Oxidation and epoxidation of hydrocarbons with O_2 catalysed by $EuCl_3$

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Abstract

Oxidation of cyclohexane and epoxidation of 1-hexene with O_2 by $EuCl_3$ catalytic systems ($EuCl_3$, Zn powder, carboxylic acid, and solvent) were studied in detail. Combination of proton donors and solvents strongly affected the turnover number (TON) and the selectivity of the monooxygenation. The maximum TON of 11.7 in 1 h for oxidation of cyclohexane to cyclohexanol and cyclohexanone ($\approx 100\%$ total selectivity) was obtained using acetic acid and dichloromethane at $P(O_2) = 101$ kPa and $T = 40°C$. The selectivity to cyclohexanone increased with increasing the yield for sum of the products. A successive reaction of cyclohexanol to cyclohexanone became obvious at higher yields in oxidation of cyclohexane. In the case of epoxidation, the maximum TON of the epoxide (81.4% selectivity) of 14.2 in 1 h was obtained using 1,2-dichloroethane and propionic acid at $P(O_2) = 101$ kPa and $T = 40°C$. The selectivity to the epoxide did not change with the total yield. A successive reaction of 1,2-epoxyhexane to by-products was not observed in the oxidation of 1-hexene. A small amount of CO_2 was produced from carboxylic acid, but none from the reactant. The efficiency of Zn powder used to the monooxygenations was not more than 5%.

Keywords: Europium; Epoxidation; Oxidation; Rare earth; Monooxygenation

1. Introduction

Development of new catalytic systems for monooxygenation of alkanes, alkenes and aromatics at ambient temperature is one of the most attractive subjects in the field of catalytic, organic syntheses. Variety of catalytic systems using transition metal complexes is known for monooxygenations. We have very recently reported a new catalytic system ($EuCl_3$, Zn powder, proton donor, and solvent) for monooxygenation of hydrocarbons with O_2 [1,2]. It is well known that lanthanide complexes catalyse the activation of C–H bonds of CH_4 and benzene [3], the polymerization and the hydrogenation of alkenes [4], and the aldol condensation [5]. Ce^{4+} ($Ce(NH_4)_2(NO_3)_6$) works as an oxidant for the oxidation of toluene to benzaldehyde [6]. However, it is unusual that $EuCl_3$, one of the rare earth elements, works as a catalyst for the oxidation of hydrocarbons under mild conditions.

The components of our reaction system reported recently are similar to those of the Gif(IV)

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system, except for the absence of $FeCl_3$ and pyridine in our system [7]. A combination of Zn powder and carboxylic acid as a reductant has already been reported by Gif(IV) system [7] and Metalloporphyrin system [8,9]. Gif–Orsay–Texas system is effective for oxidation of alkanes but not for oxidation of alkenes and aromatics [7]. In the case of our $EuCl_3$ catalytic system, the epoxidation of alkenes, the hydroxylation of aromatics and the oxidation of alkanes proceed [1]. A reductively activated dioxygen with electrons (from Zn powder) and protons (from carboxylic acid) was postulated to be responsible in the monooxygenation in this $EuCl_3$ catalytic system (Eq. 1). However, further studies on these monooxygenations in detail are needed to clarify the characteristic feature of the system.

$$C_mH_n + O_2 + 2e^-(Zn) + 2H^+(MeCO_2H)$$

$$\xrightarrow{EuCl_3 \text{ catalyst}} \cdots \rightarrow C_mH_nO + H_2O \tag{1}$$
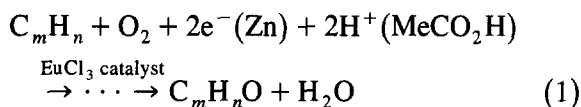
Therefore, the aim of this paper is to study the various kinetic factors for the oxidation of cyclohexane and the epoxidation of 1-hexene and to get a whole picture of the monooxygenation in $EuCl_3$ catalytic system.

2. Experimental

The standard experimental procedure for the oxidation of cyclohexane was as follows. Rare earth salts (ex. $EuCl_3 \cdot 6H_2O$) of 0.03 mmol was dissolved in a mixed solution of carboxylic acid of 2 ml (ex. $MeCO_2H$ 35.3 mmol) and a solvent of 2 ml (ex. CH_2Cl_2) in a three-necked flask with a reflux condenser. After cyclohexane of 1 ml (9.25 mmol) or 1-hexene of 1 ml (8.00 mmol) and Zn powder of 1.0 g (15.3 mmol) had been added to the solution, the reaction was started by stirring the solution and the slurry with a magnetic stirrer under a stream of O_2 (1 atm, 5 ml STP·min^{-1}) at 40°C. The reaction was continued for 1 h. The crude reaction mixture after the reaction was filtered and

was neutralized by NaOH aq. (10 wt%). The products were analyzed by a gas chromatography (Shimazu GC-14A) and a GC–mass spectrometer (Shimazu QP2000A) with PEG-20M and OV-1 capillary columns (0.25 mm i.d. × 25 m).

In experiments for mass balances of reactants, organic compounds in the stream of O_2 were collected by a cold trap (−78°C). The quantitative analysis of the organic compounds was determined by GC.

The efficiency of Zn powder used for the monooxygenation was defined as $\phi(Zn) =$ [amount of the products (mol)]/[amount of the Zn powder reacted (mol)] × 100 (%). Zn powder was recovered from the residue that might involve Zn^0 and $Zn(MeCO_2)_2$ as below. The residue was washed with H_2O repeatedly to remove the components soluble in water. The washed residue Zn^0 that was confirmed by XRD. An amount of Zn^0 was evaluated from the weigh of the residue. Moreover, volume of H_2 produced from the dried residue (Zn^0) and HCl aq. was measured using a gas burette. The amount of H_2 obtained was consistent with that of the residue (Zn^0) within experimental error of ±5%. The aqueous filtrate described above was dried slowly to allow crystallization. The transparent crystal obtained was identified as $Zn(MeCO_2)_2 \cdot 2H_2O$ by XRD.

3. Results and discussion

3.1. Oxidation of cyclohexane catalysed by rare earth salts

Fig. 1 shows the catalytic activities of various rare earth salt for the oxidation of cyclohexane. The products were cyclohexanone (CyO) and cyclohexanol (CyOH) in the liquid phase, and CO_2 in the gas phase. Other partial oxidation products, such as dicyclohexyl and cyclohexane-diol, were not detected. The sum of the turnover number (TON) of CyO and CyOH in 1 h based on rare earth salt was used for a mea-

sure of the catalytic activity. As shown in Fig. 1, most of the rare earth chlorides catalysed the oxidation of cyclohexane. Among rare earth chlorides, $LaCl_3$, $NdCl_3$, $SmCl_3$ and $EuCl_3$ were active in the reaction. The catalytic activity of $EuCl_3$ was especially high. It should be noted that the catalytic activity of $EuCl_3$ was quite high compared with those of the transition metal chlorides, $FeCl_3$, $CuCl_2$, $PdCl_2$. Other Eu salts also exhibited high activity except for $Eu_2(SO_4)_3$ which did not dissolve in the mixture. There were large differences in the activity among the Eu salts, implying that the counter anion of the salts might affect the activity of Eu catalysts for the oxidation of cyclohexane.

In a separate experiment, a mass balance for cyclohexane was studied during the oxidation catalysed by $EuCl_3$ under the standard condi-
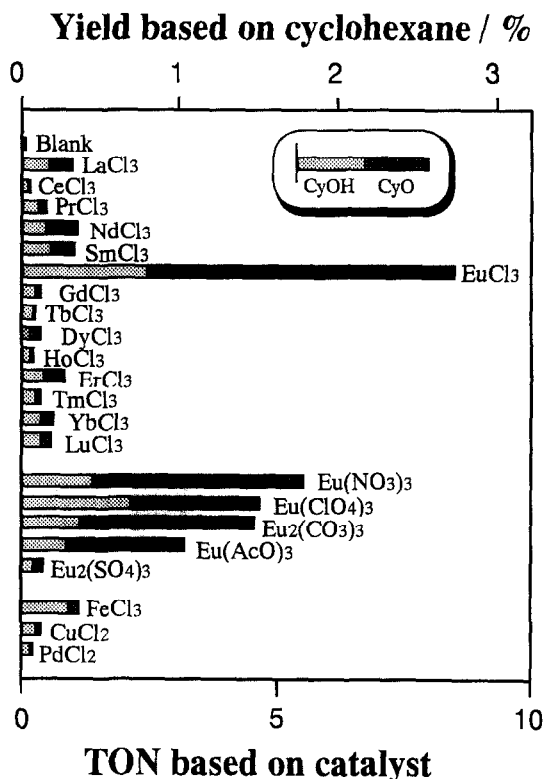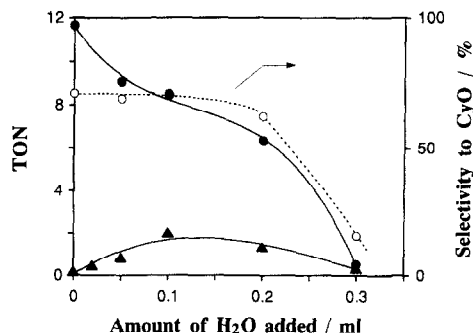

Fig. 2. Inference of the amounts of H_2O added on oxidation of cyclohexane catalysed by $EuCl_3$. ● TON for sum of the products of cyclohexane oxidation based on $EuCl_3$, ▲ TON for sum of the products of cyclohexane oxidation based on $SmCl_3$, ○ selectivity to cyclohexanone in the $EuCl_3$ catalytic system. $T = 40°C$, reaction time 1 h, cyclohexane 1 ml, catalysts 0.03 mmol, O_2 1 atm (5 ml STP·min^{-1}), Zn powder 1 g, $MeCO_2H$ 2 ml, CH_2Cl_2 2 ml.

Fig. 1. Oxidation of cyclohexane with O_2 by various rare-earth salts and transition-metal salts catalysts. $T = 40°C$, reaction time 1 h, cyclohexane 1 ml, catalyst 0.03 mmol, O_2 1 atm (5 ml STP·min^{-1}), Zn powder 1 g, $MeCO_2H$ 2 ml, CH_2Cl_2 2 ml, H_2O 0.1 ml.

tions. The initial amount of cyclohexane of 94.4% was recovered as the products and unreacted cyclohexane. The recovery efficiency for our experimental procedure was 95.0% for cyclohexane. Thus, cyclohexane of 61 μmol (0.6%) was not determined what form converted. A good mass balance was obtained for the oxidation of cyclohexane.

In this reaction system, H_2O may be produced during the oxidation, as indicated in Eq. 1. Fig. 2 shows an influence of H_2O addition on the oxidation of cyclohexane for the $EuCl_3$ catalytic system. The TON decreased with increasing the amount of H_2O added. When H_2O of 0.3 ml (16.7 mmol) was added in the reaction mixture, the catalytic activity for the oxidation of cyclohexane decreased dramatically. An agglomeration of Zn powder to a ball shape was observed during the oxidation when the amount of H_2O above 0.2 ml were added. The decrease in the yield with increasing the amount of H_2O may be due to the decrease in the surface area of Zn powder agglomerated. Therefore, the maximum TON of 11.7 in 1 h for CyO and CyOH (3.8% yield based on cyclohexane) together was obtained without addition of H_2O in the $EuCl_3$ catalytic system. We have reported previously that the maximum TON was obtained with addition of H_2O of 0.1 ml in the

$SmCl_3$ catalytic system [2]. In this system, $SmCl_3$ dissolved only slightly in the reaction mixture without addition of H_2O. The increase in the TON with increase in the amount of H_2O added may be due to the increase in the solubility of $SmCl_3$ in the reaction mixture ($H_2O < 0.1$ ml). The decrease in the TON ($H_2O > 0.1$ ml) may be due to the agglomeration of Zn powder.

3.2. Epoxidation of 1-hexene catalysed by rare earth salts

Fig. 3 shows the TON and the yields based on 1-hexene for the epoxidation under standard conditions without addition of H_2O. The products other than the epoxide are hexanal > 1,2-hexane-dial $\approx$ 1-hexene-3-ol > 1-hexanol $\approx$ 2-hexanol, some oxygenates that could not be identified by GC–MS, and CO_2 in the gas phase. The highest yield of the epoxide was

obtained by using $EuCl_3$. Among other rare earth salts, $LaCl_3$ and $LuCl_3$ exhibited fairly high TON > 2.0 in 1 h. Other Eu salts exhibited good TON except for $Eu_2(SO_4)_2$ and EuF_3 which did not dissolve in the mixture, similar to the results in Fig. 1. The selectivities to the epoxide differed among the Eu salts, $Eu_2(CO_3)_3$: 74% > $Eu(NO_3)_3$: 67%, $EuCl_3$: 66% > $Eu(MeCO_2)_3$: 61% > $Eu(ClO_4)_3$: 38%. Both catalytic activity and the selectivity to the epoxide were affected by the counter anion species of the Eu salts. This result suggests that actual active forms of Eu catalysts during the oxidation are different for each Eu salt and that may be the effect of the counter anions.

In a separate experiment, a mass balance for 1-hexene was studied during the epoxidation catalysed by $EuCl_3$ under the standard conditions. The initial amount of 1-hexene of 93.8% was recovered as products and unreacted 1-
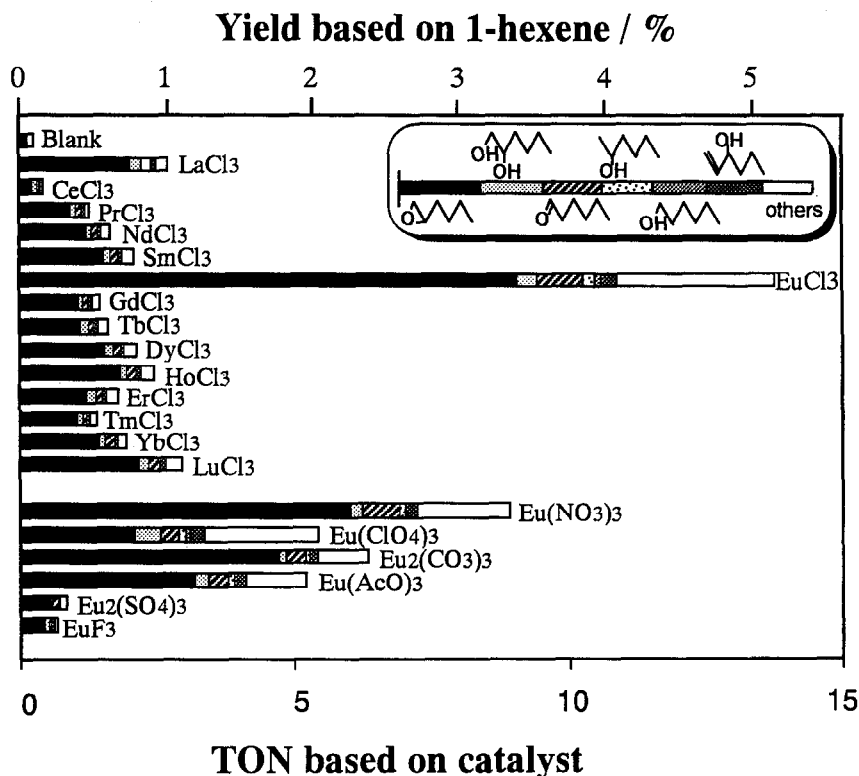

Fig. 3. Epoxidation of 1-hexene with O_2 by various rare-earth salts and transition-metal salts catalysts. $T = 40°C$, reaction time 1 h, 1-hexene 1 ml, catalyst 0.03 mmol, O_2 1 atm (5 ml STP·min^{-1}), Zn powder 1 g, $MeCO_2H$ 2 ml, CH_2Cl_2 2 ml.

hexene. The recovery efficiency for our experimental procedure was 94.7% for 1-hexene. Thus, 1-hexene of 74 μmol (0.9%) was not determined what form converted. However, a good mass balance was also obtained for the epoxidation of 1-hexene, as similar to the oxidation of cyclohexane.

3.3. Kinetic curves of monooxygenation

Fig. 4 shows the kinetic curves for the oxidation of cyclohexane and the epoxidation of 1-hexene catalysed by EuCl$_3$ without addition of H$_2$O. The oxidation of cyclohexane occurred smoothly with reaction time because the TON for the sum of products increased linearly and an induction period for the oxidation was not observed. However, the selectivity to CyO increased from 26% at 5 min to 65% at 80 min. In contrast, the selectivity to CyOH decreased with reaction time. This observation suggests that the selectivity to CyO depends on the total yield. The selectivity to CyO did not reach to 0% by an extrapolation to 0 min. This result suggests that most of CyO and CyOH are produced in parallel at the early stage. However, a successive oxidation path of CyOH to CyO is not negligible at a later stage of the reaction when the concentration of CyOH increases. The TON of CO$_2$ based on Eu was 1.2 in 1 h, corresponding to the yield of 0.07% based on cyclohexane. However, the TON of CO$_2$ of 2.0 in 1 h was observed during the oxidation without cyclohexane, that was larger than TON of 1.2 obtained under the standard condition. This observation suggests that CO$_2$ is produced from acetic acid but not from cyclohexane. Thus, the selectivity to the sum of CyO and CyOH was almost 100%.

In the case of the epoxidation of 1-hexene, the TON for the sum of the products increased with reaction time. An induction period was not observed for the oxidation of 1-hexene. The selectivity to the epoxide and that to other by-products were almost constant with reaction time. This result suggests that the products were produced in parallel. The formation of CO$_2$ (1.1 TON in 1 h) was observed during the epoxidation, that was smaller than that (2.0) without 1-hexene. This result also suggests that CO$_2$ is produced from acetic acid during epoxidation, similar to the oxidation of cyclohexane.

3.4. Efficiency of Zn powder for monooxygenation

As described above, the TON of 11.7 (351 μmol) for the sum of CyO and CyOH was obtained in 1 h. The amount of Zn powder recovered was 7132 μmol (0.4664 g) after the oxidation. Thus, the amount of Zn powder reacted during the oxidation was estimated to be 8160 μmol (0.5536 g). This amount was roughly correspond to the amount of Zn(MeCO$_2$)$_2$ · 2H$_2$O of 7180 μmol (1.577 g) obtained after the oxidation. Therefore, the efficiency of Zn powder used for the oxidation of cyclohexane through Eq. 2, ϕ(Zn), was 4.3%. Therefore, most of the Zn(MeCO$_2$)$_2$ may be produced without forming oxygenates probably through Eq. 3. If Zn powder and acetic acid reacted through Eq. 2 and 3, the conversions of Zn powder and acetic acid were estimated to be 53% and 46%, respectively, at 1 h. These large consumption of Zn powder and acetic acid may be responsible for the decrease in the rate of
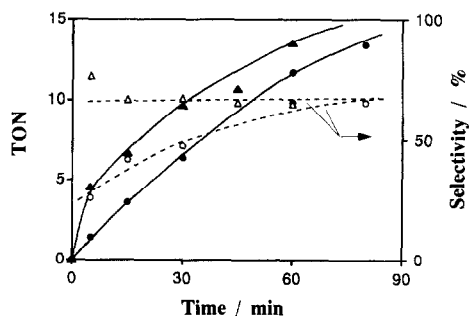
Fig. 4. Kinetic curves for oxidation of cyclohexane and epoxidation of 1-hexene catalysed by EuCl$_3$. ● TON for sum of the products of cyclohexane oxidation based on EuCl$_3$. ○ selectivity to cyclohexanone, ▲ TON for sum of the products of 1-hexene epoxidation, △ selectivity to 1,2-epoxyhexane. $T = 40$°C, cyclohexane 1 ml, EuCl$_3$·6H$_2$O 0.03 mmol, O$_2$ 1 atm (5 ml STP·min^{-1}), Zn powder 1 g, MeCO$_2$H 2 ml, CH$_2$Cl$_2$ 2 ml.

formation of the products. Moreover, the amount of H_2O produced in 1 h was estimated to be 0.15 ml through Eq. 2 and 3. This is another reason for the decrease in the rate, as described in Fig. 2.

$$C_mH_n + O_2 + Zn + MeCO_2H$$

$$\rightarrow \cdots \rightarrow C_mH_nO + Zn(MeCO_2)_2 + H_2O \tag{2}$$

$$O_2 + 2Zn + 2MeCO_2H$$
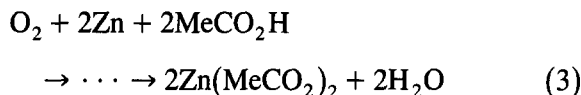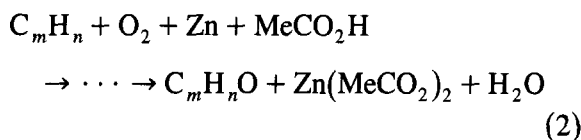
$$\rightarrow \cdots \rightarrow 2Zn(MeCO_2)_2 + 2H_2O \tag{3}$$

In the case of the epoxidation of 1-hexene, the TON of 9.05 (285 μmol) in 1 h for the epoxide and the TON of 13.5 (406 μmol) in 1 h for the sum of the products were obtained. The Zn powder remained after the epoxidation was 6148 μmol (0.402 g) and the $Zn(MeCO_2)_2 \cdot 2H_2O$ recovered was 8778 μmol (1.927 g). Thus, ϕ(Zn) of 3.1% for the epoxide and that of 4.4% for the sum of the products through Eq. 2 were obtained. These values indicate that most of the Zn powder are consumed through Eq. 3 in this $EuCl_3$ catalytic system.

3.5. Effect of partial pressure of O_2 on monooxygenation

Fig. 5 shows the effects of the partial pressure of O_2 on the monooxygenations of cyclohexane and 1-hexene. The oxidations of cyclohexane and 1-hexene did not occur without O_2. In the case of the oxidation of cyclohexane, the TON for the sum of the products increased with increasing $P(O_2)$. The selectivity to CyO increased from 45% at 25 kPa to 65% at 101 kPa according to the increase in the cyclohexane conversion. This result suggests again that the selectivity to CyO depends on the total TON.

In the case of the epoxidation of 1-hexene, the TON for the sum of the products increased with increasing $P(O_2)$ similar to the results for the oxidation of cyclohexane. However, the selectivity to the epoxide was constant, 66 ± 2%,
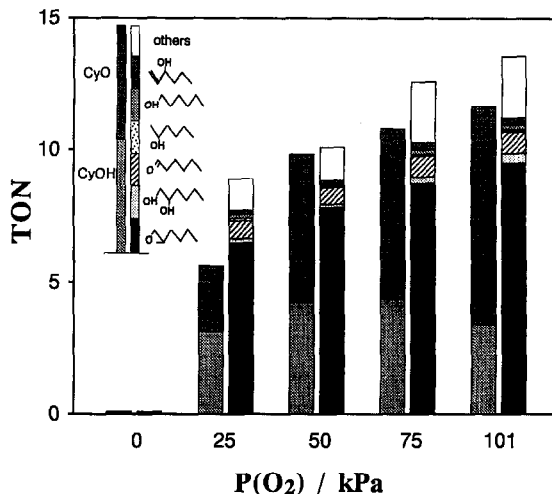

Fig. 5. Effects of partial pressure of O_2 on oxidation of cyclohexane and on epoxidation of 1-hexene catalysed by $EuCl_3$. $T = 40°C$, reaction time 1 h, reactants 1 ml, $EuCl_3 \cdot 6H_2O$ 0.03 mmol, Zn powder 1 g, $MeCO_2H$ 2 ml, CH_2Cl_2 2 ml.

and the selectivities to the by-products did not depend on $P(O_2)$. In contrast with the oxidation of cyclohexane, the selectivities to the products did not depend on the total TON.

The results obtained in Figs. 4 and 5 were replotted in Fig. 6 (the selectivities to CyO and the epoxide versus the total TON). As shown in Fig. 6, the plots in both case are on good straight lines. These results suggest that the effect of $P(O_2)$ on both reactions is essentially equal to that of reaction time. Moreover, an increase in $P(O_2)$ does not vary the character of active species in the $EuCl_3$ catalytic system. CyO is produced from CyOH successively at an high TON because the selectivity to CyO becomes higher at an high TON. However, the selectivity to CyO does not reach to zero by the extrapolation of the TON to zero in Fig. 6. Thus, CyO and CyOH are produced in parallel at a lower TON, as mentioned before. While, the selectivity to the epoxide was constant in Fig. 6. This result suggests that the products are produced in parallel for the epoxidation of 1-hexene, and further oxidation of the products can be neglected.
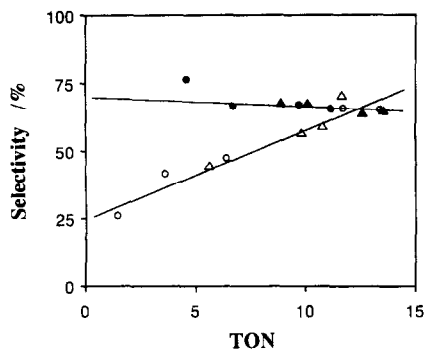
Fig. 6. The functions of the selectivities and the yields in monooxygenations of cyclohexane and 1-hexene catalysed by $EuCl_3$. ● data of oxidation of cyclohexane from Fig. 4, ▲ data of oxidation of cyclohexane from Fig. 5, ○ data of epoxidation of 1-hexene from Fig. 4, △ data for the epoxidation of 1-hexene from Fig. 5.

Fig. 7. Temperature dependence of the oxidation of cyclohexane and on epoxidation of 1-hexene catalysed by $EuCl_3$. Reaction time 1 h, reactants 1 ml, $EuCl_3 \cdot 6H_2O$ 0.03 mmol, O_2 1 atm (5 ml STP·min^{-1}), Zn powder 1 g, $MeCO_2H$ 2 ml, CH_2Cl_2 2 ml.

3.6. Temperature dependence on monooxygenation

Fig. 7 shows the dependence of temperature on the monooxygenations of cyclohexane and 1-hexene. The oxidation of cyclohexane exhibited the maximum TON of 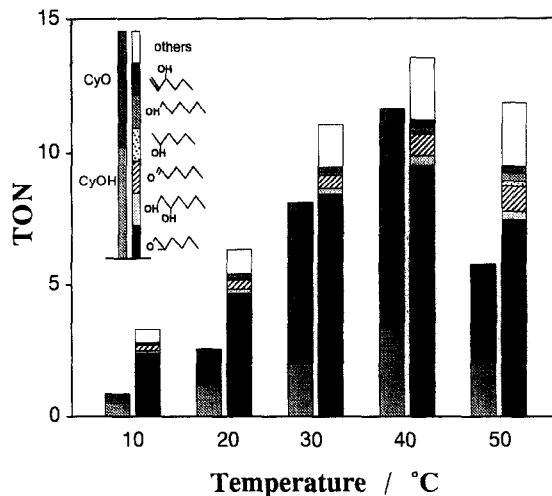the sum of the products at 40°C. The sum TON decreased with decreasing temperature. The selectivity to CyO decreased with decreasing temperature. When these results were replotted into Fig. 6, these points were not on and above the line. This result suggests that the formation rate of CyOH
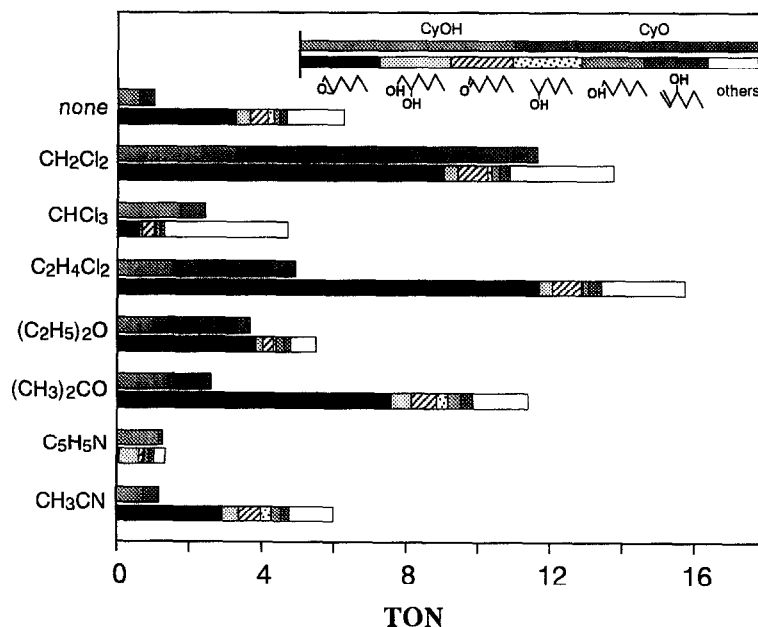

Fig. 8. Solvent effects on oxidation of cyclohexane and on epoxidation of 1-hexene catalysed by $EuCl_3$. $T = 40°C$, reaction time 1 h, reactants 1 ml, $EuCl_3 \cdot 6H_2O$ 0.03 mmol, O_2 1 atm (5 ml STP·min^{-1}), Zn powder 1 g, $MeCO_2H$ 2 ml, solvents 2 ml.

more decreased with decreasing temperature compared with that of CyO, an apparent activation energy for the formation of CyO is lower than that of CyOH.

In the case of the epoxidation of 1-hexene, the maximum TON for the sum of the products was also obtained at 40°C. The catalytic activity decreased more gradually with decreasing temperature than that observed in the oxidation of cyclohexane. This result suggests that an apparent activation energy for the epoxidation of 1-hexene was lower than that for the oxidation of cyclohexane. The selectivity to the epoxide increased slightly with decreasing temperature.

3.7. Effects of solvents on monooxygenations

Fig. 8 shows the effect of solvents on the monooxygenations of cyclohexane and 1-hexene. The reactions were carried out using various solvents of 2 ml (trichloromethane, 1,2-dichloroethane, diethyl ether, acetone, acetonitrile, and pyridine) under the standard conditions.

The oxidation of cyclohexane proceeded without solvent, though the TON was very low compared to the experiment with dichloromethane. Good enhancements of the TON were observed by using the solvents except for pyridine and acetonitrile. dichloromethane is the most suitable solvent for oxidation of cyclohexane.

In the case of the epoxidation of 1-hexene, the epoxidation occurred smoothly without addition of any solvent; epoxide TON was 3.3 in 1 h. The positive effect on the yield was observed for 1,2-dichloroethane, acetone, diethyl ether, and dichloromethane. When 1,2-dichloroethane was used for the epoxidation, a good result (TON 11.8, selectivity 74%, and ϕ(Zn) 3.8%) was obtained compared with that using dichloromethane (9.05, 66%, and 3.1%).

Therefore, 1,2-dichloroethane was the most suitable solvent for the epoxidation of 1-hexene. The enhancement factors by the solvents defined as the ratio of the TON for the epoxidation of 1-hexene with and without the solvent were 2.5 (1,2-dichloroethane) and 2.2 (dichloromethane) and that for the oxidation of cyclohexane were 12 (dichloromethane) and 5 (1,2-dichloroethane). The enhancement effect by the solvent in the epoxidation was relatively small compared with that observed in the oxidation of cyclohexane.

When pyridine, an effective solvent in Gif–Orsay–Texas system [7], was used in this $EuCl_3$ catalytic system, the monooxygenations were not enhanced. This result suggests that the solvents of low coordination affinity are suitable for monooxygenation in the $EuCl_3$ catalytic system. When the results obtained in Fig. 8 were replotted into Fig. 6, these data did not fit the lines. This implies that the reactivity of the active species in $EuCl_3$ catalytic system is varied by different solvents.

3.8. Effects of carboxylic acids on monooxygenations

Effects of various proton donors (carboxylic acids, alcohols, etc.) of 2 ml instead of acetic acid on the monooxygenations of cyclohexane and 1-hexene were studied, as shown in Fig. 9. When higher carboxylic acids than acetic acid were used for the oxidation of cyclohexane, these TON were less than 1/3 of that achieved by using acetic acid. A stronger acid (trifluoroacetic acid ($pK_a = 0.9$)) and weaker acids (hexafluoroacetone and acetylacetone) than acetic acid gave the TON less than 20% for acetic acid. When simple alcohols such as methanol, ethanol and 2-propanol, were used as proton donor, TON for the oxidation of cyclohexane was dramatically decreased. Thus, acetic acid was the most suitable proton donor for the oxidation of cyclohexane in this system.

The epoxidation of 1-hexene was also examined using different proton donors. The TON of the epoxide observed by using propionic acid (8.92 in 1 h) was comparable to that using acetic acid (9.05 in 1 h). The TON for the sum of by-products propionic acid was used was
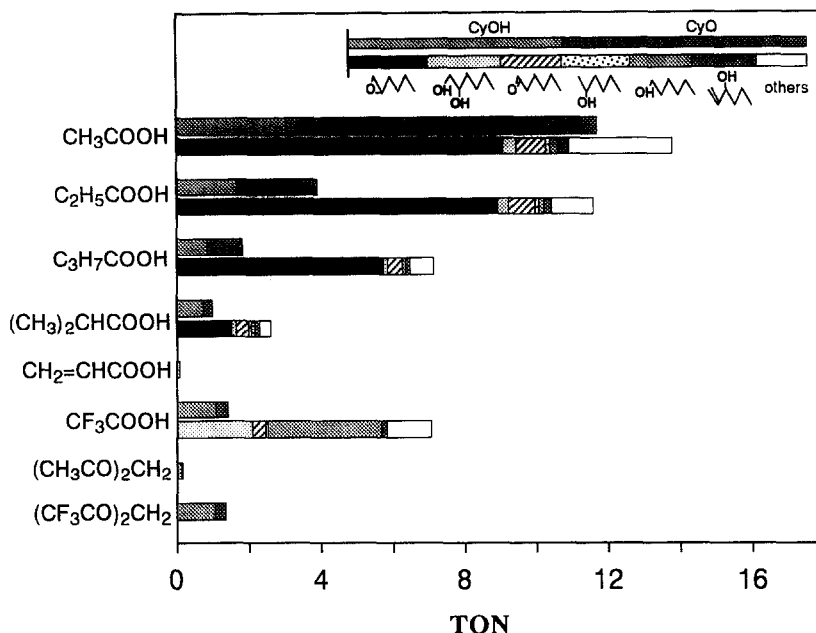
Fig. 9. Influences of proton donors on oxidation of cyclohexane and on epoxidation of 1-hexene catalysed by $EuCl_3$. $T = 40°C$, reaction time 1 h, reactants 1 ml, $EuCl_3 \cdot 6H_2O$ 0.03 mmol, O_2 1 atm (5 ml STP $\cdot$ min^{-1}), Zn powder 1 g, proton donor 2 ml, CH_2Cl_2 2 ml.

lower than that when acetic acid was used. Therefore, the selectivity to the epoxide for propionic acid (77%) was higher than that for acetic acid (65%). When butyric acid was used for the epoxidation, the epoxide TON of 5.74 in 1 h was lower than those with acetic acid and propionic acid. However, the selectivity to the epoxide using butyric acid was highest (81%) among the results in Fig. 9. When trifluoro-acetic acid was used for the epoxidation, the epoxide was not produced at all. However, 2-hexanol (TON 3.16 in 1 h) and 1,2-hexane-diol (2.07 in 1 h) were produced as major products. Therefore, propionic acid was the most suitable carboxylic acid for the epoxidation of 1-hexene.

As described above, the proton donors of $pK_a = 4-5$ may be suitable for the monooxy-genations in the $EuCl_3$ catalytic system. However, detailed differences in the TON and the selectivities of the products for the acids in this pK_a range can not be explained only by pK_a value (25°C) of each acid; trifluoroacetic acid $(pK_a = 0.9) \ll$ acrylic acid (4.26) < acetic acid (4.76) < butyric acid (4.82) < isobutyric acid

(4.85) < propionic acid (4.87) $\ll$ acetyl ace-tone. This result suggests that the effect of released protons of carboxylic acids (pK_a 4–5) is not a key factor, but the character of alkyl groups of carboxylic acids must affect the reac-tivity of active oxygen species. The character of active species is varied by using each acid because the results in Fig. 9 also did fit the lines in Fig. 6. If the coordination of carboxylic acids to Eu cation is prerequisite for the generation of active oxygen, the hydrophilic properties and electronic properties of the carboxylic groups may affect the reactivity.

As described above, the most suitable combi-nation of the solvent and the proton donor for the monooxygenation of cyclohexane were dichloromethane and acetic acid, the TON of 11.7 in 1 h for the sum of CyO and CyOH. In the case of the epoxidation of 1-hexene, 1,2-di-chloroethane and propionic acid were the most suitable solvent and proton donor, respectively. When the epoxidation of 1-hexene was carried out using this combination, the maximum TON of 14.2 in 1 h for the epoxide were obtained

(5.3% yield based on 1-hexene, 81.4% selectivity, and $\phi(Zn)$ of 4.4%).

3.9. Conclusion

As described above, this $EuCl_3$ catalytic system was active for the monooxygenations under mild conditions. Reaction mechanism is not elucidated in this paper. The standard redox potential of Eu^{3+}/Eu^{2+} (-0.35 V vs. SHE) is higher than that of Zn^{2+}/Zn^0 (-0.77 V vs. SHE). Therefore, Eu^{3+} may be reduced to Eu^{2+} by Zn^0 in $EuCl_3$ catalytic system during the monooxygenation. Among the rare earth (RE) salts tested in Figs. 1 and 2, only europium has a redox potential RE^{3+}/RE^{2+} higher than that of Zn^{2+}/Zn^0. Thus, only europium may exhibit an especially high catalytic activity for the monooxygenation compared with the other rare earth elements. However, a low efficiency of Zn powder for the monooxygenation is a problem still to be solved. Further investigations are needed to determine the actual active form of europium species and reaction mechanisms for monooxygenations.

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