

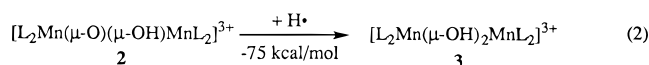
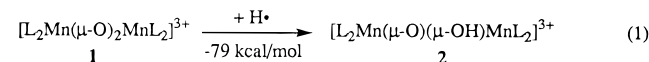
Oxidation of Hydrocarbons by [(phen)₂Mn(μ-O)₂Mn(phen)₂]³⁺ via Hydrogen Atom Abstraction

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The oxidation of hydrocarbons by homogeneous, heterogeneous, and enzymatic reagents is of much fundamental and technological interest. We report here the first example of C–H bond oxidation by a (μ-oxo)manganese complex, [L₂Mn(μ-O)₂MnL₂](PF₆)₃ (**1**; L = 1,10-phenanthroline).¹ Activation of C–H bonds by μ-oxo compounds has been suggested to occur in the catalytic cycles of iron and copper enzymes.² This study complements a recently characterized diiron system that oxidizes cumene^{2a} and methylcyclohexadiene,^{2b} as well as dicopper^{2c} and dicobalt³ systems that undergo intramolecular C–H activation. Mixed valent **1** (Mn³⁺Mn⁴⁺) has long been considered a model for a part of the oxygen-evolving complex in photosystem II, where oxidation of water has been proposed to occur by H[•] abstraction from metal-bound water or hydroxide by an adjacent tyrosine radical.⁴ We have proposed that the ability of metal oxo species such as MnO₄[−] and CrO₂Cl₂ to oxidize hydrocarbons by initial hydrogen atom abstraction is directly related to the thermodynamic affinity of these reagents for H[•], rather than any radical character in the oxidant.^{5,6} With this approach, we accurately predicted that **1** and **2** would abstract hydrogen atoms from weak C–H bonds because of its affinity for H[•] (eqs 1 and 2, L = phen) based on electrochemical and pK_a data.^{7,8}



(1) Complex **1** was prepared and fully characterized (with water of crystallization) following previous reports (see Supporting Information). (a) Manchanda, R.; Brudvig, G. W.; de Gala, S.; Crabtree, R. H. *Inorg. Chem.* **1994**, 33, 5157–5160. (b) Stebler, M.; Ludi, A.; Bürgi, H.-B. *Inorg. Chem.* **1986**, 25, 4743–4750. (c) Cooper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, 99, 6623–6630.

(2) For leading references, see: (a) Dong, Y.; Fuji, H.; Hendrich, M. P.; Leising, R. A.; Pan, G.; Randall, C. R.; Wilkinson, E. C.; Zang, Y.; Que, L., Jr.; Fox, B. G.; Kauffmann, K.; Münck, E. *J. Am. Chem. Soc.* **1995**, 117, 2778–2792. (b) Que, L., Jr., 1996, personal communication. (c) Zang, Y.; Pan, G.; Que, L., Jr.; Fox, B. G.; Münck, E. *J. Am. Chem. Soc.* **1994**, 116, 3653–3654. (d) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Cramer, C. J.; Que, L., Jr.; Tolman, W. B. *Ibid.* **1995**, 117, 8865–8866. (e) Halfen, J. A.; Mahapatra, S.; Wilkinson, E. C.; Kaderli, S.; Young, V. G., Jr.; Que, L., Jr.; Zuberbühler, A. D.; Tolman, W. B. *Science* **1996**, 271, 1397–1400. (f) For recent reviews, see: Que, L., Jr.; Dong, Y. *Acc. Chem. Res.* **1996**, 29, 190–196. Feig, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, 94, 759–805. Fox, S.; Karlin, K. D. In *Active Oxygen in Biochemistry*; Valentine, J. S., Foote, C. S., Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall: Glasgow, Scotland, 1995; pp 188–231.

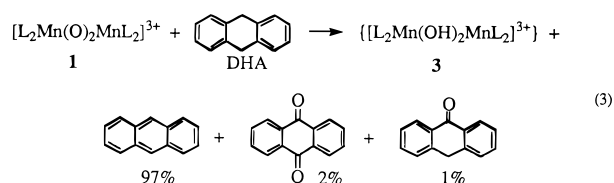
(3) Reinaud, O. M.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, 116, 6979–6980.

(4) (a) Hoganson, C. W.; Lydakis-Simantiris, N.; Tang, X.-S.; Tommos, C.; Warneke, K.; Babcock, G. T.; Diner, B. A.; McCracken, J.; Styring, S. *Photosynth. Res.* **1995**, 46, 177–184. (b) Manchanda, R.; Brudvig, G. W.; Crabtree, R. H. *Coord. Chem. Rev.* **1995**, 144, 1–38 and references therein. (c) Baldwin, M. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1996**, 118, 11325–11326.

(5) (a) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1995**, 117, 7139–7156. (b) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, 116, 1855–1868. (c) Correction. *Ibid.* **1994**, 116, 8859.

(6) (a) Gardner, K. A.; Mayer, J. M. *Science* **1995**, 269, 1849–1851. (b) Gardner, K. A.; Kuehnert, L. L.; Mayer, J. M. Submitted for publication. (c) Gardner, K. A. Ph.D. Thesis, University of Washington, 1996.

A solution of **1** in acetonitrile (20 mM) reacts with 9,10-dihydroanthracene (DHA, 40 mM) over 11 h at 65 °C, with a change in color from olive green to light brown (eq 3; all reactions done in the absence of air). GC analysis of the organic products revealed anthracene (19.4 mM) and traces of anthraquinone (0.4 mM) and anthrone (0.15 mM). Iodometric



titration⁹ of the isolated manganese product gave an average oxidation state of 2.37(4), roughly consistent with the formation of the Mn³⁺Mn²⁺ dimer **3**. The observed products account for 98% of the oxidizing equivalents of **1** consumed. When only half an equivalent of DHA is used (10 mM), the manganese product has an average oxidation state of 2.92(4), consistent with predominant formation of the Mn³⁺Mn³⁺ dimer **2**. The organic products (8 mM anthracene, 0.9 mM anthraquinone, and trace anthrone) account for 93% of the manganese oxidizing equivalents consumed. An isotope effect of 4.2(3) was found on analyzing the products of the oxidation of a 50/50 mixture of DHA-*h*₁₂ and DHA-*d*₁₂ by **1** at 55 °C. The reaction, as monitored by UV/vis spectroscopy, shows no induction period, and there are no isosbestic points. Absorbance vs time traces indicate a consecutive reaction pattern, suggested to be **1** → **2** → **3**. Species **2** and **3** are generated independently from **1** and respective stoichiometric amounts of hydroquinone.¹⁰

The reaction of **1** with fluorene in MeCN at 55 °C gives roughly equal yields of bifluorenyl and 9-fluorenone, accounting for 76% of the oxidizing equivalents consumed. The formation of bifluorenyl indicates that fluorenyl radicals are involved, as was confirmed by trapping with CBrCl₃ to give 9-bromofluorene, as well as 9-fluorenone and bifluorenyl. The reaction with DHA is similarly proposed to involve 9-hydroanthracenyl radicals (HA[•]), by H atom transfer from DHA to **1**, forming **2** (Scheme 1). In order to explain the kinetic traces, it is necessary to propose that **2** can also react with DHA by H[•] abstraction. HA[•] is then rapidly oxidized by **1** or **2** to give anthracene and **2** or **3**. The kinetic traces for the DHA reaction are successfully simulated with this scheme using the computer programs KINSIM/FITSIM.¹¹ At 25 °C, *k*₁ and *k*₃ are well defined as 1.56(2) × 10^{−3} M^{−1} s^{−1} and 4.2(7) × 10^{−4} M^{−1} s^{−1}, but the fit is not sensitive to the much faster rate constants for trapping of HA[•] (*k*₂, *k*₄ roughly 10⁴–10⁵ M^{−1} s^{−1} from the fit). Independent

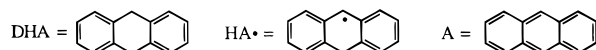
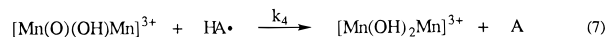
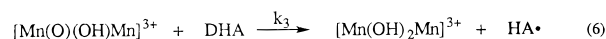
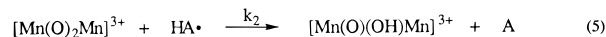
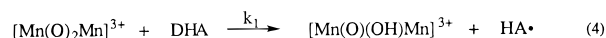
(7) Our initial estimates of the O–H bond strengths were based on aqueous electrochemical data reported (Manchanda, R.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H. *Inorg. Chem.* **1992**, 31, 4040–4041). However, a reviewer opined that these data are not for **1** but rather for a phosphate-bridged complex. In our hands, **1** reacts immediately on dissolution in phosphate buffer, apparently confirming the reviewer's view. We thank the reviewer for this information.

(8) (a) The O–H bond strengths were calculated using the equation described by Parker and Tilsen^{8b} for measurements in MeCN and Cp₂Fe^{+/0} couple as the reference: BDE = 23.06*E*_{1/2} + 1.37p*K*_a + 59.5 (kcal/mol). Baldwin and Pecoraro^{4c} used a related approach based on their measurement of *E*_{1/2} for H₂ in MeCN vs aqueous SCE, which is apparently equivalent to using a constant 3 kcal/mol lower (Baldwin, M. J. Personal communication, 1996). *E*_{1/2} values (in MeCN, vs Cp₂Fe^{+/0}): for Mn^{III}(O)₂Mn^{IV} → Mn^{III}(O)₂Mn^{III}, −0.01 ± 0.05 V; for Mn^{III}(O)(OH)Mn^{III} → Mn^{III}(O)(OH)Mn^{II}, −0.03 ± 0.05 V. The p*K*_a values in MeCN were determined electrochemically following the method of Baldwin and Pecoraro:^{4c} **2**, 14.6 ± 0.5; **3**, 11.5 ± 0.5. See Supporting Information for details. (b) Parker, V. D.; Handoo, K. L.; Roness, F.; Tilsen, M. *J. Am. Chem. Soc.* **1991**, 113, 7493–7498.

(9) Jeffery, G. H.; Bassett, J.; Mendham, J.; Denney, R. C. *Vogel's Textbook of Quantitative Chemical Analysis* 5th ed.; Wiley: New York, 1989; pp 384–391.

(10) Following related chemistry of the bipyridine analog of **1**: Ghosh, M. C.; Reed, J. W.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1994**, 33, 73–78. For detailed characterizations of **2** and **3**, see Supporting Information.

Scheme 1



oxidations of DHA with **2** (prepared from **1** + hydroquinone) occur with a rate constant of $4.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 50 °C, in excellent agreement with the simulation result ($3.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 50 °C). Over the temperature range of 25–55 °C, the activation parameters are $\Delta H^\ddagger_1 = 14.5(10) \text{ kcal/mol}$, $\Delta S^\ddagger_1 = -23(3) \text{ eu}$; $\Delta H^\ddagger_3 = 16.0(10) \text{ kcal/mol}$, $\Delta S^\ddagger_3 = -21(3) \text{ eu}$. The negative entropies of activation are consistent with bimolecular rate-limiting steps and are similar to what we have observed in other hydrogen atom transfer processes.^{5,6} $\Delta H^\ddagger_3$ is larger than $\Delta H^\ddagger_1$ presumably because the O–H bond formed on converting **1** to **2** is stronger than that formed from **2** to **3**.

Rates of hydrogen atom abstraction by main group radicals such as $\text{tBuO}\cdot$ and $\text{tBuOO}\cdot$ have long been known to correlate with the ΔH° for the $\text{H}\cdot$ transfer step (the Evans–Polanyi equation).¹² This ΔH° for reaction $\text{A–H} + \text{B} \rightarrow \text{A} + \text{B–H}$ is the difference in the bond strength between A–H and B–H. We have previously found that this relation connects the rate constants for $\text{H}\cdot$ abstraction by MnO_4^- and CrO_2Cl_2 with abstraction by oxygen radicals.^{5,6} Figure 1 shows this correlation, $\log k$ vs the strength of the O–H bond formed by the oxidant, for $\text{H}\cdot$ abstraction from DHA.¹³ The rate constants for $\text{H}\cdot$ abstraction by both **1** and **2** roughly correlate with those for $\text{tBuO}\cdot$ and $\text{secBuOO}\cdot$ (the straight line is defined by the rate constants for the oxygen radicals). It appears that **1** and **2** react slightly slower than predicted, while the MnO_4^- oxidation may be slightly faster, although this kind of correlation is rarely precise.¹² It is surprising, however, that **1** reacts only three times

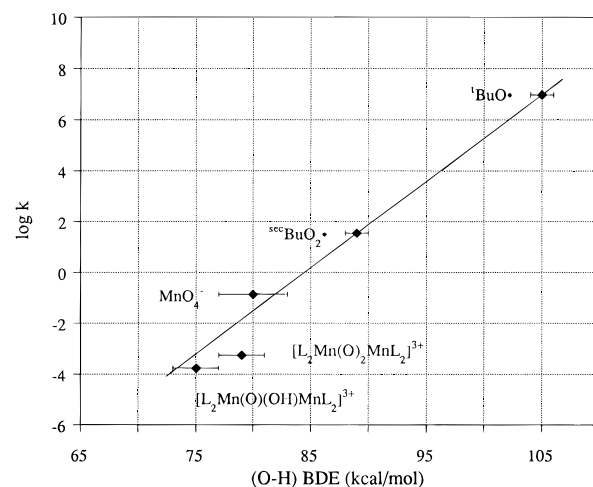


Figure 1. Rate constants for hydrogen atom abstraction from dihydroanthracene (30 °C) vs the strength of the O–H bond formed by $\text{tBuO}\cdot$, $\text{secBuOO}\cdot$, MnO_4^- , $[\text{L}_2\text{Mn}(\text{O})_2\text{MnL}_2]^{3+}$, and $[\text{L}_2\text{Mn}(\text{O})(\text{OH})\text{MnL}_2]^{3+}$.¹³ The straight line is defined by the values for $\text{tBuO}\cdot$ and $\text{secBuOO}\cdot$.

faster than **2** given the 4 kcal/mol stronger O–H bond formed. These deviations from a simple correlation with driving force may reflect different intrinsic barriers,¹⁴ perhaps due to structural reorganizations on transferring an $\text{H}\cdot$ to a bridging oxygen. Structural reorganizations have been implicated as the cause of slow proton transfer to some μ -oxo groups.¹⁵

In summary, both $[\text{L}_2\text{Mn}(\mu\text{-O})_2\text{MnL}_2]^{3+}$ (**1**) and $[\text{L}_2\text{Mn}(\mu\text{-O})(\mu\text{-OH})\text{MnL}_2]^{3+}$ (**2**; L = 1,10-phenanthroline) can abstract $\text{H}\cdot$ from hydrocarbons. The rate constants for these reactions can be roughly predicted based on the strengths of the O–H bonds that are formed. Studies with related substrates and oxidants are in progress to define the scope of these reactions and to understand the activation barriers in more detail.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this work. We thank Drs. M. Balwin and V. Pecoraro for valuable comments and an advance copy of ref 4c. We thank Jim Roe and Bob Morley for technical support, Tom Crevier for a sample of dihydroanthracene-*d*₁₂, Darin DuMez for assistance, and Dr. K. A. Gardner for valuable comments.

Supporting Information Available: Full experimental details, including preparation and characterization of **1–3**, kinetics and simulations, electrochemical measurements of $E_{1/2}$ and pK_a values, and a description of the O–H bond strengths estimation (8 pages). See any current masthead page for ordering and Internet access instructions.

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(14) Intrinsic barriers for an individual redox couple are widely used in electron transfer reactions (Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148–13168 and references therein), but their utility in hydrogen atom transfer reactions has yet to be established.

(15) Kramarz, K. W.; Norton, J. R. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1994; Vol. 42, pp 1–65 and references therein.

(11) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134. The KINSIM/FITSIM programs were obtained from Washington University (St. Louis, MO) and run on an SGI computer. We thank Prof. Carl Frieden for allowing us to use the programs.

(12) (a) *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973. See especially: Ingold, K. U. *Ibid.* Vol. 1, Chapter 2, pp 67–83. Russell, G. A. *Ibid.*; Vol. 1, Chapter 7, pp 275–331. (b) Knox, J. H. In *Oxidation of Organic Compounds*; Mayo, R. R., Ed.; American Chemical Society: Washington, DC, 1968; pp 1–22. See refs 5 and 6 for more detailed discussions.

(13) (a) For the rate constant (21 °C) for $\text{tBuO}\cdot$ see: Mulder, P.; Arends, I. W. C. E.; Clark, K. B.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 8182–8189. Rates are relatively insensitive to small temperature changes for this type of fast reactions, therefore the rate was assumed to be the same at 30 °C. For example, only 6% increase in rate from 21 to 30 °C for the reaction of $\text{tBuO}\cdot$ with 1,3-cyclopentadiene (Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106). (b) For the rate constant for $\text{secBuOO}\cdot$ (30 °C), see: Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1968**, *46*, 2661. (c) The O–H bond strength in secBuOOH is taken as 89 kcal/mol, equal to that in tBuOOH (Colussi, A. J. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; p 33. (d) Data for $\text{tBu}_4\text{NMnO}_4$ in toluene from ref 6b,c.