

# Epoxidation of olefins catalyzed by $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3[\text{PW}_4\text{O}_{16}]$ with molecular oxygen and a recyclable reductant 2-ethylanthrahydroquinone

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Received 19 June 2000; received in revised form 10 September 2000; accepted 10 September 2000

## Abstract

In the epoxidation system of  $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3[\text{PW}_4\text{O}_{16}]$ /molecular oxygen/recyclable reductant (2-ethylanthrahydroquinone), cyclohexene, terminal olefins and allyl chloride all underwent epoxidation reactions smoothly under mild conditions. Good selectivities to epoxides and high reductant utilization efficiencies (72.6–94.5%) were achieved. From 1-dodecene to 1-hexene, the epoxidation reactivity of the olefin and the utilization efficiency of the reductant increased with the decrease of carbon atoms in terminal olefins. Studies showed that  $\text{H}_2\text{O}_2$  produced by the oxidation of 2-ethylanthrahydroquinone with molecular oxygen was the key intermediate that afforded the direct epoxidation of the substrate. © 2001 Elsevier Science B.V. All rights reserved.

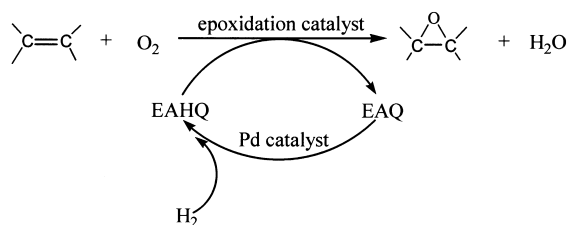
**Keywords:** Epoxidation; Molecular oxygen; Recyclable reductant (2-ethylanthrahydroquinone); Hydrogen peroxide

## 1. Introduction

Selective epoxidation of olefins with molecular oxygen is a great challenge to chemists for both academic and industrial interests. Unfortunately, direct epoxidation of olefins with dioxygen is difficult because of the poor selectivity under the conventional severe oxidation conditions. According to the catalytic oxidation model of cytochrome P-450, a reductant is needed in the epoxidation of olefins with dioxygen under mild conditions, just like the NAD(P)H in the above model [1,2]. Many compounds, such as  $\text{NaBH}_4$  [3–5],  $\text{H}_2$ -Pt [6,7], ascorbic acid [8,9] and zinc powder [10], have been used as reductants in the epoxidation of olefins with dioxygen catalyzed by metallo-

porphyrins, but the yields of the epoxides based on olefins and on reductants were both poor. In the 1990s, Mukaiyama and co-workers developed an epoxidation system with dioxygen, using aldehydes or alcohols as the reductants [11–14]. Sometimes the epoxides could be obtained quantitatively. But after the epoxidation reaction the reductant used was converted to its corresponding oxidation product (carboxylic acid), which could not be easily regenerated. Thus, the reductant was consumed and a large amount of less useful co-product was produced. At the same time, only a few less reactive terminal olefins or allyl chlorides have been tested and the results obtained were not so good. Terminal epoxides and epichlorohydrins are particularly important for the commodity chemicals [15,16]. Even for a reaction giving a quantitative yield of the epoxide based on the olefin, two or more equivalents of the reductant with respect to the olefin were needed

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in Mukaiyama's epoxidation system. Up to now, the yield of the epoxide based on the reductant (the utilization efficiency of the reductant) was still not higher than 50% in the reported molecular oxygen/reductants epoxidation systems.

Recently, we have reported on an epoxidation system, (heteropolyoxometalates catalyst/molecular oxygen/recyclable reductant (including 2-ethylanthrahydroquinone (EAHQ) and 2,3,5-trimethylhydroquinone)) [17]. The unique characteristic of this system is the use of a recyclable reductant. After the epoxidation reaction, the oxidation product of the reductant, for example 2-ethylanthraquinone (EAQ), can be easily regenerated to the original reductant via a simple catalytic hydrogenation and then can be reused (Scheme 1). Thus, only dioxygen, hydrogen and the olefin are consumed in the overall process and no co-products are formed from the reductant.

In the present work, as a part of our research on the catalytic epoxidation of olefins with dioxygen, various olefins, including cyclohexene, terminal olefins and allyl chloride, were tested as substrates in the epoxidation system of  $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3[\text{PW}_4\text{O}_{16}]$  (**M**)/molecular oxygen/EAHQ. The reaction mechanism of this epoxidation system was also investigated.

## 2. Experimental

Unless specially mentioned, the chemicals used in this work were at least of the C.P. grade and were used as purchased.

### 2.1. Preparation of **M**

A suspension of tungstic acid (2.50 g, 10 mmol) in 10 ml of 30% aqueous  $\text{H}_2\text{O}_2$  was heated to  $60^\circ\text{C}$  and stirred for 60 min. To the obtained colorless solution,

at room temperature, was added 85%  $\text{H}_3\text{PO}_4$  (0.29 g, 2.5 mmol) dissolved in 1 ml of water and the whole was diluted with another 20 ml of water and then stirred for 30 min. To the resultant solution, 1.80 g of cetylpyridiniumammonium chloride (5 mmol) in dichloromethane (40 ml) was added dropwise with stirring over about 2 min. Stirring was continued for an additional 60 min. The organic phase was then separated, dried over  $\text{Na}_2\text{SO}_4$ , filtered and distilled at  $50\text{--}60^\circ\text{C}$  (water bath) at atmospheric pressure. The dried yellow powder (85.0% yield by weight based on the quaternary ammonium salt charged) was obtained by further evaporating under reduced pressure. IR (neat, KBr plates) 3413, 2914, 2849, 1700, 1636, 1487, 1472, 1380, 1319, 1210, 1179, 1073, 934, 883, 777, 717, 683,  $541\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{63}\text{H}_{114}\text{O}_{16}\text{PN}_3\text{W}_4$ : C, 39.08; H, 5.95; N, 2.17. Found: C, 38.10; H, 6.07; N, 2.44. Determining of active oxygen showed that no peroxo bridge existed in the molecule [18].

### 2.2. Reaction and analysis

#### 2.2.1. Preparation of EAHQ

5.00 g of EAQ (ca. 20 mmol) was dissolved in the mixed solvent of 16 ml of toluene and 12 ml of tributylphosphate. Then in the presence of 0.1250 g of 5% Pd/C, hydrogenation was carried out at  $45^\circ\text{C}$  under 6 atm of  $\text{H}_2$ . The reaction was terminated when about 8–10 mmol of EAHQ was formed. The hydrogenation solution was then filtrated to remove Pd/C. The exact concentration of EAHQ was determined by chemical analysis<sup>1</sup> and the hydrogenation solution was stored under  $\text{N}_2$ .

#### 2.2.2. General procedure for the epoxidation of olefins with $\text{O}_2$

In a glass reactor, 0.0968 g of the epoxidation catalyst **M** (0.05 mmol), 2.46 g of cyclohexene (30 mmol) and a certain volume of the hydrogenation solution containing 10 mmol of EAHQ were mixed. Then 1 atm of  $\text{O}_2$  was introduced. The reaction was maintained at

<sup>1</sup> At room temperature, EAHQ can be oxidized completely with  $\text{O}_2$  to EAQ. At the same time quantitative  $\text{H}_2\text{O}_2$  is produced. The amount of  $\text{H}_2\text{O}_2$  can be titrated using the classical  $\text{KMnO}_4$  method. Thus, the exact concentration of EAHQ in the hydrogenation solution can be obtained.

Table 1  
Epoxidation of olefins catalyzed by **M** with O<sub>2</sub> and EAHQ at 35°C<sup>a</sup>

Entry	Substrate	Time (h)	Based on EAHQ		Based on the olefin	
			Conversion (%)	Yield (%)	Conversion (%)	Selectivity (%)
1	Allyl chloride	8		0		
2	1-Dodecene	15	82.8	74.4	27.6	89.8
3	1-Octene	14	100	83.4	33.6	82.7
4	1-Hexene	13	98.4	88.5	32.8	90.0
5	Cyclohexene	2.5	100	93.0	34.0	91.2

<sup>a</sup> Reaction conditions: hydrogenation solution containing 10 mmol of EAHQ, olefin:EAHQ:**M** = 600:200:1 (molar ratio), 1 atm of O<sub>2</sub>, 35°C.

35°C with vigorous stirring for 2.5 h. After the reaction, the reaction solution was analyzed by GC with the internal standard method. Gas chromatographic analyzes were performed with a SF-102 gas chromatograph equipped with FID and columns filled with SE-30.

A similar procedure was employed for the epoxidation of 1-hexene, 1-octene, 1-dodecene and allyl chloride.

### 3. Results and discussion

The results of the epoxidation of various olefins in the epoxidation system of **M**/O<sub>2</sub>/EAHQ at 35°C are shown in Table 1.

Under the reaction conditions employed, no epoxidation reaction occurred even after 8 h when allyl chloride was used as the substrate (entry 1). Comparing with the epoxidation results of terminal olefins having different carbon atoms, the yield of the epoxide based on EAHQ went up from 74.4 to 88.5% with the decrease of carbon atoms from 1-dodecene to 1-hexene (entries 2–4), while at the same time the reaction time required to reach maximum yield of the epoxide, based on EAHQ, dropped from 15 to 13 h, as shown in Fig. 1. These indicate that both the epoxidation reactivity of the olefin and the epoxidation results were enhanced with the decrease of carbon atoms from 1-dodecene to 1-hexene in this epoxidation system. Thus, the epoxidation reactivity follows the sequence: 1-dodecene < 1-octene < 1-hexene.

For cyclohexene, epoxidation exhibited the highest epoxide yield (93.0%, based on EAHQ) and the shortest reaction time required (2.5 h, entry 5).

Comparing with the results at 35°C, the epoxidation results at 45°C for various olefins were very similar, as shown in Table 2. After 8 h at 45°C, there was also no epichlorohydrin detected for the epoxidation of allyl chloride (entry 1). With regard to terminal olefins, elevating of the reaction temperature reduced the disparities in the reaction time required, due to the difference of epoxidation reactivities of terminal olefins. But from 1-dodecene to 1-hexene, the yield of the epoxide, based on EAHQ, also rose from 72.6 to 94.5% (entries 2–4). The epoxidation of cyclohexene resulted in 92.7% of epoxide yield based on EAHQ after 1.5 h (entry 5).

Since the molar ratio between the substrate and EAHQ of all the reactions listed in Tables 1 and 2 was 3:1, the theoretical maximum conversion of the olefin was 33.3%. So the resulting conversions of

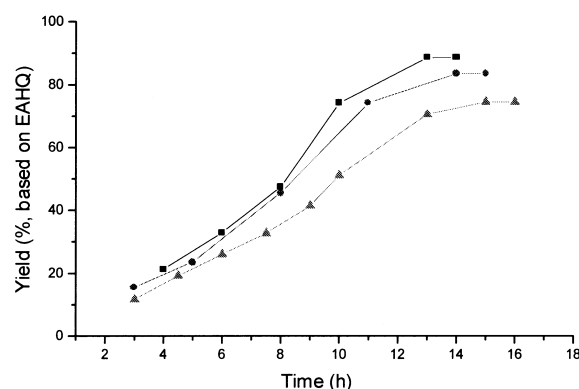


Fig. 1. Influence of reaction time on the epoxidation of terminal olefins catalyzed by **M** with O<sub>2</sub> and EAHQ at 35°C. Reaction conditions are all the same as those in Table 1, square: 1-hexene, circle: 1-octene, triangle: 1-dodecene.

Table 2  
Epoxidation of olefins catalyzed by **M** with O<sub>2</sub> and EAHQ at 45°C<sup>a</sup>

Entry	Substrate	Time (h)	Based on EAHQ		Based on the olefin	
			Conversion (%)	Yield (%)	Conversion (%)	Selectivity (%)
1	Allyl chloride	8		0		
2	1-Dodecene	7	86.4	72.6	28.8	84.0
3	1-Octene	7	93.3	79.2	31.1	84.9
4	1-Hexene	7	100	94.5	34.0	92.6
5	Cyclohexene	1.5	100	92.7	34.0	90.9

<sup>a</sup> Except for the reaction temperature (45°C), other reaction conditions are the same as those in Table 1.

the olefins based on the olefins (27.6–34.0%) were high. At the same time good epoxide selectivities (82.7–92.6%) and high olefin conversions based on EAHQ (82.8–100%) were obtained. Thus, high yields of the epoxides based on EAHQ (72.6–94.5%) were achieved in the epoxidation system of **M**/molecular oxygen/EAHQ. This is another characteristic of this new epoxidation system, with which high utilization efficiency of the reductant, which is much higher than 50%, could generally be obtained.

The reaction mechanism of the epoxidation system of **M**/molecular oxygen/EAHQ was also studied. The question usually raised is that whether the epoxidation of the olefin comes from the concerted interaction of EAHQ, molecular oxygen and the olefin with catalyst **M** or molecular oxygen interacts with the reductant EAHQ at first to give H<sub>2</sub>O<sub>2</sub> then the olefin undergoes the epoxidation reaction with the help of

the epoxidation catalyst **M**. So it is important to investigate whether H<sub>2</sub>O<sub>2</sub> plays an important role or not in this epoxidation system. The experiments and results are summarized in Table 3. In entry 2, the hydrogenation solution containing EAHQ was oxidized with O<sub>2</sub> at 35°C at first to give EAQ and H<sub>2</sub>O<sub>2</sub>. After cutting off of the O<sub>2</sub>, cyclohexene and **M** were added and the epoxidation reaction was carried out at 35°C for 2.5 h. The epoxidation results thus obtained were just the same as those achieved from the ‘normal’ procedure (entry 1). If 30% aqueous H<sub>2</sub>O<sub>2</sub> was directly used as the oxidant, similar conversion of cyclohexene was obtained under the same reaction conditions, but the selectivity of cyclohexene oxide dropped from 94.0 to 87.6% (entry 1 versus 3). When the reaction temperature was decreased to 20°C, similar dropping of the selectivity was found (entry 5 versus 6). This decrease in selectivity may be due to the existence

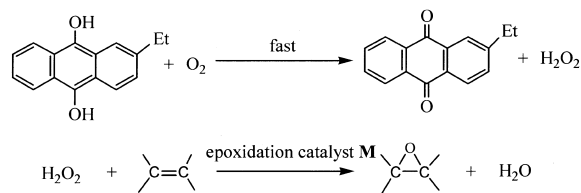
Table 3  
Influence of different oxidants on the epoxidation of olefins

Entry	Substrate	Oxidant	<i>t</i> (°C)	Time (h)	Based on EAHQ or H <sub>2</sub> O <sub>2</sub>		Based on the olefin	
					Conversion (%)	Yield (%)	Conversion (%)	Selectivity (%)
1	Cyclohexene <sup>a</sup>	O <sub>2</sub>	35	2.5	99.3	93.3	33.1	94.0
2	Cyclohexene <sup>b</sup>	O <sub>2</sub>	35	2.5	99.3	93.6	33.1	94.2
3	Cyclohexene <sup>c</sup>	30% H <sub>2</sub> O <sub>2</sub>	35	2.5	98.4	86.2	32.8	87.6
4	Cyclohexene <sup>c</sup>	15% H <sub>2</sub> O <sub>2</sub>	35	2.5	100	72.0	34.1	70.4
5	Cyclohexene <sup>a</sup>	O <sub>2</sub>	20	8	96.6	87.3	32.2	90.4
6	Cyclohexene <sup>c</sup>	30% H <sub>2</sub> O <sub>2</sub>	20	8	97.2	77.2	32.4	79.4
7	1-Hexene <sup>a</sup>	O <sub>2</sub>	35	13	98.4	88.5	32.8	90.0
8	1-Hexene <sup>c</sup>	30% H <sub>2</sub> O <sub>2</sub>	35	13	100	90.8	33.8	89.6

<sup>a</sup> Except for the reaction temperature, other reaction conditions are the same as those in Table 1.

<sup>b</sup> Hydrogenation solution containing EAHQ was oxidized with O<sub>2</sub> completely at 35°C to give H<sub>2</sub>O<sub>2</sub>, then O<sub>2</sub> was switched off, cyclohexene and **M** were added to the solution and the epoxidation reaction was carried out at 35°C. The other reaction conditions are the same as those in Table 1.

<sup>c</sup> O<sub>2</sub>/EAHQ was replaced by aqueous H<sub>2</sub>O<sub>2</sub>. Except for the reaction temperature, other reaction conditions are the same as those in Table 1.



Scheme 2.

of water in the aqueous  $\text{H}_2\text{O}_2$ , which could make the cyclohexene oxide (very sensitive to water) to be hydrolyzed. When more diluted aqueous  $\text{H}_2\text{O}_2$  (15%) was used, the selectivity of cyclohexene oxide decreased further to 70.4% (entry 4). If 1-hexene was used as the substrate, no notable difference was found between the epoxidation results using  $\text{O}_2/\text{EAHQ}$  or 30% aqueous  $\text{H}_2\text{O}_2$  as the oxidants (entry 7 versus 8). This can be explained as that 1,2-epoxyhexane is stable enough towards water under the reaction conditions employed. From the above results and discussion, it can be concluded that  $\text{H}_2\text{O}_2$  produced from the oxidation of EAHQ with molecular oxygen is the key intermediate in the epoxidation system of **M**/molecular oxygen/EAHQ, which affords the direct epoxidation of the substrate. The reaction mechanism can be illustrated as follows (Scheme 2).

It can also be concluded that this epoxidation system might be much advantageous for the preparation of the epoxides which are sensitive to water, such as cyclohexene oxide and so on.

Since  $\text{H}_2\text{O}_2$  is the key intermediate for the epoxidation of the olefin in the epoxidation system of **M**/molecular oxygen/EAHQ, then the epoxidation reaction temperature employed can be much higher than the permitted temperature of EAHQ oxidation<sup>2</sup> [19,20]. This elevated temperature can be of great help for the epoxidation of the inactive allyl chloride. For example, the hydrogenation solution containing 10 mmol of EAHQ was oxidized with  $\text{O}_2$  at 35°C at first to give  $\text{H}_2\text{O}_2$ , then 25 mmol of allyl chloride and 0.13 mmol of catalyst **M** were added and the epoxidation reaction was run at 75°C for 1.5 h. A

<sup>2</sup> During the industrial 2-ethylanthraquinone process for the production of  $\text{H}_2\text{O}_2$ , the temperature in the oxidation step is usually controlled (usually < 55°C) to avoid the decomposition of  $\text{H}_2\text{O}_2$  and to prevent the side reaction between  $\text{H}_2\text{O}_2$  and EAHQ at catalytic sites. See references [19,20].

Table 4

The reusing of EAHQ for the epoxidation of cyclohexene catalyzed by **M** with air and EAHQ<sup>a</sup>

Use times of EAHQ <sup>b</sup>	Based on EAHQ		Based on cyclohexene	
	Conversion (%)	Yield (%)	Conversion (%)	Selectivity (%)
1	97.8	90.8	39.1	92.9
2	99.8	91.3	39.9	91.5
3	95.0	90.4	38.0	95.2

<sup>a</sup> For the preparation of EAHQ, mixed trimethylbenzenes was employed instead of toluene. A certain volume of the hydrogenation solution containing 10 mmol of EAHQ was oxidized by air (1 atm) at 35°C with vigorous stirring until a bright yellow solution was obtained. After switching off of the air, 0.0242 g of epoxidation catalyst **M** (0.0125 mmol) and 2.14 g of cyclohexene (industrial purity, 96% GC, 25 mmol) were added, and the epoxidation reaction was carried out at 70°C with stirring for 3 h.

<sup>b</sup> The epoxidation catalyst **M** was soluble in the reaction solution. After the epoxidation reaction, it precipitated from the reaction solution, which was then removed. Then the unconverted cyclohexene and the product cyclohexene oxide were recovered by distillation. EAHQ was then regenerated according to the preparation conditions of EAHQ described in the experimental section.

93.5% conversion of the allyl chloride and a 80.5% yield of epichlorohydrin (both based on EAHQ) were achieved. This good result manifests another unique feature of this epoxidation system. When the aqueous  $\text{H}_2\text{O}_2$ , instead of  $\text{O}_2$ , was used directly as the oxidant, at 75°C similar epoxidation results were obtained for the epoxidation of allyl chloride.

Under these conditions, EAHQ was oxidized to EAQ completely after the reaction. After separation of the unconverted olefin, the product and the epoxidation catalyst **M**, EAQ (together with the mixed solvent) could be easily hydrogenated over a Pd/C catalyst to regenerate the EAHQ for recycle uses. Results in Table 4 show that there is no significant influence on the conversion and selectivity of the epoxidation of cyclohexene in the system of **M**/molecular oxygen/EAHQ after recycling.

#### 4. Conclusions

In the epoxidation system of **M**/molecular oxygen/EAHQ, various olefins (including cyclohexene, 1-hexene, 1-octene, 1-dodecene and allyl chloride) underwent epoxidation reactions smoothly under mild conditions. Good selectivities (82.7–92.6%) and high

yields of epoxides (based on EAHQ, 72.6–94.5%) were achieved. The utilization efficiencies of the reductant were all much higher than 50%. It was also found that from 1-dodecene to 1-hexene, the epoxidation reactivity of the olefin and the yield of the epoxide based on EAHQ increased with decrease of the carbon atoms in the terminal olefins. The results showed that H<sub>2</sub>O<sub>2</sub> produced by the oxidation of EAHQ with molecular oxygen was the key intermediate that afforded the direct epoxidation of the substrate.

### Acknowledgements

The authors acknowledge the National Nature Science Foundation of China for the financial support of this research (No. 29673042). Y. Sun is grateful to Dr. M. Ricci of EniChem for the provision of the detailed procedure for determining active oxygen in the epoxidation catalyst **M**.

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