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Kinetics and Mechanism of the Epoxidation of Allylic Alcohols by Hydrogen Peroxide with Methyltrioxorhenium as Catalyst

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The title reaction was carried out in aqueous acetonitrile (5% and 20% water) and in nitromethane. Provided acid was not added, the product was mostly the epoxide, accompanied by small amounts of the triol that results from acid-catalyzed ring opening of the epoxide. With added acid, only the triol was detected. The kinetic study afforded a striking result: only the diperoxorhenium compound was an epoxidation catalyst; the monoperoxo compound $CH_3Re(O)_2(\eta^2\text{-}O_2)$ was inactive; no other substrates, including nonallylic alkenes, show that reactivity difference. This, together with the realization of high diastereoselectivity for 2-cyclohexen-1-ol in chloroform, suggests a particular mode of hydrogen bonding: an O atom of one peroxo group engages in oxygen transfer, in a transition state that is stabilized by hydrogen bonding between the allylic OH group and O atom of the *other* peroxo group. Calculations supported that conclusion.

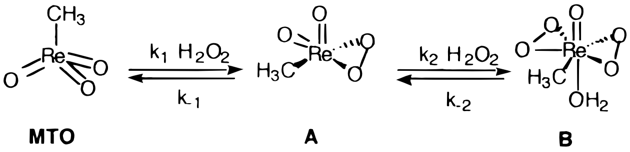
Introduction

Owing to the importance of epoxides as starting materials in organic synthesis, much effort has been devoted to their study. Allylic alcohols are important substrates because the additional functional group of the resulting epoxy alcohol makes these compounds more useful as starting materials in the synthesis of many natural products and pharmaceuticals.[1] Several systems that epoxidize allylic alcohols have been explored, generally with the aim of asymmetric epoxidation.

One of the best known asymmetric epoxidation reactions for allylic alcohols requires (+)- or (−)-diethyl tartrate, titanium tetraisopropoxide, and anhydrous *tert*-butyl hydroperoxide (TBHP).[2] The reaction is carried out at −20 °C in dry CH_2Cl_2 under an inert atmosphere to prevent catalyst decomposition. Good conversions and enantioselectivity can be obtained with as little as 5−10% of the Ti(O-*i*-Pr)$_4$ catalyst and 3−4 Å molecular sieves[3] to remove water from the system. The earliest oxidants used to epoxidize allylic alcohols are peracids such as *p*-nitroperbenzoic acid (NPBA) and *m*-chloroperbenzoic acid (MCPBA).[4−6] These reactions require a stoichiometric amount of the peracid and are typically carried out at 0 °C in ether (for NPBA) or methylene chloride (for MCPBA). Conversions are generally high, but these reactions are slower than transition-metal-catalyzed epoxidation reactions.[7]

Molybdenum- or titanium-containing zeolites can also be used.[6,8,9] The transition-metal catalyst is heterogenized by attachment to zeolites such as Ti-beta and TS-1. The oxidants used in these systems are urea−hydrogen peroxide (UHP) for TS-1, 85% hydrogen peroxide for Ti-beta, and TBHP for the Mo-containing zeolite. Conversions are generally high, except for the TS-1 zeolite, whose small pore size does not allow entry of the larger substrates. The zeolitic catalyses allow for the easy recovery of the products and the ability to recycle the catalyst. Other important systems for allylic alcohols use transition-metal catalysts such as VO(acac)$_2$/TBHP;[4,5,8] the oxygen source is >90% TBHP.

Scheme 1



This work presents a study of the kinetics of the epoxidation reaction of allylic alcohols using methyltrioxorhenium (CH_3ReO_3, abbreviated as MTO) as the catalyst. It is suitable for room temperature reactions in aqueous or organic solvents; with hydrogen peroxide the only byproduct is water. Hydrogen peroxide and MTO form the peroxorhenium species $CH_3ReO_2(\eta^2\text{-}O_2)$ (**A**) and $CH_3ReO(\eta^2\text{-}O_2)_2(H_2O)$ (**B**), Scheme 1. Both **A** and **B** are comparably active[10] for nucleophilic substrates including alkenes,[11,12] phosphines,[13] sulfides,[14] amines,[15] etc. The reactivity of MTO as a catalyst for selective oxidations with hydrogen peroxide has been reviewed.[16−18] Earlier work

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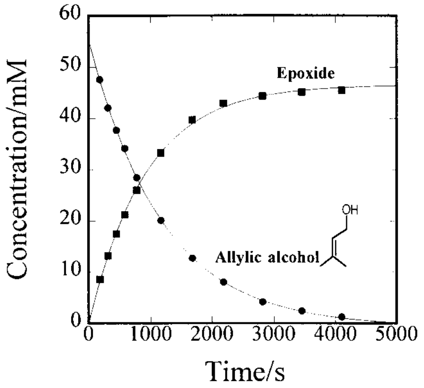

Figure 1. ^{1}H NMR data showing the loss of the olefinic proton signal and the increase in the epoxide signal. The solid lines are the fits to first-order kinetics. Conditions: $[\mathrm{Re}]_T = 2$ mM, [3-methyl-2-buten-1-ol] = 50 mM, $[H_2O_2] = 0.5$ M; 80/20 acetonitrile/water at 22.5 °C.

with the MTO/H_2O_2 system showed that allyl alcohol was epoxidized by MTO/H_2O_2.[19] This study sought to extend the study to other allylic alcohols and to define more fully the reaction mechanism.

Experimental Section

Reagents. Methyltrioxorhenium was purified by vacuum sublimation and pyridine *N*-oxide by recrystallization. 3-Methyl-1-cyclohexene, glacial acetic acid, and the other reagents were used as received. Hydrogen peroxide (30%, Fisher) was stored in a refrigerator when not in use. Its concentration was determined by titration with Ce^{4+}. Deuterium oxide (Aldrich) and acetonitrile-d_3 (CIL) were used as purchased.

Kinetics. Kinetics experiments on the epoxidation of allylic alcohols were carried out at 22.5 °C by ^{1}H NMR spectroscopy with a Bruker DRX-400 spectrometer. The ^{1}H NMR spectra were recorded at 400.13 MHz. ^{1}H chemical shifts were measured relative to the residual ^{1}H resonance of the solvent: CD_2HCN ($\delta = 1.92$ ppm) or CD_2HNO_2 ($\delta = 4.33$ ppm). In a typical kinetics experiment, **B** was formed first (as indicated by its yellow color); the allyl alcohol was added last. Immediately upon its addition, the NMR kinetics program was started. The data so acquired were analyzed by following the loss of the olefinic proton signal. (While it was generally possible to follow epoxide formation, subsequent ring opening of the epoxide to form the triol does not make this as useful an option for data analysis.) The concentration−time data were analyzed by pseudo-first-order methods. The pseudo-first-order rate constants (k_ψ) were evaluated by a nonlinear least-squares fitting of the concentration−time curves to the single-exponential equation $\mathrm{Conc}_t = \mathrm{Conc}_0 e^{-kt}$ or, when product buildup kinetics was used to confirm the data, to the equation $\mathrm{Conc}_t = \mathrm{Conc}_\infty + (\mathrm{Conc}_0 - \mathrm{Conc}_\infty)e^{-kt}$. Representative concentration−time profiles for one substrate, showing both consumption of starting material and buildup of one product and the fits to first-order kinetics, are presented in Figure 1.

The rate constants for the formation of **A** and **B** in acetonitrile were evaluated by UV−visible methods using a Shimadzu UV-3101PC spectrophotometer. The absorbance changes at 320 nm, the maximum for **A** ($\epsilon_{320} = 700$ L mol^{-1} cm^{-1}) and 360 nm, the maximum for **B** ($\epsilon_{360} = 1200$ L mol^{-1} cm^{-1}) were monitored with time at room temperature in a 1 cm cell. Relevant spectra for MTO and **B** are given in Figure S-1; the absorbance−time profile at 320 nm for the formation and loss of **A** is given in Figure S-2, and that at 360 nm for the formation of **B** is given in Figure S-3 (Supporting Information). When k_f and k_s are used to represent the pseudo-first-order rate constants for the respective fastand slow stages, the biexponential equation takes the form

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + \alpha e^{-k_f t} + \beta e^{-k_s t} \tag{1}$$

The biexponential fit of the absorbance−time data obtained at 320 nm gave the values of k_f. The peroxide dependence of k_f was analyzed according to the equation

$$k_f = k_1[H_2O_2] + k_{-1} = k_1\{[H_2O_2] + K_1^{-1}\} \tag{2}$$

Results

Rate Constants for the Interconversion of MTO, A, and B. The rate constants for the formation and dissociation of the two peroxorhenium compounds **A** and **B** have now been determined in a number of solvent systems, often in the presence of a strong acid such as perchloric or triflic acid to stabilize MTO against reaction with OH^-. In the absence of hydrogen peroxide, that is the only reaction by which it decomposes:[20−22]

$$CH_3ReO_3 + OH^- \rightarrow ReO_4^- + CH_4 \tag{3}$$

In solutions containing peroxide, however, MTO is much more prone to decomposition. The greater instability has been shown to arise not from reactions of **A** or **B** but from a reaction of MTO with the more powerful and more abundant nucleophile HOO^-.[20] In MTO/H_2O_2 solutions, the significant pathway for MTO decomposition is

$$CH_3ReO_3 + HOO^- \rightarrow ReO_4^- + CH_3OH \tag{4}$$

In the present instance, it was necessary to avoid added acid, which causes ring opening of the epoxide. With acid present, the allylic alcohol would form a triol. Indeed, we confirmed that the presence of acid, or its subsequent addition, would do just that. The triol was easily identified among the products. Even without added acid, a small amount of triol was unavoidable.

That being the case, it was necessary to redetermine the rate constants k_1, k_{-1}, k_2, and k_{-2}, defined in Scheme 1, under the solvent and pH conditions used in this research. New values were determined from the analysis of absorbance−time data collected at 320 and 360 nm. In the first case, a biexponential analysis by eq 2 was needed for the rise and fall of [**A**]. The data at 360 nm, except in the very earliest part of the curve, corresponded quite closely to the buildup of **B**, allowing use of a single-exponential form.

The plot of k_f (eq 1) against $[H_2O_2] + K_1^{-1}$, shown in Figure 2, defines the value of k_1 as 3.75 ± 0.15 L mol^{-1} s^{-1}. From the independently known value of $K_1 = 93.4$ L mol^{-1}, in 80/20 acetonitrile/water,[23] we have the value of $k_{-1} = k_1/K_1 = (4.07 \pm 0.16) \times 10^{-2}$ s^{-1}. A single-exponential expression was used to fit the data for the buildup of **B** at 360 nm. A plot of k_s against $[H_2O_2] + K_2^{-1}$, taking $K_2 = 5.85 \times 10^2$ L mol^{-1}, also shown in Figure 2, gives $k_2 = (1.21 \pm 0.06) \times 10^{-1}$ L mol^{-1} s^{-1}; from that, $k_{-2} = (2.07 \pm 0.10) \times 10^{-4}$ s^{-1}, given $k_{-2} = k_2/K_2$. This method of calculation of the reverse rate constants takes the equilibrium constants K_1 and K_2 to remain acid-

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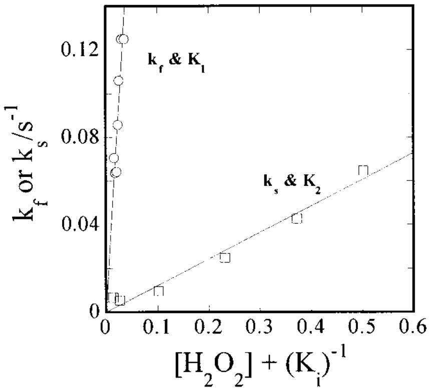

Figure 2. Resolution of the fast and slow components of the biphasic kinetics with the concentration of hydrogen peroxide and the respective equilibrium constants for formation of **A** (K_1) and **B** (K_2).

independent at low [H$^+$], just as they are at high [H$^+$].[24,25] Without acid to stabilize MTO against reactions 3 and 4, the rate constants were all about 4 times smaller than those in 0.1 M triflic acid.[23]

Kinetics of the Oxidation of Allylic Alcohols. Treatment of the allylic alcohols with hydrogen peroxide in the absence of MTO was used to show that the uncatalyzed reaction is negligible. In processing the data for the MTO-catalyzed reaction, it was therefore unnecessary to correct the experimental data for an uncatalyzed reaction. Many of the determinations of the rate constants for the catalytic system were carried out under conditions chosen such that pseudo-first-order kinetics would apply. This entailed the use of $[H_2O_2]_0 \gg [AA]_0$, with the catalyst, of course, at a constant concentration. Even then, only with certain concentration ranges would the rate constants pertaining to a given system generate a curve for the first-order loss of allylic alcohol (AA).

Consider the case of 3-methyl-2-buten-1-ol as an example, with $[AA]_0 = 50$ mM and $[H_2O_2] = 0.50$ M. The simplest case anticipated was that in which the reaction rate is given by

$$\frac{d[\text{epoxide}]}{dt} = k_4[AA][Re]_T \qquad (5)$$

where k_4 represents the rate constant for the bimolecular reaction between **B** and AA and the notation $[Re]_T$ represents the summation of all three forms of the catalyst, [MTO] + [**A**] + [**B**]. This equation requires that the kinetic time course fit first-order kinetics. A more stringent and therefore more critical criterion for first-order kinetics is that the rate constant be independent of $[AA]_0$. The rate constants for 3-methyl-2-buten-1-ol were evaluated at constant $[Re]_T = 2.00$ mM and $[H_2O_2]_0 = 0.500$ M in acetonitrile over a range of 10−50 mM AA. The value of k was indeed independent of [AA] over this range, with a mean value of $(4.02 \pm 0.01) \times 10^{-4}$ s^{-1}. A graphical display of these data appears in Figure S-4 (Supporting Information). Another necessary test for eq 5 is that the rate constant must vary linearly with $[Re]_T$. At the high peroxide concentrations used, $[Re]_T$ was essentially equal to [**B**], *provided reactions 1 and 2 remain in equilibrium*. (This consideration introduces a factor that was important in some cases, as will be discussed in due course.) The data for the same allylic alcohol shown in Figure S-5 (Supporting Information) confirm the expectation that k is a linear function of $[Re]_T$.

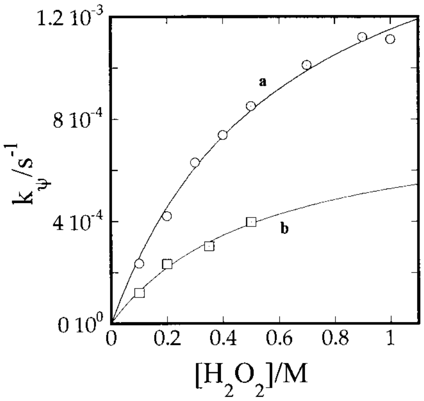

Figure 3. Rate constants for the epoxidation of 3-methyl-2-buten-1-ol (50 mM) with MTO (2.0 mM) as a function of $[H_2O_2]$ in 80/20 acetonitrile/water (a) and in 95/5 acetonitrile/water (b).

The final test of this method for analyzing the kinetic data is that the rate be independent of the concentration of hydrogen peroxide. Although that was true for many other allylic alcohols examined, it is certainly not so for this particular one, as Figure 3 shows. A kinetic dependence on $[H_2O_2]$ suggests that eq 5 is too gross an approximation in those cases. Earlier work with other substrates in the MTO/H_2O_2 catalytic system has shown that the reaction kinetics can be described by a reaction scheme composed of the steps forming the two active peroxorhenium compounds, **A** and **B**, along with the pair of reactions between each of them and the substrate. The latter reactions have rate constants designated k_3 and k_4. With that, the rate equation becomes

$$v = \frac{k_1k_3[Re]_T[AA][H_2O_2] + \dfrac{k_1k_2k_4[Re]_T[AA][H_2O_2]^2}{k_4[AA] + k_{-2}}}{k_{-1} + k_3[AA] + k_1[H_2O_2] + \dfrac{k_1k_2[Re]_T[H_2O_2]^2}{k_4[AA] + k_{-2}}} \qquad (6)$$

This equation results from applying the "improved steady-state" method[26] to the intermediates. Provided the described scheme is valid, this full form of the rate law will apply. This equation was used to analyze the different sets of kinetic data. Repeated trials showed that acceptable fits could be obtained only with $k_4 \gg k_3$. In other words, k_3 is effectively zero for allylic alcohols. This inequality is unprecedented: none of the now-numerous studies of other substrates have given the result that k_3 was negligible in comparison with k_4. Indeed, for nearly every substrate whose kinetics has been examined, the rate constants k_3 and k_4 are of comparable magnitudes. This finding has important implications for the chemical mechanism of allylic alcohols to which we shall return in the Discussion. Here we continue the analysis of the data. If k_3 is dropped from eq 6 and explicit account is taken of k_{-2} being quite small compared to k_4[AA], the expression for the reaction rate becomes

$$v = \frac{k_1k_2k_4[AA][Re]_T[H_2O_2]^2}{(k_{-1} + k_1[H_2O_2])k_4[AA] + k_1k_2[H_2O_2]^2} \qquad (7)$$

and the pseudo-first-order rate constant, assuming for the moment that first-order dependence on [AA] is at least approximately applicable despite the form of the denominator term

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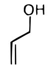
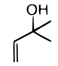
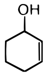
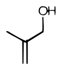
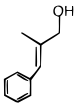
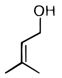
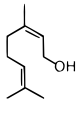
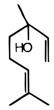
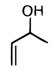
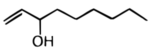
Table 1. Second-Order Rate Constants for the Epoxidation of Allylic Alcohols by **B**

Substrate	Structural formula	k_4/L mol^{-1} s^{-1} at 22.5 °C		
		AN/H_2O, 80/20	AN/H_2O, 95/5	CH_3NO_2
Allyl alcohol		3.3×10^{-3}	3.0×10^{-3}	3.9×10^{-3}
2-Methyl-3-buten-2-ol		7.6×10^{-3}	—	a
2-Cyclohexen-1-ol		3.28×10^{-2}	—	—
2-Methyl-2-propen-1-ol		4.66×10^{-2}	2.4×10^{-2}	2.5×10^{-2}
trans-2-Methyl-3-phenyl-2-propen-1-ol		9.5×10^{-2}	—	—
3-Methyl-2-buten-1-ol		7.0×10^{-1}	2.0×10^{-1}	a
Geraniol		0.25 (allylic alkene) 0.95 (remote alkene)	—	—
Linalool		b	—	—
3-Buten-2-ol		—	—	3.6×10^{-3}
1-Octen-3-ol		—	—	4.4×10^{-3}

[a] rearranged product [b] cyclized product

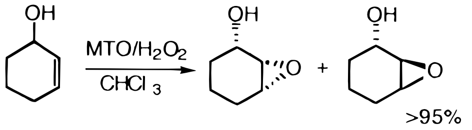
in eq 7, is

$$k_\psi = \frac{k_1 k_2 [\text{Re}]_\text{T} [H_2O_2]^2}{(k_{-1} + k_1[H_2O_2])k_4[\text{AA}] + k_1 k_2 [H_2O_2]^2} \tag{8}$$

In the approximation being made, first-order kinetics remains an adequate albeit imperfect description of the time course. The rate constant determined from a first-order analysis of the time course data will in this model rise with $[H_2O_2]$, eventually tending toward a plateau. This is the behavior that is depicted in Figure 3. The only unknown in eq 8 is k_4; fitting of the data gave $k_4 = 0.69_5$ L mol^{-1} s^{-1} for 3-methyl-2-buten-1-ol in 80/20 acetonitrile/water. An analogous set of kinetics experiments in 95/5 acetonitrile/water gave $k_4 = 0.20$ L mol^{-1} s^{-1}. The values of k_4 for the reactions between different allylic alcohols and **B** are summarized in Table 1. In many cases, especially those with smaller rate constants, the approximate form of eq 5 provides an adequate description. The difficulties in the more complicated cases just described arise when the conversion of **A** to **B** is too slow compared to the epoxidation step. This gives rise to a situation in which the kinetic step with the rate constant labeled k_2 becomes part of the overall rate equation. This point, too, will be elaborated in the Discussion.

Diastereoselectivity. Since it has been proposed that hydrogen bonding plays a role in the transition state,[6] parallel experiments were carried out with 3-methyl-1-cyclohexene and 2-cyclohexen-1-ol. These two substrates are similar in many ways and in all steric aspects. The differences lie in the electronic effects, which make the allylic alcohols much slower to react, and in the ability of the latter to participate in a hydrogen-bonded transition state.

Experiments with these two materials were carried out to determine whether hydrogen bonding in the transition state for the allylic alcohol could lead to concrete differences. If so, one would expect to see a prevalence of one diasteromeric product for it, but only a single product from the hydrocarbon. Positive results were obtained for experiments carried out in chloroform. Indeed, a >95% excess of the one diastereomer was found for 2-cyclohexen-1-ol, whereas a 1/1 product ratio was obtained from 3-methyl-1-cyclohexene. The results for the allylic alcohol are depicted in the equation



(9)

On the other hand, 2-cyclohexen-1-ol formed a 1/1 ratio of the diastereomers in 80/20 acetonitrile/water. In a solvent capable of hydrogen bonding to solutes, such as acetonitrile/water, the interaction of the solute can be realized through solute–solvent interactions. Only in a nonpolar solvent, such as chloroform, can hydrogen bonding be employed to direct the steric course of the epoxidation reaction.

Discussion

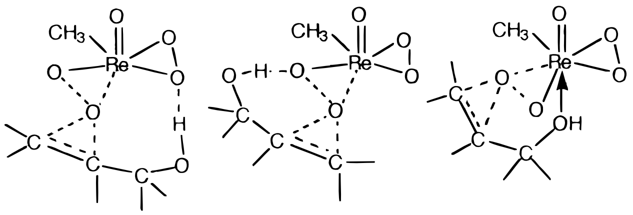
Rate Constant Trends. The pattern of reactivity among the different allylic alcohols must now be examined to delineate the structure–reactivity relationships. For one thing, the allylic alcohols are much slower to react as compared to their hydrocarbon analogues. For example, compare the epoxidation of 2-cyclohexen-1-ol ($k_4 = 0.033$ L mol^{-1} s^{-1}) with that of 3-methyl-1-cyclohexene (0.182 L mol^{-1} s^{-1}).[19] Indeed, within one molecule, the epoxidation of geraniol (see Table 1) occurs with different rate constants at the two double bonds: $k_4 = 0.25$ L mol^{-1} s^{-1} at the allylic position and 0.95 L mol^{-1} s^{-1} at the remote double bond.

A further indication of electron flow in the transition state comes from a comparison of the substituent effects. As with alkenes,[19] substituting one or more hydrogens on the double bond with alkyl groups gives rise to an increase in the rate of epoxidation. For example, compare entries 4 and 6 from Table 1: a 15-fold rate enhancement was found when one additional methyl group was added in place of a hydrogen atom of the substrate.

Conversely, replacing an olefinic hydrogen with an electron-withdrawing substituent, such as an aryl group, decreases the rate of epoxidation. The comparison of rate constants between entries 5 and 6 of Table 1 illustrates the reactivity difference. In this case, Ph in place of CH_3 lowers the rate constant by a factor of 7.

The Hydrogen-Bonded Transition State. There are several experimental observations, taken together, that allowed us to formulate in greater detail the structure of the transition state. To summarize the facts: (1) There is an unusual kinetic dependence on $[H_2O_2]$, even above 0.1 M, where the rates of nearly all other substrates are peroxide-independent. (2) The values of k_3 for **A** are much smaller than those of k_4 for **B**, to the point that **A** appears to be of negligible importance in the

Chart 1



1 2 3

epoxidation of allylic alcohols. This carries two implications. First, **A** is much less reactive with 3-hydroxyalkenes than with other alkenes; second, **B** is able to react with both compound types. (3) The diastereoselectivity found for **B** indicates a high level of steric order in the transition state.

It is our contention that all of these points admit of a single explanation. We propose that the transition state for **B** is hydrogen bonded in a way not possible for **A**. In particular, the OH group appears to participate in hydrogen bonding to an oxygen of the *other* peroxide, the one not engaged in oxygen atom transfer (Chart 1, structure **1**), and not to an oxygen atom of the same peroxide (structure **2**) or to the rhenium center (structure **3**). After each round of **B** transferring an oxygen atom to substrate, **A** is formed; but the data show that **A** is ineffective. Thus propagation of the catalytic cycle depends on the relatively slow conversion of **A** back to **B** by the relative inefficient k_2 step. Thus this set of substrates show peroxide-dependent rates, unlike most, for which the much faster k_1 step for restoring **A** from MTO poses a minor barrier.

The OH group lowers the reactivity of **A** and **B** by virtue of its electron-withdrawing ability. The true measure of this is to compare the two forms of the catalyst with a pair of substrates, one with OH and the other with H (or CH_3). Three comparisons can be made; in the remainder of this paragraph the numbers quoted are second-order rate constants at 25 °C in aqueous acetonitrile with the units L mol^{-1} s^{-1}. First, compare 2-methyl-3-phenyl-2-propen-1-ol ($k_4 = 9.5 \times 10^{-2}$) and β,β-dimethylstryene ($k_3 = 1.00$, $k_4 = 0.70$).[19] The latter pair of values reinforces the earlier-made claim that, except for those of allylic alcohols, k_3 and k_4 are generally close in value. Conservatively, the experimental analysis for the allylic alcohol might have failed to detect a k_3 value no greater than 5% of k_4; for 2-cyclohexen-1-ol, $k_3 \le 5 \times 10^{-3}$. Thus the hydrocarbon is favored over the allylic alcohol by a factor of 1.00/0.005 or 200. Since the same mechanism operates on both substrates, this comparison provides a valid measure of the extent of the (presumably) electronic effect. We then assert that the value of k_4 *along the same pathway* would have been, like k_3, of the order 10^{-3}. The fact that the real value of k_4 is ≥20-fold larger indicates that the actual reaction of the allylic alcohol has adopted a modified or a different mechanism. The other pairs of compounds to be compared are 3-methyl-2-buten-1-ol ($k_4 = 0.70$) and 2-methyl-2-pentene ($k_4 = 3.92$); the third consists of 2-cyclohexenol ($k_4 = 3.28 \times 10^{-2}$) and cyclohexene ($k_4 = 1.06$). The same analysis clearly applies; for each, the experimental value of k_4 is many times larger than might be anticipated.

The data suggest, therefore, that the structure of the transition state is one that only **B** can access. Since hydrogen bonding to an oxygen of the same peroxide engaged in O atom transfer would be as accessible to **A** as to **B**, this picture, **2** in Chart 1, is deemed less likely. As to the possibility that one might use coordination of the allylic OH group to the rhenium atom of the catalyst, **3** in Chart 1, it should be more, not less, available for **A** than for **B**, given that **B** has a higher coordination number. For that reason, structure **3** seems unlikely. The lower energy for structure **1** relative to **2** was supported by calculational results from the program HyperChem.

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Supporting Information Available: Plots and tables of kinetic data. This material is available free of charge on the Internet at http://pubs.acs.org.

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