J|A|C|S
COMMUNICATIONS

Understanding the Selectivity of a Moderate Oxidation Catalyst: Hydrogen Abstraction by a Fully Characterized, Activated Catalyst, the Robust Dihydroxo Manganese(IV) Complex of a Bridged Cyclam

Guochuan Yin,† Andrew M. Danby,† David Kitko,‡ John D. Carter,‡ William M. Scheper,‡ and Daryle H. Busch*,†

Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045, and The Procter and Gamble Company, Cincinnati, Ohio 45202

Received October 12, 2006; E-mail: busch@ku.edu

Hydrogen atom transfer and oxygen transfer are among the most studied topics in chemistry because they provide promise of understanding the basic events controlled by biological oxidases and oxygenases and because these reactions are basic to many industries, ranging from oil refining to home care products and pharmaceuticals.[1,2] Studies in this laboratory have produced useful selective oxidation catalysts[3] through design features that (1) favor oxygen transfer via a clean Lewis acid pathway[4] and (2) limit hydrogen atom transfer to relatively reactive substrates. Here we characterize the selective hydrogen abstraction with empirically based BDE calculations and experiments demonstrating two distinct Polanyi correlations attributable to catalytic species differing only in their levels of protonation. Whereas those two catalyst species react at different rates, their thermodynamic oxidizing powers are very similar (i.e., $\mathrm{BDE_{OH}}$ of 83 and 84 kcal/mol). Further, they both show a remarkable inability to oxidize substrates having $\mathrm{BDE_{CH}} \geq \mathrm{BDE_{OH}}$ of the catalyst. The work of decades, beginning with Bordwell and culminating with Mayer, produced a method, based on redox potentials and $\mathrm{p}K_\mathrm{a}$ values, for evaluating the bond dissociation energy (BDE) of OH and related groups ligated to transition metal centers.[5] Sequences of substrates with known $\mathrm{BDE_{CH}}$ values have been studied to test and make use of this so-called *Polanyi correlation*.[5b,6] This report is about a rare successful application of this relationship in the design of oxidation catalysts.[6]

These new catalysts are manganese complexes with a rigid, cross-bridged, cyclam ligand, 4,11-dimethyl-1,4,8,11-tetraazabicyclo-[6.6.2]hexadecane (abbreviated as $\mathrm{Me_2EBC}$).[7] The corresponding manganese(IV) complex,[7c] $\mathrm{Mn^{IV}(Me_2EBC)(OH)_2{}^{2+}}$, is doubly unique (1) as the first thoroughly characterized monomeric Mn(IV) complex containing a pair of hydroxo ligands (Figure 1), and (2) it constitutes the activated form of the catalyst (vide infra). Earlier studies on catalytic epoxidation of olefins by $\mathrm{Mn(Me_2EBC)Cl_2}$ identified the $\mathrm{H_2O_2}$ adduct of the manganese(IV) complex as the species responsible for the epoxidation.[4] This Lewis acid intermediate performs clean selective epoxidation reactions, like high valent early transition metal ions.[8] Further, this work proved that $\mathrm{Mn(Me_2EBC)(O)(OH)^+}$ is not capable of oxygen transfer to olefins (Groves' rebound mechanism). A remaining issue has been the hydrogen abstracting ability of the $\mathrm{Mn^{IV}{=}O}$ or $\mathrm{Mn^{IV}{-}OH}$ groups in this manganese(IV) complex. Having access to thoroughly characterized, pure crystalline salts of the activated catalyst facilitated the determination of BDE values for the $\mathrm{Mn^{IV}{=}O}$ or $\mathrm{Mn^{IV}{-}OH}$ groups and the experimental study of their hydrogen abstracting abilities. These studies show that, for these systems, the rate of hydrogen abstraction becomes vanishingly slow as the thermodynamic driving force approaches zero.

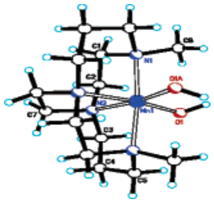
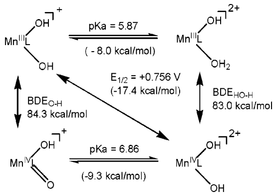


Figure 1. The X-ray structure of $\mathrm{Mn(Me_2EBC)(OH)_2{}^{2+}}$.

Scheme 1



The $\mathrm{BDE_{OH}}$ values for the reduced forms of the oxidizing agents were calculated by the Mayer/Bordwell method (Scheme 1; see Supporting Information for details).[5] $\mathrm{[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2}$ was synthesized as reported.[7c] The $\mathrm{p}K_\mathrm{a}$ values were measured in aqueous solution by titration[7b,c] ($\mathrm{p}K_\mathrm{a} = 5.87$ for $\mathrm{Mn^{III}(Me_2EBC)(OH)(H_2O)^{2+}}$ and 6.86 for $\mathrm{Mn^{IV}(Me_2EBC)(OH)_2{}^{2+}}$), and the reduction potential (+0.756 V vs NHE,[7c] corrected to aqueous media) was measured for the $\mathrm{Mn^{IV}(Me_2EBC)(OH)_2{}^{2+}/Mn^{III}(Me_2EBC)(OH)_2{}^{+}}$ couple by cyclic voltammetry. Calculations gave surprisingly similar results for the reduced forms of the two oxidizing species: $\mathrm{Mn^{III}(Me_2EBC)(OH)(H_2O)^{2+}}$, $\mathrm{BDE_{OH}} = 83.0$ kcal/mol and $\mathrm{Mn^{III}(Me_2EBC)(OH)_2{}^{+}}$, $\mathrm{BDE_{OH}} = 84.3$ kcal/mol. The close similarity in magnitude of these two values indicates that the hydrogen abstracting abilities of $\mathrm{Mn^{IV}{=}O}$ and $\mathrm{Mn^{IV}{-}OH}$ are thermodynamically very similar, even though the charges on $\mathrm{Mn^{IV}(Me_2EBC)(OH)_2{}^{2+}}$ and $\mathrm{Mn^{IV}(Me_2EBC)(O)(OH)^{+}}$ are different and the abstracting functional groups are different.

To learn the significance of the calculated $\mathrm{BDE_{OH}}$ values for water and hydroxide bound to the manganese(III) complex, hydrogen atom abstraction reactions were performed on a small synthetic scale by treating solutions containing predominantly $\mathrm{Mn^{IV}(Me_2EBC)(OH)_2{}^{2+}}$ with selected substrates (Table 1). As the reaction proceeds, the original purple color of $\mathrm{Mn^{IV}}$ gradually changes to red-brown, revealing the conversion to the corresponding $\mathrm{Mn^{III}}$ species. As the substrate $\mathrm{BDE_{CH}}$ value is increased, the reaction rate decreases dramatically. For example, in neutral 4:1 acetone/water, the second-order rate constant for the reaction between Mn(IV) and fluorene ($\mathrm{BDE_{CH}} = 80$ kcal/mol) is 2 orders slower than that of the reaction between Mn(IV) and xanthene ($\mathrm{BDE_{CH}} = 75.5$ kcal/mol). When the $\mathrm{BDE_{CH}}$ value exceeds ~80 kcal/mol, no reaction is observed over periods of weeks (e.g.,

---

† The University of Kansas.
‡ The Procter and Gamble Company.

10.1021/ja0673229 CCC: $37.00

Table 1. Hydrogen Abstraction from Selected Substrates by Manganese(IV) Complex[a]

substrate	BDE_{CH} (kcal/mol)	product	yield (mmol)	k_2 ($M^{-1}\,s^{-1}$)
xanthene[b]	75.5	xanthone	0.071	1.8×10^{-3}
1,4-cyclohexadiene[b]	76	benzene	0.16	8.7×10^{-4}
9,10-dihydro anthracene[b]	78	anthracene anthraquinone	0.14 0.0069	3.7×10^{-4}
fluorene[b]	80	9-fluorenone	0.083	2.6×10^{-5}
diphenyl methane[b,c]	82		0.00	
toluene[b,c]	90		0.00	
cyclohexane[b,c]	99		0.00	

[a] Reactions were run in a wet glovebox at room temperature. [b] 0.25 mmol of Mn^{IV} complex and 0.5 mmol of substrate. Solvent: acetone/water (4:1). [c] No hydrogen abstraction detected after stirring reactant solution for >19 days.

Table 2. Pseudo-First-Order Rate Constants for Hydrogen Abstraction with Manganese Complex at pH 4.0 and 8.4[a]

substrate	k_{1OH} at pH 4.0 (s^{-1})	k_{1oxo} at pH 8.4 (s^{-1})	k_{1oxo}/k_{1OH}
xanthene	$(1.59 \pm 0.01) \times 10^{-4}$	$(2.45 \pm 0.02) \times 10^{-3}$	15.4
1,4-cyclohexadiene	$(5.4 \pm 0.3) \times 10^{-5}$	$(8.9 \pm 0.20) \times 10^{-4}$	16.5
9,10-dihydroanthracene	$(4.39 \pm 0.09) \times 10^{-5}$	$(6.64 \pm 0.06) \times 10^{-4}$	15.1
fluorene	$(2.86 \pm 0.06) \times 10^{-5}$	$(3.02 \pm 0.07) \times 10^{-4}$	10.6

[a] Solvent: acetone/water (4:1), initial concentration of Mn(IV), 2 mM, initial concentration of substrate, 40 mM.

diphenylmethane, toluene, cyclohexane in Table 1). The corresponding Polanyi correlation is observed; see Supporting Information for details. The termination of hydrogen abstraction at diphenylmethane with $BDE_{CH} = 82$ kcal/mol is remarkable in two respects. First, it is consistent with the totally independent calculated BDE_{OH} values for $Mn^{IV}-OH_2$ (83.0 kcal/mol) or $Mn^{IV}-OH$ (84.3 kcal/mol) ligated to the manganese(III) complex within the 1−2 kcal/mol uncertainties of the BDE values; the reaction stops when the driving force stops. Second, while extensive earlier studies have confirmed the Polanyi relationship, termination of the hydrogen abstraction reaction in the manner reported here is rare.[9]

The existence of two forms of the activated catalyst that differ only in their degree of protonation at the active catalyst site presents a unique opportunity to probe intrinsic hydrogen abstraction factors. Preliminary studies of the pH dependence of the oxidation rates reveal two distinctive Polanyi correlations for this novel catalyst system (Table 2). Even with this limited data, it is reasonable to conclude that the $LMn^{IV}{=}O$ and $LMn^{IV}-OH$ moieties react at sharply different hydrogen abstraction rates despite the fact that they have very similar BDE_{OH} values (83.0 vs 84.3 kcal/mol). For a solution having an initial pH of 8.4, in which $LMn^{IV}(O)(OH)^+$ is estimated to be the dominant species, the reaction rate was 10−20 times faster than that found for a solution at an initial pH of 4.0 in which $LMn^{IV}(OH)_2^{2+}$ is the dominant species (see Supporting Information for details). For example, the reaction rate at the initial pH of 8.4 is 15 times faster than that conducted at the initial pH of 4.0 for hydrogen abstraction from 9,10-dihydroanthracene. The results summarized in Table 2 clearly show that the $Mn^{IV}{=}O$ moiety abstracts hydrogen at faster reaction rates than does the corresponding $Mn^{IV}-OH$ moiety even though the two species have almost identical BDE_{OH} values and, therefore, thermodynamic hydrogen abstracting abilities. Also, the data presented here add this $Mn^{IV}-OH$ group to the growing list of transition metal ion−hydroxo moieties with the ability to abstract hydrogen atoms from substrates.[5,6]

The observation that even the $LMn^{IV}{=}O$ moiety failed to oxidize substrates whose $BDE_{CH} > BDE_{OH}$ for the catalyst is rare (reaction conducted at pH 8.6 with diphenylmethane; see Supporting Information for details). The failure to cross the thermodynamic barrier strongly suggests an extraordinary selectivity of definable mechanistic origins. Ordinarily one might expect that a strong follow-up reaction could drive the reaction even when the equilibrium for formation of the hydrogen abstraction transition state is unfavorable. In the case of $Mn(Me_2EBC)Cl_2$, we suggest that such a follow-up reaction is mechanistically unavailable. Indeed, the oxidation of substrates having $BDE_{CH} > BDE_{OH}$ for $HOMnO_3$ (for example) may be driven by energetic follow-up reactions.[5b] These results may help in understanding and controlling synthetic, biomimetic, and biological oxidations.

In summary, this manganese complex is a highly selective oxidation catalyst because of mechanistic constraints, both in oxygen atom transfer and hydrogen abstraction. Polanyi correlations are observed for both groups ($Mn^{IV}-OH$ and $Mn^{IV}{=}O$), but hydrogen abstractions for the $Mn^{IV}{=}O$ group average ∼14 times faster than those for $Mn^{IV}-OH$. This illustrates intrinsically different oxidizing abilities for distinctly different functional groups when all else is about equal. Remarkably, the hydrogen abstracting abilities of both manganese complexes disappear when the thermal driving force becomes very small (i.e., BDE_{CH} for the substrate $\geq BDE_{OH}$ for the manganese complex). Although the slopes of the Polanyi correlations are substantially different, the thermodynamically controlled termination of oxidation is approximately the same since the BDE_{OH} values are similar for the two oxidizing groups. While intuitively appealing, the thermodynamic control of hydrogen abstraction described here appears to be rare.[9] Finally, its selective moderate oxidizing power makes this catalyst valuable for demanding applications.

Acknowledgment. Support by the Procter and Gamble Company is deeply appreciated, and we also acknowledge the National Science Foundation Engineering Research Center Grant (EEC-0310689) for partial support. GC−MS analysis of reaction products was performed by R. C. Drake.

Supporting Information Available: Methods used for calculations of BDE values; experimental procedures for hydrogen abstraction; kinetic results from hydrogen abstraction studies with different substrates under various conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Meunier, B., Ed. *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Imperial College Press: London, 2000. (b) Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*; Wiley: New York, 1995.

(2) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180. (b) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (c) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550.

(3) Busch, D. H.; Collinson, S. R.; Hubin, T. J. Catalysts and Methods for Catalytic Oxidation; WO98/39098, 1998.

(4) Yin, G.; Buchalova, M.; Danby, A. M.; Perkins, C. M.; Kitko, D.; Carter, J.; Scheper, W. M.; Busch, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 17170.

(5) (a) Bordwell, F. G.; Cheng, J. P.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1229. (b) Mayer, J. M. *Acc. Chem. Res.* **1998**, *37*, 441. (c) Mayer, J. M. *J. Mol. Catal. A: Chem.* **2006**, *251*, 24.

(6) (a) Gupta, R.; Borovik, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 13234. (b) Goldsmith, C. R.; Jonas, R. T; Stack, T. D. P. *J. Am. Chem. Soc.* **2002**, *124*, 83.

(7) (a) Hubin, T. J.; McCormick, J. M.; Collinson, S. R.; Buchalova, M.; Perkins, C. M.; Alcock, N. W.; Kahol, P. K.; Raghunathan A.; Busch, D. H. *J. Am. Chem. Soc.* **2000**, *122*, 2512. (b) Hubin, T. J.; McCormick, J. M.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **2001**, *40*, 435. (c) Yin, G.; McCormick, J. M.; Buchalova, M.; Danby, A. M.; Rodgers, K.; Smith, K.; Perkins, C.; Kitko, D.; Carter, J.; Scheper, W. M.; Busch, D. H. *Inorg. Chem.* **2006**, *45*, 8052.

(8) (a) Deubel, D. V.; Frenking, G.; Gisdakis, P.; Herrmann, W. A.; Rösch, N.; Sundermeyer, J. *Acc. Chem. Res.* **2004**, *37*, 645. (b) Xi, Z.; Zhou, N.; Sun, Y.; Li, K. *Science* **2001**, *292*, 1139.

(9) The following is a recent example: Feng, Y.; Gunnoe, T. B.; Grimes, T.; Cundari, T. R. *Organometallics* **2006**, *25*, 5456.

JA0673229