

Catalytic Oxidations and Comparative Kinetics in Room-Temperature Ionic Liquids

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One of the major goals for chemists in the twenty-first century is the development of 'green' chemical transformations. Ionic liquids are new reaction media that could be utilized for various types of organic and organometallic reactions.<sup>1</sup> These media holds many advantages, such as high thermal stability and negligible volatility, over conventional noxious organic solvents. We have been interested in the use of ionic liquids as solvents for homogeneous transition metal-catalyzed processes, since the inefficient separation of costly catalysts from products hampers the utility of homogeneous catalysis in industrial settings. Our initial efforts have focused on developing a truly 'green' catalytic oxidation system that employs hydrogen peroxide, an environmentally friendly reagent since its only oxidation byproduct is water.

Alkenes and allylic alcohols have been epoxidized in ambient-temperature ionic liquids using methyltrioxorhenium (MTO) as a catalyst and urea hydrogen peroxide;<sup>2</sup> excellent conversions and selectivities for the epoxides of a wide number of substrates are observed. When aqueous hydrogen peroxide is used in place of the water-free urea hydrogen peroxide, olefin oxidation proceeds smoothly to give the diol rather than epoxide. Recovery of the organic products is achieved by a simple extraction step leaving the catalyst behind in the ionic media. The environmental advantages of this catalytic system are numerous.

Time-resolved <sup>2</sup>H NMR spectroscopy is used to monitor the progress of and gain kinetic information for a variety of reactions in different ionic media.<sup>3</sup> In our work <sup>2</sup>H NMR is used to monitor the progress of several fundamental organic reactions in protreated ionic liquids. Using deuterated reactants, one is able to directly and quantitatively monitor the conversion of reactants to products in real time. Using this method also allows for the detection and structural characterization of intermediates that accumulate to a reasonable concentration (mM) during the course of reaction. The required initial concentrations of the deuterated reactants for excellent signal to noise ratio is only around 10-50 mM in each case as long as an external standard is present as a reference for chemical shifts and integrations.

The kinetics and thermodynamics of the reaction of MTO with hydrogen peroxide in ambient temperature ionic liquids have been investigated.<sup>4</sup> The rate constant for the formation of the diperoxorhenium complex,

CH<sub>3</sub>ReO(h<sup>2</sup>-O<sub>2</sub>)<sub>2</sub>, from the monoperoxorhenium complex, CH<sub>3</sub>ReO<sub>2</sub>(h<sup>2</sup>-O<sub>2</sub>), and hydrogen peroxide in [bmim]NO<sub>3</sub> is 0.053 ± 0.002 L mol<sup>-1</sup> s<sup>-1</sup>. The equilibrium constants for the consecutive binding of two peroxo ligands to MTO have been determined in [emim]BF<sub>4</sub> to be K<sub>1</sub> = 110 ± 28 and K<sub>2</sub> = 160 ± 38 L mol<sup>-1</sup>. Similar rate 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 water concentration in the solvent. These results indicate that the ionic liquids behave like organic solvents when water is present at very low concentrations (mM), and like aqueous solutions of high salt concentrations when water is present in abundance (≥1.0 M).

<sup>1</sup> (a) T. Welton, *Chem. Rev.*, 1999, **99**, 2071. (b) M. M. Abu-Omar, "Green Chemistry" In *2002 McGraw-Hill Yearbook of Science & Technology*, McGraw-Hill: New York, 2001, pp 148-151.

<sup>2</sup> G. S. Owens and M. M. Abu-Omar, *Chem. Commun.*, 2000, 1165.

<sup>3</sup> A. Durazo and M. M. Abu-Omar, *Chem. Commun.*, 2002, in press.

<sup>4</sup> G. S. Owens and M. M. Abu-Omar, submitted for publication.

