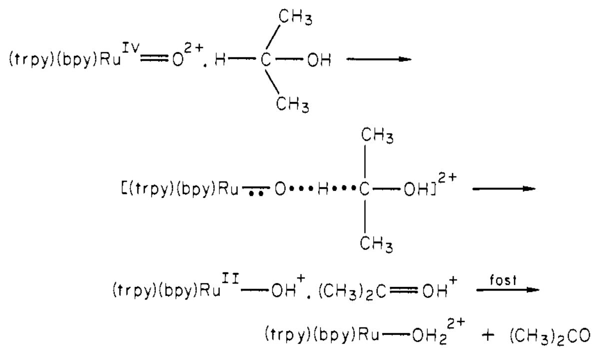
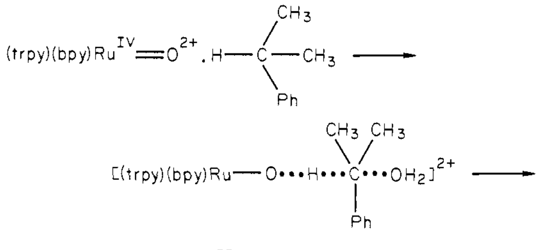

(17)


(18)

in water are within a few kilocalories of each other within the range −20 to −25 kcal/mol.[9b] Given the similarity in ΔG between the two reactions, if the same σ-C–H "lead-in" pathway exists for both substrates, a deciding factor in determining relative rates could be the electronic influence of the adjacent phenyl group. On an energy surface dominated by hydride transfer and the buildup of positive charge, electronic stabilization by the adjacent phenyl group could play a major role in determining rate constants. The importance of an adjacent aryl group is easily seen synthetically, as shown, for example, by the selective α-carbon oxidation of the ethylbenzene derivative in eq 2.

Given the proven catalytic capabilities of the $Ru(trpy)(bpy)O^{2+}$, $Ru(trpy)(bpy)OH_2^{2+}$ couple, the rate information obtained here has important implications for synthesis, and the following points are worth noting: (1) Rate discriminations based on functional group types that point to a clear element of oxidative selectivity are beginning to emerge. (2) For substrates like aromatic hydrocarbons, where groups must be added as a consequence of oxidation, strong solvent or added nucleophile effects are to be expected. (3) In weakly nucleophilic solvents the addition of added nucleophiles could lead to oxidatively catalytic pathways like

$$ArCHR_2 + D \xrightarrow{-H:^-} ArC(D^+)R_2$$

and a general route for the direct oxidative insertion of the added group D into the substrate.

Acknowledgement is made to the National Science Foundation under Grant CHE-8002433 for support of this research.

Registry No. p-$NaO_2CC_6H_4CH(CH_3)_2$, 1009-60-5; p-$NaO_2CC_6H_4CH_2CH_3$, 2046-83-5; p-$NaO_2CC_6H_4CH_3$, 17264-54-9; $C_6H_5CH(CH_3)_2$, 98-82-8; $C_6H_5CH_3$, 108-88-3; $Ru(trpy)(bpy)O^{2+}$, 73836-44-9.

Oxidation of Hydrocarbons. 11. Kinetics and Mechanism of the Reaction between Methyl (*E*)-Cinnamate and Quaternary Ammonium Permanganates

Donald G. Lee* and Keith C. Brown

Contribution from the Department of Chemistry, The University of Regina, Regina, Saskatchewan, Canada S4S 0A2. *Received December 21, 1981*

Abstract: A study of the reaction of methyl (*E*)-cinnamate with quaternary ammonium permanganates in methylene chloride solutions has been completed. The rate of reaction is fastest for those ions which permit the interionic distance in the quaternary ammonium ion pair to be minimized. The Hammett ρ value for the reaction is 0.95 at 20 °C, and an inverse secondary deuterium isotope effect is observed at the β-position but not at the α-position. The sign of the ρ value for this reaction is in direct contrast to the reported value (−0.6) for the oxidation of alkyl vinyl ethers in aqueous dioxane solutions. On the other hand, the fact that the activation parameters for the two reactions are almost identical suggests that the reaction mechanisms cannot be widely divergent. An attempt has been made to visualize a mechanism in which the reactions can proceed through similar intermediates but via either an electron-rich or an electron-deficient transition state depending on the demands of the substituents. The apparent change in mechanism is considered to be simply a reflection of nature's ability to find the lowest energy surface between two points.

Introduction

The mechanism of the reaction between carbon–carbon double bonds and permanganate ion has been a subject of interest for nearly one century.[1] Wagner,[2] noting that the oxidation of unsaturated dicarboxylic acids by basic permanganate solutions resulted in the syn addition of two hydroxyl groups to the double bond, suggested that the intermediate in the reaction could be a cyclic manganate(V) diester, **1**, which would undergo hydrolysis with liberation of a diol in aqueous alkaline solutions (eq 1).

In more modern times Wiberg and Saegebarth[3] substantiated this mechanism by showing, with the aid of isotopic tracers, that

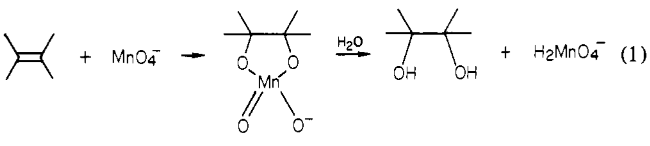
---

[1] Stewart, R. "Oxidation Mechanisms"; W. A. Benjamin: New York, 1964; p 62.

[2] Wagner, G. *J. Russ. Phys. Chem. Soc.* **1895**, *27*, 219.

[3] Wiberg, K. B.; Saegebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 2822.

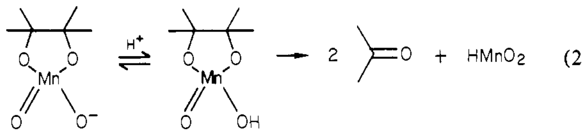
0002-7863/82/1504-5076$01.25/0


(1)

1

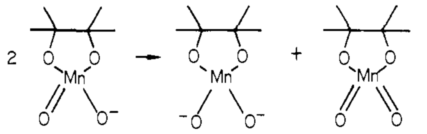
the oxygen in the diol came from permanganate and not from the solvent.

This mechanism also accounts for the formation of cleavage products which are found when the reaction is carried out under acidic conditions.[4] Protonation of **1** would increase the oxidation potential of manganate(V)[5] and provoke an oxidative decomposition as depicted in eq 2.


(2)

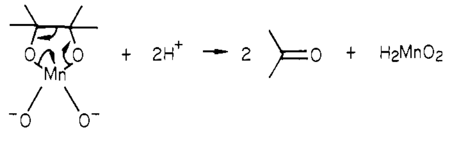
1

Wiberg[6] and Brownridge[7] also observed (independently) that intermediates can be detected when crotonic or cinnamic acid is oxidized by permanganate. Although it was initially believed that these intermediates were the previously proposed cyclic manganate(V) diesters, **1**, other workers[8,9] subsequently presented evidence which they interpreted as indicating that the detectable intermediates were actually in a +4 oxidation state. A manganate(IV) intermediate could be formed in a number of ways, the most direct being a rapid disproportionation of the manganate(V) diester (eq 3) as suggested by Wolf, Ingold, and Lemieux.[10]

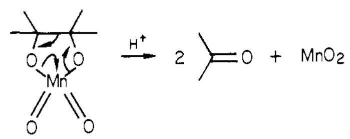

(3)

2 3

The intermediates **2** and **3** could then undergo rapid oxidative decompositions giving Mn^{2+} and molecular MnO_2 (alleged to be the detectable intermediate[8,9]) as in eq 4 and 5.

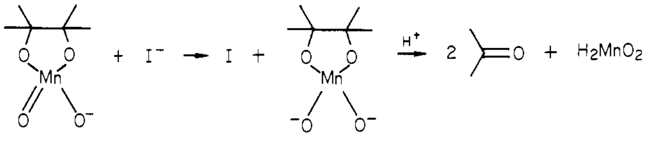

(4)

2


(5)

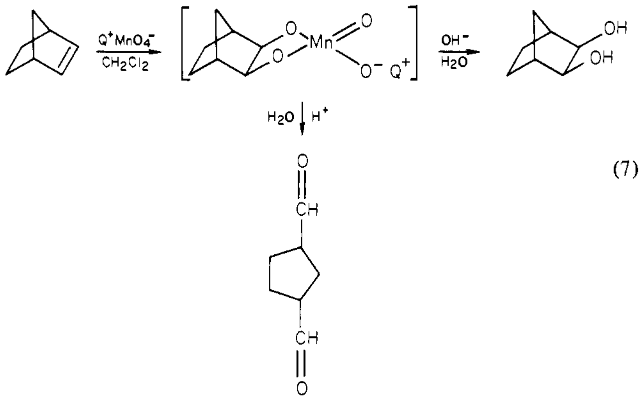
3

The quantitative data on which this argument rests is the observation that the intermediate could be reduced, under acidic conditions, by iodide ion with the formation of 1 equiv (0.5 mol) of iodine per mole of permanganate consumed. Since MnO_2 is reduced to Mn^{2+} by 2 equiv of iodide ion, the above reaction sequence appears to be consistent with the experimental data. However there are other quite plausible reaction sequences that also result in the formation of 1 equiv of iodide without involving MnO_2. For example, it is possible that the manganate(V) diester, **1**, would accept one electron from I^- to give a reactive manganate(IV) diester, **2**, which could undergo a rapid oxidative decomposition directly to Mn^{2+} as in eq 6.


2

(6)

In fact, there are several experimental observations that are more consistent with reaction 2 than the sequence portrayed in eq 3–5. First, the reaction is very simple from a spectrophotometric point of view; i.e., Freeman[9] has shown that excellent isosbestic points are obtained when the progress of the reaction is monitored by using absorption spectroscopy. This suggests that the reaction does not involve a complicated sequence of events as suggested by Jāky and Simāndi.[8] Second, a scrutiny of the published data[9] reveals that the amount of iodide required to titrate the intermediate is very often greater than the theoretical amount that would be needed to reduce molecular manganese dioxide. In some cases the excess required seems to be well outside the limits of experimental error.[9] Third, as will be shown, the intermediate detected in nonaqueous solvents has the same spectral characteristics as the one found in aqueous solutions, and an examination of its reactions provides unequivocal proof that it cannot be molecular manganese dioxide. The identity of the products is dependent on the way in which the solution is treated *after* the intermediate forms: if the solution containing the intermediate is treated with aqueous base, diols are produced; if it is treated with aqueous acid, cleavage products are obtained.[11] In the event that the intermediate was just molecular manganese dioxide, the way in which the solution was treated following its formation could have no effect on the nature of the products obtained. Instead, it is more likely that the intermediate is a manganate(V) diester as illustrated by eq 7.[11]


(7)

Sharpless[12] and his co-workers have pointed out that the reaction mechanism may be further complicated by the intervention of an organometallic complex between the reactants and the first detectable intermediate (eq 8).

The evidence suggesting this possibility comes from a comparison with an analogous reaction (between olefins and chromyl chloride) which proceeds via a similar organometallic intermediate[12] and from a consideration of the fact that carbon–carbon double bonds are not usually subject to nucleophilic attack as

---

(4) Allen, M. B.; Ruben, S. *J. Am. Chem. Soc.* **1942**, *64*, 948. Simāndi, L. I.; Jāky, M. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1856. Jāky, M.; Simāndi, L. I.; Maros, L.; Molnār-Perl, I. *Ibid.* **1973**, 1565.

(5) Stewart, R. In "Oxidation in Organic Chemistry, Part A"; Wiberg, K. B., Ed.; Academic Press: New York, 1965; p 35.

(6) Wiberg, K. B.; Deutsch, C. J.; Roček, J. *J. Am. Chem. Soc.* **1973**, *95*, 3034.

(7) Lee, D. G.; Brownridge, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 3033; **1974**, *96*, 5517.

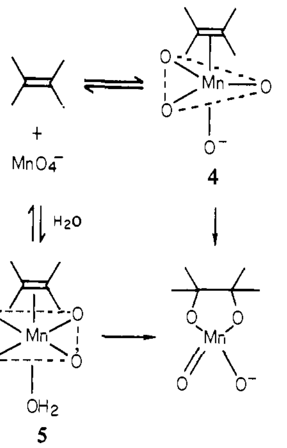
(8) Simāndi, L. I.; Jāky, M. *J. Am. Chem. Soc.* **1976**, *98*, 1995.

(9) Freeman, F.; Fuselier, C. O.; Armstead, C. R.; Dalton, C. E.; Davidson, P. A.; Karchefski, E. M.; Krochman, D. E.; Johnson, M. N.; Jones, N. K. *J. Am. Chem. Soc.* **1981**, *103*, 1154.

(10) Wolf, S.; Ingold, C. F.; Lemieux, R. U. *J. Am. Chem. Soc.* **1981**, *103*, 938.

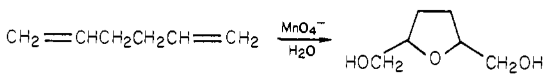
(11) Ogino, T.; Mochizuki, K. *Chem. Lett.* **1979**, 443.

(12) Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.



(8)

implied by eq 1. Instead it is more likely that the initial interaction would be between the electropositive metal and the electron-rich double bond as in eq 8.[13] As this equation indicates, two possible structures for the organometallic complex could be considered, a trigonal bipyramid, **4**, or an octahedron, **5**. Of these two possibilities there is both theoretical and experimental evidence favoring the octahedral complex, **5**, which incorporates solvent as an additional ligand. The experimental evidence favoring this structure comes from work by Wolf and Ingold,[14] who studied the oxidation of 1,5-hexadiene in oxygen-18 enriched water. From an analysis of the product of this reaction (eq 9) they found that



(9)

17% of the oxygen in the product came from the solvent and the stereochemistry of the reaction indicated that this oxygen must have been delivered from the coordination shell of the manganese, thus establishing that manganese expands its coordination shell by incorporation of one molecule of water as the reaction proceeds. Furthermore, since **5** is an 18-electron organometallic system, whereas **4** is a 16-electron system, theoretical considerations would also favor **5**.[15]

In the present work we have attempted to expand our understanding of this reaction by studying the rates at which various quaternary ammonium permanganates react with methyl cinnamate in anhydrous methylene chloride solutions.

Experimental Section

The quaternary ammonium permanganates were prepared from the reaction of quaternary ammonium chlorides with potassium permanganate by using published procedures.[16] They were crystallized to analytical purity by using a mixed-solvent system consisting of methylene chloride and toluene.[17]

Substituted methyl cinnamates were prepared by methylation of the corresponding cinnamic acids and purified by distillation or recrystallization. The physical properties of these esters corresponded well with those reported in the literature. Cinnamic-α-d and cinnamic-β-d acids were prepared essentially as previously described[18] and then methylated.

Methylene chloride, which was used as the solvent in the kinetic runs, was purified by treatment with tetrabutylammonium permanganate followed by fractional distillation from the solution.

In a typical kinetic experiment methyl *m*-methylcinnamate (0.734 g, 4.17×10^{-3} mol), dissolved in 5.0 mL of methylene chloride, and tetra-*n*-butylammonium permanganate (0.0139 g, 3.85×10^{-5} mol), dissolved in 100 mL of the same solvent, were first thermostated at 20.0 °C for 15 min. Then an aliquot (3.0 mL) of the oxidant solution was transferred

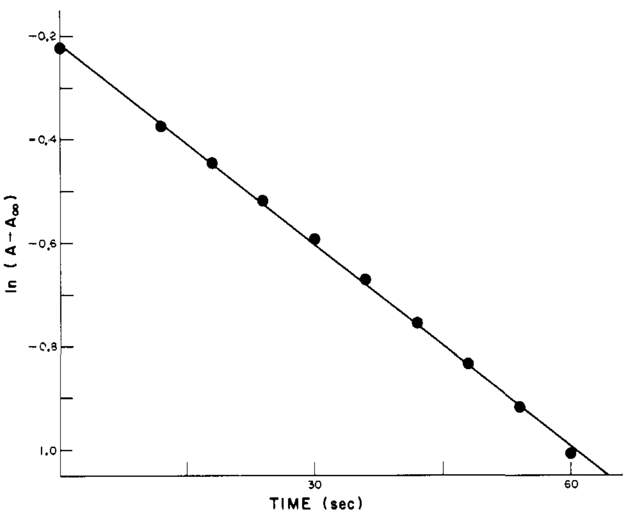


Figure 1. Typical pseudo-first-order plot for the oxidation of methyl cinnamate (8.44×10^{-3} M) by methyltributylammonium permanganate (4.42×10^{-4} M) in methylene chloride at 20.0 °C (slope = -0.781 s^{-1}).

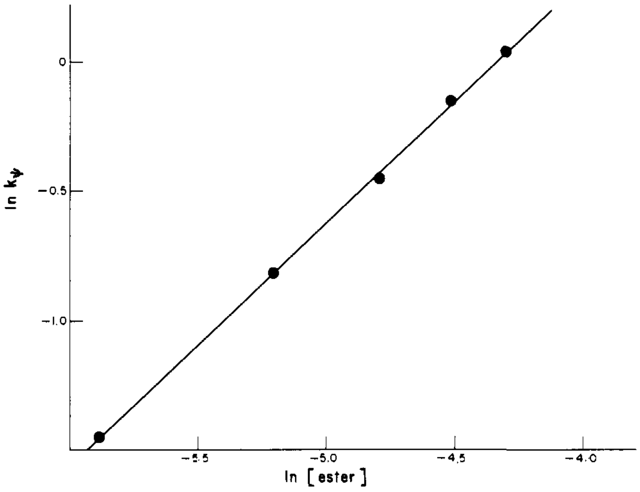


Figure 2. Plot used for determining the order of the reaction with respect to methyl cinnamate (slope = 0.94 ± 0.04).

Table I. Activation Parameters for the Oxidation of Various Alkenes by Permanganate

alkene	solvent	condins	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
methyl cinnamate[a]	methylene chloride	neutral	5.6 ± 0.8	−38 ± 3
n-butyl vinyl ether[b]	aqueous THF	alkaline	4.4 ± 1.1	−31 ± 4
cinnamic acid[c]	water	acidic	4.2 ± 0.5	−30 ± 2
cinnamate ion[d]	water	alkaline	3.3 ± 0.7	−36 ± 2
fumarate ion[e]	water	alkaline	3.1 ± 0.3	−34 ± 3
uracil[f]	water	pH 6.7	5.3 ± 0.8	−40 ± 3
crotonate ion[d]	water	alkaline	4.8 ± 0.7	−32 ± 2

[a] This work. [b] Reference 22. [c] Reference 7. [d] Wiberg, K. B.; Geer, R. D. *J. Am. Chem. Soc.* 1966, *88*, 5827. [e] Reference 4. [f] Reference 9.

to a 10-mm thermostated cuvette, 30 μL of the ester solution was injected from a syringe, and the transmittance was recorded at various time intervals. Plots of ln ($A - A_\infty$) against time were observed to be linear (Figure 1), thus confirming that the rate law is first order in oxidant. The pseudo-first-order rate constants obtained from the slopes of these plots were found to be directly proportional to the concentration of reductant (Figure 2), thus indicating that the reaction is also first order in ester concentration.

Results and Discussion

When the progress of the reaction was monitored by using UV–vis spectroscopy a series of curves were obtained as illustrated

---

(13) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(14) Wolf, S.; Ingold, C. F. *J. Am. Chem. Soc.* **1981**, *103*, 940.

(15) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 17.

(16) Schmidt, H. J.; Schäfer, H. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 787.

(17) Karaman, H., unpublished results.

(18) Lee, D. G.; Brownridge, J. R. *Can. J. Chem.* **1973**, *51*, 2102.

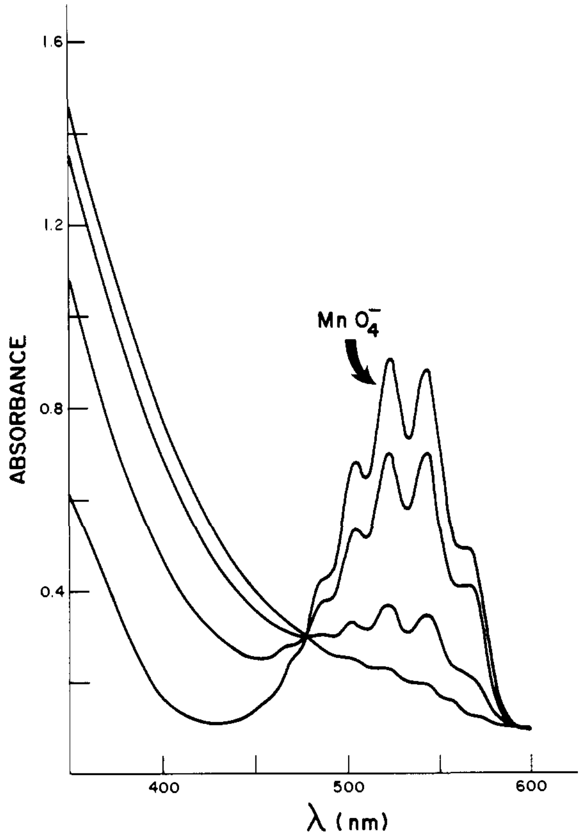


Figure 3. Successive scans for the oxidation of methyl cinnamate (4×10^{-4} M) by tetrabutylammonium permanganate (3.8×10^{-4} M) in methylene chloride at 20.0 °C (isosbestic point at 477 nm).

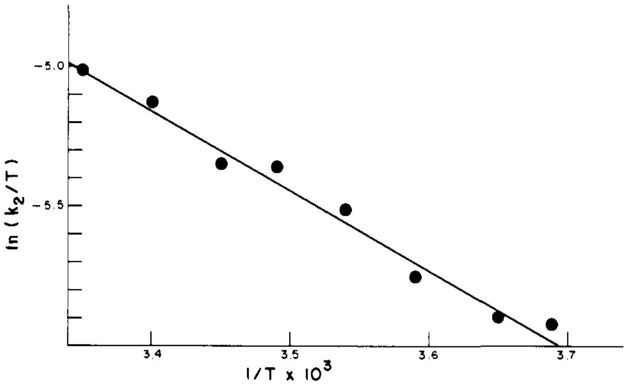


Figure 4. Plot used for determining activation parameters for the oxidation of methyl cinnamate (8.4×10^{-3} M) by methyltrioctylammonium permanganate (4.2×10^{-4} M).

in Figure 3. These curves are remarkably similar to those reported by Freeman[9] for the oxidation of uracils in aqueous solutions, and it seems almost certain that similar reactions are occurring in both aqueous and nonaqueous solvents.

Additional confirmation of this conclusion comes from an examination of the activation parameters which were obtained from a plot of log k/T vs. $1/T$ for the oxidation of methyl cinnamate by tetra-*n*-butylammonium permanganate (Figure 4). When the calculated values for the enthalpy and entropy of activation were compared with those obtained for similar reactions in aqueous solutions (Table I), it becomes apparent that the reaction which occurs under nonaqueous conditions must not be radically different from those in aqueous solutions.

The data in Table II indicate that the identity of the quaternary ammonium ion has a surprizingly large effect on the rates of reaction. This observation is in accord with theoretical calculations which indicate that quaternary ammonium permanganates exist as ion pairs in nonaqueous solutions.[19] It would only be possible for the nature of the quaternary ammonium ions to influence the reaction rates to such an extent if they were intimately involved in the structure of the ground state and/or the transition state. It was found that addition of excess quaternary ammonium ion did not produce a change in rates, thus establishing that the ionic strength of the solution was not responsible for these rate variations.

Table II. Rate Constants for the Oxidation of Methyl Cinnamate by Various Quaternary Ammonium Permanganates in Methylene Chloride Solutions[a]

oxidant	k_2, M^{-1} s^{-1}
tetra-*n*-propylammonium permanganate	1.23 ± 0.04
tetra-*n*-butylammonium permanganate	1.15 ± 0.02
tetra-*n*-pentylammonium permanganate	1.06 ± 0.05
tetra-*n*-hexylammonium permanganate	1.03 ± 0.01
tetra-*n*-heptylammonium permanganate	0.97 ± 0.03
tetra-*n*-octylammonium permanganate	0.91 ± 0.02
methyltri-*n*-butylammonium permanganate	1.54 ± 0.02
methyltri-*n*-octylammonium permanganate	1.54 ± 0.05

[a] Temperature = 20.0 ± 0.1 °C; [oxidant] = 4×10^{-4} M; [methyl cinnamate] = 8×10^{-3} M.

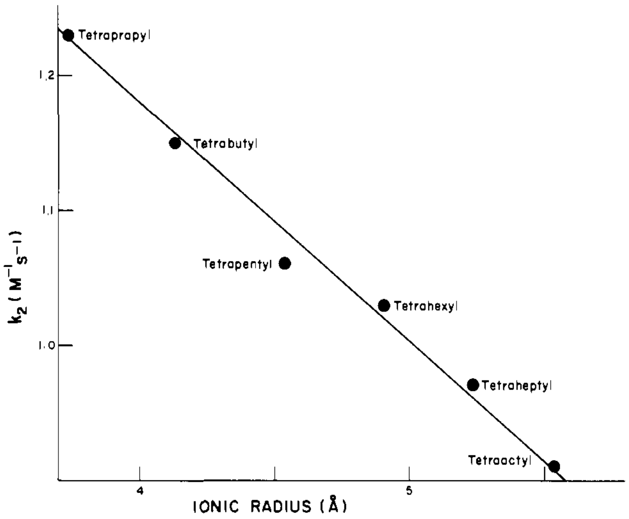


Figure 5. Relationship between ionic size and the corresponding rate constants for the oxidation of methyl cinnamate by symmetrical quaternary ammonium permanganates.

For the symmetrical tetraalkylammonium ions there is an inverse relationship between the size of the cations and the rates of reaction. As Figure 5 indicates, there appears to be a linear relationship between the second-order rate constants and the radius of the cation.[20] Since the stability derived from ion pairing would be inversely dependent on the interionic distance between the centers of positive and negative charge in the structures concerned, this result suggests that the transition state must form a tighter (more intimate) ion pair than the ground state; i.e. the transition state must derive more stability from close association with the cation than does the ground state. Hence, this observation is consistent with the mechanism proposed below (Scheme I), where the ground state is a highly delocalized anion in which the charge is spread over the four permanganate oxygens, while the transition state is a more localized enolate ion. Since the interaction with the quaternary ammonium ion would be stronger for the structure in which there is greater localization of negative charge, it follows that the transition state would benefit more from interaction with the cation. Hence smaller cations would promote a faster reaction.

A notable observation is the large rate constants obtained for oxidation with the two methyltrialkylammonium permanganates.

---

(19) Brandstrom, A. *Adv. Phys. Org. Chem.* **1977**, *15*, 267.

(20) Hughes, S. R. C.; Price, D. H. *J. Chem. Soc. A* **1967**, 1093. Krumgalž, B. S. *Russ. J. Phys. Chem.* **1971**, *45*, 1448.

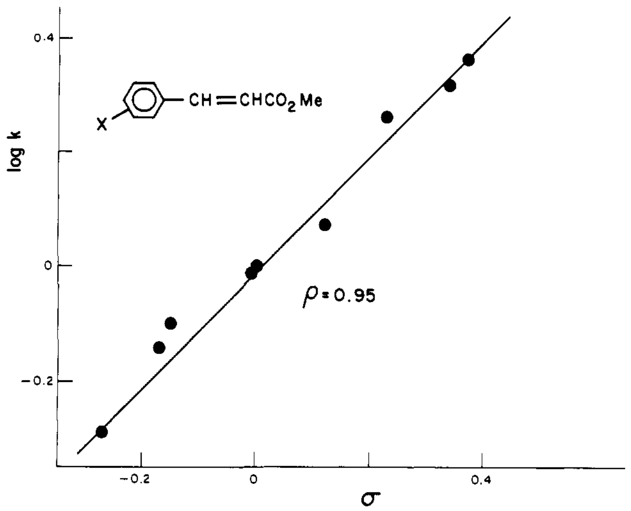
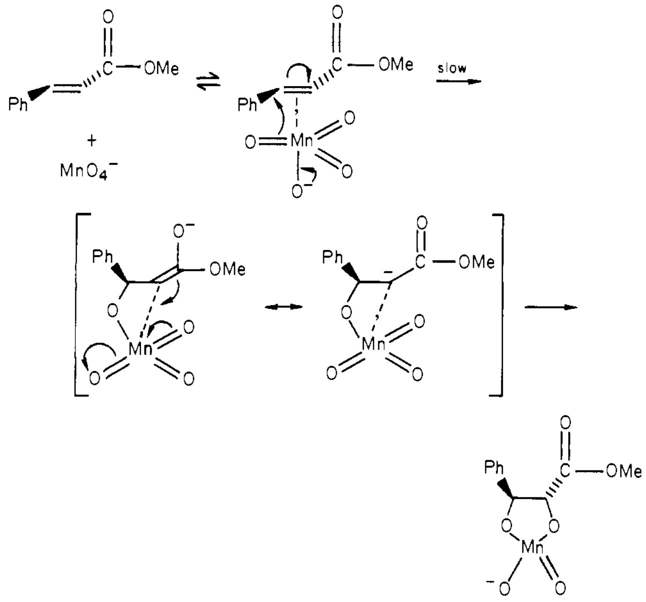


Figure 6. Hammett plot for the oxidation of methyl cinnamates by tetrabutylammonium permanganate in methylene chloride at 20.0 °C.

Scheme I



The observation that methyltri-*n*-butylammonium permanganate and methyltri-*n*-octylammonium permanganate react at the same high rate suggests that these two cations can adopt a similar orientation with respect to the anions (in both ground and transition states). Presumably the interionic distance is the same in both cases because the anions can penetrate the quaternary ammonium ions more easily when one of the alkyl groups is methyl. Such penetration effects have also been observed for other quaternary ammonium ion pairs.[20]

The introduction of substituents into the aromatic ring of the reductant also causes marked changes in the rate of reaction with the Hammett ρ value being 0.95 (Figure 6). These results indicate that the transition state contains a greater concentration of negative charge near the aromatic ring than does the ground state. Although the development of negative charge in the transition state would correspond formally to nucleophilic attack on the double bond,[21] it is unlikely that permanganate ion is a sufficiently strong nucleophile to bring about such a reaction. Instead it seems more likely that the reaction is initiated by an electrophilic attack followed by a slower step in which the organometallic π complex, **4** or **5**, is converted into a cyclic manganate(V) diester via a reaction pathway similar to that depicted in Scheme I.

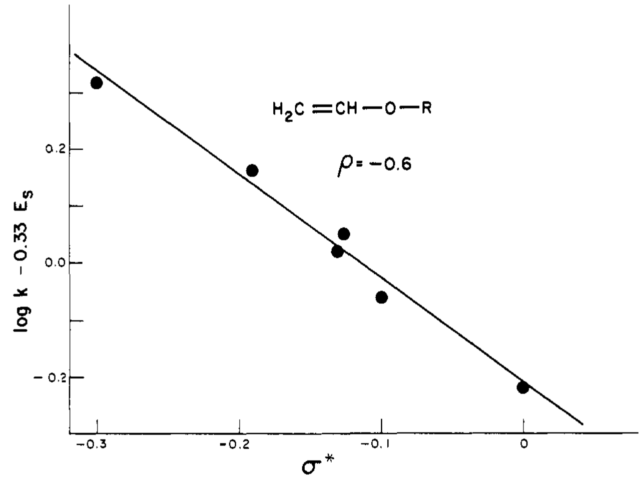


Figure 7. Taft plot for the oxidation of vinyl alkyl ethers by permanganate in aqueous THF (data from ref 22).

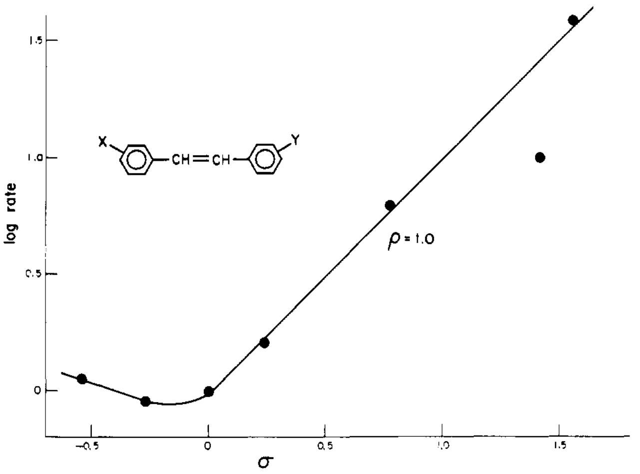
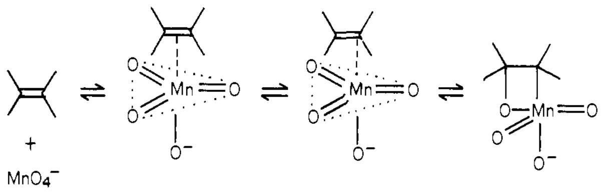


Figure 8. Hammett plot for the oxidation of stilbenes by permanganate in aqueous dioxane (data from ref 24).

Theoretical calculations reported by Eisenstein and Hoffman[13] confirm that transition-metal-complexed olefins are more susceptible to nucleophilic attack than the uncomplexed olefins. For the reaction under consideration, the oxygen ligand on the maganese would be the nucleophile and a cyclic structure would result. Interestingly, the calculations also indicated that the double bond would become activated with respect to nucleophilic attack only when the complex becomes unsymmetrical by a "slipping" of the metal toward one end of the double bond leaving the other end open to reaction with the oxygen as shown in eq 10.



(10)

Other evidence in accord with this suggestion was obtained from a study of the effect on the reaction rate of deuterium substitution at the two vinylic positions. An inverse secondary isotope effect was observed for substitution at the β-position but not at the α-position (Table III). These results substantiate that the β-carbon is sp^3 hybridized in the transition state while the α-carbon remains sp^2.

---

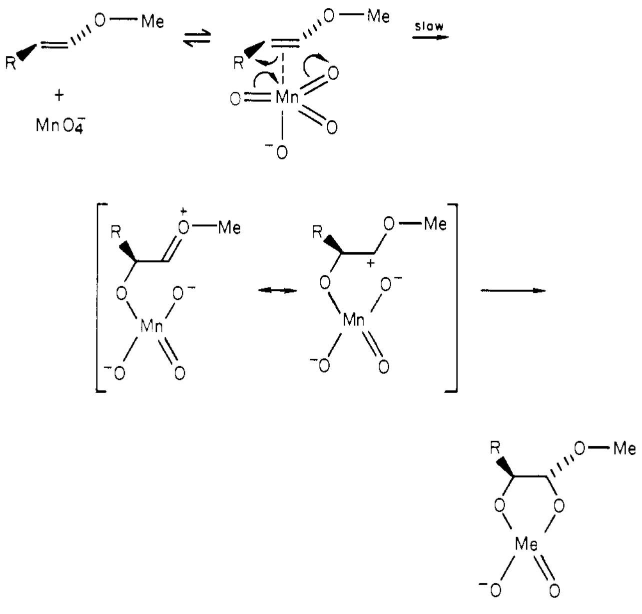
[21] Bernasconi, C. F.; Carré, D. J.; Kanavarioti, A. *J. Am. Chem. Soc.* **1981**, *103*, 4850.

Table III. Isotope Effects[a]

reductant	oxidant[b]	k_2, M^{-1} s^{-1}	k_H/k_D
methyl cinnamate	TBAP	1.25 ± 0.01	
methyl cinnamate-α-d	TBAP	1.25 ± 0.01	1.0
methyl cinnamate-β-d	TBAP	1.37 ± 0.01	0.91
methyl cinnamate	FBTEAP	2.32 ± 0.01	
methyl cinnamate-α-d	FBTEAP	2.31 ± 0.02	1.0
methyl cinnamate-β-d	FBTEAP	2.48 ± 0.01	0.94

[a] Temperature = 20.0 ± 0.1 °C; solvent = methylene chloride. [b] TBAP = tetra-*n*-butylammonium permanganate. [c] FBTEAP = (*p*-fluorobenzyl)triethyl ammonium permanganate.

Scheme II



1

The substituent effects obtained in this study are in dramatic contrast with those reported by Toyoshima, Okuyama, and Fueno[22] for the oxidation of alkyl vinyl ethers in aqueous dioxane. A proper analysis of the rate data presented by these authors indicates that it conforms to a Taft equation[23] (Figure 7) with a steric parameter, E_s, of 0.33 and a ρ value of −0.6. Furthermore a careful reexamination of the rate data for the oxidation of a series of substituted stilbenes reported over a decade ago[24] indicates that the Hammett plot is concave upward (Figure 8). A positive slope is observed when electron-withdrawing substituents are present and a negative slope when electron-donating substituents are present.

Such a concave upward Hammett plot is indicative of a reaction that is undergoing a change in mechanisms.[25] Apparently the reaction can proceed via an electron-deficient or an electron-rich transition state, depending on the demands of the substituents. With electron-withdrawing substituents such as the carboxyl group discussed above, the reaction proceeds (as in Scheme I) along a profile that takes advantage of the ability of these groups to delocalize negative charges. Conversely, when electron-donating substituents are present carbocation-like transition states can be stabilized as in Scheme II.

A comparison of Schemes 1 and 2 reveals that both reactions proceed through the same organometallic intermediate, but via different transition states, to the cyclic diester **1**. The nature of the transition state is controlled by the different abilities of the substituents to stabilize positive and negative charges. The principle difference in the transition states is associated with the timing of the reduction of manganese(VII): in Scheme I reduction occurs after the transition state is achieved; in Scheme II reduction occurs during the formation of the transition state. The apparent change in mechanism must simply be a reflection of nature's ability to find the lowest potential energy surface between two points.

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

Registry No. Methyl (*E*)-cinnamate, 1754-62-7; methyl *m*-methylcinnamate, 82444-40-4; methyl cinnamate-*α*-*d*, 55836-65-2; methyl cinnamate-*β*-*d*, 60975-76-0; tetra-*n*-propylammonium permanganate, 35638-40-5; tetra-*n*-butylammonium permanganate, 35638-41-6; tetra-*n*-pentylammonium permanganate, 35638-42-7; tetra-*n*-hexylammonium permanganate, 35638-43-8; tetra-*n*-heptylammonium permanganate, 34293-34-0; tetra-*n*-octylammonium permanganate, 82444-41-5; methyltri-*n*-butylammonium permanganate, 82444-42-6; methyltri-*n*-octylammonium permanganate, 82444-43-7; (*p*-fluorobenzyl)triethylammonium permanganate, 82444-45-9.

---

(22) Toyoshima, K.; Okuyama, T.; Fueno, T. *J. Org. Chem.* **1980**, *45*, 1600.

(23) Taft, R. W. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 597. Shorter, J. *Q. Rev., Chem. Soc.* **1970**, *24*, 433.

(24) Henbest, H. B.; Jackson, W. R.; Robb, B. C. G. *J. Chem. Soc. B* **1966**, 803.

(25) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 187.