was then added, and the mixture was further degassed by three freeze–thaw cycles. After the reaction mixture was cooled in a dry ice/acetone bath to −78 °C, butadiene (6 g, 110 mmol) was condensed into the pressure bottle and the apparatus was sealed. After the reaction mixture was heated to 100 °C with stirring for 8 h, the reaction mixture was cooled and the resulting suspension was transferred by forced siphon with a cannula into a 30-mL centrifuge tube. Centrifugation was then used to separate **5** from the solution of products. During the entire process, **5** was continuously kept under an inert atmosphere. After centrifugation, the supernatant containing the product acetoxylated butadiene dimer was separated from the solid **5** by forced siphon. The recovered catalyst **5** was washed twice with 20-mL aliquots of degassed toluene and finally transferred back into the pressure bottle as a toluene suspension with an additional 30 mL of degassed toluene. The identity of the products and their relative amounts were found to be the same as those produced by the use of $Pd(OAc)_2(PPh_3)_2$ (generated in situ) based on GC analysis. The products' identities were confirmed by GCMS; (*E*)-1-acetoxy-2,7-octadiene (68%) ($M^+ = 168$, major fragments at *m/e* 126 and 108), 3-acetoxy-1,7-octadiene (26%) ($M^+ = 168$, major fragments at *m/e* 126 and 99), 1-acetoxy-2-butene (3%) ($M^+ = 114$), 3-acetoxy-1-butene (3%) ($M^+ = 114$).

Palladium Analysis. The procedure used was a modification of Shanina's.[21] The filtrate from a reaction between morpholine and allyl benzoate was concentrated and transferred to a 20-mL quartz crucible. After evaporation to dryness, 4 mL of concentrated H_2SO_4 was added, and the mixture was gently heated on a hot plate until the sample was completely homogeneous. Then, 10 mL of concentrated HNO_3 was added dropwise followed by further heating on the hot plate for an additional 24 h with occasional shaking. After this solution was cooled to 25 °C, the solution was diluted with distilled water in a 25-mL volumetric flask and analyzed for palladium content by ICP analysis by the Agricultural Analytical Services Laboratory at Texas A&M University. A blank palladium analysis using the same amount of reagents excluding the filtrate residue was also carried out along with a Pd sample of known concentration. The standardized solution of Pd containing 31 μg of Pd/mL analyzed correctly as having 30 μg of Pd/mL. These analyses of the residue of the filtrate from a reaction showed that there was <1 μg of Pd/mL present. Analysis of a blank solution that supposedly did not contain palladium similarly analyzed as having <1 μg of Pd/mL. Thus, the amount of Pd left in the residue from the filtrate of the first cycle of a catalytic reaction was too small to measure and corresponded to less than 0.001% of the charged catalyst. Similar analyses were also performed on a sample of oligomer **4**. In this case, the same procedure described above was followed except that solid **4** was used in place of the filtrate residue. The result showed that a 0.07-g sample of oligomer **4** contained 1.07×10^{-3} mmol of Pd which was 95.5% of that calculated for a complete exchange of palladium as shown in eq 3.

Acknowledgment. Support of this research by the Robert A. Welch Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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Permanganate Ion Oxidations. 19. Hexadecyltrimethylammonium Permanganate Oxidation of Cycloalkenes[1]

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Received September 27, 1988

The kinetics of hexadecyltrimethylammonium permanganate (cetyltrimethylammonium permanganate, CTAP) oxidation of cycloalkenes in dichloromethane have been studied. The relative rates of oxidation versus ^{13}C NMR chemical shifts, vertical ionization potentials, and strain energies are discussed. A comparison of the relative rate of permanganate ion oxidation with the relative rates of addition of other reagents to carbon–carbon double bonds suggests that it may act as a 1,3-dipole.

Although no unequivocable evidence has been reported, several cyclic structures, including oxametallocyclobutane **1** and manganate(V) diester **2**, have been proposed as intermediates during the permanganate ion oxidation of carbon–carbon double bonds.[1-19] The philicity (ambiphilic, electrophilic, nucleophilic) of permanganate ion during the oxidation of alkenes is also of interest. Moreover, the relative rates of alkenes and cycloalkenes (e.g., cyclopentene, cyclohexene, bicyclo[2.2.1]hept-2-ene (norbornene), 7,7-dimethylbicyclo[2.2.1]hept-2-ene) in electrophilic addition reactions have been suggested as possible criteria to distinguish between mechanisms involving acyclic and cyclic activated complexes and for determining the sizes of cyclic activated complexes.[20-26] Thus, we

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[1] For Paper 18 in the series, see: Freeman, F.; Chang, L. Y.; Kappos, J. C.; Sumarta, L. *J. Org. Chem.* **1987**, *52*, 1460.

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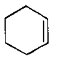
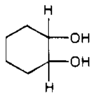
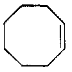
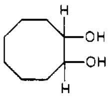
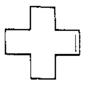
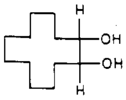
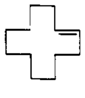
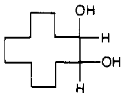
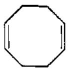
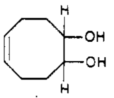
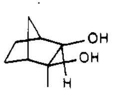
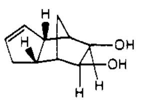
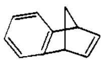
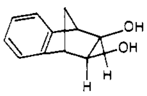
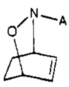
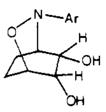
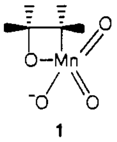
0022-3263/89/1954-2730$01.50/0 © 1989 American Chemical Society

Table I. Permanganate Ion Oxidation of Cycloalkenes to 1,2-Diols

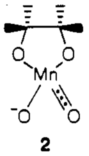
cycloalkene	product	yield, %
		86[a] 86[b]
		73[a] 70[c] 50[d]
		65[a]
		50[d]
		35[a]
		69[c] 40[e] 37[f]
		86[a] 83[c]
		73[a]
		50[g]

[a] Hexadecyltrimethylammonium permanganate (CTAP, 3) in CH_2Cl_2; ref 32. [b] Potassium permanganate in H_2O–CH_3OH–NaOH; ref 23c. [c] Benzyltriethylammonium permanganate in CH_2Cl_2; ref 18c. [d] Benzyltriethylammonium permanganate in H_2O–NaOH; ref 33. [e] Potassium permanganate in H_2O-t-BuOH–NaOH; ref 10. [f] Potassium permanganate in H_2O–CH_3OH–NaOH; ref 23. [g] Potassium permanganate, ref 36.

obtained relative rate data from a study of the hexadecyltrimethylammonium permanganate (cetyltrimethylammonium permanganate, CTAP, 3) oxidation of cycloalkenes in dichloromethane in order to obtain structure–reactivity correlations, in order to assess the size of the cyclic activated complex, and in order to elucidate the philicity of permanganate ion.



1



2

$C_{16}H_{33}\overset{+}{N}(CH_3)_3MnO_4^-$

3

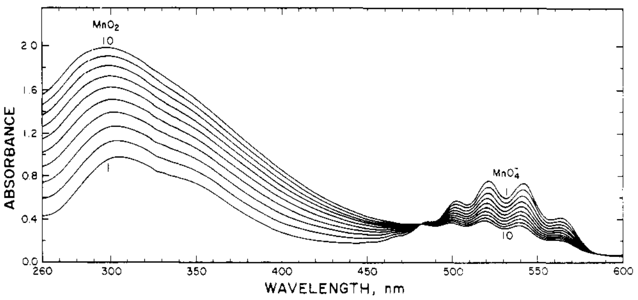


Figure 1. Ten sequential scans (scan rate = 10 nm s^{-1}) for the hexadecyltrimethylammonium permanganate (CTAP, 3, 4.00 × 10^{-4} M) oxidation of cyclohexene (0.20 M) in dichloromethane at 25.0 °C (isosbestic point 482 nm).

Table I shows the yields of 1,2-diols from the permanganate ion oxidation of cyclic and bicyclic alkenes under diverse experimental conditions. Permanganate ion oxidizes bicyclo[2.2.1]hept-2-ene to the exo diol under a wide variety of experimental conditions. It is known that concerted cycloaddends, electrophiles, nucleophiles, and radicals preferentially add to bicyclo[2.2.1]hept-2-ene from the exo face.

Experimental Section

^1H NMR spectra were recorded at 80 MHz on a Varian FT-80A spectrometer or at 300 MHz on a GE-Nicolet spectrometer.

Kinetics were determined on a Durrum Model D-110 stopped-flow spectrometer that was connected to a Tracor-Northern 1710 multichannel analyzer. The data were transferred to a computer for analysis and printing as previously described.[1] Temperature was maintained with a Forma Model 2095-2 refrigerated and heated bath circulator.

Solutions were prepared immediately before use in purified or spectral grade dichloromethane (Fisher Scientific Certified A.C.S. Spectranalyzed).[14,27,28]

Kinetic experiments were performed under pseudo-first-order conditions with a large excess of cycloalkene. The rates were determined by monitoring the disappearance of permanganate ion at 526 nm. The pseudo-first-order rate constants (k_ψ) were calculated from plots of $-\ln(A_t - A_\infty)$ on a first-order kinetics program. All rate constants are the average of two or more experiments.

Spectra of manganese dioxide were obtained on a Cary 219 spectrophotometer.

Hexadecyltrimethylammonium permanganate (CTAP, 3) was freshly prepared as previously described.[17,28,29]

The purity of the distilled commercially available cycloalkenes was checked by ^1H NMR spectroscopy.[30]

***cis*-Norbornene-5,6-*endo*-dicarboxylic anhydride,** mp 164–165 °C [lit.[31] mp 164–165 °C], was prepared from cyclopentadiene and maleic anhydride.

Results and Discussion

The ^1H NMR spectrum of hexadecyltrimethylammonium permanganate (CTAP, 3) in acetone-d_6 (dielectric constant = 20.7) shows sharp resonances at δ 1.25

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(27) (a) Essentially the same rate constant was obtained in spectral grade dichloromethane or in dichloromethane that was fractionally distilled after treatment with CTAP (3) overnight.[14,28] (b) Pestemer, M. *Angew. Chem.* **1951**, *63*, 121.

(28) (a) Karaman, H.; Barton, R. J.; Robertson, B. E.; Lee, D. G. *J. Org. Chem.* **1984**, *49*, 4509. (b) Lee, D. G.; Brown, K. C.; Karaman, H. *Can. J. Chem.* **1986**, *64*, 1054.

(29) *Caution: Although we have not experienced any difficulties, quaternary ammonium permanganates should never be allowed to stand in a warm place and care must be exercised when they are being transferred.*[28a,b]

(30) We thank the Columbian Carbon Company, a subsidiary of Cities Service Company, for generous samples of cyclododecene, 1,5,9-cyclododecatriene, cyclooctene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene.

(31) (a) Craig, D. *J. Am. Chem. Soc.* **1951**, *73*, 4889. (b) We thank Jeffrey Dodge (UCI) for a sample of *cis*-norbornene-5,6-*endo*-dicarboxylic anhydride.

Table II. Kinetics of the Hexadecyltrimethylammonium Permanganate (CTAP, 3) Oxidation of Cycloalkenes[a]

cycloalkene	k,[b] M^{-1} s^{-1}	k,[c] rel
cyclopentene	1.22	14.4
cyclohexene	0.09	1.0
1-methylcyclohexene	0.04	0.4
1-acetylcyclohexene	3.30	38.8
1,3-cyclohexadiene	6.70	78.8
1,4-cyclohexadiene	0.52	6.1
cycloheptene	0.83	9.8
(*Z*)-cyclooctene	0.76	8.9
1,3-cyclooctadiene	0.14	1.7
1,5-cyclooctadiene	3.11	37.0
cyclodecene	0.04	0.5
cyclododecene	0.27	3.2
(*E*,*E*,*E*)-1,5,9-cyclododecatriene	0.31	3.6
bicyclo[2.2.1]hept-2-ene[d]	46.2	544
bicyclo[2.2.1]hepta-2,5-diene[d]	87.0	218
cis-norbornene-5,6-*endo*-dicarboxylic anhydride[e]	77.0	193
bicyclo[2.2.2]oct-2-ene	0.40	4.7
bicyclo[3.3.0]oct-2-ene	0.33	3.9
endo-dicyclopentadiene[d]	47.8	120

[a] Temperature = 25.0 °C, λ = 526 nm; $[R_4N^+MnO_4^-] = 4.00 \times 10^{-4}$ M; [cycloalkene] = 0.10 M. [b] Second order rate constant = $k = k_\psi$/cycloalkene. [c] Rate relative to cyclohexene. [d] [cycloalkene] = 0.05 M. [e] [cycloalkene] = 0.04 M.

Table III. Comparison of the Reactivity of Cyclopentene, Cyclohexene, and Bicyclo[2.2.1]hept-2-ene (Norbornene) with Several Reagents[26]

reaction	proposed size of cyclic activated complex	$\frac{k_{\text{cyclopentene}}}{k_{\text{cyclohexene}}}$	$\frac{k_{\text{norbornene}}}{k_{\text{cyclohexene}}}$
chromic acid oxidation	3	1.3	5.5
chromyl chloride oxidation	3, 4, 5	4.1	511
epoxidation	3	1.5	1.2
CBr_2 addition	3	1.25	
bromination	3	1.4	13
2,4-dinitrobenzenesulfenyl chloride addition	3	3.3	33
hydroboration	4	110	
nitrosyl chloride addition	4	88	660
permanganate ion oxidation	5	14.4	544
osmium tetraoxide oxidation	5	21.9	320
benzophenone imine addition	5	12	280
benzonitrile addition	5	19	1800
phenyl azide addition	5	64	6500
diimide reduction	6	15.5	450

and 3.30 ppm. The δ 1.25 ppm resonance is less sharp in CD_2Cl_2 (dielectric constant = 8.9) and even less well resolved in $CDCl_3$ (dielectric constant = 4.8). Thus it appears that CTAP (**3**) exists as ion pairs or solvent-separated ion pairs in acetone-d_6 and as intimate ion pairs or aggregates in CD_2Cl_2.[28] The ultraviolet–visible spectrum of CTAP (**3**) in CH_2Cl_2 is similar to the spectrum of potassium permanganate in water.

The order of reaction with respect to cycloalkene was determined under pseudo-first-order conditions (large excess of substrate), by measuring the rate of oxidation at several different concentrations of cyclopentene or bicyclo[2.2.1]hept-2-ene while the concentration of CTAP (**3**) was held constant. The order of reaction with respect to permanganate ion is unity and the direct proportionality of the pseudo-first-order rate constants (k_ψ) to the concentration of substrate indicates that the rate of reaction is also first order in cycloalkene. Moreover, plots of ln k_ψ versus ln [cycloalkene] are linear with slopes of unity for cyclopentene and bicyclo[2.2.1]hept-2-ene, respectively.[32]

Repetitive scanning of the ultraviolet–visible region during the CTAP (**3**) oxidation of cyclohexene (Figure 1) and 1,5-cyclooctadiene suggests the absence of a long-lived intermediate such as **1** or **2**. Indeed, the spectra of the manganese product from the reaction of CTAP (**3**) with several cycloalkenes were essentially the same as the spectrum of soluble (colloidal) manganese dioxide obtained from the permanganate ion oxidation of alkenes in aqueous solution.[1,3-5] The colloidal nature of manganese dioxide is supported by the increase in absorption with time,[33] by the linear plot of −log absorbance of product versus the log of the wavelength, and by the linear plot of absorbance at 526 nm versus the absorbance at 418 nm.[1,13,34]

The kinetic data (Table II) are consistent with an initial interaction between cycloalkene and permanganate ion (charge-transfer complex formation) with [2 + 2] cycloaddition leading to oxametallocyclobutane **1** or with [4 + 2] cycloaddition leading to cyclic diester **2**. A very fast reaction of the product-determining intermediate manganate(V) diester **2** affords 1,2-diol and manganese dioxide.[13,35]

Cyclopentene, cycloheptene, and (*Z*)-cyclooctene react faster with permanganate ion than does cyclohexene. Steric factors may account for the lower rate of oxidation of 1-methylcyclohexene compared to cyclohexene. The large tetraalkylammonium cation in the tight ion pair in CTAP (**3**) offers considerable steric hindrance to the approach of oxidant to the double bond. The slower rate of 1-methylcyclohexene and the faster rate of 1-acetylcyclohexene may suggest that permanganate ion is acting as a nucleophile.

From an examination of the data in Table III, a correlation appears between the size of the cyclic activated complex and the relative rates cyclopentene:cyclohexene and norbornene:cyclohexene. Relatively high ratios of cyclopentene:cyclohexene and of norbornene:cyclohexene are observed for five- and six-membered cyclic activated complexes. It has been postulated that a considerable part of the strain energy of cyclopentene and norbornene is lost in going to a four-, five-, or six-membered cyclic activated complex.[20-26] Consequently, cyclopentene and norbornene, which have about 16.7 kJ mol^{-1} and 41.8 kJ/mol^{-1} more strain energy, respectively, than cyclohexene are also more reactive than cyclohexene in hydroboration, 1,3-dipolar additions, and diimide reduction. Thus, it appears permanganate ion may be acting as a 1,3-dipole.[1,6,21,36,37]

Although excellent correlations of vertical ionization potentials (IP_v)[38] of alkenes with log k (relative reactivities) have been observed for a large number of addition reac-

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[32] The rate of oxidation appears to be slower at high concentrations (>0.25 M) with some cycloalkenes.

[33] In some experiments the rate of oxidation was followed by monitoring the rate of formation of manganese dioxide at 418 nm.

[34] (a) Mata-Perez, F.; Perez-Benito, J. F. *Can. J. Chem.* **1985**, *63*, 988. (b) Narita, E.; Okabe, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 525.

[35] Although reaction of the long sought elusive manganate(V) diester **2** with solvent is reasonable, one could expect it to be more stable in anhydrous organic solvents.[13]

[36] Cycloadditions of several 1,3-dipoles with carbon–carbon double bonds follow second-order kinetics, which are characterized by moderate activation enthalpies from about 33 to 71 kJ mol^{-1} and large negative entropies of about −84 to −168 eu.[6,37] These data are similar to the activation parameters observed in the permanganate ion oxidation of carbon–carbon double bonds under a wide variety of experimental conditions.

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Table IV. Comparison of the Relative Rates of Cetyltrimethylammonium Permanganate (CTAP) Oxidation of Cycloalkenes with Their Physical Properties[a]

cycloalkene	log k_{rel}	IP_v, eV[b]	δ_c, ppm[c]	strain energy,[d] kcal mol^{-1}
cyclopentene	1.16	9.18	130.8	6.93
cyclohexene	0.00	9.12	127.4	2.61
cycloheptene	0.99	9.04	130.4	7.35
cyclooctene	0.95	8.98	130.4	8.81
cyclodecene	−0.30	8.98		11.63
cyclododecene	0.51			
1-acetylcyclohexene	1.59			
1-methylcyclohexene	−0.40		126.95	2.68
1,3-cyclohexadiene	1.90		125.85	
1,3-cyclooctadiene	0.23		129.3	
1,4-cyclohexadiene	0.79	8.80	125.5	0.70
1,5-cyclooctadiene	1.57		128.5	13.28
(*E*,*E*,*E*)-1,5,9-cyclododecatriene	0.31		132.7	
bicyclo[2.2.1]hept-2-ene	2.74	8.97	135.2	23.62
bicyclo[2.2.1]hepta-2,5-diene	3.01	8.69	143.5	31.59
cis-norbornene-5,6-*endo*-dicarboxylic anhydride	2.29			
bicyclo[3.3.0]oct-2-ene	0.33			
bicyclo[2.2.2]oct-2-ene	0.67	9.71	134.1	15.99
endo-dicyclopentadiene	2.1			

[a] Rates relative to cyclohexene. [b] Reference 45. [c] Reference 39. [d] Reference 40.

tions to unsaturated systems,[21,39] a plot of log k_{rel} for the permanganate ion oxidation of nine cycloalkenes (Table IV) versus IP_v did not show a simple linear relationship.

Carbon-13 NMR chemical shifts (δ_C) may be used to estimate the charge density at carbon in the ground state. A plot of log k_{rel} for permanganate ion oxidation versus the average value of δ_C for the carbon atoms of the double bond[40] in seven cycloalkenes is linear (Figure 2). Similarly, a plot of the limited available log k_{rel} values for phenyl azide addition to cycloalkenes versus the ^{13}C NMR chemical shifts of the sp^2-hybridized carbon atoms in 1-methylcyclopentene, cyclohexene, norbornadiene, and bicyclo[2.2.2]oct-2-ene is linear (slope = 0.24, correlation coefficient = r = 0.995).

A plot of log k_{rel} versus strain energy[41-44] is linear (Figure 3). It is seen that the greater the strain in the substrate, the faster is the rate of oxidation. This may be an oversimplification since one must also consider the location of the activated complex along the reaction coordinate and the strain energies of the compounds that are formed as reaction intermediates or products.[43] Moreover, it has been suggested that the small reduction in the π IP of norbornene is attributable to vertical electronic factors that may account for its increased reactivity in processes involving electrophilic addition to the π bond.[38a]

There is a similarity between the relative reactivity of a series of cycloalkenes toward phenyl azide and toward permanganate ion. An *ambiphilic* or dipolar permanganate ion is expected to exhibit a parabolic dependence on alkene π electron availability that is characterized by high reactivity toward both electron-poor and electron-rich alkenes and low reactivity toward alkenes of intermediate electronic character. This ambiphilicity of permanganate ion has been observed in the rates of oxidation of vinyl ethers, which are accelerated by both

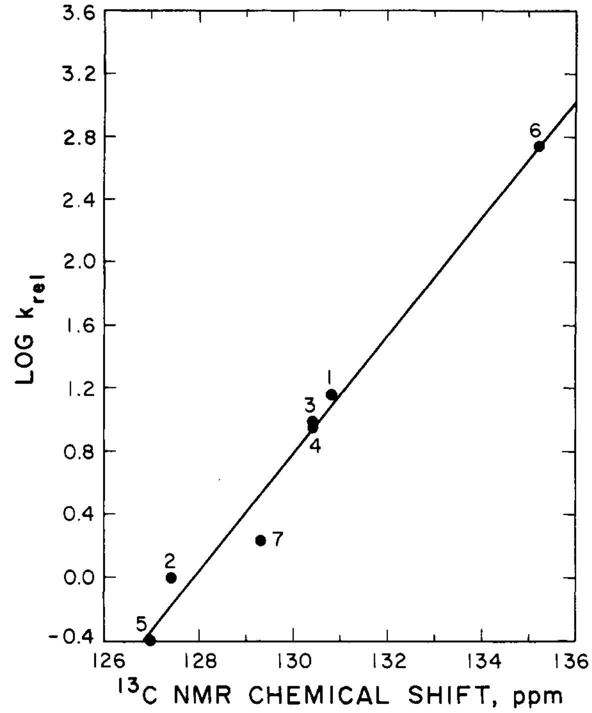

Figure 2. Plot of log k_{rel} (relative to cyclohexene) for the hexadecyltrimethylammonium permanganate (CTAP, 3) oxidation of cycloalkenes versus ^{13}C chemical shifts (δ in ppm): 1, cyclopentene; 2, cyclohexene; 3, cycloheptene; 4, cyclooctene; 5, 1-methylcyclohexene; 6, bicyclo[2.2.1]hept-2-ene; 7, 1,3-cyclooctadiene; slope = 0.37, correlation coefficient = 0.990.

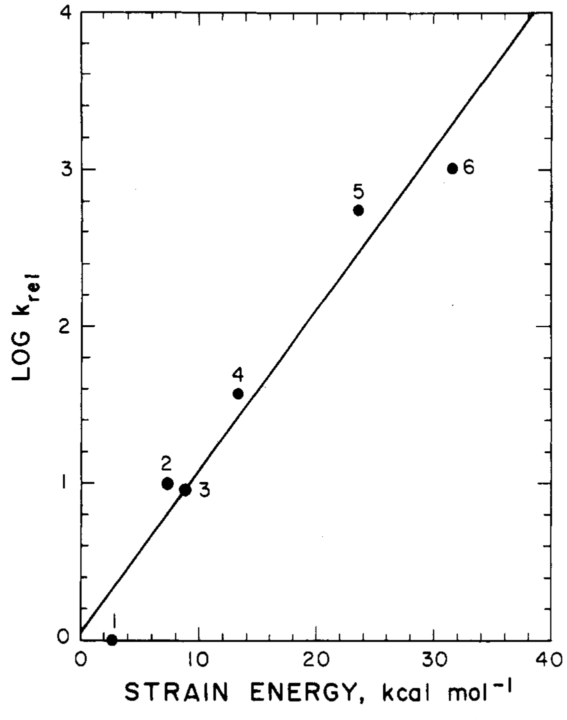

Figure 3. Plot of log k_{rel} (relative to cyclohexene) for the hexadecyltrimethylammonium permanganate (CTAP, 3) oxidation of cycloalkenes in dichloromethane at 25.0 °C versus strain energies: 1, cyclohexene; 2, cycloheptene; 3, cyclooctene; 4, 1,5-cyclooctadiene; 5, bicyclo[2.2.1]heptene; 6, bicyclo[2.2.1]hepta-2,5-diene; slope = 0.10, correlation coefficient = 0.976.

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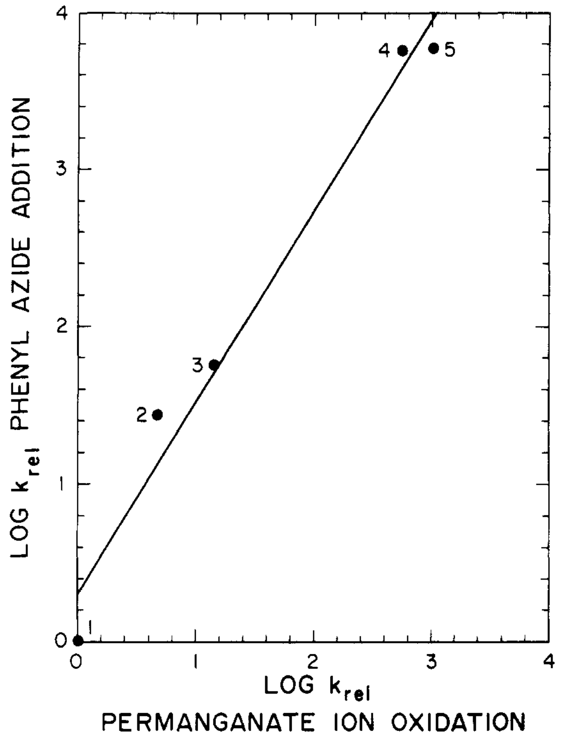

Figure 4. Plot of log $k_{\rm rel}$ (relative to cyclohexene) phenyl azide addition to cycloalkenes versus log $k_{\rm rel}$ permanganate ion oxidation of cycloalkenes (slope = 1.22, correlation coefficient = r = 0.988). The cycloalkenes are 1, cyclohexene; 2, bicyclo[2.2.2]oct-2-ene; 3, cyclopentene; 4, bicyclo[2.2.1]hept-2-ene; 5, bicyclo[2.2.1]-hept-2-ene.

electron-withdrawing and electron-attracting groups,[12] and in the concave upward Hammett plot for the oxidation of substituted 1,2-diphenylethylenes.[10,28a] A plot of ln $k_{\rm rel}$ versus IP$_{\rm v}$ of olefins for the addition of phenyl azide shows a parabolic curve.[39] Although these data do not provide a clear distinction between the four-membered (1) and five-membered (2) cyclic activated complexes, the linear correlation from the plot of log $k_{\rm rel}$ phenyl azide addition versus log $k_{\rm rel}$ permanganate ion oxidation (Figure 4) suggests a similarity between the activated complexes in permanganate ion oxidation of cycloalkenes and phenyl azide addition to cycloalkenes.[6]

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Registry No. 3, 73257-07-5; MnO$_4^-$, 14333-13-2; MnO$_2$, 1313-13-9; cyclopentadiene, 542-92-7; maleic anhydride, 108-31-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1-acetylcyclohexene, 932-66-1; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; cycloheptene, 628-92-2; (*Z*)-cyclooctene, 931-87-3; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; cyclodecene, 3618-12-0; cyclododecene, 1501-82-2; (*E,E,E*)-1,5,9-cyclododecatriene, 676-22-2; bicyclo[2.2.1]hept-2-ene, 498-66-8; bicyclo[2.2.1]hepta-2,5-diene, 121-46-0; *cis*-norbornene-5,6-*endo*-dicarboxylic anhydride, 129-64-6; bicyclo[2.2.2]oct-2-ene, 931-64-6; bicyclo[3.3.0]oct-2-ene, 5549-09-7; *endo*-dicyclopentadiene, 1755-01-7.

Supplementary Material Available: Figure 5, ultraviolet–visible spectrum of hexadecyltrimethylammonium permanganate in dichloromethane; Figure 6, Beer–Lambert law plot of hexadecyltrimethylammonium permanganate in dichloromethane; Figure 7, typical pseudo-first-order plot for the rate of disappearance of permanganate ion in dichloromethane; Figure 8, effects of cyclopentene concentration on the hexadecyltrimethylammonium permanganate ion oxidation in dichloromethane; Figure 9, effects of bicyclo[2.2.1]hept-2-ene concentration on the hexadecyltrimethylammonium permanganate ion oxidation in dichloromethane; Figure 10, sequential scans for the hexadecyltrimethylammonium permanganate oxidation of 1,5-cyclooctadiene in dichloromethane; Figure 11, log absorbance *versus* log wavelength for manganese dioxide obtained from the reduction of hexadecyltrimethylammonium permanganate by cyclopentene in dichloromethane; and Figure 12, absorbance at 526 nm *versus* absorbance at 418 nm from the hexadecyltrimethylammonium permanganate oxidation of cyclopentene in dichloromethane (8 pages). Ordering information is given on any current masthead page.

Amino- and Alkoxysulfonyl Radicals[1]

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Amino- and alkoxysulfonyl radicals were generated by chlorine abstraction from dialkylsulfamoyl chlorides and alkyl chlorosulfates. Absolute rate constants for these reactions in solution were measured by using laser flash photolysis techniques. The structural characteristics of the sulfonyl radicals were determined from their optical and electron paramagnetic resonance (EPR) spectra.

Alkane- and arenesulfonyl radicals, $\mathrm{R\dot{S}O_2}$, are reactive intermediates that participate in numerous reactions both in organic and biological systems.[2] We have investigated the structures of these radicals and their reactions using optical absorption and electron paramagnetic resonance, EPR, spectroscopy[3-7] and the basic features of their chemistry are now fairly well understood.

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