

# Permanganate Ion Oxidations. 15. Additional Evidence for Formation of Soluble (Colloidal) Manganese Dioxide During the Permanganate Ion Oxidation of Carbon-Carbon Double Bonds in Phosphate-Buffered Solutions<sup>1</sup>

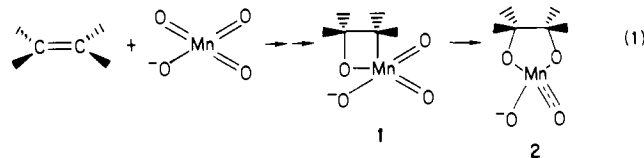
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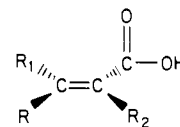
**Abstract:** The permanganate ion oxidation of the anions of propenoic acid (3), 2-methyl-2-propenoic acid (4), (*E*)-3-aryl-2-propenoic acids, (*E*)-2-butenoic acid (6), and (*E*)-3-methyl-2-butenoic acid (7) was studied in phosphate-buffered solutions. The influences of methyl substitution at the double bond and the effects of electron-releasing groups and electron-withdrawing groups on the rate of oxidation are discussed. The kinetic, spectral, and iodometric data are consistent with formation of a soluble (colloidal) manganese dioxide species which adsorbs phosphate ions on its surface.

Although permanganate ion has been extensively used and studied as an oxidant, there is considerable controversy concerning the oxidation state of the manganese species observed during the oxidation of carbon-carbon double bonds.<sup>3-30</sup> Theoretical cal-

culations<sup>27,28</sup> suggest that permanganate ion could react with carbon-carbon double bonds to give a metallocyclohexane (1)<sup>29</sup> which can rearrange to the five-membered cyclic hypomanganate [manganate(V)] diester 2. Formation of the cyclic manganate(V) diester is expected to be enhanced by the simultaneous formation of a triply-bonded spectator oxo group, which forms when two d orbitals are available for bonding to a single oxygen.<sup>27</sup>



We have observed spectrophotometrically (418 nm) the formation of a relatively stable manganese species during the permanganate ion oxidation of carbon-carbon double bonds.<sup>13-18</sup> Although this intermediate was regarded as a soluble (colloidal) manganese(IV) species (MnO<sub>2</sub>),<sup>6,17,18</sup> other reports have suggested that it is the long-sought elusive cyclic hypomanganate diester (2).<sup>8,9,21</sup> We now report additional evidence from the permanganate ion oxidation of the anions of propenoic acid (3), 2-methyl-2-propenoic acid (4), (*E*)-3-phenyl-2-propenoic acid (5) and its derivatives, (*E*)-2-butenoic acid (6), and (*E*)-3-methyl-2-butenoic acid (7) in phosphate-buffered solutions which also supports our previous assignment of soluble (colloidal) manganese dioxide to the observed manganese species (product).<sup>17,18</sup>



- 3, R = R<sub>1</sub> = R<sub>2</sub> = H  
 4, R = R<sub>1</sub> = H; R<sub>2</sub> = CH<sub>3</sub>  
 5, R = C<sub>6</sub>H<sub>5</sub>; R<sub>1</sub> = R<sub>2</sub> = H  
 6, R = CH<sub>3</sub>; R<sub>1</sub> = R<sub>2</sub> = H  
 7, R = R<sub>1</sub> = CH<sub>3</sub>; R<sub>2</sub> = H

## Experimental Section

Solutions were prepared immediately before use in water which had been deionized and then distilled from an all-glass Corning mega-pure apparatus. Appropriate quantities of KH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> to maintain pH and ionic strength were dissolved in the substrate solution. Ionic strength was also adjusted with KCl in some experiments. Standard

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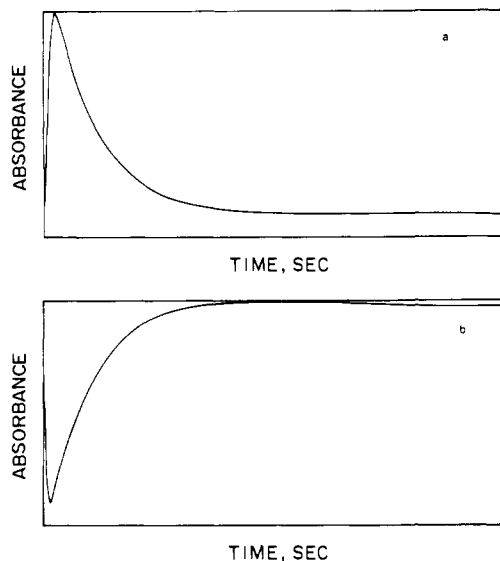
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**Figure 1.** (a) Typical curve for the disappearance of permanganate ion at 526 nm at 25.0 °C.  $[\text{MnO}_4^-] = 4.00 \times 10^{-4} \text{ M}$ ;  $[(E)\text{-}2\text{-butenoate}] = 4.00 \times 10^{-3} \text{ M}$ ;  $[\text{KH}_2\text{PO}_4] = [\text{Na}_2\text{HPO}_4] = 0.20 \text{ M}$ ; pH 6.86;  $\mu = 0.80$ . (b) Typical curve for the formation of manganese dioxide at 418 nm. Experimental conditions are the same as in part a.

(Titrisol) potassium permanganate solutions were used. The pH values were determined on an Altex  $\phi 60$  pH meter in the substrate solution before reaction and in the product mixture after oxidation.

Phosphate buffers were dried for 2 h at 110 °C and stored in a desiccator. Solid substrates were recrystallized from aqueous ethanol, and liquid substrates were fractionally distilled under reduced pressure. The physical and spectral properties of the substrates agreed with literature values.

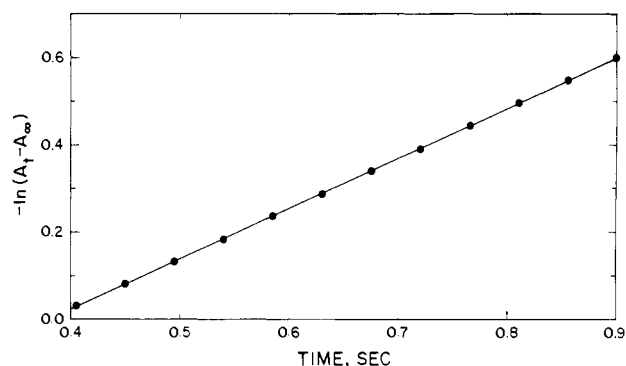
The kinetics were determined on a Durrum Model D-110 stopped-flow spectrometer which was connected to a Tracor-Northern 1710 multi-channel analyzer. The data were transferred to an IBM PC for analysis and printing. The pseudo-first-order rate constants ( $k_\psi$ ) for most of the (*E*)-3-aryl-2-propenoates were calculated by the computer program LSKINI.<sup>31</sup> The other rate constants were calculated by a first-order kinetic program on an IBM PC. All rate constants are the average of two or more experiments. Temperature was maintained with a Forma Model 2095-2 refrigerated and heated bath circulator.

Spectra of manganese dioxide were obtained on a Beckman ACTA III or a Cary 219 spectrophotometer by recording the absorbance vs. time curves at preselected wavelengths and/or by repetitive scanning of the ultraviolet-visible region.

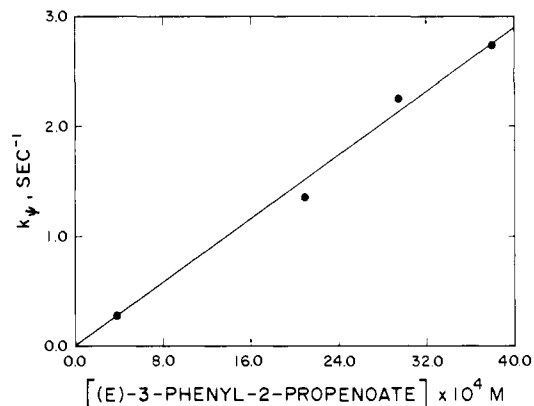
The oxidation state of manganese ( $\text{MnO}_2$ ) in the product mixture was determined by adding acidified (HCl) potassium iodide and titrating the iodine released against standard sodium thiosulfate solution.<sup>6,18</sup> In a typical procedure an alkene (3.4 mmol) was reacted with potassium permanganate ((1.5 g, 9.5 mmol) in distilled water with continuous stirring for 1 h. The product mixture was filtered through a sintered glass frit and the solid was washed with 250 mL of distilled water and 500 mL of dichloromethane and then dried for 12 h at 105 °C. Small portions (ca. 0.040 g) of the dried solid were accurately weighed, acidified with 50 mL of 2.0 M HCl, treated with excess KI (ca. 2 g), and titrated with 0.10 M sodium thiosulfate (Baker analyzed) in the presence of starch indicator to a transparent end point.

## Results

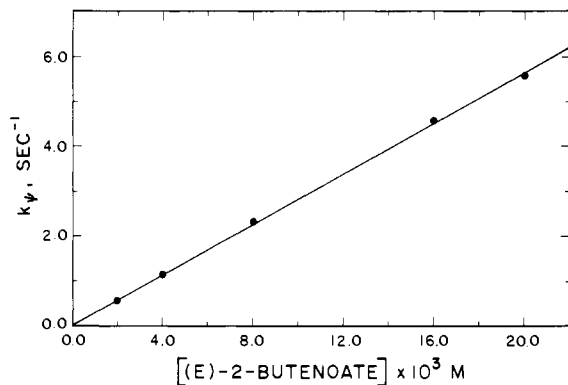
**Order of Reaction.** The kinetics of the permanganate ion oxidation of the anions of  $\alpha,\beta$ -unsaturated carboxylic acids 3-7 were determined under pseudo-first-order conditions in phosphate-buffered solutions.<sup>18</sup> The rate of disappearance of permanganate ion was monitored at 526 nm (Figure 1a), and the rate of formation of the manganese species was observed at 418 nm (Figure 1b). Pseudo-first-order rate constants ( $k_\psi$ ) were calculated from the slopes of plots of  $-\ln(A_t - A_\infty)$  (Figure 2) or  $-\ln(A_\infty - A_t)$  vs. time. A first-order dependence on the concentration of permanganate ion is suggested by the linearity of the pseudo-first-order plots and by the consistent values of the pseudo-first-order



**Figure 2.** Typical pseudo-first-order plot for the rate of disappearance of permanganate ion at 526 nm. Experimental conditions are the same as in Figure 1a.



**Figure 3.** Effects of (*E*)-3-phenyl-2-propenoate (**5**) concentration on the pseudo-first-order rate constants ( $k_\psi$ ) for the permanganate ion oxidation in 0.20 M  $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$  (pH 6.80) at 25.0 °C.



**Figure 4.** Effect of (*E*)-2-butenoate (**6**) concentration on the pseudo-first-order rate constants ( $k_\psi$ ) for the permanganate ion oxidation in 0.20 M  $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$  (pH 6.80) at 25.0 °C.

rate constant ( $k_\psi$ ) at 526 nm when the concentrations of (*E*)-3-phenyl-2-propenoate (**5**) or (*E*)-2-butenoate (**6**) and buffer were held constant and the concentration of permanganate ion was varied (Tables I and II). The consistent values of the second-order rate constant at different concentrations of **5** or **6** and constant buffer and permanganate ion concentration are in accord with a first-order dependence on the concentration of (*E*)-3-phenyl-2-propenoate (**5**) or (*E*)-2-butenoate (**6**). Plots of  $k_\psi$  vs. [anion of **5** or **6**] give straight lines which pass through the origin with slopes =  $k$ , which is indicative of a first-order dependence on the concentration of anion (Figures 3 and 4). Moreover, plots of  $\ln k_\psi$  vs.  $\ln$  [anion of **5** or **6**] were linear with slopes of 1.0

$$-d[\text{MnO}_4^-]/dt = k[\text{carboxylate ion}][\text{MnO}_4^-] \quad (2)$$

**Buffer Concentration and Ionic Strength.** Tables I and III show the effects of buffer concentration and ionic strength on the rate of permanganate ion oxidation of **5**, (*E*)-3-(4-methoxyphenyl)-

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**Table I.** Kinetic Data from the Permanganate Ion Oxidation of (*E*)-3-Phenyl-2-propenoates<sup>a</sup>

[( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CHCHCO <sub>2</sub> ] <sup>-</sup> , × 10 <sup>3</sup> M	[MnO <sub>4</sub> <sup>-</sup> ], × 10 <sup>4</sup> M	[KH <sub>2</sub> PO <sub>4</sub> ], <sup>b</sup> M	pH	μ <sup>c</sup>	k, <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>	
					418 nm	526 nm
3.80	0.40	0.20	6.65	0.80		569 ± 59
3.80	1.30	0.20	6.72	0.80	560 ± 42	637 ± 8
3.80	2.20	0.20	6.74	0.80	499 ± 15	584 ± 5
3.80	3.10	0.20	6.72	0.80	522 ± 18	588 ± 10
3.80	4.00	0.20	6.54	0.80	582 ± 51	494 ± 27
0.38	0.40 <sup>e</sup>	0.20	6.81	0.80		736 ± 13
2.09	0.40 <sup>e</sup>	0.20	6.73	0.80		493 ± 29
2.95	0.40 <sup>e</sup>	0.20	6.67	0.80		603 ± 69
3.80	4.00	0.05	6.70	0.20	405 ± 16	422 ± 17
3.80	4.00	0.10	6.77	0.40	599 ± 1	517 ± 12
3.80	4.00	0.30	6.76	1.20	727 ± 5	774 ± 2
3.80	2.20	0.40	6.76	1.60		613 ± 2
3.80	3.10	0.40	6.76	1.60		556
3.80	4.00	0.40	6.76	1.60	601 ± 48	618 ± 45
3.80	4.00	0.60	6.70	2.40	943 ± 24	880 ± 13
3.80 <sup>f</sup>	4.00	0.20	6.76	0.80	628 ± 92	430 ± 2
3.80 <sup>g</sup>	4.00	0.40	6.77	1.60	532 ± 5	801 ± 40
3.80 <sup>h</sup>	4.00	0.20	6.76	0.80	940 ± 10	767 ± 36
3.80 <sup>h</sup>	4.00	0.40	6.79	1.60	885 ± 22	1183 ± 32

<sup>a</sup> Temperature = 25.0 °C. <sup>b</sup> [KH<sub>2</sub>PO<sub>4</sub>] = [Na<sub>2</sub>HPO<sub>4</sub>]. <sup>c</sup> Ionic strength. <sup>d</sup> Second-order rate constant =  $k = k_{\psi}/[\text{anion}]$ . <sup>e</sup> Rate of formation of manganese dioxide is not observable at [MnO<sub>4</sub><sup>-</sup>] = 4.0 × 10<sup>-5</sup> M. <sup>f</sup> 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHCHCO<sub>2</sub><sup>-</sup> substrate. <sup>g</sup> 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CHCHCO<sub>2</sub><sup>-</sup> substrate.

**Table II.** Kinetic Data from the Permanganate Ion Oxidation of Anions of α,β-Unsaturated Carboxylic Acids<sup>a</sup>

substrate	compd no.	[anion], × 10 <sup>3</sup> M	[KH <sub>2</sub> PO <sub>4</sub> ], <sup>b</sup> M	pH	μ <sup>c</sup>	k, <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>	
						418 nm	526 nm
propenoate	3	4.0	0.20	6.79	0.80		442 ± 1
2-methyl-2-propenoate	4	4.0	0.20	6.84	0.80		450 ± 2
( <i>E</i> )-2-butenate	6	2.0	0.20	6.79	0.80	306 ± 4	277 ± 3
	6	4.0	0.20	6.81	0.80	279 ± 1	286 ± 1
	6	8.0	0.20	6.80	0.80	306 ± 10	290 ± 1
	6	16.0	0.20	6.76	0.80	362 ± 2	286 ± 1
	6	20.0	0.20	6.74	0.80	378 ± 6	280 ± 2
	6	4.0	0.05	6.76	0.20	209 ± 1	190 ± 1
	6	4.0	0.40	6.84	1.60	384 ± 2	399 ± 4
	6	4.0	0.60	6.84	2.40	578 ± 4	521 ± 2
3-methyl-2-butenate	7	4.0	0.20	6.79	0.80	67 ± 1	57 ± 1

<sup>a</sup> Temperature = 25.0 °C; [MnO<sub>4</sub><sup>-</sup>] = 4.00 × 10<sup>-4</sup> M. <sup>b</sup> [KH<sub>2</sub>PO<sub>4</sub>] = [Na<sub>2</sub>HPO<sub>4</sub>]. <sup>c</sup> Ionic strength. <sup>d</sup> Second-order rate constant =  $k = k_{\psi}/[\text{anion}]$ .

**Table III.** Effects of Buffer Concentration and Ionic Strength on the Rate of Permanganate Ion Oxidation of (*E*)-3-Phenyl-2-propenoate (**5**)<sup>a</sup>

[( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CHCHCO <sub>2</sub> ] <sup>-</sup> , × 10 <sup>3</sup> M	[MnO <sub>4</sub> <sup>-</sup> ], × 10 <sup>4</sup> M	[KH <sub>2</sub> PO <sub>4</sub> ], <sup>b</sup> M	pH	μ <sup>c</sup>	k, <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>
					526 nm
3.80	4.00	0.025	6.54	0.80	704 ± 3
3.80	4.00	0.05	6.60	0.80	704 ± 2
3.80	4.00	0.075	6.51	0.80	715 ± 1
3.80	4.00	0.10	6.62	0.80	717 ± 9
4.00	4.00	0.20	6.76	0.80	691 ± 1

<sup>a</sup> Temperature = 25.0 °C. <sup>b</sup> [KH<sub>2</sub>PO<sub>4</sub>] = [Na<sub>2</sub>HPO<sub>4</sub>]. <sup>c</sup> Ionic strength adjusted with KCl. <sup>d</sup> Second-order rate constant =  $k = k_{\psi}/[\text{anion}]$ . Calculated on IBM PC first-order kinetics program.

2-propenoate, and (*E*)-3-(4-methylphenyl)-2-propenoate. The effects of buffer concentration on the rate of permanganate ion oxidation of (*E*)-2-butenate (**6**) are shown in Table II.

**Thermodynamic Parameters.** Values of 14.7 and 57.0 kJ mol<sup>-1</sup> and -152.7 J K<sup>-1</sup> mol<sup>-1</sup> were obtained for  $E_a$ ,  $\Delta G^\ddagger$ , and  $\Delta S^\ddagger$ , respectively, for the permanganate ion oxidation of **5** in 0.05 M buffer at 20.0 and 30.0 °C.

**Substituent Effects.** Tables II and IV show the effects of substituents on the rate of permanganate ion oxidation of the carbon-carbon double bonds in α,β-unsaturated carboxylates.

**Oxidative State of Manganese after Oxidation.** The oxidation state of manganese in the product mixtures immediately after the reduction of permanganate ion by α,β-unsaturated carboxylate ions was determined titrimetrically (Table V).<sup>32</sup> Application of this iodometric method to manganese dioxide (Mallinckrodt AR) gave an oxidation state of 3.97.

**Table IV.** Kinetic Data for the Permanganate Ion Oxidation of Substituted (*E*)-3-Aryl-2-propenoates<sup>a</sup>

Ar in [( <i>E</i> )-ArCH=CHCO <sub>2</sub> ] <sup>-</sup>	k, <sup>b</sup> M <sup>-1</sup> s <sup>-1</sup>
	526 nm
C <sub>6</sub> H <sub>5</sub>	618 ± 45
2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	881 ± 3
3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1335 ± 190
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1183 ± 3
2-ClC <sub>6</sub> H <sub>4</sub>	1205 ± 8
4-ClC <sub>6</sub> H <sub>4</sub> <sup>c</sup>	1038 ± 3
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	801 ± 40
3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	1045 ± 1
4- <i>i</i> -C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> <sup>c</sup>	966 ± 12

<sup>a</sup> Temperature = 25.0 °C; [MnO<sub>4</sub><sup>-</sup>] = 4.00 × 10<sup>-4</sup> M; [KH<sub>2</sub>PO<sub>4</sub>] = [Na<sub>2</sub>HPO<sub>4</sub>] = 0.40 M; [(*E*)-ArCH=CHCO<sub>2</sub>]<sup>-</sup> = 3.8 × 10<sup>-3</sup> M; μ = 1.60. <sup>b</sup> Second-order rate constant =  $k = k_{\psi}/[(E)\text{-ArCHCHCO}_2^-]$ . <sup>c</sup> [MnO<sub>4</sub><sup>-</sup>] = 0.4 × 10<sup>-4</sup> M; [substrate] = 0.38 × 10<sup>-3</sup> M.

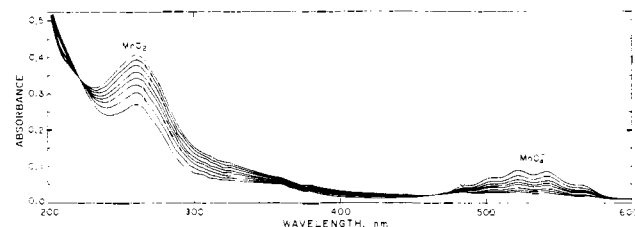
**Spectra of Manganese Species after Oxidation.** The observed manganese species in the product mixture after the reduction of

(32)  $\text{MnO}_2 + 2\text{I}^- + 4\text{H}^+ \rightarrow \text{I}_2 + \text{Mn}^{2+} + 2\text{H}_2\text{O}$ ;  $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$ .

**Table V.** Data for the Reduction of Permanganate Ion by Carbon-Carbon Double Bonds<sup>a</sup>

substrate	compd no.	slope <sup>b</sup>	oxidation state <sup>c</sup>
uracil			3.60 <sup>d</sup>
5-methyluracil			3.40 <sup>d</sup>
6-methyluracil			3.77 <sup>d</sup>
5-fluorouracil			3.33 <sup>d</sup>
propenoate	3	6.2	3.37
2-methyl-2-propenoate	4	7.0	3.39
( <i>E</i> )-3-phenyl-2-propenoic acid	5		3.08 <sup>e</sup>
( <i>E</i> )-3-phenyl-2-propenoate	5	5.0	3.08
( <i>E</i> )-2-butenolate	6	6.6	3.46
3-methyl-2-butenolate	7	5.9	3.43

<sup>a</sup> Temperature = 25.0 °C; [KH<sub>2</sub>PO<sub>4</sub>] = [Na<sub>2</sub>HPO<sub>4</sub>] = 0.20 M;  $\mu$  = 0.80. <sup>b</sup> Slope for plot of  $-\log(\text{absorbance})$  vs.  $\log \lambda$ . <sup>c</sup> Oxidation state of manganese species determined titrimetrically. <sup>d</sup> In phosphate buffers, ref 17 and 18. <sup>e</sup> In perchloric acid, ref 6.

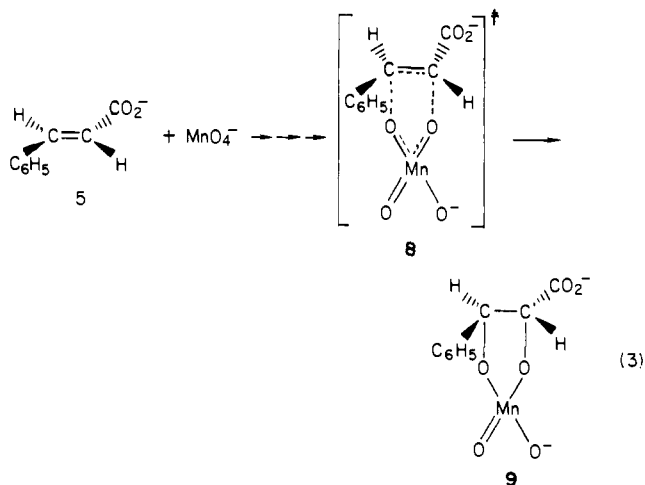


**Figure 5.** Successive UV-vis spectra (chart speed 10 nm s<sup>-1</sup>) for the reaction of  $4.00 \times 10^{-5}$  M 3-methyl-2-butenolate (7) and  $4.00 \times 10^{-5}$  M KMnO<sub>4</sub> in 0.20 M KH<sub>2</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub>. The reference cell contained 0.20 M KH<sub>2</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub>. Isosbestic point at 465 nm.

permanganate ion by  $\alpha,\beta$ -unsaturated carboxylates exhibited absorption maxima at about 260 to 280 nm and isosbestic points near 465 nm (Table V; Figure 5).<sup>14-16</sup>

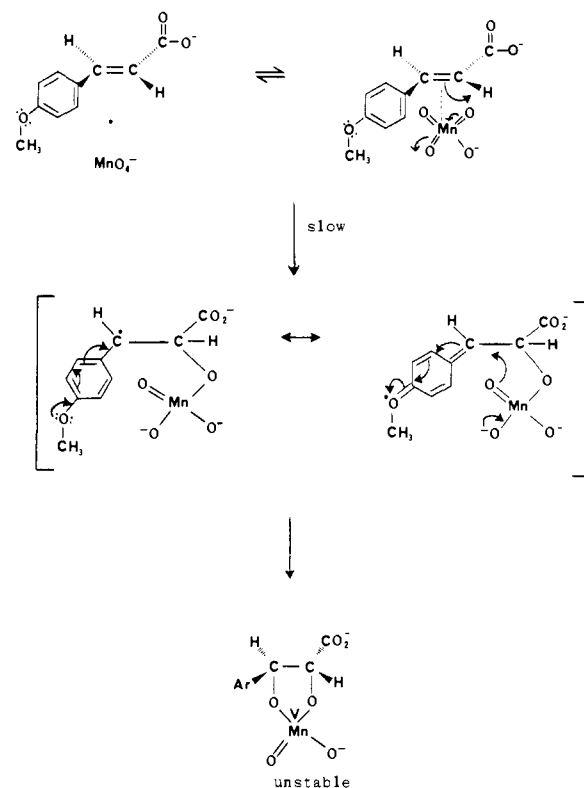
### Discussion

The data presented above are consistent with a concerted bimolecular reaction between the carbon-carbon double bond and permanganate ion. Charge-transfer complexes (CTC) and/or metallocyclooxetanes **1** may be involved prior to the rate-determining step, and the long sought elusive cyclic manganese(V) diester **9** is also a plausible intermediate (eq 1 and 3). Moreover, the small positive  $\rho$  value, the large negative entropy of activation, and the inverse secondary kinetic deuterium isotope effects previously reported<sup>7,9,11,12</sup> for the oxidation of **5** are also consistent with an activated complex which resembles **8**.

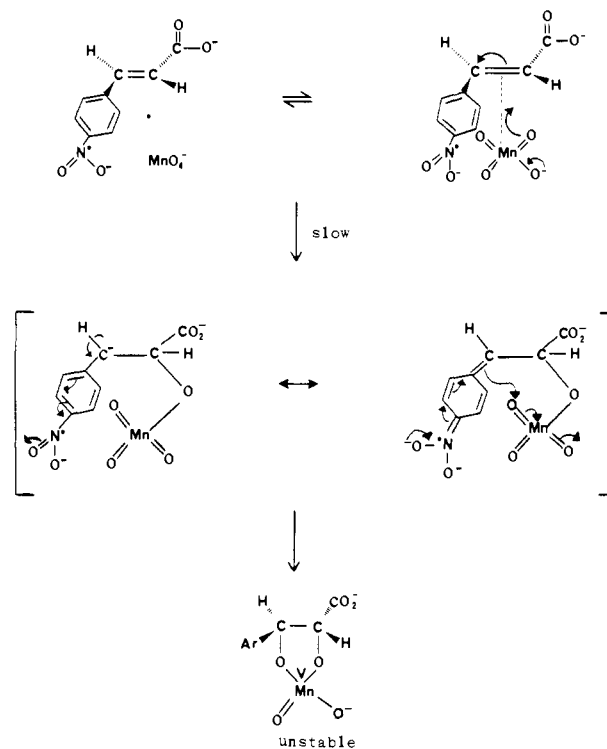


The small effects of substituents on the rates of permanganate ion oxidation of (*E*)-3-aryl-2-propenoates are of interest since both electron-releasing and electron-withdrawing groups increase the rate of oxidation (Table III; Scheme I and II). These data suggest the following: (1) an ambiphilic nature for permanganate ion; (2) an activated complex which is more stabilized than reactant

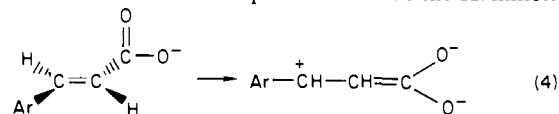
### Scheme I



### Scheme II



by electron-withdrawing or electron-releasing groups; (3) a reactant that is stabilized by electron-releasing groups; and (4) a reactant that is destabilized by electron-withdrawing groups (eq 4).<sup>8,9,11,12</sup> Lee and Brown<sup>9</sup> have pointed out that the Hammett

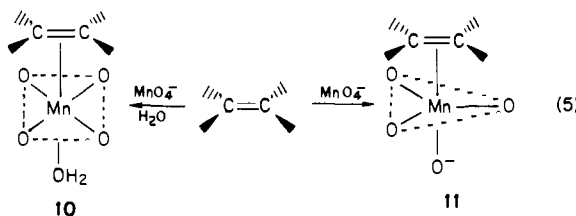


plot for the permanganate ion oxidation of 1,2-diarylethenes in

aqueous dioxane is concave upward ( $\rho = 1.0$ ), which is indicative of a change in mechanisms.<sup>33,34</sup>  $\rho$  values of 0.95 and -0.6 have been observed for the permanganate ion oxidation of methyl cinnamates by tetrabutylammonium permanganate in dichloromethane<sup>9</sup> and of alkyl vinyl ethers by permanganate ion in aqueous tetrahydrofuran, respectively.<sup>9,23</sup>

Table IV shows that permanganate ion reacts fastest with the least substituted double bond (**3**) and that substitution of a methyl group for a hydrogen at the  $\alpha$ -carbon atom of **3** (to give **4**) does not affect the rate.<sup>13,20,23,35,36</sup> Substitution of a methyl group for a  $\beta$  hydrogen in **3** (to give **5**) slows the rate by a factor of 0.65, while substitution of a second methyl group at the  $\beta$ -carbon atom (to give **6**) slows the rate by a factor of 0.12.<sup>13,14</sup> These relative reactivities, which are influenced by steric factors, are consistent with the results of Sharpless and Williams,<sup>36</sup> who oxidized alkenes with permanganate ion in ethanoic anhydride, and of Simándi and Jáky,<sup>5</sup> who oxidized methyl-substituted maleic and fumaric acids in aqueous acid media. Different relative reactivity data have been reported for the permanganate ion oxidation of enol ethers.<sup>23</sup>

The permanganate ion oxidation of olefins may involve an initial interaction between the double bond and the metal to give an octahedral (**10**) or a trigonal-bipyramidal (**11**) organometallic complex which can rearrange to a metallocyclohexane (**1**) or to a five-membered cyclic manganate(V) diester (eq 1 and 7). It is of interest to note that Sharpless and coworkers<sup>29</sup> suggested that



organometallic intermediates are involved in the oxidation of olefins by oxo metals. Thus, formation of  $\pi$  (**10**, **11**) and/or  $\sigma$  (**1**) complexes should precede the formation of manganate(V) diester **2**. If the cyclic intermediate **2** is relatively stable, the transition state should resemble the  $\pi$  or  $\sigma$  metal complex. The structure-activity relationship observed in the permanganate ion oxidations of carbon-carbon double bonds is similar to those observed for the Pd<sup>II</sup>-catalyzed oxidation of olefins and for the stabilities of Ag<sup>+</sup>-olefin complexes.<sup>1,35,37-39</sup> The Ag<sup>+</sup> and Pd<sup>II</sup> reactions proceed via metal complexation with the carbon-carbon double bond.

The increase in rate of oxidation with increasing ionic strength (Tables II and III) is consistent with a reaction between two negatively charged ions. A plot of  $\log(k/k_0)$  vs. the square root of ionic strength is linear. The energies and entropies of activation are similar in magnitude to the values observed for the permanganate ion oxidation of carbon-carbon double bonds in aqueous and in nonaqueous systems.

Owing to the controversy concerning the reported oxidation states of the observed manganese species from the permanganate ion oxidation of carbon-carbon double bonds in different systems, the reaction was studied at 418 and 526 nm. Since permanganate ion is almost transparent at 418 nm and shows a maximum of absorption at 526 nm, one can express the absorbance ( $A$ ) at 418 nm as

$$A_{418} = \epsilon_{\text{MnO}_2}^{418}(c_0 - c_t) \quad (6)$$

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(35) Structural effects (methyl substitution and phenyl conjugation) which stabilize double bonds usually give rate accelerations in electrophilic addition reactions.<sup>13</sup>

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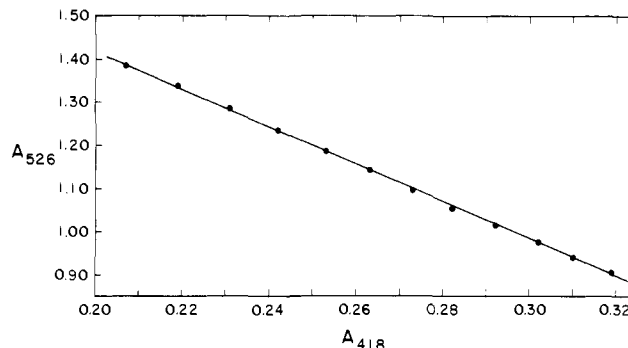


Figure 6. Absorbance at 526 nm vs. absorbance at 418 nm for the (*E*)-2-butenate (**6**,  $4.00 \times 10^{-3}$  M) reduction of permanganate ion ( $4.00 \times 10^{-4}$  M) in 0.20 M  $\text{KH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$ .

where  $\epsilon_{\text{MnO}_2}^{418}$  is the molar absorptivity of the manganese species at 418 nm,  $c_0$  is the initial permanganate ion concentration, and  $c_t$  is the concentration of permanganate ion at time  $t$ .

Since both permanganate ion and the observed manganese species absorb light at 526 nm, the absorbance at this wavelength is given by the following equation:

$$A_{526} = \epsilon_{\text{MnO}_4^-}^{526}c_t + \epsilon_{\text{MnO}_2}^{526}(c_0 - c_t) \quad (7)$$

where  $\epsilon_{\text{MnO}_4^-}^{526}$  and  $\epsilon_{\text{MnO}_2}^{526}$  are respectively the molar absorptivities of permanganate ion and the observed manganese species at 526 nm. From eq 6 and 7, it is easy to deduce:

$$A_{526} = \epsilon_{\text{MnO}_4^-}^{526}c_0 + \left[ \frac{\epsilon_{\text{MnO}_4^-}^{526} - \epsilon_{\text{MnO}_2}^{526}}{\epsilon_{\text{MnO}_2}^{418}} \right] A_{418} \quad (8)$$

Thus a plot of  $A_{526}$  against  $A_{418}$  is expected to be linear (Figure 6). Linear plots were obtained from the permanganate ion oxidation of **3-7**, uracil, 5-fluorouracil, and 5-methyluracil (thymine). The linear relationship between absorbances at 418 and 526 nm also indicates that product formation occurs at the same rate as the reaction of permanganate ion<sup>40</sup> and that the species which absorbs light at 418 and 526 nm is soluble (colloidal) manganese dioxide.<sup>41-43</sup>

If the product (manganese dioxide) were an ordinary non-colloidal species,  $\epsilon_{418}$  and  $\epsilon_{526}$  would be constant and a linear relationship would be expected. On the other hand, if the product is colloidal manganese dioxide, the spectrum will be mainly due to the scattering of light (Rayleigh's law:  $A = C/\lambda^4$ ) instead of absorption on light.<sup>44</sup> Thus,  $\epsilon_{418}$  and  $\epsilon_{526}$  will appear to increase in time as a consequence of flocculation of colloidal species and a decrease in the absolute value of the slope in the  $A_{418}$  vs.  $A_{526}$

(40) It is possible that permanganate ion is converted to highly unstable manganate(V) which goes very rapidly to manganese dioxide. This possibility is also consistent with the isosbestic points.

(41) The  $d^3$  electronic configuration of the manganese(IV) oxidation state is inherently inert and is dominated by  $\text{MnO}_2$ . Although stable manganese(IV) complexes may be polymeric, an oxomanganese(IV) cluster incorporating the tridentate macrocyclic amine 1,4,7-triazacyclonane (tacn) with an adamantane-like geometry has been characterized.<sup>42,43</sup>

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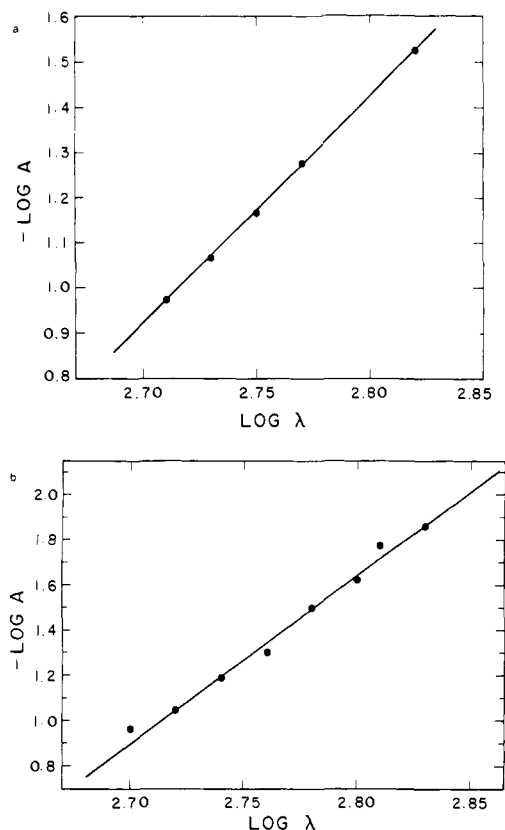
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(44) If Rayleigh's law ( $A = C/\lambda^4$ ) holds, the slope of the line should equal to four. However, the slopes are generally greater than four which implies

$$\log A = \log C_t - (4 + \alpha) \log \lambda$$

$$A = C_t/\lambda^{(4+\alpha)}$$

where  $A$  is the observed absorbance and  $C_t + \alpha$  are constants which depend on the properties of soluble (colloidal) manganese dioxide.



**Figure 7.** (a)  $-\log$  absorbance vs.  $\log \lambda$  for the product ( $\text{MnO}_2$ ) obtained from the oxidation of (*E*)-3-phenyl-2-propenoate (**5**,  $3.80 \times 10^{-3}$  M) by permanganate ion ( $4.00 \times 10^{-4}$  M) in 0.20 M  $\text{KH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$  at 25.0 °C. Slope = 5.1 (correlation coefficient = 0.999). (b)  $-\log$  absorbance vs.  $\log \lambda$  for the product ( $\text{MnO}_2$ ) obtained from the permanganate ion ( $4.00 \times 10^{-4}$  M) oxidation of (*E*)-2-butenate (**6**,  $4.00 \times 10^{-3}$  M) in 0.20 M  $\text{KH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$  at 25.0 °C. Slope = 7.5 (correlation coefficient = 0.997).

plot will yield a concave curve. However, this is not observed. Linear relationships are observed in dilute (0.05 M) and more concentrated (0.60 M) phosphate buffer solutions (Figure 6).

The apparent constancy of  $\epsilon_{418}$  and  $\epsilon_{526}$  in phosphate buffer solution may be due to the stabilization of aqueous particles of

colloidal manganese dioxide via adsorption of phosphate anions on their surface. Consequently, the flocculation process is slowed owing to the high density of negative electrostatic charge on the surface of the colloidal particles. If this hypothesis is true, the higher the concentration of phosphate ions in the system the more constant will be the apparent molar absorptivities  $\epsilon_{418}$  and  $\epsilon_{526}$  and the closer will be the  $A_{526}$  vs.  $A_{418}$  plot to a linear relationship. Moreover, one can predict that the absolute value of the slope of the plot  $A_{526}$  vs.  $A_{418}$  will be higher in the presence of concentrated phosphate ions than in the presence of diluted phosphate ions. In the former case, the size of the colloidal particles should be smaller since the flocculation process has been almost suppressed and the apparent molar absorptivities ( $\epsilon_{418}$  and  $\epsilon_{526}$ ) of scattering of light are smaller.

A linear relationship between  $-\log A$  and  $\log \lambda$  is expected if the soluble manganese dioxide species is present in the form of colloidal particles (Rayleigh's law). Plots of  $-\log A$  vs.  $\log \lambda$  were all linear with slopes greater than the theoretical value of 4 (Figure 6 and Table IV).<sup>11,25,45-47</sup> Thus, it can be seen that the available data are consistent with the formation of soluble (colloidal) manganese dioxide as the observed inorganic product during the permanganate ion oxidation of carbon-carbon double bonds (Figure 7).<sup>9,17,18,26,48-51</sup>

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(45) The manganese dioxide can also be stabilized by absorption of alkenes on its surface.<sup>11,46,47</sup>

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