Epoxidation of Olefins by Cobalt-Containing Polyoxotungstate and Potassium Monopersulfate in Aqueous Solution

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The controlled and selective epoxidation of olefins by metal complexes has been extensively studied to develop new synthetic methodologies for industrial applications.1 Often-used catalysts for the epoxidation reactions are metalloporphyrins, since these metal complexes as model compounds of heme-containing monooxygenase enzymes show high catalytic activity and selectivity under mild reaction conditions.2 However, a problem often encountered in the metalloporphyrin-catalyzed oxidation reactions is the deactivation of the catalytic species by the ring oxidation of porphyrin ligand. In order to solve the instability of the metalloporphyrins due to the porphyrin ligand degradation, an approach to prepare effective catalysts has been attempted to synthesize oxidatively resistant “inorganic porphyrin” analogues such as transition metal-substituted polyoxometalates.3 It has been proved that the polyoxometalates are resistant to oxidative degradation and that the catalytic systems are remarkably effective in various oxidation reactions.3 In the present study, we report that a cobalt-substituted polyoxotungstate, [Co(PW11O39)]6−, is a competent catalyst for the epoxidation of olefins by potassium monopersulfate (KHSO5) in buffered aqueous solution.3

Experimental Section

Materials. All chemicals obtained from Aldrich Chemical Co. were of the best available purity and used without further purification. Potassium monopersulfate, available as 2KHSO5·KH2O·2H2O·O3 (Oxone), was obtained from Aldrich. H2O2 (30%) and tert-butyl hydroperoxide (70%) were purchased from Fluka and Sigma, respectively. H318O (95% 18O enriched) was obtained from Aldrich Chemical Co. The polyoxotungstate Na-PW11O39 was prepared by a literature method.4 The transition metal-substituted polyoxotungstates used in this study were prepared from the reaction of corresponding metal salts and Na–PW11O39.6 CBZ-10,11-oxide (CBZ = carbamazepine) prepared as an authentic sample for the determination of product yields was synthesized by the published method.6

Instrumentation. HPLC analyses of the reaction solutions were performed on a Shimadzu 2000 high performance liquid chromatography equipped with a variable wavelength detector. Reaction mixtures were separated by using a C18 column, eluted by a mixture of methanol-water (70:30, v/v) at a flow rate of 1.2 mL/min. Detection was made at 215 nm. 18O analysis for H218O experiment was performed on VG70-VSEQ mass spectrometer (VG ANALYTICAL, UK) by using the electronic impact method at 70 eV.

Epoxidation of CBZ. In a typical experiment, KHSO5 (1 mM) was added to a reaction solution containing [Co(PW11O39)]6− (0.04 mM) and CBZ (1 mM, introduced as a 0.1 M solution in methanol) in buffered aqueous solution (5 mM). Reactions at pH 3 were performed in formate buffer (0.1 M), at pH 4-5 in acetate buffer (0.1 M), and at pH 6-7 in phosphate (0.1 M), and the pH of the reaction solutions was adjusted by adding either HCl (3 N) or NaOH (3 N) solutions whenever it was necessary. The reaction mixture was stirred for 30 min at room temperature and analyzed by HPLC. The yield of CBZ-10,11-oxide was determined by comparison with standard curves of the authentic CBZ-10,11-oxide.

Epoxidation of cis- and trans-Stilbenes. Epoxidation of cis-stilbene by varying pH of the reaction solution was performed in a solvent mixture (5 mL) consisting of buffered H2O (64%), CH3CN (16%), and CH3OH (20%) to make the reaction solution homogeneous. All reaction procedures were the same as described in the CBZ oxidation reaction except that cis-stilbene (1 mM) was used instead of CBZ.

Competitive epoxidation of cis- and trans-stilbenes were performed with a solution containing [Co(PW11O39)]6− (0.04 mM) and equal amounts of substrates (1 mM each, introduced as a 0.1 M solution in methanol) in a solvent mixture (5 mL) of 50% H2O (0.25 M acetate buffer, pH 5). 40% CH3CN, and 10% CH3OH at pH 5. After KHSO5 (1 mM) was added to the reaction mixture, the resulting solution was stirred for 30 min followed by the direct analysis with HPLC.

CBZ Epoxidation in Buffered H218O Solution. Isotopically labeled water experiment was run in a buffered solution (0.1 M formate consisted of 160 μL of H218O (95% 18O enriched) and 16 μL of H2O containing [Co(PW11O39)]6− (0.1 mM) and CBZ (0.5 mM). KHSO5 (0.5 mM) was added to the reaction solution, and the solution was stirred for 30 min at room temperature. The reaction solution was taken to dryness using a Speed-Vac. Then, CH3CN (160 μL) was added to the residue followed by filtration. 18O and 16O compositions in CBZ-10,11-oxide product were determined by the relative abundances of mass peaks at m/z = 252 for
Results and Discussion

The catalytic epoxidation of CBZ by KHSO₅ carried out in the presence of [Co(PW₁₀O₃₉)]⁶⁻ in buffered aqueous solution yielded the corresponding oxide product CBZ-10,11-oxide (eq. 1). The results in Figure 1 show that the yields of the oxide product varied depending on the pH of the reaction solutions, in which the yield of the oxide product was high at pH 5, whereas only small amounts of CBZ-10,11-oxide were yielded at low and high pHs (e.g., < pH 3 and > pH 6). The pH dependence of the reactions by metal complexes with terminal oxidants in aqueous solutions has been observed in metalloporphyrin-catalyzed oxidation reactions by H₂O₂, t-BuOOH, KHSO₅, and m-CPBA.⁶,⁷,¹¹,¹² Interestingly, other transition metal-substituted polynuclear complexes (M = Mn²⁺, Fe³⁺, Ni²⁺, and Cu²⁺) were ineffective in the CBZ epoxidations in the pH ranges of 3 to 8 under the reaction conditions employed. The formation of the oxide product was not detected in the absence of the cobalt complex, and other oxidants such as hydrogen peroxide and tert-butyl hydroperoxide did not yield the oxide product in the epoxidation of CBZ by [Co(PW₁₀O₃₉)]⁶⁻.

cis-Stilbene was also used as a substrate in a semi-aqueous solvent system (i.e., a solvent mixture of H₂O, CH₃OH, and CH₃CN) to make the reaction solution homogeneous. Interestingly, cis-stilbene oxide was yielded as a major product with trace amounts of trans-stilbene oxide and benzaldehyde formation, indicating that radical type of oxidation reactions was not involved in the epoxidation reaction (Table 1, entry 1).¹¹,¹² The conversion of cis-stilbene was also found to depend on the pH of the reaction solutions reaction (Figure 1). As observed in the CBZ epoxidation, high yields of the oxide product was obtained at pHs 5-6 and only small amounts of CBZ-10,11-oxide were yielded at low and high pHs (e.g., < pH 3.5 and > pH 7). In the epoxidation of trans-stilbene performed at pH 5, a high yield of trans-stilbene oxide was observed with the formation of a trace amount of benzaldehyde and no cis-stilbene oxide as well (Table 1, entry 2). Since it has been known that cis-stilbene is much more reactive than trans-stilbene in most oxidation reactions¹¹ and we found recently that, in certain cases, trans-stilbene is more reactive than cis-stilbene in iron porphyrin complex-catalyzed epoxidation reactions in aqueous and organic solvent systems,¹³ we compared the relative reactivities of cis- and trans-stilbenes by performing competitive reaction with these substrates and found that cis-stilbene was slightly more reactive than trans-stilbene in this cobalt complex-catalyzed epoxidation reaction (Table 1, entry 3).

In order to understand the structure of the intermediate responsible for the olefin epoxidations, we studied the CBZ epoxidation in buffered H₂¹⁸O solution, since isotopically labeled water, H₂¹⁸O, was often used as a mechanistic probe for the intermediacy of high-valent metal-oxo complexes in the catalytic oxygenation reactions of organic substrates.¹⁵ Especially, a number of recent reports showed that hydrocarbon oxygenations by metalloporphyrins carried out in buffered H₂¹⁸O solution afforded significant ¹⁸O-incorporation from the labeled water into products, suggesting that high-valent metal-oxo complexes are the oxygenating intermediates.⁴,⁹,¹³,¹⁴,¹⁵ By conducting the epoxidation of CBZ with [Co(PW₁₀O₃₉)]⁶⁻ and KHSO₅ in buffered H₂¹⁸O solution, we obtained result that there was no ¹⁸O-incorporation from the labeled water into the CBZ-10,11-oxide product (eq. 2). The absence of ¹⁸O-incorporation may rule out the possibility of the high-valent cobalt-oxo complex as an epoxidizing intermediate in the cobalt-mediated oxygen transfer reaction.

Table 1. Stereospecificity and Competitive Reactivity Studied with cis- and trans-Stilbenes in Olefin Epoxidations by [Co(PW₁₀O₃₉)]⁶⁻ and KHSO₅ at pH 5⁶

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>products (yields, mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cis-stilbene</td>
<td>0.43 (trace)</td>
</tr>
<tr>
<td>2</td>
<td>trans-stilbene</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>cis and trans-stilbene</td>
<td>0.19 (0.15)</td>
</tr>
</tbody>
</table>

⁶See experimental section for detailed experimental procedures. All reactions were run at least in triplicate and the data reported represent the average of these reactions. No or only a trace amount of benzaldehyde formation was observed. Less than 0.02 mM.

Figure 1. Plot of the percent yields of CBZ-10,11-oxide (•) and cis-stilbene oxide (○) vs pH of reaction solutions for the catalytic epoxidation reaction by [Co(PW₁₀O₃₉)]⁶⁻ and KHSO₅ in buffered aqueous solutions. Yields were calculated based on KHSO₅ added.
However, it may also be possible that a high-valent cobalt-oxo intermediate formed in the reaction of $\text{[Co(PW}_{12}\text{O}_{40}]^{3+}$ and $\text{KHSO}_4$ does not exchange its oxygen with labeled water since a binding site for water may not be available in the cobalt complex. Khenkin and Hill indeed showed that an isolated oxo-Cr(V) heteropolytungstate complex does not exchange its oxygen with water due to that the axial position opposite to the oxo group of the high-valent chromium-oxo species was not available for binding labeled water. Thus, blocking of the axial position prevents the oxygen exchange in the oxo-Co(V) heteropolytungstate complex. At this moment, two plausible epoxidizing intermediates such as $\text{PW}_{12}\text{O}_{40}\text{Co}^{-}$ and $\text{PW}_{12}\text{O}_{40}\text{Co}^{-}\text{O}^{-}$ are postulated. The former intermediate transfers an oxygen to olefins prior to O-O bond cleavage, and a number of recent studies suggested that oxygen atom transfer by this type of oxidants can occur in olefin epoxidations as well as in alkane hydroxylations.

The latter intermediate is the well-known high-valent metal-oxo complex, which has been widely proposed as an intermediate in metal complex-catalyzed oxidation reaction, and we have suggested recently that a high-valent cobalt-oxo porphyrin intermediate is a plausible hydroxylating species in the hydroxylation of alkanes by m-chloroperbenzoic acid catalyzed by an electron-deficient cobalt porphyrin complex.

In summary, we have shown that a water-soluble cobalt-substituted polyoxotungstate is an effective catalyst for the epoxidation of olefins by potassium monopersulfate in aqueous solution and that the reaction of the cobalt complex with the oxidant depends on the pH of reaction solution. On the basis of the results of the cis-stilbene epoxidation and radical scavenger reactions, we conclude that the olefin epoxidation does not occur via radical type of oxidation reactions.

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References
11. In order to ensure that the oxidant generated in the reaction of $\text{[Co(PW}_{12}\text{O}_{40}]^{3+}$ and $\text{KHSO}_4$ is distinct from those found in typical radical-type of oxidation reactions, we used common radical scavengers such as mannitol and tert-butyldihydroperoxide in the epoxidation of CBZ. The radical scavengers did not diminish the product yields, demonstrating again that the involvement of radical scavengers as an epoxidizing agent can be ruled out.