

Kinetics of MTO-Catalyzed Olefin Epoxidation in Ambient Temperature Ionic Liquids: UV/Vis and ^2H NMR Study**

Gregory S. Owens, Armando Durazo, and Mahdi M. Abu-Omar*[a]

Abstract: The kinetics of oxygen-atom transfer from the peroxo complexes of methyltrioxorhenium (MTO) to alkenes in ionic liquids have been investigated. Noncatalytic conversions of alkenes to epoxide were monitored by UV/Vis at 360 nm, where the monoperoxorhenium (mpRe) and diperoxorhenium (dpRe) complexes absorb. Water- and peroxide-free dpRe was prepared in situ by the reaction of MTO and urea hydrogen peroxide (UHP) in dry THF. The observed biexponential time profiles in conjunction with kinetic modeling allow

the assignment of the fast step to the reaction of olefin with dpRe (k_4) and the slow step to the analogous reaction with mpRe (k_3). In most of the studied ionic liquids, $k_4 \approx 5 \times k_3$. ^2H NMR experiments conducted with $[\text{D}_3]\text{dpRe}$ under non-steady-state conditions confirm the speciation of the catalytic system in ionic liquids and assert the validity of the UV/

Vis kinetics. Deuteriated alkenes were used to study the catalytic epoxidation and dihydroxylation of alkenes by ^2H NMR spectroscopy. The values of k_4 for α -methylstyrene in several ionic liquids exceed what is observed in acetonitrile by an order of magnitude. While the rate of olefin epoxidation is unaffected by the nature of the ionic liquid cation, a discernable kinetic effect is observed with coordinating anions such as nitrate.

Keywords: ionic liquids • kinetics • NMR spectroscopy • oxidations • rhenium

Introduction

The need for developing environmentally friendly chemical technologies is more important than ever. At the forefront in the push for green chemistry are catalytic processes employing transition metals, benign reagents such as molecular oxygen and hydrogen peroxide, and nonvolatile, recyclable reaction media.

Interest in hydrogen peroxide as an oxidant when activated by transition metal catalysts has expanded rapidly in the past two decades.^[1] One of the most useful organometallic complexes for the activation of hydrogen peroxide is methyltrioxorhenium (MTO). MTO has been shown in recent years to be an exceptionally versatile oxygen transfer catalyst when used with either aqueous hydrogen peroxide or urea hydrogen peroxide (UHP).^[2–6]

Ionic liquids have received a great deal of attention as alternative reaction media. In particular, 1,3-dialkylimidazolium- and 1-alkylpyridinium-based ionic liquids have been the focus of much investigation.^[7–9] Negligible vapor pressures,

polar yet noncoordinating anions (in general), tunable melting points and solvent miscibilities, and the ability to dissolve a wide range of inorganic and organic materials are among the most desirable characteristics of these room-temperature liquids.^[7]

UHP was first used by Adam and co-workers as an oxidant for the MTO catalytic system in chloroform.^[3] Recently, the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($[\text{emim}]\text{BF}_4$) has been shown to be a suitable solvent for the MTO-catalyzed epoxidation of olefins using UHP.^[10] Electron-rich olefins such as styrenes are particularly easy to oxidize with this system, giving conversions and yields up to and exceeding 99 %. The use of UHP yields the corresponding epoxide product, whereas the use of aqueous hydrogen peroxide (30 %) with MTO quantitatively converts the olefin to the 1,2-diol. These oxidation reactions were found to proceed on a time scale similar to that reported for the same reactions in molecular solvents.

To gain further insight into the applicability of ionic liquids for organic synthesis and industrial oxidations, this group has undertaken the kinetic study of the MTO/peroxide system in these relatively unexplored solvents. The interactions of MTO with aqueous hydrogen peroxide and UHP will be reported elsewhere.^[11] Herein we focus on the kinetics of olefin oxidation using the MTO catalyst, and examine the effect of these new media on the rates of oxygen-atom transfer from the catalytically active peroxorhenium complexes.

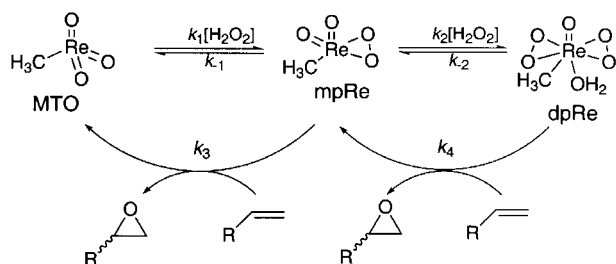
Both UV/Vis spectrophotometry and NMR spectroscopy have been used previously to characterize the MTO/peroxide/

[a] Prof. M. M. Abu-Omar, Dr. G. S. Owens, A. Durazo
Department of Chemistry and Biochemistry
607 Charles E. Young Drive, East University of California
Los Angeles, CA 90095-1569 (USA)
Fax: 310-206-4038
E-mail: mao@chem.ucla.edu

[**] MTO = methyltrioxorhenium.

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olefin system and its kinetics in aqueous and organic media (Scheme 1).^[12–14] Unfortunately, the UV-cutoff for 1,3-dialkylimidazolium- and 1-alkylpyridinium-based ionic liquids is approximately 300 nm, which precludes the direct observation



Scheme 1. Reaction of MTO with hydrogen peroxide to form two peroxorhenium complexes.

of substrate or product spectroscopic features in the UV for monitoring reaction kinetics. However, it is possible to monitor the non-steady-state kinetics of these reactions by observing the spectral changes in the visible region due the diperoxo-rhenium complex, dpRe. In this work, the kinetics of substrate oxidation in water-miscible ionic liquids as well as in acetonitrile were studied by monitoring the decrease in absorbance at 360 nm, which is attributable to the reactions of both dpRe and the monoperoxo-rhenium complex, mpRe, with the olefinic substrates. Non-steady-state kinetics was used to elucidate the rate constants k_3 and k_4 .

Additionally, while reports of perdeuterated ionic liquids have appeared in the literature,^[15] these liquids are difficult and expensive to make. Recently, however, techniques have been developed in this laboratory to measure kinetics in ionic liquids using ^2H NMR spectroscopy.^[16] These techniques include using deuterated substrates such as $[\text{D}_8]\text{styrene}$ under steady-state conditions as well as the peroxo complexes of $[\text{D}_3]\text{MTO}$ for non-steady-state kinetics. The data collected from the UV/Vis and NMR studies combined fully describe the kinetics of olefin oxidation in ionic liquids.

Results

Non-steady-state UV/Vis kinetics: The goal of this study is to determine the rates of oxygen transfer from the catalytically active peroxorhenium complexes (k_3 and k_4 in Scheme 1) to olefinic substrates in ionic liquids, and contrast these values to those obtained in water and organic solvents. It had become evident early on that two complications needed to be addressed here. First, the effects of water on the kinetics^[11] and physical properties^[17] of room temperature ionic liquids

(RTILs) have been documented. Hence, a water-free source of hydrogen peroxide had to be employed to minimize the deleterious effects of water as a co-solvent. Second, the UV cutoff of 300 nm imposed by the ionic media necessitated the development of a new and reliable method to monitor these reactions under single turnover conditions. Many solvents were screened for the preparation of essentially water- and peroxide-free dpRe. The best results were obtained with anhydrous THF and UHP, since in this solvent dpRe is stable for prolonged periods of time and UHP is nearly insoluble. Hence, filtration of excess UHP affords a concentrated solution (ca. 40 mM) of dpRe in THF; such solutions are well behaved and display negligible degradation of dpRe as observed at 360 nm (λ_{max} for dpRe) even after two days.

For the non-steady-state kinetics with alkenes, the THF solution of dpRe was diluted into the desired RTIL to about 1 mM such that the final concentration of THF was less than 3 % of the ionic solvent. Upon addition of excess alkene (40–150 mM), the reaction progress was followed at 360 nm. The non-steady-state time profiles are biexponential (a typical time profile for the epoxidation of α -methylstyrene is shown in the Supporting Information in Figure S1). The absorbance at the end of reaction is essentially zero. This indicates that all of the dpRe and mpRe have reacted with the substrate. The kinetic traces are fitted using Equation (1), in which both α and β are constants.

$$\text{ABS}_t - \text{Abs}_\infty = \alpha \exp(-k_f t) + \beta \exp(-k_s t) \quad (1)$$

Both k_f and k_s (the fast and slow pseudo-first-order rate constants, respectively) exhibit linear dependences on the alkene concentration. Representative plots of k_f and k_s versus [alkene] for the oxidation of *trans*- β -methylstyrene (TBMS) in $[\text{emim}]\text{BF}_4$ ($\text{emim} = N,N'$ -ethylmethyylimidazolium) are shown in Figure S2 and S3 in the Supporting Information.

The intercepts of these plots represent k_{-1} and k_{-2} ; however, these measurements are not particularly reliable since their values are negligible in comparison to the slopes. The second-order rate constants for the reaction of mpRe (k_3) and for the reaction of dpRe (k_4) with the substrate were obtained from the slopes of the above plots. However, as the data is presented, the fast and slow steps cannot be assigned. The kinetics simulation program KINSIM^[18] was used to determine that the k_4 step, the oxidation of alkene with dpRe, is faster than the k_3 step. The details of these simulations are provided in the Discussion.

The values of k_3 and k_4 for several olefins have been determined previously in 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$.^[13] These constants are compared with new values for k_3 and k_4 in acetonitrile and in $[\text{emim}]\text{BF}_4$ in Table 1. α -Methylstyrene was chosen as the

Table 1. Values of k_3 and k_4 [$\text{L mol}^{-1} \text{s}^{-1}$] in different solvents for several alkenes.

Solvent	Styrene		<i>trans</i> - β -Methylstyrene		α -Methylstyrene		Cyclohexene	
	$k_3 \times 10^2$	$k_4 \times 10^2$	$k_3 \times 10^2$	$k_4 \times 10^2$	$k_3 \times 10^2$	$k_4 \times 10^2$	$k_3 \times 10^2$	$k_4 \times 10^2$
$[\text{emim}]\text{BF}_4$ ^[a]	1.3 ± 0.1	13 ± 1	5.8 ± 0.4	26 ± 1	10 ± 1	44 ± 1	3.1 ± 0.2	13 ± 1
CH_3CN ^[a]	0.20 ± 0.04	1.5 ± 0.1	2.1 ± 0.2	5.2 ± 0.2	4.5 ± 0.1	4.5 ± 0.1	3.1 ± 0.2	22 ± 1
$\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ^[b]	–	11 ± 1	51 ± 7	22 ± 2	–	47 ± 2	–	106 ± 2

[a] Conditions: 0.91 mM dpRe, 38–154 mM substrate, 23 °C. [b] 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v) ref. [13].

substrate for comparative kinetics in different ionic liquids. The rate constants k_3 and k_4 for the oxidation of α -methylstyrene are shown in Table 2.

Table 2. Rate constants for the oxidation of α -methylstyrene in various ionic liquids.^[a]

Entry	Solvent	k_3 [L mol ⁻¹ s ⁻¹]	k_4 [L mol ⁻¹ s ⁻¹]
1	CH ₃ CN	0.045 ± 0.001	0.045 ± 0.001
2 ^[b]	1:1 CH ₃ CN/H ₂ O	–	0.47 ± 0.02
3	[emim]BF ₄	0.10 ± 0.01	0.44 ± 0.01
4	[bmim]BF ₄	0.074 ± 0.002	0.35 ± 0.02
5	[bmim]NO ₃	0.016 ± 0.004	0.12 ± 0.02
6	[bupy]BF ₄	0.13 ± 0.01	0.58 ± 0.01

[a] Conditions: 0.91 mM dpRe, 38–154 mM substrate, 23 °C. bmim = *N,N'*-butylmethylimidazolium, bupy = *N*-butylpyridinium. [b] 1:1 CH₃CN/H₂O (v/v). Reference [13].

²H NMR kinetics: Deuteriated alkenes can be used as substrates in pre-treated ionic liquids to study the MTO-catalyzed oxidation of alkenes under steady-state conditions. The integrals of the ²H resonance signals for deuteriated reactants (alkenes) and products (epoxide or diol) were monitored over time to obtain kinetic information. UHP is soluble in RTILs, a fact that makes the MTO/UHP system homogeneous in ionic liquids and amenable to kinetic investigations. However, in order to avoid complex kinetics and minimize catalyst degradation, one is forced to employ high hydrogen peroxide concentrations (0.5–1.0 M).^[19] A representative NMR stack plot for the epoxidation of [D₁₀]cyclohexene in [emim]BF₄ is shown in Figure 1. Under these conditions, the kinetic traces follow a single-exponential decay and are fit with Equation (2).

$$I_t - I_\infty = a \exp(-k_p t) \quad (2)$$

The kinetics are first-order in [alkene] and show no dependence on [H₂O₂]. Hence, $k_p = k_3$ [mpRe] + k_4 [dpRe] simplifies to $k_p \approx k_4$ [dpRe], since at these high [H₂O₂], the major rhenium species is dpRe and (as shown above by UV/Vis kinetics) $k_3 < k_4$ in RTILs. Table 3 displays k_4 values obtained by ²H NMR spectroscopy for the epoxidation and dihydroxylation of [D₈]styrene and [D₁₀]cyclohexene.

In an alternative method that more closely resembles the conditions used in the UV/Vis kinetic studies, CD₃ReO₃ ([D₃]MTO) was allowed to react with two equivalents of UHP in RTILs to generate [D₃]dpRe. The latter was used for single turnover reactions with alkenes, and monitored by ²H NMR

Table 3. Values of k_4 for the epoxidation and dihydroxylation of several alkenes as determined by ²H NMR spectroscopy.

Entry	Alkene	Solvent ^[a]	Method ^[b]	k_4 [L mol ⁻¹ s ⁻¹]
1	[D ₈]styrene	[emim]BF ₄	A	0.034 ± 0.004
2	[D ₈]styrene	[bupy]BF ₄	A	0.040 ± 0.008
3	[D ₈]styrene	[etpy]BF ₄	B	0.20 ± 0.02
4	styrene	[emim]BF ₄	C	0.059 ± 0.006
5	2-fluorostyrene	[emim]BF ₄	C	0.027 ± 0.002
6	2,6-difluorostyrene	[emim]BF ₄	C	0.012 ± 0.001
7	[D ₁₀]cyclohexene	[emim]BF ₄	A	0.20 ± 0.01
8	[D ₁₀]cyclohexene	[bupy]BF ₄	A	0.23 ± 0.02
9	[D ₁₀]cyclohexene	[emim]BF ₄	B	1.75 ± 0.06

[a] etpy = *N*-ethylpyridinium. [b] Method A (steady-state epoxidation conditions): [UHP] = 1.0 M, [MTO] = 0.008 M, [deuteroalkene] = 0.10 M, $T = 298$ K. Method B (steady-state dihydroxylation conditions): [H₂O₂] (30 % aqueous) = 0.50 M, [MTO] = 8.0×10^{-4} M, [deuteroalkene] = 0.10 M, $T = 298$ K. Method C (non-steady-state epoxidation conditions): [[D₃]dpRe] = 0.048 M, [alkene] = 0.50 M, $T = 298$ K.

spectroscopy. The relatively long time scale inherent to NMR kinetic experiments mandated the use of more deactivated styrenes as epoxidation substrates. For this study, styrene, 2-fluorostyrene, and 2,6-difluorostyrene were used. Over the course of a reaction, the intensity of the [D₃]dpRe resonance signal ($\delta = 2.9$ ppm) decreases and the intensity of the [D₃]MTO resonance signal ($\delta = 2.4$ ppm) increases. The ²H resonance signals due to products of peroxorhenium complex decompositions, namely CD₃OH and CD₃OOH ($\delta = 3.4$ and 3.3 ppm, respectively), increase during the course of reaction.^[19, 20] An NMR stack plot for the epoxidation of 2-fluorostyrene is shown in Figure 2.

The integration for the [D₃]dpRe resonance signal is plotted as a function of time. The kinetic traces obtained are exponential, and the integration for the [D₃]dpRe resonance

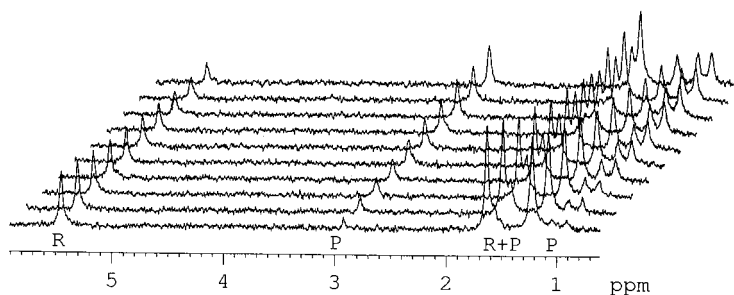


Figure 1. ²H NMR stack plot for the steady-state epoxidation of [D₁₀]cyclohexene in [emim]BF₄. Conditions: [Re]_T = 5.0 mM, [[D₁₀]cyclohexene] = 100 mM, [UHP] = 1.0 M. Spectra are shown at 60 s intervals.

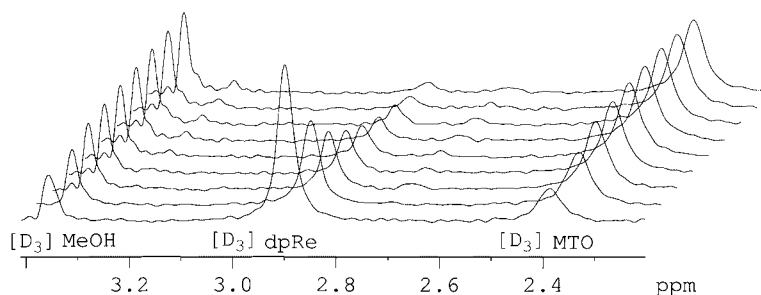


Figure 2. ²H NMR stack plot for the single-turnover epoxidation of 2-fluorostyrene in [emim]BF₄. Conditions: [Re]_T = 36 mM, [2-fluorostyrene] = 364 mM, [UHP] = 72 mM. Spectra are taken at 165 s intervals.

signal is nearly zero at the end of the reactions, which demonstrates that the reaction between $[D_3]dpRe$ and substrate proceeds to completion. The kinetic traces are treated with a standard exponential decay equation (vide supra) to obtain k_4 from the pseudo-first-order rate constant, $k_p = k_4 [\text{alkene}]$. Table 3 lists the values of k_4 obtained for the epoxidation of three different styrenes alongside the data acquired under steady-state conditions with deuteriated substrates. The k_4 values reflect a multiplicative decrease in rate depending on the number of fluorine atoms present in the *ortho* positions on the aromatic ring.

Discussion

UV/Vis kinetic experiments and simulations: MTO reacts with hydrogen peroxide to form two peroxorhenium complexes, as shown in Scheme 1. In ionic liquids, the peroxide binding constants are approximately $K_1 = 40$ and $K_2 = 120$, and the rate constant k_2 is approximately $0.20 \text{ M}^{-1}\text{s}^{-1}$.^[11] These constants necessitate a large excess of hydrogen peroxide to convert all of the rhenium to $dpRe$. Hence, a typical procedure involves making $dpRe$ in situ and then reacting it with an olefinic substrate. It is important to note that the concentrations needed for this type of experiment are generally $0.75\text{--}1.00 \text{ mM}$ MTO, $\geq 50 \text{ mM}$ H_2O_2 , and $50\text{--}300 \text{ mM}$ substrate; the latter would be added after the complete formation of $dpRe$. However, because of the excess of peroxide used to form $dpRe$, H_2O_2 remains in the solution after the substrate is added. Thus, once steady state is achieved, there is an appreciable concentration of $dpRe$ as well as $mpRe$ in the solution due to the reactions with H_2O_2 (k_1 and k_2), and hence the rate constants k_3 and k_4 are not easily resolved.

Making $dpRe$ in THF (in which UHP is nearly insoluble) alleviates the problem described above. When $dpRe$ is isolated by removing the THF solution from the solid UHP, the only Re compound in solution is $dpRe$; essentially zero hydrogen peroxide is present in the solution. Hence, when $dpRe$ reacts with the substrate to form $mpRe$, there is negligible amount of peroxide to re-form $dpRe$. Therefore, the change in absorbance is attributable only to the reactions of both peroxorhenium complexes with the substrate. It should be noted that $dpRe$ re-establishes the equilibrium with $mpRe$ (and $mpRe$ with MTO) once the THF solution is removed from the solid UHP and diluted into the ionic liquid. However, the re-establishment of these equilibria is much slower than the reactions of the peroxorhenium complexes with the substrate, so the effects on the absorbance at 360 nm (A_{360}) are essentially negligible with respect to reactions with substrate. Therefore, the major reactions taking place using this method are the epoxidation of olefin by $dpRe$ (k_4) and by $mpRe$ (k_3).

To gain insight into which is the faster step, the modeling program KINSIM was used to create simulated kinetic traces.^[18] The mechanism shown in Equations (3)–(5) was used in the simulations, and the rate constants for the oxidation of α -methylstyrene (AMS) with both of the peroxorhenium complexes were used alongside the known



value for $k_{-2} \approx 2.0 \times 10^{-3} \text{ s}^{-1}$ in $[\text{emim}]\text{BF}_4$.^[11] For simplicity, the disproportionation of $mpRe$ to H_2O_2 and MTO and the decomposition pathways for $dpRe$ and $mpRe$ were omitted from the mechanism. Figure 3 shows the reaction of $dpRe$ and the formation and subsequent reaction of $mpRe$.

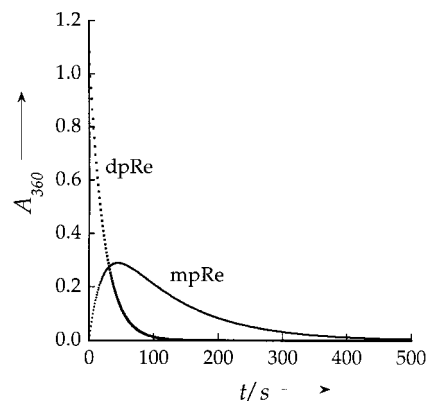


Figure 3. Simulation of the reaction of $dpRe$ and $mpRe$ with α -methylstyrene using KINSIM. Conditions: $[dpRe]_0 = 0.98 \text{ mM}$, $[mpRe]_0 = 0.00 \text{ mM}$, $[\text{AMS}] = 96 \text{ mM}$, $k_4 = 0.44 \text{ M}^{-1}\text{s}^{-1}$, $k_3 = 0.10 \text{ M}^{-1}\text{s}^{-1}$, and $k_{-2} = 2.0 \times 10^{-3} \text{ s}^{-1}$.

Since both $mpRe$ and $dpRe$ absorb at 360 nm ,^[11, 19] their simulated contributions were added together to generate a simulated kinetic trace that should, in theory, be similar to the time profile that is observed experimentally at comparable conditions. Since it was still unknown up to this point which rate constant was faster, simulations were performed using both $k_4 > k_3$ and $k_3 > k_4$. The contributions of both $mpRe$ and $dpRe$ were added together as described above, and the results were plotted alongside the actual experimental data for comparison. Figure 4 compares the experimental data to the simulated kinetic traces for $k_4 > k_3$ and $k_3 > k_4$.

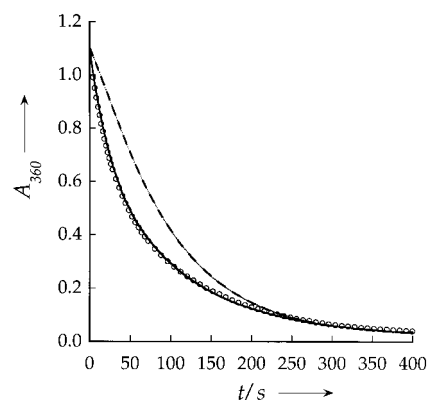


Figure 4. Comparison of experimental data ($\circ$) and simulated kinetic traces ($k_4 > k_3$, —; and $k_3 > k_4$, ---) for the oxidation of α -methylstyrene (AMS). Simulation conditions: $[dpRe]_0 = 0.98 \text{ mM}$, $[mpRe]_0 = 0.00 \text{ mM}$, $[\text{AMS}] = 96 \text{ mM}$, k_4 , $k_3 = 0.44$ and $0.10 \text{ M}^{-1}\text{s}^{-1}$, and $k_{-2} = 2.0 \times 10^{-3} \text{ s}^{-1}$. Experimental conditions: $[dpRe]_0 = 0.98 \text{ mM}$, $[\text{AMS}] = 96 \text{ mM}$ in $[\text{emim}]\text{BF}_4$ at 23°C .

Figure 4 shows good agreement between the experimental data and the simulated kinetic trace when $k_4 > k_3$. The simulated and experimental profiles begin to deviate slightly after 150 s. This deviation is probably attributable to the decomposition of mpRe to methanol and methyl hydroperoxide as observed by ^2H NMR spectroscopy. These reactions, due to their minimal contribution and for the sake of simplicity, do not appear in the mechanism used for the KINSIM simulations.

The point to be made here is that Figure 4 shows rather poor agreement between the experimental data and the simulated kinetic trace when $k_3 > k_4$. The two profiles deviate substantially from the outset and never agree at any point in the reaction/simulation. Therefore, in light of the good agreement between experiment and simulation when $k_4 > k_3$, we concluded that k_4 is greater than k_3 for the oxidation of α -methylstyrene in $[\text{emim}]\text{BF}_4$. The kinetic data for α -methylstyrene in other RTILs and for other alkenes in $[\text{emim}]\text{BF}_4$ are again in excellent agreement with simulations that employ $k_4 > k_3$ values.

As shown in Table 1, the k_4 values in $[\text{emim}]\text{BF}_4$ for the three styrene substrates are quite similar to those values in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$. The notable exception is the oxidation of cyclohexene for which k_4 in $[\text{emim}]\text{BF}_4$ is lower by an order of magnitude than k_4 in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and lower even than k_4 in CH_3CN . This result is anomalous but is explained by considering the limited solubility of cyclohexene in $[\text{emim}]\text{BF}_4$. This limited solubility lowers the effective concentration of cyclohexene in the ionic liquid, which in turn causes the k_4 value to be artificially low. The low solubility of several other substrates, including 1-methylcyclohexene, 1-phenylcyclohexene, and 1-decene, precluded their use in kinetic studies.

The values of k_3 in $[\text{emim}]\text{BF}_4$ for the oxidation of the styrenes are only slightly higher than the corresponding k_3 values in acetonitrile. There is, however, a significant difference between the k_3 values obtained in $[\text{emim}]\text{BF}_4$ versus those in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$. This is in contrast to k_4 for which the values in the ionic liquid and in the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixture are virtually the same.

The results in Table 1 show clearly that k_4 is significantly greater than k_3 when the reactions are done in $[\text{emim}]\text{BF}_4$. This trend holds for the same reactions done in other water-miscible ionic liquids, shown in Table 2. The reactivity of the styrenes with the peroxorhenium complexes shows the expected trend for electrophilic oxygen transfer from rhenium: styrene < TBMS < α -methylstyrene (AMS). The additional methyl groups of TBMS and AMS increase the styrenes' reactivities relative to $\text{PhCH}=\text{CH}_2$, and the sterics of TBMS make this substrate slightly less reactive than AMS.

Table 2 shows the k_3 and k_4 values that have been determined for the oxidation of α -methylstyrene in several ionic liquids and in molecular solvents. Entries 3, 4, and 6 in Table 2 show essentially the same rate constants for the ionic liquids $[\text{emim}]\text{BF}_4$, $[\text{bmim}]\text{BF}_4$, and $[\text{bupy}]\text{BF}_4$. This indicates that the cations of these liquids do not affect the reaction of the rhenium complexes with the olefin. However, both k_3 and k_4 are substantially lower when the reaction is done in $[\text{bmim}]\text{NO}_3$ (Table 2, entry 5). This result is rationalized by

considering that NO_3^- has much higher coordination ability than BF_4^- and thus interferes with the oxidation reactions.

In contrast to what is observed here for RTILs and CH_3CN , k_3 in general is larger than k_4 for reactions done in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$.^[5] The relative reactivities of mpRe and dpRe are apparently dependent on the water content of the solvent. This is likely so because of a couple of different factors: 1) Additional water in the solution makes the solvent more polar, which stabilizes the more polar dpRe over mpRe toward reaction with the substrate. 2) Water participates in hydrogen bonding more with dpRe than with mpRe because of the two peroxy groups, rendering dpRe less reactive.

^2H NMR studies under steady-state conditions: Deuteriated alkenes were used to monitor the kinetics of alkene epoxidation (with UHP) and dihydroxylation (with aqueous H_2O_2) under steady-state conditions. The advantages of using ^2H NMR spectroscopy include the ability to observe product(s) formation in real time, characterize the kinetics of reaction under catalytic conditions, and use easily prepared preteated ionic liquids. Nevertheless, this method differs from the non-steady-state kinetics in that the concentration of water in the ionic liquid is significant. Even for the MTO/UHP system, the concentration of water, being a by-product, increases as the reaction proceeds. The profound effects of water on the physical properties of RTILs have been documented previously.^[17] Since water increases the polarity of the ionic solvent, the rate of oxygen transfer from dpRe to the substrate is expected to increase as $[\text{H}_2\text{O}]$ increases. This effect is reflected in the k_4 values for the dihydroxylation of $[\text{D}_8]\text{styrene}$ and $[\text{D}_{10}]\text{cyclohexene}$ (entries 3 and 9, Table 3) in comparison to the values for epoxidation of the same substrates (entries 1, 2, 7, and 8, Table 3).

The k_4 values determined by ^2H NMR spectroscopy under steady-state conditions for $[\text{D}_8]\text{styrene}$ and $[\text{D}_{10}]\text{cyclohexene}$ (Table 3) are not in full agreement with those measured by UV/Vis kinetics (Table 1). In the case of styrene, the k_4 value from the ^2H NMR experiments is one third the value determined by UV/Vis. On the other hand, in the case of cyclohexene, the k_4 value from the ^2H NMR experiments is twice the value determined by UV/Vis. These discrepancies are attributed to the differences in solvent composition between the NMR and UV/Vis experiments. While the UV/Vis experiments are essentially anhydrous and contain < 3% THF, the water concentration in the NMR experiments increases as more product (epoxide) forms. Even though water is expected to enhance the rate of alkene oxidation by dpRe, it also accelerates the degradation of the peroxorhenium complexes. Furthermore, the need for higher $[\text{MTO}]$ in the steady-state experiments results in an ionic liquid that contains 10–20% CH_3CN ; an MTO stock solution in acetonitrile is normally diluted into the ionic liquid in order to maintain the homogeneity of the catalyst at these concentrations. The presence of an acetonitrile co-solvent in the ^2H NMR experiments also explains the improved rates for cyclohexene epoxidation, since the solubility of cyclohexene is improved.

Despite all of the mentioned differences between the UV-vis (non-steady-state) and ^2H NMR (steady-state) kinetic

experiments, the general agreement within a factor of 2 between the two sets of rate constants is remarkable.

Non-steady-state kinetics by ^2H NMR spectroscopy: The addition of a stock solution of $[\text{D}_3]\text{MTO}$ in anhydrous THF to UHP in a RTIL yields deuteriated diperoxorhenium ($[\text{D}_3]\text{dpRe}$). The ^2H spectrum shows the exclusive presence of $[\text{D}_3]\text{dpRe}$ ($\delta = 2.9$ ppm). However, over time the deactivation products CD_3OH ($\delta = 3.4$ ppm) and CD_3OOH ($\delta = 3.3$ ppm) become evident.

In the absence of excess peroxide, the monoperoxorhenium complex ($[\text{D}_3]\text{mpRe}$) decomposes quickly, and hence no NMR signal for this species is observed. Due to the decomposition of $[\text{D}_3]\text{mpRe}$ the observed stoichiometry of epoxidation is always above 1:1 and below 2:1—namely, 1 mole of $[\text{D}_3]\text{dpRe}$ will convert between 1 and 2 moles of alkene into epoxide. The stoichiometry depends on both the concentration and the nature of the alkene undergoing epoxidation.

Based on ^2H NMR kinetic data, the value of k_4 for the epoxidation of styrene in $[\text{emim}]\text{BF}_4/\text{THF}$ (27% v/v THF) is $0.059\text{ M}^{-1}\text{s}^{-1}$ (entry 4, Table 3). This value is half the value of k_4 obtained from UV/Vis kinetics for this epoxidation in $[\text{emim}]\text{BF}_4$ ($0.13\text{ M}^{-1}\text{s}^{-1}$). The modest decrease in rate between the NMR study and the UV/Vis study in $[\text{emim}]\text{BF}_4$ is attributable to the relatively large amount of THF used in the NMR study, which is imposed by the need of concentrated $[\text{D}_3]\text{dpRe}$ (ca. 40 mM) for reliable detection over short (ca. 3 min) collection times.

Conclusion

The reaction of MTO and UHP in dry THF yields essentially water- and peroxide-free methyldiperoxorhenium (dpRe), which can be diluted into room temperature ionic liquids (RTILs) after the removal of the remaining solid UHP. The homogeneous solution of dpRe in RTILs was reacted with various olefins under pseudo-first-order conditions. The kinetic profiles are biexponential, and the observed rate constants display first-order dependences on [olefin]. Based on kinetic simulations and their agreement with experimental data, the fast step was assigned to the reaction of olefin with dpRe (k_4) and the slow step to the reaction of olefin with the monoperoxorhenium complex (mpRe) (k_3). While the mpRe, in general, is more reactive towards alkenes than the dpRe in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, the opposite is true for the reactions conducted in several RTILs. For example, in all of the investigated RTILs, $k_4 = 4.5 \times k_3$. The rate constants k_3 and k_4 are unaffected by the cation of the ionic liquid, but are sensitive to the anion. The kinetics of the reaction of dpRe with deuteriated alkenes have been characterized by ^2H NMR spectroscopy under steady-state conditions. Also, $[\text{D}_3]\text{dpRe}$, prepared in situ from $[\text{D}_3]\text{MTO}$ and UHP, has been employed to characterize the system and determine k_4 by ^2H NMR spectroscopy under single turnover experiments. The NMR rate constants are in general agreement (within a factor of about 2) with those obtained by UV/Vis spectroscopy. The difference in solvent composition between the NMR study and the UV/Vis study accounts for the modest variations in rate constants.

Experimental Section

Materials: MTO was prepared by the standard literature method.^[21] $(n\text{Bu})_3\text{Sn}(\text{CD}_3)$ ^[22] was used in the synthesis of $[\text{D}_3]\text{MTO}$. Stock solutions of MTO were prepared in tetrahydrofuran and stored at -10°C ; concentrations were determined spectrophotometrically. The ionic liquids $[\text{emim}]\text{BF}_4$, $[\text{bmim}]\text{BF}_4$, $[\text{bmim}]\text{NO}_3$, $[\text{etpy}]\text{BF}_4$, and $[\text{bupy}]\text{BF}_4$ were prepared as described previously.^[11] Hydrogen peroxide solutions were standardized by iodometric and permanganate titrations. Urea hydrogen peroxide was standardized by permanganate titration as a stock solution in $[\text{bmim}]\text{BF}_4$. The olefinic substrates were used as received (Aldrich).

UV/vis kinetics: Kinetic measurements were obtained on a Shimadzu UV-2501PC at $23 \pm 1^\circ\text{C}$. Small-volume (0.5 mL) quartz cuvettes with 1.0 cm optical path length were used. The formation and reaction of the diperoxorhenium complex was monitored by observing the absorbance change at 360 nm, the λ_{max} of the dpRe complex ($\epsilon = 1100\text{ M}^{-1}\text{cm}^{-1}$). The monoperoxorhenium complex mpRe also features an absorbance at 360 nm ($\epsilon = 500\text{--}700\text{ M}^{-1}\text{cm}^{-1}$).^[12, 19] The kinetics of the reactions of dpRe and mpRe with substrates were measured by monitoring the decline in absorbance at 360 nm using the following method.

MTO (40.0 mM in dry THF) was mixed with an excess of urea hydrogen peroxide (UHP), which is insoluble in tetrahydrofuran. After the reaction was complete, the solution containing the dpRe was removed from the remaining solid UHP. An aliquot of the 40.0 mM dpRe solution was added to the ionic liquid of interest to make about 1.0 mM solution. The initial absorbance was recorded, the substrate was added, and the absorbance change at 360 nm was monitored with respect to time. Kaleidagraph 3.0 was used to analyze the kinetic data. The kinetics simulation program KINSIM was used to model the reactions.^[18]

^2H NMR kinetics: Kinetic measurements were obtained on Brüker Avance and ARX 500 MHz (^1H) spectrometers at ambient temperature. A sealed capillary containing a 0.346 M solution of $[\text{Cr}(\text{acac})_3]$ in $\text{CD}_3\text{CN}/\text{toluene}$ (5% v/v CD_3CN) was used as a standard for chemical shifts ($\delta = 9.80$ ppm) and integrations.

The following is a typical procedure for collecting steady-state kinetics with a deuteriated alkene ($[\text{D}_8]\text{styrene}$): An NMR tube was charged with $[\text{emim}]\text{BF}_4$ (0.5 mL), UHP (47 mg), and about 100 μL of a 0.040 M MTO stock solution in CH_3CN . After 10 min, a sealed capillary tube containing the external standard was added, along with $[\text{D}_8]\text{styrene}$ (6 μL). The contents of the tube were mixed well, and ^2H NMR spectra were subsequently collected about every 5 min.

For non-steady-state kinetics, 150 μL of 0.13 M $[\text{D}_3]\text{MTO}$ solution in dry THF was added to 0.10 M UHP in 400 μL of $[\text{emim}]\text{BF}_4$. The reaction solution was mixed well, and monitored by ^2H NMR spectroscopy until all the starting $[\text{D}_3]\text{MTO}$ had converted to $[\text{D}_3]\text{dpRe}$. At this time, a tenfold molar excess of an olefinic substrate was added to ensure pseudo-first order conditions.

Under these conditions, the ^2H resonance signal of $[\text{D}_3]\text{dpRe}$ appears at $\delta = 2.9$ ppm. The extent of reaction between $[\text{D}_3]\text{dpRe}$ and substrates is indicated by the decrease in the integral for this resonance signal over time. Kaleidagraph 3.0 was used in the analysis of the kinetic data.

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