Mechanism of Permanganate Oxidation of Alkanes: Hydrogen Abstraction and Oxygen "Rebound"

Thomas Strassner* and K. N. Houk*

Technische Universität München
Institut für Anorganische Chemie
Lichtenbergstrasse 4, D-85747 Garching, Germany
Department of Chemistry and Biochemistry
University of California, Los Angeles, California 90095-1569

Received March 20, 2000
Revised Manuscript Received June 9, 2000

Despite the venerable reputation of permanganate as an oxidant, the details of mechanism have remained unclear. Permanganate is known to oxidize alkanes to ketones and aldehydes or carboxylic acids.[1] Although a simple hydrogen atom abstraction has gained popularity based upon the correlation of rates with heats of reaction for MnO_4^- and a series of alkoxy radicals,[2] other alternatives have been proposed to account for experimental observations. Electron-transfer followed by proton transfer has recently been proposed,[3] while a concerted $[\pi^2 + \sigma^2]$ process, involving insertion into a CH bond has been considered for a variety of metal−oxo bonds.[4] Brauman and Pandall provided evidence that the reaction occurs by hydrogen abstraction to give a caged radical pair which collapses to a Mn(V) ester with partial retention of configuration.[5] The first step of the oxidation resembles a hydrogen abstraction by alkoxy radicals; Mayer describes the reaction as a molecule-assisted homolysis.[2] The reaction of Cr−oxo species with radicals has recently been described.[6] Reactions of metal−oxo species with alkanes is a subject of burgeoning interest.[7]

We have explored the transition state of the permanganate oxidation of alkanes computationally and have computed the H−O bond dissociation energy in $HMnO_4^-$ to compare with estimates based on experimental data.[2] We report the nature of the transition states of permanganate oxidations of alkanes and their relationships to those involved in hydrogen abstraction by alkoxy radicals. We provide a mechanism which accounts for the experimental data.[1−6] The mechanism has some features in common with alkoxy radical mechanisms, and others in common with the "oxygen rebound" mechanism proposed for metal−oxo reactions in biological systems and model systems.[7] The hybrid density functional/Hartree−Fock model Becke3LYP[8,9] together with the 6-311+G(d,p) basis set implemented in GAUSSIAN-94[10] has been used throughout this study.[11] This level of theory provides reasonable activation energies and transition states for permanganate reactions with alkenes.[12] The computed energies of reaction are generally less exothermic than the best experimental values by 2−8 kcal/mol.[2b]

Mayer has studied permanganate in aprotic organic media; he found similar rate constants in organic media with very different dielectric constants.[2] He concluded that his experimental results rule out an electron transfer or hydride transfer mechanism. The Polanyi correlation of rate constants with C−H bond strength provided evidence for a rate determining H-atom transfer. Mayer estimated the $H-OMnO_3^-$ bond strength of 80.3 kcal/mol using a thermochemical cycle.[2]

From B3LYP computed energies, zero point energies, and thermal corrections, we have computed an HO bond dissociation energy of 83.3 kcal/mol for $HOMnO_3^-$. This compares favorably with Mayer's estimate and deviates in the direction expected for these B3LYP results. This dissociation energy is remarkably high for a radical and is comparable to that of an OH group of an alkyl hydroperoxide.

We have also located the transition state for reaction of MnO_4^- with methane and compared that to the transition states for the reactions of various oxyradicals with methane. The data are given in Table 1.

Figure 1 is a plot of the activation energies versus the energies of reaction, both computed theoretically for the reactions of $HO^\bullet$, $MeO^\bullet$, t-$BuO^\bullet$, t-$BuOO^\bullet$ radicals, and of permanganate with methane. The theoretical Polanyi relationship between activation energies and energies of reaction (both corrected for zero point energies) is satisfactorily linear, as found by Mayer from experimental data.[2] The activation energy of the permanganate reaction is about 6 kcal/mol higher than the correlation based upon the oxyradicals, consistent with the lack of diradical character for permanganate (see below). The slope of the Polanyi correlation is about 0.8, indicating that a significant fraction of the change in heat of reaction is manifested in the activation energy change.

The earliest transition state is expected for the reaction of hydroxyl—which has a low activation energy corresponding to a high exothermicity. The $MeO^\bullet$, t-$BuO^\bullet$, and t-$BuOO^\bullet$ radicals should have later transition states—corresponding to higher activation energies and low exothermicities. Permanganate is expected to possess a very late transition state and high activation energy, due to the relatively low O−H bond strength.

The transition states calculated for these reactions confirm these ideas (Figure 2). The bond length for the forming bond in the transition state decreases from 1.325 Å for the hydroxyl radical to 1.115 Å for the *t*-BuOO radical. The permanganate transition state is predicted to be even later, with a calculated bond length of 1.084 Å; this reaction is endothermic by 33.8 kcal/mol.

Accordingly, the breaking C−H bond length increases from 1.216 Å for the hydroxyl radical to 1.542 Å for permanganate. The activation energy increases from 1.1 kcal/mol to 32.3 kcal/mol as shown in Table 1; a 30 kcal/mol variation in activation energy corresponds to a 0.3 Å alteration in transition state bond length.

The $Mn(VII)O_4^-/CH_4$ transition state shown in Figure 2a leads to a radical ion pair $HMn(VII)O_4^{\bullet-}/CH_3^\bullet$. The sum of the energies

---

(1) Stewart, R. *Oxidation in Organic Chemistry, Part A*, K. B. Wiberg, Ed.; Academic Press: New York, 1965; Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*; Open Court: La Salle, 1981.

(2) (a) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441−450. (b) Gardner, K. A.; Kuehnert, L. L.; Mayer, J. M. *Inorg. Chem.* **1997**, *36*, 2069−2078. (c) Gardner, K. A.; Mayer, J. A. *Science* **1995**, *269*, 1849−1851.

(3) Bockman, T. M.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 2826−2830.

(4) Lee, D. G.; Chen, T. *J. Am. Chem. Soc.* **1993**, *115*, 11231−11236 and references therein.

(5) Brauman, J. I.; Pandall, A. J. *J. Am. Chem. Soc.* **1970**, *92*, 329−335.

(6) Wistuba, T.; Limberg, C.; Kircher, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 3037−3039.

(7) Filatov, M.; Harris, N.; Shaik, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3510−3512.

(8) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785−789.

(9) (a) Becke, A. D. *J. Am. Chem. Soc.* **1992**, *97*, 9173−9177. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(11) All geometries have been fully optimized. The stability of the wave function has been verified. The transition states have been confirmed by frequency calculations to have one negative eigenvalue.

(12) Strassner, T.; Houk, K. N. *J. Org. Chem.* **1999**, *64*, 800−802.

10.1021/ja000981f CCC: $19.00

Table 1. Bond Lengths in the Transition States and Calculated Activation Energies

	^{r}O- -H	^{r}C- -H	$\Delta H^{\ddagger}$ (kcal/mol)	ΔH_{rxn} (kcal/mol)
HO$^{\bullet}$	1.325	1.216	1.1	−12.2
MeO$^{\bullet}$	1.202	1.307	11.2	3.8
t-BuO$^{\bullet}$	1.207	1.312	11.3	2.2
t-BuOO$^{\bullet}$	1.115	1.447	26.1	23.9
MnO_4^-	1.084	1.542	32.3	24.3

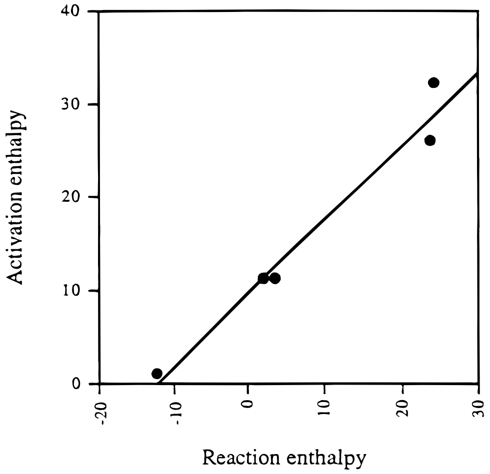
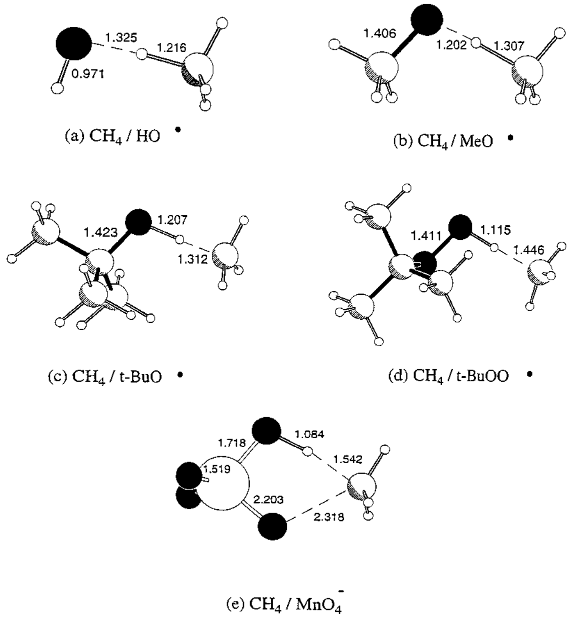


Figure 1. Polanyi relationship between calculated activation energies and energies of reaction for oxyradicals and permanganate.



(a) CH_4 / HO $^{\bullet}$ (b) CH_4 / MeO $^{\bullet}$

(c) CH_4 / t-BuO $^{\bullet}$ (d) CH_4 / t-BuOO $^{\bullet}$

(e) CH_4 / MnO_4^-

Figure 2. UB3LYP/6-311+G** transition states for hydrogen abstractions from CH_4.

of these two radicals is 6.3 kcal/mol below the transition state. The IRC[13] shows that the radical pair collapses without a barrier to the manganese(V) product, $Mn(OH)(OMe)O_2^-$, which is 20.7 kcal/mol more stable than the reactants. This Mn(V) species will disproportionate to Mn(IV) and Mn(VI) or Mn(VII) species. In solution, the radical pair might be stabilized enough to diffuse out of the cage, accounting for Brauman's observation of only partial retention of configuration with an optically active tertiary alkane. However, the preferred mechanism is a hydrogen atom abstraction followed by immediate collapse (oxygen rebound) of the radical pair to alkyl manganate ester.

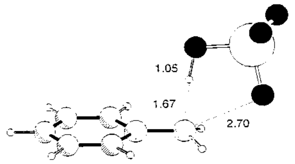


Figure 3. UB3LYP/6-311+G** transition state for the hydrogen abstraction from toluene.

Mayer compared the rates of reactions of different oxygen radicals and permanganate with toluene. The transition state for the hydrogen abstraction of toluene by permanganate is shown in Figure 3. The benzyl radical is nearly formed; the breaking CH bond length is 1.671 Å, and the forming H−O bond length is 1.05 Å. The interaction between the permanganate O and the CH_2 group stabilizes the transition state. The activation energy of the reaction is calculated to be 21.8 kcal/mol.

In both permanganate transition states, two oxygens of the permanganate are involved significantly in the transfer of the hydrogen. The hydrogen is clearly transferred to one, but a second oxygen is in the vicinity of the forming radical. The bond lengths of two Mn═O are significantly elongated for the oxygens near the C−H. The Mn−O bond to which the hydrogen is transferred to is elongated to 1.721 Å in the reaction with methane and 1.732 Å for the reaction with toluene. The Mn−O bond to the other nearby oxygen is 1.636 Å in the methane reaction and 1.617 Å in the toluene reaction.

The correlation of activation energy and energy of reaction for permanganate with those of alkoxy radicals leads to the impression that the permanganate has some radical character or that the reaction is a typical hydrogen abstraction leading to alkyl radicals. However, permanganate is well described by a closed shell wave function; the lowest triplet state is 20.8 kcal/mol higher in energy.

The reaction resembles that of other closed-shell oxidants which insert into CH bonds of alkanes. For example, we and Bach et al. have studied the reactions of dioxiranes with alkanes;[14] the processes have transition states involving mainly CH abstraction but lead to oxygen insertion. This is consistent with experimental evidence for stereospecificity in oxygen insertion reactions of dioxiranes[15] and some metal−oxo species.[4] Whether the reaction is stereospecific or not depends on whether the radical pair has a lifetime sufficient for dissociation or diffusion out of the solvent cage. The incipient radical pair may separate in some circumstances, but "rebound" to covalent products is the preferred pathway. Collman, Brauman et al. have proposed that H_2 and CH_4 form agostic complexes with the high-valent iron−oxo species in cytochrome P-450.[16] However, with permanganate we are unable to find such complexes. The permanganate mechanism fits the oxygen rebound mechanism.

Acknowledgment. We are grateful to Dr. Karl Wamsler-Stiftung (T.S.) and the National Science Foundation for financial support of this research and to Professor James P. Collman and Allis Chien for helpful discussions.

JA000981F

---

[13] The intrinsic reaction coordinate traces the minimum energy pathway from transition state to reactants and products.

[14] (a) Du, X. H.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 6480−6483. (b) Glukhovtsev, M. N.; Canepa, C.; Bach, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 10528−10533.

[15] Bakke, J. M.; Bethell, D. *Acta Chem. Scand.* **1992**, *46*, 644−649.

[16] Collman, J. P.; Chien, A. S.; Eberspacher, T. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1998**, *120*, 425−426.