate catalytic behavior involving dihydrogen.

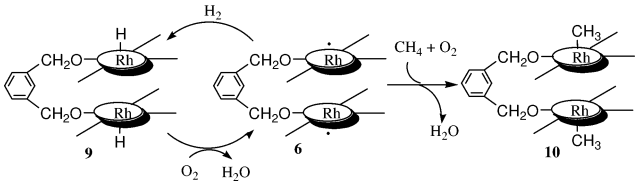
The *m*-xylyl-tethered dirhodium(II) diporphyrin complex (•Rh(*m*-xylyl)Rh• (**6**)) reacts reversibly with O_2 to form mono- and bis-dioxygen complexes (•Rh(*m*-xylyl)Rh−O_2• (**7**) and •O_2−Rh(*m*-xylyl)Rh−O_2• (**8**)) (Scheme 1). The equilibrium constants ($K_6 = 1.5(0.4) \times 10^4$; $K_7 = 7.4(0.2) \times 10^3$; $T = 300$ K)[6] for the sequential dioxygen complex formation were evaluated from the nonlinear least-squares curve fitting of the observed mole fraction averaged chemical shifts to the equation: $\delta_{obs} = (\delta_6 + K_6[O_2]\delta_7 + K_6K_7[O_2]^2\delta_8)/(1 + K_6[O_2] + K_6K_7[O_2]^2)$, where δ_6, δ_7, and δ_8 are the ^{1}H NMR shifts for species **6**, **7**, and **8**, respectively. The observed ratio of approximately 2 for K_6/K_7 is the expected statistical result when the two rhodium(II) centers are fully independent.

Reaction of •Rh(*m*-xylyl)Rh• (**6**) with H_2 forms the dihydride derivative H−Rh(*m*-xylyl)Rh−H (**9**) rapidly, and **9** reacts readily with O_2 to form water and regenerate **6** without observing a hydroperoxy intermediate. Mixtures of H_2 ($P_{H_2} > 300$ Torr) and O_2 ($P_{O_2} < 30$ Torr) react with **6** to produce water catalytically until the O_2 is essentially consumed, and the residual H_2 reacts with **6** to form the dihydride complex **9** (Scheme 2). Reaction of **6** with CH_4 and O_2 ($P_{CH_4} > 300$ Torr, $P_{O_2} < 30$ Torr) produces only a stoichiometric quantity of H_2O and the dimethyl complex CH_3−Rh(*m*-xylyl)Rh−CH_3 (**10**) (Scheme 2), which does not react thermally with O_2 at a finite rate at 300 K.

Scheme 1



Scheme 2



More complete thermodynamic and mechanistic studies for dioxygen and hydroperoxy complex formation and an effort to evaluate the utility of these species in substrate oxidation reactions are in progress.

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Supporting Information Available: Equilibrium measurements for the dioxygen binding process to rhodium(II) metalloradicals, the expressions for the kinetics study of (TMP)Rh−H with dioxygen, and characterization data for compounds **1**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) (TMP)Rh−OO−Rh(TMP) (**4**): ^{1}H NMR (C_6D_6) δ (ppm) 8.27 (s, 8H, pyrrole), 7.21 (s, 4H, *m*-phenyl), 6.93 (s, 4H, *m*-phenyl), 2.41 (s, 12H, *p*-CH_3), 1.92 (s, 12H, *o*-CH_3), 1.20 (s, 12H, *o*′-CH_3).

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(6) All equilibrium constants (K_1, K_2, K_3, K_6, K_7) are based on the standard state of 1 M for each constituent. Equilibrium constants are dimensionless, but are sometimes given nominal units associated with the standard state. (Nominal units are M^{-1} for K_1, K_2, K_6, and K_7, and M^{-2} for K_3).

(7) (TMP)Rh−OOH (**5**): ^{1}H NMR (C_6D_6) δ (ppm) 8.90 (s, 8H, pyrrole), 2.45 (s, 12H, *p*-CH_3), 2.24 (s, 12H, *o*-CH_3), 1.99 (s, 12H, *o*′-CH_3), −0.30 (br, 1H, Rh−OO*H*), the *m*-phenyl hydrogens are obscured by solvent peak.

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