

Letter

Direct epoxidation of olefins catalyzed by heteropolyoxometalates with molecular oxygen and recyclable reductant

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Received 8 January 2000; received in revised form 6 February 2000; accepted 25 February 2000

Abstract

A new epoxidation system is reported in this communication. Heteropolyoxometalates catalyst/recyclable reductant — 2-ethylanthrahydroquinone/O₂ is employed for epoxidation of olefins. The reductant can be regenerated by catalytic hydrogenation without consumption. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Epoxidation; Heteropolyoxometalate; Molecular oxygen; Reductant; 2-Ethylanthrahydroquinone

1. Introduction

Epoxides are useful intermediates. It is widely used for petrochemicals, fine chemicals and polymers. Except ethylene, direct catalytic epoxidation of olefins with high selectivity by molecular oxygen is difficult, because side reactions occur obviously under conventional severe reaction conditions. Selective epoxidation under mild conditions usually needs the presence of a reductant to accept one oxygen atom from the dioxygen molecule. When porphyrin complexes are used as catalysts, many reductants such as NaBH₄ [1], zinc powder [2], H₂-Pt [3] and ascorbic acid [4,5] are reported. But the utilization efficiencies of all these reductants are low (generally < 50%). Groves and Quinn [6,7] and Groves and Ahn [8] reported an epoxidation system without any reductants, with Ru^{VI}(TMP)(O)₂

(TMP=tetramesitylporphyrin) as catalyst some olefins could be epoxidized by molecular oxygen, but the reaction rate is too slow and the catalyst is not stable enough. Mukaiyama and Yamada [9] reported a method with high yield for epoxidation of olefins catalyzed by β-diketone metal complexes with O₂ and with an aldehyde as the reductant. In 1993, Hamamoto [10] used heteropolyoxometalate as catalyst for epoxidation of olefins with O₂ in the presence of an aldehyde. In the reaction, aldehyde is completely oxidized to acid, and large amount of reductant is consumed, with a lot of co-products produced. Yamanaka et al. [11,12] reported a system for epoxidation of propylene with EuCl₃ as catalyst and Zn in CH₃COOH as reductant, the selectivity for propylene oxide is high, but the yield and the utilization efficiency of Zn are low.

In this communication, we report a new method for selective epoxidation of olefins catalyzed by

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Table 1
Catalytic epoxidation of cyclohexene with O₂ and the reductant

Reductant	Conversion ^a (%)	Selectivity ^a (%)
TMHQ ^b	14.2	85.0
EAHQ ^c	25.2	94.0

^aConversion and selectivity are based on cyclohexene.

^bOxidation conditions: cyclohexene 30 mmol, TMHQ 20 mmol, mixed solvent 15 ml, epoxidation catalyst J 0.07 mmol, 45°C, 1 atm O₂, 5 h.

^cCyclohexene 30 mmol, EAHQ about 10 mmol, mixed solvent 23.5 ml, epoxidation catalyst J 0.07 mmol, 1 atm O₂, 35°C, 3.5 h.

heteropolyoxometalates catalysts with molecular oxygen and a recyclable reductant — hydroquinone. Oxidized hydroquinone can be regenerated through catalytic hydrogenation. Thus, the reductant will not be consumed and no co-product is produced by this method.

2. Results and discussion

Table 1 shows the results of the epoxidation of cyclohexene catalyzed by $[\pi\text{-C}_5\text{H}_5\text{NC}_{14}\text{H}_{29}]_7[\text{PW}_{12}\text{O}_{42}]\cdot x\text{H}_2\text{O}$ (J) with molecular oxygen and with trimethylhydroquinone (TMHQ) or 2-ethylanthrahydroquinone (EAHQ) as the reductant. Because the solubility properties of quinone and hydroquinone are quite different, a mixed solvent containing aromatics and alcohols or esters is usually employed for this system. For instance, a mixed solvent of trimethylbenzenes and trioctylphosphate is used commercially for the hydrogenation–oxidation recycle system

Table 3

The reusing of EAHQ for epoxidation of cyclohexene with O₂ by catalyst L. Reaction conditions: Cyclohexene 30 mmol, EAHQ about 10 mmol, mixed solvent 23.5 ml, epoxidation catalyst J 0.07 mmol, 1 atm O₂, 35°C, 3.5 h

Using times	Conversion (%)	Selectivity (%)
1	34.7	96
2	35.1	95
3	33.7	95

of 2-ethylanthraquinone (EAQ)/2-ethylanthrahydroquinone. This kind of mixed solvent is also suitable for our reaction system.

The conversion and the selectivity of epoxidation of cyclohexene with EAHQ were obviously higher than that with TMHQ. Thus, EAHQ was chosen as the reductant for investigation of the epoxidation performance of several heteropolyoxometalates catalyst.

Table 2 shows that the epoxidation reaction did not take place in the absence of catalyst. The catalytic performance of J (containing W) is better than that of K (containing Mo). The molar ratio of EAHQ to cyclohexene added in the reaction system is 1:3, it means that the maximum conversion of cyclohexene is about 33%. So, the conversion and selectivity are all good when the catalyst L or M is employed.

EAHQ is oxidized to EAQ during the process of epoxidation. After separation of the unconverted olefin, the product and the epoxidation catalyst, EAQ can be hydrogenated by a Pd catalyst to regenerate EAHQ for recycle use. Results in Table 3 show that there is no influence on the conversion and the selectivity of epoxidation of cyclohexene by using the

Table 2

Epoxidation of cyclohexene with O₂ and EAHQ by different catalysts. Reaction conditions: cyclohexene 30 mmol, EAHQ about 10 mmol, mixed solvent 23.5 ml, epoxidation catalyst J 0.07 mmol, 1 atm O₂, 35°C, 3.5 h

Entry	Catalyst	Conversion ^a (%)	Selectivity ^a (%)
1	no	0	0
2	$[\pi\text{-C}_5\text{H}_5\text{NC}_{14}\text{H}_{29}]_7[\text{PW}_{12}\text{O}_{42}]\cdot x\text{H}_2\text{O}$ (J)	25.2	94
3	$[\pi\text{-C}_5\text{H}_5\text{NC}_{14}\text{H}_{29}]_7[\text{PMo}_{12}\text{O}_{42}]\cdot x\text{H}_2\text{O}$ (K)	18.5	90
4	$[\pi\text{-C}_5\text{H}_5\text{NC}_{14}\text{H}_{29}]_3[\text{PW}_4\text{O}_{16}]$ (L)	34.4	97
5	$[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3[\text{PW}_4\text{O}_{16}]^b$ (M)	33.1	94

^aConversion and selectivity are based on cyclohexene.

^bCyclohexene 30 mmol, EAHQ about 10 mmol, mixed solvent 23.5 ml, epoxidation catalyst J 0.07 mmol, 1 atm O₂, 35°C, 3.5 h., but catalyst M 0.05 mmol.

Table 4
Epoxidation of olefins^a catalyzed by M with O₂ and EAHQ

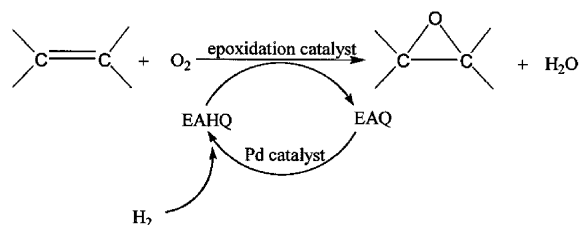
Entry	Olefin	Time (h)	Conversion (%)	Yield	Conversion (%)	Selectivity (%)
			(based on EAHQ)		(based on olefin)	
1	cyclohexene	2	100	92.7	34.0	90.9
2	1-dodecene	7	86.4	72.6	28.8	84.0
3	1-octene	7	93.3	79.2	31.1	84.9
4	1-hexene	7	100	94.5	34.0	92.6
5	propene ^b	6	–	78.0	–	–
6	styrene ^c	4	40.0	36.0	20.0	90.0

^a 10 mmol EAHQ, olefin:EAHQ:catalyst=600:200:1 (molar ratio), mixed solvent, 1 atm O₂, 45°C.

^b 5 mmol EAHQ, propene:EAHQ:catalyst=1000:100:1, mixed solvent, 6 atm air, 45°C.

^c Styrene:EAHQ:catalyst=400:200:1, half of the amount of aromatic solvent is replaced by dimethyl phthalate the others are the same as in footnote (a).

regenerated EAHQ as the reductant. Thus, EAHQ in the overall reaction forms a catalytic cycle without any consumption. The overall catalytic reaction is as follows:



The consumed materials in this method are only olefin, oxygen and hydrogen. The main products are epoxides and H₂O, and no co-product forms.

The catalytic epoxidation of various olefins using this method was investigated, as shown in Table 4. Except styrene, the conversions (based on EAHQ) were high (between 84–92%). So the epoxide yields (based on EAHQ) for internal olefins and linear terminal olefins are good. It means that the utilization efficiency of the EAHQ reductant in this reaction system is high. Comparing with the result of the epoxidation of liquid linear terminal olefins having different carbon atoms, the conversion and the yield (all based on EAHQ) increased with the decrease of carbon atoms from 1-dodecene to 1-hexene. It indicates that the linear terminal olefin having lower carbon atom is easier to proceed for epoxidation in this reaction system. The catalytic epoxidation of

propene was carried out with air in autoclave with a yield (based on EAHQ) of propene oxide of 78.0%.

Further investigation on the epoxidation of olefins by this method and the reaction mechanism is now under way.

Acknowledgements

We are grateful to the financial support of the National Natural Science Foundation of China (No. 29673042).

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