Computational and Experimental Studies of Olefin Epoxidation by Hydrogen Peroxide Catalyzed by $[\gamma\text{-}(SiO_4)W_{10}O_{32}H_4]^{4-}$

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Introduction

Epoxidation of olefins - used to manufacture surfactants, epoxy resins and paints - by hydrogen peroxide has been one of the most researched processes in chemical industry [1]. Hydrogen peroxide has a high content of active oxygen and produces water as the only by-product. Polyoxometalates have been used as homogeneous catalysts for a wide variety of thermal organic substrate oxidations [2-3]. A large number of transition metal compounds including polyoxometalates (POM) has been used to catalyze homogeneous and heterogeneous epoxidation [4]. The Ishii-Venturello and closely related biphasic H_2O_2-based processes have been extensively examined [3-4]. Phosphotungstic acid, $H_3PW_{12}O_{40}$, was primarily used as a catalyst precursor, while several peroxotungstates and peroxophosphotungstates have been identified as reactive species in these systems. A divacant lacunary Keggin-type silicodecatungstate $[\gamma\text{-}(SiO_4)W_{10}O_{32}H_4]^{4-}$ (**1**) has been found to catalyze the epoxidation of olefins with 99% selectivity, 99% H_2O_2 utilization efficiency, and high stereospecificity while the catalyst is easily recovered [5]. Here we report detailed experimental and computational studies of this and analogous systems.
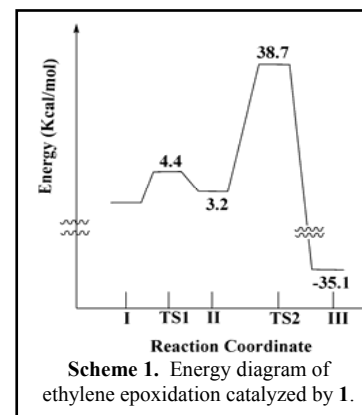
Materials and Methods

Experimental and computational procedures used in this work were similar to those of described earlier [5-6]. Simulation of the reaction kinetics was performed using a free Gepasi 3.3 software package (www.gepasi.org, [7-8]).

Results and Discussion

According to our B3LYP study, [6] compound **1** possesses four terminal hydroxyl ligands and therefore is formulated as $[\gamma\text{-}(SiO_4)W_{10}O_{28}(OH)_4]^{4-}$. The same formulation was used in this computational study, while C_2H_4 was utilized as a model olefin. Briefly, the following sequence of transformations has been found. First, H_2O_2 and C_2H_4 bond to **1** forming an intermediate I. In this complex, H_2O_2 forms strong hydrogen bonds with a W-OH hydroxy and a terminal W=O oxo group of **1**. Subsequent cleavage of an O-H bind in H_2O_2 results in formation of hydroperoxy W-O-OH species (intermediate II) and H_2O via a transition state TS1. This step has a relatively small barrier of 4.4 kcal/mol. The resulting W-O-OH species reacts with ethylene to form epoxide in a concerted fashion via a transition state TS2. TS2 lies 38.7 kcal/mol higher than complex I. The data are summarized on Scheme 1. We thought that a counter cation effect (ion-pairing) may decrease the activation barrier. Indeed, an explicit inclusion of Me_4N^+ as a model cation into the calculations decreases the barrier by 7.6 kcal/mol. However, we believe that the calculated activation barriers are too large to be consistent with a high catalytic activity of **1**. In experimental studies cyclooctene was used as

a model compound. Typically, the reaction was carried out in CH_3CN at 40 °C with 0.5-5.0 mM catalyst, 0.05-0.5 M H_2O_2 and 0.05-0.8 M olefin. The selectivity of cyclooctene epoxidation was >97% (ketone and alcohol were minor products), and the yield of cyclooctene oxide (based on hydrogen peroxide) was 95±3%. Importantly, the IR spectrum of the recovered catalyst is close to that of **1**. In general, these

data are consistent with those reported by Mizuno et al [5]. However, the reaction always proceeds with a *noticeable induction period*. Detailed kinetic studies revealed that the reaction rate (after induction period) increases with catalyst, olefin and hydrogen peroxide concentrations, and decreases with water concentration. Numerous attempts to fit all experimental data (even ignoring the presence of induction period) to the reaction mechanism based on calculations as depicted on Scheme 1 were unsuccessful. The presence of induction period may indicate a slow formation of reactive species. A premixing of catalyst with hydrogen peroxide (0.5-1.5 hr) either significantly decreases or completely eliminates the induction period, but does not affect the maximal reaction

Scheme 1. Energy diagram of ethylene epoxidation catalyzed by **1**.

rate. No decrease in induction period was observed if catalyst was premixed with water. Thus decomposition of **1** by hydrogen peroxide is implicated. Based on such a mechanism the reaction kinetics can be quantitatively fitted. So far, all experimental attempts to identify catalytic species were unsuccessful. However, we believe that low-molecular-weight peroxotungstates are likely involved.

Significance

The fast, highly selective H_2O_2-efficient epoxidation of olefins catalyzed by silicotungstates is more complex than previously thought and likely involves multiple low-molecular-weight catalytically active species.

References
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