

Permanganate Oxidation of Alkenes. Substituent and Solvent Effects. Difficulties with MP2 Calculations

Kenneth B. Wiberg,^{*,†} Yi-gui Wang,[†] Stepan Sklenak,^{†,§} Carol Deutsch,^{†,||} and Gary Trucks[‡]

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107, and Gaussian, Inc., 340 Quinnipiac Street, Bldg 40, Wallingford, Connecticut 06492

Received May 1, 2006; E-mail: kenneth.wiberg@yale.edu

Abstract: The permanganate oxidation of alkenes has been studied both experimentally and computationally. Transition state structures were located for the reaction of permanganate ion with a variety of monosubstituted alkenes at the B3LYP/6-311++G** level. Although the calculated activation energy for the reaction with ethene was reasonable, the calculated effect of substituents, based on the energies of the reactants, was much larger than that experimentally found. This was shown to be due to the formation of an intermediate charge–dipole complex which led to the transition state. Reaction field calculations found the complex to disappear in a high dielectric constant medium, and the range of activation energies for the reaction in solution became quite small. MP2 calculations were carried out in order to have a comparison with the DFT results. MP2–MP4 gave unusual results for calculations on permanganate ion as well as chromate ion and iron tetraoxide. They also gave markedly unreasonable results for the activation energy of the reaction of permanganate with ethane. CCSD/6-311++G** calculations gave satisfactory results for permanganate ion and chromate ion. At this level of theory, the reaction of permanganate with ethene was found to have a very early transition state, when the bond lengths of the reactants just began to change. The reaction was calculated to be very exothermic (–69 kcal/mol), and this was confirmed via calorimetry. The rates of permanganate oxidation of allyl alcohol and acrylonitrile were determined, and they had similar reactivities. The kinetics and the products of the reaction of permanganate with crotonate ion were examined in some detail.

1. Introduction

One might expect that the permanganate oxidation of an alkene such as crotonate ion would be a relatively slow reaction. First, it is a bimolecular reaction, and in addition, both reactants have a negative charge. Thus there will be two unfavorable entropy of activation terms. Second, alkenes normally react readily with electrophilic species, and not nucleophiles. In permanganate ion, the oxygens are more electronegative than manganese,¹ and as a result each oxygen bears about a one-half negative charge. In the initial stages of the reaction, permanganate ion should appear as a nucleophile when approaching an alkene. Despite this, the reaction is remarkably rapid with rate constants on the order of $100 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, requiring the use of a stopped-flow reactor and dilute solutions in order to study the kinetics.^{2,3}

Much is known about the permanganate oxidation of alkenes. It leads to cis-hydroxylation,⁴ and ¹⁸O labeling experiments show

that both oxygens are derived from permanganate.⁵ This suggests a cyclic five-membered ring intermediate, as originally proposed by Wagner.⁶ Substituent effects on the rate of reaction are generally small.^{2,3,7} The products of the reaction depend on pH, with diol formation favored at high pH, ketol formation favored in neutral solution,⁸ and C=C bond cleavage occurring in acidic solutions.^{3,9} Spectrometric studies have located a Mn(V) intermediate in the reaction.^{3,10} Kinetic isotope effects have also been studied.^{10,11}

One approach to gaining further information concerning this reaction is computational, and Houk and Strassner have located a transition state for the oxidation of ethene at the B3LYP/6-31G* level.¹¹ They showed that the alternative [2 + 2] cycloaddition mechanism had a much higher activation energy.

[†] Yale University.

[‡] Gaussian, Inc.

[§] Present address: J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic.

^{||} Present address: Department of Physiology, University of Pennsylvania, Philadelphia, PA.

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Table 1. Results of B3LYP/6-311++G** Calculations for the Permanganate Oxidation of Monosubstituted Alkenes^a

X	ν^b	ΔH^\ddagger^c	ΔG^\ddagger^c	ΔS^\ddagger^c	ΔH_r^d	ΔG_r^d	ΔS_r^d
H ^e	427i	11.1	21.3	-34.2	-39.8	-28.7	-37.1
CH ₃	420i	12.1	23.2	-37.4	-40.7	-28.9	-39.6
F	466i	9.2	20.3	-37.3	-54.3	-42.8	-38.5
CH ₂ OH	395i	8.7	19.9	-37.6	-44.6	-32.5	-23.4
SiH ₃	403i	6.9	18.2	-37.8	-38.2	-26.7	-38.7
CF ₃	379i	4.0	15.4	-38.2	-48.6	-36.8	-39.8
CCl ₃	361i	3.9	15.2	-37.6	-48.3	-36.4	-39.8
CN	391i	0.7	11.7	-37.1	-45.2	-33.7	-38.7

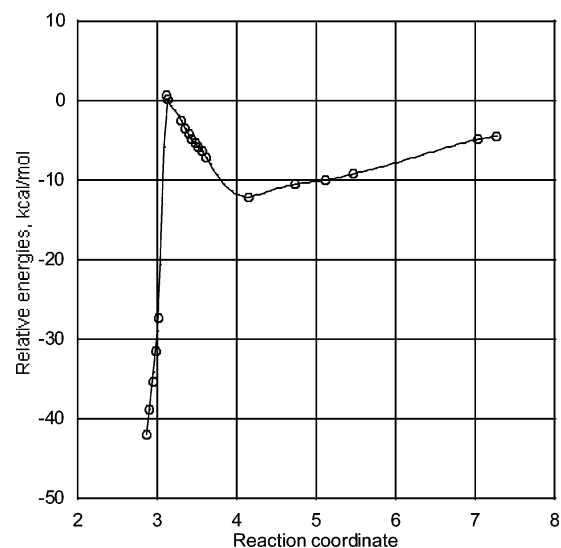
^a Units: ν , cm⁻¹; ΔH , ΔG , kcal/mol; ΔS , cal/mol/deg, $T = 298$ K. ^b Calculated imaginary frequencies for the transition states, cm⁻¹. ^c Activation energies are relative to the energies of the two reactants. ^d Energy changes for the overall reaction. ^e HF/6-311++G**: $\nu = 1301i$, $\Delta H^\ddagger = 20.4$, $\Delta G^\ddagger = 31.6$, $\Delta S^\ddagger = -37.6$, $\Delta G_r = -141.8$.

At about the same time, we obtained corresponding results at the B3LYP/6-311++G** level. The activation energy derived from these calculations is compatible with the kinetic studies. Subsequent calculations by Strassner and Busold dealt with the effect of alkyl substituents on the oxidation of crotonic acids¹² and with the reaction of permanganate ion with alkynes.¹³

Our primary interest was in studying the reason for the very small substituent effects. We located the transition state for the reaction of permanganate with acrylonitrile and other monosubstituted ethylenes using B3LYP/6-311++G**. The results are given in Table 1. A very large effect of substituents was calculated suggesting that acrylonitrile should react about 10⁶ faster than allyl alcohol. A kinetic study (see below) indicated that acrylonitrile was only 1.9 times as reactive as allyl alcohol, in contradiction to the results of the calculations. A difference between experiment and calculations also is found in the work of Strassner and Busold.⁹ The experimental data of Freeman and Kappos⁷ gave a range of 1.5 kcal/mol for the ΔG^\ddagger for the oxidation of substituted crotonic acids, whereas the calculations gave a range of 3.9 kcal/mol for these compounds.

The above calculations are for the gas phase. CCSD calculations described below made it apparent that there was an initial charge-dipole complex that could be significantly stabilized with respect to the reactants. This type of complex has been observed in other gas-phase reactions such as S_N2 displacements.¹⁴ One might have expected it to be small for the present reaction, since the permanganate ion is large and the negative charge is distributed over four oxygens. However, it was found to be significant. The B3LYP calculated energy changes along the reaction coordinate for the acrylonitrile reaction are shown in Figure 1. In the reaction, the initial approach of acrylonitrile to MnO₄⁻ has a terminal H directed toward the MnO₄⁻ oxygens. As the distance becomes smaller, the cis hydrogens are directed toward the MnO₄⁻ oxygens. Near the transition state, acrylonitrile rotates to direct the π -electrons toward the MnO₄⁻ oxygens. Snapshots of the structures along the reaction coordinate may be found in the Supporting Information. In view of the complex changes that occur, the reaction coordinate was just taken as the average distance between the Mn and the acrylonitrile carbons.

With acrylonitrile, the initial complex is 12 kcal/mol stabilized with respect to the reactants. The complexes were located for each of the substituents, and their energies relative to the

**Figure 1.** Changes in energy along the reaction coordinate for the reaction of acrylonitrile with permanganate in the gas phase. The energy of the reactants is given as zero.**Table 2.** Intermediate Complexes and Solvent Effects for the Permanganate Oxidation of Monosubstituted Alkenes^a

X	ΔH_c^b	ΔG_c^b	ΔH_s^c	ΔG_s^c	ΔH_p^d	ΔG_p^d
H	-1.9	0.3	9.9	20.1	-42.4	-31.3
CH ₃	-2.8	2.5	10.8	22.0	-42.8	-30.9
F	-6.4	-0.8	10.1	21.2	-51.0	-39.6
CH ₂ OH	-10.9	-5.7	10.7	21.9	-41.9	-29.8
SiH ₃	0.4	-3.8	9.8	21.1	-39.2	-27.6
CF ₃	-0.9	-1.8	9.9	21.4	-43.0	-31.2
CCl ₃	-7.8	-2.5	11.5	22.9	-43.2	-31.3
CN	-10.9	-6.7	8.5	17.7	-39.0	-29.2

^a Energies are given as kcal/mol, $T = 298$ K. ^b Calculated energies of complexes relative to the reactants in the gas phase. ^c Calculated activation parameters for the reaction in aqueous solution. ^d Calculated overall energy changes in aqueous solution.

reactants are given as ΔH_c and ΔG_c in Table 2. The unusually high stability of the complex derived from allyl alcohol is due to the formation of a hydrogen bond between the OH proton and a permanganate oxygen. The complex formation is, as expected, generally large with alkenes having large dipole moments. It should be noted that ΔG values are in general less reliable than ΔH because the former is more strongly affected by the low vibrational frequencies that are not accurately calculated.

In a polar solvent, the charge on permanganate ion will be stabilized, and the intermediate complex would be expected to disappear, as was found with the S_N2 reaction. The structure of the complex in the reaction with acrylonitrile was reoptimized using the PCM reaction field model¹⁵ for water as the solvent. The two reactants were found to move away from each other, and the final energy was within 0.1 kcal/mol of that for the individual reactants. Thus, the complex was found to disappear in solution.

Estimates of the energies of the reactants, the transition state, and the products of the reactions of the alkenes with permanganate in aqueous solution were obtained using the PCM model, and the results are summarized in Table 2. Here, ΔH_s^\ddagger and ΔG_s^\ddagger ,

(12) Strassner, T.; Busold, M. *J. Org. Chem.* **2001**, *66*, 672.(13) Strassner, T.; Busold, M. *J. Phys. Chem. A* **2004**, *108*, 4455.(14) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672.(15) Cappelli, S.; Corni, B.; Mennucci, B.; Cammi, R.; Tomasi, J. *J. Phys. Chem. A* **2002**, *106*, 12331. Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43.

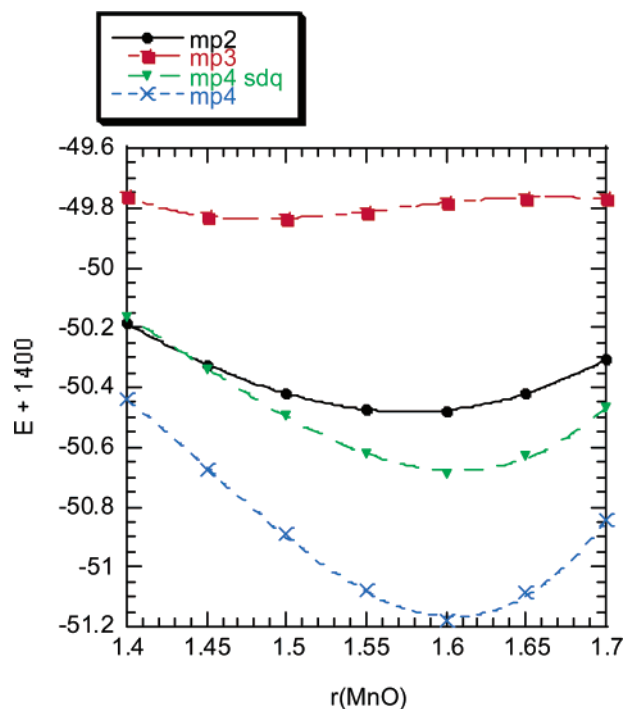


Figure 2. Effect of MP level on the calculated energy and bond length for the permanganate ion. Energies are given in $H =$ atomic units (hartrees).

are the activation parameters for the reaction in solution, and ΔH_p and ΔG_p are the overall energy changes for the reactions carried out in solution. The range of activation energies has been markedly reduced. The PCM reaction field model has some uncertainty, especially for aqueous solutions. With this in mind, the results suggest that the rates of reaction of most of the alkenes might be expected to be similar in water. However, acrylonitrile is still calculated to be more reactive than the other alkenes.

2. Permanganate Ion. DFT methods provide one way in which the HF energies may be corrected for the correlation energy, and MP2 provides a different way in which to do so. It is often helpful to compare the results using these two procedures.¹⁶

The results of MP/6-311+G** calculations for permanganate ion are shown in Figure 2 and Table 3. Different levels lead to different equilibrium bond lengths. There is a remarkably large calculated increase in energy on going from MP2 to MP3, whereas a decrease is normally found.¹⁷ The energy does decrease with MP4(SDQ), but the full MP4 (including triple excitations) leads to a remarkably large further decrease in energy. The unusual energy changes found with the MP series are not improved on going to QCISD and QCISD(T), and if anything, the results are even less satisfactory (cf. Table 2 and Supporting Information).

The coupled cluster methods are generally considered to be among the more successful approaches using a single reference determinant.¹⁹ Both CCSD/6-311+G* and CCSD(T) give similar bond lengths for the permanganate ion that are in satisfactory agreement with the experiments (Figure 3). The decrease in energy on going from CCSD to CCSD(T) is only

Table 3. Calculated M–O Bond Lengths of MO_4 Species, 6-311+G*

level	FeO_4	MnO_4^-	CrO_4^{2-}
experiment		1.610(6) ^a	1.65 ^b
HF	1.516	1.540	1.602
B3LYP	1.576	1.601	1.658
MP2	1.501	1.580	1.692
MP3	1.660	1.489	1.574
MP4(SDQ)	1.523	1.606	1.770
MP4(SDQT)	1.520	1.560	1.750
QCISD	> 1.8	> 1.8	> 1.8
QCISD(T)	1.555	1.562	1.650
CCSD	1.602	1.590	1.636
CCSD(T)	^c	1.607	1.660

^a Average Mn–O bond length for tetraethylammonium permanganate (Whang, D.; Chung, S.-K.; Kim, K. *Acta Crystallogr.* **1991**, C47, 2674). $KMnO_4$ gave 1.607 (Palenik, G. J. *Inorg. Chem.* **1967**, 6, 503). ^b Average value from several chromate salts (Deeth, R. J. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 3745). ^c High level calculations find FeO_4 to not be tetrahedral.¹⁸

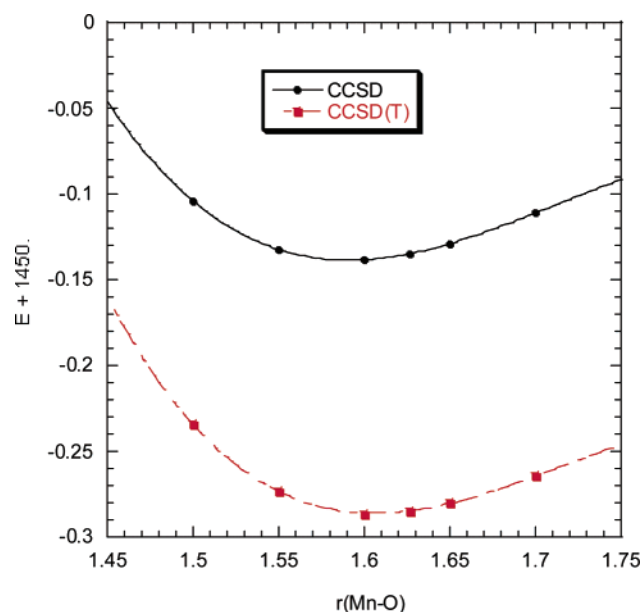


Figure 3. Results of CCSD and CCSD(T) calculations for the permanganate ion. Energies are given in atomic units (hartrees).

about 0.15 H, much smaller than the difference between MP4-(SDQ) and MP4(SDTQ).

Permanganate ion is not the only species that leads to problems with commonly used theoretical methods. The iso-electronic chromate ion and iron tetroxide behave in a similar fashion. The results of these calculations are given in Table 3. CCSD calculations are again more satisfactory for the chromate ion, with both CCSD and CCSD(T) giving similar calculated Cr–O bond lengths that are in satisfactory agreement with the experimental data.

Iron tetroxide is different than the other compounds in that high level calculations find that it is not tetrahedral.¹⁸ There does not appear to be any experimental data regarding its structure.

3. Computational Studies for the Permanganate Oxidations

a. MP2 and MP4. In a number of cases, MP2 gives somewhat more satisfactory geometries and relative energies

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(17) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 90ff.

(18) Cao, Z.; Wu, W.; Zhang, Q. *THEOCHEM* **1999**, 489, 165.

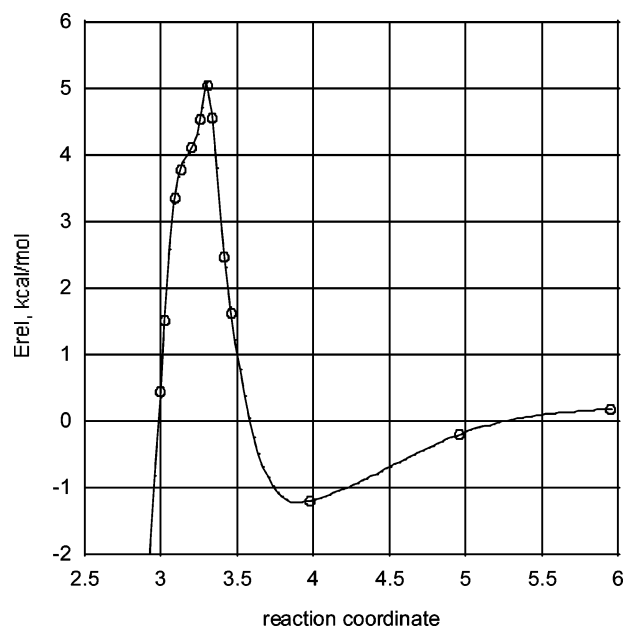


Figure 4. Change in energy along the reaction coordinate for the ethene–permanganate reaction.

than DFT.¹⁶ Despite the problems noted above in using MP2 for the permanganate ion itself, the oxidation of ethene was studied at this level of theory. The B3LYP transition state was taken as the starting point, and an MP2/6-311+G* optimization to a transition state was carried out. It was shown to be a transition state by observing only one imaginary frequency (1254i), which is unusually large. The structure was close to that of the B3LYP transition state. The energies of ethene and permanganate ion were obtained at the same level of theory (Table S3, Supporting Information). From these results, at 25 °C, $\Delta H^\ddagger = 111$ kcal/mol and $\Delta G^\ddagger = 121$ kcal/mol. In addition, the reactants were calculated to be 37 kcal/mol lower in energy than the product! These results clearly indicate that MP2 is not satisfactory for a study of this reaction.

In view of the large change in energy for the permanganate ion on going from MP2 to MP4, MP4/6-311+G* calculations were carried out for the reaction of ethene using the MP2 geometries. Now ΔH^\ddagger increased to 266 kcal/mol! The energy of the permanganate ion is reduced more than that of the transition state on going from MP2 to MP4. Clearly, these levels of theory are not satisfactory.

b. CCSD. CCSD appeared to be satisfactory in the calculations for the permanganate ion, and therefore it was used to study the oxidation of ethene and allow a comparison with B3LYP. It was not possible for us to directly optimize to the transition state since CCSD analytical second derivatives were not available, and it was not practical to calculate the force constants numerically. Instead, we calculated a series of points along the reaction coordinate that was taken as the distance between the manganese and the center of the C=C. The energy changes are shown in Figure 4, and the geometry changes are shown in Figure 5. As the reactants approach each other, there is an initial drop in energy as is common for the gas-phase reactions of ions with neutral compounds. The subsequent energy increase before 3.4 Å is probably mainly a repulsive steric interaction between the two reactants as they approach each other.

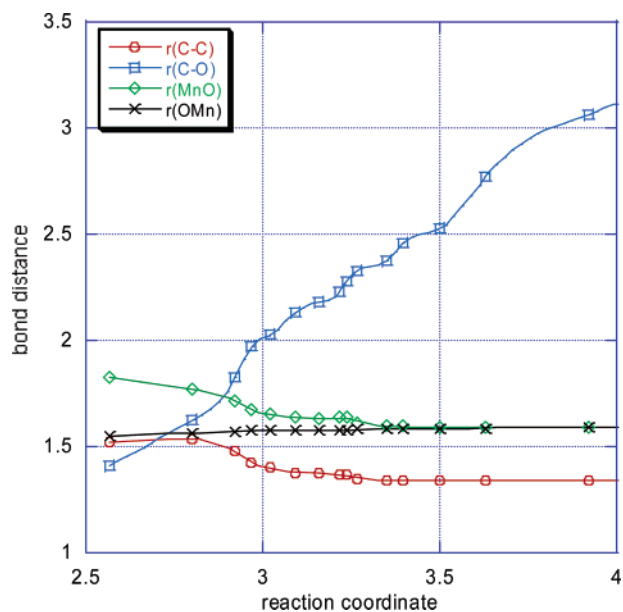


Figure 5. Change in structural parameters along the reaction coordinate.

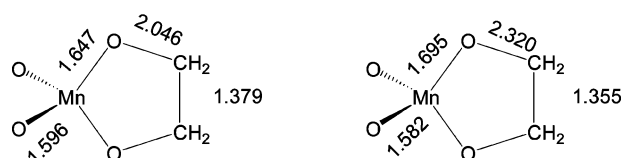


Figure 6. Calculated transition state geometries: (left) B3LYP; (right) CCSD.

Table 4. CCSD/6-311++G** Calculated Energies for the Reaction of MnO_4^- with Ethene

compound	energy (H)	E_{rel} (kcal/mol)	
MnO_4^-	-1450.138 42		
ethene	-78.374 29		
reactants	-1528.512 71	0.0	
initial complex	-1528.514 61	-1.5	0.0
TS	-1528.504 66	5.1	6.2
product	-1528.621 95	-68.5	

The transition state is found just after the electronic effects begin to appear and has a distance close to 3.25 Å, with an energy of -1528.504 66 H. The energies of the reactants and the product are listed in Table 4, and indicate a ΔE^\ddagger of 6.2 kcal/mol starting from the initial energy minimum. The overall change in energy for the reaction is very large (-69 kcal/mol), in accord with finding a very early transition state. The changes in the NBO²⁰ atomic charges along the reaction coordinate are negligible before 3.3 Å and then change monotonically to those of the product.

What is the difference between the B3LYP and CCSD calculations? Some information can be obtained by comparing the calculated geometries of the transition state and the products (Figure 6). It is clear that the B3LYP transition state is more advanced than that found using CCSD, and this provides an opportunity for substituent effects to become somewhat more important.

(19) Bartlett, R. J. In *Modern Electronic Structure Theory*; Yarkony, D. R. Ed.; Advanced Series in Physical Chemistry, Vol. 2; World Scientific: Singapore, 1995. Crawford, T. D.; Schaefer, H. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 2000.

(20) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899.

Table 5. CCSD/6-31+G* Calculated Energies for the Reaction of Acrylonitrile with Permanganate

compound	energy (H)	E_{rel} (kcal/mol)	
MnO ₄ ⁻	-1449.947 49		
acrylonitrile	-170.330 61		
reactants	-1620.278 10	0.0	
initial complex	-1620.297 70	-12.3	0.0
TS	-1620.286 02	-5.0	7.3
product	-1620.395 88	-73.9	

The compound that was found to give the largest effect on the rate of reaction in the B3LYP calculations is acrylonitrile. It was not practical to examine the reaction at the CCSD/6-311++G** level because of its increased size and lower symmetry as compared to the ethene oxidation. CCSD/6-31+G* appeared to be the highest level that was at all practical. Some calculations for the permanganate–ethene reaction were carried out at this level and gave results essentially the same as those with the larger basis set ($\Delta E^\ddagger = 6.2$ kcal/mol, initial complex = -1.2 kcal/mol). The results of the calculations for the permanganate–acrylonitrile reaction are summarized in Table 5.

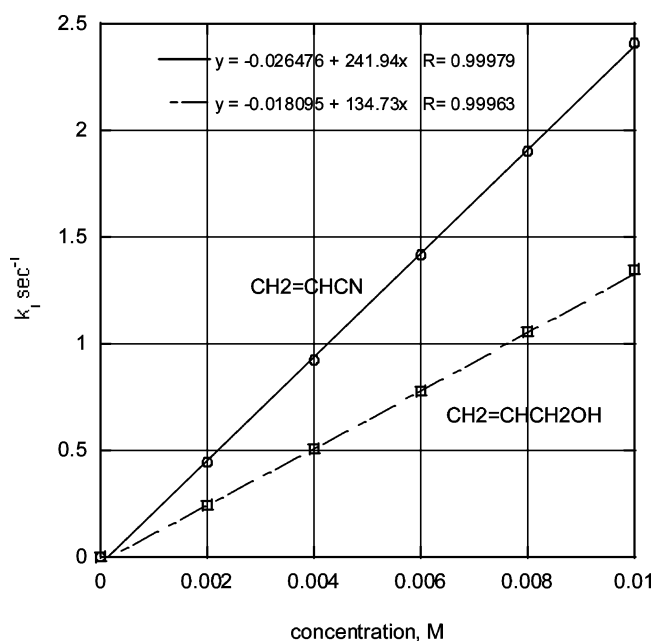
The initial complex is stabilized by an amount similar to that found in the B3LYP calculations. This is followed by an increase in energy of 7 kcal/mol leading to a transition state with a reaction coordinate distance of 3.2 Å. Here, the C=C bond length has increased to 1.375 Å indicating that the reaction has started to occur. The relative energies are comparable to those for the ethene reaction and are in agreement with the experimental observation that allyl alcohol²¹ and acrylonitrile have similar reactivities toward permanganate. This clearly results from a very early transition state that is followed by a remarkably large decrease in energy on going to the products. With acrylonitrile, the latter is calculated to be -74 kcal/mol.

4. Kinetic Studies

There are two aspects of the reaction that could profitably be studied via an examination of the kinetics of the reaction. The first is the relative reactivity of allyl alcohol and acrylonitrile. It is not possible to study ethene because of its low solubility. Allyl alcohol would appear to be a satisfactory water soluble substitute.

The rates of reaction were determined in neutral aqueous solutions in order to avoid the base-catalyzed addition of water to acrylonitrile. The rates of reaction were determined at 525 nm using a stopped-flow reactor. The permanganate concentration was 4×10^{-4} M, and the concentration of the organic compounds was between 0.002 and 0.01 M. The observed pseudo-first-order rate constants are plotted against the alkene concentration in Figure 7 and leads to a second-order rate constant of $135 \text{ M}^{-1} \text{ s}^{-1}$ for allyl alcohol and $242 \text{ M}^{-1} \text{ s}^{-1}$ for acrylonitrile. Thus, acrylonitrile is 1.9 times as reactive as allyl alcohol.

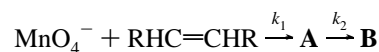
The steps that follow the initial reaction are also of interest, and they can be examined via a kinetic study. Here, a crotonate ion was chosen as the reactant because it would facilitate the product studies. Our previous report showed that the reaction

**Figure 7.** Effect of reactant concentration of the pseudo-first-order rate constants for permanganate oxidation in neutral solutions.

between the crotonate ion and permanganate ion under pseudo-first-order conditions using an excess of the former is first-order in permanganate.² The rate of reaction is also first-order in the crotonate ion, and it is relatively independent of pH. The reaction has now been studied at a number of wavelengths.²² When a large excess of crotonate ion was used at pH 7, the absorbance at 525 nm (permanganate maximum) decreased in a first-order fashion, as the absorbance at 420 nm increased in a corresponding fashion. The intermediate thus formed (**A**) is relatively stable and presumably is a Mn(V) species. When a 2:1 ratio of permanganate to crotonate was used, the final spectrum corresponded to that of the manganate ion (absorption maxima at 439 and 606 nm).

When the reaction was carried out in 0.1 M sodium hydroxide and a high crotonate concentration, the change in absorbance at 525 nm with time was the same as that at pH 7, but the absorbance at 420 nm first increased and then decreased, whereas the absorbance at 584 nm first decreased and then increased. Again, when a low crotonate concentration was used, the final absorbance corresponded to that of the manganate ion.

These data indicate that there are two intermediate species, **A** (420 nm) and **B** (584 nm). The spectra of these two species were derived from a run using 0.1 M crotonate ion in 0.1 M sodium hydroxide, collecting a set of data for 28 wavelengths. The data were analyzed using the following kinetic scheme:



Here, k_1 and k_2 are the same for all wavelengths, and the absorbancy indices of Mn(VII) (the initial point) and of the intermediates **A** and **B** were derived for each wavelength. The rate constants were obtained using the program LORAK.²³ The integrated form of the rate expression for a pair of consecutive reactions may be reduced to an exponential decay function:

(21) It would have been desirable to carry out CCSD calculations for the reaction of allyl alcohol. However, it has an additional rotational degree of freedom, and the DFT calculations indicate that the location of the proton is important. As a result, it was beyond our present computational capabilities.

(22) For a preliminary report on this study, see ref 10.

(23) Deutsch, C. J. In *Computer Programs for Chemistry*; DeTar, D. F., Ed.; Benjamin: New York, 1972; Vol. IV.

$$y_{ij} = a_{1j} e^{a_2 t_i} + a_{3j} e^{a_4 t_i} + a_{5j}$$

Here the y_{ij} terms are the absorbance values at a series of wavelengths (j) and a set of times (i). The constants may be obtained by a nonlinear least-squares fitting procedure. The rate constants k_1 and k_2 are given by a_2 and a_4 , and the absorbance indices of the reactant (ϵ_{Aj}), intermediate (ϵ_{Bj}), and product (ϵ_{Cj}) are derived from a_1 , a_3 , and a_5 :

$$A_0 \epsilon_{Cj} = a_{5j}$$

$$A_0 \epsilon_{Bj} = A_0 \epsilon_{Cj} - a_{3j} \left(\frac{k_2 - k_1}{k_1} \right)$$

$$A_0 \epsilon_{Aj} = a_{1j} + \frac{A_0 \epsilon_{Cj} k_2 - A_0 \epsilon_{Bj} k_1}{k_2 - k_1}$$

Here A_0 is the initial concentration of the reactant.

The spectra derived from the kinetic data are summarized in Figure 8. The spectrum of **A** agreed with that found in the pH 7 runs.

The dependence of k_2 on the hydroxide ion concentration was examined and gave the data shown in Figure 9. The experimental error at low hydroxide concentration is relatively large. The data suggest a linear dependence on base, with possibly a slow water catalyzed reaction.

The above kinetic runs were carried out using a large excess of crotonate ion vs permanganate in order to avoid the oxidation of the intermediate by permanganate. This latter reaction could be studied by carrying out the reaction using a constant permanganate concentration (4×10^{-4} M) and varying the crotonate concentration. When the permanganate had just disappeared, the ratio of Mn(V) to Mn(VI) could be estimated from the absorbance at 420 nm (mainly Mn(V)) and 600 nm (mainly Mn(VI)). The results of such a study are shown in Figure 10.

5. Thermochemical Study

One significant difference between the DFT and CCSD calculations is found in the predicted overall energy changes for the reaction with acrylonitrile: -45 kcal/mol for DFT and -73 kcal/mol for CCSD. These values are, of course, for the gas phase, and the energy change in solution will differ as a result of the heats of solution of the reactants and products. The results in Table 1 suggest that the overall energy change may decrease somewhat on going to an aqueous solution.

The kinetic results described above show that, in neutral solution, permanganate reacts with a large excess of an alkene (to avoid oxidation of the intermediate by permanganate) to give a rather stable Mn(V) intermediate. The heat of reaction of permanganate with a large excess of allyl alcohol in aqueous solution was determined calorimetrically giving $\Delta H_r = -87 \pm 2$ kcal/mol. This is in accord with the results of the CCSD calculations and considerably larger than the DFT prediction. It should be recognized that although the species formed in the reaction is a Mn(V) derivative, it does not necessarily have the structure that was calculated. It may well include a molecule of water making a five-coordinate Mn. The highly exothermic nature of the reaction is clearly consistent with a very early transition state. It was not practical for us to try to calculate the energy of a hydrated Mn(V) intermediate at the CCSD level.

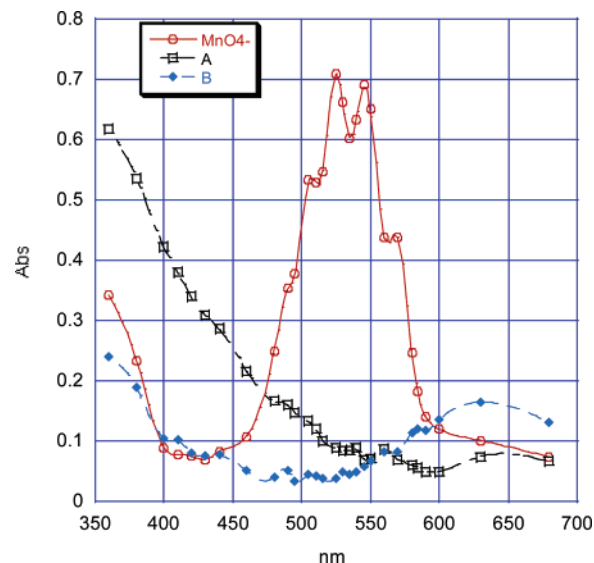


Figure 8. Spectra of the permanganate ion and the two Mn(V) species derived from the kinetic data.

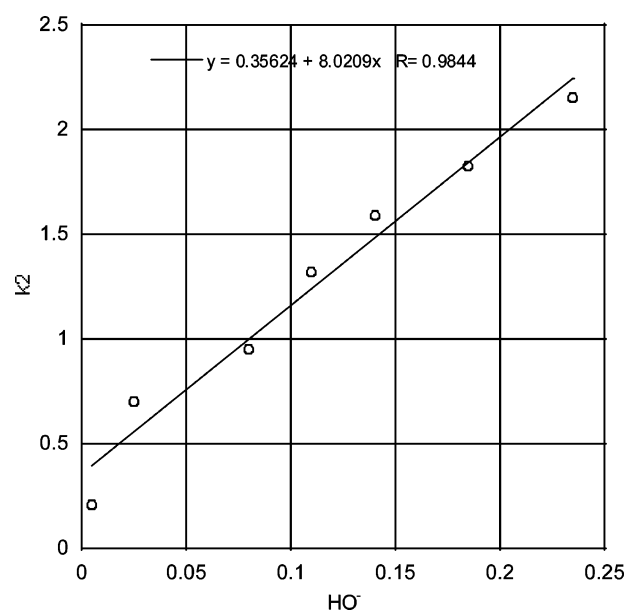


Figure 9. Effect of hydroxide ion concentration on k_2 .

6. Product Study

The products of the oxidation of crotonate ion were studied using ^{14}C labeled crotonic acid. The reaction was carried out under two sets of reaction conditions. In the first, 250 mL of a 6×10^{-4} M crotonate solution were placed in one bulb and 250 mL of 8×10^{-4} M permanganate were placed in the second. The two solutions were allowed to flow at a controlled rate into a small mixing chamber with a stirrer, and the mixed solution was collected in a flask. Under these conditions, the final manganese species was Mn(VI). The excess oxidant was reduced with bisulfite. To the product solution was added known amounts of crotonic acid and threo-2,3-dihydroxybutyric acid. The solution was made basic and evaporated to dryness. Methanolic HCl and trimethylorthoformate were added, and the mixture was warmed to facilitate ester formation. After removal of the more volatile material, the residue was separated by gas chromatography giving methyl 2,3-dihydroxybutyrate and

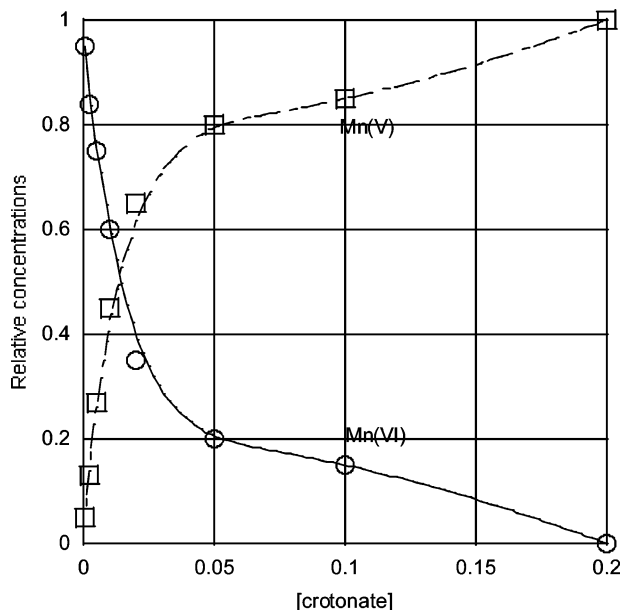


Figure 10. Effect of crotonate concentration on the final ratio of Mn(V) to Mn(VI) with an initial permanganate concentration of 4×10^{-4} M.

Table 6. Results of Product Studies at 0 °C

[crotonate], M	[HO ⁻], M	%dihydroxybutyric acid ^a	%crotonic acid ^b
6×10^{-4}	0.2	64 ± 1	6 ± 1
6×10^{-4}	0.0	33 ± 1	4 ± 3
0.2	0.2	96 ± 1	99 ± 1
0.2	0.0	90 ± 5	98 ± 1

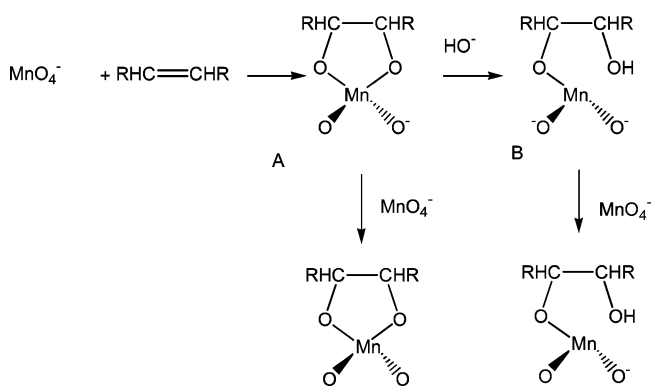
^a Based on the amount of permanganate ^b With a large excess of crotonic acid, little of the acid undergoes reaction.

methyl crotonate. The determination of the ¹⁴C concentration was carried out with a scintillation counter, and this allowed the determination of the amount of crotonic acid that remained and the amount of dihydroxybutyric acid that had been formed. In the second set of reactions, the permanganate solution was added to an excess of crotonate with stirring over a period of 4–5 h. Here, Mn(V) is the final product. The reaction solution was worked up as above. The results are summarized in Table 6.

With the low crotonate concentrations, the amount of permanganate was not sufficient to effect complete reaction (a 1:2 ratio would be required for the formation of manganate as the product), and as a result, some unreacted crotonic acid was found. With 0.2 M sodium hydroxide, the major product is dihydroxybutyric acid, whereas, in neutral solution, the amount of this acid is markedly reduced. The remaining product is presumably largely a ketol, formed by the conversion of the Mn(V) intermediate to Mn(VI) followed by the conversion of the latter to the ketol and Mn(IV).

When a large excess of crotonate is used, the major product is the dihydroxy acid in both neutral and basic solutions. Thus, the Mn(V) intermediate leads only to the dihydroxy product. A reasonable hypothesis (see Scheme 1) is that, in basic solution, the initial Mn(V) intermediate is opened by the hydroxyl ion at a rate competitive with the permanganate oxidation of the intermediate, and the subsequent oxidation of the opened Mn(V) species to Mn(VI) and hydrolysis of the latter lead mainly to the dihydroxy acid.

Scheme 1



7. Summary

It is known from several studies that substituent effects on the oxidation of alkenes are relatively small. A substituent effect study for cinnamic acids leads to a Hammett ρ value of 0.1,² and in the present work, acrylonitrile was found to be only 2 times as reactive as allyl alcohol.

The reaction was studied computationally. It was found that B3LYP/6-311++G** predicted much larger substituent effects, based on the energies of the reactants, than are found. This was shown to be due to the formation of an initial charge–dipole complex that leads to products via the rate-determining step. PCM calculations indicated that the complex should disappear in aqueous solution, and under these conditions, most of the alkenes were predicted to have about the same activation energy. The activation energy for acrylonitrile was somewhat lower than that for the other alkenes. MP2–MP4 were found to be unsatisfactory for calculations for the permanganate ion itself and gave very large calculated activation energies.

CCSD/6-311++G** calculations for the permanganate ion gave a satisfactory result, and therefore the transition state for the reaction of permanganate with ethene was studied at this level of theory. It was found that there were no significant structural changes until just before the transition state, indicating a very early transition state. This is in agreement with the very large exothermic reaction that follows the transition state. A calorimetric study gave a very large overall change in energy.

The kinetics of the reactions of allyl alcohol and acrylonitrile were studied, and the latter was found to be only 1.9 times as reactive as the former. A CCSD study of the oxidation of acrylonitrile found the reaction to proceed in a fashion very similar to that for ethene.

Kinetic data indicate that the initial reaction between permanganate ion and crotonic acid has a first-order dependence on both reactants and is independent of hydroxide ion concentration. The initially formed Mn(V) species (**A**) is relatively stable at pH 7 and can be observed when a high crotonate concentration is used. With lower concentrations, the oxidation of **A** to Mn(VI) by permanganate becomes competitive with the oxidation of crotonate, and with a 2:1 ratio of permanganate to crotonate, the product is a manganate species.

At higher hydroxide concentrations, **A** is converted to a second Mn(V) species (**B**) at a rate proportional to the hydroxide ion concentration. These data suggest the process shown in Scheme 1.

Oxidation of intermediate **A** by permanganate leads to a cyclic species that can lose a proton from carbon to give a ketol and

Mn(IV). The product study suggests that oxidation of intermediate **B** by permanganate leads to an open species that largely gives diol as the product. Hydrolysis of either **A** or **B** gives only the diol product.

The study by Lee and Brownridge³ of the permanganate oxidation of cinnamic acid in an acidic solution also found a Mn(V) species as a transient intermediate, and here the product of the reaction was benzaldehyde, formed by cleavage of the C=C bond. The inorganic product was found to be Mn(III). Thus, it appears that the intermediate **A** in Scheme 1 decomposes in an acid solution (1 M HClO₄) to directly give Mn(III) and benzaldehyde. Under the acidic conditions, **A** is probably protonated, and this may account for the change in mode of reaction as compared to a neutral solution.

8. Experimental Section

a. Kinetics of the Permanganate Oxidation of Crotonate Ion. A fresh potassium permanganate solution was prepared for each series of experiments. The concentration was 8×10^{-4} M, and it had a pH of 8.3. Sodium hydroxide solutions were prepared from 1 N standard solutions, and the kinetic experiments were carried out with an ionic strength of 0.7 M via the addition of sodium nitrate. In the stopped-flow studies, equal quantities of crotonate solutions containing sodium hydroxide were mixed with the permanganate solution. Thus, the concentration of permanganate in the flow cell was 4×10^{-4} M. The stopped-flow apparatus used a 0.7 cm cell that was cooled to the desired temperature, and the storage containers were kept at the same temperature. The absorbance data at a given wavelength were digitized and stored in a computer using 100 points per run. The time intervals were chosen so that at least 15 points would be collected for the first half-life, and longer time intervals could be used for the latter part of each run. The runs were replicated from 5 to 20 times, and the data for a given wavelength were averaged.

Data were collected for a number of wavelengths and were analyzed simultaneously to obtain k_1 and k_2 along with the initial absorbance and the absorbance indices of the intermediates **A** and **B**. The program LORAK²³ was used for the calculations.

b. Relative Rates of Oxidation of Allyl Alcohol and Acrylonitrile. The rates of oxidation were determined with a stopped-flow system using pseudo-first-order conditions with a large excess of the organic reagent. The permanganate concentration was 8×10^{-4} M, and the reactant concentrations ranged from 0.004 to 0.02 M. Since equal volumes of the two solutions are introduced into the stopped-flow cell, the reacting concentrations are one-half of the above values. The

acrylonitrile solutions were freshly prepared, and it was shown that acrylonitrile is quite stable in neutral aqueous solutions.¹⁸ The rate of oxidation of allyl alcohol agreed with that obtained in our earlier study.²

c. Calorimetric Study. The calorimeter consisted of a 30 mL polyethylene bottle with a 100 ohm (0 °C) thin film platinum resistance thermometer inserted into its side and a magnetic stirrer. The thermometer had a temperature coefficient of 0.385 ohm/deg. The bottle, along with a similar bottle for the reagent to be added, was placed in tight fitting holes in a Styrofoam block. The first solution (20 mL) was added to the calorimeter flask, and the second solution was placed in the other flask. The system was allowed to equilibrate for 30–60 min while the resistance was measured with a 6-digit ohmmeter. The resistance became constant to ± 0.001 ohm. The second solution (2 mL) was then added with stirring, and after a short while the stirrer was stopped. The final resistance was noted.

The calorimeter was calibrated using the known heat of reaction of hydrochloric acid with sodium hydroxide (-13.76 kcal/mol).²⁴ To the calorimeter flask was added 10 mL of 1 N hydrochloric acid and 10 mL of 1 M allyl alcohol in water. It was assumed that allyl alcohol would not significantly affect the heat of reaction. After equilibration, 2 mL of 1 N sodium hydroxide solution were added. The change in resistance was 0.445 ± 0.004 ohm (4 runs), leading to an effective heat capacity of the system containing 22.00 mL of an aqueous solution of 23.78 ± 0.24 cal/deg.

In the oxidation of allyl alcohol, 20 mL of 0.5 M allyl alcohol were added to the calorimeter flask. After equilibration, 2.00 mL of 0.1 M potassium permanganate were added dropwise with stirring in order to avoid oxidation of the intermediate by permanganate. Stirring was stopped, and the final resistance was noted. The change in resistance was 0.288 ± 0.005 ohm (3 runs), which leads to a heat of reaction of -88.7 ± 2.0 kcal/mol.

d. Calculations: The ab initio and PCM calculations were carried out using Gaussian-03.²⁵

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Supporting Information Available: Tables of structural data and energies, and the complete list of authors for ref 25. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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