

Hydrogen Atom Abstraction by Permanganate: Oxidations of Arylalkanes in Organic Solvents

Kimberly A. Gardner, Linda L. Kuehnert, and James M. Mayer*

Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

Received October 25, 1996[®]

Oxidations of arylalkanes by ^tBu₄NMnO₄ have been studied in toluene solvent: toluene, ethylbenzene, diphenylmethane, triphenylmethane, 9,10-dihydroanthracene, xanthene, and fluorene. Toluene is oxidized to benzoic acid and a small amount of benzaldehyde; other substrates give oxygenated and/or dehydrogenated products. The manganese product of all of the reactions is colloidal MnO₂. The kinetics of the reactions, monitored by UV/vis spectrometry, show that the initial reactions are first order in the concentrations of both ^tBu₄NMnO₄ and substrate. No induction periods are observed. The same rate constants for toluene oxidation are observed in neat toluene and in *o*-dichlorobenzene solvent, within experimental errors. The presence of O₂ increases the rate of ^tBu₄NMnO₄ disappearance. The reactions of toluene and dihydroanthracene exhibit primary isotope effects: $k_{C_7H_8}/k_{C_7D_8} = 6 (\pm 1)$ at 45 °C and $k_{C_{14}H_{12}}/k_{C_{14}D_{12}} = 3.0 (\pm 0.6)$ at 25 °C. The rates of oxidation of substituted toluenes show only small substituent effects. In the reactions of dihydroanthracene and fluorene, the MnO₂ product is consumed in a subsequent reaction that appears to form a charge-transfer complex. The rate-limiting step in all of the reactions is hydrogen atom transfer from the substrate to a permanganate oxo group. The enthalpies of activation for the different substrates are directly proportional to the ΔH° for the hydrogen atom transfer step, as is typical of organic radical reactions. The ability of permanganate to abstract a hydrogen atom is explained on the basis of its ability to form an 80 ± 3 kcal/mol bond to H[•], as calculated from a thermochemical cycle. (This bond strength is slightly lower than given in earlier calculations.) Rates of H[•] abstraction by ^tBu₄NMnO₄ correlate with rates of abstraction by oxygen radicals.

Introduction

The selective oxidation of hydrocarbons is a fundamental transformation in chemistry, important in a wide range of areas from biological to industrial chemistry.¹ A recurrent theme is the use of metal–oxo species, both catalytically and stoichiometrically, as the active oxidants. Commercially, for example, a vanadium phosphorus oxide is used as a heterogeneous catalyst for the conversion of butane to maleic anhydride.² One of the most intensively studied metalloenzyme families, cytochrome P-450, utilizes a ferryl (FeO) group to selectively oxidize hydrocarbons to alcohols under mild conditions.³ The classic examples of stoichiometric hydrocarbon oxidation by metal–oxo species are those of permanganate and chromium(VI) reagents, which have been used for this purpose for over a century.⁴ These heterogeneous, enzymatic, and molecular oxidants likely share some common features which enable them to attack C–H bonds, but the proliferation of literature in these fields has made a comprehensive understanding of the chemistry a daunting task. Additionally, many of the systems that are most effective at selective hydrocarbon oxidation are also the most complex.

We have been studying reactions of the relatively simple and well-defined oxidants chromyl chloride⁵ and permanganate⁶ in order to develop an understanding of C–H bond oxidations. Permanganate has been widely used as a strong, easily handled, readily available, and versatile oxidant, reacting with alcohols, alkenes, aldehydes, saturated C–H bonds, and other functionalities.⁷ The lack of selectivity of permanganate is due, at least in part, to its ability to react readily by either one-electron or two-electron pathways, and its conversion to even stronger oxidants such as “MnO₃⁺”.⁸ The reaction pathway is influenced by solvent, pH, substrate, and other variables, complicating mechanistic understanding.

Most of the mechanistic studies of C–H bond oxidation by permanganate date from the 1950s and 1960s.^{7a–d} Organic radical intermediates feature prominently in many of the mechanistic proposals, as, for instance, in the formation of 3,4-diphenylhexane from *n*-propylbenzene and succinic anhydride from acetic anhydride.^{7d} The partial retention of stereochemistry observed in the oxidation of tertiary C–H bonds has been explained using radical mechanisms.⁹ However, it is unclear how the organic radicals are formed. As stated in a 1958

[®] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

- (1) (a) Olah, G. A.; Molnár, Á. *Hydrocarbon Chemistry*; Wiley-Interscience: New York, 1995. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (c) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley-Interscience: New York, 1989.
- (2) Haggin, J. *Chem. Eng. News* **1995**, 73, 20–23.
- (3) (a) *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1995. (b) Watanabe, Y.; Groves, J. T. In *The Enzymes*, 3rd ed.; Academic Press: New York, 1992; Vol. XX, pp 405–452.
- (4) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985.

- (5) (a) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, 116, 1855–1868; (b) correction, **1994**, 116, 8859. (c) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1995**, 117, 7139–7156.
- (6) A preliminary report on the oxidation of toluene by permanganate has appeared: Gardner, K. A.; Mayer, J. M. *Science* **1995**, 269, 1849–1851.
- (7) (a) Waters, W. A. *Q. Rev. (London)* **1958**, 277–300. (b) Carrington, A.; Symons, M. C. R. *Chem. Rev.* **1963**, 63, 443–460. (c) Stewart, R. In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Part A, pp 1–68. (d) Stewart, R. *Oxidation Mechanisms*; Benjamin: New York, 1964. (e) Fatiadi, A. J. *Synthesis (Stuttgart)* **1987**, 85–127. (f) *Comprehensive Organic Synthesis, Vol. 7 (Oxidation)*; Trost, B. M., Ed.; Pergamon: New York, 1991.
- (8) Stewart, R.; Spitzer, U. A. *Can. J. Chem.* **1978**, 56, 1273–1279.

review:^{7a} "Ions derived from every valence state of manganese from VII to III, as well as the hydroxyl radical and other oxygenated species (e.g., O⁻ and HO₂) have been proposed as the active entities responsible for oxidation by permanganate." In addition, nonradical pathways have been suggested for C–H bond oxidation by permanganate, such as hydride abstraction.⁶ It has also been suggested that C–H bonds add in a [2 + 2] fashion across a Mn=O π bond to give alkylmanganese species,¹⁰ as originally suggested in theoretical studies of CrO₂-Cl₂ oxidations.¹¹

Presented here are studies of permanganate oxidations of alkyl-substituted aromatic hydrocarbons in organic solvents,⁶ using the soluble tetrabutylammonium salt ⁿBu₄NMnO₄.¹² The use of organic solvents allows the substrate and solvent to be the same and avoids some of the complications of aqueous permanganate reactions, such as decomposition at high¹³ and autocatalysis at low^{14a} pH, involvement of water in the rate-determining step,⁶ and limited solubility of the organic substrates of interest.¹⁵ There are previous reports of C–H bond oxidation by organic soluble permanganate salts,¹⁶ but this is the first mechanistic study. It is concluded that the first step in these reactions is abstraction of a hydrogen atom by permanganate, as we have found in related CrO₂Cl₂ reactions.⁵ The data support our proposal that the occurrence and rate of these reactions are a direct result of the strength of the O–H bond formed on addition of a hydrogen atom to the oxidant.^{5,6}

Experimental Section

All reactions were carried out in the absence of air unless otherwise noted. Reactions were typically set up in a drybox dedicated to this oxidation project. It was found necessary to exclude all reductants other than alkanes and arylalkanes from this drybox. ⁿBu₄NMnO₄ was prepared by a literature procedure¹² and recrystallized from CH₂Cl₂/Et₂O. The crystalline solid was stored in a sealed container in the laboratory freezer as it decomposes at 20 °C over several days. The container and its contents were always warmed to room temperature before opening to avoid condensing water onto the solid. **CAUTION:** ⁿBu₄NMnO₄ is reported¹² to be prone to violent spontaneous decomposition. Care should be taken in handling the dry solid.

Materials were purchased in the highest possible purity, and they were purified¹⁷ immediately before use and/or were stored in the drybox. Toluene (100.0%, Baker), ethylbenzene (99.8%, Aldrich), cumene (99%, Aldrich), and *tert*-butylbenzene (99%, Aldrich) were washed with ice-cold concentrated H₂SO₄, followed by water and then aqueous base (PhMe, 5% NaHCO₃; PhCH₂Me and PhCHMe₂, 10% NaHCO₃;

PhCMe₃, 10% NaOH), and finally rinsed with water until the washings were neutral. Drying was carried out in two stages, followed by vacuum transfer or distillation under N₂ and a purity check by GC. Toluene: CaSO₄, then Na. Ethylbenzene: MgSO₄, then Na (100.0% by GC). Cumene: Na₂SO₄, then Na or CaH₂ (99.96% GC purity). PhCMe₃: CaSO₄, then CaH₂ (99.8%). Cumene and *tert*-butylbenzene were stored in the glovebox, the former in an amber bottle, protected from light. *d*₈-Toluene (100.0% by GC/MS, Cambridge Isotope) was dried over Na and vacuum transferred prior to use.

o-Dichlorobenzene was purified by shaking with concentrated H₂SO₄ until clear and then washing with an equal portion of water. After preliminary drying over CaCl₂, the *o*-dichlorobenzene was refluxed over CaH₂ for 3 days and distilled from CaH₂. In a fume hood (excluding all light except a red safelight), the solvent was run down a column of activated alumina, degassed, and stored in the drybox. The purity by GC was 99.9%. Immediately before each use, the solvent was further purified by being run down a 1 cm × 10 cm alumina column in the drybox. The alumina was activated by heating under vacuum at 190 °C for 7 h and was stored in the glovebox.

p-Xylene (99.7%, Aldrich) was dried over Na and vacuum transferred prior to use. *p*-Chlorotoluene (Aldrich) was refluxed over CaH₂ and fractionally distilled (GC purity: 99.6%). 4-Methylbenzophenone (99.8%, Aldrich), xanthene (99.4%, Aldrich), and fluorene (99%, Fluka) were used as received (purification of fluorene concentrated the impurities). 9,10-Dihydroanthracene (99.97%, Aldrich) was recrystallized four times from EtOH. Diphenylmethane (100.0%, Aldrich) was a solid at room temperature after sublimation. Triphenylmethane (99.95%, Aldrich) was recrystallized from hot EtOH. *d*₁₂-Dihydroanthracene was prepared¹⁸ by reduction of *d*₁₀-anthracene by Na/EtOD (>98% GC purity; 98% isotopic purity by GC–MS).

Kinetics. Kinetic experiments were monitored with a Hewlett-Packard 8452A diode array spectrophotometer scanning over the range 400–640 nm. Temperature control (± 0.1 °C) was accomplished using either a custom-built aluminum block cell holder connected to a Peltier electronic control module or a water-jacketed cell holder connected to a circulating water bath. Solutions were prepared in the glovebox by adding toluene to an excess of ⁿBu₄NMnO₄, stirring for several minutes, and filtering off the undissolved solid. This solution was used directly for toluene oxidation experiments, or it was mixed with a known quantity of another substrate, either neat or as a concentrated toluene solution (e.g., 1.0 mL of ⁿBu₄NMnO₄ in toluene plus 1.0 mL of neat PhEt). A quartz cuvette sealed to a Teflon needle valve was charged with this solution and shaken to ensure mixing. Data collection was started immediately after the cuvette was placed in the preheated cell holder. The initial MnO₄⁻ concentration was calculated from the first spectrum using $\epsilon_{526} = 2530 \text{ M}^{-1} \text{ cm}^{-1}$ (which assumes that the solution was at approximately ambient temperature).¹² For experiments above room temperature, the data collected in the first 5 min were not used to allow for temperature equilibration.

Xanthene reacts so quickly with MnO₄⁻ that experiments used a specially designed cuvette (described elsewhere¹⁹) which is sealable and injectable. In a typical procedure, the cuvette was charged with 2 mL of a saturated solution of ⁿBu₄NMnO₄ in toluene and equilibrated at 10.0 °C in the spectrometer. By syringe, 15 μ L of concentrated xanthene solution was added (101.4 mg of xanthene in 5 mL of toluene). The cuvette was shaken, and data collection was started. Reactions in *o*-dichlorobenzene solvent were assembled in the glovebox. In a typical procedure, a sealable cuvette was loaded with 1.0 mL of toluene and 2.0 mL of a solution of ~ 1.5 mg of ⁿBu₄NMnO₄ in 10 mL of freshly purified *o*-dichlorobenzene. The cell was sealed and removed from the drybox, and data collection was started immediately.

Data Analysis. For all reactions, optical spectra in the range 400–640 nm show the disappearance of MnO₄⁻ and the appearance of a broad absorbance due to colloidal MnO₂. Despite its colloidal nature, the absorbance/scattering of MnO₂ follows Beer's law fairly well as evidenced by the formation of isosbestic points (eq 1; Figure 1). The *d*₈-toluene reactions are an exception where the colloidal MnO₂ absorption is not well-behaved. Since neither [MnO₂] nor ϵ_{MnO_2} is well-defined, [MnO₄⁻] is calculated from the absorbance at two different

- (9) (a) Brauman, J. I.; Pandell, A. J. *J. Am. Chem. Soc.* **1970**, *92*, 329–335. (b) Wiberg, K. B.; Fox, A. S. *J. Am. Chem. Soc.* **1963**, *85*, 3487–3491.
- (10) (a) Lee, D. G.; Chen, T. *J. Org. Chem.* **1991**, *56*, 5341–5345. (b) Lee, D. G.; Chen, T. *J. Am. Chem. Soc.* **1993**, *115*, 11231–11236. (c) Lee, D. G.; Congson, L. N. *Can. J. Chem.* **1990**, *68*, 1774–1779.
- (11) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 3287–3294.
- (12) Karaman, H.; Barton, R. J.; Robertson, B. E.; Lee, D. G. *J. Org. Chem.* **1984**, *49*, 4509–4518. ⁿBu = CH₂CH₂CH₂CH₃. According to this paper and references therein, the molar extinction coefficient for permanganate at 526 nm is approximately the same in all organic solvents (at 25 °C).
- (13) Vepřek-Siška, J.; Ettl, V.; Regner, A. J. *Inorg. Nucl. Chem.* **1964**, *26*, 1476–1477.
- (14) (a) Cullis, C. F.; Ladbury, J. W. *J. Chem. Soc.* **1955**, 555–560. (b) Cullis, C. F.; Ladbury, J. W. *J. Chem. Soc.* **1955**, 1407–1412. (c) Cullis, C. F.; Ladbury, J. W. *J. Chem. Soc.* **1955**, 2850–2854. (d) Cullis, C. F.; Ladbury, J. W. *J. Chem. Soc.* **1955**, 4186–4190.
- (15) Wiberg, K. B.; Stewart, R. *J. Am. Chem. Soc.* **1955**, *77*, 1786–1795.
- (16) (a) Sala, T.; Sargent, M. V. *J. Chem. Soc., Chem. Commun.* **1978**, 253–254. (b) Leddy, B. P.; McKervey, M. A.; McSweeney, P. *Tetrahedron Lett.* **1980**, *21*, 2261–2264. (c) Schmidt, H.-J.; Schäfer, H. *J. Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 68–69.
- (17) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980.

- (18) By T. J. Crevier. Crevier, T. J.; Mayer, J. M. Manuscript in preparation.
- (19) Gardner, K. A. Ph.D. Thesis, University of Washington, 1996.

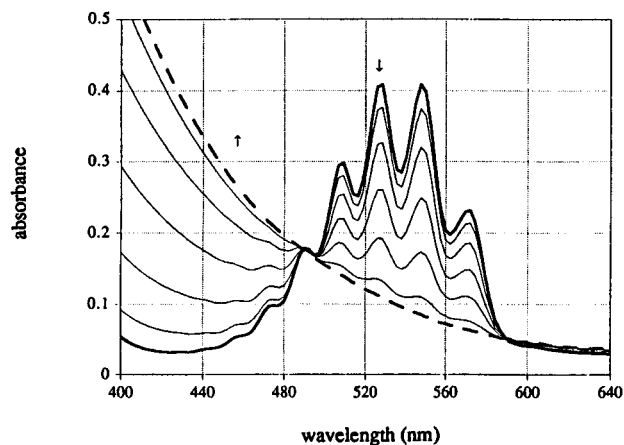


Figure 1. Overlay of UV/vis spectra from the reaction of ${}^n\text{Bu}_4\text{NMnO}_4$ with toluene at 25 °C. Spectra are at 1, 5, 15, 30, 50, 75, and 99 $\times 10^3$ s.

wavelengths, x and y , using only the relative MnO_2 absorbance, Q , at these wavelengths (eqs 2 and 3).

$$A_x = [\text{MnO}_4^-] \epsilon_{\text{MnO}_4^-;x} + [\text{MnO}_2] \epsilon_{\text{MnO}_2;x} \quad (1)$$

$$[\text{MnO}_4^-] = \frac{A_y - QA_x}{\epsilon_{\text{MnO}_4^-;y} - Q\epsilon_{\text{MnO}_4^-;x}} \quad (2)$$

where

$$Q = \frac{\epsilon_{\text{MnO}_2;y}}{\epsilon_{\text{MnO}_2;x}} \quad (3)$$

The ratio Q cannot be determined from the end of the reaction because of changes in the colloid. Instead, the ratio is calculated from a spectrum obtained after 2–3 half-lives by fitting the absorbance in the ranges 438–478 and 598–638 nm to a third-order polynomial (usually $R > 0.9999$, always $R > 0.999$), as an estimate of the smooth MnO_2 spectrum. The absorbance in these ranges is due almost entirely to MnO_2 , with essentially no contribution due to MnO_4^- .

The concentration of MnO_4^- at time t has been determined from eq 2 at a wavelength where MnO_4^- strongly absorbs ($\lambda_{\text{max}} = 526$ or 546 nm) and at a reference wavelength where the effective absorbance due to MnO_2 is strong ($\lambda = 450$ or 494 nm). Each λ_{max} was analyzed with respect to each reference wavelength, yielding four different $[\text{MnO}_4^-]_t$ data sets and four apparent rate constants for each kinetics experiment (526 vs 450; 546 vs 450; 526 vs 494; 546 vs 494). The rate constants reported in Table S1 (Supporting Information) are the average of the four derived values, and the errors are 3 σ of the distribution of the four values as a percentage of the average rate constant (all errors given in this paper are 3 σ errors).

First-order plots of $\ln [\text{MnO}_4^-]$ vs time are curved downward for all reactions (Figure S1), with the degree of curvature toward the end of the reaction (>2 half-lives) largely dependent on which spectrum is chosen to model for the calculation of the ratio Q . The initial slope of the first-order plots is independent of the later curvature, within experimental error, so only initial rate constants are reported. It is uncertain whether the curvature is real or simply an artifact of colloid changes and the data analysis procedure. Therefore it was deemed unreliable to analyze the curvature as due to the buildup of an intermediate organic species (e.g., PhCHO from PhCH₃).

For reactions of substrates in toluene or *o*-dichlorobenzene solvent, the observed rate constants were corrected to account for solvent oxidation, and second-order rate constants were calculated by dividing by the substrate concentration. For the *o*-dichlorobenzene reactions, either the rate of ${}^n\text{Bu}_4\text{NMnO}_4$ decomposition in the neat solvent was measured simultaneously with a substrate oxidation experiment or the solvent correction was derived from rates measured at 45, 55, and 75 °C. The rate of ${}^n\text{Bu}_4\text{NMnO}_4$ decay in *o*-dichlorobenzene is very

sensitive to the purity of the solvent, especially its water content and the extent of its exposure to light.²⁰

Product Analyses. Manganese Oxidation State Determination. Traditional iodometric titrations are unreliable here due to the interference of organic compounds with the starch indicator.²¹ Instead, a spectroscopic technique developed by Lee²² was adapted. At the end of a kinetics experiment, a 1.0 mL aliquot of the reaction solution was placed in a 10 mL volumetric flask with 0.019 g of ${}^n\text{Pr}_4\text{Ni}$ (${}^n\text{Pr} = \text{CH}_2\text{-CH}_2\text{CH}_3$). Glacial acetic acid (1 mL) was added, followed by enough CH_2Cl_2 to bring the total volume to 10.00 (± 0.02) mL. After thorough mixing, an aliquot of the solution was promptly transferred to a cuvette and the visible spectrum recorded. The concentration of I_3^- formed was calculated using $\epsilon_{365}(\text{I}_3^-) = 26\,200 \text{ M}^{-1} \text{ cm}^{-1}$.²¹

Organic Product Analyses. The colloidal MnO_2 was reduced by acidic aqueous sulfite or iodide, resulting in a two-phase system. Organic products in the aqueous layer were identified and quantified by HPLC, comparing with authentic samples and using calibration curves with potassium hydrogen phthalate (KHP) as an internal standard. HPLC analyses were performed on a Hitachi system consisting of an L-6200 pump, an L-4250 UV/vis detector, and a D-2500 integrator with a Beckman Ultrasphere ODS (25 cm/4.6 mm) reverse phase column. Analyses were performed under isocratic conditions with a mobile phase of 80% Millipore water, 20% acetonitrile, and 0.1% trifluoroacetic acid. The organic layer was analyzed by GC, and the organic products were identified and quantified by using authentic samples and one-point calibration using an internal standard, typically benzyl alcohol. GC analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph with a 30 m HP-5 fused silica capillary column and an FID detector interfaced to a personal computer running HP GC ChemStation software.

In a representative procedure, a 2–3 mL aliquot of a saturated solution of ${}^n\text{Bu}_4\text{NMnO}_4$ in toluene was transferred to a cuvette and the $[\text{MnO}_4^-]$ calculated from the absorbance at 526 nm.¹² A 20 mL aliquot was transferred to a greaseless Pyrex vessel with a Teflon needle valve, which was sealed and heated in a thermostated water bath at 57 °C for 5 h. After cooling to room temperature, 5 mL of a 0.02 M NaHSO_3 solution was added to reduce the colloidal MnO_2 to Mn^{2+} . The layers were shaken until colorless. Solid NaHCO_3 was added until the solution pH was ~ 9 , to convert benzoic acid to benzoate, which should partition into the aqueous layer.²³ A 1.2 mL portion of the aqueous layer was mixed with 0.2 mL of a 0.989 mM KHP solution and 40 μL of concentrated HCl, and the mixture was analyzed by HPLC. The organic layer was analyzed by GC. For reactions where carboxylic acids were not expected as products, reaction mixtures were prepared for product analysis by adding 3–4 drops of concentrated aqueous NaHSO_3 solution to reduce the MnO_2 . Benzyl alcohol was added as an internal standard, and the organic layer was separated. Analysis of the organic layer was by GC; the small aqueous layer was not analyzed.

Experiments in the Presence of O_2 . A saturated solution of ${}^n\text{Bu}_4\text{NMnO}_4$ in toluene was prepared, and equal amounts were placed into two reaction vessels, which were removed from the box and cooled to -78 °C. The headspace of one vessel was evacuated on the vacuum line and backfilled with O_2 . The reactions were monitored visually in a room temperature water bath by the disappearance of the permanganate purple color and appearance of the orange color of the colloid.

Results

${}^n\text{Bu}_4\text{NMnO}_4$ has sufficient solubility in toluene, approximately 0.3 mM, for analysis of the solutions by optical spectroscopy (Figure 1). The solubility is much higher in *o*-dichlorobenzene but substantially lower in ethylbenzene, generally making

- (20) The exposure of *o*-dichlorobenzene to fluorescent light results in the generation of a number of new organic species. Robinson, G. E.; Vernon, J. M. *J. Chem. Soc. D* **1969**, 977–980. Fox, M.-A.; Nichols, W. C., Jr.; Lemal, D. M. *J. Am. Chem. Soc.* **1973**, 95, 8164–8166.
- (21) Harris, D. C. *Quantitative Chemical Analysis*; Freeman: New York, 1982; p 383.
- (22) Lee, D. G.; Perez-Benito, J. F. *J. Org. Chem.* **1988**, 53, 5725–5728.
- (23) The pK_a of benzoic acid is 4.2,²⁴ so at pH 9 essentially only benzoate is present.
- (24) *CRC Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1982; p D-142.

Table 1. Rates and Activation Parameters for $n\text{Bu}_4\text{NMnO}_4$ Reactions

substrate	exptl values ^a		values for the H [•] transfer step ^b					BDE(C–H) (kcal/mol) ^d
	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (eu)	k (M ⁻¹ s ⁻¹) ^c (298 K)	ΔG^\ddagger (kcal/mol)	ΔS^\ddagger (eu)	E_a (kcal/mol)	$\log A$	
PhCH ₃	21.0 (±1.0)	-16 (±3)	1.4×10^{-7}	26 (±1)	-20 (±3)	11.2 (±0.7)	24.6 (±0.9)	88.5 ^e
PhCH ₂ CH ₃	20.8 (±0.6)	-17 (±3)	3.3×10^{-6}	25 (±1)	-19 (±3)	13.1 (±0.7)	25.4 (±0.9)	84.7 ^f
Ph ₂ CH ₂	17.1 (±0.5)	-19 (±3)	6.5×10^{-5}	23 (±1)	-21 (±3)	11.2 (±0.9)	21.1 (±1.2)	82 ^g
Ph ₃ CH	16.5 (±0.8)	-16 (±5)	2.7×10^{-3}	21 (±2)	-15 (±5)	12.0 (±0.7)	19.9 (±0.9)	81 ^g
DHA ^h	13.8 (±1.0)	-15 (±7)	1.2×10^{-1}	19 (±2)	-17 (±7)	11.5 (±0.9)	16.9 (±1.2)	78 ^{d,g}
xanthene	11.7 (±1.2)	-18 (±8)	5.6×10^{-1}	18 (±3)	-20 (±8)	10.4 (±1.1)	14.5 (±1.4)	75.5 ^g

^a Derived from an Eyring plot of experimental k_2 values. ^b Values are at 298 K, corrected per reactive hydrogen of the substrate and adjusted for the idealized reaction stoichiometry (see text and footnote 39). The adjustment does not affect the ΔH^\ddagger values. ^c Extrapolated from best fit straight line of Eyring plot and adjusted (see note b). ^d Footnote 73. ^e Reference 74a. ^f Reference 74b. ^g Reference 61a. ^h DHA is 9,10-dihydroanthracene.

reactions in this solvent impractical. Neither *o*-dichlorobenzene nor toluene is an ideal solvent for these reactions, as both are reactive with permanganate, but in our hands alternative solvents were either more reactive (CH₂Cl₂, CH₃CN, pyridine) or showed insufficient solubility (benzene).²⁵ The reactions were found to be sensitive to trace impurities in solvents and substrates, so materials were rigorously purified and a drybox was established with no extraneous reductants.

The manganese product of all of these reactions is colloidal MnO₂, as indicated by its characteristic optical spectrum.²⁶ In the toluene and ethylbenzene reactions, the average manganese oxidation states of the products were determined to be 4.05 (±0.08) and 3.96 (±0.08) by a spectroscopic iodometric technique (see Experimental Section). Under most of the reaction conditions, the colloid is fairly well-behaved optically, obeying Beer's law closely enough to show isosbestic points (as has been observed in related studies^{22,27}). Quantification of the organic products is difficult because the low solubility of $n\text{Bu}_4\text{NMnO}_4$ means that very little of the products are formed, usually 1 μmol or less, in concentrations ≤ 10⁻⁴ M. The organic products are typically bound in and/or on the colloidal particles of MnO₂,²⁸ so analysis requires destruction of the MnO₂(s) by reduction to Mn²⁺ with an acidic aqueous bisulfite or iodide solution. The products then partition between the aqueous and organic phases, which are analyzed by HPLC and GC, respectively (see Experimental Section).

1. Oxidation of Toluene. $n\text{Bu}_4\text{NMnO}_4$ decays in toluene over 1 week at 25 °C. Analysis of the optical data required modeling of the MnO₂ absorbance (see Experimental Section). None of the kinetic runs showed an induction period. The first-order plots are all slightly curved downward, corresponding to as much as a doubling of the observed rate constant over the course of the reaction. Initial rates are therefore used. The rate constants (Table S1, Supporting Information) are reproducible to ca. ±10%, which is somewhat larger than the error associated with the data analysis from one kinetic experiment. At 45 °C, the same initial rate constant was obtained from experiments with more than a factor of 2 difference in initial $n\text{Bu}_4\text{NMnO}_4$ concentration, showing the first-order dependence. The dependence on toluene concentration could not be examined

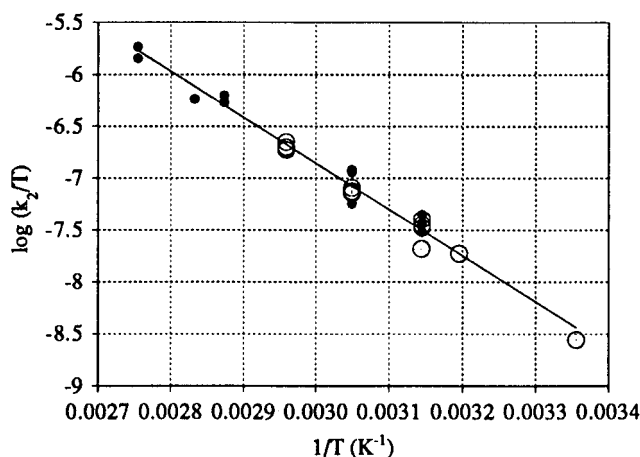


Figure 2. Combined Eyring plot, $\log(k_2/T)$ vs $1/T$, for reaction of $n\text{-Bu}_4\text{NMnO}_4$ with toluene, both in neat toluene (open circles) and in *o*-dichlorobenzene (filled circles), over the temperature range 25–90 °C.

in toluene solvent, but is assumed to be first order by analogy to toluene oxidation in *o*-dichlorobenzene and to the oxidations of other hydrocarbons (see below). Second-order rate constants from 25 to 65 °C give the activation parameters in Table 1, via an Eyring plot (Figure 2). Oxidation of *d*₈-toluene is significantly slower: $k_{C_7H_8}/k_{C_7D_8} = 6 (\pm 1)$ at 45 °C.²⁹

As a test for the intermediacy of radicals, a reaction was run in the presence of oxygen gas; all other reactions were performed with careful exclusion of air. More common radical traps such as CBrCl₃ are problematic in this system as the expected products (*i.e.*, benzyl bromide) are subject to further oxidation by permanganate and/or are reactive with the aqueous acidic workup (PhCH₂Br → PhCH₂OH). Reductive traps, such as $n\text{-Bu}_3\text{SnH}$, are not compatible with permanganate. Oxygen is known to react with radicals at near the diffusion limit,³⁰ as does permanganate.³¹ O₂ should compete with MnO₄⁻ in reacting with any radicals present, as the concentration of dissolved oxygen in toluene under 1 atm pressure of O₂ at 20 °C is 5.7 mM,³² more than an order of magnitude larger than the permanganate concentration. If organic radicals are intermediates, the presence of O₂ should have an effect on the

(25) Previous studies suggest that $n\text{Bu}_4\text{NMnO}_4$ is not reactive with pyridine;^{16a} however, under our conditions, it seems to react at approximately the same rate as toluene. Benzene was deemed unacceptable as a solvent because, when a saturated solution of $n\text{Bu}_4\text{NMnO}_4$ in benzene was passed through a frit, the salt began crystallizing out of solution.

(26) Perez-Benito, J. F.; Arias, C. *J. Colloid Interface Sci.* **1992**, *152*, 70–84.

(27) (a) Lee, D. G.; Brown, K. C. *J. Am. Chem. Soc.* **1982**, *104*, 5076–5081. (b) Freeman, F.; Kappos, J. C. *J. Org. Chem.* **1989**, *54*, 2730–2734.

(28) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 943.

(29) The value given here for the kinetic isotope effect, $k_H/k_D = 6$, is larger than previously reported by us, $k_H/k_D = 2.5$.⁶ Presumably the earlier value was too low as a result of impurities in the atmosphere of the glovebox or in the *d*₈-toluene used which caused the deuterio reaction to proceed too rapidly.

(30) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095.

(31) Steenken, S.; Neta, P. *J. Am. Chem. Soc.* **1982**, *104*, 1244–1248.

(32) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds, Volume I Binary Systems, Part 1*; Macmillan: New York, 1963; p 573.

kinetics, although it is unclear whether the presence of O₂ should accelerate or decelerate the disappearance of MnO₄⁻. Visually monitored, the reaction containing oxygen showed complete loss of permanganate in 1 day compared to almost 1 week for an identical reaction under nitrogen.

Toluene oxidation forms benzoic acid and a trace of benzaldehyde, as determined by HPLC analysis of the aqueous layer resulting from MnO₂ reduction. No organic products were observed in the toluene layer by GC, but any benzaldehyde present would have been below our detection limit of 0.23 mM, corresponding to a benzaldehyde yield of 87%, based on MnO₄⁻ to MnO₂. (For ease of interpretation, detection limits are reported below in terms of the minimum detectable yield.) Benzyl alcohol was not detected above our sensitivity of 20% yield. The benzoic acid and benzaldehyde observed account for 62% of the permanganate oxidizing equivalents consumed. Some of the "missing" oxidative equivalents are likely in undetected PhCHO and/or PhCH₂OH. A small amount of complete oxidation of toluene (or an impurity) to CO₂ and H₂O could also consume a large number of permanganate oxidative equivalents (as observed in other systems^{9,14}). It is also possible that there is some oxidation of the ⁿBu₄N⁺ counterion. ⁿBu₄NMnO₄ is tightly ion paired in toluene,³³ giving a high local concentration of butyl C–H bonds. The reaction of ⁿBu₄NMnO₄ in benzene with benzyltributylammonium bromide (ⁿBu₃NCH₂Ph⁺Br⁻) gives large amounts of benzoic acid, showing that counterion oxidation can be a facile process. Attempts to use PPN⁺MnO₄⁻³⁴ were prevented by its lack of solubility in toluene.

The oxidation of toluene by ⁿBu₄NMnO₄ in *o*-dichlorobenzene, 10–35% toluene by volume, also gives MnO₂ and benzoic acid as the predominant products.³⁵ The presence of O₂ results in a slight increase in the apparent rate of permanganate disappearance, under conditions where [O₂] ≅ [ⁿBu₄NMnO₄].³⁶ Addition of 24 equiv of ⁿBu₄NBr to a reaction mixture of ⁿBu₄NMnO₄ (0.24 mM) and toluene in *o*-dichlorobenzene caused an increase of 12% in the observed rate constant, within the experimental error. This suggests that ion-pairing effects are not dominant and that counterion oxidation is not a major factor. First-order plots are again curved downward, roughly a 30% increase in the apparent rate constant after 2 half-lives. The pseudo-first-order initial rate constants are corrected for solvent oxidation (typically about 10%; see Experimental Section). The reproducibility of the initial rate constants is not very good (±50%). The second-order rate constants, derived by dividing the corrected *k*_{obs} by the toluene concentration, are the same as those obtained in neat toluene, within the large error bars. This is best illustrated by the combined Eyring plot (Figure 2).

The rate constants for oxidation of substituted toluenes in *o*-dichlorobenzene at 55 °C are as follows: toluene, 2.5 × 10⁻⁵; *p*-xylene, 4.2 × 10⁻⁵; *p*-chlorotoluene, 2.0 × 10⁻⁴; 4-methylbenzophenone, 2.4 × 10⁻⁴ (with statistical adjustment for the number of methyl groups in *p*-xylene; estimated errors ±50%; Table S1). The range of substituents is limited by the high reactivity of permanganate; for instance, *p*-nitrotoluene was found to react autocatalytically with ⁿBu₄NMnO₄ in *o*-dichlorobenzene. Increases in rate constants are observed for both electron-donating and electron-withdrawing substituents, so there

is no correlation with either Hammett σ or σ^+ values.³⁷ The relative rates do vary monotonically with σ^+ values, although the correlation is poor.³⁸

2. Ethylbenzene, *tert*-Butylbenzene, Diphenylmethane, Triphenylmethane, 9,10-Dihydroanthracene, Xanthene, and Fluorene. These substrates (except *tert*-butylbenzene) are more reactive than toluene, so kinetic experiments were performed in toluene solvent under pseudo-first-order conditions. First-order plots, as in the reaction of pseudo-toluene, are curved downward. Initial rates are calculated in all cases, and reproducibility of <±25% is observed. None of the first-order plots show an induction period, although an initial fast reaction was observed (~5% of the reaction for all substrates except diphenylmethane) and was omitted from the data analysis. This is likely due to oxidation of an impurity. The initial rate constants all show a first-order dependence on both substrate and permanganate concentrations.

The bimolecular rate constants (Table S2) increase in the order PhCMe₃ < PhCH₃ < PhCH₂CH₃ < Ph₂CH₂ < Ph₃CH < fluorene < dihydroanthracene < xanthene. Fluorene can only be placed tentatively on this list because kinetic experiments showed poor reproducibility, with *k* ≅ 6 × 10⁻² M⁻¹ s⁻¹ at 25 °C. Dihydroanthracene reacts 3.0 (±0.6) times faster than its *d*₁₂ isotopomer at 25 °C. Dihydroanthracene and fluorene also show some unusual features in the later stages of their oxidation (see below). Most of the reactions were examined over a 30–40 °C temperature range to derive activation parameters (Table 1). In order for the rate constants and entropies of activation to be comparable, the values in Table 1 have been divided by the number of reactive hydrogen atoms in each substrate and adjusted for the idealized stoichiometry of the reactions. In toluene oxidation, for example, there are three reactive hydrogens and the idealized stoichiometry is that 2 equiv of MnO₄⁻ are consumed for every toluene molecule that is activated (assuming 100% yield of benzoic acid).³⁹ The values in Table 1 therefore correspond fairly closely to the activation parameters for the hydrogen atom abstraction step.

The organic products from ethylbenzene oxidation were determined from a reaction in neat ethylbenzene to avoid toluene oxidation products.⁴⁰ The aqueous layer contained acetophenone, accounting for approximately 30% of the permanganate oxidizing equivalents. Within the detection limits, benzoic acid (<5% yield) and *sec*-phenethylalcohol (< 10%) were absent in the aqueous layer. The remaining oxidizing equivalents were likely in the form of acetophenone left in the organic layer (undetectable with our GC protocol, <4 μM, <107% yield), as acetophenone has little water solubility. Xanthene is oxidized to xanthone in ~80% yield; no other organic products are observed by GC. Diphenylmethane forms benzophenone in 44% yield. These yields were determined by GC of the organic layer after destruction of the MnO₂ colloid; any products that partitioned into the aqueous layer were not observed. The expected product from Ph₃CH oxidation, Ph₃COH, is unstable under the conditions of the acid workup. GC analysis of the

(33) Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 4024–4025.

(34) Martinsen, A.; Songstad, J. *Acta Chem. Scand. A* **1977**, *31*, 645–650. PPN⁺ = Ph₃PNPh₃⁺.

(35) The presence or absence of benzyl alcohol could not be determined in the presence of a huge excess of *o*-dichlorobenzene.

(36) No data are available for the solubility of O₂ in *o*-dichlorobenzene, but the concentration of O₂ in chlorobenzene at 20 °C under 1 atm of O₂ is 8.3 mM.³² The solubility of O₂ in toluene at 20 °C under 1 atm of O₂ is 5.7 mM.³²

(37) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; pp 439–540.

(38) σ^+ values from Wayner and Arnold: Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2378.

(39) The correction for reaction stoichiometry is necessary but is not very accurate because products are not quantitatively formed (~60% yield of benzoic acid from toluene). If the remainder of the MnO₄⁻ is consumed in production of benzyl alcohol or benzaldehyde, then the idealized correction is too big, but if it is consumed in overoxidation of benzoic acid or counterion oxidation, then the correction is too large. The correction does not influence the ΔH^\ddagger values in Table 1, as long as it is constant over the temperature range studied.⁵

(40) Ethylbenzene and toluene are both reported to give benzoic acid: ref 4, p 1072.

reaction solution without destruction of the colloid showed a 9% yield of Ph_3COH ; when the MnO_2 was reduced with a slightly acidic solution (pH 5), the observed yield increased to 19%. Dihydroanthracene gives anthracene as the only apparent organic reaction product (by GC and ^1H NMR), in approximately 65% yield based on the anthracene absorbance at 380 nm.⁴¹

The disappearance of $^n\text{Bu}_4\text{NMnO}_4$ was slower in a 1:2 *tert*-butylbenzene/*o*-dichlorobenzene mixture (v/v) as compared with pure *o*-dichlorobenzene at 75 °C. The $^n\text{Bu}_4\text{NMnO}_4$ appears to react primarily with the *o*-dichlorobenzene, as the same second-order rate constant for *o*-dichlorobenzene oxidation is derived in the two cases (within the sizable error bars). The rate constant for *tert*-butylbenzene oxidation is thus estimated as $\leq 3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, at least 2 orders of magnitude less than the rate constant for toluene oxidation. This is consistent with the correlations below, which predict an extremely slow reaction based on a *tert*-butylbenzene C–H bond strength of $\geq 100 \text{ kcal/mol}$.⁴³ Despite repeated efforts, reactions of cumene with $^n\text{Bu}_4\text{NMnO}_4$ in toluene and *o*-dichlorobenzene gave irreproducible kinetic results. The reason for this erratic behavior is unclear. Some of the reactions were slower than expected from the toluene and ethylbenzene results, which suggests that the problems were not solely the result of oxidation of an impurity.

3. Charge-Transfer Complexes. The reaction of excess dihydroanthracene (2.5 mM) with $^n\text{Bu}_4\text{NMnO}_4$ in toluene at 25 °C proceeds initially as described above, with a roughly first order decay until all of the MnO_4^- is converted to MnO_2 (ca. 2000 s at 25 °C). At that point, a second, faster reaction occurs, with disappearance of the MnO_2 absorption and the formation of a new species within ~ 200 s (Figure 3a,b). The new species has a strong absorbance in the visible region with maxima at 524 and 560 nm, whose extinction coefficients are comparable to those of permanganate. There is a vibrational progression between 300 and 400 nm which partially overlaps the vibrational progression of anthracene, but is shifted to longer wavelength. The 1100 cm^{-1} spacing of the bands in the progression is lower in energy than the spacing of 1400 cm^{-1} in free anthracene. Removal of the solvent gives a pale pink residue, unexpected considering the intense purple color of the solution. The purple color is also rapidly bleached on exposure to air or light. Similar behavior is observed in acetonitrile solvent, but the new product absorbances are blue-shifted by 30 nm, with maxima at 494 and 530 nm.

The reaction of fluorene with $^n\text{Bu}_4\text{NMnO}_4$ in toluene similarly forms an air-sensitive, intensely colored product (λ_{max} 454, 374 nm). In this case the reaction is quite variable, and the permanganate does not need to be consumed prior to formation of the new product. Some of the time the fluorene oxidation resembles a clock reaction, proceeding smoothly until a point at which there is rapid consumption of MnO_4^- and formation of the new species. In other cases, with identical batches of $^n\text{Bu}_4\text{NMnO}_4$, fluorene, and vacuum-transferred toluene, the dark species forms immediately or never forms.

The characteristics of the new products are suggestive of charge-transfer (CT) complexes: the high extinction coefficients, sensitivity to light, and difficulty in isolation.⁴⁴ While formation of CT complexes is without precedent in permanganate chem-

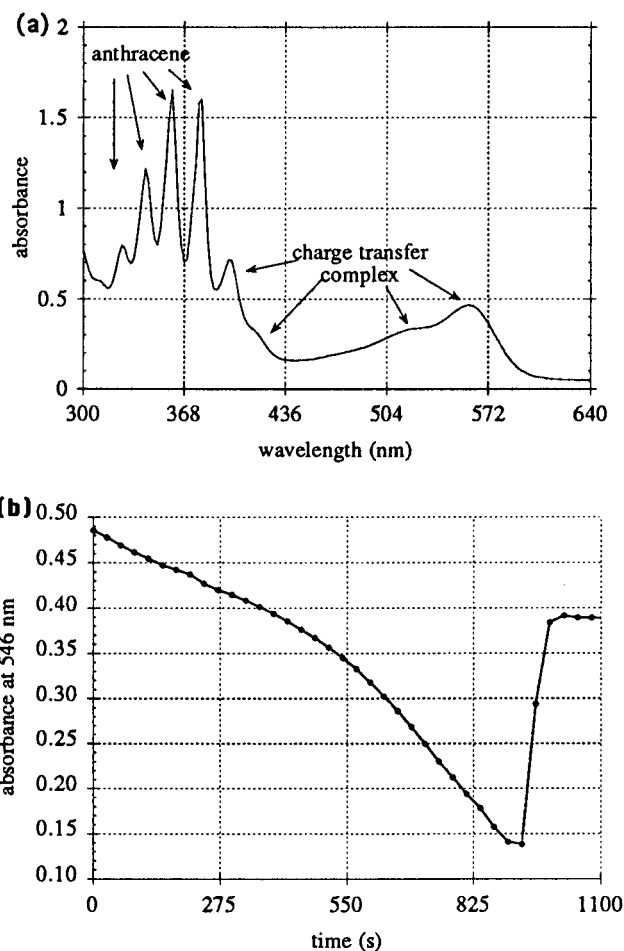


Figure 3. (a) Final UV/vis spectrum from the reaction of $^n\text{Bu}_4\text{NMnO}_4$ with 9,10-dihydroanthracene in toluene at 25 °C, showing the charge-transfer absorbance. (b) Plot of absorbance at 546 nm vs time, showing the rapid formation of the charge-transfer complex.

Table 2. Comparison of Charge-Transfer Complexes of “ MO_x ” Species with Arenes

arene	IP (eV) ^c	λ_{max} (nm) in different solvents			
		complexes with OsO_4^a $^n\text{C}_6\text{H}_{14}$	CH_2Cl_2	complexes with “ MnO_x ” ^b toluene	CH_3CN
mesitylene	8.39	390			
fluorene	8.63			454/374	
anthracene	7.23	520	510	560/524	530/494

^a Reference 44a. ^b This work. ^c Reference 47b.

istry, CT complexes are observed with aromatic hydrocarbons and CrO_2Cl_2 ⁴⁵ or OsO_4 .^{44a} The 30 nm blue shift between toluene and acetonitrile for the complex derived from $^n\text{Bu}_4\text{NMnO}_4$ and dihydroanthracene is similar to the shifts observed for anthracene– OsO_4 complexes in polar vs nonpolar solvents (Table 2).^{44a} The energy of the optical transition is related to the ionization potential of the aromatic donor (Table 2), as is typical of CT absorbances.⁴⁴ The observed vibrational progression between 300 and 400 nm is most likely due to an anthracene ring-breathing mode, and its lower frequency vs free anthracene is seen in other anthracene CT complexes.^{44c} The final optical spectra indicate a yield of 1 mol of free anthracene per mole of permanganate consumed, suggesting the reaction stoichiometry

(41) Anthracene has a vibrational progression between 300 and 400 nm. The most intense band at 380 nm ($\epsilon = 8500 \text{ M}^{-1} \text{ cm}^{-1}$)⁴² was used to calculate the amount of anthracene in the solution.

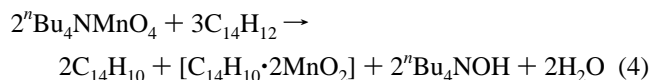
(42) *UV Atlas of Organic Compounds*; Butterworths: London, 1966; Vol. 2, p E2/T1.

(43) The C–H bond strength in *tert*-butylbenzene is not known, but is likely to be at least as high as in ethane (101.1 kcal/mol^{74a}), as the value for neopentane is higher than that for ethane: Holmes, J. L.; Lossing, F. P.; Maccoll, A. *J. Am. Chem. Soc.* **1988**, *110*, 7339–7342.

(44) (a) Wallis, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 8207–8223. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969. (c) Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: New York, 1969.

(45) Reference 5c and references therein.

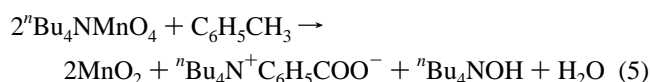
of eq 4 (dihydroanthracene = C₁₄H₁₂; anthracene = C₁₄H₁₀). The water and hydroxide formed are likely associated with the manganese product.



Efforts to generate the apparent CT complex by other routes have not been successful. Attempts include reactions of colloidal MnO₂ (from ⁿBu₄NMnO₄ + toluene) with anthracene, dihydroanthracene, or both, and the addition of anthracene to a ⁿBu₄NMnO₄/toluene reaction. These negative results may indicate that the CT complex is formed at the colloid surface, consistent with the variability of the rate of the fast reaction and with the loss of the MnO₂ absorbance in the 400–600 nm region on complex formation. The MnO₂ spectrum is due to absorbance of light by the surface and can be strongly affected by reactions there.²⁶ Such a reaction could be surface complex formation or reduction of the MnO₂ by additional dihydroanthracene.

Discussion

1. Overview of the Reactions. Permanganate is a versatile multielectron oxidant, able to oxidize a variety of substrates in one- or two-electron steps.⁷ In the reactions studied here, manganese undergoes a three-electron change from Mn(VII) to Mn(IV) and the substrates are oxidized by two, four, or six electrons. For instance, toluene to benzoic acid is a six-electron oxidation. The idealized stoichiometry is given in eq 5, with the products largely associated with the colloidal MnO₂. The observed benzoic acid yield is 60% of that predicted by eq 5. The reactions closely follow the second-order rate law of eq 6 over the first half-life, as indicated by the dependence of the pseudo-first-order *k*_{obs} on substrate concentrations and the independence of *k*_{obs} on the starting ⁿBu₄NMnO₄ concentration. No induction periods are observed for any of the substrates.



$$d[\text{MnO}_4^-]/dt = -k_2[{}^n\text{Bu}_4\text{NMnO}_4][\text{substrate}] \quad (6)$$

2. The Rate-Determining Step. The rate expression (eq 6) and the primary isotope effects imply that the rate-determining step of these reactions is bimolecular attack of permanganate on a substrate C–H bond. There is no support for the suggestion that other manganese species are involved in the initial hydrocarbon activation. Similar conclusions were reached by Brauman and Pandell in their study of the oxidation of γ -phenylvaleric acid in aqueous base and by Wiberg and Fox in their studies of *p*-sec-butylbenzoic acid and 4-methylhexanoic acid in neutral and basic aqueous solutions.⁹

Outer-sphere electron transfer from arene to permanganate (eq 7) cannot be the initial step in these reactions, as has been discussed in the context of OsO₄^{44a} and cytochrome P-450 oxidations.⁴⁶ First, this path is not consistent with the isotope effects or substituent effects. For instance, *p*-xylene reacts only about 3 times as fast as toluene despite being 0.42 V easier to

oxidize⁴⁷ (0.42 V corresponds to a difference of 10⁷ in *K*_{eq}). It should be more difficult to form the radical cation of 4-methylbenzophenone than to form that of toluene, yet this substrate is oxidized faster than toluene. Second, outer-sphere electron transfer is a difficult process in nonpolar media such as toluene because of the difficulty in stabilizing the charged species which result. Permanganate has a less positive redox potential in toluene than in water (*E*^o = +0.56 V vs NHE in H₂O⁴⁸), and formation of the toluene radical cation would be less favorable in toluene solvent than in acetonitrile (*E*^o > +2.5 V vs NHE^{47b}). Therefore, on the basis of the aqueous and MeCN potentials, outer-sphere electron transfer is at least 1.9 V or 44 kcal/mol uphill in toluene. Since this is larger than the observed ΔG^\ddagger of 26 kcal/mol, eq 7 cannot be either the rate-limiting step or a pre-equilibrium step. Put another way, the equilibrium constant for electron transfer is <10⁻³², which implies, on the basis of the forward rate constant of 10⁻⁶ M⁻¹ s⁻¹, that the reverse reaction (back electron transfer) would have to proceed at the impossible bimolecular rate of 10²⁶ M⁻¹ s⁻¹.



Rate-limiting C–H bond cleavage could occur by proton, hydrogen atom, or hydride transfer to a permanganate oxo group or by [2 + 2] addition across a Mn–O bond. Proton transfer can be immediately dismissed given the very low acidity of toluene and the low basicity of permanganate. [2 + 2] addition to metal oxo bonds has been suggested on the basis of *ab initio* calculations of CrO₂Cl₂ reactions¹¹ and experimental studies of manganate reactions.¹⁰ The analogous addition across a metal–imido linkage is well preceded for early transition metal systems.⁴⁹ In this case, however, the implied formation of the five-coordinate intermediate [Mn(R)(O)₃OH⁻] is very unlikely. There is little precedent for such an expansion of coordination number in the chemistry of permanganate so this mechanism would predict a sizable steric effect, with particular difficulty in forming a tertiary alkyl complex. (For this reason, the imido complexes do not activate tertiary C–H bonds.⁴⁹) As shown below, no such effect is observed. Similarly, the entropies of activation reported here ($\Delta S^\ddagger = -16$ eu for toluene oxidation) are not as negative as expected for a constrained [2 + 2] transition state.¹⁰

Hydride transfer from organic substrates to permanganate is well preceded, most clearly in the oxidation of alcohols,^{50,51} and has been proposed for the oxidation of toluene by MnO₄⁻ in water⁶ (and for the oxidation of hydrocarbons by (trpy)(bpy)-RuO₂²⁺⁵²). Abstraction of H⁻ from toluene would form HMnO₄²⁻ and benzyl cation (eq 8), an unlikely process given the observed substituent effects. *p*-Xylene is only 3 times more reactive than toluene while it should be much more reactive. *p*-Chlorotoluene and 4-methylbenzophenone react faster than toluene but should react much more slowly. In addition, the

(46) See, for instance: Traylor, T. G.; Nakano, T.; Miksztal, A. R.; Dunlap, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 3625. Ostrovic, D.; Bruice, T. C. *Acc. Chem. Res.* **1992**, *25*, 314–320. Kim, T.; Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 7653. Gross, Z.; Nimri, S. *J. Am. Chem. Soc.* **1995**, *117*, 8021.

(47) (a) *E*^o_{ox} = 1.54 V for *p*-xylene vs 1.96 V for toluene (potentials in MeCN, vs Ag⁺/AgNO₃:^{47a}) (b) Kochi, J. K. In ref 7f, pp 849–855. (c) The conversion of Ag/AgNO₃ (MeCN) to aqueous NHE is roughly +0.5 V (Sawyer, D. T.; Sobkowiak, A.; Robers, J. L., Jr. *Electrochemistry for Chemists*, 2nd ed.; Wiley: New York, 1995; pp 201, p 192).

(48) Latimer, W. M. *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, 2nd ed.; Prentice Hall: New York, 1952.

(49) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591–611 and references therein.

(50) Stewart, R. J. *J. Am. Chem. Soc.* **1957**, *79*, 3057–3061. See also ref 7.

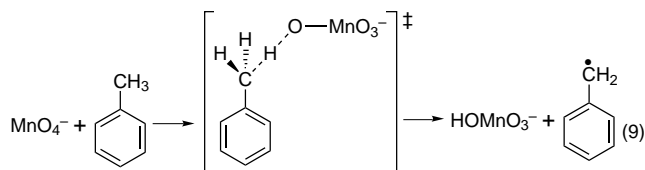
(51) Haight, G. P. Unpublished results (personal communication, 1996).

(52) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5070–5076.

formation of higher-charged species such as benzyl cation is unfavorable in such a nonpolar solution.



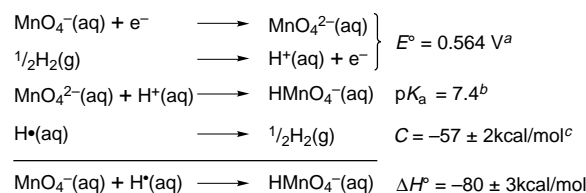
Rate-limiting hydrogen atom transfer from the substrate (eq 9) to a permanganate oxo group is consistent with all of the experimental evidence. This is probably the most commonly proposed mechanism for permanganate oxidations of C–H bonds.^{7–10,14} The lack of a solvent effect is characteristic of



radical reactions⁵³ and is not consistent with polar transition states or products. The observed influence of added O₂ is an indicator of radical intermediates (see above). Hydrogen atom abstraction reactions exhibit small substituent effects and often do not show a correlation with Hammett σ or σ^+ values.⁵⁴ Previous studies of permanganate oxidations of toluene in aqueous acetic acid, which proceed much faster than the reactions described here and therefore likely involve a different mechanism (involving “MnO₃⁺⁺”), have reported Hammett ρ values of -1.57^c and $-2.8.^{55}$ A more valuable comparison is with hydrogen atom abstraction by ‘BuOO•’, where the relative rates are (after the statistical adjustment for the number of methyl groups in *p*-xylene) as follows: *p*-xylene, 1.8; toluene, 1; *p*-chlorotoluene, 1; 4-methylacetophenone, 0.3.⁵⁶ The analogous values for ⁵⁴Bu₄NMnO₄ are 1.7:1:8:10 (the last for 4-methylbenzophenone). Permanganate is a slower and more selective hydrogen atom abstractor than ‘BuOO•’ (see below), so larger substituent effects are observed. The permanganate rates are monotonic with σ^* values,³⁸ although the correlation is poor. The primary isotope effects are consistent with this mechanism, although the measured $k_{\text{H}}/k_{\text{D}}$ values are not the same as the isotope effects for the H• transfer step. The slower activation of the deuterated substrates means that more permanganate is likely consumed in side reactions, implying that the measured $k_{\text{H}}/k_{\text{D}}$ underestimates the isotope effect of the rate-limiting step. Secondary isotope effects may also be significant.

3. Understanding the Rate Constants: Bond Strengths and Enthalpy Correlations. We have proposed that permanganate and related oxidants can abstract hydrogen atoms (H•) from organic substrates because of the strong bond they form on addition of H•.^{5,6} The data reported here provide strong support for this hypothesis. Our perspective based on enthalpy changes contrasts with the standard chemical intuition that a reagent needs to be a radical in order to perform hydrogen atom abstraction. This intuition may be reflected in many proposed mechanisms for hydrocarbon oxidation, from metalloenzymes to industrial heterogeneous catalysts.⁵⁷ Permanganate does not fit this intuition because it is a closed-shell species, whose lowest lying triplet state lies roughly 18 000 cm⁻¹ (51 kcal/mol) above

Scheme 1. Calculation of the O–H Bond Strength in [O₃MnO–H]–



^a Footnote 48. ^b Footnote 62. ^c $C = \Delta H^\circ\{\text{H}^+(\text{g}) \rightarrow \frac{1}{2}\text{H}_2(\text{g})\} - \Delta H^\circ\{\text{H}^+(\text{g}) \rightarrow \text{H}^+(\text{aq})\} - \frac{1}{2}TS^\circ\{\text{H}_2(\text{g})\}.$ ⁶⁵

the ground state.⁵⁸ Since this energy is much larger than the observed energies of activation, a triplet state cannot be an intermediate in the reactions. It should be noted that it is spin-allowed for two diamagnetic species to react and form a singlet radical pair, as in eq 9. Examples of H• transfer between closed-shell organic molecules have been described by Rüchardt and others.⁵⁹

The affinity of MnO₄⁻ for H• is equivalent to its affinity for an electron (its redox potential, E°) and a proton (the acid dissociation constant, K_a of HMnO₄⁻), following the thermochemical cycle in Scheme 1 [$\text{BDE}(\text{H}-\text{OMnO}_3^-) = 23.06E^\circ + 1.37 pK_a + C$].⁶⁰ Such cycles have been used by Bordwell and others to determine bond strengths to hydrogen in many organic and organometallic compounds.⁶¹ Scheme 1 is slightly different from what we have used previously,^{5,6} in part because a recent pulse radiolysis study provides a new value for the pK_a of HMnO₄⁻.^{62,63} The constant C is calculated as 57 ± 2 kcal/mol.⁶⁴ With the common assumption that the entropies of MnO₄⁻ and HMnO₄⁻ are equal,⁶¹ a value of 80 ± 3 kcal/mol

(57) See, for instance, refs 1 and 3 and the following: (a) Stubbe, J.; Kozarich, J. W. *Chem. Rev.* **1987**, *87*, 1107–1136. (b) Hecht, S. M. *Acc. Chem. Res.* **1986**, *19*, 383–391. (c) Stewart, L. C.; Klinman, J. P. *Annu. Rev. Biochem.* **1988**, *57*, 551–592. (d) Tian, G.; Berry, J. A.; Klinman, J. P. *Biochemistry* **1994**, *33*, 226–234. (e) Lin, C. H.; Ito, T.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4808 and references therein.

(58) Blasse, G. *Struct. Bonding (Berlin)* **1980**, *42*, 1–42, especially p 11.

(59) (a) Rüchardt, C.; Gerst, M.; Nölke, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1523–1525. Gerst, M.; Morgenthaler, J.; Rüchardt, C. *Chem. Ber.* **1994**, *127*, 691–696 and references therein. Reference 74c. (b) For earlier discussions of the formation of organic radicals from diamagnetic precursors, see: Pryor, W. A. in *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symposium Series 69; Washington, DC, 1978; pp 33–62; Harmony, J. A. K. *Methods Free-Radical Chem.* **1974**, *5*, 101–176.

(60) (a) A reviewer and other authors^{60b,61c} have pointed out complications in this approach (see also footnote⁶⁴). We use Scheme 1 to calculate the *solution phase* bond strength, so that the $\Delta H_{\text{sol}}^\circ$ of MnO₄⁻ and HMnO₄⁻ are not needed. We assume that $S(\text{MnO}_4^-\text{aq}) = S(\text{HMnO}_4^-\text{aq})$ and that the aqueous $D(\text{H}-\text{OMnO}_3)$ can be used to understand reactions in toluene solvent in the Polanyi correlations (Figure 5, which also assumes that gas phase RO–H values can be used in the condensed phase). (b) Wayne, D. D. M.; Luszyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737–8744.

(61) For leading references, see: (a) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790–9795. (b) Bordwell, F. G.; Liu, W.-Z. *J. Am. Chem. Soc.* **1996**, *118*, 8777–8781. (c) Parker, V. D. *J. Am. Chem. Soc.* **1992**, *114*, 7458–7462; correction, **1993**, *115*, 1201. (d) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6717; correction, **1990**, *112*, 2843. (e) Reference 60b.

(62) (a) $pK_a(\text{HMnO}_4^-) = 7.4$: Rush, J. D.; Bielski, B. H. *Inorg. Chem.* **1995**, *34*, 5832–5838. (b) The previously accepted value of 10.5 was taken from the following: Lister, M. W.; Yoshino, Y. *Can. J. Chem.* **1960**, *38*, 2342–2348. Heckner, K.-H.; Landsberg, R. *J. Inorg. Nucl. Chem.* **1967**, *19*, 423–430.

(63) There is also an error in the calculation of ΔG° for H• + MnO₄⁻ in the scheme reported in ref 5b (in addition to the use of the older pK_a value⁶²). This scheme used an incorrect reference state for $\Delta G_{\text{sol}}^\circ(\text{H}_2)$, unit mole fraction instead of 1 M. We thank Professors John Brauman (Stanford) and Neil Bartlett (Berkeley) for bringing this to our attention (personal communications, January 1995).

(53) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Luszyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466–470.

(54) Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972; p 20. See also refs 37, 38, and 71.

(55) Radhakrishnamurti, P. S.; Mahapatro, S. N. *Indian J. Chem.* **1975**, *13*, 1294–1296.

(56) Howard, J. A.; Chenier, J. H. B. *J. Am. Chem. Soc.* **1973**, *95*, 3054–3055.

for the H–OMnO₃[−] bond strength is obtained. Alternatively, the constant is not needed if relative bond strengths are calculated from a thermodynamic cycle where H• is transferred from another species, HA, as in eq 10 (HA = PhOH or PhNH₂). The standard free energy ΔG° is calculated (eq 11) from the known E° and K_a values⁶⁷ and is taken to be equal to ΔH° because ΔS° ≈ 0. The derived ΔH° is the difference between the H–OMnO₃[−] and H–A bond strengths. The solution H–A bond strengths are derived from the gas phase values and estimates of differential solvation of HA and A•. Both calculations are in good agreement with D(H–OMnO₃[−]) = 80 ± 3 kcal/mol.⁶⁷



$$\begin{aligned} \Delta H^\circ = \text{BDE}(\text{H}-\text{A}) - \text{BDE}(\text{H}-\text{OMnO}_3^-) = \\ 23.06[E^\circ(\text{A}^\bullet) - E^\circ(\text{MnO}_4^-)] + 1.37 [\text{p}K_a(\text{HA}) - \\ \text{p}K_a(\text{HMnO}_4^-)] \quad (11) \end{aligned}$$

The O–H bond strength of 80 kcal/mol in HMnO₄[−] is 9 kcal/mol less than the O–H bond strength in ^tBuOOH (89 kcal/mol)⁶⁸ and is between the H–Br and H–I bond strengths of 87 and 71 kcal/mol. Since ^tBuOO• and Br• readily abstract H• from alkyl aromatic compounds, it is not surprising that permanganate does as well. (Slower rates can be observed for permanganate because it is a stable species, not a fleeting intermediate.) ΔH° for the H• transfer step—the difference between the strengths of the bond being broken and that being formed—is a lower bound for ΔH‡. Therefore, formation of a strong bond to H• is a necessary condition for hydrogen atom abstracting reactivity. The reactions discussed here vary from 9 kcal/mol uphill for H• abstraction from toluene to 6 kcal/mol downhill for abstraction from xanthene (Table 1). The data suggest that formation of a strong O–H bond is not only necessary but also a sufficient condition for H• abstraction. It is well established that rates of H• abstraction by main-group radicals are directly related to bond strengths. OH• reacts with almost all organic compounds at close to the diffusion limit,⁶⁹ in part because it forms such a strong bond to H• (119 kcal/mol⁶⁸). ^tBuOO• is a much less reactive oxidant,⁷⁰ because it forms a weaker O–H bond of 89

kcal/mol.⁶⁸ Evans and Polanyi suggested in 1936 a linear relationship between activation energies and net enthalpy change in hydrogen atom transfer reactions (eq 12), and this correlation works quite well over a narrow range of ΔH° for similar radicals and substrates.⁷¹ Over a wider range, α → 0 as the reactions become very exothermic and α → 1 as the reactions become very endothermic.⁷²

$$E_a = \beta + \alpha(\Delta H) \quad \text{or} \quad \log k \propto \Delta G^\ddagger = \beta + \alpha(\Delta H) \quad (12)$$

The data reported here fit the Polanyi equation well, in two different ways. First, ΔH‡ (and log k₂) for oxidation of the different arylalkanes by ^tBu₄NMnO₄ are proportional to ΔH° (Figure 4a,b;⁷³ rate constants for the H• transfer step,³⁹ from Table 1). The linearity of these relations over the 15 kcal/mol range of ΔH° is quite good, given the large uncertainties in some of the C–H bond strengths. Both log k₂ and ΔH‡ correlate with ΔH° because the entropies of activation are essentially constant. These correlations strongly support the assignment of the rate-determining step as H• transfer from carbon to an oxo group. If there were any Mn–C bond formation, as in a [2 + 2] mechanism for instance, there would be substantial steric effects. Rather, rates of abstraction from primary, secondary, and tertiary C–H bonds all fit on the same line.

The rates of hydrogen atom transfer from alkyl aromatic compounds to ^tBu₄NMnO₄ also correlate with rates of abstraction by OH•, ^tBuO•, and ^tBuOO• (Figure 5). This is the second kind of Polanyi correlation, for reactions of one substrate with a range of oxidants. The plots level off at the right because the OH• reactions approach the diffusion limit (> 10⁹ M^{−1} s^{−1}). The correlations are not precise, with uncertainties of at least an order of magnitude over the ca. 10¹⁶ range of rate constants plotted. But the permanganate reactions fit on the lines. Thus, permanganate acts just as would be predicted for an

- (64) $H^\circ\{\text{H}^\bullet(\text{g}) \rightarrow \frac{1}{2}\text{H}_2(\text{g})\} = -52.1$ kcal/mol (half of the bond dissociation energy of H_{2(g)}) and $S\{\text{H}_2(\text{g})\} = 31.2$ eu.⁶⁵ Following ref 61c (including correction), the solvation of H• is well modeled by the solvation of H₂, giving $\Delta H^\circ\{\text{H}^\bullet(\text{g}) \rightarrow \text{H}^\bullet(\text{aq})\} \approx \Delta H^\circ\{\text{H}_2(\text{g}) \rightarrow \text{H}_2(\text{aq})\} = -1.0$ kcal/mol⁶⁶ (which gives $C = 55.75$ kcal/mol). However, a reviewer suggested using the value of +2 kcal/mol (quoted in ref 60b apparently for H• in MeCN). Given this uncertainty, we use 57 ± 2 kcal/mol for the constant, with E° vs NHE. This agrees well with constants calculated by others for similar cycles.^{61,67b}
- (65) JANAF Thermochemical Tables, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.
- (66) *Solubility Data Series*; Young, C. L., Ed.; Pergamon: New York, 1981; Vol. 5/6, p 2.
- (67) (a) For phenol: Lind et al. (Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479–482) give $\Delta\Delta G_{\text{solv}} = \Delta G_{\text{solv}}(\text{PhO}^\bullet) - \Delta G_{\text{g-aq}}(\text{PhOH}) \approx 3 \pm 1$ kcal/mol and $D(\text{PhO}-\text{H})_{\text{g}} = 86.5 \pm 2$ kcal/mol (see also ref 60b), yielding $D(\text{H}-\text{OMnO}_3^-) = 80.7 \pm 3$ kcal/mol. (b) For aniline, a slightly different thermochemical cycle is used involving E°(PhNH₂) and pK_a(PhNH₂⁺), as described by Jonsson et al.: Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1994**, *116*, 1423–1427. [$\Delta\Delta G_{\text{g-aq}} = \Delta G_{\text{g-aq}}(\text{PhNH}^\bullet) - \Delta G_{\text{g-aq}}(\text{PhNH}_2) \approx 0.5$ kcal/mol and $D(\text{PhNH}-\text{H})_{\text{g}} = 89$ kcal/mol yield $D(\text{H}-\text{OMnO}_3^-) = 80 \pm 2$ kcal/mol.
- (68) (a) $D(\text{HO}-\text{H}) = 119.2$ kcal/mol, $D(\text{H}-\text{Br}) = 87.4$ kcal/mol, $D(\text{H}-\text{I}) = 71.4$ kcal/mol derived from data in ref 65. (b) $D(\text{tBuO}-\text{H}) = 104.8$, $D(\text{MeO}-\text{H}) = 104.4$, and $D(\text{tBuOO}-\text{H}) = 89.4$ kcal/mol from Colussi (Colussi, A. J. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; p 33). Other $D(\text{ROO}-\text{H})$ are assumed to be the same as $D(\text{tBuOO}-\text{H})$.
- (69) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

- (70) (a) Howard, J. A.; Scaiano, J. C. Oxy-, Peroxy- and Related Radicals. In *Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Landolt-Börnstein New Series; Springer Verlag: New York, 1984; Vol. 13, Subvol. d. (b) Mulder, P.; Arends, I. W. C. E.; Clark, K. B.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 8182–8189.
- (71) (a) Ingold, K. U. Chapter 2, p 69 ff in ref 71b. (b) *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1. (c) Russell, G. A. Chapter 7, pp 283–293 of ref 71b. (d) For an example involving ^tBuOO•: Korcek, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1972**, *50*, 2285–2297. (e) Knox, J. H. In *Oxidation of Organic Compounds Vol. II*; Mayo, F. R., Ed.; Advances in Chemistry 76; American Chemical Society: Washington, DC, 1968; pp 1–22. The correlation of rates with driving force holds for similar kinds of radicals, when polar effects are not significant.^{71c,f} (f) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401–410. (g) A discussion of free energy relationships in radical reactions is also given by Korzekwa et al.: Korzekwa, K. R.; Jones, J. P.; Gillette, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 7042–7046.
- (72) The detailed interpretation of α in Polanyi and Brønsted relations as indicating the position of the transition state along the reaction coordinate is not thought to be generally applicable: Pross, A. *Theoretical and Physical Principles of Organic Reactivity*; Wiley: New York, 1995; pp 175–182. Lowry, R. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; pp 671–676 and references therein.
- (73) ΔH° is the difference between the strengths of the MnO–H bond formed (80 kcal/mol) and the C–H bond broken. Compiling a consistent set of C–H bond strengths is not straightforward because there is no complete compendium, because data from different sources do not agree for the same substrate, and because values for only some of the substrates have been recently re-evaluated (typically upward^{74a}). The Bordwell values^{61a} are supported by a gas-phase study obtaining the same value for dihydroanthracene (78 ± 1^{61a} vs 78.4 ± 1.8^{74c} kcal/mol).
- (74) (a) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D. *Gas-Phase Ion and Neutral Thermochemistry*; *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. (c) Billmers, R.; Griffith, L. L.; Stein, S. E. *J. Phys. Chem.* **1986**, *90*, 517–523.

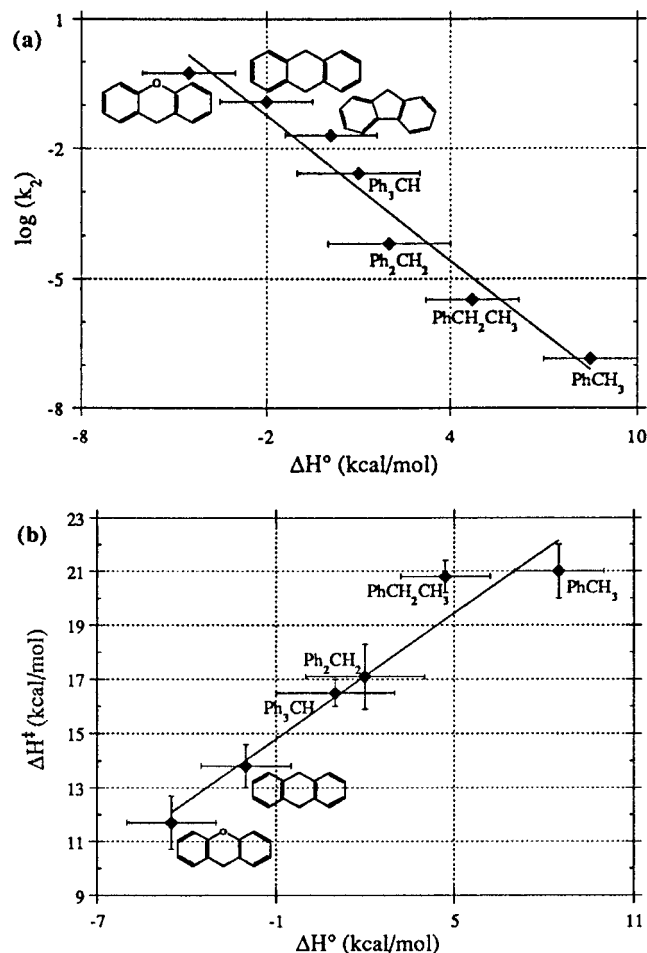


Figure 4. Plots of (a) $\log k_2$ and (b) ΔH^\ddagger vs ΔH° for the hydrogen atom transfer step in reactions of ${}^t\text{Bu}_4\text{NMnO}_4$ with toluene, ethylbenzene, diphenylmethane, triphenylmethane, 9,10-dihydroanthracene, and xanthene. ΔH^\ddagger , k_2 , and ΔH° values are from Table 3. The error bars for the $\log k_2$ values are approximately the size of the data points.

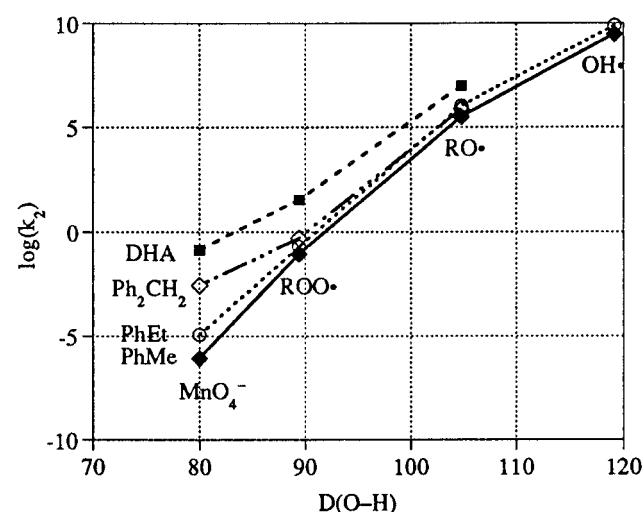


Figure 5. Rate constants for hydrogen atom abstraction by HO^\bullet , RO^\bullet , ROO^\bullet , and MnO_4^- at 30 °C vs the strength of the O–H bond formed for toluene, ethylbenzene, diphenylmethane, and dihydroanthracene. Data were obtained from refs 68–70, ref 71d (XO^\bullet), and Scheme 1 and were calculated from Eyring plots (MnO_4^-).

oxygen radical that makes an 80 kcal/mol bond to a hydrogen atom. The similarity of permanganate to oxygen radicals is remarkable given that permanganate is a closed-shell species. The frontier orbitals involved in H^\bullet transfer are different in the radical vs the closed-shell case, as described elsewhere.^{5c} These

data indicate that, at least for metal–oxo species such as permanganate and CrO_2Cl_2 ,⁵ the primary determinant of hydrogen atom abstraction reactivity is the strength of the O–H bond formed, rather than details of the electronic structure of the oxidant. These conclusions should apply equally well to metal–oxo species in enzyme active sites and on the surface of a heterogeneous catalyst. An ongoing study of μ -oxo compounds is supportive of these ideas.⁷⁵ As a final comment, the reactions described as hydrogen atom transfers could be equivalently called proton-coupled electron transfer. The data only show that the rate-limiting step involves transfer of both a proton and an electron. We favor the H^\bullet transfer terminology in this case because it facilitates the comparison with organic radicals.

Conclusions

${}^t\text{Bu}_4\text{NMnO}_4$ oxidizes arylalkanes in toluene solvent by dehydrogenation and/or oxygenation. For instance, toluene is converted mostly to benzoic acid, xanthene to xanthone, and dihydroanthracene to anthracene. In all cases, the initial reactions are first order in the concentrations of both ${}^t\text{Bu}_4\text{NMnO}_4$ and substrate. No induction periods are observed. There are primary isotope effects on oxidation of toluene and dihydroanthracene. Added O_2 enhances the rate of ${}^t\text{Bu}_4\text{NMnO}_4$ disappearance in toluene, consistent with the presence of organic radicals. The rate-limiting step for these reactions is H^\bullet transfer from the substrate to a manganese oxo group. The enthalpies of activation correlate with the strength of the C–H bond being cleaved, as is typical of H^\bullet abstraction by main group radicals such as ${}^t\text{BuOO}^\bullet$. This correlation includes primary, secondary, and tertiary C–H bonds, with no evidence of any steric effects that would accompany formation of a metal–carbon bond.

Permanganate can abstract a hydrogen atom from organic substrates because it has a high thermodynamic affinity for H^\bullet . The ΔH° for addition of H^\bullet to MnO_4^- to give HMnO_4^- in aqueous solution is calculated to be -80 ± 3 kcal/mol using a thermochemical cycle (Scheme 1). Using this value, the rates of ${}^t\text{Bu}_4\text{NMnO}_4$ oxidation of toluene, ethylbenzene, and diphenylmethane are shown to correlate with the rates of hydrogen atom abstraction by the oxygen radicals OH^\bullet , ${}^t\text{BuO}^\bullet$, and ${}^t\text{BuOO}^\bullet$ (Figure 5). Permanganate reacts just as one would predict for an oxygen radical that makes an 80 kcal/mol O–H bond. This behavior is in spite of the fact that permanganate is a closed-shell species, with no radical character. For metal–oxo oxidants, a high thermodynamic affinity for H^\bullet is necessary and appears to be sufficient for hydrogen atom abstracting reactivity.

Acknowledgment. We are grateful to the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support. Jim Roe, Bob Morley, and Dr. William Howald provided invaluable technical support, and Tom Crevier supplied the sample of d_{12} -dihydroanthracene. We thank Dr. G. K. Cook (Union Carbide Corp.) and Professors S. N. Brown (University of Notre Dame), Jeanne McHale (University of Idaho), John Brauman (Stanford University), and Neil Bartlett (University of California, Berkeley) for advice and comments and Dr. K. Wang for assistance. Use of HPLC instruments was graciously provided by the Gouterman and Sasaki research groups of the University of Washington.

Supporting Information Available: Tables of rate constants and a representative first-order kinetics plot (6 pages). Ordering information is given on any current masthead page.

IC961297Y

(75) (a) Wang, K.; Mayer, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 1470–1471.