Biomimetic Oxidation of 3,5-Di-tert-butylcatechol by Dioxygen via Mn-Enhanced Base Catalysis

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The 6-coordinate dioximatomanganese(II) complex [Mn(HL)(CH₃OH)]⁺ (2, where H₂L is [HON=C(CH₃)₂CH₂=CH₂]NH), formed by instant solvolysis of [Mn₂(HL)₂][BPh₄]₂ (1) in methanol, accelerates the triethylamine (TEA)-catalyzed oxidation of 3,5-di-tert-butylcatechol (H₂dtbc) by O₂ to the corresponding o-benzoquinone. Significantly, 2 alone has no catalytic effect. The observed rate increase can be explained by the interaction of 2 with the hydroperoxo intermediate Hdtbco₂⁻ formed from Hdtbc⁻ and O₂ in the TEA-catalyzed oxidation. The kinetics of the TEA-catalyzed and Mn-enhanced reaction has been studied by gas-volumetric monitoring of the amount of O₂ consumed. The initial rate of O₂ uptake (Vₒ₂) shows a first-order dependence on the concentration of 2 and O₂ and saturation kinetics with respect to both H₂dtbc and TEA. The observed kinetic behavior is consistent with parallel TEA-catalyzed and Mn-enhanced oxidation paths. The 3,5-di-tert-butylsemiquinone anion radical is an intermediate detectable by electron spin resonance (ESR) spectroscopy. The dimeric catalyst precursor has been characterized by X-ray diffraction and electrospray ionization mass spectrometry and the monomeric catalyst by ESR spectroscopy.

Introduction

Mn-containing redox enzymes are ubiquitous in nature and perform a number of vital functions.¹ The most notable examples are manganese superoxide dismutase,²a manganese catalases,²b peroxidase,²c and manganese-dependent dioxygenases.²d Photosynthetic water oxidation by photosystem II is controlled by a tetramanganese cluster.²e,f The modeling approach has been extensively used to elucidate the structure and function of Mn redox enzymes.³ The reactions of O₂ and its reduced forms with Mn have been reviewed by Pecoraro et al.⁴

Catechol oxidases are plant enzymes containing dinuclear Cu centers, which catalyze the oxidation of catechols to quinones.⁵ Catecholases are also involved in the formation of melanin pigments and the enzymatic browning of fruits.⁶ Functional catecholase models based on Cu,⁷ Fe,⁸ Co,⁹ and Zn¹⁰ have been investigated to shed light on the reaction mechanisms involved and to help design “bioinspired” catalyst systems for various reactions requiring activation of O₂.

The abundance of O₂-activating Co, Cu, and Fe catalysts¹¹ is in contrast with the relative rarity of Mn complexes capable of that function under homogeneous conditions. Reversible O₂ additives have been reported and characterized as metal–peroxo species for manganese(II) porphyrin derivatives,¹² a manganese(III) diene complex,¹³ and a dinuclear manganese-

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(3) Pecoraro, V. L.; Hsieh, W.-Y. Reference 1; Chapter 14, pp 429–504.
Additional examples of O₂ binding are manganese phthalocyanines, a Mn complex of 3,5-di-tert-butylcatecholate, and a series of [Mn₃X₃(PR₃)] complexes. Manganese(II) tris[(R)-pyrazolyl]borates complexes undergo oxidation with O₂ to the MnIII derivative. The peroxomanganese(III) complex [Mn(O₂)(3,5-Pr₂Ph)(H₂O)₂] was made using H₂O₂ rather than O₂. MnIII(salpr) reacts with O₂, affording the bridged [MnVI(salpr)(H₂O)] dimer via a MnII intermediate. MnIII(salpp) reacts similarly but is assumed to bypass the MnIII stage. Further MnII complexes reacting irreversibly with O₂ are those of anionic O-donor ligands in preference over neutral N-donor ligands.

Manganese porphyrins undergo irreversible oxidation upon reaction with O₂ in nondonor solvents. The air oxidation of manganese(II) tetrphenylporphyrin in chlorobenzene yields a monooxo-bridged MnIIIL mixed-valence complex.

The kinetics and mechanisms of metal-catalyzed autoxidation reactions, including Mn systems, have been recently reviewed. Aerobic catechol oxidation catalysis has been reported by Funabiki et al. for a bis(µ-oxo)dimanganese(III) complex via a manganese(II) semiquinonato intermediate.

Our earlier work was concerned with the biomimetic catalytic oxidation of 3,5-di-tert-butylcatechol (H₂dbc), using the functional catecholase model bis(dimethylglyoximato)cobalt(II) and -iron(II) complexes [also known as cobaloxime (II)c₉ and ferroxime(II) derivatives]. Kinetic investigations of these models were carried out to help elucidate the mechanism of the underlying biological catecholase reaction. As an extension of the scope of oximate(II) models beyond ferroximes, some new dioximatoiron complexes with less rigid coordination spheres have been synthesized, which turned out to possess catecholase activity.

The general mechanistic pattern typical for these dioximato-metal(II) complexes is the formation of a ternary catalyst−O₂−substrate intermediate, which in the rate-determining step undergoes H-atom transfer, generating a semiquinone anion radical.

In this paper, we report the (a) synthesis and characterization of the dimeric MnIII complex [Mn₂(HL)₂(BPh₄)₂], where H₂L is [H₂O₂]+(CH₃C₆H₄O)₆−(C₆H₅)₃C₆H₄O₂⁻, and (b) a kinetic study of the remarkable accelerating effect that monomeric [Mn(HL)(CH₃OH)]+ (2) exerts on the triethylamine (TEA)-catalyzed (base-catalyzed) oxidation of 3,5-dibenoazoxy methanol (MeOH).

**Experimental Section**

The ligand H₂L was synthesized by the condensation of 2 equiv of diacetylmonoxime with 1 equiv of diethylenetriamine in methanol (MeOH) according to a reported procedure. The product gave satisfactory elemental analyses for C₁₉H₁₄N₂O₂. Its purity was checked by ¹H NMR spectroscopy.

Electron spin resonance (ESR) spectra were recorded on a Bruker ELEXY S500 CW-EPR spectrometer in a MeOH solution. The catalytic oxidation of 3,5-di-tert-butylcatechol (H₂dbc) was monitored under O₂, keeping the solution saturated with O₂ throughout the reaction with ELEXYS E500 CW-EPR spectrometer in a MeOH solution. The ligand H₂L was synthesized by the condensation of 2 equiv of diacetylmonoxime with 1 equiv of diethylenetriamine in methanol (MeOH) according to a reported procedure. The product gave satisfactory elemental analyses for C₁₉H₁₄N₂O₂. Its purity was checked by ¹H NMR spectroscopy.

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...the experiments. Spectra were accumulated over the initial 30 min of the reaction.

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a PE-SCIEX API 2000 triple-quadrupole mass spectrometer. Spectra were acquired in positive mode with a 4800-V spray voltage and a 30-V orifice voltage; the source housing was kept at room temperature. Samples were dissolved in MeOH. The instrument was used in Q1 scan mode in the range of m/z 50–1000.

The oxidation was followed by (i) recording the time evolution of UV/vis spectra on a Hewlett-Packard 8453 diode-array spectrophotometer and (ii) measuring the volume of O2 absorbed.

The rates of O2 uptake were measured in a constant-pressure gas-volumetric apparatus, described earlier. The reaction was started by dropping the solid MnII catalyst precursor into a vigorously stirred, thermally equilibrated MeOH solution of H2dtbc from a sample holder manipulated from the outside. The rate of O2 absorption was independent of the stirring rate, excluding eventual diffusion control effects.

Throughout this paper, M = mol dm−3.

[Mn(HL)][B(C6H5)4]2 (I) was prepared by dissolving H2L (538 mg, 2 mmol) and MnCl2·4H2O (198 mg, 1 mmol) in MeOH at 25 °C. The resulting red solution was stirred for 30 min. After the addition of Na[B(C6H5)4] (342 mg, 1 mmol) in 5 mL of MeOH, an orange precipitate formed, which was collected by filtration and dried at ambient temperature. The complex was recrystallized from MeOH/CH2Cl2 (1:1) to give red single crystals suitable for analysis by X-ray diffraction. Yield: 55%. Anal. Calcd for [Mn(HL)][B(C6H5)4]2: C, 67.01; H, 6.64; N, 10.92. IR (KBr disk): ν 3441(m), 3058(m), 1645(m), 1424(m), 1054(s), 735(s), 711(s), 612(m) cm−1.

Crystal Structure Determination of Complex 1. Crystal data:27–30 C20H28B2MnN4O2, M = 642.50, monoclinic, a = 14.143(1) Å, b = 14.226(2) Å, c = 17.800(2) Å, β = 130.2(1)°, space group P21/c, Z = 4, μ = 3.552 mm−1, 4849 reflections measured, 4551 unique [R(int) = 0.0297], which were used in all calculations. Final R indices [I > 2σ(I)] were R1 = 0.0569 and wR2 = 0.1122. The C3 atom splits into two positions in a 0.81:0.19 ratio.

Results and Discussion

X-ray Structure of 1. The molecular structure of the dimeric catalyst precursor 1 is shown in Figure 1 (the two BPh4− ions are omitted for clarity). Each monomeric unit contains one HL− ligand, having one oximato(1−) and one oxime group. The coordination spheres of both Mn atoms (that of Mn1 shown in Figure 2) are strongly distorted octahedra with four N atoms (N1−N4) in the quasi-equatorial plane and the N5 atom in the pseudoaxial position. The other axial position is occupied by a bridging oximate O atom from the other monomeric unit. The result is a bis(μ-oximato-1N:2O) dimer formed around the inversion center. There is intramolecular H bonding between the oxime H atoms and the O atoms of the oximato moiety [O1−H1⋯O2: H−O 0.71 Å, H⋯O 1.98 Å, O⋯O 2.568(6) Å, <(O–H⋯O) 141°] and a rather weak H bond between the same donor and the N4 of the same ligand [O1−H11⋯N4: H−O 0.71 Å, H⋯N 2.62 Å, O⋯O 3.062(7) Å, O−H⋯N 123(8)°], conferring additional stability on the dimer.

ESI-MS. For ESI-MS, the dimeric MnII complex 1 was dissolved in MeOH and measured in positive ion mode. In the spectra, an intensive singly charged ion was observed, corresponding to the 5-coordinate monomeric MnII[HL]+ structure (m/z = 323.2). Besides this, the 6-coordinate methanolate complex [MnII(HL)(CH3OH)]+ (m/z = 355) could also be observed in medium intensity. The free protonated ligand [H2L + H]+ (m/z = 270.1) was detected in low intensity only. These results strongly indicate that the predominant species in MeOH should be [MnII(HL)(CH3-}

![Figure 1. Molecular diagram of the dication of 1, [Mn(HL)x]2+,
with the numbering of atoms. The minor disorder component [C(3×), H(3× 1), H(3× 2)], and H(1×1)] is omitted for clarity. Atomic displacement parameters are represented at the 50% probability level.

![Figure 2. Coordination sphere of Mn1 with distances (Å) and angles (deg).](image-url)
OH])⁺, a large percentage of which loses coordinated CH₃OH upon evaporation, generating the m/z = 323.2 species.

**ESR Spectroscopy.** The ESR spectra in a MeOH solution also provide information upon the nature of Mn species present. The solid dimer 1 dissolved in acetonitrile is ESR-silent. However, immediately upon dissolution of complex 1 in MeOH at room temperature, the typical six-line pattern of monomeric Mn II appears (Figure 3) and persists for several hours, indicating that 1 dissociates into monomeric units 2 (eq I), which are stabilized by coordination of MeOH as the sixth ligand. Because the intensity of the ESR spectrum does not change in time, the dissociation can be regarded as complete. Dissociation does not take place in acetonitrile.

**Base-Catalyzed Oxidation of H₂dtbc.** The base-catalyzed oxidation of H₂dtbc to 3,5-di-tert-butyl-1,2-benzoquinone (dtbq) by O₂ is known to take place in the presence of dilute (<0.06 M) NaOH in MeOH at room temperature (Scheme 1).31

<table>
<thead>
<tr>
<th>Scheme 1. NaOH-Catalyzed Oxidation of H₂dtbc</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₂dtbc] + 0.5O₂ → [dtbq] + H₂O</td>
</tr>
</tbody>
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**Scheme 2. Base-Catalyzed Equilibrium Binding of O₂, Leading to a Peroxy Intermediate**

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The reactive species in this process is the catecholato monoanion, Hdtbc⁻, which can be generated by the known reaction of H₂dtbc with a hydroxide ion. It binds O₂ at room temperature, affording the hydroperoxo adduct HdtbcO₂⁻ (Scheme 2).31

Deprotonation of H₂dtbc can also be effected by N bases of suitable strength, an approach we used in this work. Figure 4 shows the spectral changes (3) observed during TEA-catalyzed oxidation of H₂dtbc together with the spectra of H₂dtbc (2) and TEA itself (1). The series of spectra (3) corresponds to rapid deprotonation of H₂dtbc by TEA to Hdtbc⁻, followed by oxidation to dtbq. The simultaneous increase of the bands at 203, 282, and 404 nm and of the shoulder at 220 nm, as well as the lack of isosbestic points, indicates the absence of absorbing products other than dtbq.

An important feature of the base-catalyzed oxidation is the appearance of the 3,5-di-tert-butyl-1,2-benzoquinonate (1⁻) anion radical (dbsq⁻) as an intermediate detectable by ESR spectroscopy (Figure 5). No detection is possible spectrophotometrically because of its low concentration reached during the oxidation (the sodium salt of dbsq⁻ has λ_max = 730 nm and ε_730 = 680 M⁻¹ cm⁻¹).32 This should be taken into account by the proposed reaction mechanism.

When other N bases are used as catalysts, the rate varies as a function of the base strength. Some examples are shown

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| Table 1. Initial Rate of \( \text{H}_2 \text{dtbc} \) Oxidation Catalyzed by N Bases of Different Strength (Solvent MeOH, \([\text{H}_2 \text{dtbc}]_0 = 3.86 \times 10^{-3} \text{ M}, [\text{Base}]_0 = 3.86 \times 10^{-3} \text{ M, under Air} \)) |
|-----------------|--------------|----------------|
| Base            | \( pK_a \)   | Initial rate/M s\(^{-1} \) |
| none            | na           | 1.68 \times 10^{-9}    |
| pyridine        | 5.33 \(^{33a}\) | 1.83 \times 10^{-9}    |
| 1-methylimidazole | 7.06\(^{33a}\) | 3.79 \times 10^{-9}    |
| triethylamine   | 9.73 \(^{33a}\) | 4.34 \times 10^{-7}    |
| 1,8-bis(dimethylamino)napthalene | 12.34\(^{33b}\) | 3.41 \times 10^{-7}    |
| (proton sponge) |              |                        |

in Table 1, indicating that the rate of base-catalyzed oxidation depends on the \( pK_a \) of the added N base. This is in line with the generalized Scheme 2, where protonation of \( \text{H}_2 \text{dtbc} \) takes place by the added base, generating the monoanion \( \text{Hdtbc}^- \), which is the reactive intermediate toward \( \text{O}_2 \). In the presence of a proton sponge, the rate does not increase further, indicating that the dianion has about the same reactivity as \( \text{Hdtbc}^- \).

Individual volumetric \( \text{O}_2 \) absorption curves show the saturation behavior leveling off at the stoichiometric amount corresponding to Scheme 1, i.e., upon reduction of both O atoms to \( \text{H}_2 \text{O} \). The reaction can be restarted by repeated addition of \( \text{H}_2 \text{dtbc} \) to mixtures in which the \( \text{O}_2 \) uptake has already ceased. For further work, we have selected TEA to ensure significant deprotonation to the monoanion.

**Effect of Added \([\text{Mn}^{II}(\text{HL})(\text{MeOH})]^+\)** on the Oxidation of \( \text{H}_2 \text{dtbc} \). When present alone in MeOH, the complex \([\text{Mn}^{II}(\text{HL})(\text{MeOH})]^+\) does not react with \( \text{O}_2 \) nor does it catalyze catechol oxidation. However, when added to a solution in which the TEA-catalyzed oxidation of \( \text{H}_2 \text{dtbc} \) is in progress, it brings about a remarkable increase (ca. 2.5-fold) in the oxidation rate. This acceleration is illustrated by the absorbance at 404 nm displayed in Figure 6 as a function of time. The corresponding two series of spectra are given in the Supporting Information as Figures 1S and 2S. Series 1 refers to the TEA-catalyzed oxidation, whereas series 2 was recorded after the addition of \( 5.2 \times 10^{-3} \text{ M } [\text{Mn}^{II}(\text{HL})(\text{MeOH})]^+ \) in MeOH to the reacting solution.

Upon the addition of \( \text{MnCl}_2 \) instead of \([\text{Mn}^{II}(\text{HL})(\text{MeOH})]^+\) to the reacting solution, a dark-brown solution formed, but no oxidation of \( \text{H}_2 \text{dtbc} \). Instead, \( \text{MnO}_2 \) gradually precipitated, indicating oxidation of \( \text{Mn}^{III} \) followed by disproportionation.

In another experiment, complex 1 was dissolved in \( \text{O}_2 \)-saturated MeOH, containing \( \text{H}_2 \text{dtbc} \). According to ESR spectroscopy of this solution, the six-line pattern of monomeric \([\text{Mn}^{II}(\text{HL})(\text{MeOH})]^+\) appeared, but no oxidation of \( \text{H}_2 \text{dtbc} \) (\( \text{O}_2 \) absorption) took place. However, upon the addition of TEA, the oxidation of \( \text{H}_2 \text{dtbc} \) started immediately as shown by (a) the absorption of \( \text{O}_2 \), (b) development of a strong absorption band centered at 404 nm, and (c) the appearance of the characteristic ESR spectrum of \( \text{dbsq}^+ \), which is a narrow doublet at \( g = 2.0032 \) (Figure 5)\(^{34}\).


The kinetic dependences shown in Figures 7-10 can be described by the empirical rate equation (II), where \( A \), \( B \), and \( C \) are constants.

\[
V = \frac{A + B[Mn]_0[O_2]_0[H_{dtbc}]_0}{1 + C[H_{dtbc}]_0/[TEA]_0} 
\]

Empirical rate law (II) is consistent with the following reaction mechanism:

\[
\text{H}_2\text{dtbc} + \text{TEA} \rightleftharpoons \text{Hdtbc}^- + \text{TEAH}^+ \quad K_C/K_T \quad (1)
\]

\[
\text{Hdtbc}^- + \text{O}_2 \rightleftharpoons \text{HdtbcO}_2^- \quad K_B \quad (2)
\]

\[
\text{HdtbcO}_2^- \rightarrow \text{dbsq}^- + \text{HO}_2 \quad k_B \quad (3)
\]

\[
\text{dbsq}^- + \text{O}_2 \rightarrow \text{dtbq} + \text{O}_2^- \quad \text{fast} \quad (4)
\]

\[
\text{HO}_2 + \text{TEA} \rightleftharpoons \text{O}_2^- + \text{TEAH}^+ \quad \text{fast} \quad (5)
\]

\[
[(\text{HL})\text{Mn}^{II}(\text{MeOH})]^{+} + \text{HdtbcO}_2^- \xrightarrow{\text{MeOH}} [(\text{HL})\text{Mn}(\text{O}_2\text{dtbcH})]^{X} \quad K_6 \quad (6)
\]

\[
\text{X} \rightarrow \text{dbsq}^- + [(\text{HL})\text{Mn}^{III}\text{O}_2\text{H}]^{+} \quad k_7 \quad (7)
\]

\[
[(\text{HL})\text{Mn}^{III}\text{O}_2\text{H}]^{+} + \text{MeOH} \rightarrow [(\text{HL})\text{Mn}^{II}(\text{MeOH})]^{+} + \text{HO}_2 \quad (8)
\]

\[
2\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^2- \quad \text{fast} \quad (9)
\]

\[
\text{H}_2\text{O} + \text{O}_2^2- \rightarrow 0.5\text{O}_2 + 2\text{OH}^- \quad \text{fast} \quad (10)
\]

According to the proposed mechanism (1)–(10), the oxidation of \( \text{H}_2\text{dtbc} \) in the presence of \( \text{TEA} \) takes place via deprotonation to the monoanion (1) followed by the formation of the \( \text{O}_2 \) adduct \( \text{HdtbcO}_2^- \) in step 2 (for the structure of this hydroperoxide, see Scheme 2). It decomposes in rate-limiting step 3 to \( \text{HO}_2 \) (stabilized as \( \text{O}_2^- \)) and the semiquinonato anion radical \( \text{dbsq}^- \), which is rapidly oxidized to the product \( \text{dtbq} \) by \( \text{O}_2 \) (step 4). At this point interference by \( [(\text{HL})\text{Mn}^{II}(\text{MeOH})]^{+} \) becomes operative via displacement of coordinated \( \text{MeOH} \) by \( \text{HdtbcO}_2^- \) in step 6, leading to the formation of \( [(\text{HL})\text{Mn}(\text{O}_2\text{dtbcH})]^{X} \). Rapid elimination of \( \text{dbsq}^- \) in step 7 and of \( \text{HO}_2 \) in step 8 (with immediate deprotonation to \( \text{O}_2^- \)) regenerates \( [(\text{HL})\text{Mn}^{II}(\text{MeOH})]^{+} \) and
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Table 2. Summary of the Rate and Equilibrium Constants (MeOH, 25 °C)

<table>
<thead>
<tr>
<th>source</th>
<th>C = K_c/K_T</th>
<th>B = k_bK_cK_T/[M]_0/[O_2]</th>
<th>A = k_b/[M]_0 s^{-1}</th>
<th>slope/s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[TEA] dep. (Figure 12)</td>
<td>1.72 ± 0.03</td>
<td>895 ± 27</td>
<td>0.84 ± 0.025</td>
<td>na</td>
</tr>
<tr>
<td>[Mn]_0 dep. (calcd) (Figure 9)</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>[Mn]_0 dep. (calcd) (Figure 9)</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>(6.69 ± 0.33) x 10^{-3}</td>
</tr>
<tr>
<td>[Mn]_0 dep. (calcd) (Figure 9)</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>(5.25 ± 0.16) x 10^{-3}</td>
</tr>
<tr>
<td>[Mn]_0 dep. (calcd) (Figure 9)</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>(5.39 ± 0.14) x 10^{-3}</td>
</tr>
</tbody>
</table>

clones the Mn-enhanced cycle. The dbsq^- released is rapidly oxidized to dtbq by O_2 in step 4.

While steps 1–7 account for the formation of intermediate dbsq^- and of the observed oxidation product (dtbq), fast steps 9 and 10 describe how intermediate O_2^- is converted to OH^- (the final reduction product of O_2) via the peroxo (O_2^2-) oxidation state.

The kinetic equation based on the proposed mechanism can be obtained as follows. If the initial concentration of [(HL)Mn^{II}(MeOH)]^+ is denoted by [Mn]_0, the rate of oxidation (V_m) can be written as

\[ V_m = k_b[HdtbcO_2^-] + k_bK_c[Mn]_0[HdtbcO_2^-] = k_bK_B [Hdtbc^-][O_2] + k_bK_cK_T[Hdtbc][O_2][Mn]_0 = (k_b + k_bK_c[Mn]_0K_B[Hdtbc^-][O_2]) \] (11)

An approximate expression for [Hdtbc^-] (eq 12) can be obtained from the mass balance for H_2dtbc and TEA in combination with the required protonation constants (see the Supporting Information, eqs 1S–12S).

\[ [Hdtbc^-] = \frac{[H_2dtbc]_0}{1 + (K_c/K_T)[H_2dtbc]/[TEA]_0} \] (12)

Upon substitution of eq 12 into eq 11, we obtain the kinetic equation (13).

\[ V_m = \frac{(k_b + k_bK_c[Mn]_0)[O_2][H_2dtbc]_0}{1 + (K_c/K_T)[H_2dtbc]/[TEA]_0} \] (13)

On comparison of eq 13 with the constants of empirical rate law (II), we can calculate the following kinetic and equilibrium constants:

\[ A = k_bK_B = 0.84 ± 0.025 \text{ M}^{-1} \text{s}^{-1} \]
\[ B = k_bK_cK_B = 895 ± 27 \text{ M}^{-2} \text{s}^{-1} \]
\[ C = K_c/K_T = 1.73 ± 0.05 \]
\[ B/A = k_bK_cK_B/k_bK_B = 1065 ± 60 \text{ M}^{-1} \]

Kinetic equation (13) has the same form as the empirical rate law (II); therefore, mechanism (1)–(10) is consistent


Scheme 3. Rate-Controlling Elimination of [(HL)Mn^{III}(O_2H)]^+ from Intermediate X in Step 7 of the Mn-Enhanced Path

with the observed kinetic behavior. Figures 7–10 have been used to determine the parameters of eq 13. The independent parameters are k_b, k_bK_cK_T, and K_c/K_T. They can be determined by fitting eq 13 to the curves in both Figures 9 and 10. The results are shown in Table 2. Consistency with the catalyst and O_2 dependence (Figures 7 and 8) was demonstrated by calculating the slopes of those straight lines using the average best-fit parameters of Figures 9 and 10. The agreement is rather good, as can be seen from Table 2. The intercepts of both lines are too small to permit any reliable calculations; therefore, they were not used for showing the consistency.

Discussion

This work demonstrates that the base-catalyzed catecholase-type oxidation of H_2dtbc by O_2 is accelerated by the dioximatomanganese(II) complex, [Mn^{II}(HL)(MeOH)]^+, which by itself does not catalyze the catecholase reaction. There is no interaction between [Mn^{II}(HL)(MeOH)]^+ and O_2 in the absence of base, but when the complex is added to a solution in which the TEA-catalyzed oxidation of H_2dtbc by O_2 is in progress, a distinct acceleration can be observed.

A detailed kinetic analysis of the Mn^{II}-enhanced, TEA-catalyzed reaction has shown the validity of kinetic equation (13), which is consistent with the reaction mechanism (1)–(10). It involves two reaction paths, viz., base-catalyzed and Mn-enhanced oxidation. In the base-catalyzed path, the catalyst is TEA, deprotonating H_2dtbc to the monoanion. O_2 is activated via binding to Hdtbc^-, generating the hydroperoxo species Hdtbco_2^- (Scheme 2), which either decomposes directly to the semiquinone anion radical or, alternatively, is first bonded to [(HL)Mn^{III}(CH_3OH)]^+, generating the intermediate [(HL)Mn(O_2dtbcH)] and only then does it yield dbsq^- in the rate-controlling step 7 (Scheme 3). The latter, together with step 6, is the Mn-enhanced oxidation pathway, in which the active intermediate of the base-catalyzed path is made more reactive by complexation with [(HL)Mn^{III}(CH_3OH)]^+. The dbsq^- generated via these paths is thereafter oxidized to dtbq by O_2.

An additional source of useful mechanistic information about the nature of the rate-determining step is the kinetic isotope effect (KIE). Previous examples of dioximatomanganese-
(II) complexes, viz., cobaloxime(II) and ferroxime(II), acting as functional catecholase and phenoxazinone synthase models\(^{36}\) exhibited deuterium KIEs in the interval of 1.8–3.5, indicating a variable extent of H-atom transfer from 3,5-dtbc or 2-aminophenol hydroxy groups to coordinated O\(_2\) in the rate-limiting step.\(^{7d}\) These KIEs are close to the theoretical values,\(^{37}\) corrected by equilibrium effects, for nonlinear O\(\cdots\)H\(\cdots\)O transition states involving the rigid, square-planar cobaloxime(II) and ferroxime(II). Lower values of ca. 1.2–1.1 were observed for Fe\(^{II}\) complexes of more flexible dioximato ligands.\(^{7d}\) Significantly, the KIE of the combined base-catalyzed and Mn-enhanced catecholase reaction was found to be 1.02 even after correction for equilibrium effects.\(^{7d}\)

The lack of a significant KIE indicates no direct transfer of a H atom from the aromatic OH group to the superoxo ligand in the rate-controlling step.

Work is in progress to further elucidate the mechanistic features of oxidative dehydrogenation mechanisms in biomimetic oxidations.

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**Supporting Information Available:** Evolution of visible spectra, initial rates of O\(_2\) uptake as a function of the catalyst, O\(_2\), substrate, and TEA concentration, derivation of an approximate expression for [Hdtbc\(^-\)], and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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