

Semiquantitative FMO Analysis of Substituent Effect on the Reaction of Permanganate Ion with Unsymmetrical Alkenes

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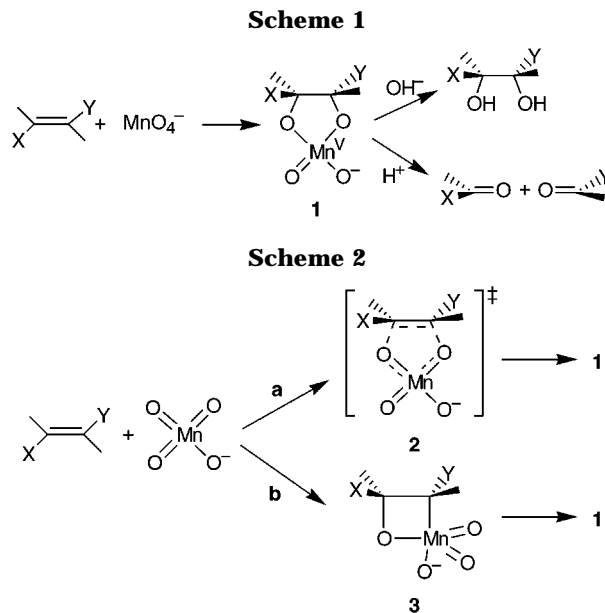
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Abstract: The substituent effects on the reactions of permanganate ion with unsymmetrical alkenes are analyzed on the assumption of a concerted (3 + 2) cycloaddition model by using an equation obtained by approximation based on the FMO theory in which development and localization of the frontier molecular orbitals at the reaction sites with progress of the reaction are considered. The Hammett plots are successfully reproduced with the newly obtained rate data for the reactions of *trans*-chalcone and its derivatives and the data for methyl cinnamates, cinnamate ions, and alkyl vinyl ethers taken from the literature using FMO energies and orbital coefficients calculated by the PM3 method. It was indicated that a factor introduced to the basic equation in order to estimate the extent of localization of the molecular orbitals at the transition state is closely related to the position of the transition state along the reaction path.

Introduction

It has been widely accepted that permanganate ion (MnO_4^-) reacts with alkenes in a cycloaddition to form the transient cyclic manganese(V) ester intermediate **1**, which subsequently decomposes into a 1,2-diol or carbonyl compounds depending on the reaction conditions (Scheme 1).^{1,2} A remarkable feature of the permanganate oxidation is that the reactions are accelerated not only by electron-releasing groups but also, in certain cases, by electron-withdrawing groups, while other oxidative reagents such as osmium tetroxide (OsO_4) react to alkenes only in an electrophilic manner.^{3–5}

Two different pathways, both of which lead to the manganese(V) intermediate **1**, have been proposed.⁶ The (3 + 2) pathway **a** in Scheme 2 involves concerted attack of the oxygen atoms to the unsaturated carbons and proceeds via a five-membered cyclic transition state **2**.^{7,8} This mechanism was also suggested by theoretical speculations based on the frontier molecular orbital (FMO) theory⁹ and the Zimmerman treatment.¹⁰ The other mechanism, pathway **b**,¹⁶ in which a four-membered organometallic intermediate **3** is formed first via [2 + 2] cycloaddition and then rearranges to **1**, is based on the general proposal by Sharpless and co-workers¹¹ for the



reactions between alkenes and oxo transition-metal species. Goddard and Rappé¹² gave theoretical support for this mechanism in analogy with a study on the reaction between ethylene and chromyl chloride.

For the oxidation of alkenes by other oxo transition-metal reagents, in particular for the dihydroxylation by OsO_4 , a similar mechanistic question, namely, whether the reaction proceeds by a (3 + 2) cycloaddition mechanism or by a stepwise mechanism that involves [2 + 2] cyclization, has been studied more extensively since Sharpless's proposal for the metallaoxetane intermediate. It was indicated by Jørgensen and Hoffmann that the frontier orbitals of OsO_4 have the right symmetry for interactions with π and π^* orbitals of alkenes.¹³ Houk

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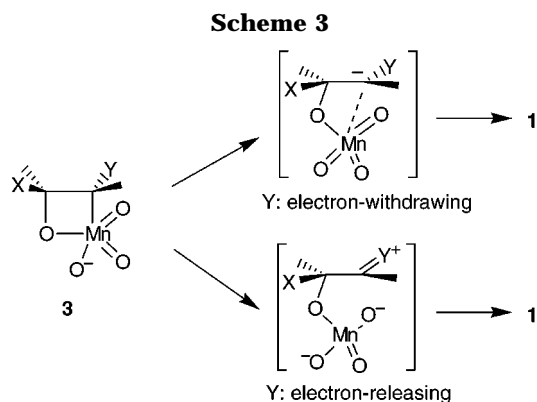
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and co-workers showed that MM2 calculations based on a symmetrical five-membered transition model reproduce the stereoselectivities observed with several chiral diamine ligands.¹⁴ Furthermore, Corey and Noe proposed a (3 + 2) model for the origin of the high enantioselectivity of the dihydroxylation attained by an amine-OsO₄ complex.¹⁵ Although the [2 + 2] mechanism for the reaction of OsO₄ can also rationalize the stereoselectivities caused by chiral ligands,¹⁶ and the rearrangement of the metallaoxetane to a five-membered diolate was also supported by theoretical considerations,^{12,17} many of recent theoretical and experimental studies that appeared during the course of this study support the (3 + 2) cycloaddition mechanism.¹⁸

In connection with the ambiphilic reactivity of permanganate ion, Lee and Brown³ gave an explanation by assuming the occurrence of two different ionic transition states in the [2 + 2] cycloaddition pathway depending on the electronic nature of the substituent on alkenes (Scheme 3).

In this paper, we present the semiquantitative frontier molecular orbital analysis of the substituent effects on permanganate oxidation of aryl-substituted alkenes. We have assumed the concerted (3 + 2) cycloaddition model and used newly introduced rate equations derived from the general perturbation equation by approximations based on the FMO theory. The results obtained by PM3 calculations well reproduced Hammett plots theoretically for all the reactions examined and strongly support the (3 + 2) cycloaddition mechanism.

Experimental Section

The solvent (dichloromethane) used in the kinetic experiments was purified before use by refluxing with potassium permanganate and benzyltriethylammonium chloride followed by distillation from the solution.

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The following *trans*-chalcones were prepared by condensation of acetophenone and a corresponding derivative of benzaldehyde in the presence of NaOH in EtOH at room temperature and purified by crystallization from EtOH; 4-methoxy-*trans*-chalcone, mp 76–77 °C (lit.¹⁹ mp 77–78.5 °C), 4-methyl-*trans*-chalcone, mp 96–98 °C (lit.²⁰ mp 97–98 °C), 4-chloro-*trans*-chalcone, mp 112–113 °C (lit.²¹ mp 112–114 °C), 4-bromo-*trans*-chalcone, mp 125–126 °C (lit.¹⁹ mp 127–128 °C), 4-nitro-*trans*-chalcone, mp 163.5–164 °C (lit.²² mp 157–159 °C). *trans*-Chalcone was purchased from Tokyo Kasei Kogyo Co., Ltd, and crystallized from ethanol. *trans*-Chalcone- α -*d* was prepared by condensation of benzaldehyde and acetophenone- α -*d*₃ (Nippon Sanso Corp.) in EtOH containing a catalytic amount of EtONa. *trans*-Chalcone- β -*d* was obtained by the reaction of benzaldehyde- α -*d* (Nippon Sanso Corp.) and acetophenone in a similar manner. Similarly, 4-nitro-*trans*-chalcone- α -*d* was prepared from 4-nitrobenzaldehyde and acetophenone- α -*d*₃ and 4-nitro-*trans*-chalcone- β -*d* from acetophenone and 4-nitrobenzaldehyde- α -*d*, which was obtained from 4-nitrobenzoyl chloride by the reduction with LiAlD(*t*-BuO)₃ in diglyme at –78 °C. All the deuterated compounds were confirmed to give satisfactory 200 MHz ¹H NMR spectra (no proton signals at the position of replaced protons), respectively.

Permanganate ion solutions were prepared as follows. Powdered potassium permanganate (50 mg, 0.32 mmol) and benzyltriethylammonium chloride (172 mg, 0.76 mmol) were dissolved in 5 mL of dichloromethane, and the solution was allowed to stand overnight in a refrigerator. After suitable dilution of the supernatant solution, the accurate concentration of permanganate ion was determined by a spectrophotometric method immediately before use.

The reactions were performed by mixing a solution of permanganate ion (2 mL) with a solution of chalcone (2 mL) in a 10 mm cuvette, and the kinetics were determined by monitoring the changes in absorbance at 526 nm (disappearance of permanganate ion) on a JASCO Ubest-35 spectrophotometer connected to a floppy disk drive for data storage. The temperature was maintained at 25.0 °C with a refrigerated and heated bath circulator. The data were transferred to an Apple Macintosh computer, and a correction was made at each moment by subtracting the background absorbance of the manganese product estimated from the observed absorbance at 420 nm. All the rate constants are the average of three or more experiments. Activation parameters for the reactions of *trans*-chalcone and 4-nitro-*trans*-chalcone were obtained from the plots of ln *k*₂/*T* vs 1/*T* using *k*₂ values determined at 15, 20, 25, and 30 °C, respectively.

Molecular orbital calculations were carried out by the PM3 method²³ in MOPAC as implemented in the MacSpartan Plus, Chem3D Pro, or CAChe Work System ver. 3.7 on an Apple Macintosh computer. Calculations for the optimization of the transition structure for the reaction between permanganate ion and ethylenethene and graphical modeling for the orbitals were accomplished by use of the PM3(tm) method²⁴ in the MacSpartan Plus.

Results and Discussion

Approximation of Basic Equation. On the basis of the general perturbation method,^{25,26} the second-order energy change caused by the FMO interactions between two molecules (R and S) reacting in a cycloaddition is

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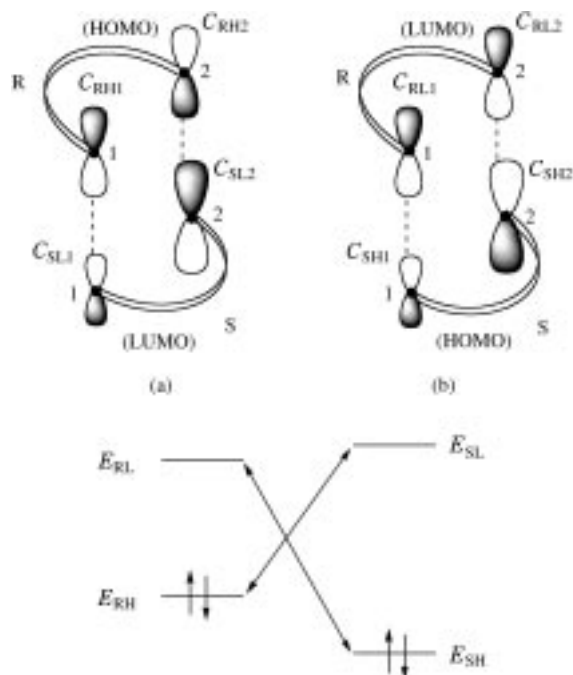


Figure 1. FMO interactions when two molecules (R and S) react in a cycloaddition.

given by eq 1.^{27,28} In this equation, ΔE is the interaction

$$\Delta E = 2\beta^2 \left[\frac{(C_{RH1}C_{SL1} + C_{RH2}C_{SL2})^2}{E_{RH} - E_{SL}} + \frac{(C_{RL1}C_{SH1} + C_{RL2}C_{SH2})^2}{E_{SH} - E_{RL}} \right] \quad (1)$$

energy; β is the resonance integral for the two interacting MO pairs; C and E refer, respectively, to eigenvector coefficients and eigenvalues specified by the subscripts; subscripts R and S refer, respectively, to the reacting molecules R and S; subscripts 1 and 2 refer, respectively, to the reaction sites 1 and 2; and subscripts H and L refer, respectively, to HOMO and LUMO (Figure 1).

For a series of reactions where one component of the reactant differs from one another only in electronic effects of the substituents, the relative reaction rate would be expressed by eq 2, which has been given by Mok and Nye

$$\ln k = C + \frac{2\beta^2}{RT} \left[\frac{(C_{RH1}C_{SL1} + C_{RH2}C_{SL2})^2}{|E_{RH} - E_{SL}|} + \frac{(C_{RL1}C_{SH1} + C_{RL2}C_{SH2})^2}{|E_{SH} - E_{RL}|} \right] \quad (2)$$

through connecting eq 1 with the Eyring equation for rate constant (k) and activation energy (ΔE^\ddagger).²⁸ This equation is based on the assumption that the stabilization energy at the transition state is proportional to that given by eq 1.

Eq 2 would be simplified to eq 3 if $|E_{RH} - E_{SL}|$ is smaller than $|E_{SH} - E_{RL}|$ or to eq 4 if $|E_{SH} - E_{RL}|$ is smaller than $|E_{RH} - E_{SL}|$. As pointed out by Mok and Nye,²⁸ this simplification is rationalized by the FMO

$$\ln k = C + \frac{2\beta^2}{RT} \left[\frac{(C_{RH1}C_{SL1} + C_{RH2}C_{SL2})^2}{|E_{RH} - E_{SL}|} \right] \quad (3)$$

$$\ln k = C + \frac{2\beta^2}{RT} \left[\frac{(C_{RL1}C_{SH1} + C_{RL2}C_{SH2})^2}{|E_{SH} - E_{RL}|} \right] \quad (4)$$

theory,²⁹ which states that the more closely lying HOMO–LUMO pair plays the most important role at the transition state and dominates the reaction.

For Diels–Alder reactions where R = diene and S = dienophile, for example, eq 3 dominates the reactions with normal electron demand, while eq 4 dominates the reactions with inverse electron demand.³⁰ If β and the numerators in parentheses of eqs 3 and 4 could be assumed constant for the reactions between a diene and a series of dienophiles, one can expect a linear correlation between $\ln k$ and $1/|E_{RH} - E_{SL}|$, or $\ln k$ and $1/|E_{SH} - E_{RL}|$. However, few examples for which such a linear relationship is established have been known.^{28,30b}

In order to apply eqs 3 and 4 more quantitatively to permanganate oxidations of alkenes (R = MnO_4^- , S = alkene) it is necessary to consider the changes in frontier orbital coefficients at the transition state, and hence, we have further modified these equations in the following manner. First, it was assumed that frontier orbital coefficients at the reaction sites of the symmetrical component, MnO_4^- in this case, are equal and constant for the transition states of the reactions with similar alkenes ($C_{RH1} = C_{RH2} = C_{RH}$, $C_{RL1} = C_{RL2} = C_{RL}$). Thus, eqs 3 and 4 are reduced to simpler forms as eqs 5 and 6, respectively, where C_{RH} and C_{RL} are constant. Second,

$$\ln k = C + \frac{2\beta^2 C_{RH}^2}{RT} \left[\frac{(|C_{SL1}| + |C_{SL2}|)^2}{|E_{RH} - E_{SL}|} \right] \quad (5)$$

$$\ln k = C + \frac{2\beta^2 C_{RL}^2}{RT} \left[\frac{(|C_{SH1}| + |C_{SH2}|)^2}{|E_{SH} - E_{RL}|} \right] \quad (6)$$

in order to indicate to what extent the frontier orbital coefficients of the unsymmetrical component have developed and localized at the reaction sites when the transition state is reached, we introduced a factor, d , and obtained eqs 7 and 8 as the final equations.

$$\ln k = C + \frac{2\beta^2 C_{RH}^2}{RT} \left[\frac{(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d}{|E_{RH} - E_{SL}|} \right] \quad (7)$$

$$\ln k = C + \frac{2\beta^2 C_{RL}^2}{RT} \left[\frac{(1-d)(|C_{SH1}| + |C_{SH2}|)^2 + 2d}{|E_{SH} - E_{RL}|} \right] \quad (8)$$

The value of d varies from 0 to 1 with the position of the transition state along the reaction path. The numerator in the parentheses of the equations linearly changes from the minimum value $[(|C_{SL1}| + |C_{SL2}|)^2]$ or $[(|C_{SH1}| + |C_{SH2}|)^2]$ to the theoretical maximum value of

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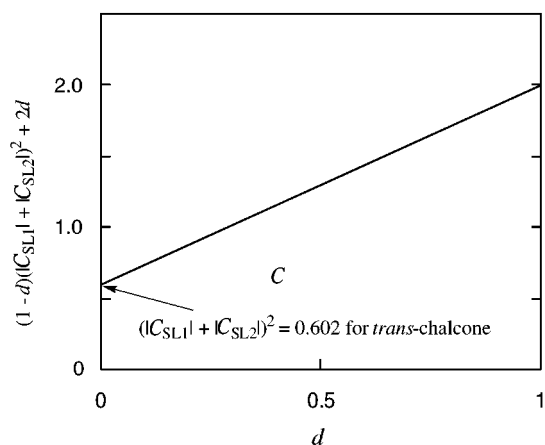


Figure 2. Changes in $(1 - d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d$ against d for the case of *trans*-chalcone.

²³¹ with increasing d (Figure 2). If one can determine the right value of d for a series of related cycloadditions, a linear relationship can be expected between $\ln k$ and $[(1 - d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d]/|E_{RH} - E_{SL}|$ or $[(1 - d)(|C_{SH1}| + |C_{SH2}|)^2 + 2d]/|E_{SH} - E_{RL}|$. A relatively small value of d implies that the reaction rate is dependent not only on the HOMO–LUMO energy difference but also to some extent on the frontier orbital coefficients, while a relatively large value of d implies that the reaction rate is dependent primarily on the HOMO–LUMO energy difference. Furthermore, for the reaction of alkenes whose frontier orbital coefficients are significantly unsymmetrical, a value of d close to zero indicates an early, unsymmetrical transition state, while a value of d close to 1 indicates a symmetrical, product-like transition state.

Molecular Orbitals of MnO_4^- . In spite of many papers on semiempirical³² and ab initio MO calculations³³ for MnO_4^- , it seems to be difficult to find the proper FMO energies of MnO_4^- from the currently available data, since there remains considerable disagreement in the orbital energies and even in the order of energy levels. It is still worthwhile, however, to presume a roughly estimated value for the FMO energy since the purpose here is to approximate the relative energies of the transition state for a series of closely related reactions. The $1t_1$ orbitals (Figure 3) have been placed on the highest level of filled orbitals by many calculations, and one of these orbitals meets the symmetry requirement for the FMO interaction with the LUMO of an alkene in the same manner as suggested for the reaction of osmium tetroxide.¹³ Despite the disagreement among the MO calculations as to the order of the first unfilled orbitals, it has been supported by ESR measurements of MnO_4^{2-}

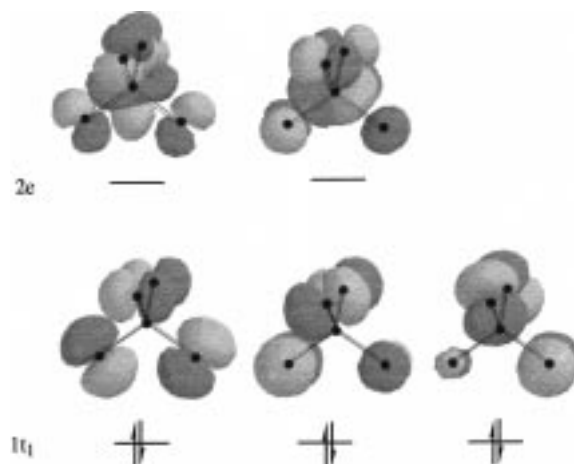


Figure 3. Surface drawings of the PM3(tm)-calculated frontier molecular orbitals for MnO_4^- .

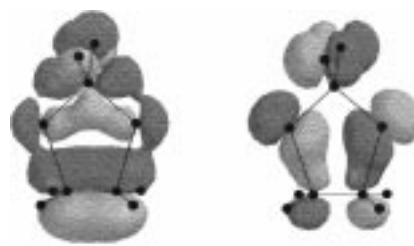


Figure 4. Drawings of the first and second highest filled orbitals of the transition state optimized by the PM3 (tm) method for the reaction between MnO_4^- and ethylene.

and its theoretical analysis that the $2e$ orbitals (Figure 3) are in the lowest unfilled level,³⁴ and one of these orbitals fulfills the symmetry requirement for the FMO interaction with the HOMO of an alkene. It is noteworthy that the transition state optimized by PM3 (tm)²⁴ calculations for the reaction between MnO_4^- and ethylene exhibits surface drawings of the first and second highest filled orbitals, which are just made up of the combination of π orbital of ethylene and one of $2e$ orbitals and of the combination of the π^* orbital of ethylene and one of the $1t_1$ orbitals, respectively (Figure 4).

In this paper, we tentatively take the orbital energies for HOMO and LUMO of MnO_4^- as -8.5 and -0.5 eV, respectively. The satisfactory results of this work are little affected by changing these values in the range of ± 3 eV or somewhat more, since the ambiguity introduced in eqs 7 and 8 is weakened by changing d value as described below in the practical discussions. Therefore, the d value determined for a series of reactions has no absolute meaning at present so long as the reliable MO energies of MnO_4^- are unknown.

Reaction of MnO_4^- with *trans*-Chalcones. The second-order rate constants obtained for the reactions of permanganate ion with a series of 4-substituted *trans*-chalcones in CH_2Cl_2 are listed in Table 1 together with the MO data calculated by the PM3 method. A good linear Hammett plot with a positive slope ($\rho = 1.28$) was obtained (Figure 5). These results indicate that the reactions are nucleophilic, and hence, the kinetic data could be analyzed on the basis of eq 7 as the normal

(31) At this point, the frontier orbital coefficients at the reaction sites of the alkene are completely grown up and equalized to $1/\sqrt{2}$, respectively.

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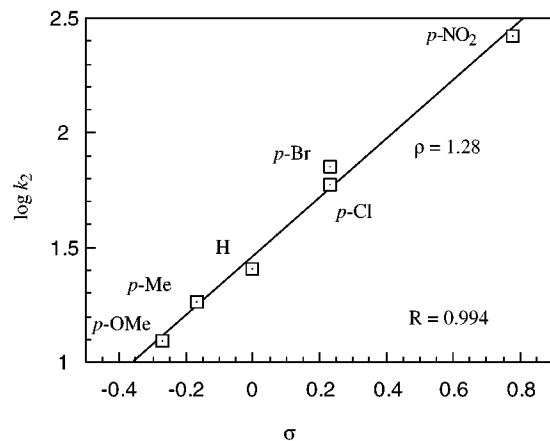
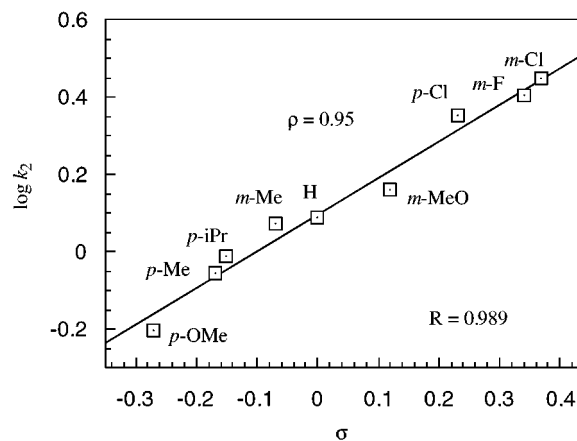
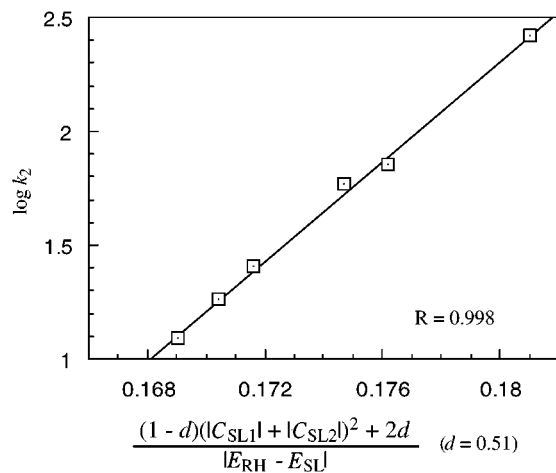
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Table 1. Second-Order Rate Constants and MO Data for Reactions between MnO_4^- and *trans*-Chalcones ($\text{XPhCH}=\text{CHCOPh}$)

X	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	orbital energy (eV)		eigenvector		$ E_{\text{RH}} - E_{\text{SL}} ^a$	$ E_{\text{SH}} - E_{\text{RL}} ^b$
		E_{SH}	E_{SL}	C_{SL1}	C_{SL2}		
<i>p</i> -OMe	12.3	-8.965 78	-0.795 41	-0.347 06	0.412 31	7.704 59	8.465 78
<i>p</i> -Me	18.3	-9.187 04	-0.829 05	-0.355 46	0.410 50	7.670 95	8.687 04
H	25.4	-9.376 54	-0.836 97	-0.362 55	0.413 63	7.663 03	8.876 54
<i>p</i> -Cl	59.0	-9.225 87	-0.987 36	-0.374 17	0.398 61	7.512 64	8.725 87
<i>p</i> -Br	71.3	-9.492 06	-1.011 79	-0.381 47	0.400 28	7.488 21	8.992 06
<i>p</i> -NO ₂	265.0	-10.158 01	-1.711 16	-0.360 58	0.292 67	6.788 84	9.658 01

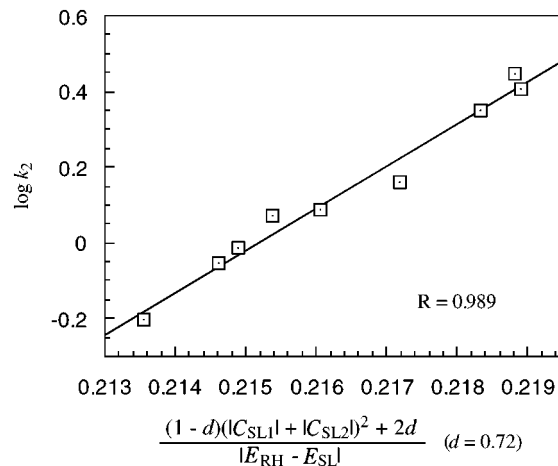
^a E_{RH} is taken as -8.5 eV. ^b E_{RL} is taken as -0.5 eV.

**Figure 5.** Hammett plot for the reactions of MnO_4^- with *trans*-chalcones.**Figure 7.** Hammett plot for the reactions of MnO_4^- with methyl cinnamates (data from refs 3 and 35).**Figure 6.** Plots of $\log k_2$ vs $[(1-d)(|C_{\text{SL1}}| + |C_{\text{SL2}}|)^2 + 2d]/|E_{\text{RH}} - E_{\text{SL}}|$ for the reactions of MnO_4^- with *trans*-chalcones, $d = 0.51$.

electron-demand cycloaddition. When d is taken as 0.51, the plot of $\log k_2$ vs $[(1-d)(|C_{\text{SL1}}| + |C_{\text{SL2}}|)^2 + 2d]/|E_{\text{RH}} - E_{\text{SL}}|$ follows a straight line with the best correlation, and this is remarkably similar to the Hammett plot (Figure 6). Very similar plots with nearly the same correlation were also obtained even when E_{RH} was taken as -10.5 or -6.5 eV but using alternate d values (Supporting Information). However, when $\log k_2$ is plotted against $2/|E_{\text{RH}} - E_{\text{SL}}|$ on the assumption that C_{SL1} and C_{SL2} have completely localized at the reaction sites when the transition state is reached ($d = 1$), the plot considerably deviates from the straight line (Supporting Information).

Reaction of MnO_4^- with Methyl Cinnamates.

Further attempts to test eqs 7 and 8 have been made by taking kinetic data from the literature. Figure 7 shows

**Figure 8.** Plots of $\log k_2$ vs $[(1-d)(|C_{\text{SL1}}| + |C_{\text{SL2}}|)^2 + 2d]/|E_{\text{RH}} - E_{\text{SL}}|$ for the reactions of MnO_4^- with methyl cinnamates, $d = 0.72$ (rate data from refs 3 and 35).

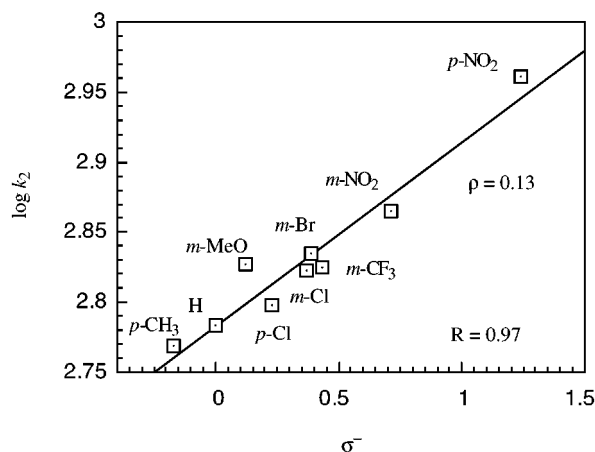
the Hammett plot given by Lee and Brown for the reactions of permanganate ion with a series of methyl cinnamates in CH_2Cl_2 .^{3,35} The Hammett plot is reproduced with good fidelity when $\log k_2$ is plotted against $[(1-d)(|C_{\text{SL1}}| + |C_{\text{SL2}}|)^2 + 2d]/|E_{\text{RH}} - E_{\text{SL}}|$ with the d value taken as 0.72 (Figure 8). Although, as indicated in Table 2, the magnitude of the eigenvector coefficients at the reaction sites of methyl cinnamates ($|C_{\text{SL1}}|$, $|C_{\text{SL2}}|$) appear roughly symmetrical and unchanged by the substituent, the plot obtained by taking d as unity exhibits more widely scattered points (Supporting Information). These results indicate that even a slight difference in eigenvector coefficients between methyl cin-

(35) Lee, D. G.; Brown, K. C.; Karaman, H. *Can. J. Chem.* **1986**, *64*, 1054.

Table 2. MO Data for Methyl Cinnamates (XPhCH=CHCOOCH₃) by PM3 Calculations^a

X	orbital energy (eV)		eigenvector	
	E_{SH}	E_{SL}	$ C_{SL1} $	$ C_{SL2} $
<i>p</i> -OMe	-9.0357	-0.727 28	0.436 62	0.449 63
<i>p</i> -Me	-9.2741	-0.775 52	0.438 40	0.443 66
<i>p</i> -iPr	-9.3282	-0.775 21	0.440 37	0.445 86
<i>m</i> -Me	-9.4127	-0.759 04	0.446 17	0.454 85
H	-9.4777	-0.793 46	0.445 50	0.450 98
<i>m</i> -MeO	-9.2404	-0.813 59	0.450 57	0.454 38
<i>p</i> -Cl	-9.3050	-0.978 75	0.431 82	0.417 90
<i>m</i> -F	-9.7104	-1.023 25	0.426 89	0.411 40
<i>m</i> -Cl	-9.4939	-0.946 44	0.440 77	0.431 27

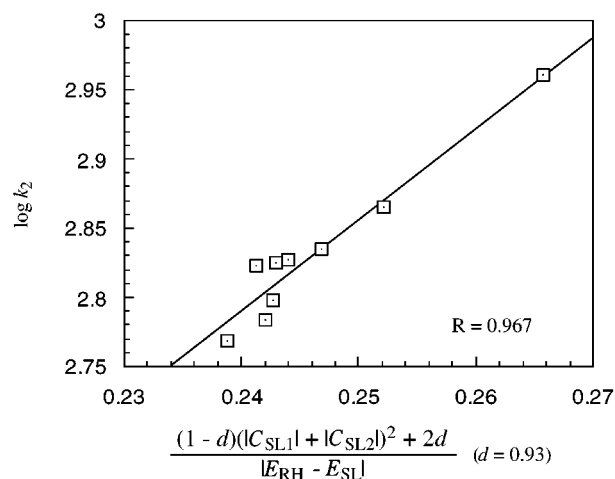
^a MPOAC 93 in MacSpartan Plus was used. For the *m*-fluoro derivative, PM3 calculations in the other package programs gave somewhat different values of the eigenvectors, and the point in Figure 8 appreciably deviates from the straight line.

**Figure 9.** Hammett plot for the reactions of MnO₄⁻ with cinnamate ions in alkaline solution (from ref 36).

namates significantly influences their reactivity, and the semiempirical MO calculation is precise enough to detect such differences.

Reaction of MnO₄⁻ with Cinnamate Ions in Alkaline Solution. We next applied eq 7 to the rate data for the reaction of permanganate ion with cinnamate ions in aqueous alkaline solution as elaborated by Lee and Nagarajan.³⁶ The reaction is also nucleophilic since the Hammett plot follows a straight line of positive slope (Figure 9). A very similar straight line was obtained with the best correlation for the plot of log *k*₂ against [(1 - *d*)(|*C*_{SL1}| + |*C*_{SL2}|)² + 2*d*]/|*E*_{RH} - *E*_{SL}| when *d* is taken as 0.93 (Figure 10). The fairly large value of *d* indicates that the lobes of the LUMO of cinnamate ions develop and localize to a considerable extent at the reaction sites when the transition state is reached, and the structure of the transition state is more symmetrical and product-like than those for the reactions of chalcones and methyl cinnamates. It should be noted, however, that differences in size of the LUMO coefficient between the reaction sites of cinnamate ions (|*C*_{SL1}| and |*C*_{SL2}|) are more significant than those of methyl cinnamates (Table 3).

It has been observed that there are distinct differences in magnitude of *d* among the three reactions above discussed. According to the definition of *d*, the degree of bond formation at the transition state should be in the order of the magnitude of *d*, namely, cinnamate ions, methyl cinnamates, and chalcones. This conclusion is

**Figure 10.** Plots of log *k*₂ vs [(1 - *d*)(|*C*_{SL1}| + |*C*_{SL2}|)² + 2*d*]/|*E*_{RH} - *E*_{SL}| for the reactions of MnO₄⁻ with cinnamate ions; *d* = 0.93 (rate data from ref 36).**Table 3. MO Data for Cinnamate Ions (XPhCH=CHCOO⁻) in Aqueous Solution by the PM3 Method^a**

X	orbital energy (eV)		eigenvector	
	E_{SH}	E_{SL}	$ C_{SL1} $	$ C_{SL2} $
<i>p</i> -CH ₃	-9.268 16	-0.528 87	0.453 50	0.332 68
H	-9.453 19	-0.612 97	0.454 01	0.383 25
<i>m</i> -MeO	-9.399 19	-0.681 79	0.449 23	0.372 39
<i>p</i> -Cl	-9.281 21	-0.681 46	0.431 59	0.297 81
<i>m</i> -Cl	-9.465 21	-0.621 96	0.445 64	0.313 08
<i>m</i> -Br	-9.555 07	-0.781 21	0.435 10	0.372 67
<i>m</i> -CF ₃	-9.621 74	-0.717 15	0.395 08	0.269 89
<i>m</i> -NO ₂	-9.626 20	-1.103 24	0.166 55	0.106 89
<i>p</i> -NO ₂	-9.814 93	-1.422 40	0.332 60	0.216 16

^a The solvent (water) was specified by the COSMO option in CACHEMOPAC version 94.

Table 4. Comparison of *d* Value with Activation Entropy and *k*_H/*k*_D

compd	<i>d</i>	ΔS^\ddagger (eu)	<i>k</i> _H / <i>k</i> _D	
			α - <i>d</i>	β - <i>d</i>
<i>t</i> -chalcone ^a	0.51	-31.1	0.96 ± 0.02	0.93 ± 0.02
4-NO ₂ - <i>t</i> -chalcone ^a		-30.0	0.94 ± 0.02	0.96 ± 0.02
methyl cinnamate ^b	0.72	-38	1.0	0.91
cinnamate ion ^c	0.93	(-29)	0.87	0.89

^a This work, in CH₂Cl₂. ^b From ref 3, in CH₂Cl₂. ^c From ref 36, in 0.5 M NaOH.

also supported by comparing the *d* values with the activation entropies and secondary deuterium isotope effects as shown in Table 4. The relatively small negative value of activation entropies and relatively insignificant inverse secondary isotope effects observed for the reaction of chalcone derivatives indicate a loosely bonded and sp²-dominant early transition state in accord with the small value of *d*. On the other hand, the relatively significant inverse secondary isotope effects observed for the reaction of cinnamate ion³⁶ suggest a sp³-dominant later transition state in accord with the relatively large value of *d*. In addition, this sp³ dominant transition state also explains the small ρ value for the reaction of cinnamate ions since the electronic effects from the substituents may be blocked by an sp³-like carbon more significantly than by an sp²-like carbon.

Reaction of Permanganate Ion with Electron-Releasing Alkenes. The rate data reported by Okuya-

(36) Lee, D. G.; Nagarajan, K. *Can. J. Chem.* **1985**, *63*, 1018.

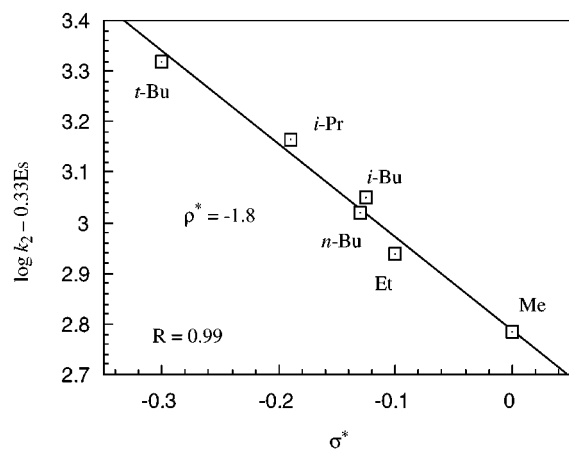


Figure 11. Taft plot for the reactions of MnO_4^- with alkyl vinyl ethers in aqueous dioxane (from refs 3 and 4).

Table 5. MO Data for Alkyl Vinyl Ethers ($\text{CH}_2=\text{CHOR}$)^a

R	orbital energy (eV)		eigenvector	
	E_{SH}	E_{SL}	$ C_{\text{SH1}} $	$ C_{\text{SH2}} $
CH_3	-9.515 08	1.301 70	0.495 30	0.670 89
C_2H_5	-9.458 51	1.329 90	0.488 14	0.669 52
<i>i</i> - C_3H_7	-9.442 51	1.365 74	0.499 09	0.680 18
<i>t</i> - C_4H_9	-9.427 08	1.390 78	0.503 56	0.682 36
<i>n</i> - C_4H_9	-9.465 34	1.322 40	0.487 96	0.669 08
<i>i</i> - C_4H_9	-9.452 22	1.326 04	0.485 77	0.668 26

^a Calculated by PM3 in CACheMOPAC ver. 94.

ma and co-workers for the reaction of permanganate ion with alkyl vinyl ethers in aqueous dioxane indicate that the reaction is electrophilic.⁴ It was shown later by Lee and Brown³ that the rate data conform to a Taft equation with a steric parameter of $0.33E_{\text{S}}$ and ρ^* value of -1.8 ³⁷ (Figure 11). The PM3 calculation disclosed that LUMO energies of the alkyl vinyl ethers are 2 eV or somewhat more higher than those of electron-withdrawing alkenes such as chalcone and cinnamate derivatives (Table 5). This fact will make it likely that the FMO interaction between HOMO of an alkyl vinyl ether and LUMO of MnO_4^- is more favorable than that between the HOMO of MnO_4^- and the LUMO of an alkyl vinyl ether, and hence, the reactions will be analyzed by eq 8 as inverse-electron-demand reactions. The straight line of the Taft plot is well reproduced when $\log k_2 - 0.33E_{\text{S}}$ is plotted against $-[(1-d)(|C_{\text{SH1}}| + |C_{\text{SH2}}|)^2 + 2d]/|E_{\text{SH}} - E_{\text{RL}}|$, taking the d factor as 0.91 on the basis of the presumed LUMO energy of -0.5 eV for MnO_4^- (Figure 12). When the LUMO energy was taken as $+1.5$ and -2.5 eV, very similar plots with nearly the same correlation were also obtained using alternate d values, 0.93 and 0.89, respectively (Supporting Information).

Test of Eqs 7 and 8 with Other Concerted Cycloaddition Reactions. Since eqs 7 and 8 cannot inherently apply to the (2 + 2) cycloaddition reaction model of permanganate ion oxidation (Scheme 2b), our results cannot definitely exclude this mechanism. However, these equations can apply in general to other concerted cycloadditions such as Diels–Alder reactions if one component of the reactants has a symmetrical structure. We have analyzed some rate data of Diels–Alder reactions in the literature on the basis of eq 7 or 8 using MO data obtained by PM3 calculations. It was

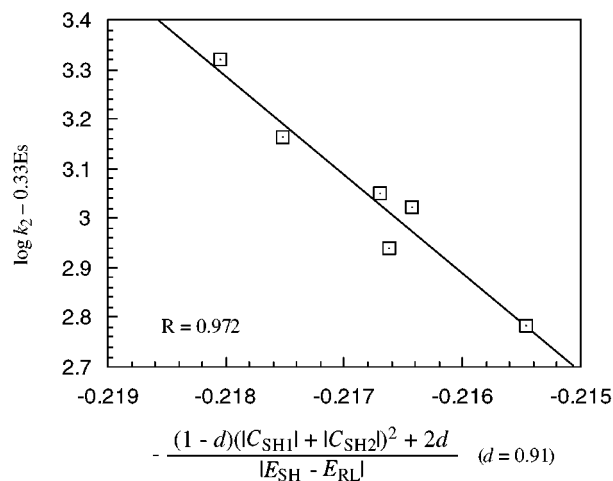


Figure 12. Plots of $\log k_2 - 0.33E_{\text{S}}$ vs $-[(1-d)(|C_{\text{SH1}}| + |C_{\text{SH2}}|)^2 + 2d]/|E_{\text{SH}} - E_{\text{RL}}|$ for the reactions of MnO_4^- with alkyl vinyl ethers; $d = 0.91$ (rate data from ref 4).

found that this method not only reproduces simple Hammett plots but also reproduces extended Hammett plots and other linear free-energy relationship for Diels–Alder reactions (Supporting Information). The detailed comparative studies of permanganate ion oxidations and Diels–Alder reactions of the same sets of alkenes will appear elsewhere.

Conclusion

The substituent effects on the reactions of permanganate ion with unsymmetrical alkenes were analyzed with the newly proposed rate equations, eq 7 or 8, on the assumption of concerted (3 + 2) cycloaddition mechanism. The linear free-energy relationships obtained as the results are remarkably similar to those obtained from Hammett equation or its correction forms, supporting the (3 + 2) mechanism for the formation of cyclic manganese(V) diesters. Equations 7 and 8 are generally applicable to other concerted cycloadditions such as Diels–Alder reactions without any corrections. The factor d , which was introduced to the equations to estimate the extent of localization of the frontier orbitals at the reaction sites of the transition state, agrees with other parameters that are closely related to the position of the transition state such as activation entropy or secondary deuterium isotope effect.

Supporting Information Available: Figures of the plots of $\log k_2$ vs $[(1-d)(|C_{\text{SL1}}| + |C_{\text{SL2}}|)^2 + 2d]/|E_{\text{RH}} - E_{\text{SL}}|$ for the reactions of chalcone derivatives plotted with alternate E_{RH} and d values, a figure of the plot of $\log k_2$ vs $[(1-d)(|C_{\text{SL1}}| + |C_{\text{SL2}}|)^2 + 2d]/|E_{\text{RH}} - E_{\text{SL}}|$ for the reactions of methyl cinnamate derivatives plotted with $d = 1$, figures of the plots of $\log k_2 - 0.33E_{\text{S}}$ vs $-[(1-d)(|C_{\text{SH1}}| + |C_{\text{SH2}}|)^2 + 2d]/|E_{\text{SH}} - E_{\text{RL}}|$ for the reactions of alkyl vinyl ethers plotted with alternate E_{RL} values, and the results of the analysis for the Diels–Alder reactions between 9,10-dimethylanthracene and a set of seven directly substituted *trans*-dienophiles and between maleic anhydride and six anthracene derivatives (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(37) The ρ^* value of -0.6 in ref 3 may be incorrect.