

# Highly selective epoxidation of cyclohexene by reductive activation of molecular dioxygen using hexylviologen as catalyst

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## Abstract

Cyclohexene oxide, 2-cyclohexene-1-one, and 2-cyclohexene-1-ol were produced as oxidation products of cyclohexene by adding  $\text{Br}^-$  ions into an air-equilibrated acetonitrile suspension containing zinc powder, hexylviologen, benzoic anhydride, and cyclohexene. With increasing the concentration of  $\text{Br}^-$  ions, the epoxidation selectivity increased up to 85% with about 60% of the Zn-utilizing efficiency. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Viologen catalyst; Cyclohexene epoxidation; Reductively activated dioxygen

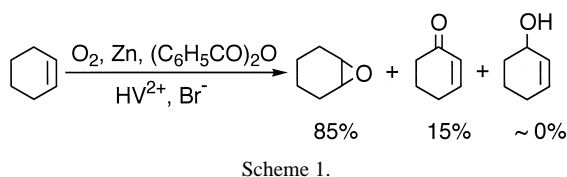
## 1. Introduction

Epoxide compounds such as propylene oxide, a raw material for urethane rubber, were produced industrially by the oxidation of olefin with peroxide or the chlorohydrin method. Recently, several new catalytic systems for the epoxidation of olefin by reductive activation of molecular dioxygen using transition metal complexes [1–6], copper salts [7], or rare earth salts [8–10] as a catalyst under mild conditions have been reported. Further, a few non-catalytic systems using aldehyde as a reductant have been

reported [4,11,12]. When a transition metal complex was used as the catalyst, a high selectivity to epoxide of cyclic olefin such as cyclohexene has been reported [2–6], but when a rare earth salt was used as the catalyst, the epoxidation selectivity of the cyclic olefin was low because the active oxygen species generated in the catalytic system attacked the two allyl positions as well as the double bond [8]. Therefore, the design of active oxygen species is most important for the selective epoxidation of olefin.

We report here that in the new catalytic system containing molecular dioxygen, zinc powder, benzoic anhydride, hexylviologen ( $\text{HV}^{2+}$ ), and  $\text{Br}^-$  ions, namely in the system containing viologen compound as catalyst, the concentration of  $\text{Br}^-$  ions has limited the selec-

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tivity of epoxide for oxidation products of cyclohexene as shown in Scheme 1.

## 2. Experimental

The oxidation of cyclohexene was carried out as follows. An air-equilibrated acetonitrile suspension of 10.5 cm<sup>3</sup> containing zinc powder (50 mg,  $7.3 \times 10^{-2}$  M (M = mol dm<sup>-3</sup>)), HV(ClO<sub>4</sub>)<sub>2</sub> (0.57 mg,  $1 \times 10^{-4}$  M), benzoic anhydride (100 mg,  $4.2 \times 10^{-2}$  M), cyclohexene (0.5 cm<sup>3</sup>, 0.47 M), and different amount of tetrabutylammonium bromide (Bu<sub>4</sub>NBr) was stirred at a constant rate with a magnetic stirrer at 30°C during 3 h. The quantitative analysis and the identification for the oxidation products were performed by a Yanaco G-2800 Gas Chromatograph with a silicon DC 550 column. To estimate the Zn-utilizing efficiency, the amount of consumed zinc powder was determined by EDTA titration [3].

## 3. Results and discussion

When Bu<sub>4</sub>NBr was not added in the reaction system, no oxidation product was obtained. However, products of  $4 \times 10^{-3}$  M cyclohexene oxide (epoxide),  $5 \times 10^{-3}$  M 2-cyclohexene-1-one (1-one), and  $1.6 \times 10^{-3}$  M 2-cyclohexene-1-ol (1-ol) were obtained by adding  $5 \times 10^{-3}$  M Bu<sub>4</sub>NBr. Then, the epoxidation selectivity (molar ratio of [epoxide] to [total amount of the oxidation products]) had a low value of about 34%. The turnover number of HV<sup>2+</sup> (molar ratio of [total amount of the oxidation products] to [HV<sup>2+</sup>]) for the reaction time of 3 h reached about 100, thus it was found that HV<sup>2+</sup> acted as

a catalyst. When either molecular dioxygen, zinc powder, HV<sup>2+</sup>, or benzoic anhydride was not contained, no oxidation product of cyclohexene was obtained. This result suggests that molecular dioxygen, zinc powder, and HV<sup>2+</sup> acted as the oxygen source, the reductant, and the mediator for the electron transfer from zinc powder to molecular dioxygen, respectively, and benzoic anhydride and Bu<sub>4</sub>NBr acted very effectively for the oxidation of cyclohexene as described later. Further, the Zn-utilizing efficiency (molar ratio of [total amount of the oxidation products] to [consumed zinc powder]) was 110% at  $5 \times 10^{-3}$  M Bu<sub>4</sub>NBr, suggesting that two kinds of reductive elementary reactions, one and two electron-transfer reactions, were involved in this catalytic system.

The effect of the addition of Bu<sub>4</sub>NBr on the amount of oxidation product and the Zn-utilizing efficiency is shown in Fig. 1. The total amount of oxidation products and the amount of epoxide increased with increasing [Bu<sub>4</sub>NBr], but the amount of 1-one and 1-ol, and the Zn-utilizing efficiency had a maximum at  $5 \times$

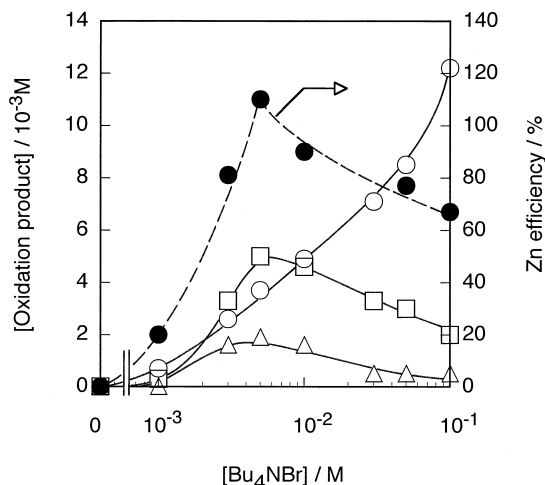
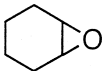
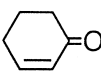
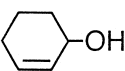


Fig. 1. Effect of the addition of Bu<sub>4</sub>NBr on the amount of the oxidation products (epoxide (○), 1-one (□), and 1-ol (△)) and Zn-utilizing efficiency (●) in air-equilibrated acetonitrile suspension containing  $1 \times 10^{-4}$  M HV(ClO<sub>4</sub>)<sub>2</sub>,  $7.3 \times 10^{-2}$  M zinc powder,  $4.2 \times 10^{-2}$  M benzoic anhydride, and 0.47 M cyclohexene at 30°C (reaction time; 3 h).

Table 1

Amount of oxidation products<sup>a</sup> ( $Q/10^{-3}$  M) and Zn-utilizing efficiency<sup>b</sup> ( $E/\%$ ) obtained by adding a salt containing either  $\text{Bu}_4\text{N}^+$  ions or halogen ions

Salt	Q			E
				
non	n.d. <sup>c)</sup>	n.d.	n.d.	-
$\text{Bu}_4\text{NBr}$	4.0	5.0	1.6	110
$\text{Bu}_4\text{NClO}_4$	n.d.	n.d.	n.d.	-
$\text{Bu}_4\text{NCF}_3\text{SO}_3$	n.d.	n.d.	n.d.	-
$\text{Bu}_4\text{NBF}_4$	n.d.	n.d.	n.d.	-
$\text{LiCl}$	3.4	1.8	0.9	86
$\text{LiClO}_4$	0.6	n.d.	n.d.	9

<sup>a</sup>Concentration of reactants:  $1 \times 10^{-4}$  M  $\text{HV}(\text{ClO}_4)_2$ ,  $5 \times 10^{-3}$  M salt,  $7.3 \times 10^{-2}$  M zinc powder,  $4.2 \times 10^{-2}$  M benzoic anhydride, and 0.47 M cyclohexene. Reaction temperature: 30°C, reaction time: 3 h.

<sup>b</sup>(Molar ratio of [total amount of oxidation products] to [consumed zinc powder])  $\times$  100.

<sup>c</sup>Not detected.

$10^{-3}$  M  $\text{Bu}_4\text{NBr}$ . At 0.1 M  $\text{Bu}_4\text{NBr}$ , the epoxidation selectivity reached about 85% and the Zn-utilizing efficiency was about 60%. This improvement of the epoxidation selectivity was apparently correlated with the addition of a large amount of  $\text{Bu}_4\text{NBr}$ . The epoxidation selectivity and the Zn-utilizing efficiency of our catalytic system were comparable to those of the systems using transition metal complexes as a catalyst [2,3,5,6].

To clarify which of  $\text{Bu}_4\text{N}^+$  ions or  $\text{Br}^-$  ions effectively acted to produce the oxidation product, some salts containing either  $\text{Bu}_4\text{N}^+$  ions or halogen ions were added to this system instead of  $\text{Bu}_4\text{NBr}$ . The amount of the oxidation products and the Zn-utilizing efficiency are summarized in Table 1. When either  $\text{Bu}_4\text{NClO}_4$ ,  $\text{Bu}_4\text{NCF}_3\text{SO}_3$ , or  $\text{Bu}_4\text{NBF}_4$  was added, no oxidation product was obtained despite zinc powder was consumed, while the oxidation products

were obtained by adding  $\text{LiCl}$ <sup>1</sup> with 86% of the Zn-utilizing efficiency. When  $\text{LiClO}_4$  was added in a control experiment, the epoxide was obtained as the single oxidation product, but the Zn-utilizing efficiency remained very low value of about 9%. These results indicate that halogen ions took part in the oxidation of cyclohexene.

3,5-Di-*tert*-butyl-*p*-hydroxytoluene (BHT) as a radical inhibitor was added into our catalytic system to examine whether this oxidation reaction was radical reaction or not. The effect of BHT addition on the amount of oxidation product and the Zn-utilizing efficiency is shown in Fig. 2. The amount of 1-one and 1-ol, and the Zn-utilizing efficiency decreased with increasing [BHT], but the amount of epoxide changed hardly. By adding  $1 \times 10^{-2}$  M BHT, the epoxi-

<sup>1</sup> Since  $\text{LiBr}$  was insoluble in acetonitrile,  $\text{LiCl}$  was added in this system instead of  $\text{LiBr}$ .

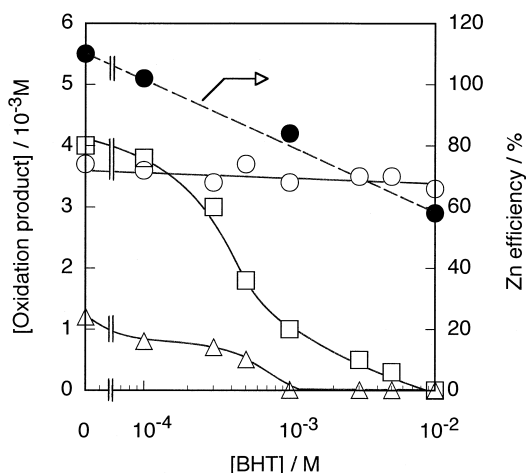


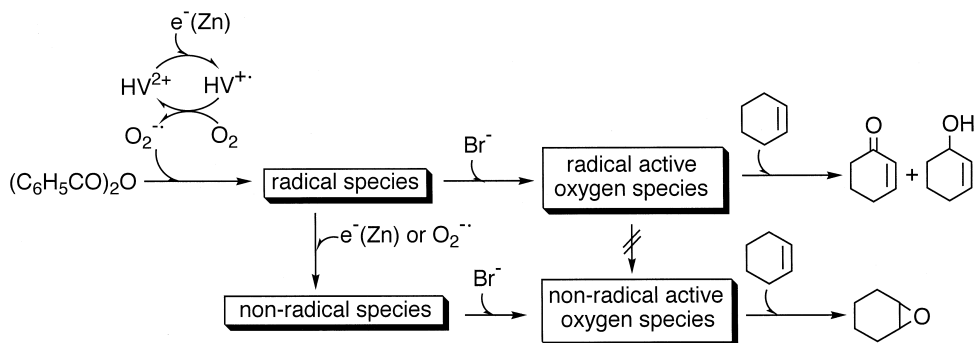
Fig. 2. Effect of the addition of BHT on the amount of the oxidation products (epoxide (○), 1-one (□), and 1-ol (△)) and Zn-utilizing efficiency (●) in air-equilibrated acetonitrile suspension containing  $1 \times 10^{-4}$  M  $HV(ClO_4)_2$ ,  $7.3 \times 10^{-2}$  M zinc powder,  $4.2 \times 10^{-2}$  M benzoic anhydride,  $5 \times 10^{-3}$  M  $Bu_4NBr$ , and 0.47 M cyclohexene at 30°C (reaction time; 3 h).

dation selectivity of 100% was attained even at low concentration of  $5 \times 10^{-3}$  M  $Bu_4NBr$  with 60% of the Zn-utilizing efficiency. This result indicates that only the active oxygen species which produces 1-one and 1-ol was deactivated by BHT, but other active oxygen species which produces epoxide was not deactivated by BHT. We named former species 'radical active oxygen species', and later species 'non-radical active oxygen species'.

A characteristic blue color of  $HV^{+}$  radical ions [13,14], produced by reducing colorless  $HV^{2+}$  ions with zinc powder, readily returned to colorless in acetonitrile by an air-oxidation

producing superoxide anion by one electron transfer from  $HV^{+}$  to molecular dioxygen [15]. Therefore, we assume that a radical species such as benzoylperoxy radical ( $C_6H_5COOO\cdot$ ) produced by a reaction between benzoic anhydride and superoxide anion [1], and successively a radical active oxygen species such as hypobromous radical ( $BrO\cdot$ ) produced by a reaction between the  $C_6H_5COOO\cdot$  radicals and  $Br^-$  ions. Thus, 1-one and 1-ol were produced by a reaction between  $BrO\cdot$  and cyclohexene. On the other hand, epoxide was produced by a reaction between non-radical active oxygen species and cyclohexene. The non-radical active oxygen species was not produced by the reduction of the radical active oxygen species such as  $BrO\cdot$  which was deactivated by BHT, because the amount of epoxide did not change by adding BHT. We infer that since zinc powder has large reducing power in the presence of a large amount of  $Br^-$  ions according to a complex formation between zinc ion and halogen ion [16],  $C_6H_5COOO\cdot$  produced by one electron reduction of benzoic anhydride was further reduced by zinc powder or a large amount of superoxide anion [17] produced by the mediation of  $HV^{2+}$  ions, producing species such as benzoylperoxide ion ( $C_6H_5COOO^-$ ). Then, the  $C_6H_5COOO^-$  ions may react with  $Br^-$  ions, and the non-radical active oxygen species such as hypobromous ion ( $BrO^-$ ) may be produced. The  $BrO^-$  reacted with cyclohexene, producing epoxide.

The catalytic system assumed by this study is summarized in Scheme 2. Further investigation



Scheme 2.

is being carried out to clarify the active oxygen species in our catalytic system.

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