

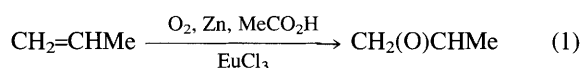
Direct Synthesis of Propene Oxide by using an EuCl_3 Catalytic System at Room Temperature

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Epoxidation of propene to propene oxide with O_2 is catalysed by an EuCl_3 -Zn-MeCO₂H 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 molybdenum¹ and titanium² 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)].



Epoxidation of C_3H_6 was carried out by batch-type procedures using an autoclave reactor (volume = 44 ml). $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (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

Table 1 Epoxidation of C_3H_6 with O_2 using the EuCl_3 -Zn-MeCO₂H catalytic system

Run	$P(\text{C}_3\text{H}_6)$	$P(\text{O}_2)$	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), MeCO₂H (2 ml), CH_2Cl_2 (2 ml).

increasing the pressure. The results in runs 4–7 show the effect of pressure of O_2 on the formation of propene oxide at $P(\text{C}_3\text{H}_6) = 8$ 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-MeCO₂H 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 $\phi(\text{Zn}) = 100 \times [\text{amount of the sum of products (mol)}] / [\text{amount of Zn powder reacted (mol)}]$ (%). 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 $\text{Zn}(\text{MeCO}_2)_2 \cdot 2\text{H}_2\text{O}$ (6958 μmol , 1.53 g) obtained after the oxidation. Therefore, $\phi(\text{Zn})$ for propene oxide and the sum of oxygenates were 5.1 and 5.7%, respectively. If the reactions proceeded *via* eqns. (2)

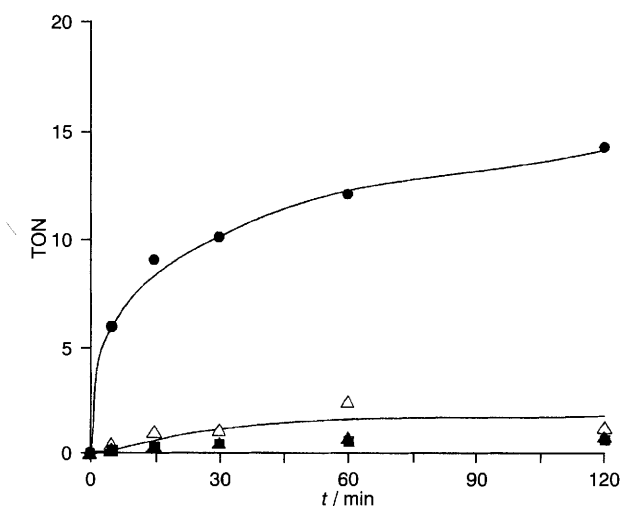
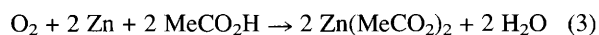
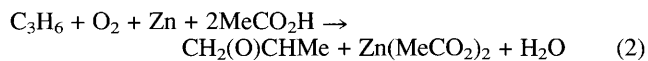


Fig. 1 Kinetic curves for epoxidation of C_3H_6 with O_2 using a EuCl_3 -Zn-MeCO₂H catalytic system. $T = 30$ °C, EuCl_3 (30.0 μmol), MeCO₂H (2 ml), CH_2Cl_2 (2 ml), Zn powder (1 g), C_3H_6 (10 atm), O_2 (4 atm); (●) propene oxide, (▲) allyl alcohol, (■) propan-2-ol, (△) CO_2 .

and (3) (the main process probably *via* the latter pathway), the conversions of Zn powder, acetic acid and O₂ 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).



As described above, our EuCl₃-Zn-MeCO₂H catalytic system is effective for epoxidation of C₃H₆ with O₂. 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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