

# Reduction of Manganate(VI) by Mandelic Acid and Its Significance to Development of a General Mechanism for Oxidation of Organic Compounds by High-Valent Transition Metal Oxides

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**Abstract:** Results obtained from a study of the oxidation of mandelic acid and cyclobutanol by manganate(VI) indicate that reaction mechanisms traditionally applied to oxidations of this type (i.e., hydrogen atom or hydride ion transfers) may not be correct. Instead it appears that the reaction may be initiated by a 2 + 2 addition of the  $\alpha$ -C-H bond to a manganese oxo double bond. This interpretation may be useful in the development of a general mechanism for the oxidation of organic compounds by high-valent transition metal oxides including more common oxidants such as permanganate, ruthenium tetroxide, and chromic acid.

## Introduction

Manganate(VI) ion ( $\text{MnO}_4^{2-}$ ) is an oxidant that may be used for the preparation of ketones from secondary alcohols or glycols from alkenes under alkaline conditions.<sup>1</sup> In solutions less basic than approximately 1 M NaOH, however, manganate(VI) disproportionates in a second-order reaction to give manganate(V) and permanganate.<sup>2</sup> Because of this rapid disproportionation reaction, manganate(VI) cannot be used as an oxidant in acidic solutions and is therefore less versatile than permanganate ( $\text{MnO}_4^-$ ).<sup>3</sup> It is, nevertheless, an interesting oxidant from a theoretical point of view because it provides for a direct comparison with other dianionic oxidants such as ruthenate<sup>4</sup> and ferrate<sup>5</sup> (which may also be used for the oxidation of alcohols under basic conditions) and chromate<sup>6</sup> (which reacts with organic compounds only under acidic conditions).

The oxidation of alcohols by high-valent transition metal oxides such as manganate(VI) has traditionally been considered to involve an initial transfer of electrons, usually along with a hydrogen nucleus, i.e., hydrogen atom or hydride ion transfers. In many cases the experimental results are not sufficiently restrictive to make a conclusive choice between various mechanistic possibilities. For example, the oxidation of alcohols by ferrate ion has variously been interpreted to support electron transfer unaccompanied by a hydrogen nucleus, hydrogen atom transfer, hydride ion transfer, or the formation of ferrate ester intermediates.<sup>5</sup> The difference of opinion on the nature of this reaction does not arise because of any contradictions in the experimental results reported by various authors but from the fact that the results are open to a broad range of mechanistic interpretations. Results which are

more restrictive insofar as mechanistic choices are concerned increase the confidence in the correctness of a proposed mechanism.

## Experimental Section

**Kinetic Methods.** Reduction of manganate(VI) by alcohols is accompanied by a well-defined change in the visible region (400-700 nm) of the electromagnetic spectrum. The characteristic spectrum of manganate(VI) with an absorption maximum at 606 nm is replaced by the spectrum of manganate(V) with an absorption maximum at 670 nm.<sup>3</sup> The observation of a precise isosbestic point at 657 nm (Figure 1) indicates that manganate(VI) is reduced to manganate(V) without formation of intermediates with detectable lifetimes in 3-10 M KOH. At lower basicities manganate(V) disproportionates with the precipitation of manganese dioxide.<sup>3</sup>

From the measured extinction coefficients for manganate(VI) at 606 and 670 nm (1710 and 660, respectively) and manganate(V) at the same wavelengths (565 and 900, respectively), it is possible to derive an expression for the concentration of  $\text{MnO}_4^{2-}$  as in eqs 1-3.

$$A_{606} = 1710[\text{MnO}_4^{2-}] + 565[\text{MnO}_4^{3-}] \quad (1)$$

$$A_{670} = 660[\text{MnO}_4^{2-}] + 900[\text{MnO}_4^{3-}] \quad (2)$$

$$[\text{MnO}_4^{2-}] = (A_{606} - 0.628A_{670})/1296 \quad (3)$$

In order to avoid solubility problems in highly basic solutions, the kinetic studies were completed using mandelic acid as the reductant.

In a typical experiment, a solution of manganate(VI) ( $8.88 \times 10^{-4}$  M) and mandelate ion ( $8.00 \times 10^{-3}$  M) in 4.0 M KOH were thermostated in a constant-temperature bath for 15 min. Aliquots (1.0 mL) of each solution were then transferred to a 10-mm glass spectrophotometer cell in the thermostated cell compartment of a Hewlett Packard 8450 A spectrophotometer and spectra recorded at regular intervals as in Figure 1. Plots of  $\ln[\text{MnO}_4^{2-}]$  (calculated by the use of eq 3) against time were then prepared, as in Figure 2, and the slopes used to calculate pseudo-first-order rate constants.

**Materials.** Manganate(VI) solutions used in these experiments were prepared, in analogy with the work of Carrington and Symons,<sup>7</sup> The water used was doubly distilled from alkaline permanganate in an all-glass still and reboiled to remove carbon dioxide. In a typical procedure, potassium permanganate was added to 10 or 5 M potassium hydroxide solutions at room temperature and then the mixture was stirred for about 24 h in the dark. The spectrum of the solution obtained was examined

(7) Carrington, A.; Symons, M. C. R. *J. Chem. Soc.* 1956, 3373.

\* Abstract published in *Advance ACS Abstracts*, October 15, 1993.

(1) Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*; Open Court: La Salle, IL, 1981; p 175-181.

(2) Lee, D. G.; Chen, T. *J. Am. Chem. Soc.* 1989, 111, 7534.

(3) Stewart, R. In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Part A.

(4) Lee, D. G.; Congson, L. N. *Can. J. Chem.* 1990, 68, 1774.

(5) Bielski, B. H. J. *Free Radical Res. Commun.* 1991, 12, 13, 469. Audette, R. J.; Quail, J. W.; Smith, P. J. *J. Chem. Soc., Chem. Commun.* 1972, 38. Cyr, J. E.; Bielski, B. H. J. *Free Radical Biol. Med.* 1991, 11, 157. Audette, R. J.; Quail, J. W.; Smith, P. J. *Tetrahedron Lett.* 1971, 279. Bartzatt, R.; Tabatabai, A.; Carr, J. *Synth. React. Inorg. Met.-Org. Chem.* 1985, 15, 1171.

(6) Freeman, F. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum: New York, 1986; Chapter 2.

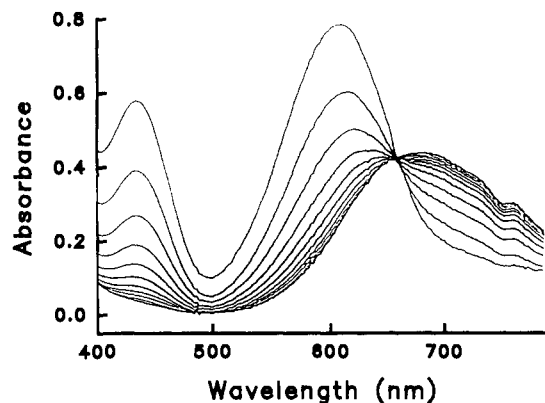


Figure 1. Sequential scans (top to bottom at 600 nm) recorded during the oxidation of mandelate ion ( $1 \times 10^{-2}$  M) by manganate(VI) oxide ( $5.45 \times 10^{-4}$  M) in 10.0 M KOH solutions at 25 °C.

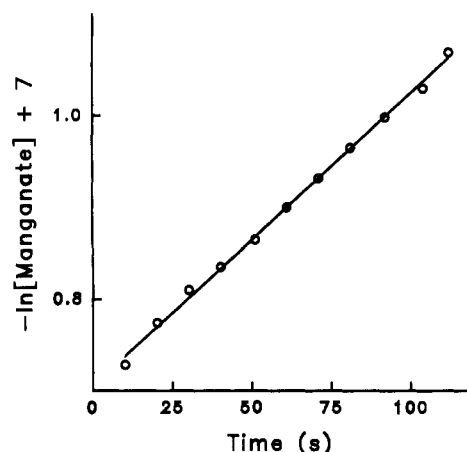
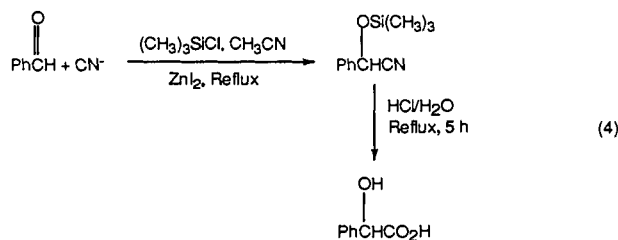


Figure 2. Typical pseudo-first-order rate plot for the oxidation of mandelate ion ( $1 \times 10^{-2}$  M) by manganate(VI) oxide ( $4.44 \times 10^{-4}$  M) in 4.0 M KOH solutions at 25 °C. Slope =  $3.46 \times 10^{-3} \text{ s}^{-1}$ ;  $r = 0.996$ .

to ensure that all of the permanganate had been converted into manganate(VI).

Substituted mandelic acids were prepared using a new procedure that has some advantage over those previously reported.<sup>8</sup> In this preparation, cyanotrimethylsilane is initially added to substituted benzaldehydes to form silyl ethers of the corresponding cyanohydrins<sup>9</sup> which are then hydrolyzed as in eq 4. Overall yields from 66 to 93% were realized.



In a typical experiment, potassium cyanide (17.3 g, 0.27 mol) and  $\text{ZnI}_2$  (0.050 g, 0.16 mmol) were dried in an oven overnight and then transferred to a flame-dried 100-mL round-bottomed flask. Acetonitrile (25 mL) which had previously been distilled from  $\text{P}_2\text{O}_5$  was added as the solvent. Chlorotrimethylsilane (14.2 mL, 0.13 mol) and 10.0 mL (0.066 mol) of 3-fluorobenzaldehyde (freshly purified and stored under nitrogen) were introduced. The flask was then attached to a refluxing condenser equipped with a  $\text{CaCl}_2$  drying tube, and the mixture was stirred and heated under reflux. The reaction was monitored by use of GLC (12% carbowax, 20 M) until the peak for fluorobenzaldehyde disappeared. The unreacted KCN was removed by filtration through a Buchner funnel, the solvent was evaporated, and the silyl ether of 3-fluorobenzaldehyde

(8) Jenkins, S. S. *J. Am. Chem. Soc.* 1931, 53, 2341. Klingenberg, J. J. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. 4, p 110.

Table I. Melting Points (°C) of Substituted Mandelic Acids

substituent	mp (lit.)	substituent	mp (lit.)
unsubstituted	119–120 (121.3) <sup>a</sup>	3-fluoro	96–97
4-methoxy	106.5–108 (107–109) <sup>b</sup>	4-chloro	119–121 (120.5–121) <sup>f</sup>
3-methoxy	60–61 (63–65) <sup>c</sup>	3-chloro	113.5–115 (115–115.5) <sup>g</sup>
4-methyl	145–146 (145–145.5) <sup>d</sup>	4-bromo	116.5–118 (117–119) <sup>e</sup>
3-methyl	93–94	a-deuterio	119–120 (118.5–120) <sup>a</sup>
4-fluoro	138–139 (138.5) <sup>e</sup>		

<sup>a</sup> *CRC Handbook of Chemistry and Physics*. <sup>b</sup> Klingberg, J. J.; Thole, J. P.; Lingg, R. D. *J. Chem. Eng. Data* 1966, 11, 94. <sup>c</sup> *Aldrich Catalog Handbook of Fine Chemicals*, 1988–89. <sup>d</sup> Riebsomer, J. L.; Irvine, J.; Andrews, R. *J. Am. Chem. Soc.* 1938, 60, 1015. <sup>e</sup> Klingenberg, J. J. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. 4, p 110. <sup>f</sup> Jenkins, S. S. *J. Am. Chem. Soc.* 1931, 53, 2341. <sup>g</sup> Barger, G.; Evins, A. J. *J. Chem. Soc.* 1909, 95, 552.

cyanohydrin was collected under reduced pressure (110 °C, 10 Torr). The yield was 14.4 g (98%).

The silyl ether of 3-fluorobenzaldehyde cyanohydrin (5 g, 22.4 mmol) and 5 mL of water were placed in a 100-mL three-necked round-bottomed flask equipped with a refluxing condenser. Hydrochloric acid (35%, 45 mL) was then added from a dropping funnel, and the solution was stirred and heated under reflux for 5 h. The mixture was cooled, and concentrated KOH was slowly added until the solution became slightly basic. Extraction with 50 mL of ether removed unreacted starting material. The aqueous solution was acidified and extracted with  $4 \times 50$  mL portions of ether. The combined ether extracts were dried over anhydrous  $\text{MgSO}_4$  and evaporated to yield a crude product (2.5 g, 95%) which was recrystallized from benzene. Mp: 96–97 °C. IR (nujol):  $\nu$  3451 (m), 2921 (vs), 2853 (s), 1704 (s), 1595 (m). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  2.53 (s, 1H), 5.12 (s, 1H), 7.27 (m, 4H).

All substituted mandelic acids prepared in this way exhibit consistent NMR and IR spectra and have sharp melting points that are in agreement with literature values (Table I).

**Product Studies.** For the oxidation of mandelic acid,  $\text{KMnO}_4$  (2.28 g, 14.5 mmol) was first added to 70 mL of 10.0 M KOH solution which was then stirred at room temperature until all of the permanganate had been reduced to manganate(VI) (about 12 h). A solution of mandelic acid (1.0 g, 6.57 mmol) in 30 mL of 1.0 M KOH was added and the mixture stirred continuously at room temperature for about 6 h. The flask was immersed in an ice bath, and an excess of 98% sodium sulfite (2.73 g) added. Concentrated HCl was carefully added with stirring until all of the manganate had been reduced to colorless manganese(II). The pH of the solution was about 3. Extraction with  $4 \times 100$  mL portions of ether was followed by drying of the combined extracts over anhydrous  $\text{MgSO}_4$  for 10 min. A crude solid (0.80 g, 81%) was obtained after evaporation of the solvent. After recrystallization from carbon tetrachloride, its melting point was 66–68 °C. IR (nujol):  $\nu$  3100–3300 (vs), 2922 (vs), 2854 (s), 1739 (m), 1660 (s), 1593 (m), 1452 (s). <sup>1</sup>H NMR ( $\text{DMSO}-d_6$ ):  $\delta$  7.41 (m, 2H), 7.74 (m, 1H), 7.90 (m, 2H). The reported melting point of the expected product, benzoylformic acid, is 66 °C.<sup>10</sup>

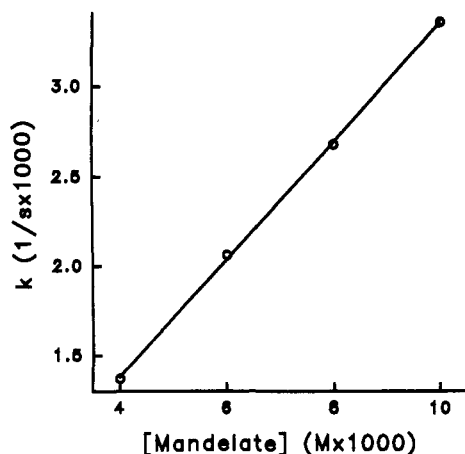
Cyclobutanol (1.0 g, 12 mmol) in 100 mL of 6.0 M KOH was allowed to react with 200 mL of aqueous manganate(VI) solution (0.155 M) which had been prepared as described above. The mixture was held in the ice-water bath and stirred for about 5 min. When the reaction had gone to completion, an excess of sodium sulfite (10 g, 79.3 mmol) was introduced. HCl was carefully added until all of the manganate had been reduced to colorless manganese(II). The solution was saturated with sodium chloride, made slightly basic, and extracted with  $5 \times 100$  mL portions of ether. The ethereal extract was dried over anhydrous magnesium sulfate for a few minutes and evaporated to give a liquid product that was identified to be cyclobutanone by comparison of its IR spectrum and GC retention time (12% carbowax, 20 M) with an authentic sample. The yield was 0.83 g (10 mmol, 83%) with 0.07 g (7%) of unreacted starting material recovered.

## Results

**Rate Law.** When an excess of mandelic acid was used, the resulting pseudo-first-order rate constants (Figure 2) were found

(9) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: Toronto, 1981; p 296. Neef, H.; Muller, R. *J. Prakt. Chem.* 1973, 315, 367. Rasmussen, J. K.; Heilmann, S. M. *Synthesis* 1978, 219. Evans, D. A.; Truesdale, L. K. *Tetrahedron Lett.* 1973, 4929. Lidy, W.; Sundermeyer, W. *Chem. Ber.* 1973, 106, 587. Corey, E. J.; Crouse, D. N.; Anderson, T. E. *J. Org. Chem.* 1975, 40, 2140.

(10) Weast, R. C.; Astle, M. J.; Beyer, W. H. *CRC Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, FL, 1985; p C-292.



**Figure 3.** Plot for determination of the order with respect to mandelate ion when oxidized by manganate(VI) oxide ( $4.44 \times 10^{-4}$  M) in 4.0 M KOH solutions at 25 °C. Slope =  $3.34 \pm 0.03 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ ;  $r = 1.000$ .

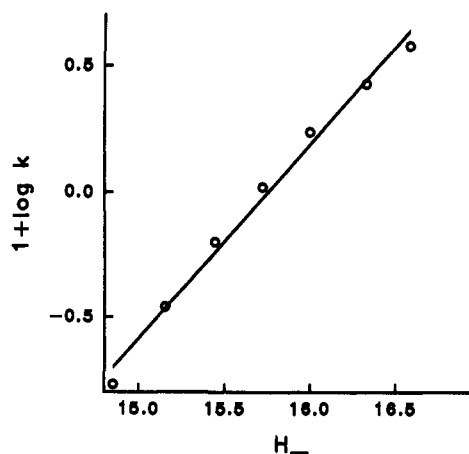
**Table II.** Rate Constants for the Oxidation of Mandelate Ion by Manganate(VI) Oxide

[MnO <sub>4</sub> <sup>2-</sup> ] (M × 10 <sup>4</sup> )	[mandelate] (M × 10 <sup>3</sup> )	[KOH] (M)	k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>
4.31	1.82	10.0	4.59 ± 0.13
4.31	3.50	10.0	4.56 ± 0.22
4.31	5.36	10.0	4.94 ± 0.15
4.31	8.80	10.0	4.72 ± 0.26
4.31	10.6	10.0	4.62 ± 0.37
4.31	12.3	10.0	4.72 ± 0.08
3.57	5.30	10.0	4.58 ± 0.21
2.20	5.30	10.0	4.83 ± 0.17
1.73	5.30	10.0	4.74 ± 0.09
4.77	2.00	8.0	2.73 ± 0.06
4.77	4.00	8.0	2.79 ± 0.12
4.77	6.00	8.0	2.77 ± 0.04
4.77	8.00	8.0	2.79 ± 0.05
4.77	10.0	8.0	2.79 ± 0.02
5.56	6.03	8.0	2.62 ± 0.02
4.77	6.08	8.0	2.77 ± 0.07
4.19	6.11	8.0	2.58 ± 0.03
2.40	6.09	8.0	2.67 ± 0.08
4.75	4.02	6.0	1.02 ± 0.04
4.75	6.12	6.0	1.05 ± 0.04
4.75	8.0	6.0	1.03 ± 0.01
4.75	10.1	6.0	1.01 ± 0.01
4.75	12.0	6.0	1.09 ± 0.08
5.58	6.02	6.0	1.04 ± 0.03
3.80	6.09	6.0	1.03 ± 0.05
2.97	5.98	6.0	1.09 ± 0.01
4.44	4.02	4.0	0.340 ± 0.010
4.44	6.13	4.0	0.338 ± 0.011
4.44	8.04	4.0	0.335 ± 0.005
4.44	10.1	4.0	0.337 ± 0.009
5.49	10.0	4.0	0.389 ± 0.011
2.90	10.3	4.0	0.383 ± 0.08
1.95	10.6	4.0	0.336 ± 0.28

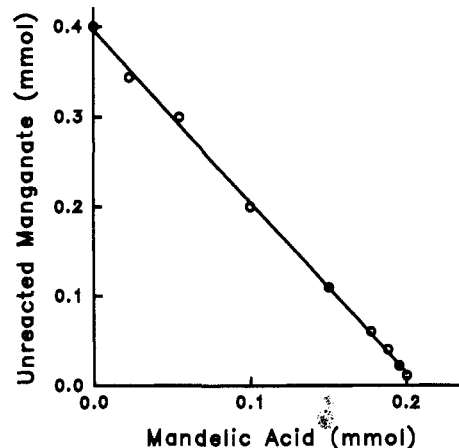
<sup>a</sup> Each rate constant is the average of three determinations at 25.0 ± 0.1 °C.

to be directly proportional to the concentration of reductant (Figure 3), thereby indicating a second-order rate law. The observed second-order rate constants,  $k_2$ , increased with increasing basicity of the solutions (Table II). A plot of  $\log k_2$  vs the basicity function,  $H_-$ , is approximately linear with a slope near unity between 4 and 8 M NaOH (Figure 4). It is not clear if the deviation from linearity is related to the fundamental nature of the reaction or to uncertainties in the function.<sup>11</sup>

**Stoichiometry.** The stoichiometry of the reaction, determined



**Figure 4.** Dependence of the magnitude of the second-order rate constants on the basicity of the solution. Slope =  $0.77 \pm 0.08$ ;  $r = 0.994$ .



**Figure 5.** Determination of the stoichiometry for the oxidation of mandelate ion by manganate(VI) oxide in 10.0 M KOH.

**Table III.** Deuterium Isotope Effects for the Oxidation of Mandelate by Manganate(VI)

reductant <sup>a</sup>	[KOH] (M)	k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )	k <sub>H</sub> /k <sub>D</sub>
mandelate	10.0	4.70 ± 0.24	7.3 ± 0.3
mandelate-2-d	10.0	0.64 ± 0.02	
mandelate	8.0	2.72 ± 0.14	8.8 ± 0.2
mandelate-2-d	8.0	0.31 ± 0.01	
mandelate	6.0	1.05 ± 0.04	7.5 ± 0.1
mandelate-2-d	6.0	0.14 ± 0.01	
mandelate	4.0	0.35 ± 0.04	8.3 ± 0.1
mandelate-2-d	4.0	0.042 ± 0.001	

<sup>a</sup> [reductant] = 0.11 M.  $T = 25.0 \pm 0.1$  °C.

by reacting limited amounts of mandelic acid with an excess of manganate, is clearly 2:1 as indicated by the plot reproduced in Figure 5.

**Isotope Effect.** A primary deuterium kinetic isotope effect<sup>12</sup> was observed when the rate constant for the oxidation of mandelic acid was compared with that for  $\alpha$ -deuteriomandelic acid (Table III).

**Substituent Effects.** A Hammett plot<sup>13</sup> for the oxidation of substituted mandelic acids (Figure 6) exhibits a positive  $\rho$  value.

**Activation Parameters.** The activation parameters for the reaction of the substituted mandelate ions with manganate(VI), determined by measuring the rate constant at various temperatures and application of the Eyring equation,<sup>14</sup> are characterized by low enthalpies of activation (4–6 kcal/mol) and very negative

(11) Rochester, C. H. *Acidity Functions*; Academic Press: New York, 1970; Chapter 7.

(12) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum: New York, 1990; Part A, p 216.

(13) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley-Interscience: New York, 1975.

(14) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford: New York, 1985; p 247.

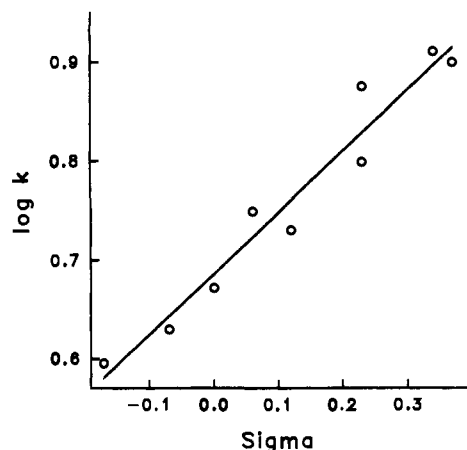


Figure 6. Hammett plot for the oxidation of substituted mandelate ions by manganate(VI) oxide in 10.0 M KOH solutions at 25 °C. Slope =  $0.63 \pm 0.06$ ;  $r = 0.967$ .

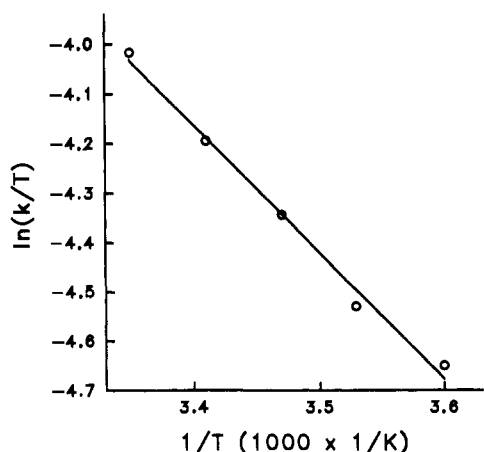
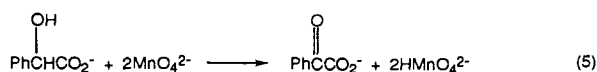


Figure 7. Typical plot used for the calculation of activation parameters. Slope =  $2.65 \pm 0.16$  K; intercept =  $-4.86 \pm 0.57$ ;  $r = 0.998$ .

entropies of activation as indicated by the data in Table IV. It should be noted that these Eyring plots were constructed using pseudo-second-order rate constants,  $k_2$ , measured under conditions of constant basicity.

## Discussion

The stoichiometry determination (Figure 5) clearly indicates that the overall reaction involves reduction of 2 mol of manganate(VI) by 1 mol of mandelate ion as in eq 5.



The reaction is subject to specific base catalysis, giving the rate law depicted in eq 6.

$$\text{rate} = k_3[\text{MnO}_4^{2-}][\text{mandelate}]a_{\text{OH}^-} \quad (6)$$

Alkoxide ion formation (eq 7), which is known to increase the rate of reaction of alcohols with other oxidants such as permanganate,<sup>3</sup> is likely responsible for the acceleration depicted in Figure 4.

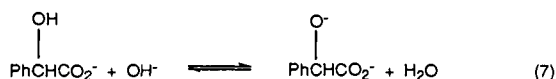
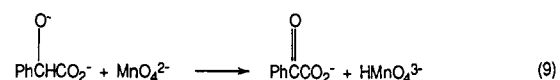
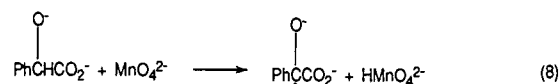


Table IV. Rate Constants and Activation Parameters for the Oxidation of Substituted Mandelate Ions by Manganate(VI)<sup>a</sup>

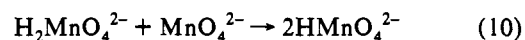
substituent	$k_2$ ( $\text{M}^{-1} \text{s}^{-1}$ ) <sup>b</sup>	$\Delta H^\ddagger$ ( $\text{kcal mol}^{-1}$ ) <sup>c</sup>	$\Delta S^\ddagger$ ( $\text{cal mol}^{-1} \text{K}^{-1}$ ) <sup>c</sup>	$r^d$
4-methyl	$3.94 \pm 0.02$	$3.9 \pm 0.4$	$43 \pm 1$	0.982
3-methyl	$4.26 \pm 0.01$	$5.7 \pm 0.6$	$37 \pm 2$	0.985
none	$4.70 \pm 0.08$	$4.5 \pm 0.8$	$40 \pm 3$	0.968
4-fluoro	$5.61 \pm 0.46$	$4.5 \pm 0.4$	$40 \pm 1$	0.990
3-methoxy	$5.37 \pm 0.05$	$5.3 \pm 0.3$	$37 \pm 1$	0.994
4-bromo	$7.80 \pm 0.06$	$5.4 \pm 0.3$	$36 \pm 1$	0.996
4-chloro	$6.30 \pm 0.18$	$5.5 \pm 0.5$	$37 \pm 2$	0.987
3-chloro	$7.95 \pm 0.08$	$4.0 \pm 1.2$	$41 \pm 4$	0.885
3-fluoro	$8.14 \pm 0.15$			

<sup>a</sup>  $[\text{KOH}] = 10.0 \text{ M}$ .  $[\text{manganate(VI)}] = 3.99 \times 10^{-4} \text{ M}$ .  $[\text{mandelate}] = 1.0 \times 10^{-2} \text{ M}$ . <sup>b</sup>  $T = 25.0 \pm 0.1$  °C. All rate constants are averages of three determinations. <sup>c</sup> Temperature ranges: 5–25 °C. <sup>d</sup> Correlation coefficient of Eyring plot.

Because manganate(VI) does not attack aromatic rings, it is apparent that there is only one site in the alkoxide ion, **1**, at which the oxidant could react—the  $\alpha$ -C–H bond. The observed primary kinetic deuterium isotope effect (Table III) establishes that cleavage of this remaining C–H bond must occur in the rate-limiting step. Such an oxidative cleavage of a C–H bond can, theoretically, occur in a number of different ways<sup>15</sup>—the two most obvious being hydrogen atom transfer (eq 8) and hydride ion transfer (eq 9).



Hydrogen atom transfer, although it results in formation of the observed inorganic product, manganate(V), is not acceptable because the high yield of cyclobutanone obtained from the oxidation of cyclobutanol indicates that free radicals are not involved.<sup>16</sup> Hydride transfer, on the other hand, would produce cyclobutanone directly, but result in the formation of manganate(IV) instead of manganate(V), the observed product. The kinetic data are consistent with a sequence of reactions that involves hydride transfer followed by a rapid oxidation of manganate(IV) to manganate(V) as in eq 10. The observation



that manganate(IV) generated by the photolytic reduction of permanganate<sup>17</sup> was found not to react with manganate(VI) does not entirely eliminate the possibility of a hydride transfer; manganate(IV) generated photolytically may be less reactive than manganate(IV) produced in an electron-transfer reaction.<sup>18</sup>

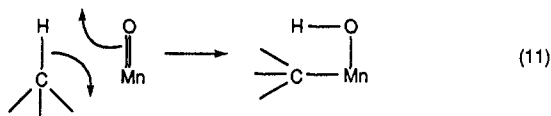
A third cleavage mode, 2 + 2 addition of a manganese oxo double bond to the carbon–hydrogen bond as in eq 11, appears to be more consistent with all of the experimental evidence. Such

(15) March, *J. Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; Chapter 19.

(16) Rocek, J.; Radkowsky, A. E. *J. Am. Chem. Soc.* 1968, 90, 2986; 1973, 95, 7123. Meyer, K.; Rocek, J. *J. Am. Chem. Soc.* 1972, 94, 1209. Rocek, J.; Aylward, D. E. *J. Am. Chem. Soc.* 1975, 97, 5452.

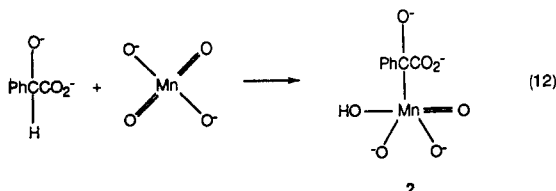
(17) Lee, D. G.; Moylan, C. R.; Hayashi, T.; Brauman, J. I. *J. Am. Chem. Soc.* 1987, 109, 3003.

(18) A reviewer has advanced the suggestion that manganate(IV) generated photolytically from permanganate<sup>17</sup> may not be identical to manganate(IV) produced in a hydride-transfer reaction. If it is assumed, despite the unreactivity of photolytically generated manganate(IV), that manganate(IV) produced in reaction 9 could react with manganate(VI) so rapidly that it would not cause an observable effect on the isosbestic point (Figure 1), a mechanism involving hydride transfer could not be conclusively eliminated. Calculations indicate that the reaction between manganate(VI) and manganate(IV) would have to be very fast, but not beyond the limits of a diffusion-controlled reaction.



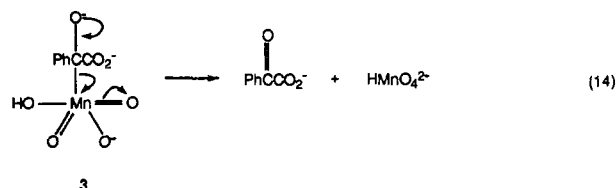
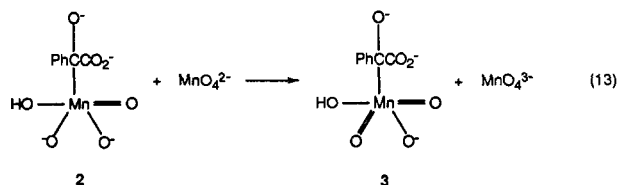
a process, which was originally proposed on the basis of molecular orbital calculations,<sup>19</sup> has been suggested to occur when oxides of iron,<sup>20</sup> ruthenium,<sup>4</sup> chromium,<sup>19</sup> and manganese<sup>21</sup> react with alkanes and alcohols.

Subsequent cleavage of the C-Mn bond of the organometallic intermediate, **2**, formed from the reaction of mandelate ion with manganate(VI) as in eq 12, could then yield either a free radical



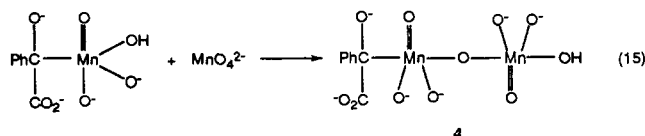
and manganate(V) (if the cleavage is homolytic) or a carbocation and manganate(IV) (if the cleavage is heterolytic). Both of these possibilities, however, lead to products that do not appear to be in agreement with the experimental facts.

Alternatively, **2** could be oxidized by manganate(VI), as in eq 13, prior to heterolytic cleavage of the C-Mn bond (eq 14) to give



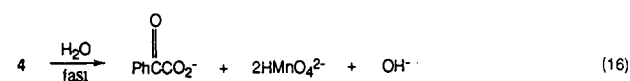
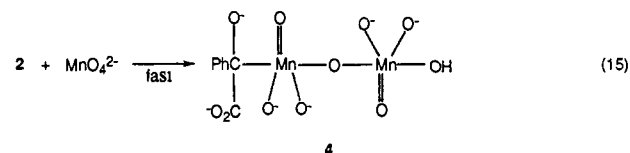
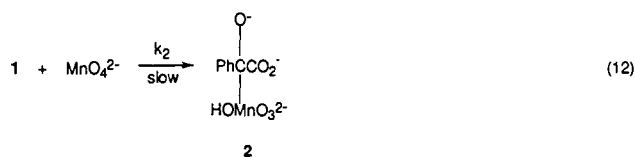
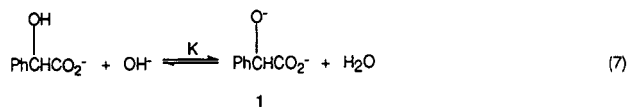
the experimentally observed products. However, this possibility must also be rejected from a consideration of an analogous reaction of permanganate. The intermediate, **3**, is actually the initial product that would be obtained from a 2 + 2 oxo addition of permanganate with mandelate ion, which is known from previous work to decompose with homolytic cleavage of the C-Mn bond, yielding a radical anion and manganate(VI).<sup>21</sup>

It is therefore necessary to consider alternative processes, one of which, formation of a dimanganate(VI) ion (eq 15) prior to electron transfer, appears to readily accommodate all of the experimental facts.



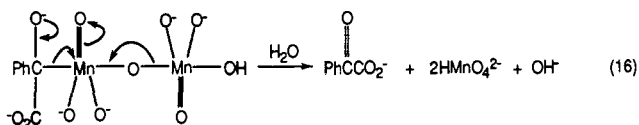
The intermediate, **4**, would be analogous to the well-characterized dichromate ion, and its formation would be consistent with the observation that disproportionation of manganate(VI)

### Scheme I. Probable Reaction Sequence for the Oxidation of Mandelate Ion by Manganate(VI) in Alkaline Solutions



under these conditions involves formation of a dimer prior to electron transfer.<sup>2</sup>

A possible mode for the electron-transfer process has been suggested in eq 16. Since no spectral change (manganate(VI)



→ manganate(V)) would occur during the proposed reaction sequence (Scheme I) until the formation of manganate(V) in reaction 16, it must be assumed that reactions 15 and 16 are fast relative to the rate-limiting step which is known to involve C-H cleavage.

It can also be noted that formation of a manganate(VI) dimer prior to reaction with the reductant would lead to a rate law that is second order in manganate(VI) and, therefore, not in accord with the experimental data.

The observation of a positive Hammett  $\rho$  value (Figure 6) is unusual for hydride-transfer oxidation reactions which are generally accelerated by electron-donating substituents.<sup>22</sup> Furthermore, the 2 + 2 addition proposed as the rate-limiting step would not be expected to result in a Hammett plot with a large  $\rho$  value because no charges are developed near the ring in the transition state. (See eq 11.) In this particular reaction sequence (Scheme I), it is, however, quite possible that the positive Hammett  $\rho$  is a consequence of the initial equilibrium which causes the transition state, formed during reaction 12, to bear a negative charge.

The very low enthalpy of activation for this reaction ( $\Delta H^\ddagger = 4.5 \pm 0.8$  kcal/mol) is consistent with a rate-limiting step in which bond cleavage and bond formation occur coincidentally as in eq 11, and the unfavorable entropy of activation ( $\Delta S^\ddagger = -40 \pm 3$  eu) is to be expected for a transition state that occurs during a bimolecular reaction between two anions.

### Conclusions

The results of this study place severe restrictions on the type of mechanism that can be proposed for this reaction. Direct

(19) Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 3287.  
 (20) Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Cshai, E.; Doller, D.; Liu, W.-G. *J. Am. Chem. Soc.* **1992**, *114*, 2147. Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504.

(21) Lee, D. G.; Chen, T. *J. Org. Chem.* **1991**, *56*, 5341.

(22) Che, C.-M.; Tang, W.-T.; Lee, W.-O.; Wong, K.-Y.; Lau, T.-C. *J. Chem. Soc., Dalton Trans.* **1992**, 1551.

hydrogen atom transfer is eliminated because it would produce free radicals and result, contrary to the experimental facts, in the formation of acyclic products when cyclobutanol is oxidized.<sup>16</sup> Hydride transfer must also be considered unlikely because it would result in the production of manganese(IV) and not manganate(V) as is experimentally observed. Similarly, the 2 + 2 addition of a manganese oxo double bond to the  $\alpha$ -C-H bond, which has been proposed to occur in a number of analogous reactions,<sup>19-21</sup> would give an organometallic intermediate, **2**, whose "normal" reactions (homolytic or heterolytic cleavage of the C-Mn bond) would be expected to produce products other than those observed experimentally. The reaction of **2** with  $\text{MnO}_4^{2-}$  to form a dimanganate(VI) ion (analogous to other dimeric anions such as dichromate) does, however, provide a reaction pathway which accommodates all experimental evidence.

The restrictiveness of the mechanistic choices in this reaction aids in our attempt to define the course of the reaction and allows us to be fairly specific in our description of the reaction sequence (Scheme I). Having arrived in an experimentally well-defined mechanism for this reaction, is it reasonable to suggest that the

reactions of other high-valent transition metal oxides, where the experimental evidence is not so mechanistically restrictive, would also be expected to proceed in similar ways? For example, is it reasonable to suggest, on the basis of this one example, that none of the high-valent transition metal oxide oxidations involve either hydrogen atom or hydride ion transfer? Such an idea is revolutionary in comparison with the commonly held views as expressed in a legion of journal articles and numerous textbooks. However, we believe it is a suggestion that has considerable merit, especially for very similar oxidants such as ruthenate ( $\text{RuO}_4^{2-}$ )<sup>4</sup> or ferrate ( $\text{FeO}_4^{2-}$ ),<sup>23</sup> but that additional evidence is required before it will be possible to conclude whether or not a similar mechanism is also applicable to more common oxidants such as permanganate, ruthenium tetroxide, and chromic acid.

**Acknowledgment.** Financial assistance from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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(23) Lee, D. G.; Gai, H. *Can. J. Chem.*, in press.