Epoxidation of Styrenes by Hydrogen Peroxide As Catalyzed by Methylrhenium Trioxide

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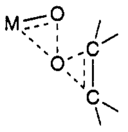
Abstract: Methylrhenium trioxide, CH_3ReO_3, catalyzes the oxidation of styrenes by hydrogen peroxide. Kinetic studies by three methods were carried out in acidic CH_3CN/H_2O (1:1 v/v) solutions. The catalytically-active species are the mono-peroxide, $CH_3Re(O)_2(O_2)$, **A**, and the bis-peroxide, $CH_3Re(O)(O_2)_2$, **B**, which epoxidize a given styrene at a similar rate. The rate constants are relatively insensitive to steric hindrance, but increase with the nucleophilicity of the styrene, electron-donating groups on the olefinic carbons or on the aromatic ring enhancing the rate. The rate constants for meta- and para-substituted styrenes follow a linear Hammett relationship; correlation with σ^+ gave $\rho = -0.93 \pm 0.05$. In CD_3CN, epoxides were observed by ^1H NMR spectroscopy. *cis*-β-Methylstyrene and *trans*-β-methylstyrene led to the *cis* epoxide and the *trans* epoxide, respectively. In acidic CH_3CN/H_2O, the major products were 1,2-diols. In some cases C−C bond cleavage products were also observed, the extreme case being β-methoxystyrene where the C−C bond was completely cleaved to yield benzaldehyde, formaldehyde, and methanol.

The use of aqueous organometallic catalysts poses a challenge, since many are unstable to hydroxylic solvents. The research reported here utilizes the water-stable methylrhenium trioxide as an epoxidation catalyst. Epoxidations by peroxides are catalyzed by complexes of high-valent d^0 metals, such as Mo(VI), V(V), and Ti(IV),[1−3] which heterolyze the peroxides by way of an electron deficient peroxometal.[2c]

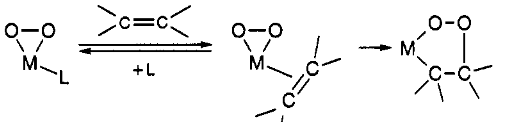
Nucleophilic olefins are the most reactive toward metal−peroxo complexes. The oxygen transferred to the olefin comes exclusively from the peroxo group,[1a,4] and epoxidation is mostly stereoselective.[5,6] In protic solvents 1,2-diols and β-methoxy alcohols are obtained.[7] Alkyl-substituted styrenes are more prone to oxidative cleavage than are aliphatic olefins.[5]

The epoxidation mechanism remains controversial. Three proposals have been made for oxygen transfer from the peroxide, and plausibly each may be valid in certain circumstances. The mechanisms are the following:

(1) External nucleophilic attack of the olefin on the electrophilic peroxy oxygen through a three-membered ring transition state:[2,12]



(2) Olefin binding, followed by insertion into the M−O bond to form a five-membered peroxometallacycle intermediate, eq 1:[1a]



(1)

(3) Nucleophilic attack of one olefinic carbon (α or β) on the peroxy oxygen, followed by intramolecular attack of the same oxygen on the other carbon.[8]

External nucleophilic attack was preferred for Mo(VI) peroxides.[2,9] The epoxide, while still complexed to the metal, is easily displaced by solvent or peroxide, although it may undergo further oxidation.[5,10] The second mechanism[1a,3] has been supported by the lack of reactivity of catalysts lacking an adjacent coordination site for a labile monodentate ligand.[5] The reactions are inhibited in the presence of basic ligands or solvent, such as water and alcohols.[1c] With no electrons available for back-bonding to the olefin, its nucleophilicity is lost upon coordination. The electron density on the peroxy oxygens increases and then nucleophilic attack of the peroxy oxygen on the metal-coordinated olefin leads to a peroxometallacycle intermediate, as isolated from reactions of Pt and Rh peroxo complexes with tetracyanoethene.[11] This mechanism has, however, not been found for d^0 metals.[12] A frontier orbital investigation[13] found the metal-bound olefin slipping toward the peroxy oxygen, with a three-membered, rather than five-membered, ring transition state.

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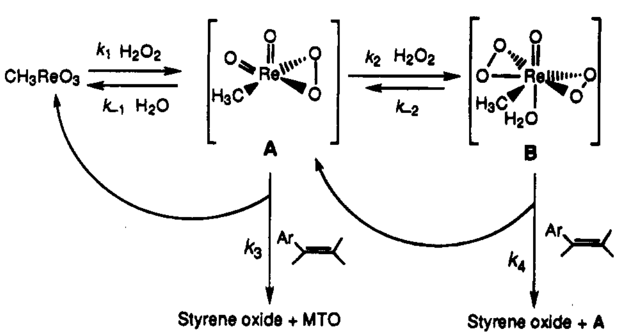
Scheme 1



Methylrhenium trioxide[14] activates hydrogen peroxide through the formation of mono- and bis-peroxides, **A** and **B**, as given in Scheme 1.[15,16] The crystal structure of **B** has been reported.[15] Both **A** and **B** are efficient oxygen donors, transferring oxygen to $ArNMe_2$,[17] Br^-,[18] PR_3,[19] and R_2S [20] at rates 10^4–10^6 times those of free hydrogen peroxide.

The catalytic epoxidation of olefins by hydrogen peroxide using CH_3ReO_3 as a catalyst in *tert*-butyl alcohol has been reported,[21] although no detailed kinetic studies were reported. Others have suggested that only **B** is active in the epoxidation of olefins.[15] In the oxidations of most other species, however, both **A** and **B** react, **A** usually somewhat faster.[16-20] Indeed, we have demonstrated that the same holds for styrenes.

A kinetic study of catalytic epoxidation of a series of styrenes by CH_3ReO_3–H_2O_2 has been carried out in acidic CH_3CN/H_2O to determine the reactivities of **A** and **B** and other features of the mechanism. The mixed solvent was chosen to promote solubility of the styrenes, and water and acidic conditions greatly increased catalyst stability in peroxide solutions. The major products were isolated and identified by ^{1}H-NMR experiments; some of these determinations were made in neat acetonitrile.

We have conducted detailed kinetic studies of the complicated catalytic system shown in Scheme 1. It involves two active species, **A** and **B**, formed from H_2O_2 and MTO. These rhenium peroxides react independently with the styrene. Similar catalytic systems have been observed and studied before.[1d,3] We have used four different methods to determine the rate constants k_3 and k_4 of Scheme 1. In some cases the steady-state approximation was applied; in others, the equilibrium concentrations of **A** and **B** were applicable.

Experimental Section

Materials. Water was purified by a Millipore-Q water purification system. HPLC grade acetonitrile (Fisher) was used, and a low pH, usually 1, was maintained with perchloric acid to stabilize catalyst–peroxide solutions. The catalyst itself, however, was stable for long periods in the absence of hydrogen peroxide. Methylrhenium trioxide[14a] was purified first by sublimation, then by recrystallization from CH_2Cl_2/hexane, and finally by a second sublimation. Solutions of CH_3ReO_3 in water or in CH_3CN were stored at 5 °C and used within 1–2 weeks. Concentrations were determined spectrophotometrically: 239 nm (ϵ 1900 L mol^{-1} cm^{-1}) or 270 nm (ϵ 1300 L mol^{-1} cm^{-1}).[16] Styrenes were purchased commercially from Aldrich, except *cis*-β-methylstyrene which were from TCI America. β-Methoxystyrene was purified by vacuum distillation. Other styrenes were used without further purification. Stock solutions of hydrogen peroxide were prepared by diluting 30% or 3% H_2O_2 (Fisher) and standardized daily by iodometric titration.

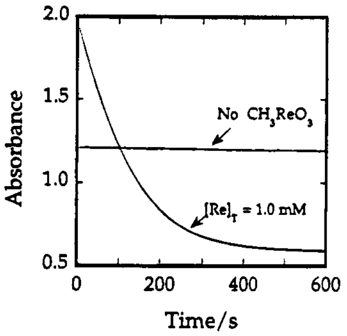


Figure 1. Typical absorbance–time data at 295 nm for β-methoxystyrene (2.0 mM) with H_2O_2 (50 mM) at 25 °C in 0.1 M $HClO_4$, CH_3CN/H_2O (1:1 v/v), in the presence and absence of CH_3ReO_3.

^{1}H NMR spectra were obtained with a Nicolet 300 MHz spectrometer referenced to $(CH_3)_4Si$. A Magnum GC/MS spectrometer was used for GC/MS results.

Kinetics. The kinetic studies were carried out in CH_3CN/H_2O (1:1 v/v) solutions at 25 °C. The concentration of perchloric acid and the ionic strength were maintained at 0.1 M unless specified otherwise. Quartz cuvettes with optical paths of 0.01–2 cm were used. The temperature was maintained at 25.0 °C, or another desired temperature, by immersing the reaction cell in a thermostated water-filled holder positioned in the light beam of the spectrophotometer throughout the experiment. Air (oxygen) had no effect on the reactions and was not excluded. The kinetic data were obtained by following the loss of styrene absorption in the region 265–300 nm using a Shimadzu UV–visible spectrometer.

Reaction mixtures were prepared in a spectrophotometric cell with the last reagent added being H_2O_2 (Method I) or the styrene (Methods II and III) to optimize the kinetic conditions as explained later. Initial rate and pseudo-first-order conditions applied in different protocols; in the latter case the pseudo-first-order rate constants were evaluated by nonlinear least-squares fitting of the absorbance–time curves to a single exponential function, eq 2.

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)e^{-k_\psi t} \qquad (2)$$

Products. 1,2-Diols. The styrene (10 mmol in 5 mL of CH_3CN) was added dropwise to a flask containing CH_3ReO_3 (0.1–1 mmol) and H_2O_2 (12 mmol) in 1:1 CH_3CN/H_2O containing 0.1 M $HClO_4$. The reactions were protected from light and stirred for 1–4 h at room temperature. The acetonitrile was removed under low pressure at 40–50 °C and the products, after extraction into CH_2Cl_2, were dried over $MgSO_4$ and crystallized from CH_2Cl_2/hexane. The percentage yields were then calculated based on styrene, the limiting reactant. The major products were characterized by their ^{1}H-NMR spectra, GC-MS, and melting point.

Epoxides were formed in CD_3CN without added acid or water. To an NMR tube containing the styrene (0.2 M) and CH_3ReO_3 (0.01 M), 0.25 M H_2O_2 was added as a 30% stock solution. The ^{1}H-NMR spectra were recorded intermittently over 12 h.

Results

The reactions of β-methoxystyrene with H_2O_2 in the presence and in the absence of CH_3ReO_3 showed that the uncatalyzed reaction is relatively so slow (Figure 1) that it was not necessary to correct for the uncatalyzed process. The equilibrium and

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Table 1. Rate Constants and Equilibrium Constants for the Reactions of CH_3ReO_3 with Hydrogen Peroxide, Scheme 1[a]

rate constants		
forward (L mol^{-1} s^{-1})	reverse (s^{-1})	equilibrium constants (L mol^{-1})
$k_1 = 32.5^b$	$k_{-1} = 3.0^b$	$K_1 = 10.8^b$
$k_2 = 1.05^c$	$k_{-2} = 0.008^c$	$K_2 = 136^b$

[a] In 0.1 M $HClO_4$, CH_3CN/H_2O (1:1 v/v) at 25 °C. [b] Reference 19. [c] This work.

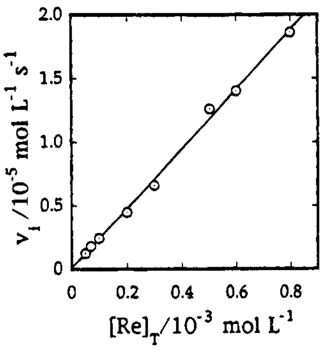


Figure 2. The initial rate of oxidation of β-methoxystyrene (4.0 mM) by $[H_2O_2]$ (50 mM) varies linearly with $[Re]_T$ in 0.1 M $HClO_4$,CH_3CN/H_2O (1:1 v/v) at 25 °C.

rate constants of Scheme 1 are given in Table 1.[19] The catalytic system involves two reactive species, **A** and **B**. By themselves they are in equilibrium with the catalyst, but during the catalytic cycle either the steady-state approximation (Method Ia and Ib) or the equilibrium condition (Methods II and III) defines their concentrations. The rate of epoxidation resulting according to Scheme 1 is expressed by eq 3, in which it is assumed that both **A** and **B** react independently with the styrene.

$$v = -\frac{d[\text{styrene}]}{dt} = (k_3[\mathbf{A}] + k_4[\mathbf{B}])[\text{styrene}] \qquad (3)$$

The rate equation was derived by means of the steady-state approximation for [**A**] and [**B**]. With the mass balance expression, $[Re]_T = [CH_3ReO_3] + [\mathbf{A}] + [\mathbf{B}]$, the rate of the reaction can be expressed as follows:

$$v = \frac{k_1[\text{Re}]_T[\text{styrene}][\text{H}_2\text{O}_2]\left\{k_3 + \dfrac{K_2k_4[\text{H}_2\text{O}_2]}{1 + (k_4/k_{-2})[\text{styrene}]}\right\}}{k_{-1} + k_3[\text{styrene}] + k_1[\text{H}_2\text{O}_2] + \left\{\dfrac{k_1K_2[\text{H}_2\text{O}_2]^2}{1 + (k_4/k_{-2})[\text{styrene}]}\right\}} \qquad (4)$$

Under conditions in which [**A**] is much greater than [**B**] ($[H_2O_2] \leq 2.0$ mM) eq 4 simplifies to eq 5. Actually the determinant is k_3[**A**] versus k_4[**B**], but the use of concentrations is not incorrect since the values of k_3 and k_4 are quite close.

$$v = \frac{k_1k_3[\text{Re}]_T[\text{styrene}][\text{H}_2\text{O}_2]}{k_{-1} + k_3[\text{styrene}] + k_1[\text{H}_2\text{O}_2]} \qquad (5)$$

Kinetics with Variable $[Re]_T$. Values of the initial rate (v_i) were calculated from experiments in which $[Re]_T$ varied over a range of 0.05−1.0 mM. Hydrogen peroxide and β-methoxystyrene were held constant at 50 and 4.0 mM, respectively. As shown in Figure 2, the initial rates showed a linear dependence on $[Re]_T$ as expected from eqs 4 and 5. The rate constants for the reaction of the styrenes with **A** and **B**, k_3 and k_4, respectively, were determined by four different methods.

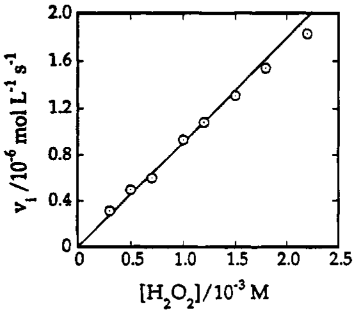


Figure 3. The initial rate of oxidation of β-methoxystyrene (3.0 mM) with $[H_2O_2]$ fits eq 5 at low $[H_2O_2]$ (involving only **A**) at $[Re]_T$ = 2.0 mM.

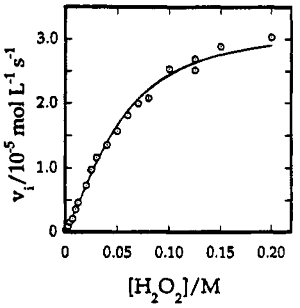


Figure 4. The initial rate of oxidation of β-methoxystyrene (2.0 mM) with $[H_2O_2]$ fits eq 7 under conditions involving both **A** and **B**, at $[Re]_T$ = 1.0 mM.

Method Ia: Initial Rates with Involvement of A Only. The reaction of β-methoxystyrene was studied at constant concentrations of CH_3ReO_3 and β-methoxystyrene of 2.0 and 3.0 mM, respectively. To minimize [**B**], the variable concentration of hydrogen peroxide was kept ≤2.0 mM, and it was added last to minimize [**B**] in the pre-reaction period. The initial rate at each $[H_2O_2]$ was calculated from the initial rate of absorbance change from the loss of styrene in the region 265−300 nm:

$$v_i = \frac{1}{b\Delta\epsilon_\lambda} \times \frac{\Delta Abs}{\Delta t} \qquad (6)$$

where $\Delta\epsilon$ is the difference in the molar absorptivities of the reactants and the products at wavelength λ, and b the optical path length. The dependence of v_i on $[H_2O_2]$, shown in Figure 3, was fit to eq 5 giving $k_3 = 14.6 \pm 0.4$ L mol^{-1} s^{-1}, the other quantities being fixed at the specified values.

Method Ib: Initial Rates with Involvement of A and B. Kinetic measurements were carried out with a constant $[Re]_T$ of 1.0 mM and a constant concentration of β-methoxystyrene of 2.0 mM. The concentration of H_2O_2 was varied in the range 1−200 mM. The nineteen values (see Figure 4) were fit to eq 4 and yielded values for the unknown rate constants: $k_3 = 14.2 \pm 0.5$ L mol^{-1} s^{-1}, $k_4 = 15.7 \pm 0.75$ L mol^{-1} s^{-1}, and $k_{-2} = 0.008 \pm 0.001$ s^{-1}. From K_2 and k_{-2}, we obtained $k_2 = 1.05$ L mol^{-1} s^{-1}. Fitting of k_2 was needed, as it was previously unknown in this medium.

The reactions of *trans*-4-propenylanisole and *trans*-2-methyl-3-phenyl-2-propen-1-ol were studied similarly. With k_{-2} fixed at 0.008 s^{-1}, the kinetic data were fitted to eq 4. The values of k_3 and k_4 are summarized in Table 2.

Method II: First-Order Kinetics Involving B Only. In the epoxidation of the styrenes with $[H_2O_2] > 0.5$ M, the absorbance-time values followed first-order kinetics. Indeed, at high $[H_2O_2]$, the amount of **A** present is negligible, and the

Table 2. Rate constants for the Reactions of Styrenes with **A** [$CH_3Re(O)_2(O_2)$, k_3] and **B** [$CH_3Re(O)(O_2)_2(H_2O)$, k_4][a] by Various Methods[b]

styrene	k_3/L mol^{-1} s^{-1}	k_4/L mol^{-1} s^{-1}
$PhCH{=}CH_2$		0.11 ± 0.02 (II)[a]
3-MeC_6H_4-$CH{=}CH_2$		0.12 ± 0.01 (II)
4-MeC_6H_4-$CH{=}CH_2$	0.38 ± 0.06 (III)	0.16 ± 0.01 (II) 0.19 ± 0.01 (III)
2,4-$Me_2C_6H_3$-$CH{=}CH_2$		0.38 ± 0.02 (II)
2,4,6-$Me_3C_6H_2$-$CH{=}CH_2$	0.13 ± 0.05 (III)	0.12 ± 0.01 (III)
$PhC(Me){=}CH_2$		0.47 ± 0.02 (II)
trans-$PhCH{=}CHMe$	0.51 ± 0.07 (III)	0.22 ± 0.02 (III)
cis-$PhCH{=}CHMe$	0.74 ± 0.08 (III)	0.28 ± 0.01 (III)
$PhCH{=}CMe_2$	1.00 ± 0.17 (III)	0.70 ± 0.04 (III)
$PhCH{=}CH(CH_2OH)$		0.14 ± 0.01(II)
trans-$PhCH{=}C(Me)CH_2OH$	0.73 ± 0.07 (I)	0.40 ± 0.03 (I) 0.45 ± 0.03 (II)
4-$MeOC_6H_4$-$CH{=}CH_2$	0.67 ± 0.12 (III)	0.63 ± 0.01 (II) 0.57 ± 0.04 (III)
trans-MeO-4-C_6H_4-$CH{=}CHMe$	2.79 ± 0.05 (I) 2.80 ± 0.11 (III)	0.80 ± 0.03 (I) 1.20 ± 0.03 (II) 0.92 ± 0.03 (III)
$PhCH{=}CH(OMe)$	14.1 ± 0.5 (I)	15.7 ± 0.8 (I) 18.0 ± 0.7 (II)

[a] In CH_3CN/H_2O (1:1 v/v), 0.1 M $HClO_4$ at 25 °C. [b] The methods are given by the Roman numerals (see text).

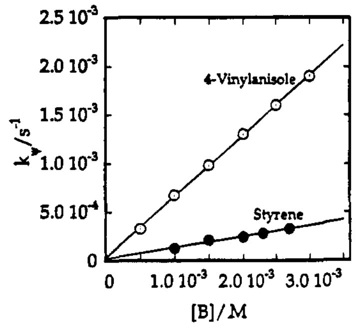


Figure 5. The pseudo-first-order rate constants for the oxidation of 5.0 mM styrene and 4-methoxystyrene with [H_2O_2] (0.8 M) varied with **B** ($\cong[Re]_T$) are fitted by eq 7, $k_\psi = k_4[\mathbf{B}]$.

formation of **B** during the reaction is much faster than the reaction of **B** with styrene; i.e. $k_2[H_2O_2] \gg k_4$[styrene]. The concentration of **B** was constant during the reaction and essentially equal to $[Re]_T$. Under these conditions the rate of the reaction becomes:

$$v = k_4[\mathbf{B}][\text{styrene}] = k_4[\text{Re}]_T[\text{styrene}] = k_\psi[\text{styrene}] \quad (7)$$

A series of experiments was done with constant [H_2O_2] = 0.5−1 M and [styrene] = 2−5 mM, with $[Re]_T$ varied from 0.3 to 3 mM. The solutions of CH_3ReO_3 and H_2O_2 were allowed to equilibrate with **B** for 3−5 min before adding the styrene. The rate constants k_ψ from eq 2 varied linearly with [**B**] = $[Re]_T$ at each $[Re]_T$, Figure 5. The value of k_4 is given by the slope of the line. Their values are summarized in Table 2.

Method III: First-Order Kinetics with A and B. Inspection of Scheme 1 reveals that the equilibrium concentrations of **A** and **B** will not change during the reaction if the following conditions are maintained throughout the reaction time:

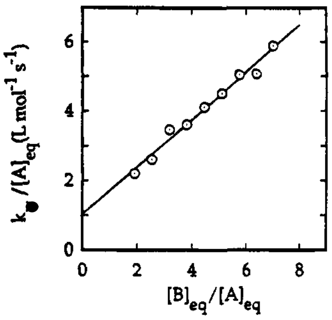


Figure 6. A plot of $k_\psi/[A]_{eq}$ against $[B]_{eq}/[A]_{eq}$ for the oxidation of 2-methyl-1-phenyl-1-propene (1.0 mM) by **A** and **B** at $[Re]_T$ = 1.0 mM, and [H_2O_2] 15−60 mM. The fit to eq 13 gave k_3 = 1.03 ± 0.17 L mol^{-1} s^{-1} and k_4 = 0.68 ± 0.04 L mol^{-1} s^{-1}. Fitting the same data to two independent variables, $[A]_{eq}$ and $[B]_{eq}$, gave k_3 = 1.00 ± 0.17 and k_4 = 0.70 ± 0.04 L mol^{-1} s^{-1}.

$$k_1[H_2O_2] + k_{-1} \gg k_3[\text{styrene}] \quad \text{and} \quad k_2[H_2O_2] + k_{-2} \gg k_4[\text{styrene}] \quad (8)$$

Helping to attain this condition, for all except β-methoxystyrene, is the finding $k_1 \gg k_3$ and $k_2 > k_4$. In addition to that, [H_2O_2] was at least ten times more than [Styrene]. A wide set of concentrations could be found for the styrenes where the inequalities in expression 8 were fully satisfied. Under these conditions the rate law can be written as:

$$v = (k_3[\mathbf{A}] + k_4[\mathbf{B}])[\text{styrene}] = k_\psi[\text{styrene}] \quad (9)$$

In this method, kinetic measurements were carried out with constant $[Re]_T$ of 1−2 mM and constant [styrene] of 1−3 mM, different values being used for different styrenes. To ensure a significant contribution from **A**, [H_2O_2] was not used in very large excess. The concentration of [H_2O_2] was varied between 15 and 60 mM, at least ten times more than [Styrene]. As in Method II, the solutions of CH_3ReO_3 and H_2O_2 were allowed to equilibrate with **A** and **B** for 3−5 min before adding the styrene.

The experimental observation of pseudo-first-order kinetic traces also confirms the validity of eq 9. The traces fit very well to the first-order exponential equation, eq 2, yielding $k_\psi = k_3[\mathbf{A}]_{eq} + k_4[\mathbf{B}]_{eq}$. In some cases, where the reactions were relatively slow, the initial reaction rates were calculated from the initial stage only. The observed rate constants, k_ψ, were then calculated from the initial rates, $k_\psi = v_i$ /[styrene]. The concentrations of $[\mathbf{A}]_{eq}$ and $[\mathbf{B}]_{eq}$ for each [H_2O_2] and $[Re]_T$ were calculated from the equilibrium constants, K_1 = 10.8 L mol^{-1} and K_2 = 136 L mol^{-1}. The values of k_3 and k_4, Table 2, were calculated using the nonlinear least-squares program GraFit, which allowed the simultaneous use of two independent variables, $[\mathbf{A}]_{eq}$ and $[\mathbf{B}]_{eq}$. An equation with single independent variable can also be used by dividing k_ψ by $[\mathbf{A}]_{eq}$ (eq 10) or $[\mathbf{B}]_{eq}$.

$$\frac{k_\psi}{[\mathbf{A}]_{eq}} = k_3 + k_4 \frac{[\mathbf{B}]_{eq}}{[\mathbf{A}]_{eq}} \quad (10)$$

Plots of $k_\psi/[\mathbf{A}]_{eq}$ against $[\mathbf{B}]_{eq}/[\mathbf{A}]_{eq}$ give straight lines with slopes of k_4 and intercepts of k_3, Figure 6. The values of k_3 and k_4 obtained by both types of fits are very similar, but those from the dual variable treatment are sounder statistically and are the ones tabulated.

The use of different methods for the kinetics under which different solutions to the rate laws applied allowed the various constants to be determined and to be checked independently. The initial rate method allowed the rate constant for **A** to be determined at low [H_2O_2] ($\leq$2 mM). Variation of the initial rates with [H_2O_2] over a wide range of [H_2O_2], Figure 4, allowed us to determine both k_3 and k_4. The values for the reactions of β-methoxystyrene with **A** obtained under these two conditions agreed, $k_3 = 14.6 \pm 0.4$ and 14.2 ± 0.5 L mol^{-1} s^{-1}.

At high [H_2O_2], with essentially only **B** present, the rate law simply reduces to eq 9. Method II is easily applied and is the most accurate one. The assumption $[\mathbf{B}] \approx [\mathrm{Re}]_T$ is valid throughout the reaction. The values of K_1 and K_2 are such that when $[H_2O_2] > 0.5$ M, $[CH_3ReO_3]_{eq}$ and $[\mathbf{A}]_{eq}$ are less than 2% of $[\mathbf{B}]_{eq}$ (i.e., $[\mathbf{B}]_{eq} \sim [\mathrm{Re}]_T$). To ensure that [$H_2O_2$] and $[\mathbf{B}]_{eq}$ remain essentially constant during the reaction, styrenes were used at ~2−5 mM, very low relative to [H_2O_2]. Furthermore, the experimental observation of pseudo-first-order kinetics under these conditions was confirmed by kinetic simulations using KINSIM.[24]

The values of k_4 obtained by methods I and II are in a good agreement, Table 1, except for *trans*-4-propenylanisole, 0.80 $\pm$ 0.03 (I) and 1.20 $\pm$ 0.03 (II) L mol^{-1} s^{-1}. This is more likely due to systematic errors in the experiments rather than differences in the chemistry under the two sets of conditions.

Method III applies only to substrates that react relatively slowly with **A** and **B**. This method could not be used for the reactions of PR_3[19] or R_2S.[20] Method III is permissible especially when $k_3 < k_1$ and $k_4 < k_2$, and [H_2O_2] $\gg$ [styrene], which is true except for β-methoxystyrene.

Activation Parameters. Only k_4 for 4-methoxystyrene was studied in this respect. The following are the data, T/°C (k_4/L mol^{-1} s^{-1}): 3.3 (0.133); 8.0 (0.195); 14.5 (0.273); 20.0 (0.398); 25.0 (0.626); 30.0 (0.75); 37.5 (1.18). Analysis by the TST equation $k_4 = (RT/Nh)\exp(\Delta S^{\ddagger}/R)\exp(-\Delta H^{\ddagger}/RT)$ gave $\Delta H^{\ddagger} = 42.8 \pm 1.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -106 \pm 5$ J mol^{-1} K^{-1}.

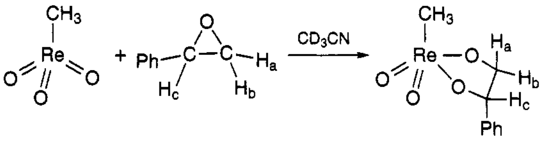
Products. The reactions of β-methoxystyrene and *trans*-4-propenylanisole with $CH_3ReO_3-H_2O_2$ in CH_3CN/H_2O at 0.1 M $HClO_4$ showed that epoxidation of 1.0 equiv of styrene required 1.0−1.2 equiv of H_2O_2. This slight mismatch is consistent with the known slow decomposition of the catalytic system, CH_3ReO_3-H_2O_2, to $HReO_4$, CH_3OH, and oxygen.[22]

In CD_3CN, ^{1}H−NMR experiments showed that the initial product from reaction of the styrenes with $CH_3ReO_3-H_2O_2$ was the styrene oxide. In the presence of aqueous acid, the epoxide ring opened, yielding 1,2-diol and other minor products. In CH_3CN/H_2O, the final product was the 1,2-diol. The catalytic reactions of 0.5 M styrene, 4-methoxystyrene, and *trans*-4-propenylanisole with H_2O_2 (0.6 M) in the presence of 2−20 mM CH_3ReO_3 yielded the corresponding 1,2−diol with isolated yields of 55%, 43%, and 35%, respectively. Other products, such as aldehydes, ketones, or alcohols, were detected by GC-MS with relatively low yields depending on the nature of the styrene.

Electron-donating groups on the aromatic ring or on the olefinic carbons enhance the C−C bond cleavage. For example, no C−C bond cleavage was observed from reaction of styrene, whereas *trans*-4-propenylanisole produced 4-methoxybenzaldehyde and 4-methoxybenzyl alcohol in 10−15% yield. Epoxidation of β-methoxystyrene, on the other hand, involved complete C−C bond cleavage. The products were benzaldehyde, identified by ^{1}H-NMR and GC-MS, and formaldehyde, characterized by chromotropic acid analysis.[23] ^{1}H-NMR experiments showed that the same products also resulted from the reaction of β-methoxystyrene with *m*-chloroperoxybenzoic acid in CD_3CN/D_2O (1:1 v/v) containing 0.1 M $HClO_4$.

The stereochemistry of these reactions was studied in CD_3CN in the absence of acid. The difference in the coupling constants in the ^{1}H NMR spectra of the cis protons, J_{AB}(cis) = 4.2 Hz, and the trans protons, J_{AB}(trans) = 2.0 Hz, was used to distinguish between the products. Epoxidation of *cis*-β-methylstyrene with the $CH_3ReO_3-H_2O_2$ system gives the cis epoxide; likewise, *trans*-β-methylstyrene is converted to the trans epoxide.

Epoxide Ring Opening. In CD_3CN, in the absence of acid, styrene oxide reacts with CH_3ReO_3 in both the presence *and absence* of H_2O_2 to yield a Re(VII) compound with a bound diol, eq 11. Its ^{1}H−NMR spectrum in CD_3CN showed six signals: δ 2.45 ppm (s, 3H, Re-CH$_3$), 4.78 ppm (dd, 1H, H$_a$), 5.23 ppm (t, 1H, H$_b$), 5.54 ppm (dd, 1H, H$_c$), 7.32 ppm (m, 3H, *p*- and *m*-Ph), and 7.47 ppm (m, 2H, *o*-Ph). The coupling constants for the protons H$_a$, H$_b$, and H$_c$ are $J_{cb} \sim J_{ab} = 9.6$ Hz and $J_{ac} = 8.3$ Hz. Reaction 11 occurs only when water is absent. In the presence of water (~1 M), the Re-diol adduct hydrolzed slowly to CH_3ReO_3 and the 1,2-diol.



(11)

In addition to the bound diol, free phenyl-1,2-ethanediol was also formed. The rhenium diolate adduct in eq 11 forms from the reaction of styrene epoxide with CH_3ReO_3 and not from reaction of phenyl-1,2-ethanediol with CH_3ReO_3. Under the same conditions, phenyl-1,2-ethanediol (0.10 M) and CH_3ReO_3 (0.05 M) in CD_3CN did not yield any Re-diol adduct even after two days. In CH_3CN/H_2O (1:1 v/v), 0.10 M $HClO_4$, addition of CH_3ReO_3 did not enhance the rate of formation of phenyl-1,2-ethanediol from styrene oxide. The epoxide ring-opening is much faster in the presence of 0.1 M $HClO_4$ is much faster than in the presence of 1−5 mM CH_3ReO_3.

Discussion

In organic solvents, the rhenium−catalyzed reactions of hydrogen peroxide and styrenes do yield epoxides, as established in our research and in work reported in the literature.[22] For the study of the quantitative kinetics, however, a semi-aqueous medium was employed since the rate and equilibrium constants of the initial steps, formation and dissociation of the rhenium peroxides, have been quantitatively established from earlier work and improved by subsequent experiments carried out in the course of this work. Once the activity of water is this high, acid must be added to stabilize the rhenium peroxides, even though CH_3ReO_3 itself is stable toward water. In aqueous acid, of course, the first-formed epoxide product undergoes "instant" ring opening to the diol, which is thus the identified product in the aqueous, acidic medium.

During olefin epoxidation by CH_3ReO_3-H_2O_2 in *tert*-butyl alcohol catalytic ring opening of epoxides to 1,2-diols also occurs.[21] In dry organic solvents, such as CH_2Cl_2 and THF, 1,2-diols react with CH_3ReO_3 to form Re-diol chelate complexes, eq 12.[25]

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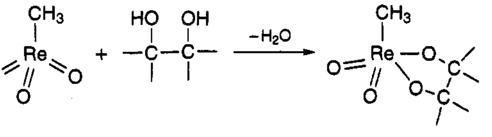
(24) Barshop, B. A.; Wrenn, C. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134.

(25) Herrmann, W. A.; Watzlowik, P.; Kiprof, P. *Chem. Ber.* **1991**, *124*, 1101.



(12)

Formation of the diolate may reduce the catalytic turnover. Epoxides bind more strongly to Mo^{VI}−peroxo complexes than the corresponding olefins do,[26] inhibiting epoxidation and leading to further oxidation of the metal-coordinated epoxide.[5,10] Formation of rhenium epoxide adducts was not observed. The coupling patterns of the aliphatic protons, H_a, H_b, and H_c, in free styrene oxide, eq 11, and in rhenium-bound styrene oxide are expected to be very similar. Free styrene oxide gives three doublet-of-doublets signals at 2.77 ppm (H_a, $J_{ac} = 2.7$ Hz and $J_{ab} = 5.4$ Hz), 3.07 ppm (H_b, $J_{bc} = 4.2$ Hz), and 3.82 ppm (H_c). The chemical shifts and the coupling constants obtained by ^{1}H-NMR from the reaction of styrene oxide with CH_3ReO_3 suggest formation of the Re-diol adduct rather than a Re-epoxide adduct. Here the Re-diol chelate complex was observed only in CD_3CN in the absence of acid. Under the conditions for the kinetics, CH_3CN/H_2O, 0.1 M $HClO_4$, CH_3ReO_3 did not react with phenyl-1,2-ethanediol or styrene oxide, nor did it enhance the opening of the styrene oxide ring. Also, addition of 1,2-diols did not alter the rate of epoxidation of styrene by $CH_3ReO_3-H_2O_2$. The epoxide ring-opening is catalyzed by the acid (0.10 M $HClO_4$) rather than by CH_3ReO_3. The reaction of 1,2-diols with Re(VII) is inhibited by water since d^0 early transition metals (Lewis acids) have high affinity for bases such as water, present in high concentration relative to the 1,2-diols.

The rate of reaction of β-methoxystyrene with $CH_3ReO_3-H_2O_2$ increases with the amount of water in the solution, consistent with the higher values of k_1, k_{-1}, k_2 and k_{-2}, in H_2O.[16,19] There is also an effect on the catalytic steps: the rate constants for *trans*-4-propenylanisole are $k_4 = 1.1$ L mol^{-1} s^{-1} in 1:1 CH_3CN/H_2O and 0.45 L mol^{-1} s^{-1} in a 4:1 solvent mixture. Another examination of solvent effects was carried out for styrene. The value of k_4 is 0.021 L mol^{-1} s^{-1} in methanol, compared to 0.11 in 1:1 CH_3CN/H_2O. Note that the results cited refer to the reactions of **B** only, and do not reflect any effect of water on the rates or equilibria of the peroxide-binding steps. Again, the catalytic step of this reaction is accelerated in the presence of water.

Clearly **A** and **B** epoxidize styrenes at similar rates. What differences exist between the two depend upon the kind of styrene being used. A recent study[17] of the oxidation of anilines by the CH_3ReO_3/H_2O_2 system in methanol has shown that **A** is more active than **B**. These results do not agree with the findings for alkenes reported recently, from studies carried out in *tert*-butyl alcohol,[21] from which it was concluded that **B** but not **A** epoxidizes olefins. Since both **A** and **B** are neutral molecules in which Re^{VII} binds to CH_3, oxo, and peroxo ligands, the medium should not greatly affect their relative reactivities. The absolute activities of **A** and **B** are, however, media dependent. In general, the relative activity of the diperoxo to the monoperoxo metal complexes depends greatly on the size of the metal and the reaction mechanism. Competitive studies of olefin epoxidation by $M(O)(O_2)_2$HMPT (HMPT = hexamethylphosphoric triamide; M = Mo and W) have shown that the diperoxo is more reactive than the monoperoxo when M = W. In the case of Mo it is the opposite, the monoperoxo being more reactive.[3] We have found that **A** is less sensitive to steric factors than **B**. For example, the rate constant for the reaction of *trans*-4-propenylanisole with **A** is about three times larger than that from the same reaction with **B** ($k_3/k_4 = 3.4$), whereas for the less sterically hindered 4-methoxystyrene, $k_3/k_4 = 1.3$.

It is pertinent to this research to comment upon the very similar reactivities of **A** and **B**, not only toward styrenes, but also with respect to several of the species cited earlier: Br^-, $ArNMe_2$, R_2S, and Ar_3P, for example. This might at first seem surprising, in that CH_3ReO_3 is the product of **A**, whereas **A** itself is formed when **B** reacts; clearly the two products, CH_3ReO_3 and **A**, are quite different. Nonetheless, the cause seems to be that these two hardly differ in free energy with respect to the extra molecule of H_2O_2/H_2O by which they differ; that is, K_1 is only 10.6 L mol^{-1}, or $\Delta G_1^\circ = -6$ kJ mol^{-1}. Both **A** and **B** contain $Re(\eta^2\text{-}O_2^{2-})$, and it this chemical unit that is the reactive one.

In both cases the rate constants increase with the presence of electron-donating groups, whether on the olefinic carbons or on the aromatic ring. For methyl-substituted styrenes the following reactivity trend was observed: styrene < *trans*-β-methylstyrene ~ *cis*-β-methylstyrene < α-methylstyrene < β-dimethylstyrene.

Steric factors have little effect. The ratio of the rate constants (k_4) for epoxidation of *cis*- and *trans*-β-methylstyrene is 1.3. Addition of one methyl group to the olefinic carbon increases the rate constant by a factor of 3−4. A large effect was observed when the substituent on an olefinic carbon donates electrons through resonance. The rate constant of β-methoxystyrene is ~150 times greater than that of styrene. Donation of electrons from the OCH_3 group through resonance enhances greatly the nucleophilicity because it develops negative charge on the olefinic carbons.

Electron-donating substituents on the aromatic ring in ortho and para positions increase the rate through resonance;[27] thus 4-methylstyrene and 2,4-dimethylstyrene have rate constants 2−5 times greater than that of styrene. On the other hand, the rate constants for styrene and 3-methylstyrene are almost the same, as given in Table 2.

The rate of epoxidation of 2,4,6-trimethylstyrene is almost equal to that of styrene and 3−4 times less than that of 2,4-dimethylstyrene. Steric factors resulting from the presence of methyl groups in both ortho positions lower the reactivity of 2,4,6-trimethylstyrene. Sterically, these substituents affect the attack of the olefinic carbons on the peroxy oxygen of **B**. They also disturb the delocalization of electrons between the aromatic and the olefinic systems. In 2,4,6-trimethylstyrene the β-carbon lies out of the plane that contains the aromatic carbons and the α-carbon. This, of course, reduces the donation of electrons from the methyl groups to the olefinic system through resonance, probably the most important path for donation of electrons in this case.

Further evidence for the importance of electron donation through resonance was obtained from a correlation of substituent effects by the Hammett equation. The rate constants for styrene, 3-methylstyrene, 4-methylstyrene, and 4-methoxystyrene were correlated by the Hammett linear free-energy relationship, σ^+ (but not σ) gave a good correlation, Figure 7, with $\rho = -0.93 \pm 0.05$. The correlation with σ^+ implies a direct interaction through resonance between the substituent and the reaction site. The relatively small negative value of ρ indicates the buildup of partial positive charge on the olefinic carbons in the transition state. Compare the epoxidation of styrenes with dimethyldioxirane ($\rho = -0.90$)[28] and by peracetic acid ($\rho = -1.3$).[8] In

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[26] Zahonyi-Budo, E.; Simandi, I. *The Role of Oxygen in Chemistry and Biochemistry* Ando, W., Moro-Oka, Y., Ed.; Elsevier Science Publishers: Amsterdam, 1988; Vol. 33, p 219.

[27] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry* 3rd ed.; Plenum Press: New York, 1990; p 199.

[28] Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1988**, *53*, 3437.

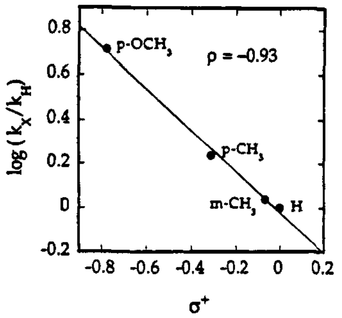


Figure 7. The Hammett correlation of k_4 for the oxidation of styrenes by **B** against σ^+. The reaction constant is $\rho = -0.93$.

both studies the rate constants correlated well with σ^+. The latter study proposed nucleophilic attack of one of the olefinic carbons (α or β) on the peroxy oxygen followed by intramolecular attack of the same oxygen on the other olefinic carbon.

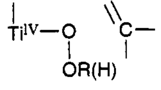
For the epoxidation of styrenes by $CH_3ReO_3-H_2O_2$ we propose for **A** the mechanism diagrammed in Scheme 2.

Reactions of **B** should adopt the same mechanism. It involves external nucleophilic attack of the π-system of the olefin on the electrophilic peroxide oxygen. This leads to the formation of a three-membered-ring transition state. This proposed mechanism is consistent with the slight effect of steric factors on the rate constant since such attack is insensitive to steric hindrance.

A similar three-membered-ring transition state has been proposed for the epoxidation of olefins by Mo(VI)−peroxo complexes.[2] Theoretical studies of epoxidations by M(VI)−peroxo complexes (M = Cr, Mo, W) show that three-membered-ring transition states are more favorable than five-membered rings which include both peroxy oxygens and the metal.[13]

The activation parameters for k_4 support this model. Bimolecular reactions will nearly always have a negative value for $\Delta S^{\ddagger}$, but the value of -106 J mol^{-1} K^{-1} is so negative as to suggest specific orientational features in the transition state formed from two uncharged species. The value of $\Delta H^{\ddagger}$ of 42.8 kJ mol^{-1} is substantial and must surely reflect a composite of bond breaking (Re−O, O−O) and bond making (C−O); without such compensation the reaction would be extraordinarily slow: witness the very slow uncatalyzed reaction between hydrogen peroxide and styrenes.

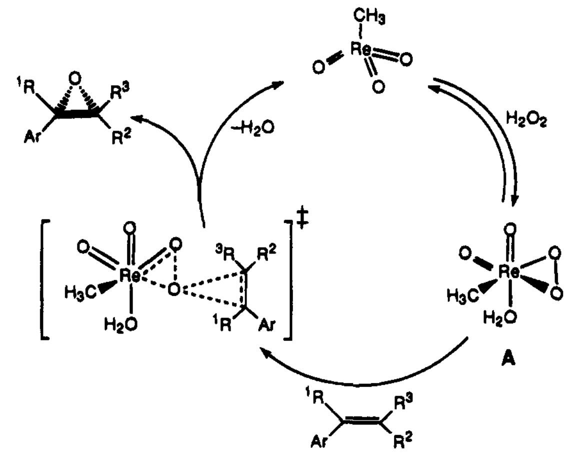
Allyl alcohols are epoxidized more readily than normal olefins by d^0-peroxides of early transition metals, such as Ti(IV) and V(V).[12] An allyl alcohol binds the metal through its OH group, **5**, before oxygen transfer. In addition, this binding leads to selective epoxidations.



5

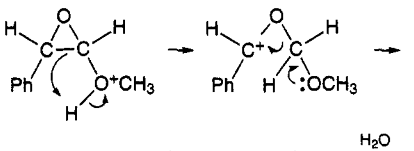
Our results for cinnamyl alcohol and *trans*-3-methyl-2-phenyl-2-propen-1-ol show that such binding to Re(VII) is not likely. The rate constants for cinnamyl alcohol and *trans*-3-methyl-2-phenyl-2-propen-1-ol are less than those of β-methylstyrene and β-dimethylstyrene, respectively. The slight changes in reactivity of allyl alcohols relative to methyl−substituted styrenes follow the trend for other alkyl-substituted styrenes; the CH_3 group is simply a better electron donor than CH_2OH. This finding confirms the observation that aqueous Re(VII)−peroxo complexes do not bind to OH groups of diols and allyl alcohols. Indirectly, it further suggests that olefins do not bind to **A** or **B** prior to the oxygen-transfer step since high oxidation state d^0 early transition metals are known to have a much higher affinity for hard ligands, such as ones with OH groups, than for π-acid ligands, such as olefins. This result suggests that the alternative mechanism, eq 1,[1a] which involves binding of the olefin to Re^{VII} before the oxygen atom transfer takes place, is not possible under these conditions. Furthermore, reactions that involve this mechanism are inhibited by basic solvents, such as water or alcohols. In the case of CH_3ReO_3/H_2O_2, however, the reactivity increases with the [H_2O] present in the solutions.

Scheme 2

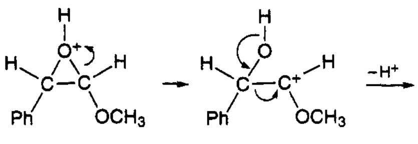


Expoxides are the initial products from these reactions. Epoxides react rapidly with acids to yield carbocation intermediates that react immediately with nucleophiles, such as H_2O, to yield 1,2-diols or other organic products. The extent of carbon−carbon bond cleavage depends on the styrene and on the experimental conditions. The amount of cleavage increased with acidity but decreased with the amount of H_2O. Electron-donating groups, especially on the olefinic carbons, enhance the C−C bond cleavage in this order: styrene < *cis*-β-methylstyrene ≤ *trans*-β-methylstyrene < *trans*-4-propenylanisole ≪ β-methoxystyrene.

β-Methoxystyrene undergoes complete C−C bond cleavage and produces benzaldehyde, formaldehyde, and methanol, assisted by the strong electron-donating group, OCH_3. Formation of the same products from oxidation of β-methoxystyrene by *m*-chloroperoxybenzoic acid under the same conditions suggested that the C−C bond cleavage is catalyzed by acid. Two reasonable mechanisms in which either the methoxy or epoxide oxygen is protonated can be advanced, eqs 13−14; it appears a further resolution cannot be made with the data at hand.



$$PhCHO + H_2CO^+Me \xrightarrow[-H^+]{H_2O} HCHO + MeOH \quad (13)$$



$$PhCHO + HC^-{=}O^+Me \xrightarrow{H_2O} HCHO + MeOH \quad (14)$$

In aqueous acid the epoxide forms slowly and reacts rapidly, and could not be observed. Although the epoxide ring-opening in organic solvent, such as alcohols, is catalyzed by CH_3ReO_3, the epoxide can be observed and isolated.[21] In the presence of basic ligands, such as pyridines, only the epoxide is formed at 25 °C in almost quantitative yield.[22] In the absence of acid, using only CD_3CN as solvent, the epoxide was detected by ^1H NMR. It reacted slowly with the water introduced with the 30% H_2O_2 and produced by the overall reaction. Under these conditions the epoxidation reactions are stereospecific. Epoxidation of *cis*-β-methylstyrene led to the *cis* epoxide, whereas epoxidation of *trans*-β-methylstyrene gave exclusively the *trans* epoxide. These results are consistent with the proposed mechanism of concerted oxygen transfer through a three-membered-ring transition state. Rotation of the C−C bond is not possible and so the reactions are completely stereospecific. Reactions that adopt radical mechanisms[1c,29] or proceed by nucleophilic attack of one of the olefinic carbon atoms on the peroxo oxygen, as in the third mechanism,[8] are partially or completely nonstereospecific. The radical mechanism has been proposed for epoxidation of allyl alcohols by $V(O)(O_2)(pic)(H_2O)_2$.[1b]

Epoxidation rates catalyzed by d^0 early transition element peroxo complexes increase in the following order, Ti(IV) < V(V) < Mo(VI).[2] Tungsten(VI) complexes are the best, but water or a polar solvent retards the reaction.[2c] Rhenium(VII) may be the most active catalyst among these d^0 early transition metals. Herrmann et al.[22] have claimed that CH_3ReO_3 is the best catalyst for epoxidation of olefins by H_2O_2; they state: "Among the epoxidation catalysts, only Groves' manganese/porphyrin systems can successfully compete with CH_3ReO_3 in terms of yields and turnover numbers (TON)."[22] The sources of oxygen in these reactions, however, are PhIO, $KHSO_5$, or very high $[H_2O_2]$ (>30%). The efficiency and selectivity of the catalyst for oxygen transfer is very important since a less effective epoxidation catalyst, such as Ti(IV), leads to free-radical formation and catalytic decomposition of the peroxide.[2] Furthermore, non-selective catalysts, such as (Por)M=O; (M = Fe[3,30] or Mn),[2,31] lead to further oxidation of the epoxides by C−C bond cleavage and hydride or hydrogen atom abstraction pathways. Although the $CH_3ReO_3-H_2O_2$ catalyst decomposes slowly under certain conditions,[32] CH_3ReO_3 is a good catalyst for epoxidation of olefins. It is easy to prepare and handle, soluble, and active in H_2O and most organic solvents. Methylrhenium trioxide activates H_2O_2 heterolytically and achieves high reactivity ($k_{cat}/k_{uncat} \sim 10^5$) and selectivity. It does not catalyze hydride or hydrogen atom abstraction reactions, or involve radical pathways. Unlike other transition metal peroxo complexes, the reactivities of the monoperoxo-Re, **A**, and diperoxo-Re, **B**, species are not inhibited by the presence of basic ligands or solvents, such as alcohols or water. The epoxidation reactions are stereospecific. Finally, CH_3ReO_3 can be used, efficiently, over a wide temperature range, below and above room temperature.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under Contract No. W-7405-Eng-82. We are grateful to a referee and to Professor W. S. Trahanovsky for guidance in the construction of eqs 13 and 14.

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[32] Methylrhenium trioxide in the presence of low $[H_2O_2]$ ($[H_2O_2]/[CH_3ReO_3] < 10$) decomposes slowly. Its stability increases with increasing $[H_2O_2]$. The product seems inactive compared with **A** and **B**.