

Comparative kinetic investigations in ionic liquids using the MTO/peroxide system

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Abstract

The kinetics and thermodynamics of the reaction of methyltrioxorhenium (MTO) with hydrogen peroxide in ambient temperature ionic liquids have been studied. The rate constant for the formation of the diperoxorhenium complex, $\text{CH}_3\text{ReO}(\eta^2\text{-O}_2)_2$, from the monoperoxorhenium complex, $\text{CH}_3\text{ReO}_2(\eta^2\text{-O}_2)$, and hydrogen peroxide in $[\text{bmim}]\text{NO}_3$ is $0.053 \pm 0.002 \text{ M}^{-1} \text{ s}^{-1}$. The equilibrium constants for the binding of two peroxide units have been determined in $[\text{emim}]\text{BF}_4$ to be $K_1 = 110 \pm 28$ and $K_2 = 160 \pm 36$. Similar rate constants and equilibrium constants are obtained in other water-miscible, dialkylimidazolium and alkylpyridinium ionic liquids. The values of the rate constants are highly dependent on the concentration of water in the solvent. These results indicate that the ionic liquids can behave like organic solvents and aqueous solutions of high salt concentrations. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Room temperature ionic liquids have gained a great deal of attention during the past few years as alternative reaction media [1–5]. Interest in the dialkylimidazolium and alkylpyridinium salts, particularly, is high because of their negligible vapor pressure and their stability to both air and moisture. The possibility of using ionic liquids as truly recyclable reaction media is exceptionally appealing because of increasing environmental concerns with respect to waste production and containment.

Many transition metal-catalyzed reactions have been shown to proceed with high yields in both water-miscible and water-immiscible ionic liquids,

including hydrogenation [6,7], hydroformylation [6,8], Heck reactions [9–11], and oxidations [12,13]. Furthermore, there have been reports of reaction acceleration in ionic liquids as opposed to molecular solvents. Palladium-catalyzed Suzuki cross-coupling reactions in 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}]\text{BF}_4$) have been described to proceed at 90–200 times faster than in a mixture of toluene, water, and ethanol [14]. Rate-enhancement has also been observed in biphasic Trost–Tsuji couplings when a biphasic mixture of $[\text{bmim}]\text{Cl}$ /methylcyclohexane is used instead of butyronitrile/water [15].

In addition to expanding the applicability of ionic liquids to various types of organic transformations, a great deal of physical data and trends has surfaced in the last 2 years. The specific conductivity of a wide range of water-immiscible ionic liquids has been studied in relevance to their potential use in photoelec-

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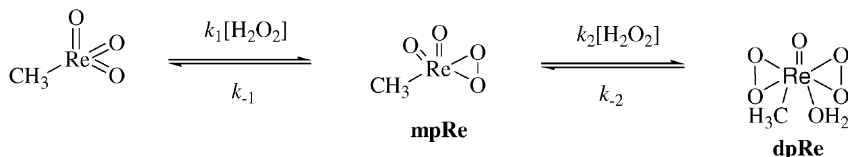
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trochemical cells [16]. The polarity of a number of ionic liquids has been investigated recently through studies that show contributions from both the cation and the anion [17,18]. The influence of water, organic solvents, and impurities, especially leftover chloride, on the viscosity and density of ionic liquids has been reported recently [19]. Additionally, pulsed-gradient spin-echo ^1H and ^{19}F NMR have been used to measure the ionic diffusion coefficient of various ionic liquids [20].

Kinetic studies on reactions in ionic liquids are conspicuously absent from the growing list of physical measurements. These studies are an important part of determining the economic viability of using ionic liquids as alternative reaction media, especially concerning industrial applications of ionic liquids.

Our research group is interested in the utility of ionic liquids for transition metal-catalyzed oxygen atom transfers. We have shown previously that the ionic liquid [emim]BF₄ can be used with urea hydrogen peroxide (UHP) and the catalyst methyltrioxorhenium (MTO) to effect the epoxidation of olefins [13]. The epoxide yields are comparable to the yields that are obtained in molecular solvents, and there seems to be a rate-enhancement compared to reactions done in dichloromethane and acetonitrile (ACN).

MTO reacts with excess hydrogen peroxide to form two η^2 -peroxo complexes [21,22]. Both intermediates are capable of transferring an oxygen atom to suitable substrates, including olefins [23,24], sulfides [25–27], phosphines [28], and aromatics [29–31]. The formation of monoperoxorhenium (mpRe) and diperoxorhenium (dpRe) complexes with accompanying rate constants k_1 and k_2 has been well established in a variety of solvents of differing polarity [22,28,32,33]. This report focuses on the formation of the catalytically active peroxorhenium intermediates, especially dpRe, in ionic liquids and examines the effect of these unusual media on this well studied system.



2. Experimental section

2.1. Materials

Bromoethane, bromobutane, 1-methylimidazole, 1-butylimidazole, and pyridine were distilled prior to use. Hydrogen peroxide solutions were standardized by iodometric and permanganate titrations. UHP was standardized by permanganate titration as a stock solution in [bmim]BF₄. MTO was prepared by the standard literature method [34]. Stock solutions of MTO were prepared in ACN and stored at -10°C ; concentrations were determined spectrophotometrically. All syntheses were performed under inert atmosphere conditions, though rigorous water-exclusion methods are unnecessary.

2.2. Solutions

Kinetic and thermodynamic measurements were obtained on a Shimadzu UV-2501PC at $23 \pm 1^\circ\text{C}$. Small-volume (0.50 ml) quartz cuvettes with 1.00 cm optical path length were used. All solutions contained 0.10 M perchloric acid to stabilize the MTO/peroxide system. The reaction solutions involving aqueous hydrogen peroxide were studied by adding perchloric acid and MTO to the particular solution, obtaining a baseline, and then adding aqueous hydrogen peroxide last.

Since UHP is a solid, stock solutions of UHP in the various ionic liquids were made and then diluted. Perchloric acid was then added, a baseline was obtained, and MTO was added last.

2.3. Kinetics and thermodynamics

The formation of the dpRe complex was monitored by observing the absorbance change at 360 nm, the λ_{max} of the dpRe complex ($\epsilon = 1100 \text{ M}^{-1} \text{ cm}^{-1}$). Plots of k_{ψ} (the pseudo rate constant) versus $[\text{H}_2\text{O}_2]$ were analyzed to obtain values of k_2 for the reactions

of MTO with hydrogen peroxide and UHP in a variety of ionic liquids and salt mixtures. The maximum absorbance values at 360 nm for variable $[H_2O_2]$ were used to calculate the peroxide binding constants K_1 and K_2 . The nonlinear least-squares program Kaleidagraph was used to analyze the kinetic and thermodynamic data.

3. Synthesis of ionic liquids

3.1. 1-Ethyl-3-methylimidazolium bromide ([emim]Br)

[emim]Br was synthesized according to a literature procedure [16] with the following modifications. With vigorous stirring, bromoethane was added via addition funnel over 1.5 h to 1-methylimidazole neat. Ambient temperature was maintained by the use of a water bath. The mixture became cloudy after complete addition of bromoethane, and a white solid formed within 1 h. The excess bromoethane was decanted, and the white solid, [emim]Br, was washed three times with tetrahydrofuran (THF) and recrystallized from ACN and THF in 96% yield. 1H NMR shifts correspond to those from the literature [16].

3.2. 1-Ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF₄)

[emim]BF₄ was synthesized according to the literature procedure [7] with the following modification. [emim]Br was dissolved in 9:1 acetone:ACN, and 1.1 equiv. of sodium tetrafluoroborate were added to the solution. The solution was vigorously stirred for 60 h at room temperature. Leftover NaBF₄ and the byproduct, sodium bromide, were removed by filtration, and the solvent was removed under reduced pressure to yield [emim]BF₄ as a clear, colorless liquid. The liquid was redissolved in ACN and stirred with neutral alumina (Brockman activity 1) for 6 h to remove traces of unreacted 1-methylimidazole from the previous step. Leftover Br⁻ was removed from the product ionic liquid by precipitation with silver tetrafluoroborate or silver nitrate. Overall yield, 92%. 1H NMR peaks correspond to those reported previously in the literature [35].

3.3. 1-Butyl-3-methylimidazolium bromide ([bmim]Br)

The same procedure was used as for [emim]Br except that the mixture was heated to 65 °C for 2 h after complete addition of 1-methylimidazole. The mixture turned cloudy and then separated into two phases: excess 1-bromobutane on top and [bmim]Br on bottom. The excess 1-bromobutane was removed under reduced pressure, leaving behind an extremely viscous, cloudy liquid, [bmim]Br. The sludgy liquid was washed three times with THF and dried in vacuo, resulting in a white solid. The solid was recrystallized from ACN and THF, giving [bmim]Br in 94% yield. 1H NMR peaks correspond to those reported previously in the literature [16].

3.4. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄)

The same synthetic and purification procedure was used as for [emim]BF₄ to yield [bmim]BF₄ in 92% overall yield. 1H NMR peaks correspond to those reported previously in the literature [35].

3.5. 1-Butyl-3-methylimidazolium nitrate ([bmim]NO₃)

[bmim]NO₃ was prepared as described in the literature by metathesis of [bmim]Br with AgNO₃ [19]. The same purification procedure as for [emim]BF₄ was used to obtain [bmim]NO₃ in 97% overall yield. 1H NMR shifts are in the range for [bmim]⁺ described in the literature [16].

3.6. 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim]OTf)

The literature procedure was used to synthesize [bmim]OTf as a clear, yellow liquid in 93% yield [16]. The liquid was redissolved in ACN and stirred with neutral alumina for 5 h. Removal of the alumina by filtration and the organic solvent by vacuum yielded the product as a clear, colorless liquid (80% yield). 1H NMR shifts correspond to those from the literature [16].

3.7. 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆)

[bmim]PF₆ was prepared as described in the literature by metathesis of [bmim]Br with NaBF₆ in water [19]. After separation from the aqueous phase of the metathesis mixture, the product ionic liquid was mixed with THF and stirred with neutral alumina for 2 h. Removal of the alumina and then of the organic solvent yielded [bmim]PF₆ as a clear, colorless liquid (68%). No residual bromide was detected through assay with hydrogen peroxide (vide infra). ¹H and ¹⁹F NMR shifts correspond to those from the literature [7].

3.8. Butylpyridinium bromide ([bupy]Br)

[bupy]Br was synthesized according to a literature procedure [36] with the following modifications. Bromobutane was used instead of chlorobutane, and the reaction was performed neat by adding pyridine via additional funnel to bromobutane. The mixture was then heated to 65 °C for 6 h, during which time the mixture turned cloudy and then separated into two phases. The excess 1-bromobutane was removed under reduced pressure, leaving behind an off-white solid, [bupy]Br. The solid was washed three times with THF and dried in vacuo. The solid was recrystallized from ACN and THF, giving [bupy]Br in 94% yield. ¹H NMR (ACN-d₃): δ (ppm) 8.72 (d, 2H), 8.50 (t, 2H), 8.03 (t, 1H), 4.52 (t, 2H), 2.01–1.86 (m, 2H), 1.45–1.27 (m, 2H), 0.98–0.90 ppm (t, 3H).

3.9. Butylpyridinium tetrafluoroborate ([bupy]BF₄)

The same synthetic and purification procedure as for [emim]BF₄ and [bmim]BF₄ was used to obtain [bupy]BF₄ as a colorless liquid in 93% overall yield. ¹H NMR shifts were the same as for [bupy]Br. ¹⁹F NMR (ACN-d₃): –152.92.

3.10. Ethylpyridinium bromide ([etpy]Br)

The same procedure was used as for [bupy]Br to obtain [etpy]Br as a white solid in 96% yield. ¹H NMR (ACN-d₃): δ (ppm) 8.60 (d, 2H), 8.39 (t, 2H), 7.94 (t, 1H), 4.41 (q, 2H), 1.98 ppm (t, 3H).

3.11. Ethylpyridinium tetrafluoroborate ([etpy]BF₄)

The same synthetic procedure as for [bupy]BF₄ was used to obtain [etpy]BF₄ as a white solid. The solid was redissolved in ACN and stirred with neutral alumina to remove organic impurities. The solvent was then removed to give [etpy]BF₄ in 90% overall yield. ¹H NMR shifts are the same as for [etpy]Br. ¹⁹F NMR (ACN-d₃): –153.0.

4. Results and discussion

4.1. Observations

A word about the color of ionic liquids in general is relevant here. Since the work described in this paper involves using UV–Vis exclusively to monitor kinetics, it was important to be able to produce ionic liquids that are colorless. The ionic liquids used in this study can range from colorless to orange (in the case of [bmim]OTf), and the major difference seems to be temperature regulation during preparation. The reaction of 1-methylimidazole with bromoethane is rather exothermic, and the product [emim]Br will be colored yellow if the reagents are mixed together too rapidly. The use of an addition funnel helps reduce this problem. Furthermore, [emim]Br can be recrystallized from ACN and THF to form long, white needles. This recrystallization serves not only to remove the yellow impurity from the product but also to remove leftover methylimidazole. Removal of the yellow impurity at this stage in the ionic liquid synthesis is key because of the ability to recrystallize the halide precursor. The 1-butyl-3-methylimidazolium salts present a similar case. While the reaction of 1-methylimidazole with bromoethane goes to completion without additional heating, the same reaction with bromobutane requires heat to go to completion within a few hours. Excessive heating of the methylimidazole/bromobutane reaction mixture causes the mixture to turn dark yellow, but recrystallization can again be employed to isolate [bmim]Br as long, white needles.

Finally, the synthesis of [bmim]OTf merits special consideration because it does not proceed through a solid intermediate, and recrystallization of the product is not practical. The reaction of methyl triflate with 1-butylimidazole is highly exothermic and should be

performed at 0 °C with an appropriate solvent such as trichloroethane or ACN; an addition funnel should also be employed. The color of the product can range from pale yellow to dark red, depending on how much care is taken to control the reaction mixture's temperature. Stirring the ionic liquid with neutral alumina at least once is required to render the ionic liquid colorless.

Solvent purity is of utmost importance for success in making kinetic measurements on the MTO/peroxide system in room temperature ionic liquids. The starting materials 1-methylimidazole, 1-butylimidazole, and pyridine react with MTO to form yellow complexes. The influence of pyridine on the MTO/peroxide system has been thoroughly examined [33], and it is assumed that methylimidazole and butylimidazole present the same advantages (and problems) as those observed with pyridine, pyrazole, bipyridine, and related compounds.

Leftover bromide is much more problematic than leftover imidazole. Bromide is oxidized by both peroxorhenium complexes to hypobromite, which in turn forms hypobromous acid [37]. In the presence of excess peroxide, hypobromous acid catalyzes the disproportionation of hydrogen peroxide to molecular oxygen and water. When excess bromide is present, hypobromous acid reacts to form bromine, which reacts with the 1,3-dialkylimidazolium cations, possibly by brominating at the 2-position. It is important to remove all traces of halide from the ionic liquids, as only 1 mol% impurity in the ionic liquid gives an impurity concentration of 79 mM. However, treatment of the ionic liquids with a large excess of Ag(I) can be problematic as well, since Ag(I) is photosensitive and will cause the liquids to turn from colorless to brown. Careful titration of the appropriate amount of Ag(I) prevents excess silver from coloring the ionic liquids.

Finally, the presence and effects of dissolved salts, especially NaBF₄, in ionic liquids have been documented [19]. These salts are removed easily by redissolving the ionic liquids in dichloromethane, which causes the precipitation of the solid salt, and subsequent filtration.

The ionic liquid [bmim]PF₆ presents an interesting case. Since many reports have been published concerning different reactions employing [bmim]PF₆ as the solvent, including catalytic epoxidations [12], we thought to include it in our study of the MTO/peroxide chemistry in ionic liquids. Though it

is called “hydrophobic” since it is not miscible with water, the ionic liquid is actually hygroscopic, as pointed out by a few authors [17,19], and will form one phase when mixed with very small amounts of aqueous hydrogen peroxide. Additionally, our system requires the use of aqueous acid in order to stabilize the η^2 -peroxorhenium complexes, and this small amount of acid is also miscible with [bmim]PF₆. However, the presence of 0.10 M perchloric acid in [bmim]PF₆ apparently promotes the formation of HF, as evidenced by etching of the glass container in which the solution was temporarily stored for kinetics studies. This observation accords with a similar result recently described involving mixtures of PF₆⁻ with HNO₃ [38].

4.2. Kinetics

The kinetics and thermodynamics of this system were studied by monitoring the absorbance changes at 360 nm, the absorption maximum of dpRe. The spectrum of dpRe and MTO in [emim]BF₄ is given in Fig. 1.

The ionic liquids used in this study all have a slight absorbance at 360 nm in the absence of peroxide and MTO. This absorbance remains constant at least in the range of 330–500 nm, so good baselines can be

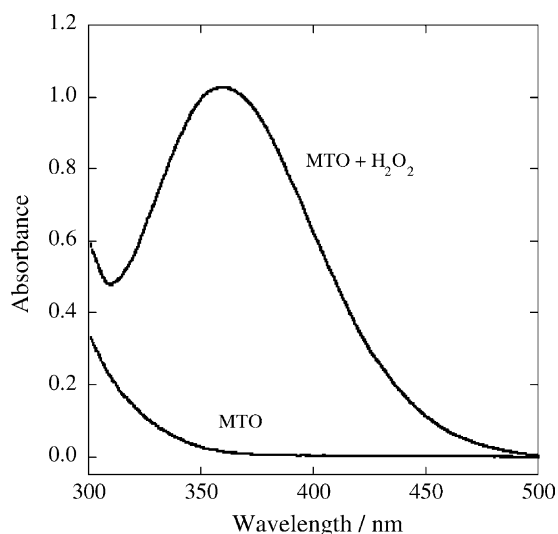


Fig. 1. UV-Vis spectrum of MTO and dpRe in [emim]BF₄. Conditions: 0.93 mM MTO, 42 mM H₂O₂, 0.10 M HClO₄, 23 °C.

obtained. However, the inherent absorbance at 360 nm changes dramatically with respect to water content, and the 1,3-dialkylimidazolium-based ionic liquids are known to be hygroscopic. Additionally, solutions of 30% hydrogen peroxide (70% water) were employed, and the reactions of MTO with peroxide themselves liberate two molecules of water per MTO. Therefore, for kinetic purposes, most of the experiments described here were done with at least 10% water (v/v) so as to maintain an essentially constant water concentration.

As pointed out earlier, the MTO/H₂O₂ system features the formation of two catalytically active peroxorhenium complexes. The rate constants k_1 and k_2 have been determined in a number of molecular solvents, including water [22], ACN [32], methanol [33], and nitromethane [33]. In aqueous solution, the reactions of MTO with hydrogen peroxide are so fast that they have to be studied using stopped-flow techniques. The kinetic profile of the reaction is biexponential, and absorbance changes at 305 nm (the λ_{\max} of mpRe) and at 360 nm have been used to determine k_1 and k_2 (80 and $5.2 \text{ M}^{-1} \text{ s}^{-1}$, respectively) [22]. In organic solvents, the reaction has been studied using conventional UV–Vis and also features biexponential traces.

Because of the viscosity of ionic liquids (generally > 60 cP), we decided against using stopped-flow techniques and resorted instead to conventional UV–Vis spectroscopy. Furthermore, the kinetics of the reaction in ionic liquids were studied exclusively at 360 nm because of the ionic liquids' absorbance at wavelengths below 330 nm. In ionic liquids, the absorbance change at 360 nm follows a single-exponential curve. It can be easily seen from the trace in Fig. 2 that the first part of the reaction, the formation of the mpRe complex, occurs extremely rapidly; at time = 0.0 s, the absorbance is already approximately 0.31. This first step is essentially completed at this stage. Hence, the reaction that is being monitored is described by the reversible process in Eq. (1), and the absorption data at 360 nm obeys Eq. (2), in which Abs_0 is the absorption at the initial dpRe concentration, that is $[\text{dpRe}]_0$, and Abs_e is the absorption at the equilibrium concentration $[\text{dpRe}]_e$. The rate expression for dpRe is given by Eq. (3) and the ratio for the equilibrium concentrations $[\text{dpRe}]_e$ and $[\text{mpRe}]_e$ by Eq. (4). With $[\text{mpRe}]_e + [\text{dpRe}]_e - [\text{dpRe}]$ in place of $[\text{mpRe}]$ and with the use of Eq. (4), integration of 3 leads to

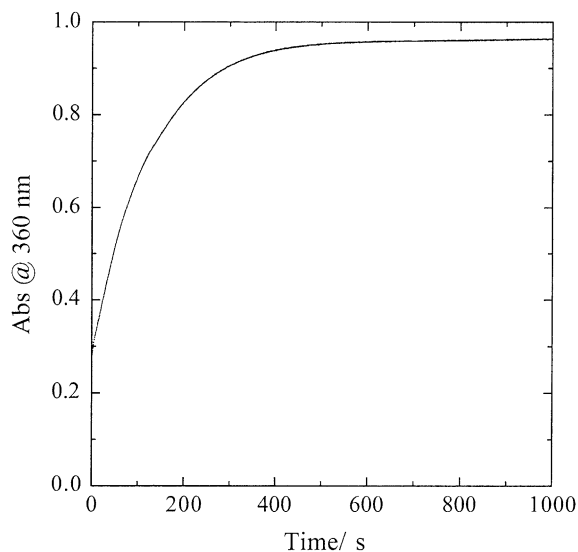
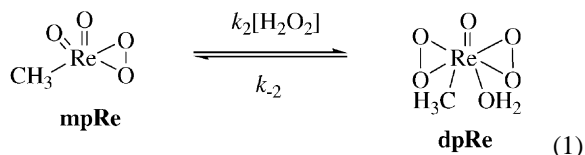


Fig. 2. Kinetic profiles of the reaction of MTO with aqueous hydrogen peroxide in CH₃CN and 9:1 [emim]BF₄:H₂O. Conditions: [MTO] = 0.85 mM, [HClO₄] = 0.100 M, [H₂O₂] = 42.6 mM, $T = 23^\circ\text{C}$.

Eq. (5). Equating the exponents in Eqs. (2) and (5) yields Eq. (6) for the observed pseudo constant k_ψ . Plots of k_ψ versus [H₂O₂] or [UHP] were then used to determine k_2 . A typical plot of k_ψ versus [H₂O₂] is given in Fig. 3. Even though the intercepts from the plots of k_ψ versus [H₂O₂] should, in principle, provide values for k_{-2} in different ionic media, the y-intercepts are significantly smaller than the corresponding slopes (Fig. 3), a fact that renders k_{-2} negligible within experimental precision. Therefore, decisive medium effects on the reversal process, k_{-2} , cannot be discerned.



$$\text{Abs}_t = \text{Abs}_e + (\text{Abs}_0 - \text{Abs}_e) \exp(-k_\psi t) \quad (2)$$

$$\frac{d[\text{dpRe}]}{dt} = k_2[\text{mpRe}][\text{H}_2\text{O}_2] - k_{-2}[\text{dpRe}] \quad (3)$$

$$\frac{[\text{mpRe}]_e}{[\text{dpRe}]_e} = \frac{k_{-2}}{k_2[\text{H}_2\text{O}_2]} \quad (4)$$

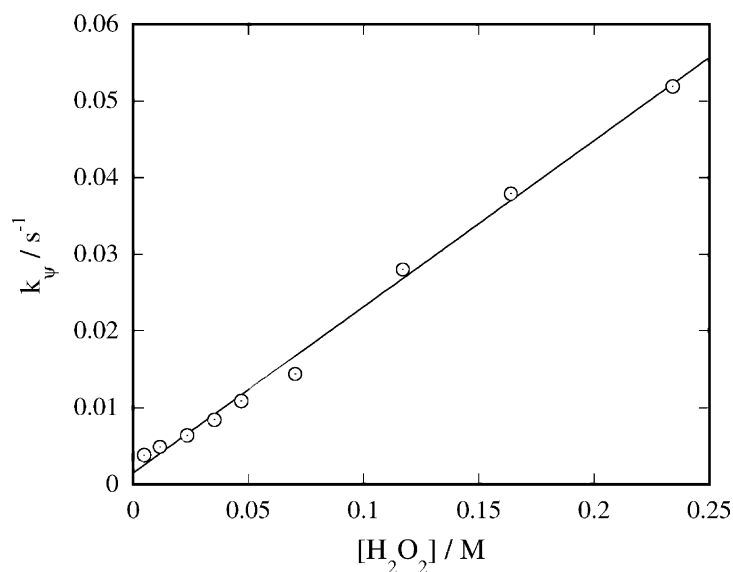


Fig. 3. Plot of aqueous H₂O₂ dependence in 9:1 [bmim]NO₃:H₂O. The slope gives k_2 , and the intercept gives k_{-2} . Conditions: 0.85 mM MTO, 0.10 M HClO₄, and 4.69–234 mM peroxide.

$$[\text{dpRe}] = [\text{dpRe}]_e + ([\text{dpRe}]_0 - [\text{dpRe}]_e) \times \exp\{-(k_2[\text{H}_2\text{O}_2] + k_{-2})t\} \quad (5)$$

$$k_\psi = k_2[\text{H}_2\text{O}_2] + k_{-2} \quad (6)$$

The kinetic treatment used to determine k_2 is based on the assumption that the formation of mpRe is completed before the time profiles for the formation of dpRe are obtained, but this treatment does not account for the fact that mpRe may not have reached

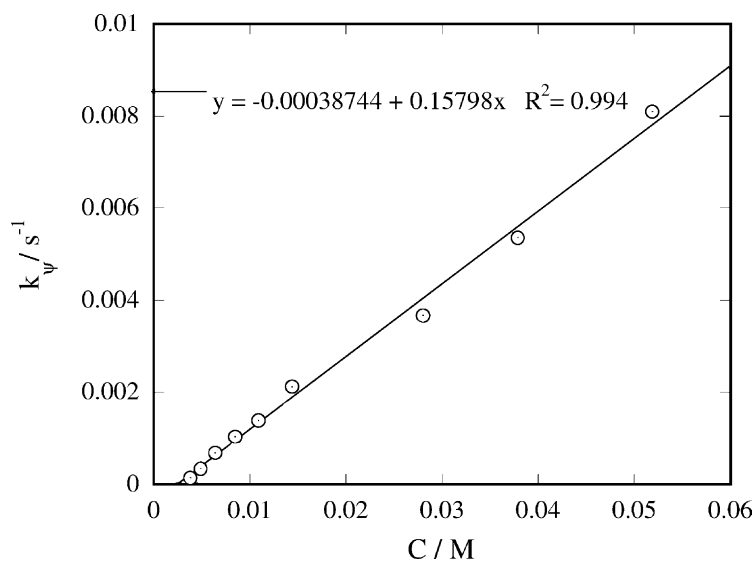


Fig. 4. Plot of k_ψ versus C (defined in text) for the reaction of MTO with aqueous hydrogen peroxide in 90% [bmim]NO₃. The slope gives k_2 . Conditions: 0.85 mM MTO, 0.10 M HClO₄, and 4.69–234 mM peroxide.

equilibrium. To verify the validity of this assumption, it is possible to determine k_2 using an expression that incorporates the equilibrium constants K_1 and K_2 , which are determined independently by thermodynamic titrations (vide infra). This treatment takes into consideration the possibility of incomplete reaction of MTO with H_2O_2 to form mpRe prior to the formation of dpRe. Assuming the reaction of MTO with H_2O_2 to be incomplete gives

$$k_\psi = k_2 \left\{ \frac{K_1[\text{H}_2\text{O}_2]^2}{1 + K_1[\text{H}_2\text{O}_2]} + \frac{1}{K_2} \right\} = k_2 C$$

Plotting k_ψ versus C gives a line whose slope is equal to k_2 . As shown in Fig. 4 for the case of 90% [bmim] NO_3 , the value of k_2 obtained is $0.16 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$. When the errors in the equilibrium constants K_1 and K_2 (Table 3) are considered, this value is essentially the same as $0.22 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$, the value that was obtained as described above (Eq. (6)). This result verifies the assumption that the first step of mpRe formation, that is $k_1[\text{MTO}][\text{H}_2\text{O}_2]$, is essentially complete prior to the formation of dpRe.

The rate constant k_2 was determined in a number of ionic liquids, ionic liquid/water mixtures, and salt solutions. Values of k_2 determined in 9:1 (v/v) solutions of ionic liquid/water with both aqueous hydrogen peroxide and UHP as oxidant are given in Table 1. Note that the rate constant k_2 was not determined for the reaction of MTO with UHP in [bupy] BF_4 because UHP is only slightly soluble in this ionic liquid.

The rate constant k_2 is the same for all five of the ionic liquids in Table 1. It is likely that this is so because of several combined factors, including the viscosity of the liquids, the coordination ability of the anion, and the hydrogen-bonding ability of the anion and cation. The dynamic viscosities of the

liquids in this study range from 66.5 cP ([emim] BF_4) to 154 cP ([bmim] BF_4) [19], and rate constants are expected to decrease with increasing solvent viscosity. However, the rate constants are small enough for this system that they are not diffusion-limited. The Stokes–Einstein equation can be used to estimate the diffusion-controlled rate constants (k_{dc}) in the investigated ionic media [39]. The values of k_{dc} at 298 K lie in the range of $\sim 1.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ for [emim] BF_4 and $\sim 4.3 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ for [bmim] BF_4 . So the viscosity of the ionic liquids is expected to have minor effects if any. The anion coordination ability is as follows: $\text{OTf} > \text{NO}_3^- > \text{BF}_4$. Higher anion coordination ability should lead to a decreased k_2 because the anion will interfere with peroxide binding to the rhenium. Finally, the hydrogen-bonding ability of both the anion and the cation (from the proton at the 2-position) may affect the kinetics by interacting with hydrogen peroxide and with the peroxide group on mpRe. However, all of these factors are expected to produce very subtle, minor effects and will not be taken up further.

It is interesting to note that the k_2 values are essentially independent of the form of hydrogen peroxide. UHP has been used previously to effect various oxidations with MTO [13,40,41], but its insolubility in organic solvents has precluded any kinetic studies to this point. The results in Table 1 are not particularly surprising considering that UHP is just a stable form of concentrated hydrogen peroxide.

In order to gain an understanding of how the high salt concentration of ionic liquids affects the kinetics of the MTO/hydrogen peroxide chemistry, it was necessary to obtain kinetic data in a number of concentrated salt solutions and compare that data to rate constants that have been determined previously in aqueous solution and organic solvents. These results are given in Table 2. The salts used for this study are [etpy] BF_4 (a solid at room temperature), [bmim] NO_3 (liquid), and [bmim] BF_4 . [etpy] BF_4 was chosen as a control because it is expected to have many of the same properties as all of the ionic liquids used in this study with respect to ion size, anion coordination ability, and hydrogen-bond donor (HBD) ability.

Comparing the rate constants in Table 2 shows several interesting points. First, the reaction in ionic liquids is much slower than in water. In the case of the pure ionic liquid without any added water (entry 4), k_2 is approximately 1% of that measured in

Table 1
Values of k_2 in 9:1 (v/v) solutions of ionic liquid:water^a

Ionic liquid	H_2O_2 , k_2 ($\text{l mol}^{-1} \text{ s}^{-1}$)	UHP, k_2 ($\text{l mol}^{-1} \text{ s}^{-1}$)
[emim] BF_4	0.20 ± 0.01	0.21 ± 0.01
[bmim] BF_4	0.23 ± 0.02	0.20 ± 0.01
[bmim] NO_3	0.22 ± 0.01	0.23 ± 0.01
[bmim]OTf	0.17 ± 0.02	0.20 ± 0.01
[bupy] BF_4	0.21 ± 0.01	–

^a Conditions: 0.10 M HClO_4 , 0.80 mM MTO, 5–250 mM peroxide, 10% water by volume, and $T = 23^\circ\text{C}$.

Table 2
Values of k_2 in various media

Entry	Solvent	k_2 ($M^{-1} s^{-1}$)	[H ₂ O] (M)
1	5.92 M [etpy]BF ₄ ^a	0.20	5.55
2	5.41 M [etpy]BF ₄ ^a	0.38	8.88
3	4.28 M [etpy]BF ₄ ^a	0.65	18.7
4	99% [bmim]NO ₃	0.053	0.555
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

^a The density for this salt was estimated to be 1.25 g/ml.

aqueous solution ($k_2 = 5.2 M^{-1} s^{-1}$ in 0.1 M HClO₄) [22]. Secondly, k_2 in 99% ionic liquid is essentially the same as k_2 in ACN ($0.045 M^{-1} s^{-1}$) [32]. This is not surprising since the polarity of ionic liquids has been estimated to be very similar to that of ACN and methanol [17].

It has been observed previously that the reaction rate of MTO with hydrogen peroxide decreases with increasing ionic strength [37]. This result seems particularly relevant to the present study, as ionic liquids themselves can be thought of as media with high salt

concentrations. However, relating reaction rates for the MTO/peroxide system strictly to solution ionic strength for these experiments is impractical for a few reasons. First, the effect of ionic strength alone on these reactions should not be very substantial, as all reactants and products are neutral. Secondly, these solutions have such high salt concentrations that all the ions are unlikely to be solvated by available water. Indeed, ion pairing must be considered at these high salt concentrations, and the extent of ion pairing versus ion solvation is difficult to estimate in this regime. For these reasons, relating the kinetic data to the activity of water is impractical as well.

It has been suggested that the acceleration in aqueous solution is attributable to the higher polarity of water and the possible involvement of water in the transition state [32]. Furthermore, the involvement of water in the reaction is clearly illustrated by its coordination to dpRe. The coordination of water onto mpRe has not been observed directly, but it is difficult to rule out since little structural information on mpRe is available.

In light of these phenomena, for kinetic purposes it is best to consider these concentrated salt solutions in terms of the concentration of water. For simplicity, [H₂O] for these experiments was calculated without

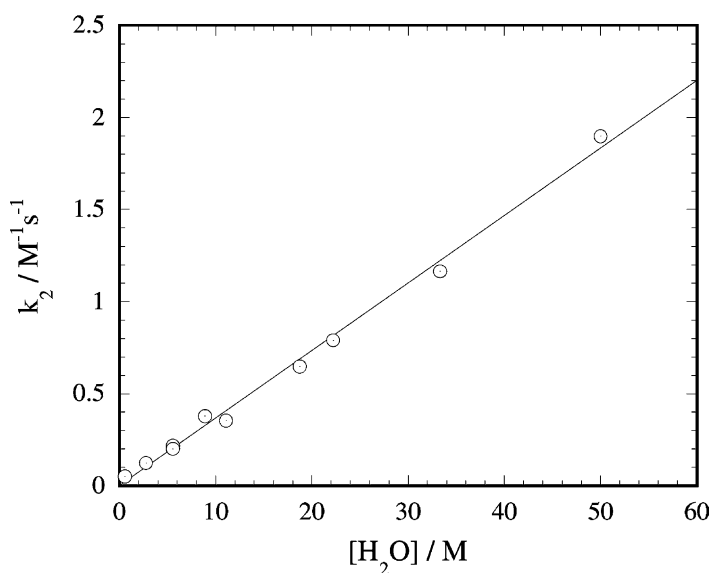


Fig. 5. Plot of k_2 versus [H₂O] for the reaction of MTO with aqueous hydrogen peroxide in various ionic liquids. Data is presented in Table 2.

Table 3

Peroxide binding constants for the MTO/H₂O₂ reaction in different solutions^a

Solvent	Form of H ₂ O ₂	<i>K</i> ₁	<i>K</i> ₂
H ₂ O ^b	30% aqueous H ₂ O ₂	16.1	132
CH ₃ CN ^c	30% aqueous H ₂ O ₂	209	660
[emim]BF ₄	30% aqueous H ₂ O ₂	49 ± 8	170 ± 29
[bupy]BF ₄	30% aqueous H ₂ O ₂	110 ± 17	140 ± 24
[bmim]BF ₄	30% aqueous H ₂ O ₂	74 ± 15	130 ± 28
[bmim]BF ₄	UHP	30 ± 10	220 ± 80
[bmim]NO ₃	30% aqueous H ₂ O ₂	28 ± 7	82 ± 20
[bmim]NO ₃	UHP	40 ± 5	50 ± 5
[bmim]OTf	30% aqueous H ₂ O ₂	34 ± 10	120 ± 30
[bmim]OTf	UHP	25 ± 12	210 ± 100

^a Ionic liquid samples are 10% water by volume. Conditions: 0.10 M HClO₄, 1.00 mM MTO, and 5.0–250 mM peroxide at 23 °C.

^b Ref. [22].

^c Ref. [32].

consideration to the contribution of water from aqueous hydrogen peroxide, since that contribution should be constant in all experiments. The data in Table 2 show that the rate constant *k*₂ increases as [H₂O] increases. A plot of *k*₂ versus [H₂O], Fig. 5, for all of the data in Table 2 shows that *k*₂ depends linearly on [H₂O]. This result provides strong evidence that the particular ionic liquids used in this study do not substantially affect the formation of dpRe; the most important consideration is the concentration of water.

4.3. Thermodynamics

The relationship of Abs₃₆₀ and [H₂O₂], derived using the equilibrium expressions for *K*₁ and *K*₂, is [22]:

$$\frac{\text{Abs}}{[\text{Re}]_{\text{T}}} = \frac{\varepsilon_{\text{A}} K_1 [\text{H}_2\text{O}_2] + \varepsilon_{\text{B}} K_1 K_2 [\text{H}_2\text{O}_2]^2}{1 + K_1 [\text{H}_2\text{O}_2] + K_1 K_2 [\text{H}_2\text{O}_2]^2}$$

where [Re]_T is the total concentration of Re species in the solution.

A nonlinear least-squares fit of the data using the above equation gives values for *K*₁ and *K*₂. The equilibrium constants *K*₁ and *K*₂ determined from the reaction of MTO with aqueous hydrogen peroxide and UHP in 9:1 (v/v) solutions of ionic liquid:water and in molecular solvents are given in Table 3.

The results of the thermodynamics experiments indicate the same general trends as the results from the kinetics. Ninety percent ionic liquid solutions tend to fall between water and ACN with respect to the equilibration of MTO with hydrogen peroxide. As expected, *K*₂ > *K*₁ for all cases, indicates cooperativity in peroxide binding [22]. Also, as expected, there is no appreciable difference in equilibrium constants for a particular ionic liquid when UHP is used instead of aqueous hydrogen peroxide.

The influence of water is not quite as dramatic for the equilibrium constants as it is for the

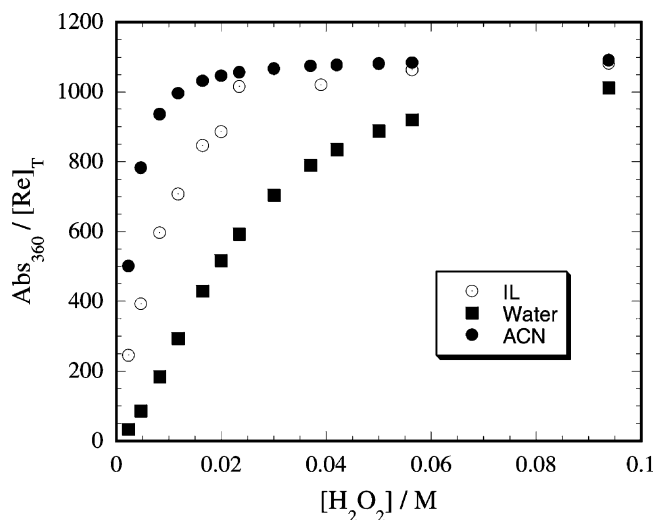


Fig. 6. Equilibration of MTO and H₂O₂. Data for H₂O and ACN are simulated based on known values for *K*₁ and *K*₂. Conditions for ionic liquid experiment: 1.03 mM MTO, 0.10 M HClO₄ in [emim]BF₄.

rate constant k_2 . The values for the reaction in vacuum-dried [emim]BF₄ are $K_1 = 110 \pm 28$ and $K_2 = 160 \pm 36$. When less water is present in the ionic liquids, the extent of peroxide binding cooperativity seems to be reduced, as is the case when the reactions are done in ACN. The plot shown in Fig. 6 contrasts the peroxide binding to MTO in ionic liquids, water, and ACN.

5. Conclusions

This work represents the first detailed study of the kinetics of a transition metal reaction in ionic liquids. With respect to formation constants and equilibrium constants of the MTO/H₂O₂ system, the water-miscible dialkylimidazolium and alkylpyridinium ionic liquids behave like ACN at low water concentrations. As [H₂O] increases, the liquids behave more like aqueous solutions with high salt concentrations. More studies of this nature are needed to determine the viability of ionic liquids as efficient reaction media. Current efforts in this lab are focused on determining the rate constants of catalytic reactions using the MTO/H₂O₂ system in ionic liquids.

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