Direct Synthesis of Propene Oxide by using an $EuCl_3$ Catalytic System at Room Temperature

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Epoxidation of propene to propene oxide with O_2 is catalysed by an $EuCl_3$–Zn–$MeCO_2H$ catalytic system at 30 °C (TON of 12.1 in 1 h).

Direct synthesis of propene oxide from C_3H_6 and O_2 without using expensive oxidants such as *tert*-butyl hydroperoxide and H_2O_2 is the one of the most desirable reactions in the current chemical industry. Epoxidation of C_3H_6 catalysed by molybdenum[1] and titanium[2] catalysts with *tert*-butyl hydroperoxide is employed industrially as the well-known Halcon process. We have very recently reported the monooxygenation of hydrocarbons (hexene, hexane and benzene *etc.*) catalysed by $EuCl_3$ with O_2 in the presence of Zn powder (e^- donor) and acetic acid (H^+ donor).[3] Here, this $EuCl_3$ catalytic system was employed in an attempt to epoxidise C_3H_6 to propene oxide [eqn.(1)].

$$\mathrm{CH_2{=}CHMe} \xrightarrow[\mathrm{EuCl_3}]{\mathrm{O_2,\ Zn,\ MeCO_2H}} \mathrm{CH_2(O)CHMe} \qquad (1)$$

Epoxidation of C_3H_6 was carried out by batch-type procedures using an autoclave reactor (volume = 44 ml). $EuCl_3{\cdot}6H_2O$ (30 μmol) was dissolved in a mixture of acetic acid (2 ml, 35.3 mmol) and CH_2Cl_2 (2 ml) in a glass tube. After Zn powder (1 g, 15.3 mmol) was added, O_2 (0–4 atm, 0–6.43 mmol) was introduced into the autoclave reactor. The reaction was initiated by introducing C_3H_6 (0–10 atm, 0–16.1 mmol) and stirring the reaction mixture at 30 °C for 1 h. After the reaction, the products were analysed by GC (PEG-20M and Solbitol columns).

Table 1 shows the effect of the pressure of C_3H_6 and O_2 on formation of propene oxide. The main product in the liquid phase was propene oxide ($>90\%$ selectivity); allyl alcohol ($<4\%$), propan-2-ol ($<4\%$) and trace amounts of propan-1-ol and acetone were also formed along with a trace of CO_2 in the gas phase. Oxidation of C_3H_6 did not occur if any one of the components ($EuCl_3$, O_2, Zn powder, acetic acid) were removed from this catalytic system. The results in runs 1–4 show the effect of pressure of C_3H_6 on the formation of propene oxide at an oxygen pressure of 1 atm. Turnover number (TON) based on $EuCl_3$ for propene oxide formation increased with increasing pressure of C_3H_6. The selectivity towards propene oxide was 100% at <2 atm of C_3H_6, and slightly decreased on further increasing the pressure. The results in runs 4–7 show the effect of pressure of O_2 on the formation of propene oxide at $P(C_3H_6)$ = 8 atm. TON for the formation of propene oxide increased with increasing pressure of O_2, but selectivity towards propene oxide slightly decreased. These results indicate that higher pressures of C_3H_6 and O_2 are favourable for the formation of propene oxide in this $EuCl_3$–Zn–$MeCO_2H$ catalytic system. The maximum TON for propene oxide of 12.1 (yield of 2.26% based on C_3H_6) was obtained under the conditions of run 8.

Fig. 1 shows the kinetic curves for epoxidation of C_3H_6 under the same reaction conditions as run 8. A rapid formation of propene oxide was observed during the early stages of reaction (yield of 1.1% at 5 min). The formation rate of propene oxide decreased between 5 and 30 min. However, TON for propene oxide increased steadily after 30 min. The selectivity towards propene oxide was almost constant (94%) during the reaction. The highest yield for the formation of CO_2 was only 0.15% (Fig. 1). However, larger amounts of CO_2 (yield of 0.45% in 1 h) were produced when the reaction was carried out under the conditions in run 8 in the absence of C_3H_6. This result suggests that CO_2 is produced from acetic acid but not from C_3H_6.

The efficiency of Zn powder for the epoxidation was defined as $\phi(\mathrm{Zn}) = 100 \times$ [amount of the sum of products (mol)]/[amount of Zn powder reacted (mol)] (%). As described above, a TON of 12.1 (363 μmol) for propene oxide and a TON of 13.4 (402 μmol) for the sum of oxygenates were obtained in 1 h. The amount of Zn powder unreacted was 8208 μmol (0.5364 g) after the epoxidation. Thus, the amount of Zn powder reacted during the monooxygenation was estimated to be 7085 μmol. This amount corresponded well to the amount of $Zn(MeCO_2)_2{\cdot}2H_2O$ (6958 μmol, 1.53 g) obtained after the oxidation. Therefore, $\phi(\mathrm{Zn})$ for propene oxide and the sum of oxygenates were 5.1 and 5.7%, respectively. If the reactions proceeded *via* eqns. (2)

Table 1 Epoxidation of C_3H_6 with O_2 using the $EuCl_3$–Zn–$MeCO_2H$ catalytic system

Run	$P(C_3H_6)$	$P(O_2)$	Propene oxide		
			TON[a]	Yield[b] (%)	Selectivity[c] (%)
1	0.7	1.0	0.65	1.73	≈ 100
2	2.0	1.0	1.78	1.66	99.9
3	4.0	1.0	2.91	1.37	93.6
4	8.0	1.0	3.60	0.84	95.3
5	8.0	0	0	0	—
6	8.0	2.0	6.24	1.46	93.3
7	8.0	4.0	9.28	2.16	92.6
8	10.0	4.0	12.1	2.26	90.0

[a] Turnover number [amount of propene oxide (mol)/amount of $EuCl_3$ (mol)] for propene oxide based on $EuCl_3$. [b] Based on C_3H_6. [c] Based on C_3H_6 converted. T = 30 °C, reaction time 1 h, $EuCl_3$ (30 μmol), $MeCO_2H$ (2 ml), CH_2Cl_2 (2 ml).

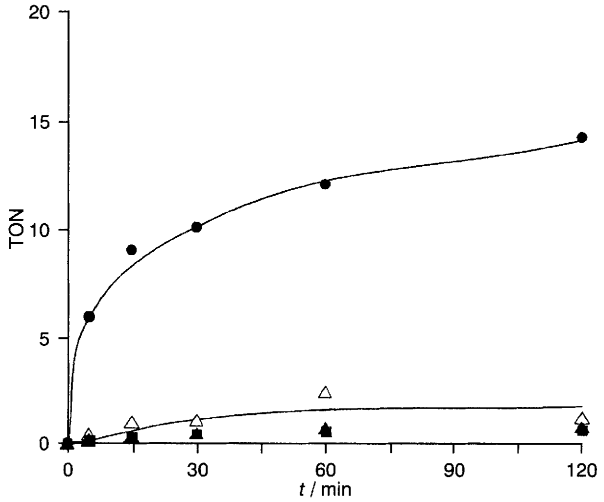

Fig. 1 Kinetic curves for epoxidation of C_3H_6 with O_2 using a $EuCl_3$–Zn–$MeCO_2H$ catalytic system. T = 30 °C, $EuCl_3$ (30.0 μmol), $MeCO_2H$ (2 ml), CH_2Cl_2 (2 ml), Zn powder (1 g), C_3H_6 (10 atm), O_2 (4 atm); (●) propene oxide, (▲) allyl alcohol, (■) propan-2-ol, (△) CO_2.

and (3) (the main process probably *via* the latter pathway), the conversions of Zn powder, acetic acid and O_2 were estimated to be 46, 40 and 58%, respectively, in 1 h. These high conversions explain the decrease in the rate of formation of the products with reaction time (Fig. 1).

$$C_3H_6 + O_2 + Zn + 2MeCO_2H \rightarrow CH_2(O)CHMe + Zn(MeCO_2)_2 + H_2O \qquad (2)$$

$$O_2 + 2\,Zn + 2\,MeCO_2H \rightarrow 2\,Zn(MeCO_2)_2 + 2\,H_2O \qquad (3)$$

As described above, our $EuCl_3$–Zn–$MeCO_2H$ catalytic system is effective for epoxidation of C_3H_6 with O_2. More investigations are needed to clarify the active oxygen species generated in this catalytic system and the reaction mechanisms for the epoxidation.

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