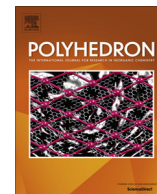




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Expanding the scope of gallium-catalyzed olefin epoxidation

Fraser Bronston, Sharon Ting, Qiao Zhang, Christian R. Goldsmith*

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, United States

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ABSTRACT

The broader use of Ga(III) complexes in the catalysis of olefin epoxidation was explored with a variety of studies. Two Ga(III) complexes with N-donor ligands were found to catalyze olefin epoxidation by peracetic acid in water. The stability of the catalyst more strongly influences the observed reactivity in water than in acetonitrile. Analysis of olefin epoxidation in buffered aqueous solutions indicates that either acidic or basic conditions are necessary for catalysis. The functional group tolerance was assessed using a variety of organic substrates. Alcohols, ketones, and alkylhalides survive the reaction conditions. Other common terminal oxidants were tested as possible replacements for peracetic acid but were not found to benefit from the presence of a Ga(III)-containing catalyst.

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1. Introduction

Much effort has been devoted to developing chemical processes capable of operating in water instead of an organic solvent [1,2]. The use of water as a solvent can potentially minimize the wastes generated by a reaction as well as its cost. Another key issue in reaction development is chemical selectivity. An ideal reaction will target a single type of chemical functionality on a substrate while leaving the remainder of the molecule unmodified. Improving the chemical selectivity also reduces waste by eliminating the need for additional steps to install and remove protecting groups and by minimizing the amounts of generated side-products.

Most reported homogeneous catalysts for olefin epoxidation are studied in organic solvents, such as acetonitrile (MeCN) [3]. The metal catalysts used in these studies generally are either unstable, insoluble, or otherwise non-functional in water [4,5]. Most reports of metal-catalyzed olefin epoxidation in solvent systems with high concentrations of water rely on simple salts [6,7]. In these systems, the structure of the catalytic species is ill-defined, with mixtures of oligonuclear complexes being implicated in some cases [6]. Furthermore, additives have been found to influence the reactivity strongly, possibly by significantly altering the composition of the catalyst [6,7]. A similar ambiguity with respect to the structure of the relevant catalyst was identified in a recent system that used a polyoxomolybdate “nanoball” to catalyze the epoxidation of olefins in water [8]. The regio- or stereoselective oxidation of alkenes is simply not feasible in water with these systems, given the possible agency of multiple oxidants and/or the lack of a ligand

capable of directing the catalyzed oxidation toward a specific product. Water-soluble iron complexes with porphyrin derivatives have been used to catalyze the asymmetric epoxidation of styrene derivatives in mixtures of water and methanol, but the activity is negligible in pure water [4]. A manganese-containing analog with the same porphyrin derivative has higher activity but produces epoxides with relatively low enantiomeric excesses [9]. The development of “green” olefin epoxidation reactions therefore remains a fertile area for exploration and improvement.

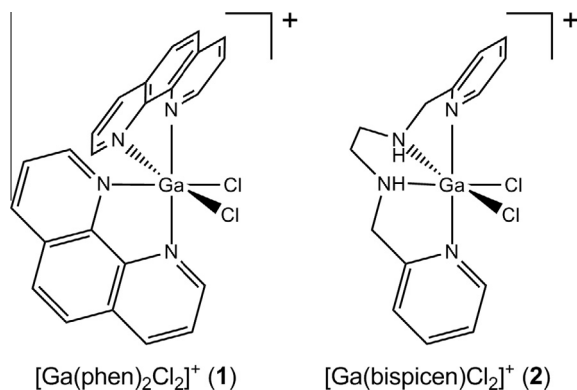
The functional group tolerance of olefin epoxidation can likewise be improved. Many first-row transition metal catalysts for olefin epoxidation are also capable of promoting allylic C–H activation and produce alcohols and ketones in addition to the target epoxides [9–13]. In rare circumstances, symmetric dihydroxylation is observed [14,15]. Other alkene epoxidation reactions can oxidize alcohols or amines in addition to C–C double bonds [16].

Recent work in our laboratory explored the use of gallium(III) complexes with N_4Cl_2 inner-spheres as catalysts for olefin epoxidation in MeCN (Scheme 1) [17–20]. In this chemistry, the activity was correlated to the electronic character of the ligand, with the most electron-poor ligands providing the best short-term activity [18]. The more highly chelating ligands better stabilize the $[GaN_4]^{3+}$ cores seemingly needed for catalysis. Although $[Ga(phen)_2Cl_2]Cl$ (**1**) led to greater yields of cyclohexene oxide from cyclohexene than $[Ga(bispiden)Cl_2]Cl$ (**2**) at 1 h, the two compounds have approximately equal activity when the oxidation reactions are allowed to proceed for 3 h [18]. At 1% mol loadings, both **1** and **2** are selective for the epoxide and do not promote C–H activation. At lower loadings, allylic C–H oxidation is observed for **1** but not **2**.

The Ga(III) complexes displayed excellent stability and solubility in water, with even the ethylenediamine complex $[Ga(en)_2Cl_2]$

* Corresponding author.

E-mail address: crgoldsmith@auburn.edu (C.R. Goldsmith).



Scheme 1.

Cl showing no sign of either ligand dissociation or speciation to $[\text{Ga}(\text{en})_3]^{3+}$ and $[\text{Ga}(\text{en})\text{Cl}_n]^{3-n}$ species in pure D_2O [18]. These properties encouraged us to assess the catalytic capabilities of **1** and **2** in aqueous solutions in the present work. We further investigated the functional group tolerance of **2**. Lastly, we performed a more systematic analysis of alternative terminal oxidants.

2. Materials and methods

2.1. Materials

Except where noted otherwise, chemicals were purchased from Sigma–Aldrich and used as received. Anhydrous acetonitrile (MeCN) was purchased from Acros Organics and stored in a glovebox free of moisture and oxygen. Hydrogen peroxide (H_2O_2 , 50% wt) was bought from Fisher. Iodosobenzene was purchased from TCI. Dry nitrogen (N_2) and oxygen (O_2) were purchased from Airgas. Chloroform-*d* (CDCl_3) and acetonitrile-*d*3 (CD_3CN) were bought from Cambridge Isotopes. *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen), $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}$ (**1**), and $[\text{Ga}(\text{bispicen})\text{Cl}_2]\text{Cl}$ (**2**) were prepared as previously described [17,18,21]. The purities of all materials were confirmed by ^1H nuclear magnetic resonance (NMR).

2.2. Preparation of custom-made peracetic acid (PA_R)

A more basic grade of peracetic acid (PA_R) that lacks the sulfuric acid impurity found in commercially available sources of PA was prepared through a modified version of a reported procedure [17,22]. At room temperature, 17 g of 50% H_2O_2 (0.25 mol) was slowly added to glacial acetic acid (150 g, 2.5 mol). After 5 min, 5.0 g of Amberlite IR-120 was added to the mixture and stirred for 24 h. The solution was subsequently filtered to remove the resin. The formation of PA was determined by ^{13}C NMR, and its concentration was determined by comparing the intensities of the PA and acetic acid resonance peaks. The solution was stored at -20°C when not in use. The content of PA was determined to be 6.6% (molar) by ^{13}C NMR analysis.

Caution: Peracids and mixtures of peroxides and organic solvents can potentially explode and should be handled with care. The dangers can be minimized by using small amounts of these materials, using proper protective equipment such as a blast shield, and working at lower temperatures.

2.3. Instrumentation

^1H and ^{13}C NMR spectra were recorded on either a 400 MHz or a 250 MHz AV Bruker NMR spectrometer at 295 K. Fischer Scientific

AB15 and Thermo Scientific Orion 3 Star pH meters were used to prepare and calibrate the described buffered aqueous solutions. A Thermo Scientific Trace GC Ultra Gas Chromatograph and Thermo Scientific TR-1 and TG-WAXMS columns were used for gas chromatography (GC). High-resolution mass spectrometry (HR-MS) data were collected at the Mass Spectrometer Center at Auburn University on a Bruker microflex LT MALDI-TOF mass spectrometer via direct probe analysis operated in the positive ion mode.

2.4. Reactivity

For the reactions performed in unbuffered water, the initial concentrations of Ga(III) catalyst, alkene, and peracetic acid were 5.0 mM, 500 mM, and 500 mM, respectively. The reactions were stirred vigorously at 298 K for 60 min, at which point methylene chloride (CH_2Cl_2) was added to extract the organic products and remaining alkene starting material. The extracts were filtered through a plug of silica gel to remove the metal complex and most of the PA and then analyzed by GC. This work-up was found to have a negligible impact on the ratios of the organic products and remaining starting material [17]. All reported numbers are the averages of at least three independent reactions. All error values and bars represent one standard deviation.

2.5. Study of pH-dependence on olefin epoxidation

The concentrations of the buffer components in each solution used in the variable pH study were 0.5 M. Acetic acid was used to buffer the pH 4.0 and pH 5.0 solutions. Piperazine-*N,N'*-bis(2-ethanesulfonic acid) (PIPES) was used for solutions buffered to pH 6.0. 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was used to prepare the pH 7.0 and pH 8.0 solutions. Boric acid was used in the pH 9.0 and pH 10.0 solutions. For all reactions catalyzed by **1**, the initial concentrations of catalyst, cyclohexene, and PA were 0.75 mM, 75 mM, and 151 mM, respectively. Reactions catalyzed by **2** had initial catalyst, cyclohexene, and PA concentrations of 0.85 mM, 85 mM, and 169 mM respectively. The reactions were stirred vigorously at 298 K for 60 min, at which point the organic products were extracted using CH_2Cl_2 . Extracts were filtered through a silica gel plug in order to remove residual Ga(III) catalyst and much of the PA. The samples were then immediately analyzed by GC; the immediate analysis was found to be critical for obtaining reproducible results.

3. Results and discussion

3.1. Catalysis of olefin epoxidation in water

Prior work from our laboratory found that Ga(III) complexes with N_4Cl_2 coordination spheres catalyze the oxidation of alkenes to epoxides in MeCN [17–19]. The compounds $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}$ (**1**) and $[\text{Ga}(\text{bispicen})\text{Cl}_2]\text{Cl}$ (**2**) were selected as representative examples of Ga(III) complexes with bidentate and polydentate N-donor ligands. Each compound has been structurally characterized [17,18]. Complexes **1** and **2** were subsequently tested for their ability to accelerate the epoxidation of alkenes by peracetic acid (PA) in water. A less acidic grade of PA was used in order to facilitate comparison to previously studied alkene epoxidations in acetonitrile (MeCN) [17–19]. All reactions occurred under air at ambient temperature and pressure. Previous reactions in MeCN were run under either air or N_2 , but the presence of O_2 and atmospheric moisture did not impact the reactivity to a significant degree [19].

Complex **2** was found to be an effective catalyst for the epoxidation of electron-rich substrates by PA (Table 1), and the high selectivity for the epoxide product that was previously observed in

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