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Kinetics and Mechanism of the Epoxidation of Alkyl-Substituted Alkenes by Hydrogen Peroxide, Catalyzed by Methylrhenium Trioxide

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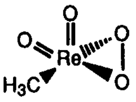
Epoxidations of alkyl-substituted alkenes, with hydrogen peroxide as the oxygen source, are catalyzed by CH_3ReO_3 (MTO). The kinetics of 28 such reactions were studied in 1:1 CH_3CN-H_2O at pH 1 and in methanol. To accommodate the different requirements of these reactions, ^{1}H-NMR, spectrophotometric, and thermometric techniques were used to acquire kinetic data. High concentrations of hydrogen peroxide were used, so that diperoxorhenium complex $CH_3Re(O)(\eta^2\text{-}O_2)_2(H_2O)$, **B**, was the only predominant and reactive form of the catalyst. The reactions between **B** and the alkenes are about 1 order of magnitude more rapid in the semiaqueous solvent than in methanol. The various trends in reactivity are medium-independent. The rate constants for **B** with the aliphatic alkenes correlate closely with the number of alkyl groups on the olefinic carbons. The reactions become markedly slower when electron-attracting groups, such as halo, hydroxy, cyano, and carbonyl, are present. The rate constants for catalytic epoxidations with **B** and those reported for the stoichiometric reactions of dimethyldioxirane show very similar trends in reactivity. These findings suggest a concerted mechanism in which the electron-rich double bond of the alkene attacks a peroxidic oxygen of **B**. These data, combined with those reported for the epoxidation of styrene (a term intended to include related molecules with ring and/or aliphatic substituents) by **B** and by the monoperoxo derivative of MTO, suggest that all of the rhenium-catalyzed epoxidations occur by a common mechanism. The geometry of the system at the transition state can be inferred from these data, which suggest a spiro arrangement.

Introduction

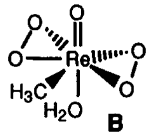
The epoxidation of olefins is a subject with a considerable history, amply explored in books and reviews.[1−5] The oxygen source may be hydrogen peroxide, an alkyl hydroperoxide, or oxygen itself. Epoxides are useful intermediates, and many of their ring-opened products, such as glycols[5] and glycol ethers,[6] are of practical value.

A catalyst, often a transition metal complex, is required in nearly every case. We have limited the scope of this research to the use of hydrogen peroxide as the oxygen source. The various transition elements that catalyze epoxidation reactions may differ as to specificity, rate, and mechanism. Compounds of some group IV−VI metals in high oxidation states, such as Ti(IV) and V(V), are converted to peroxo complexes. The intermediate from V(V) gives rise to radical pathways resulting in nonselective oxidations and catalyst decomposition, whereas Ti(IV) complexes give mainly stereospecific reactions.[7] Generally speaking, the best catalysts in this group contain Mo(VI) and W(VI).[8]

Methylrhenium trioxide (CH_3ReO_3 or MTO), a rhenium(VII) derivative and thus a powerful Lewis acid, efficiently catalyzes the epoxidation of olefins, in semiaqueous or organic solvents, at low and moderate temperatures with high activity and catalytic turnovers.[9−11] The rhenium peroxides **A** and **B** are the catalytically active intermediates. In the epoxidation of styrenes, both **A** and **B** are comparably active catalysts,[12] as they are for oxygen transfer to other substrates such as PR_3,[13] R_2S,[14] Br^-,[15] and Cl^-.[16] Having established several times that **A** and **B** are both effective catalysts, we carried out the present study at high concentrations of hydrogen peroxide, to make **B** the only rhenium species present at an appreciable concentration.



A



B

We have studied the kinetics of epoxidation of 28 alkyl-substituted alkenes in two media, acidic acetonitrile−water and methanol, using three techniques for obtaining kinetic data. Without water (other than that introduced with the peroxide or formed in the reaction), excellent yields of epoxides are obtained in methanol and unacidi-

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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fied, neat acetonitrile. The more water present, however, particularly in the acidic medium, the greater the yield of the ring-opened diol originating from the primary epoxide product. From the kinetic data we can now present a detailed picture of the reactions, including a description of their steric and electronic requirements.

Experimental Section

Materials. The solvents used for quantitative kinetic studies were 1:1 CH_3CN-H_2O at pH 1 and CD_3OD. Methanol-d_4 (Cambridge Isotopes) and HPLC-grade acetonitrile (Fisher) were used. Water was purified by a Millipore-Q water purification system. When required, 0.1 M perchloric acid, diluted from the 70% reagent (Fisher), was used to maintain pH. Occasional experiments were done in CH_3OH or CD_3CN.

Methylrhenium trioxide[17] was purified first by sublimation, then by recrystallization from methylene chloride–hexane, and finally by a second sublimation. Stock solutions of MTO in methanol-d_4 or acetonitrile were stored at 5 °C and used within 1 or 2 weeks. The concentration was determined spectrophotometrically after dilution into a large volume of water: 239 nm (ϵ 1900 L mol^{-1} cm^{-1}), 270 nm (ϵ 1300 L mol^{-1} cm^{-1}).[18]

We purchased the alkenes (Aldrich); those which proved to be pure by ^1H NMR were used as such. *trans*-4-Octene, 1-octene, and 1-hexene were purified by distillation. Aqueous solutions of hydrogen peroxide were prepared from the 30%, or occasionally the 3%, reagent. The concentrated reagent, which proved quite stable over time, was standardized by iodometric titration; the diluted peroxide solutions were much less stable and were made up daily by dilution.

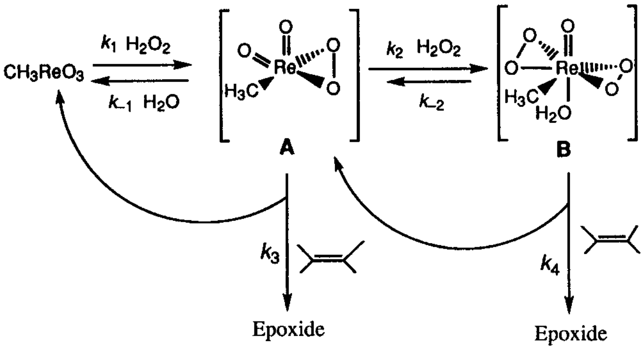
Kinetics. Three methods were applied, as required by the range of alkenes and solvents. In every case the temperature was controlled at 25 °C. (a) The reactions studied in methanol were followed by ^1H NMR in a total volume of 0.6 mL. These experiments used 0.50 M H_2O_2, 1–50 mM MTO, and 0.05–0.1 M alkene, added last. The relative amounts of peroxide and alkene were chosen with a concern for the requirements of the kinetic analysis which was carried out by a first-order kinetic equation. The proton spectrum was recorded at 2–20 min increments over the 2–5 h reaction time. The changes in intensity (Y) of the alkene signal(s) were fit to a single-exponential decay: $Y_t = Y_\infty + (Y_0 - Y_\infty) \times \exp(-k_\psi t)$.

(b) A spectrophotometric method was used for some of the reactions carried out in 1:1 CH_3CN-H_2O, in which the acid concentration and the ionic strength was maintained at 0.100 M unless specified otherwise. The acid concentration needs to be fairly high, because $MTO-H_2O_2$ solutions otherwise decompose fairly rapidly, unlike MTO itself.[19] The cuvettes had short optical paths, 0.01–0.2 cm, because the alkenes to which the method was applicable had high molar absorptivities and the other reagents contributed a large absorbance background at the wavelengths used. The reaction mixtures were prepared in the reaction cuvette which was held in a thermostatted water bath, with the last component added being the alkene. Air was not excluded, since controls showed there was no need. Hydrogen peroxide was used in large excess over the alkene, such that the bis-peroxide **B** was maintained at constant concentration throughout. The data were obtained by following the loss of the alkene absorption in the range 200–225 nm. The absorbance–time data were fitted by nonlinear least-squares to a first-order kinetic equation: $A_t = A_\infty + (A_0 - A_\infty) \times \exp(-k_\psi t)$.

(c) A number of the reactions of the alkyl-substituted alkenes were not accompanied by a useful absorbance change at an accessible wavelength (>200 nm). These reactions, along with several known systems that we used as controls, were studied in the aqueous acetonitrile medium by a thermometric method.[20] The components were placed inside two reservoirs within a Parr Model 1455 precision calorimeter, equipped with a thermistor in a platinum resistance probe. The solutions were separately allowed to reach temperature equilibration for 20–30 min. The two solutions were then mixed and stirred for 1–2 min. The stirrer was then stopped, and the temperature was recorded at 5–10 s intervals by a computer with Lotus 1-2-3 software. For each alkene, experiments were done with 1.0 M H_2O_2, with $[Re]_T$ (which is essentially equal to [**B**] at this high a peroxide concentration) being varied in the range 0.5–5.0 mM, and with [alkene] 10–50 mM. The reaction followed first-order kinetics, with temperature–time curves independent of the reaction stoichiometry; in these systems ΔT was within the range 0.2–0.8 °C. The temperature profile is in addition affected by a slow thermal leakage in the adiabatic calorimeter. With the thermal leakage expressed as a first-order function with a constant k_T, (Newton's law of cooling),[20] the expression for the temperature at a given time (T_t) is given by eq 1, where the constants m_1, m_2, and m_3 are related to the temperature factors of the experiment.

$$T_t = m_1 + m_2\, e^{-k_\psi t} + m_3\, e^{-k_T t} \qquad (1)$$

Scheme 1



Results

Catalytic Intermediates. As cited in the Introduction, quantitative kinetic data have already been reported for oxygen-transfer reactions in the MTO/H_2O_2 system. Because of that, we shall rely on the established course of these systems to provide the initial guidance for the kinetic scheme that might apply to epoxidation reactions of the alkyl-substituted alkenes. In this scheme, either or both of the previously-depicted rhenium peroxides, **A** or **B**, may transfer an oxygen atom to the alkene.

In the event that the monoperoxide **A** is reactive, then MTO is immediately recovered along with the epoxide. Similarly, if an oxygen atom is transferred from the bis-peroxide **B**, then **A** is generated along with the epoxide. This sequence of events in shown in Scheme 1.

Prior research has established that the conversion of MTO to **A** upon reaction with hydrogen peroxide constitutes a *reversible* equilibrium, likewise the conversion of **A** to **B**. With the notation in Scheme 1, these are the applicable equilibrium constants at 25.0 °C:

medium	K_1/L mol^{-1}	K_2/L mol^{-1}
1:1 CH_3CN-H_2O, pH 1[13]	1.3×10^1	1.36×10^2
CH_3OH[21]	2.61×10^2	8.14×10^2

Kinetic Design. The fact that the peroxo complex formation reactions are reversible certainly does not mean that the concentrations of the three species are necessarily sustained at equilibrium under all circumstances in which the catalytic cycles are in operation. In many of the cases already considered, especially those with reactive substrates such as phosphines[13] and sul-

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fides,[14] MTO, **A**, and **B** are interconverted, but they are not equilibrated rapidly enough to maintain the equilibria among them. These reactions must be considered as kinetic steps, along with the oxygen-transfer step. This means that the concentrations of **A** and **B** used in analysis of the kinetic data are those given by the steady-state approximation, not those described by the equilibrium constants listed.

That is to say, the immediate fate of a newly-born **A** is not *necessarily* to react further with H_2O_2 to form **B**; it might instead react with the substrate to yield product, thereby regenerating MTO. Indeed, instead of either of these, **A** might revert to MTO upon addition of water and loss of peroxide. The choice a given molecule of **A** exercises depends upon the relative rates of three reactions and therefore on the relative values of $k_2[H_2O_2]$, k_3[substrate], and k_{-1}.

One method of incorporating all of these considerations is to formulate a general expression for the rate of reaction in terms of the three independent concentration variables, which include the *total* catalyst concentration, $[Re]_T$, defined by $[Re]_T = [MTO] + [\mathbf{A}] + [\mathbf{B}]$. The resulting rate equation appears to have such a complex form (eq 2) that it might be difficult to apply in a form that would convince one that it represented a unique solution. This equation has, in fact, been applied successfully in other studies,[12,14,22] where the conditions were such that none of the terms could be neglected to simplify the expression. The use of eq 2 (alk = alkene or other substrate) was feasible in such cases because the rate constants for the rhenium−peroxide equilibrations (k_1, k_{-1}, k_2, and k_{-2}) have been determined independently.[12,14,22]

$$\frac{d[\text{epoxide}]}{dt} = \frac{k_1k_3[\text{Re}]_T[\text{H}_2\text{O}_2][\text{alk}] + \dfrac{k_1k_2k_4[\text{Re}]_T[\text{alk}][\text{H}_2\text{O}_2]^2}{k_4[\text{alk}] + k_{-2}}}{k_{-1} + k_3[\text{alk}] + k_1[\text{H}_2\text{O}_2] + \dfrac{k_1k_2[\text{H}_2\text{O}_2]^2}{k_4[\text{alk}] + k_{-2}}} \quad (2)$$

The numerical fitting of initial rate data to this equation was the procedure used in some of the experiments carried out in our earlier research dealing with the epoxidation of styrene. On the other hand, having validated this approach and the kinetic model now in several cases, including styrene, the most germane example in the present instance, it seemed preferable to move directly in the case at hand to a set of conditions in which one or another limiting form of eq 2 would be realized. This would allow the direct evaluation of the epoxidation rate constants through the use of a simplified but entirely valid kinetic treatment. In particular, consider the limiting form at a concentration of hydrogen peroxide sufficiently high that only the last term in the numerator, and the last in the denominator, is significant compared to the rest. The simplified form is

$$\frac{d[\text{epoxide}]}{dt} = -\frac{d[\text{alkene}]}{dt} = k_4[\text{Re}]_T[\text{alkene}] \quad (3)$$

The concentration of hydrogen peroxide needed to attain this limit accurately is different in the two solvents. In all of these experiments, $[H_2O_2]$ was fixed between 0.3 and 1.0 M. At the lower value, >97% of the total MTO is present as **B** in aqueous acetonitrile and >99% in methanol. One approximation made in reducing eq 2 to eq 3 is clearly satisfied. In addition, we rely on the fact that k_3 is not large compared to k_4; indeed k_3 and k_4 are of the same order of magnitude in any number of other systems, the case of the styrenes[12] being the most germane.

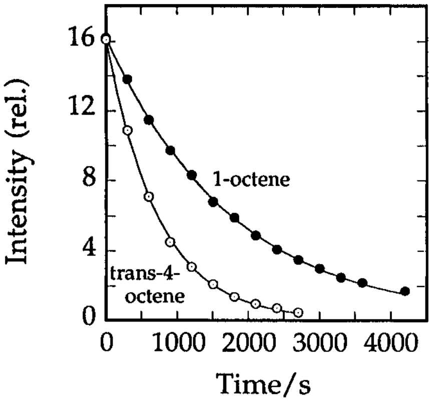

Figure 1. Kinetic data for the epoxidation of 1-octene (0.10 M, with 50 mM MTO) and *trans*-4-octene (0.10 M, with 25 mM MTO) and 0.50 M H_2O_2 in methanol-d_4 at 25 °C. The ^{1}H NMR signal intensities were recorded for an olefinic proton of 1-octene at δ 5.6 and of *trans*-4-octene at δ 5.4.

A further advantage is gained by working at constant $[H_2O_2]$, since the amount of water present in the solution remains nearly constant. This is important since the rates of epoxidation of styrene are sensitive to the amount of water.[12]

Kinetic Data. The results from the three kinetic techniques will be presented in turn, and then the comparisons made between them. The ^{1}H NMR method was applied to reaction mixtures with 0.1 M alkene, 0.50 M hydrogen peroxide, and 1−50 mM MTO. Figure 1 displays the results of two typical reactions, with 1-octene and *trans*-4-octene. The signal intensity for an olefinic proton absorption of each alkene is displayed as a function of time. The smooth curve drawn through the experimental points is the nonlinear least-squares fit to the exponential decay function given before. The values of the pseudo-first-order rate constants so obtained were divided by the total catalyst concentration. This quotient, $k_\psi/[Re]_T$, represents the value of the rate constant k_4, which applies to the reaction between **B** and the alkene (Scheme 1). These values, in methanol-d_4 at 25 °C, are presented in Table 1.

The nonconjugated alkenes, with $\lambda_{max} \leq 200$ nm, could not be studied by the spectrophotometric method. Other alkenes, such as β-pinene, α-pinene, and limonene, have absorption maxima with quite large molar absorptivities in the range 200−225 nm. Since MTO, H_2O_2, **A**, and **B** absorb significantly in this range, short-path optical cells (0.01−0.2 cm) were used. A series of experiments with $[H_2O_2] \geq 0.3$ M, [alkene] = 5−20 mM, and $[Re]_T$ varying between 0.2 and 5 mM were carried out in acidic acetonitrile. Note that the value of $[H_2O_2]$ in this range is immaterial, in that its concentration does not affect the reaction rate (eq 3); note also that $[Re]_T$ was adjusted to bring the reaction to a convenient time scale and that it was varied for each alkene to confirm that the direct proportionality of rate on $[Re]_T$ (eq 3) was followed. The

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Table 1. Second-Order Rate Constants at 25 °C for the Epoxidation of Olefins with $CH_3Re(O)(O_2)_2(H_2O)$, B, by Various Methods in Two Solvents

olefin	k_4/L mol^{-1} s^{-1} CH_3OD (method)[a]	 1:1 CH_3CN-H_2O, pH 1 (method)[a]
styrene (**1**)	0.019 ± 0.001 (N)	0.11 ± 0.01 (S)
	0.021 ± 0.002 (S)	
4-methoxystyrene (**2**)		0.62 ± 0.05 (T)
		0.57 ± 0.04 (S)
1-methylcyclohexene (**3**)	0.32 ± 0.01 (N)	4.20 ± 0.16 (T)
β-pinene (**4**)	0.35 ± 0.01 (N)	3.63 ± 0.10 (T)
	0.34 ± 0.01 (S)	3.88 ± 0.20 (S)
α-pinene (**5**)		2.21 ± 0.15 (S)
(*R*)-(+)-limonene (**6**)	0.15[b] (N)	2.79 ± 0.13 (S)
	0.09[c] (N)	
norbornylene (**7**)	0.250 ± 0.001 (N)	1.88 ± 0.04 (T)
cyclohexene (**8**)	0.108 ± 0.003 (N)	1.06 ± 0.02 (T)
methylenecyclohexane (**9**)	0.096 ± 0.001 (N)	0.97 ± 0.06 (T)
2,3-dimethyl-2-butene (**10**)	1.33 ± 0.03 (N)	8.93 ± 0.55 (T)
2-methyl-2-pentene (**11**)	0.260 ± 0.007 (N)	3.92 ± 0.04 (T)
2-methyl-1-pentene (**12**)	0.061 ± 0.001 (N)	0.55 ± 0.06 (T)
cis-3-hexen-1-ol (**13**)	0.106 ± 0.008 (N)	
trans-3-hexen-1-ol (**14**)	0.039 ± 0.001 (N)	
trans-4-octene (**15**)	0.048 ± 0.003 (N)	0.253 ± 0.003 (T)
		0.289 ± 0.005 (S)
1-octene (**16**)	0.0126 ± 0.001 (N)	0.098 ± 0.021 (T)
1-hexene (**17**)	0.0124 ± 0.0002 (N)	
3,3-dimethyl-1-butene (**18**)	0.0087 ± 0.0003 (N)	
5-hexen-2-one (**19**)		0.066 ± 0.003 (S)
4-hexen-3-one (**20**)		0.0038 ± 0.0003 (S)
allyl alcohol (**21**)	0.0033 ± 0.0002 (N)	
allyl phenyl ether (**22**)	0.0052 ± 0.0001 (N)	
2-buten-1,2-diol (**23**)		0.0326 ± 0.0004 (S)
cis-1-bromopropene (**24**)		0.012 ± 0.001 (S)
trans-1-bromopropene (**25**)		0.0051 ± 0.0003 (S)
1-chloro-2-methyl-propene (**26**)	0.0160 ± 0.0005 (N)	
1-bromo-2-methyl-propene (**27**)	0.0098 ± 0.0003 (N)	
methyl acrylate (**28**)		<0.001 (S)
1,4-dicyano-2-butene (**29**)		<0.001 (S)
acrylonitrile (**30**)		<0.001 (S)

[a] By NMR (N), spectrophotometric (S), or thermometric (T) methods. [b] For the epoxidation of the internal olefinic group. [c] For the epoxidation of the external olefinic group (see text).

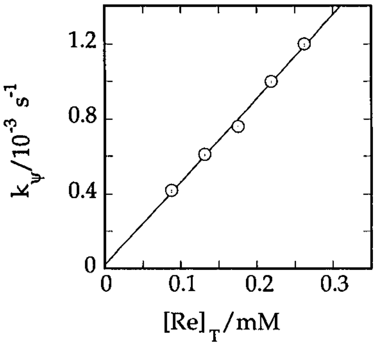


Figure 2. Spectrophotometrically-determined values of the pseudo-first-order rate constant k_ψ for the reaction of *β*-pinene (5 mM) with hydrogen peroxide (0.4 M) as a function of $[Re]_T$ (which is ~[**B**]). The data are linear through the origin as in eq 3. The medium is 1:1 acetonitrile–water at pH 1 and 25 °C.

solutions of hydrogen peroxide and MTO were allowed to equilibrate for about 5–10 min before the reaction was initiated by the addition of the alkene.

The absorbance–time data were fit to first-order kinetic functions. The values of k_ψ are a linear function of $[Re]_T$, as shown for *β*-pinene in Figure 2. The slope affords k_4. The values of k_4 determined by this method are also listed in Table 1.

Experiments carried out using the thermometric technique all employed 1.0 M H_2O_2. The other concentration ranges were 10–50 mM alkene and 0.2–5.0 mM MTO.

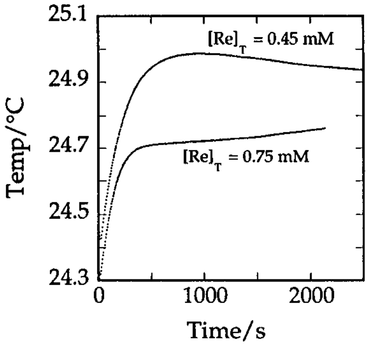


Figure 3. Typical curves of temperature *versus* time are shown for the epoxidation of 2,3-dimethyl-2-butene (~20 mM) with hydrogen peroxide (1.0 M) at $[Re]_T$ = 0.45 and 0.75 mM in aqueous acetonitrile at pH 1 and 25 °C.

Typical temperature–time data are shown in Figure 3 for the epoxidation of 2,3-dimethyl-2-butene in acidic acetonitrile–water. The data were analyzed according to first-order kinetics, after allowance for a temperature drift term, designated $\exp(-k_T t)$ in eq 1. The values of the pseudo-first-order reaction rate constants, k_ψ, are shown as a function of [**B**] ($\cong$ $[Re]_T$) in Figure 4 for norbornylene and cyclohexene. The values of k_4, given by the slope of this graph, are given in Table 1.

To show that the three methods give the same values of the rate constants, several compounds were examined by the NMR (N), spectrophotometric (S), and thermometric (T) methods. In acidic, aqueous acetonitrile and

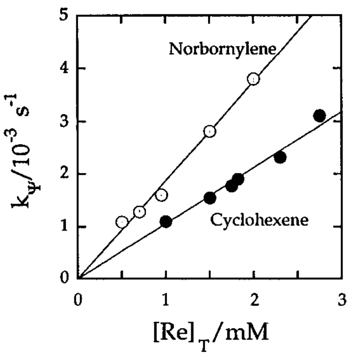


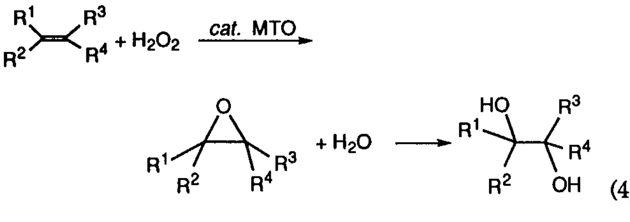
Figure 4. Thermometrically-determined rate constants for the epoxidation of cyclohexene (solid circles) and norbornylene (open circles) shown to be linear functions of $[Re]_T$, in agreement with eq 3. The data were taken in aqueous acetonitrile at pH 1 and 25 °C.

in methanol, the values of k_4 (L mol^{-1} s^{-1}) at 25 °C to which the different methods were applied are as follows:

1:1 CH_3CN/H_2O, pH 1		methanol	
β-pinene	3.63 ± 0.10 (T)	β-pinene	0.34 ± 0.01 (S)
	3.88 ± 0.20 (S)		0.35 ± 0.01 (N)
4-methoxystyrene	0.62 ± 0.05 (T)	styrene	0.021 ± 0.001 (S)
	0.57 ± 0.04 (S)		0.019 ± 0.001 (N)
trans-4-octene	0.253 ± 0.003 (T)		
	0.289 ± 0.005 (S)		

The thermometric experiments, by definition, are adiabatic, not isothermal. The temperature rise was always <0.6 °C, and usually ~0.2–0.4 °C. We may take as a guide to the effect of this variation the increase in the rate constant for 4-methoxystyrene. For this compound, values of k_4 were determined as a function of temperature, leading to the value $\Delta H^{\ddagger} = 42.8$ kJ mol^{-1}.[12] With that, a 0.6° increase will cause k_4 to increase by 4.8%, and even less for smaller temperature increases. We take this effect as fairly insignificant within the experimental errors and have therefore treated each determination by isothermal kinetics.

Products were identified by ^{1}H NMR for every alkene studied in methanol. In each case the epoxide was formed first. The epoxide then underwent ring opening to the diol upon reaction with water, of which there are two sources, the 30% stock solution of hydrogen peroxide and that produced in the overall reaction. These steps are as follows:



(4)

In the second stage, three processes are at work: uncatalyzed hydrolysis of the epoxide, which we have shown is negligibly slow (>2 d) under these conditions, catalysis by MTO alone, which certainly occurs albeit slowly, and catalysis jointly by MTO and H_2O_2, which is the most effective pathway of the three.[11,12]

The data supporting the sequence of events in eq 4 are displayed for *trans*-4-octene in Figure 5. The consumption of the alkene and increase of the epoxide occur concomitantly, as do the consumption of the epoxide and the buildup of the diol. These studies establish that MTO is a catalyst for both the epoxidation of the alkene and the conversion of epoxide to diol; it is not a catalyst, however, for direct hydration of the alkene to the diol by a pathway that would bypass the epoxide.

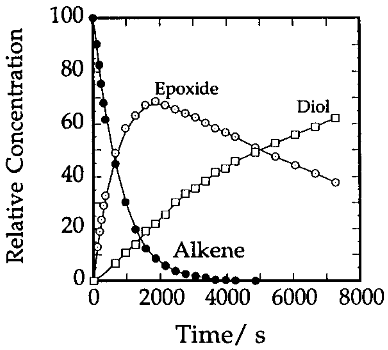
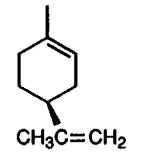
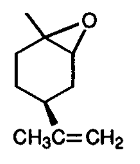


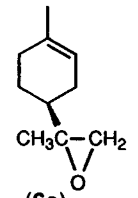
Figure 5. Time progression of concentrations for *trans*-4-octene, showing the alkene, the epoxide, and the diol. Conditions: 0.10 M alkene, 0.5 M H_2O_2, and 25 mM MTO in methanol-d_4 at 25 °C.

Neat acetonitrile was also used to examine the products, even though it was not one of the media for kinetics; here the epoxide is stable. In CH_3OD, under conditions used for kinetic studies, formation of the epoxide was faster than its hydrolysis to the 1,2-diol. For *trans*-4-octene, when $[Re]_T = 25$ mM and $[H_2O_2] = 0.5$ M, the pseudo-first-order rate constant of the epoxidation step is 1.34×10^{-3} s^{-1}. Under the same conditions, the pseudo-first-order rate constant for the ring opening is 1.70×10^{-4} s^{-1}, more strongly enhanced by MTO and H_2O_2 together than by MTO alone.

The case of limonene (**6**) is an interesting one, in that it has two sites of unsaturation, either of which can be epoxidized. The kinetics were studied by recording intensity of the ^{1}H NMR signal as a function of time. The resonance of H_a was quite distinct, since it was far removed from the water peak; H_b and H_c were also used, but were less reliable because of that interference. The value of k_ψ gave $k_4 = 0.235$ L mol^{-1} s^{-1}; the mathematics of this situation is just like that for parallel reactions,[23] in that the rate constant is the sum of those for the separate pathways, irrespective of the fact that a resonance associated with just one of the double bonds was observed. To resolve the rate constant into its components, the ratio of the two different epoxides (**6e, 6i**) was determined, giving [**6i**]/[**6e**] = 1.9. This measurement was carried out when only ca. 34% of the starting material had been consumed, to minimize the influence of formation of the double epoxide and the diols derived from all three epoxides. With this ratio, and the total rate constant, the separated values of k_4 are 0.09 L mol^{-1} s^{-1} (external) and 0.15 L mol^{-1} s^{-1} (internal).


(6)


(6i)


(6e)

Discussion

Kinetic Model. The adherence of the kinetic data to the rate equations, here and in related instances, espe-

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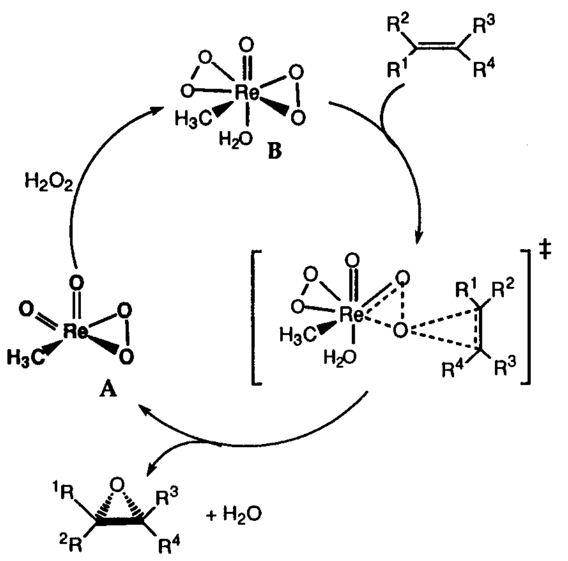
(23) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; 2nd ed.; McGraw-Hill Inc.: New York, 1995; p 277.

Scheme 2



cially for the family of styrenes,[12] serves to support the kinetic model and the general pattern of reactivity given in Scheme 1. In the earlier studies[12–16] much effort was devoted to defining separately the reactivity of **A** (the monoperoxorhenium(VII) complex) as compared to **B**, the bis-peroxo complex. In nearly every case, including styrene, the differences in reactivity between **A** and **B** were not remarkable. Having made that distinction, we therefore decided to simplify the present study by limiting the effort to **B** alone. It should be noted that this usually cannot be achieved by using a synthesized and isolated sample of **B.** This limitation is so because the step by which H_2O_2 is released from **B** is often competitive with that by which the alkene reacts; that is, it is a matter of the relative values of k_{-2} and k_4[alkene]. With this point in mind, the limited reaction scheme applicable under the conditions employed here, and which therefore involves the recycling of **B** and **A** (and not **A** and MTO), is given in Scheme 2. This will be the basis on which the molecular mechanism will be discussed.

Kinetic Effects of Substituents. The major issue is to infer from these and other data how the key step, oxygen transfer from **B** to the alkene, occurs. We are proposing that a peroxidic oxygen is attacked by the electron-rich double bond, to which it is ultimately transferred. This intermediate (or transition state, we cannot be sure) is shown by the diagram suggested for it in Scheme 2. Indeed, we have already verified by ^{18}O-labeling that exactly this happens in the MTO-catalyzed reaction between H_2O_2 and $PhSCH_3$: the sulfoxide derives its oxygen neither from a Re=O group nor from a water molecule in the semiaqueous medium but from the peroxide.[14] We have not carried out the labeling experiment here, but none of the data give us reason to suspect a change in mechanism.

For the families Ar_3P, Ar_2PR, Ar_2S, ArSR, R_2S, $ArNMe_2$, and $ArNH_2$, etc., we have shown numerous instances in which the addition of an electron-donating (or electron-attracting) substituent on the aryl ring increases (or decreases) the values of k_3 and k_4; likewise an alkyl group in place of an aryl group or a hydrogen atom increases the rate. In all of the systems studied, no exceptions to this trend have been noted.

In this diverse set of alkenes, a similar pattern emerges. This pattern can be seen first by examining the kinetic effect of substituting an alkyl group for one or more of the H's at an olefinic position. When we group the alkenes accordingly, they will have between one (N = 1) and four (N = 4) alkyl groups attached to the olefinic carbons. We limit ourselves to comparing the acyclic compounds without aryl, hydroxy, or halogen substituents to avoid the mixing in of other factors. For compounds **10**–**12** and **15**–**18** of Table 1, the plot of log (k_4) against N is shown in Figure 6. The positive correlation in each solvent is evident; indeed there appears to be an almost linear relation over some 2 orders of magnitude in reactivity, although we do not attach particular significance to the correlation being linear. The implication seems apparent: the more electron rich an alkene, other factors aside, the more rapidly it is epoxidized in the MTO/H_2O_2 system. The effect of an additional substituent in this case is, however, less marked than in the reactions of peroxy acids and α-azo hydroperoxides.[24–26]

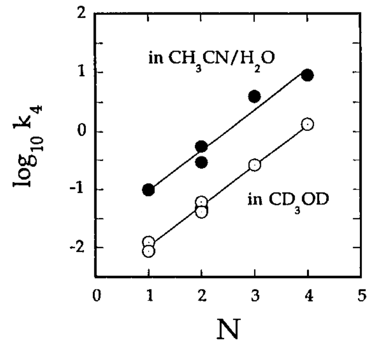
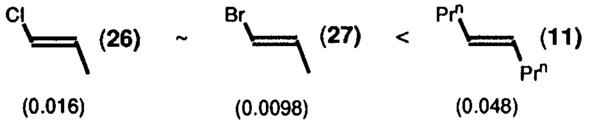
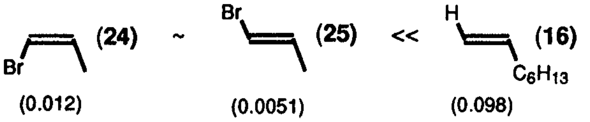


Figure 6. Correlation of the rate constants (k_4), for the reactions between aliphatic alkenes and **B**, with N, the number of aliphatic substituents on the double bond.

The marked retarding effect of halogen substituents is evident by this comparison of values of rate constants in methanol (throughout the Discussion, values of k_4 (L mol^{-1} s^{-1}) are shown as parenthetical numbers without further identification):



A somewhat analogous comparison, this time in the semiaqueous medium, is shown here, although it is less exact since it takes CH_3 as equivalent, in effect, to n-C_6H_{13}:



The effect of other electron-attracting groups can be seen by comparing the low rates of those molecules with carbonyl groups (**19**, **20**) and hydroxy groups (**14**, **15**, **21**, and **23**) to comparable alkenes that are strictly aliphatic. The limit of this trend is seen in the rates of the last three compounds in Table 1. They have very strongly electron-attracting groups. In these cases the rate constants are too small for evaluation; we place an upper limit $k_4 < 10^{-3}$ L mol^{-1} s^{-1} for the reactions of methyl acrylate (**28**), 1,4-dicyano-2-butene (**29**), and acrylonitrile (**30**).

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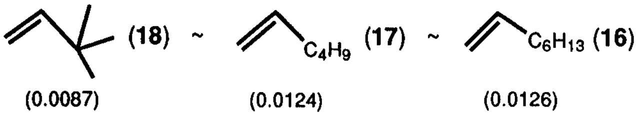
(24) Baumstark, A. L. *J. Bioorg. Chem.* **1986**, *14*, 326.
(25) Baumstark, A. L.; Pilcher, R. S. *J. Org. Chem.* **1982**, *47*, 1141.
(26) Baumstark, A. L.; Vasquez, P. C. *Tetrahedron Lett.* **1983**, 123.

All of these trends, without exception, show that the more electron rich an alkene is, the more rapidly it reacts with **B**. We also note that, uniformly, the rate of epoxidation of an alkene by **B** is 5−10 times slower in methanol than in aqueous acetonitrile. The same holds true for styrene;[12] as before, we attribute this trend to the increase in the activity of water and to an increase in solvent polarity, stabilizing a polar arrangement at the transition state.

Steric effects seem relatively mild, which allows us to make the comparisons of electronic effects just given without reference to such factors. Note, for example, these rate constants in methanol:

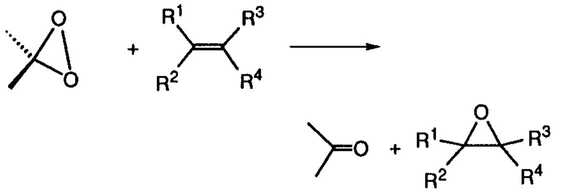


(18) (0.0087) ~ **(17)** (0.0124) ~ **(16)** (0.0126)

And, in any event, the correlation, presented in Figure 6, of reaction rate with the number of alkyl groups is exactly counter to what the trend would have been were steric effects playing a major factor. Perhaps the most cautious statement is this: electronic factors outweigh steric ones.

Consider a pair of alkenes that are 1,1-disubstituted, β-pinene (**4**) and methylenecyclohexane (**9**). Reaction of the first is about 4-fold faster than the latter. β-Pinene has a higher angle strain because it is a bicyclic system. This factor may account for the rate enhancement, since in the transition state for epoxidation the olefinic carbons change hybridization from sp^2 to sp^3. Similar comparisons could be made between norbornylene (**7**) and cyclohexene (**8**), with relative rates of 2.4 and 1.8 in the two solvents, and between norbornylene and *trans*-**4**-octene (**15**), with relative rates of 7.4.

A Linear-Free-Energy Correlation. An interesting analogy can be drawn between two cyclic peroxides, **B** and dimethyldioxirane, DMDO.[27] The kinetics of epoxidation with DMDO, eq 5, have been reported for a significant number of alkenes.[28,29]



(5)

The similarities are striking. The epoxidation reactions of both **B** and DMDO are stereospecific. Both proceed at rates that increase with the nucleophilicity of the olefin, that are but slightly sensitive to steric effects (see the report on styrene[12]), and that are enhanced by the solvent polarity and an increase in the activity of water in the solution. Moreover, Hammett constants (σ^+) are similar: $\rho = -0.92$ (**B**) and −0.90 (DMDO).

Similar kinetic factors run throughout the entire series. Figure 7 displays a plot of log k_4(**B**) versus log k(DMDO). This figure records an excellent correlation for (separately) seven alkenes and four styrenes. The respective slopes are 0.84 and 1.18, with correlation coefficients of 0.987 and 0.982. The strong correlation allows certain comparisons to be drawn between the structures of the systems at the transition states, as presented in the next section.

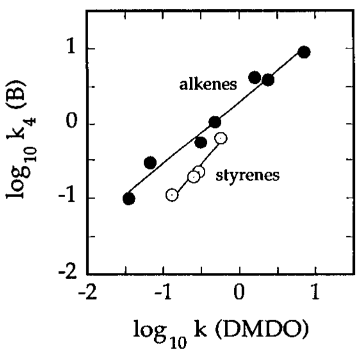
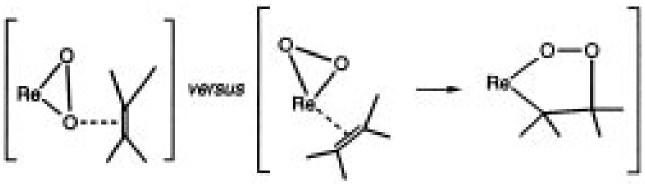


Figure 7. Correlation of the rate constants for the epoxidation of several olefins by **B**, in 1:1 CH_3CN-H_2O at pH 1, with those for dimethyldioxirane in acetone.

Structure of the Transition State. Guided by previous results for epoxidation, we envisage two possible modes by which the olefin might react with the metalloperoxide: a direct attack[30−32] of the double bond on a peroxidic oxygen of **B** or prior binding of the olefin to the rhenium, followed by the slower insertion into the M−O bond to yield a five-membered peroxometalacycle, which would then rapidly yield the epoxide.[33] We diagram the two possibilities as



From these data and earlier reports, we argue against the second formulation. The reasons, which offer different degrees of cogency, are as follows: (1) The second mechanism seems suitable for later transition metals and has been invoked for them.[34] An electron-rich metal favors olefin coordination by back-bonding. (2) No evidence was obtained for any intermediate forming transiently during the repeated NMR scans of any of the 19 alkenes studied by this technique. Although this is not a definitive argument, seeing that it depends on the rates of successive steps that would occur along this pathway, it is suggestive. (3) A five-membered peroxometallacycle has been isolated only in the instance of Pt and Rh peroxo complexes with tetracyanoethylene.[35] Such intermediates have not been found for high-valent early transition metal peroxides of Groups IV−VI.[32] The Re(VII) species, entirely lacking in d electrons, seems likely to fall in the same category. (4) One piece of evidence for prior binding of an olefin to a metal peroxide is that the reaction is inhibited by the presence of basic (coordinating) solvents and ligands.[36] In the present, the reactions of **B** are

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(32) Jørgenson, K. A. *Chem. Rev.* **1989**, *89*, 431−458.

(33) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734.

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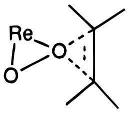
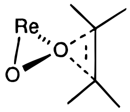
enhanced by the change to a more polar solvent (methanol to aqueous acetonitrile) and in the case of styrene[12] by the addition of water. Epoxidation reactions of DMDO are also accelerated by water.[29] (5) The very close parallel with DMDO, for which coordination is not an option, suggests that the first scheme is the valid one for **B**.

Allyl alcohols are epoxidized more rapidly than normal olefins by early transition metal peroxides. An allyl alcohol may bind to the metal through its OH group prior to oxygen transfer.[37] This feature contradicts our findings: for **B**, allyl alcohols and allyl ethers are less reactive than the corresponding olefins. It appears that this is the only major difference between **B** and other early transition metal peroxides. Perhaps the OH group does not bind; perhaps the electronic factors are dominant.

The geometrical configuration that might represent the reaction at its transition state is worthy of consideration. Consider these two geometries, the first a cyclic planar (or "butterfly") one[38] and the other a "spiro" arrangement[39,40]

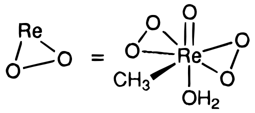


"Butterfly" (planar oxygen)



"Spiro" (tetrahedral oxygen)

where



In the spiro form, the olefinic carbon atoms are coplanar with the three-membered ring formed by the peroxo oxygen atoms and the rhenium atom. The data offer mild support for the spiro transition state. In the isomers of β-methylstyrene, the phenyl ring and the olefinic carbon atoms are coplanar and rotation about the Ph−C bond is hindered owing to π-interaction. Thus there should not be a significant difference in steric hindrance between this pair of isomers; the rate ratio is $k_{\text{cis}}/k_{\text{trans}} = 1.3$. In the case of the isomers of 3-hexen-1-ol, with $k_{\text{cis}}/k_{\text{trans}} = 2.5$, given the free rotation around the single bond between the alkyl group and its olefinic carbon atom, attack should be more sterically hindered for $R^1 = n$-Pr than for $R^1 = H$. The rate ratio of 2.5 is, however, less striking than that for DMDO,[28] where ratios of 7−9 were found, perhaps because the Re−O bonds are longer than the C−O bonds, which reduces the interactions referred to. This geometry also agrees with the finding that the 1,1-disubstituted alkenes and the 1,2-disubstituted alkenes have similar reactivities; the substituents, whether H or alkyl, do not greatly affect the attack of the olefin.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-7405-Eng-82. We gratefully acknowledge the assistance of Prof. Kenneth Kustin toward implementing the thermometric technique used in these studies.

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