CATALYTIC OXIDATION AND COMPARATIVE KINETICS IN ROOM-TEMPERATURE IONIC LIQUIDS

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

Department of Chemistry and Biochemistry, 607 Charles E. Young Drive East, Box 951569, University of California, Los Angeles, CA 90095-1569, USA

ABSTRACT

Methylrhenium trioxide (MTO) catalyzes the epoxidation of alkenes and allylic alcohols with urea hydrogen peroxide (UHP) in room-temperature ionic liquids (RTILs) that are based on N, N'-dialkylimidazolium or N-alkylpyridinium cations. The ionic liquids must be halide-free because halides catalyze the disproportionation of hydrogen peroxide to molecular oxygen and water. The kinetics and thermodynamics of the reaction of MTO with H$_2$O$_2$ in different ionic liquids have been investigated. The rate constant for the formation of the catalytically active diperoxorhenium complex, dpRe, is highly dependent on the concentration of water in the ionic solvent. Also, the rate constants for olefin epoxidation by the peroxorhenium complexes of MTO have been measured by UV-visible and $^2$H NMR spectroscopies. $^2$H NMR experiments conducted with [D$_3$]dpRe confirmed the speciation of the catalytic system and asserted the validity of the UV-vis kinetics. The dpRe is more reactive in RTILs than its analogous monperoxo species, mpRe. The rate of olefin epoxidation is unaffected by the nature of the ionic liquid’s cation; however, a discernable kinetic effect was noted for coordinating anions such as nitrate.

INTRODUCTION

A major research goal in green chemistry is the development and study of catalytic reactions that employ benign reagents and solvents. Although the first ionic liquid was reported almost 90 years ago (1), their use as alternative reaction media has attracted attention only in the past few years (2). The majority of room-temperature ionic liquids (RTILs) consist of nitrogen-containing organic cations and inorganic anions. Among the most desirable properties of ionic liquids are their (1) negligible vapor pressure, (2) high polarity, (3) weakly coordinating anions, (4) tunable melting temperatures, and (5) ability to dissolve both organic and inorganic compounds. A wide variety of catalytic reactions have been investigated in ionic liquids (3). Nevertheless, it is surprising that studies of catalytic oxidations in these media have been limited, particularly, given the importance of such reactions in the laboratory as well as in the chemical industry (4).

Hydrogen peroxide is an environmentally friendly oxidant because its only byproduct is water when targeted for oxygen atom transfer reactions. Since reactions of hydrogen peroxide are often slow and nonselective (due to free-radical side reactions), a...
catalyst is needed for activation and selectivity (5). Methylrhenium trioxide (MTO) is one of the best activators for hydrogen peroxide and the most studied organometallic compound (6). It reacts with hydrogen peroxide to form \( \eta^2 \)-peroxo complexes that are capable of transferring an oxygen atom to olefins and other suitable substrates (Figure 1). The MTO catalytic system in conventional solvents (organic and aqueous) suffers two drawbacks. Catalyst separation from product and catalyst recycling are difficult and cumbersome; for instance, the use of column chromatography is mandatory. Secondly, the peroxorhenium complexes (mpRe and dpRe in Figure 1) require addition of acid for stability. A side effect of adding aqueous acid is facile ring-opening of epoxide to diol.

\[
\begin{array}{c|c|c|c|c}
\text{MTO} & \text{mpRe} & \text{dpRe} \\
\hline
\text{H}_3\text{C} & \text{O} & \text{O} & \text{O} & \text{O} \\
\hline
\end{array}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \xrightleftharpoons[k_1\text{H}_2\text{O}_2]{k_4} \text{O} & \text{H}_3\text{C} & \xrightleftharpoons[k_2\text{H}_2\text{O}_2]{k_3} \text{O} \\
\text{R} & \equiv & \text{O} & \equiv & \text{O} \\
\end{align*}
\]

**Figure 1.** Formation and reactivity of the active catalytic species in the MTO/H\(_2\)O\(_2\) System.

We have shown that imidazolium ionic liquids such as [emim]BF\(_4\) can be used with urea hydrogen peroxide (UHP), a water-free source of H\(_2\)O\(_2\), and MTO to effect the epoxidation of olefins in high yields (4b). Furthermore, the kinetics of dpRe formation (\(k_2\)) have been determined in several ionic liquids as well as the kinetics of oxygen atom transfer from mpRe and dpRe to a wide variety of olefinic substrates (7,8). It is worth noting that kinetic studies in ionic liquids have been conspicuously scarce in the growing list of physical investigations (9). Techniques have been developed in this laboratory to monitor kinetics in ionic media by time-resolved \(^{2}\)H NMR spectroscopy (10). In this account, we summarize the chemistry of olefin epoxidation and dihydroxylation as catalyzed by the MTO-peroxide system in RTILs.

**MTO-CATALYZED EPOXIDATIONS USING UHP**

The advantages of ionic liquids and the MTO/peroxide system have been combined to create an oxidation solution that is both environmentally friendly and highly efficient. The ionic liquid N-ethyl-N'-methylimidazolium tetrafluoroborate ([emim]BF\(_4\)) was used with MTO and UHP to oxidize alkenes and allylic alcohols with high conversions to the corresponding epoxides (Table I). This system combines the advantages of heterogeneous and homogeneous catalysis: the epoxide products are easily recovered by simple extraction with diethyl ether, and the reaction times are comparable to those observed with organic solvents.

Electrochemical Society Proceedings Volume 2002-19
Table I. Epoxidation of alkenes and allylic alcohols with MTO/UHP in \([\text{emim}]\text{BF}_4\).

| Substrate | % epoxide$^b$ | Substrate | % epoxide$^b$ |
|-----------|---------------|-----------|---------------|
|            | 99            |            | 96            |
|            | 95            |            | 94            |
| Ph         | 98            |            | 95            |
| OH         | 95$^c$        |            | 85$^d$        |

$^a$ Conditions: 1.0 mmol substrate, 1.0-2.0 mmol UHP, and 0.02 mmol MTO in 2.0 mL \([\text{emim}]\text{BF}_4\) at 20 °C for 4-6 h. $^b$ % Conversion of substrate into product. $^c$ 2,3-epoxycyclohexanol (62%) and 2,3-epoxycyclohexanone (32%). $^d$ This represents the diepoxide; the remainder is the monoepoxide.

The use of a water-free source of hydrogen peroxide is important to produce epoxide products. When aqueous hydrogen peroxide is employed as oxidant, the 1,2-diol is the major product. Hence, this system is extremely versatile as both epoxides and diols can be easily accessed by simply changing the peroxide from UHP to 30% aqueous H$_2$O$_2$. A major difference between the MTO/UHP system in ionic liquids compared to that in organic solvents is the solubility of urea hydrogen peroxide. The UHP complex is sparingly soluble in aqueous and organic (CHCl$_3$ or CH$_2$Cl$_2$) media, but UHP is readily soluble in \([\text{emim}]\text{BF}_4\), giving homogeneous reaction conditions. This difference accounts for the enhanced reactivity of the MTO/UHP in RTILs. For example, the epoxidation of styrene with MTO/UHP in CHCl$_3$ under the same conditions as in Table I requires 19 h for 45% conversion to styrene oxide. The same reaction (see Table I) is complete in \([\text{emim}]\text{BF}_4\) in less than 6 h.

Solvent purity is crucial for successful epoxidations with the MTO-peroxide catalytic system in RTILs. The sensitivity of mpRe and dpRe to pyridine, pyrazole, and

\[
\begin{align*}
\text{Ph} + 2 \text{H}_2\text{O}_2 \quad \text{aqueous 30\%} & \quad \text{1 mol \% MTO} \quad \text{[emim]BF}_4, 20 ^\circ\text{C} & \quad \text{95\%} & \quad \text{(1)} \\
\text{Ph} + \text{1 UHP} & \quad \text{1 mol \% MTO} \quad \text{[emim]BF}_4, 20 ^\circ\text{C} & \quad 98\% & \quad \text{(2)}
\end{align*}
\]
imidazole is well documented in the literature (11). Hence, ILs must be absolutely free of any residual \( N \)-alkylimidazole starting materials. The most common procedure for making RTILs involves the metathesis of dialkylimidazolium halide with the desired inorganic anion. Halides (e.g. \( \text{Br}^- \) and \( \text{Cl}^- \)) are oxidized by the peroxorhenium complexes of MTO to the hypohalous acids, which in turn catalyze the disproportionation of hydrogen peroxide to molecular oxygen and water (12). Halide impurities are detrimental because they are oxidized faster than olefins. For example, \( k_4 \) for \( \text{Br}^- \) is \( \approx 2000 \) times \( k_4 \) for styrene. A simple calculation reveals that only 1 mol % residual bromide gives an impurity concentration of 80 mM in the resulting ionic liquid! This amount of halide is comparable to substrate (alkene) concentration, and sufficient to shunt epoxidation and result in complete disproportionation of hydrogen peroxide. Hence, care must be taken to remove traces of halide from the ionic liquid. Silver salts are generally most effective reagents for metathesis, but large excess of Ag(I) is also undesirable as its photosensitivity leads to brown ILs (7).

**KINETICS AND THERMODYNAMICS OF THE MTO/PEROXIDE REACTIONS**

**Kinetics of dpRe Formation**

The formation of dpRe (Figure 1) was monitored by observing the absorbance change at 360 nm, the \( \lambda_{\text{max}} \) of dpRe \( (e = 1100 \text{ M}^{-1} \text{ cm}^{-1}) \). Hydrogen peroxide was used in excess and plots of \( k_y \) versus \([\text{H}_2\text{O}_2]\) were analyzed to obtain values of \( k_2 \) in a variety of ionic liquids. The rate constants for the formation of two peroxorhenium species from the MTO/\( \text{H}_2\text{O}_2 \) reaction, \( k_1 \) and \( k_2 \), have been determined in a number of molecular solvents (6b). The kinetics of the MTO/\( \text{H}_2\text{O}_2 \) reaction feature biexponential time profiles in organic solvents. However, in ionic liquids, the absorbance change at 360 nm follows a single-exponential curve, since the formation of mpRe occurs extremely rapidly within the mixing time. Because of the viscosity of the ionic liquids \((\approx 60 \text{ cP})\), the formation of mpRe was not investigated by stopped-flow techniques. Even though the intercepts from the plots of \( k_y \) versus \([\text{H}_2\text{O}_2]\) should, in theory, give values for \( k_2 \), the \( y \)-intercepts are significantly smaller than the slopes, rendering \( k_2 \) negligible within experimental precision.

The rate constant \( k_2 \) was determined in five different ionic liquids: \([\text{emim}]\text{BF}_4\), \([\text{bmim}]\text{BF}_4\), \([\text{bmim}]\text{NO}_3\), \([\text{bmim}]\text{OTf}\), and \([\text{bupy}]\text{BF}_4\) (13). The rate constant \( k_2 \) is the same for all five ionic liquids \((k_2 = 0.20 \pm 0.02 \text{ L mol}^{-1} \text{ s}^{-1})\). This result is surprising given the differences in viscosity of the liquids and in the coordination ability of their anions. The rate constant \( k_2 \) in ionic liquids is smaller than that in water \((5.2 \text{ L mol}^{-1} \text{ s}^{-1})\) and greater than that in acetonitrile \((0.045 \text{ L mol}^{-1} \text{ s}^{-1})\). In order to gain insight into the effect of water and salt concentrations, values of \( k_2 \) were determined in a number of concentrated salt solutions. These results are summarized in Table II. Comparing the rate constants in Table II shows that \( k_2 \) in 99% ionic liquid is essentially the same as \( k_2 \) in acetonitrile. This is not surprising given that the polarity of ionic liquids has been estimated to be comparable to that of acetonitrile and methanol (14). The data in Table II correlates best with the concentration of water. The rate constant \( k_2 \) increases as \([\text{H}_2\text{O}]\) increases. This result provides evidence that in the presence of water RTILs behave like aqueous solutions of high salt concentrations. The kinetics of dpRe formation is not
affected by the nature of the ionic liquid; the most important consideration is the water concentration.

### Table II. Values of $k_3$ in various media.

| Entry | Solvent* | $k_3/\text{L mol}^{-1}\text{s}^{-1}$ | [H$_2$O]/mol L$^{-1}$ |
|-------|----------|-----------------------------------|---------------------|
| 1     | 5.92 M [etpy]BF$_4$ | 0.20                             | 5.55                |
| 2     | 5.41 M [etpy]BF$_4$ | 0.38                             | 8.88                |
| 3     | 4.28 M [etpy]BF$_4$ | 0.65                             | 18.7                |
| 4     | 99% [bmim]NO$_3$   | 0.053                            | 0.56                |
| 5     | 95% [bmim]NO$_3$   | 0.12                             | 2.77                |
| 6     | 90% [bmim]NO$_3$   | 0.22                             | 5.55                |
| 7     | 80% [bmim]NO$_3$   | 0.36                             | 11.1                |
| 8     | 60% [bmim]NO$_3$   | 0.79                             | 22.2                |
| 9     | 40% [bmim]BF$_4$   | 1.17                             | 33.3                |
| 10    | 10% [bmim]BF$_4$   | 1.90                             | 50.0                |

*Abbreviations: etpy = N-ethylpyridinium, and bmim = n-butylmethylimidazolium.

### Thermodynamics of the MTO-Peroxide Equilibria

The relationship of $A_{360}$ and [H$_2$O$_2$], derived using the equilibrium expressions for $K_1$ and $K_2$ (Figure 1), is given in eq. 1, where [Re]$_T$ = [MTO] + [mpRe] + [dpRe]. A nonlinear least-squares fit of the data using eq. 1 provides values for $K_1$ and $K_2$ (Table III).

$$
\frac{A_{360}}{[\text{Re}]_T} = \frac{\varepsilon_{\text{mpRe}}K_1[H_2O_2] + \varepsilon_{\text{dpRe}}K_1K_2[H_2O_2]^2}{1 + K_1[H_2O_2] + K_1K_2[H_2O_2]^2}
$$

[1]

The results in Table III indicate the same general trends observed for the kinetics studies. However, the influence of water is not quite as dramatic for the equilibrium constants as it is for the rate constant $k_3$. The equilibrium constants $K_1$ and $K_2$ in 90% ionic liquid solution fall between water and acetonitrile with $K_2 > K_1$, indicating cooperativity in peroxide binding. The values for the reaction in dry [emim]BF$_4$ are $K_1 = 110$ and $K_2 = 160$ L mol$^{-1}$. When less water is present in the ionic liquids, the extent of peroxide binding cooperativity is reduced, as is the case when the reaction is conducted in acetonitrile.
Table III. $K_1$ and $K_2$ for the MTO-peroxide reaction in different solutions.\(^a\)[5]

| Solvent\(^b\) | $K_1$/ L mol\(^{-1}\) | $K_2$/ L mol\(^{-1}\) |
|--------------|----------------|----------------|
| H\(_2\)O\(^c\) | 16 | 132 |
| CH\(_3\)CN\(^c\) | 209 | 660 |
| [emim]BF\(_4\) | 49 | 170 |
| [bupy]BF\(_4\) | 110 | 140 |
| [bmim]BF\(_4\) | 74 | 130 |
| [bmim]NO\(_3\) | 28 | 82 |
| [bmim]OTf | 34 | 120 |

\(^a\) Ionic liquid samples were 10% water by volume. \(^b\) Abbreviations: emim = ethylmethylimidazolium, bupy = n-butylpyridinium, bmim = n-butylmethylimidazolium, and OTf = trifluoromethane sulfonate.

\(^c\) Reference (6b).

NON-STEADY-STATE KINETICS OF OLEFIN EPOXIDATION

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 Figure 1) to olefinic substrates in ionic liquids, and contrast these values to those obtained in water and organic solvents (8). It had become evident early on that two complications needed to be addressed here. First, the effects of water on the kinetics (7) and physical properties (15) of room temperature ionic liquids have been documented. Hence, a water free source of hydrogen peroxide had to be employed in order to minimize the deleterious effects of water as a co-solvent. Secondly, 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 (~ 40 mM) of dpRe in THF.

For the non-steady-state kinetics with alkenes, the THF solution of dpRe was diluted into the desired RTIL to ~ 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. The absorbance at the end of reaction is essentially zero, which indicates that all of the dpRe and mpRe have reacted with the substrate. The kinetic traces are fitted using the biexponential treatment shown in eq 2, where both $\alpha$ and $\beta$ are constants. Both $k_1$ and $k_4$ (the fast and slow pseudo-first-order rate constants, respectively) exhibit linear dependences on the alkene concentration.

$$\text{Abs}_t - \text{Abs}_\infty = \alpha \exp(-k_1 t) + \beta \exp(-k_4 t)$$ [2]
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. In order to assign the fast and slow steps, we employed the kinetics simulation program KINSIM16 and determined that the \(k_4\) step, the oxidation of alkenes with dpRe, is faster than the \(k_3\) step \((8)\). The values of \(k_3\) and \(k_4\) for several olefins have been determined in acetonitrile and in \([\text{emim}]\text{BF}_4\), and compared to those previously measured in 1:1 \(\text{CH}_3\text{CN}:\text{H}_2\text{O}\) \((17)\) (Table IV).

### Table IV. Values of \(k_3\) and \(k_4\) (L mol\(^{-1}\) s\(^{-1}\)) in different solvents for several styrenes.

| Substrate | \([\text{emim}]\text{BF}_4^a\) | \(\text{CH}_3\text{CN}^a\) | \(\text{CH}_3\text{CN}:\text{H}_2\text{O} (\text{v/v})^b\) |
|-----------|-----------------|-----------------|-----------------|
|           | \(k_3\) | \(k_4\) | \(k_3\) | \(k_4\) | \(k_3\) | \(k_4\) |
| \(\text{C}_6\text{H}_5\text{CH}-\text{CH}_2\) | 0.013 | 0.13 | 0.0020 | 0.015 | — | 0.11 |
| \(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2\) | 0.058 | 0.26 | 0.021 | 0.052 | 0.51 | 0.22 |
| \(\text{C}_6\text{H}_5\text{CH}2\text{CH}=\text{CH}_2\) | 0.10 | 0.44 | 0.045 | 0.045 | — | 0.47 |
| \(\text{C}_6\text{H}_5\text{CH}2\text{CH}=\text{CH}2\text{CH}=\text{CH}_2\) | 0.031 | 0.13 | 0.031 | 0.22 | — | 1.06 |

\(^a\)Reference \((8)\). \(^b\)Reference \((17)\).

\(k_4\) values in \([\text{emim}]\text{BF}_4\) for the three styrene substrates in Table IV 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 \(\text{CH}_3\text{CN}\). This result is anomalous but is reconciled by considering the limited solubility of cyclohexene in \([\text{emim}]\text{BF}_4\). 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 reactivity of the styrenes with the peroxorhenium complexes shows the expected trend for electrophilic oxygen transfer from rhenium: styrene < TBMS < \(\alpha\)-methylstyrene (AMS). The additional methyl groups of TBMS and AMS increase the styrenes’ reactivities relative to PhCH=CH\(_2\), and the steric of TBMS make this substrate slightly less reactive than AMS.

The kinetics of \(\alpha\)-Methylstyrene epoxidation was investigated in different ionic liquids. The rate constants \(k_3\) and \(k_4\) for the oxidation of \(\alpha\)-methylstyrene are summarized in Table V. Entries 3, 4, and 6 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 have an effect on the reaction of the peroxorhenium complexes with the double bond. However, both \(k_3\) and \(k_4\) are substantially lower when the reaction is done in \([\text{bmim}]\text{NO}_3\) (entry 5). This result is rationalized by considering that \text{NO}_3^- has much
higher coordination ability than BF$_4^-$ and thus hinders approach of substrate to the rhenium peroxo complexes.

Table V. 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                       | 0.045                       |
| 2$^b$ | 1:1 CH$_3$CN/H$_2$O    | ___                         | 0.47                        |
| 3     | [emim]BF$_4$           | 0.10                        | 0.44                        |
| 4     | [bmim]BF$_4$           | 0.074                       | 0.35                        |
| 5     | [bmim]NO$_3$           | 0.016                       | 0.12                        |
| 6     | [bupy]BF$_4$           | 0.13                        | 0.58                        |

$^a$Reference (8). $^b$Reference (17).

$^2$H NMR KINETICS

Deuterated alkenes can be used as substrates in proteated ionic liquids to study the MTO-catalyzed oxidation of alkenes under steady-state conditions (8,10). The integrals of the $^2$H resonances for deuterated 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). Under these conditions, the kinetic traces follow a single-exponential decay and are fit with eq 3. The kinetics are first-order in [alkene] and show no dependence on [H$_2$O$_2$]. Hence, $k_y = k_3$ [mpRe] + $k_4$ [dpRe] simplifies to $k_y \approx k_4$ [dpRe], since at these high [H$_2$O$_2$], the major rhenium species is dpRe and (as shown above by UV-vis kinetics) $k_3 < k_4$ in RTILs. The $k_y$ values obtained by $^2$H NMR for the epoxidation and dihydroxylation of [D$_8$]styrene and [D$_{10}$]cyclohexene in several RTILs are comparable to values obtained by non-steady-state UV-vis kinetics (vide supra) (8).

$$I_t - I_\infty = \alpha \exp(-k_y t) \quad \text{[3]}$$

In an alternative method that more closely resembles the conditions used in the UV-vis kinetic studies, CD$_2$ReO$_3$ ([D$_3$]MTO) was reacted with 2 equivalents UHP in RTILs to generate [D$_3$]dpRe. The latter was used for single turnover reactions with
alkenes, and followed by $^2$H NMR. The relatively long timescale 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 (8). Over the course of a reaction, the intensity of the [D$_3$]dpRe resonance ($\delta = 2.9$ ppm) decreases and the intensity of the [D$_3$]MTO resonance ($\delta = 2.4$ ppm) increases. The $^2$H resonances due to products of peroxyrhenium complex decompositions, namely CD$_3$OH and CD$_3$OOH ($\delta = 3.4$ and 3.3 ppm, respectively), increase during the course of reaction.

![Figure 2. $^2$H NMR stack plot for the single-turnover epoxidation of 2-fluorostyrene with [D$_3$]dpRe in [emim]BF$_4$.](image)

When the integration for the [D$_3$]dpRe resonance is plotted as a function of time, the kinetic traces obtained are exponential, and the integration for the [D$_3$]dpRe resonance is nearly zero at the end of the reactions. This 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, $k_w = k_4$ [alkene]. The values of $k_4$ obtained by $^2$H NMR are comparable to those determined by UV-vis kinetics (8).

**SUMMARY**

Little research has been conducted on green catalytic oxidations in ionic liquids. The MTO/UHP is an effective catalytic system for the epoxidation of alkenes and allylic alcohols in different RTILs. When aqueous hydrogen peroxide is used in place of UHP, olefin oxidation proceeds smoothly to give the diol rather than epoxide. Recovery of the organic products is easily achieved by an extraction step in which the catalyst remains in the ionic medium. The purity of the ionic liquid is key to the success of the MTO/UHP system, as small impurities of leftover halide or imidazole result in diminished alkene conversion to epoxide. The kinetics and thermodynamics of the reaction of MTO with hydrogen peroxide in different ionic liquids have been studied, demonstrating the amenability of the system for quantitative measurements. The values of the rate constants are highly dependent on the concentration of water. The rate constants for oxygen atom transfer from mpRe and dpRe to alkenes have been measured by UV-vis and $^2$H NMR spectroscopy. The diperoxorhenium complex dpRe was found to be about 5 times more reactive than its analogous monoperoxo species mpRe. $^2$H NMR is an economical and
versatile technique for studying the progress of reactions in protected ionic liquids. In conclusion, we have demonstrated the suitability of ionic liquids for green catalytic oxidations with hydrogen peroxide under ambient and mild conditions. Future directions of interest would include the use of molecular oxygen, possibly the best oxidant, for selective oxidations in ionic liquids, and the employment of task specific ionic media in catalysis.

ACKNOWLEDGMENTS

We are grateful to the US National Science Foundation, the Beckman Foundation, and the University of California Toxic Substance Research and Teaching Program for supporting our work on ionic liquids.

REFERENCES

1. P. Walden, Bull. Acad. Imper. Sci. (St. Petersburg), 1800 (1914).
2. (a) T. Welton, Chem. Rev., 99, 2071 (1999). (b) P. Wassercheid and W. Keim, Angew. Chem. Int. Ed., 39, 3772 (2000). (c) M. J. Earl and K. R. Seddon, Pure Appl. Chem., 72, 1391 (2000). (d) M. M. Abu-Omar, in 2002 McGraw-Hill Yearbook of Science & Technology, p. 148, McGraw-Hill, New York, NY (2001).
3. R. Sheldon, Chem. Commun., 2399 (2001).
4. (a) C. E. Song and E. J. Roh, Chem. Commun., 837 (2000). (b) G. S. Owens and M. M. Abu-Omar, Chem. Commun., 1165 (2000). (c) S. V. Ley, C. Ramarao, M. D. Smith, Chem. Commun., 2278 (2001). (d) I. M. Ansari and R. Gree, Org. Lett., 4, in press (2002).
5. G. Strukul, in Catalytic Oxidations with Hydrogen Peroxide as Oxidant, G. Strukul, Editor, p. 1, Kluwer Academic Publishers, Dordrecht (1992).
6. (a) C. C. Romao, F. E. Kuhn, W. A. Herrmann, Chem. Rev., 97, 3197 (1997). (b) J. H. Espenson, Chem. Commun., 479 (1999). (c) G. S. Owens, J. Arias, M. M. Abu-Omar, Catal. Today, 55, 317 (2000).
7. G. S. Owens and M. M. Abu-Omar, J. Mol. Catal. A: Chemical, in press (2002).
8. G. S. Owens, A. Durazo, M. M. Abu-Omar, Chem. Eur. J., in press (2002).
9. (a) Z. J. Karpinski, S. Song, R. A. Osteryoung, Inorg. Chim. Acta, 225, 9 (1994). (b) M. T. Carter and R. A. Osteryoung, J. Electrochem. Soc., 141, 1713 (1994). (c) C. M. Gordon and A. J. McLean, Chem. Commun., 1395 (2000). (d) S. Csihony, H. Mehdi, I. T. Horvath, Green Chemistry, 3, 307 (2001).
10. A. Durazo and M. M. Abu-Omar, Chem. Commun., 66 (2002).
11. (a) W. A. Herrman, R. W. Fischer, M. U. Rauch, W. Scherer, J. Mol. Catal., 86, 243 (1994). (b) M. M. Abu-Omar, P. J. Hansen, J. H. Espenson, J. Am. Chem. Soc., 118, 4966 (1996). (c) W. Wang and J. H. Espenson, J. Am. Chem. Soc., 120, 11335 (1998).
12. (a) J. H. Espenson, O. Pestovsky, P. Huston, S. Staudt, J. Am. Chem. Soc., 116, 2869 (1994). (b) P. J. Hansen and J. H. Espenson, Inorg. Chem., 34, 5839 (1995).
13. Abbreviations: emim = ethylmethylimidazolium, bmim = n-butylmethylimidazolium, bupy = n-butylpyridinium, and OTf = trifluoromethane sulfonate.
14. S. N. V. K. Aki, J. F. Bremnecke, A. Samanta, Chem. Commun., 413 (2001).
15. K. R. Seddon, A. Stark, M.-J. Torres, Pure Appl. Chem., 72, 2275 (2000).
16. B. A. Barshop, C. F. Wrenn, C. Frieden, Anal. Biochem., 130, 134 (1983).
17. A. Al-Ajlouni and J. H. Espenson, J. Am. Chem. Soc., 117, 9243 (1995).