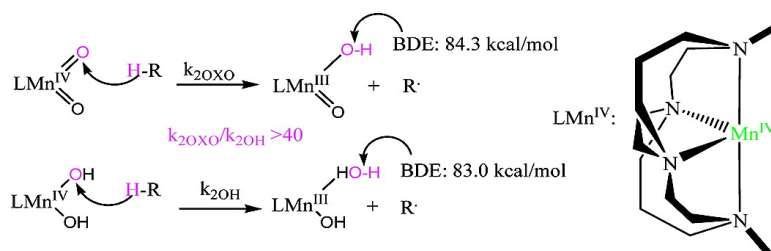


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Oxidative Reactivity Difference among the Metal Oxo and Metal Hydroxo Moieties: pH Dependent Hydrogen Abstraction by a Manganese(IV) Complex Having Two Hydroxide Ligands

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Abstract: Clarifying the difference in redox reactivity between the metal oxo and metal hydroxo moieties for the same redox active metal ion in identical structures and oxidation states, that is, $M^{n+}=O$ and $M^{n+}-OH$, contributes to the understanding of nature's choice between them ($M^{n+}=O$ or $M^{n+}-OH$) as key active intermediates in redox enzymes and electron transfer enzymes, and provides a basis for the design of synthetic oxidation catalysts. The newly synthesized manganese(IV) complex having two hydroxide ligands, $[Mn(Me_2EBC)_2(OH)_2](PF_6)_2$, serves as the prototypic example to address this issue, by investigating the difference in the hydrogen abstracting abilities of the $Mn^{IV}=O$ and $Mn^{IV}-OH$ functional groups. Independent thermodynamic evaluations of the O–H bond dissociation energies (BDE_{OH}) for the corresponding reduction products, $Mn^{III}-OH$ and $Mn^{III}-OH_2$, reveal very similar oxidizing power for $Mn^{IV}=O$ and $Mn^{IV}-OH$ (83 vs 84.3 kcal/mol). Experimental tests showed that hydrogen abstraction proceeds at reasonable rates for substrates having BDE_{CH} values less than 82 kcal/mol. That is, no detectable reaction occurred with diphenyl methane ($BDE_{CH} = 82$ kcal/mol) for both manganese(IV) species. However, kinetic measurements for hydrogen abstraction showed that at pH 13.4, the dominant species $Mn(Me_2EBC)_2(O)_2$, having only $Mn^{IV}=O$ groups, reacts more than 40 times faster than the $Mn^{IV}-OH$ unit in $Mn(Me_2EBC)_2(OH)_2^{2+}$, the dominant reactant at pH 4.0. The activation parameters for hydrogen abstraction from 9,10-dihydroanthracene were determined for both manganese(IV) moieties: over the temperature range 288–318 K for $Mn^{IV}(OH)_2^{2+}$, $\Delta H^\ddagger = 13.1 \pm 0.7$ kcal/mol, and $\Delta S^\ddagger = -35.0 \pm 2.2$ cal K^{-1} mol $^{-1}$; and the temperature range 288–308 K for $Mn^{IV}(O)_2$, $\Delta H^\ddagger = 12.1 \pm 1.8$ kcal/mol, and $\Delta S^\ddagger = -30.3 \pm 5.9$ cal K^{-1} mol $^{-1}$.

Introduction

Transition metal ions play a critical role in various oxidation and electron transfer processes in nature and in industrial and academic chemistry.¹ Generally, there are three major categories of redox metal ions when defined in terms of the active oxygen species: (1) high valent metal oxo moieties in various redox enzymes along with their synthetic counterparts, and lattice oxygen in metal oxide catalysts;² (2) metal hydroperoxide complexes in certain redox enzymes and in transition metal

peroxidation catalysts;³ and (3) high valent metal hydroxo moieties in lipoxygenases, and their models.⁴ Further, the high valent metal oxo or hydroxo functional groups may also participate in a series of electron transfer processes in biological and chemical events.¹ Because of their wide significance in biological and chemical sciences, an immediate issue is determining the reactivity differences among these related active transition metal ion species and then understanding the roles they can play in various oxidation processes. For example, in the case of iron, the $(L^{+})Fe^{IV}=O$ moiety is a general active intermediate in an oxidation process mediated by P450 enzymes and by synthetic iron porphyrin and related compounds.^{2a,5} The $Fe^{III}-OOH$ moiety has recently been proposed to serve as a second active intermediate in certain P450 enzymes and in the destruction of porphyrins in certain oxygenase enzymes.^{3,6} Also,

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in iron lipoxygenases, the $\text{Fe}^{\text{III}}\text{--OH}$ moiety has most recently been suggested as the key active species for hydrogen abstraction from 1,4-diene-containing fatty acids to form alkyl hydroperoxides.⁴ A similar issue occurs in the redox reactions involving manganese. The $\text{Mn}^{\text{V}}\text{=O}$ function is generally believed to serve as the key active species in a series of oxygen transfer process,^{5b,c,7} whereas a $\text{Mn}^{\text{III}}\text{--OH}$ moiety has recently been assigned responsibility for hydrogen abstraction in manganese lipoxygenases.⁸ In addition to these manganese reactants, a manganese(III)/manganese(II) couple has been credited with lignin degradation in manganese peroxidases, although no evidence was provided to determine whether $\text{Mn}^{\text{III}}\text{=O}$ or $\text{Mn}^{\text{III}}\text{--OH}$ served as the active species.⁹ Clarifying the reactivity differences among these active intermediates would provide a basis for enhanced understanding of nature's redox enzymes and the knowledge for matching catalyst systems to targeted oxidation processes. Unfortunately, prior to our preliminary results¹⁰ and the detailed work presented here, there was no reported example of precisely related $\text{Mn}^{\text{III}}\text{=O}$ or $\text{Mn}^{\text{III}}\text{--OH}$ moieties to address this broadly significant issue. The major obstacle has been that it is difficult to produce an effective platform, that is, an uncomplicated high valent metal complex of manganese or iron within which the metal oxo and the metal hydroxo groups could be alternatively generated and manipulated in confidence, using a single central metal ion with identical oxidation states and an otherwise identical coordination sphere. The difficulty exists because such high oxidation state iron and manganese ion moieties (M=O and M--OH) have great tendencies to form μ -oxo bridged dimers and/or higher oligomers. Following our preliminary publication,¹⁰ Fujii, et al., reported solution studies on the physical chemical property differences between $\text{O=Mn}^{\text{IV}}(\text{salen})$, $\text{HO--Mn}^{\text{IV}}(\text{salen})$ and $\text{H}_2\text{O--Mn}^{\text{IV}}(\text{salen})$ using various spectroscopic techniques. However, the poor oxidizing capability of $\text{HO--Mn}^{\text{IV}}(\text{salen})$ and $\text{H}_2\text{O--Mn}^{\text{III}}(\text{salen}^{+})$ prevented their investigation of the reactivity differences between the corresponding reaction centers,

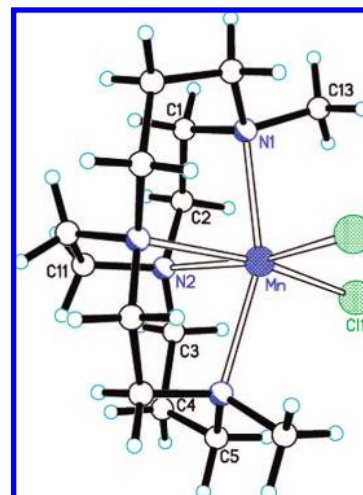


Figure 1. The structure of $\text{Mn}^{\text{II}}(\text{Me}_2\text{EBC})\text{Cl}_2$.

$\text{O=Mn}^{\text{IV}}(\text{salen})$ and $\text{HO--Mn}^{\text{IV}}(\text{salen})$, although $\text{O=Mn}(\text{salen})$ demonstrated its ability to abstract hydrogen from cyclohexene.¹¹

In these laboratories, a series of transition metal complexes having rare abilities to host stable $\text{Mn}^{\text{IV}}\text{=O}$ and $\text{Mn}^{\text{IV}}\text{OH}$ functional groups has been successfully developed with ultra rigid ethylene cross-bridged macrocyclic ligands.¹² Compared with other ligands, these cross-bridged macrocycles produce manganese(II) complexes having extreme kinetic stability in both acidic and basic media, despite the well-known lability of the high-spin d^5 Mn^{2+} ion. The complexes have rich redox chemistries and an industrial partner has demonstrated their excellent catalytic activity in demanding applications, for example in home care products.¹³ Specifically, the manganese complex, $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2$, in which Me_2EBC is 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (Figure 1), demonstrated unexpected selectivity when epoxidizing olefins with hydrogen peroxide. Epoxidations by transition metal ions known for readily displaying a range of oxidation states, such as manganese, have most often been attributed to the oxygen rebound mechanism, in which oxygen atom transfer is accompanied by 2-electron reduction of the metal ion.^{5c}

The capabilities of the high valent intermediates in these complexes include 1-electron oxidations as well, often limiting their selectivities. Detailed studies with the $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2$ catalyst system found the origin of this selectivity to be mechanistic with the epoxidation occurring by a Lewis acid

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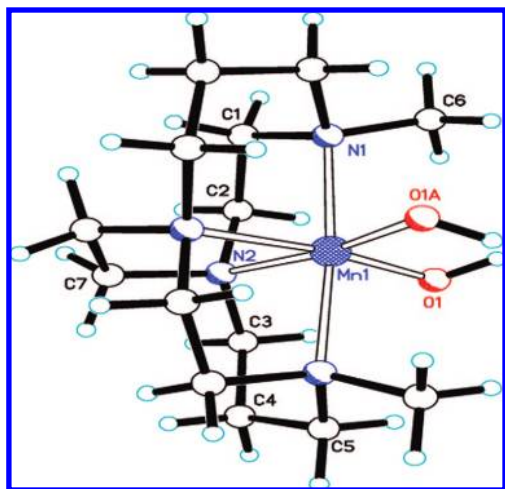
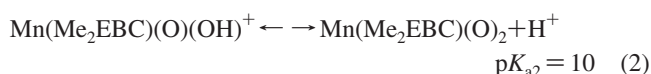
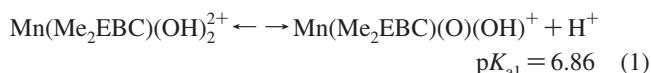


Figure 2. The structure of $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$.

pathway.¹⁴ That mechanism has generally been found for the early transition metal ions such as Ti(IV), Mo(IV), W(IV), and Re(VII), not with the elements manganese and iron.¹⁵ Through simple oxidation of $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2$ by H_2O_2 in the presence of NH_4PF_6 , the first mononuclear manganese(IV) complex having two hydroxide ligands, $[\text{Mn}(\text{Me}_2\text{EBC})(\text{OH})_2](\text{PF}_6)_2$, was synthesized and thoroughly characterized (Figure 2).¹⁶ Because of the two bulky methyl groups on the nonbridged nitrogen atoms of the ligand, the dehydration of $\text{Mn}^{\text{IV}}-(\text{OH})_2$ unit to form dimers or oligomers is prevented. The measured deprotonation constants for this manganese(IV) complex to generate $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$ and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ are 6.86 and 10, respectively (eq 1 and 2). The deprotonated manganese(IV) species, including $\text{Mn}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$ and $\text{Mn}(\text{Me}_2\text{EBC})(\text{O})_2$, slowly decompose ($\text{pH} > 7$), gradually degrading to the manganese(III) species in base with 88% yield.



Since the two $\text{p}K_{\text{a}}$ values, 6.86 and 10, are within the easily controllable pH range, this manganese(IV) complex provides a good platform to address the main issue stated above, that is, clarifying the reactivity difference between the $\text{Mn}^{\text{IV}}-\text{OH}$ vs $\text{Mn}^{\text{IV}}=\text{O}$ reactive groups on the same transition metal ion with identical ligands and oxidation states. Our preliminary results showed that the oxo derivative, $\text{Mn}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$, reacts

at least 15 times faster than does the hydroxo species $\text{Mn}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ in hydrogen abstraction processes.¹⁰ The present studies address this issue in detail, showing that, for this manganese complex, the $\text{Mn}=\text{O}$ group in $\text{Mn}(\text{Me}_2\text{EBC})(\text{O})_2$ reacts more than 40 times faster than the corresponding $\text{Mn}^{\text{IV}}-\text{OH}$ group in $\text{Mn}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ in hydrogen abstraction reactions.

Experimental Section

$\text{Mn}^{\text{II}}(\text{Me}_2\text{EBC})\text{Cl}_2$ (+99.9%) was generously supplied by the Procter and Gamble Company. $[\text{Mn}^{\text{III}}(\text{Me}_2\text{EBC})\text{Cl}_2]\text{PF}_6$ and $[\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2](\text{PF}_6)_2$, were synthesized as reported.^{12c,16} Deuterated 9,10-dihydroanthracene (DHA- d_4) was synthesized according to the literature.^{4d} Other reagents were obtained from Aldrich and used as received except 1,4-cyclohexadiene which was distilled before use.

Hydrogen Abstraction Reaction, Small Synthetic Scale. In a typical reaction, 0.25 mmol of the manganese(IV) complex was added to 0.5 mmol of 1,4-cyclohexadiene in 5 mL of acetone/water (ratio 4:1) solvent in a controlled atmosphere wet box. The reaction mixture was stirred until the purple color of the manganese(IV) species turned to the red-brown color of the corresponding manganese(III) species. Quantitative analysis of products was performed by GC using an internal standard, and the identities of the reaction products were confirmed by GC-MS.

Hydrogen Abstraction Reaction in Base, Analytical Scale. In 8 mL of acetone/water (ratio 4:1), 0.063 g (0.1 mmol) of manganese(IV) complex was dissolved. Before adding 0.4 mL (2.4 mmol) of diphenylmethane (or some other substrate) to initiate the reaction, the pH of the solution was adjusted to 8.4 by NaOH addition, making $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$ the dominant catalyst species in the solution. After stirring overnight, the manganese(IV) in the complex was reduced to manganese(III). In the case of diphenylmethane, GC and GC-MS analysis of the reaction mixture showed that no hydrogen abstraction product was formed. The identical procedure was performed at the initial pH value of 13.4, making $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ the dominant species and, for the reaction with diphenylmethane as the substrate, the GC and GC-MS analysis of the resulting reaction mixture also confirmed that no hydrogen abstraction product was formed.

Rate Measurements. (a) In a typical kinetic experiment, a 20-fold excess of substrate was used. For example, a 20-fold excess of 1,4-cyclohexadiene (CHD, 40 mM) and 2 mM of the manganese(IV) complex were dissolved in 10 mL of acetone/water (ratio 4:1, initial pH 6.1), at room temp. The disappearance of the manganese(IV) species was monitored by UV-visible spectrophotometry and the pseudo-first-order rate constant was calculated.

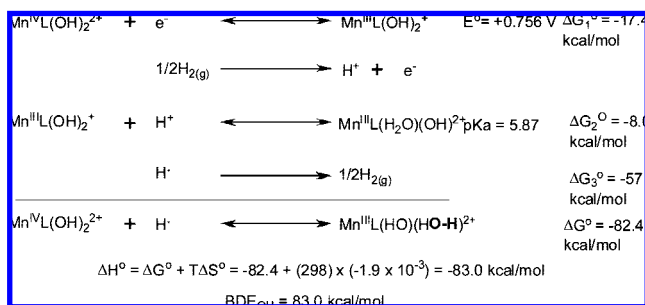
(b) To determine the reactivity differences for three distinct catalyst species, that is, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$, and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$, the oxidations of the selected substrates (40 mM) were carried out with the freshly synthesized manganese(IV) complex (4 mM) in acetone/water (ratio 4:1) at the selected initial pH value, including pH values of 4.0, 8.4, and 13.4, at the temperature of 288 K. The initial pH value was adjusted by NaOH or HCl as needed. The disappearance of the manganese(IV) species was monitored by UV-visible spectrophotometry and the pseudo-first-order rate constant was calculated. The second order constant was calculated from a set of the pseudo-first-order rate constants with the different initial substrate concentrations, including 25, 30, 35, and 40 mM.

(c) To demonstrate the influence of the pH of the reaction medium on the hydrogen abstraction rate, the hydrogen abstractions from 9,10-dihydroanthracene by Mn(IV) complexes were performed in solutions having each of the different initial pH values, and monitored by UV-visible spectrophotometer. The initial pH values were adjusted by the addition of HCl or NaOH as needed.

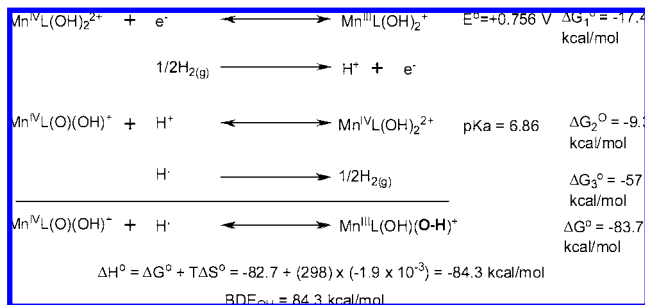
(d) To measure the activation parameters for hydrogen abstraction with $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$, and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$, 9,10-dihy-

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Scheme 1



Scheme 2



droanthracene (0.04 M) was chosen as substrate, and kinetic studies were performed at initial pH values of 4.0 and 13.4 with the manganese(IV) complex (4 mM) in acetone/water (ratio 4:1), at the temperatures of 288, 298, 303, 308, and 318 K.

Results and Discussions

Thermodynamic Evaluation of the Oxidizing Power of Manganese(IV) Oxo and Hydroxo Groups. In our earlier report, the Bordwell/Mayer analysis¹⁷ was applied to calculate the BDE_{OH} values for the OH bonds formed when Mn^{IV}(Me₂EBC)(O)(OH)⁺ or Mn^{IV}(Me₂EBC)(OH)₂²⁺ abstracts a hydrogen atom from a substrate.¹⁰ The corresponding thermochemical cycles are shown in Schemes 1 and 2. The method has been applied by others to certain oxygen evolution models for photosystem II, and to evaluate hydrogen abstraction abilities of high oxidation state transition metal complexes.^{10,18,19} The BDE_{OH} values of the reduced forms of these oxidizing agents correlate with activation energies for substrate oxidations and, in that unusual Polanyi correlation, can serve as measures of the oxidizing power of the reagent in that category of reactions. The BDE_{OH} of the water molecule ligated to the Mn³⁺ species, Mn^{III}(Me₂EBC)(OH)(H₂O)²⁺, BDE_{OH} = 83.0 kcal/mol (Scheme 1) is taken to be a measure of the oxidizing power of the Mn^{IV}-OH group in Mn^{IV}(Me₂EBC)(OH)₂²⁺. In the same way, the BDE_{OH} value for hydroxide ligated to the Mn³⁺ species in Mn^{III}(Me₂EBC)(OH)₂⁺ provided the corresponding parameter for the oxidizing power of Mn^{IV}=O group in Mn^{IV}(Me₂EBC)(O)(OH)⁺; BDE_{OH} = 84.3 kcal/mol. It is significant that the two bond dissociation energies are similar in magnitude (83 and 84.3 kcal/mol), indicating that the hydrogen

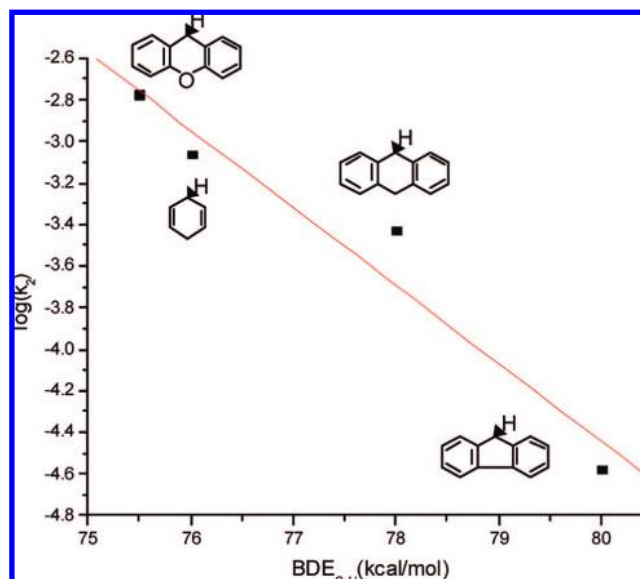


Figure 3. Plot of log(*k*_{2corr}) vs BDE_{CH} for hydrogen abstraction.

abstracting abilities of Mn^{IV}-OH and Mn^{IV}=O are very similar despite the difference in charges on the two manganese(IV) complexes, that is, +2 for Mn^{IV}(Me₂EBC)(OH)₂²⁺ vs +1 for Mn^{IV}(Me₂EBC)(O)(OH)⁺. The effect of the difference in ionic charge is largely compensated by the change in the nature of the ionizing moiety (2+ for Mn^{IV}-(OH)₂ versus 1+ for Mn^{IV}-(O)(OH)). In the calculation this is reflected by the similarities in the two p*K*_a values, 5.87 and 6.86, respectively.^{12e,16}

Interestingly, the calculated BDE_{OH} values (83.0 and 84.3 kcal/mol) for water and hydroxide ligated to this manganese ion are far below the value for bulk water (119 kcal/mol), differing by well over 30 kcal/mol. This decrease in the activation energy for the OH bond is a simple example of water activation by ligation to a monomeric manganese ion center, reflecting the expectations for water associated with the tetramanganese center in photosystem II.²⁰ A second consideration also comes from these simple results. The BDE calculations reported here show that the accumulation of a charge of one positive unit on a monomeric manganese complex need not necessarily change the energy barrier substantially (activation energy proportional to 83.0 kcal/mol for [Mn^{III}(Me₂EBC)(OH)(H₂O)]²⁺ vs 84.3 kcal/mol for [Mn^{III}(Me₂EBC)(OH)₂]⁺). This may be pertinent to the view that separate proton and electron transfer events that result in one unit of charge accumulation may be energetically feasible in processes like water oxidation.^{20c,21}

Experimental Test for the Oxidizing Power of the Manganese(IV) Complex. Our earlier study reported oxidation by [Mn^{IV}(Me₂EBC)(OH)₂](PF₆)₂ of substrates of known BDE_{CH}, giving the Polanyi correlation presented graphically in Figure 3.¹⁰ Rate constants were determined in 4:1 acetone/water solutions spectrophotometrically as the purple Mn(IV) changed

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Table 1. pK_a Values in the Reported Monomeric Redox Metal Complexes

complex ^a	pK _{a1}	pK _{a2}	medium	ref
HMnO ₄ ⁻		7.4	aqueous	22
[Mn ^{III} H ₃ I(OH)] ⁻		28.3	DMSO	23
[Fe ^{III} H ₃ I(OH)] ²⁻		25.0	DMSO	23
[(bpy) ₂ (py)Ru ^{IV} (OH ₂) ³⁺	0.85		aqueous	24
[Mn ^{IV} (Me ₂ EBC)(OH) ₂] ²⁺	6.86	10	aqueous	16
[Mn ^{II} (PY ₅)(OH ₂) ²⁺	13		acetonitrile	25
[Fe ^{II} (PY ₅)(OH ₂) ²⁺	8.1		DMSO	26a

^a H₃I: tris[(*N'*-*tert*-butylureaylato)-*N*-ethyl]aminato. PY₅: 2,6-bis(bis(2-pyridyl)methoxymethane)pyridine.

into the red-brown of Mn(III), revealing the logarithmic dependence on the strength of the targeted CH bond, as expected. The rates varied from $1.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for xanthene with a BDE of 75.5 kcal/mol to $2.6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ for fluorene with a BDE of 80 kcal/mol. Diphenylmethane with a BDE of 82 kcal/mol showed zero reaction after over 19 days in stirred solution. The observation of the termination of the hydrogen abstraction reaction is rare,^{19c} presumably because unfavorable 1-electron processes (e.g., high energy hydrogen abstractions) are often driven by irreversible follow-up reactions. In addition, a deuterated analogue of 9,10-dihydroanthracene (DHA-*d*₄) displays a significant rate decrease relative to the normal 9,10-dihydroanthracene (DHA-*h*₄). The ratio of the rate constants is 3.27 at 297 K, implying that the hydrogen abstraction by Mn^{III}(Me₂EBC)(OH)₂²⁺ is the rate determining step ($k_{\text{obs}}(\text{DHA-}d_4) = 7.79 \times 10^{-6} \text{ s}^{-1}$; $k_{\text{obs}}(\text{DHA-}h_4) = 2.55 \times 10^{-5} \text{ s}^{-1}$).

Kinetic Rate Constants for Mn^{IV}-OH in Mn^{IV}(Me₂EBC)(OH)₂²⁺ and Mn^{IV}=O in Mn^{IV}(Me₂EBC)(O)₂. Conveniently, the two deprotonation constants for [Mn^{IV}(Me₂EBC)(OH)₂](PF₆)₂, pK_{a1} = 6.86 and pK_{a2} = 10, fall in the easily controllable pH range, and this facilitates the generation of activated catalyst forms containing only Mn^{IV}=O and Mn^{IV}-OH moieties, respectively. The data in Table 1 suggest the rarity of this useful set of pK_a values. Importantly, this manganese(IV) complex is sufficiently stable in water to permit useful physicochemical measurements, including acid–base titrations, and electrochemical and kinetic measurements, providing a unique opportunity to address the open issue about the reactivity differences between metal oxo and metal hydroxo oxidants, when all else is constant. This discussion concerns the difference in hydrogen abstracting abilities of Mn^{IV}-OH and Mn^{IV}=O groups.

In preliminary work, pH values of 4.0 and 8.4 were chosen to reveal the relative reactivities of two distinct catalyst species capable of performing hydrogen abstractions, Mn^{IV}(Me₂EBC)(OH)₂²⁺ and Mn^{IV}(Me₂EBC)(O)OH⁺. These pH values were chosen on the basis of a well-defined pK_a value of 6.86 relating the two species, whereas only approximate values of ~2 and ~10 were available for the equilibria under more acidic or more basic conditions. For pK_a ≈ 2, the third proton is added to Mn^{IV}(Me₂EBC)(OH)₂²⁺ converting one bound OH to a water molecule and the pK_a ≈ 10 involves removing the second proton from Mn^{IV}(Me₂EBC)(OH)₂²⁺ to form the dioxo complex, Mn^{IV}(Me₂EBC)(O)₂. Although the calculations are rendered highly approximate because the oxidations were studied in 4:1 acetone/water in order to reliably dissolve the substrates, the range of acidities should be reasonably represented. For water at a pH of 4, Mn^{IV}(Me₂EBC)(OH)₂²⁺ is expected to be present at ≥99%, and the concentrations of both Mn^{IV}(Me₂EBC)(OH)₂²⁺ and Mn^{IV}(Me₂EBC)(O)OH⁺ are estimated to be less than 1%. Similarly, calculations in basic media pH 8.4 suggest

Table 2. The Second Order Rate Constants for Hydrogen Abstraction from Substrates with Mn^{IV}(Me₂EBC)(OH)₂²⁺ and Mn^{IV}(Me₂EBC)(O)₂ at pH 4.0 and pH 13.4^a

substrate	BDE _{CH} kcal/mol	k _{OH} at pH 4.0 M ⁻¹ s ⁻¹	k _{oxo} at pH 13.4 M ⁻¹ s ⁻¹	k _{oxo} /k _{OH}
xanthene	75.5	0.00107	0.048	44
1,4-cyclohexadiene	76	3.64×10^{-4}	0.0159	44
9,10-dihydroxyanthracene	78	3.52×10^{-4}	0.01496	43
fluorene	80	$\sim 2.5 \times 10^{-4}$	0.00912	36

^a Reaction conditions: solvent, acetone/water (ratio 4:1), initial concentration of substrate, 40 mM, initial concentration of manganese(IV) complex, 4 mM, at temperature 288 K.

that the concentration of Mn^{IV}(Me₂EBC)(O)(OH)⁺ is at the 97–98% level. Further, about 2–3% of the manganese is estimated to be present as either the dihydroxo complex, Mn^{IV}(Me₂EBC)(OH)₂²⁺, or the dioxo complex, Mn^{IV}(Me₂EBC)(O)₂. Accordingly, preliminary rate studies were conducted at pH values of 4.0 and 8.4 to demonstrate the difference in reactivities of the two catalyst forms and HCl or NaOH was used to adjust the initial pH. Buffers were not used in these preliminary studies because of the complications they introduce. Specifically, phosphate and carbonate buffers complex with the metal ions, displacing OH groups, while some organic buffers can also coordinate to the metal ion and some are subject to oxidation. Since the manganese(IV) complexes decompose slowly in the acidic solution and are quite unstable in basic solution, the calculated rate constants have been corrected for the separately determined catalyst decomposition rates in the absence of the substrate. The hydrogen abstraction reaction using 9,10-dihydroanthracene (DHA) as the substrate proceeds much faster in base than in acid. The pseudo-first-order rate constant at pH = 8.4 is $k_1 = 6.64 \times 10^{-4} \text{ s}^{-1}$, at 297 K, while that in acidic solution (pH = 4.0) is $k_1 = 4.39 \times 10^{-5} \text{ s}^{-1}$, also at 297 K. These results demonstrate the fact that the Mn^{IV}=O moiety performs hydrogen abstraction more rapidly than does Mn^{IV}-OH, even though there are two OH groups in the dihydroxo complex and only one oxo group in the oxo-hydroxy compound.¹⁰ These rates differ by an average factor of 15 and this directs attention toward the relative intrinsic efficacies of oxidizing species differing only in the level of their protonation in such fundamental chemical processes as hydrogen abstraction.

Accepting the result that hydrogen abstraction from 9,10-dihydroanthracene by Mn^{IV}(Me₂EBC)(O)(OH)⁺ proceeds more than 15 times faster than that by Mn^{IV}(Me₂EBC)(OH)₂²⁺, it is to be expected that, the reaction rate with a catalyst having two Mn^{IV}=O units (that is Mn^{IV}(=O)₂) would be much faster than the rate for a catalyst having one Mn^{IV}-OH and one Mn^{IV}=O unit (i.e., Mn^{IV}(O)(OH)). The hydrogen abstraction rate for Mn^{IV}(Me₂EBC)(O)(OH)⁺ should be a combination of the rates of both an Mn^{IV}=O and an Mn^{IV}-OH group. To explore the reactivity difference between Mn^{IV}=O and Mn^{IV}-OH groups further, hydrogen abstraction experiments were conducted at the initial pH values of 4.0 and 13.4, respectively, and the second order rate constants are listed in Table 2. As stated earlier, at the pH of 4.0, the Mn^{IV}(Me₂EBC)(OH)₂²⁺ moiety is almost certainly the dominant species and is estimated to be present at ≥99%. Correspondingly, since the second pK_a, which indicates removal of the last proton from Mn^{IV}(Me₂EBC)(O)(OH)⁺ to form Mn^{IV}(Me₂EBC)(O)₂, is 10, at pH 13.4, the fully deprotonated species, Mn^{IV}(Me₂EBC)(O)₂, is confidently estimated as ≥99%. Therefore, the reaction rates presented in Table 2 should clearly reveal the difference in hydrogen abstracting abilities between the two active manganese(IV) species, that is, Mn^{IV}=O

vs $\text{Mn}^{\text{IV}}\text{-OH}$, providing the first direct measure of this important difference in reactivities. At 288 K, as the BDE_{CH} value of the substrates increases from 75.5 to 80 kcal/mol, the second order rate constants drop from $0.00107 \text{ M}^{-1} \text{ s}^{-1}$ to $\sim 2.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Mn}^{\text{IV}}\text{-OH}$ in $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$, and for $\text{Mn}^{\text{IV}}\text{=O}$ in $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ it drops from 0.048 to $0.00912 \text{ M}^{-1} \text{ s}^{-1}$. Also, as shown in Table 2, the ratio of the more rapid $\text{Mn}^{\text{IV}}\text{=O}$ rate to that of the slower $\text{Mn}^{\text{IV}}\text{-OH}$ ranges from 36 to 44. From this result, one might suspect that the relative reactivities of these two functional groups (M-OH and M=O), as measured by rates of reaction, may vary by between 1 and 2 orders of magnitude, but, probably, not by a great deal more.

It is interesting to compare the results of these simple rate measurements with the calculated hydrogen abstracting abilities of the two complexes, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$ and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$, recalling that they operate at BDE_{OH} strengths of 84.3 and 83 kcal/mol, respectively. Viewing this small difference in enthalpies (1.3 kcal) as if it were a difference in the free energy of activation, the difference in rates of hydrogen abstraction between the two functional groups should only be a factor of a little less than 10 at room temperature. The corresponding variation in rates was found to be 15-fold for the complexes whose physical constants were used for the calculations of BDE_{OH} values. We suggest that the agreement is surprisingly good.

Since the redox potential of the $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+/\text{Mn}^{\text{III}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})$ couple is not available, the calculated BDE_{OH} value of the O-H bond associated with the $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ oxidant was not accessible. However, experimentally, the rate ratio for hydrogen abstraction between $\text{Mn}^{\text{IV}}\text{=O}$ and $\text{Mn}^{\text{IV}}\text{-OH}$, $k_{2\text{OXO}}/k_{2\text{OH}}$, is ~ 43 for 9,10-dihydroanthracene as the substrate, a number that indicates a difference of ~ 2.3 kcal/mol between the activation free energies for hydrogen abstraction, suggesting that the BDE_{OH} associated with the reaction of $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ might be 85 or 86 kcal/mol. In seeking to observe the expected greater oxidizing capability of this source of $\text{Mn}^{\text{IV}}\text{=O}$ groups, attempts were made to abstract hydrogen from diphenyl methane (BDE_{CH} value of 82 kcal/mol) at pH 8.4, where $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$ is the dominant form of the reagent and at pH 13.4, where $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ dominates, in acetone/water (ratio 4:1) at room temperature. No hydrogen abstraction reaction was observed in either case after the reaction ran overnight, with stirring. The catalyst was completely degraded to the previously studied manganese(III) derivatives in this reaction time, as expected, because of the previously reported instability of the catalyst in media at high pH.¹⁶ At this point it must be concluded that the substantial errors and approximations in both the thermodynamic model and the experiments reported here are too great to characterize the two $\text{Mn}^{\text{IV}}(\text{OH})_2$ derived functional groups further with the available information.

In addition, the kinetic isotope effect for hydrogen abstraction from 9,10-dihydroanthracene ($\text{DHA-}h_4$) and deuterated 9,10-dihydroanthracene ($\text{DHA-}d_4$) with $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ at pH 13.4 supports hydrogen abstraction by $\text{Mn}^{\text{IV}}\text{=O}$ as the rate determining step with a KIE value of 3.78 at 288 K (the pseudo-first-order rate constant for $\text{DHA-}h_4$, $k_1 = 9.37 \times 10^{-4} \text{ s}^{-1}$, and for $\text{DHA-}d_4$, $k_1 = 2.48 \times 10^{-4} \text{ s}^{-1}$). The hydrogen abstraction from $\text{DHA-}d_4$ with $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ at pH 4.0 was too slow at 288 K and was lost in the noise of the blank experiment, thus the accurate KIE value is not available, however, the KIE value of 3.27 at 297 K from the neutral acetone/water mixture

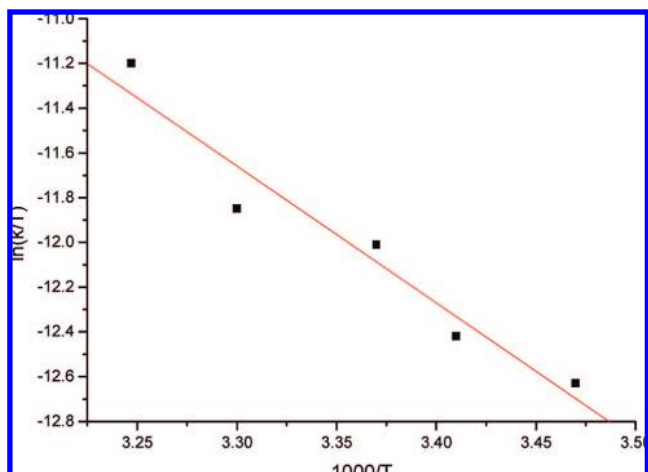


Figure 4. Eyring plot for hydrogen abstraction from 9,10-dihydroanthracene with $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ at 288 K, initial pH = 13.4.

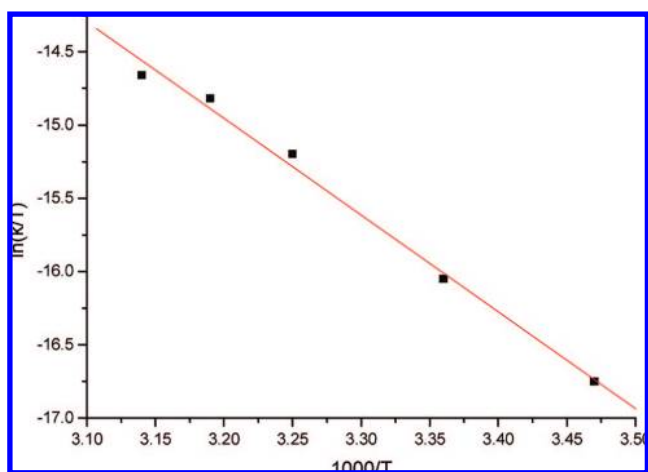


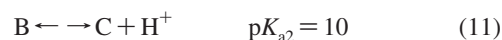
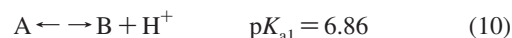
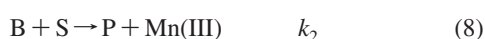
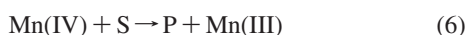
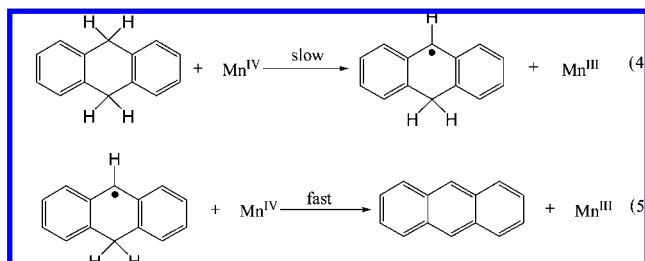
Figure 5. Eyring plot for hydrogen abstraction from 9,10-dihydroanthracene with $\text{LMn}^{\text{IV}}(\text{OH})_2^{2+}$ at 288 K, initial pH = 4.0.

is also in agreement with hydrogen abstraction from substrate by $\text{Mn}^{\text{IV}}\text{-OH}$ in the rate determining step.

Activation Parameters for $\text{Mn}^{\text{IV}}\text{-OH}$ and $\text{Mn}^{\text{IV}}\text{=O}$. The data presented above have revealed that the kinetic rates between $\text{Mn}^{\text{IV}}\text{-OH}$ and $\text{Mn}^{\text{IV}}\text{=O}$ units are distinctly different, although the thermodynamic oxidizing power of $\text{Mn}^{\text{IV}}\text{-OH}$ and $\text{Mn}^{\text{IV}}\text{=O}$ units are very similar as calculated (83.0 vs 84.3 kcal/mol). To further examine the reactivity differences between the $\text{Mn}^{\text{IV}}\text{-OH}$ and $\text{Mn}^{\text{IV}}\text{=O}$ groups, the enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of activation have been determined for hydrogen abstraction from 9,10-dihydroanthracene by $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ at the initial pH of 4.0 and by $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ at the initial pH of 13.4, over the temperature range of 288–318 K, (Figures 4 and 5). Because of the solubility limitations of 9,10-dihydroanthracene in acetone/water (ratio 4/1), the rapid degradation of the manganese(IV) species to the manganese(III) derivative¹⁶ in very strong base, and the rapid hydrogen abstraction rate of the Mn^{IV} moiety, the measurements of the activation parameters for $\text{Mn}^{\text{IV}}\text{=O}$ in base were limited to the relatively narrow temperature range from 288 to 308 K. Also, because of the same low solubility of 9,10-dihydroanthracene, the slow hydrogen abstraction rate of $\text{Mn}^{\text{IV}}\text{-OH}$ in acid, and the relatively low boiling point of acetone (56 °C), the measurements of the activation parameters for $\text{Mn}^{\text{IV}}\text{-OH}$ were limited to the temperature range from 288 to 318 K. The data are summarized in Table 3 along with the literature data for other

appropriate monomeric metal complexes. As shown in Table 3, the ΔH^\ddagger and ΔS^\ddagger values for the two manganese(IV) complexes studied here fall in the range of other reported catalytic metal complexes. Superficially, the ΔH^\ddagger values for $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ are close in value, 13.1 ± 0.7 vs 12.1 ± 1.8 kcal/mol, whereas the ΔS^\ddagger values appear different, -35.0 ± 2.2 vs -30.3 ± 5.9 cal $\text{K}^{-1} \text{mol}^{-1}$. However, the uncertainties of these thermal parameters are relatively large and the relative contributions of the two terms to the free energies of activation are comparable. A sizable ΔS^\ddagger difference could indicate that the transition state for hydrogen abstraction from $\text{Mn}^{\text{IV}}-(\text{OH})_2^{2+}$ requires a more ordered or rigid state, relative to the ground state, than that involving $\text{Mn}^{\text{IV}}=\text{O}$. This could derive from the necessity to rearrange and fix the positions of the protons in the OH groups in the transition state. A second possibility may involve more extensive ground-state solvation via hydrogen bonding for the $\text{Mn}^{\text{IV}}(\text{OH})_2$ functional group. The overall perspective is that the $\text{Mn}^{\text{IV}}(=\text{O})_2$ functional group undergoes reaction with less constraint than is the case for the corresponding hydroxo derivative. The calculated activation free energy (ΔG^\ddagger) for hydrogen abstraction from 9,10-dihydroanthracene by $\text{Mn}^{\text{IV}}=\text{O}$ of $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ at 298 K is $+21.1$ kcal/mol while for the $\text{Mn}^{\text{IV}}-\text{OH}$ unit in $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$, it is $+23.5$ kcal/mol. The difference between the two activation energies is 2.4 kcal/mol, suggesting a 58 fold reaction rate ratio to which the activation enthalpy contributes an approximate 5.4-fold rate ratio while activation entropy contributes a ~ 10.6 -fold rate ratio. With an uncertainty of at least a kilocalorie, this result includes the range of experimental values observed for the rate parameters; that is, a reaction rate ratio of 44 comes from a Δ (ΔG^\ddagger) value of 2.2 kcal/mol.

Rate Law and Kinetics of Hydrogen Abstraction by Three Active Manganese(IV) Species. Since the composition of the mixture of three active manganese forms, including $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$ and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$, in the solution is highly pH dependent (eq 1 and eq 2), it is essential to investigate the influence of proton concentration on the reaction rate. The kinetic correlation between the $[\text{H}^+]$ and the pseudo-first-order rate constant (k_{obs}) was studied with 9,10-dihydroanthracene as the substrate (eqs 4 and 5). For this substrate, the first hydrogen abstraction step, which generates the radical intermediate, is the rate determining step and the overall reaction is second order, with first-order dependences on both the substrate and the manganese(IV). The second, follow-up step is fast compared to the initial hydrogen abstraction so that eqs 4 and 5 can be abbreviated as eq 6.



Hydrogen abstraction from 9,10-dihydroanthracene with the three active manganese(IV) species can be expressed by eq 7–9. Here S is substrate, P is the product, and A, B, and C represent $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$, and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$, respectively. The corresponding second order rate constants of eqs 7–9 are k_1 , k_2 , and k_3 , and the link connecting complexes A, B, and C is provided by the two deprotonation constants, $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ (eqs 10 and 11). Under the reaction conditions, the total initial concentration of the manganese(IV) complexes was 4 mM, and the substrate was present in excess (0.04 M), imposing pseudo-first-order conditions. The overall pseudo-first-order rate law for the disappearance of manganese(IV) species is expressed as

$$-d[\text{Mn}^{\text{IV}}]/dt = \{k_1[\text{A}] + k_2[\text{B}] + k_3[\text{C}]\}[\text{S}] \quad (13)$$

Incorporation of the equilibria, material balance, and $[\text{H}^+]$ (overall, eqs 7–13) leads to

$$-\frac{d[\text{Mn}^{\text{IV}}]}{dt} = \frac{k_1[\text{H}^+] + k_2K_{\text{a}1}[\text{H}^+] + k_3K_{\text{a}1}K_{\text{a}2}}{[\text{H}^+]^2 + K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2}}[\text{S}][\text{Mn}^{\text{IV}}] \quad (14)$$

Thus:

$$k_{\text{obs}} = \frac{k_1[\text{H}^+] + k_2K_{\text{a}1}[\text{H}^+] + k_3K_{\text{a}1}K_{\text{a}2}}{[\text{H}^+]^2 + K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2}}[\text{S}] \quad (15)$$

Under the limiting conditions, at pH 4.0, the percent of $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ exceeds 99%; $k_1[\text{H}^+]^2 \gg k_2K_{\text{a}1}[\text{H}^+] + k_3K_{\text{a}1}K_{\text{a}2}$, and $[\text{H}^+]^2 \gg K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2}$, thus, $k_{\text{obs}} \approx k_1[\text{S}]$. Similarly, at pH 13.4, the presence of $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$ is greater than 99%; $k_3K_{\text{a}1}K_{\text{a}2} \gg k_1[\text{H}^+]^2 + k_2K_{\text{a}1}[\text{H}^+]$, and $K_{\text{a}1}K_{\text{a}2} \gg [\text{H}^+]^2 + K_{\text{a}1}[\text{H}^+]$, thus $k_{\text{obs}} \approx k_3[\text{S}]$. Figure 6 displays the influence of the initial proton concentration (pH) in the reaction mixture on the pseudo-first-order rate constant for hydrogen abstraction from 9,10-dihydroanthracene (DHA) with the manganese(IV) complex. The data represented by the black squares is made up of experimental observed rate constants, and the red dots represent calculated rate constants obtained by applying eq 15, beginning with the limiting second order rate constants, $k_1 = 3.52 \times 10^{-4}$, $k_2 = 0.00384$, and $k_3 = 0.01496 \text{ M}^{-1} \text{ s}^{-1}$ (Table 3), and $\text{p}K_{\text{a}1} = 6.86$ and $\text{p}K_{\text{a}2} = 10$ (eqs 10 and 11). In the range from weakly acidic to neutral pH, the two curves overlap very well, supporting the expectation that eq 15 describes the actual reaction system; that is, abstraction of the first hydrogen atom from the substrate by the manganese(IV)

Table 3. The Related Activation Parameters for Hydrogen Abstraction from 9,10-Dihydroanthracene and Various Monomeric Metal Complexes

complex ^a	activation enthalpy ΔH^\ddagger (kcal mol ⁻¹)	activation entropy ΔS^\ddagger (cal K ⁻¹ mol ⁻¹)	ref
$[\text{Fe}^{\text{III}}(\text{Hbim})(\text{H}_2\text{bim})_2]^{2+}$	11.6 ± 0.5	-36 ± 5	26b
$[\text{MnO}_4]^-$	13.8 ± 1	-15 ± 7	17b
$[\text{Fe}^{\text{III}}(\text{PY}_5)\text{OH}]^{2+}$	13.2 ± 0.5	-26 ± 5	26a
$[\text{Mn}^{\text{III}}(\text{PY}_5)\text{OH}]^{2+}$	9.3 ± 0.5	-36 ± 5	25
$[\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2]^{2+}$	13.1 ± 0.7	-35.0 ± 2.2	this work
$[\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2]$	12.1 ± 1.8	-30.3 ± 5.9	this work

^a H₂bim: 2,2'-bi-1,4,5,6-tetrahydropyrimidine. PY₅: 2,6-bis(bis(2-pyridyl)methoxymethane)pyridine.

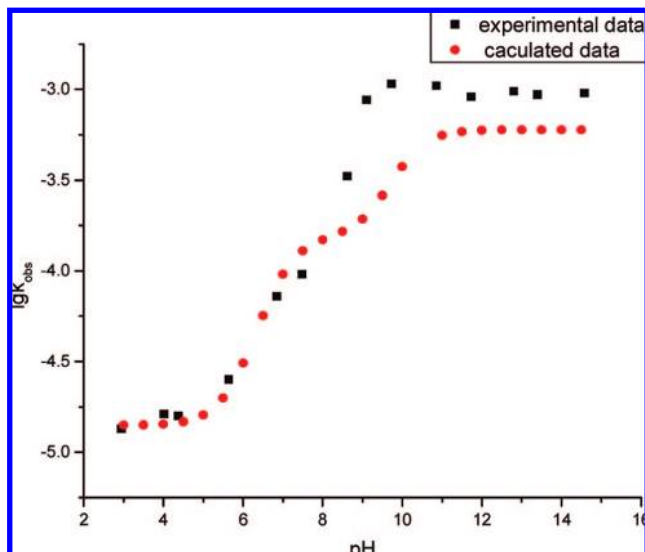


Figure 6. The influence of pH dependence of the pseudo-first-order rate, k_{obs} , for hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by the manganese(IV) complex (4 mM). Solvent: 4:1 acetone/water; 288 K.

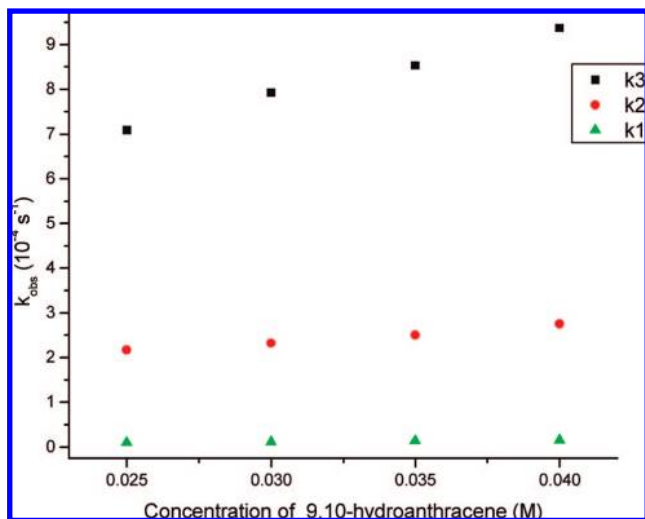


Figure 7. Correlation of substrate concentration with the pseudo-order rate constant for hydrogen abstraction from 9,10-dihydroanthracene by manganese(IV) complex at pH 4.0 (for k_1), 8.4 (for k_2) and 13.4 (for k_3). Solvent: acetone/water (ratio 4:1); $[\text{Mn}^{\text{IV}}] = 4 \text{ mM}$, 288 K.

oxidant determines the reaction dynamics for those values of the variables. However, at pH values more positive than the neutral point, the experimental and calculated curves deviate dramatically. This deviation is apparent also in the correlation of the second order rate constants, k_2 and k_3 , with the experimental pseudo-first-order rate constant (k_{obs}) data (Figure 7, eqs 16–18, see Supporting Information for details).

$$k_{1\text{obs}} = 1.26 \times 10^{-6} + 3.52 \times 10^{-4}[\text{DHA}],$$

$$k_1 = 3.52 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} \quad (16)$$

$$k_{2\text{obs}} = 1.19 \times 10^{-4} + 0.00384[\text{DHA}],$$

$$k_2 = 0.00384 \text{ M}^{-1} \text{ s}^{-1} \quad (17)$$

$$k_{3\text{obs}} = 3.36 \times 10^{-4} + 0.01496[\text{DHA}],$$

$$k_3 = 0.01496 \text{ M}^{-1} \text{ s}^{-1} \quad (18)$$

The intercepts from the graph of $k_{1\text{obs}}$, $k_{2\text{obs}}$ to $k_{3\text{obs}}$ plotted against the concentration of substrate, using the second order

rate constants listed in eqs 16–18, increase from 1.26×10^{-6} for $k_{1\text{obs}}$, to 1.19×10^{-4} for $k_{2\text{obs}}$ to $3.36 \times 10^{-4} \text{ s}^{-1}$ for $k_{3\text{obs}}$. For the initial concentration of 0.04 M 9,10-dihydroanthracene (DHA), these intercepts represent 8%, 43%, and 36% of the total k_{obs} values, respectively. Such big intercepts for $k_{2\text{obs}}$ and $k_{3\text{obs}}$ cannot be regarded as experimental error, clearly indicating a growing misfit of the chemistry and the assumed rate law. The extreme deviation at high pH values is consistent with the known slow decomposition of the deprotonated species, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})(\text{OH})^+$ and $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2$, in basic media, a supposition supported by the fact that the deviation is independent of substrate composition. Because the degradation of the manganese(IV) oxo complex at pH 13.4 is relatively slow in the absence of substrate ($k_{\text{obs}} = \sim 2 \times 10^{-5} \text{ s}^{-1}$; corrected on the basis of the blank experiment performed in the absence of substrate), as shown in blank experiments, the large intercept ($3.36 \times 10^{-4} \text{ s}^{-1}$) for the $k_{3\text{obs}}$ plot represents a relatively rapid reduction of manganese(IV) that has to be explained. One possibility is that the degradation of manganese(IV) is accelerated, or “catalyzed”, by radical intermediates generated in the course of the catalytic oxidation of the substrate by manganese(IV) (for example, eq 4). The small steady state amounts of radical intermediates may initiate a rapid degradation of manganese(IV), a complicated process that has been described elsewhere.¹⁶ The detailed investigation of the degradation of the manganese(IV) complex in base is beyond the scope of this study.

Perspective. The difference between the $\text{Mn}^{\text{IV}}\text{—OH}$ and $\text{Mn}^{\text{IV}}\text{=O}$ functional groups in this manganese(IV) complex obviously derives from the dissociation of a proton from the same manganese(IV) complex. Since proton transfer is very rapid in polar media, especially in aqueous media, the equilibrium between the M=O and M—OH functional groups with the same metal ion in the same oxidation state, and the same ligand, must be very facile. Further, this property of proton lability must carry over to the active centers of some redox enzymes. On the other hand, the chemical literature chooses to distinguish between and select each of these groups $\text{M}^{n+}\text{=O}$,^{2a,c,d} and $\text{M}^{n+}\text{—OH}$,^{4a–c,8a,10,25,26} as the key active intermediate in specific series of oxidation events in chemical or in biological systems. For example, in horseradish peroxidases, it has been argued that the relatively unreactive compound II involves the $\text{Fe}^{\text{IV}}\text{—OH}$ moiety in performing hydrogen abstractions.²⁷ The discoveries presented here on the active species in such systems provide an enhanced focus on the immediate issue of distinguishing the reactivity difference between certain metal oxo and metal hydroxo moieties, $\text{M}^{n+}\text{=O}$ and $\text{M}^{n+}\text{—OH}$. The study of this manganese(IV) complex has revealed that, given the same metal ion, the same ligand, and the same oxidation state, the oxidizing powers of metal oxo and metal hydroxo functions are not very different. As one might expect, the rates of their reactions (at least for hydrogen abstraction) are, in a relative sense, distinctly different, and the $\text{M}^{n+}\text{=O}$ group can perform oxidations substantially more rapidly than the corresponding $\text{Mn}^{n+}\text{—OH}$ group. Chemists and biologists should bear this in mind when considering the mechanisms mediated by the redox

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active transition metal ions in various enzymes, including the oxidases, dehydrogenases, and electron transfer enzymes.

Conclusions

A recently synthesized and characterized manganese(IV) complex having two hydroxide ligands, $[\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2](\text{PF}_6)_2$, has been studied to investigate the difference in oxidative reactivity of the metal oxo and metal hydroxo functional groups for the same metal ion with the same ligands and the same oxidation states, that is, $\text{LM}^{n+}=\text{O}$ and $\text{LM}^{n+}-\text{OH}$. For the systems under investigation, the calculated BDE_{OH} values for the $\text{Mn}^{\text{III}}-(\text{HO}-\text{H})$ and $\text{Mn}^{\text{III}}-\text{OH}$ moieties in the manganese(III) complexes, that are produced by hydrogen abstraction from a substrate, show that, thermodynamically, $\text{Mn}^{\text{IV}}-\text{OH}$ and $\text{Mn}^{\text{IV}}=\text{O}$ have very similar oxidizing powers (83.0 vs 84.3 kcal/mol). Close agreement was found in experiments using batch reactions, conducted for well defined reaction times and identical conditions, performing oxidations that involve the abstraction of hydrogen atoms from selected substrates having known BDE_{CH} values. Neither of these functional groups will oxidize substrates having BDE_{CH} values of 82 kcal/mol or higher. However, hydrogen abstraction by

the $\text{Mn}^{\text{IV}}=\text{O}$ group proceeds ~ 40 times faster than that of $\text{Mn}^{\text{IV}}-\text{OH}$ with the same substrate. The difference in reactivity in this case is attributed to differences in both activation entropies and enthalpies, for the case of hydrogen abstraction from 9,10-dihydroanthracene. The distinctive reactivity difference revealed by this exemplary manganese(IV) activated catalyst may provide new insights into oxidation events occurring in nature and provide guidance in the design of new oxidation catalysts for laboratory and industrial use.

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Supporting Information Available: Kinetic results of hydrogen abstraction from different substrates under various reaction conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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