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 condition.[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, $[Co(PW_{11}O_{39})]^{5-}$, is a competent catalyst for the epoxidation of olefins by potassium monopersulfate ($KHSO_5$) in buffered aqueous solution.[4]

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 $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Oxone), was obtained from Aldrich. H_2O_2 (30%) and *tert*-butyl hydroperoxide (70%) were purchased from Fluka and Sigma, respectively. $H_2{}^{18}O$ (95% ^{18}O enriched) was obtained from Aldrich Chemical Co. The polyoxotungstate $Na_7PW_{11}O_{39}$ was prepared by a literature method.[5] The transition metal-substituted polyoxotungstates used in this study were prepared from the reaction of corresponding metal salts and $Na_7PW_{11}O_{39}$.[6] CBZ-10,11-oxide (CBZ = carbamazepine) prepared as an authentic sample for the determination of product yields was synthesized by the published method.[7]

Instrumentation. HPLC analyses of the reaction solutions were performed on Orom *Vintage* 2000 high performance liquid chromatography equipped with a variable wavelength detector. Reaction mixtures were separated by using 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. ^{18}O analysis for $H_2{}^{18}O$ 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, $KHSO_5$ (1 mM) was added to a reaction solution containing $[Co(PW_{11}O_{39})]^{5-}$ (0.04 mM) and CBZ (1 mM, introduced as a 0.1 M solution in methanol) in buffered aqueous solution (5 mL). 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 H_2O (64%), CH_3CN (16%), and CH_3OH (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.

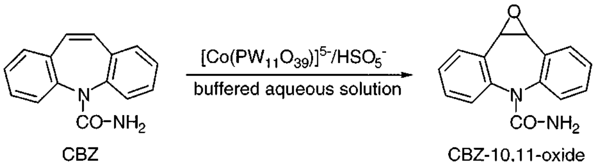
Competitive epoxidation of *cis*- and *trans*-stilbenes were performed with a solution containing $[Co(PW_{11}O_{39})]^{5-}$ (0.04 mM) and equal amounts of substrates (1 mM each, introduced as a 0.1 M solution in methanol) in a solvent mixture (5 mL) of 50% H_2O (0.25 M acetate buffer, pH 5), 40% CH_3CN, and 10% CH_3OH at pH 5. After $KHSO_5$ (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 $H_2{}^{18}O$ Solution. Isotopically labeled water experiment was run in a buffered solution (0.1 M formate consisted of 160 μL of $H_2{}^{18}O$ (95% ^{18}O enriched) and 16 μL of $H_2{}^{16}O$) containing $[Co(PW_{11}O_{39})]^{5-}$ (0.1 mM) and CBZ (0.5 mM). $KHSO_5$ (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, CH_3CN (160 μL) was added to the residue followed by filtration. ^{16}O and ^{18}O compositions in CBZ-10,11-oxide product were determined by the relative abundances of mass peaks at m/z = 252 for

^{16}O and m/z = 254 for ^{18}O. A control reaction for the stability of CBZ-10,11-oxide showed that the oxygen of CBZ-10,11-oxide did not exchange with labeled water under the reaction conditions.[8] Another control reaction for the oxygen exchange between $KHSO_5$ and $H_2{}^{18}O$ also indicated that oxygen exchange between $KHSO_5$ and $H_2{}^{18}O$ did not occur during the pre-incubation time.[8]

Results and Discussion

The catalytic epoxidation of CBZ by $KHSO_5$ carried out in the presence of $[Co(PW_{11}O_{39})]^{5-}$ 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 H_2O_2, *t*-BuOOH, $KHSO_5$, and *m*-CPBA.[7,8a,9,10] Interestingly, other transition metal-substituted polyoxotungstates (M = Mn^{2+}, Fe^{2+}, Ni^{2+}, and Cu^{2+}) 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 $[Co(PW_{11}O_{39})]^{5-}$.



(1)

cis-Stilbene was also used as a substrate in a semi-aqueous solvent system (*i.e.*, a solvent mixture of H_2O, CH_3OH, and CH_3CN) 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 reactions[13] 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,[14] 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).

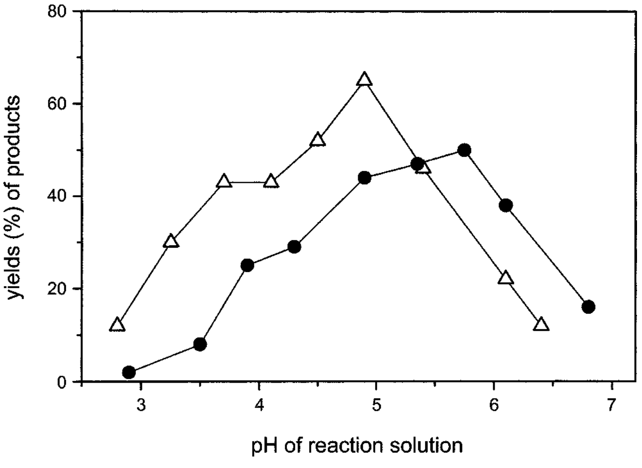


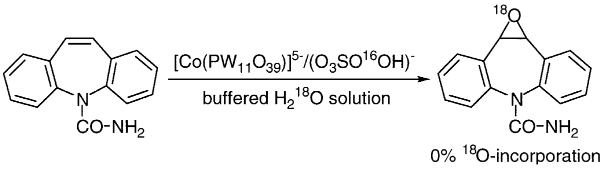
Figure 1. Plot of the percent yields of CBZ-10,11-oxide (△) and *cis*-stilbene oxide (●) *vs* pH of reaction solutions for the catalytic epoxidation reaction by $[Co(PW_{11}O_{39})]^{5-}$ and $KHSO_5$ in buffered aqueous solutions. Yields were calculated based on $KHSO_5$ added.

Table 1. Stereospecificity and Competitive Reactivity Studied with *cis*- and *trans*-Stilbenes in Olefin Epoxidations by $[Co(PW_{11}O_{39})]^{5-}$ and $KHSO_5$ at pH 5[a]

entry	substrate	products (yields, mM)[b]	
		cis-stilbene oxide	*trans*-stilbene oxide
1	*cis*-stilbene	0.43	trace[c]
2	*trans*-stilbene	0	0.32
3	*cis*- and *trans*-stilbene	0.19	0.15

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

In order to understand the structure of the intermediate responsible for the olefin epoxidations, we studied the CBZ epoxidation in buffered $H_2{}^{18}O$ solution, since isotopically labeled water, $H_2{}^{18}O$, 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 $H_2{}^{18}O$ solution afforded significant ^{18}O-incorporation from the labeled water into products, suggesting that high-valent metal-oxo complexes are the oxygenating intermediates.[4,7,8a,9a,10a] By conducting the epoxidation of CBZ with $[Co(PW_{11}O_{39})]^{5-}$ and $KHSO_5$ in buffered $H_2{}^{18}O$ solution, we obtained result that there was no ^{18}O-incorporation from the labeled water into the CBZ-10,11-oxide product (eq. 2). The absence of ^{18}O-incorporation may rule out the possibility of the high-valent cobalt-oxo complex as an epoxidizing intermediate in the cobalt-mediated oxygen transfer reaction.



(2)

However, it may also be possible that a high-valent cobalt-oxo intermediate formed in the reaction of $[Co(PW_{11}O_{39})]^{5-}$ and $KHSO_5$ does not exchange its oxygen with labeled water since a binding site for water may not be available in the cobalt complex.[16] Khenkin and Hill indeed showed that an isolated oxoCr(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.[16] Thus, blocking of the axial position prevents the oxygen exchange in the oxoCr(V) heteropolytungstate complex. At this moment, two plausible epoxidizing intermediates such $(PW_{11}O_{39})Co\text{-}HSO_5$ and $(PW_{11}O_{39})Co{=}O$ 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.[17] 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,[18] 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.[19]

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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