

Epoxidation of Cyclohexene with Oxygen in Ultrasound Airlift Loop Reactor*

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Abstract Epoxidation of cyclohexene to cyclohexene oxide was studied in a new type reactor—the ultrasound airlift loop reactor. The influences of ultrasound intensity, molar ratio of isobutyraldehyde to cyclohexene and oxygen gas flow rate on the conversion of cyclohexene and selectivity of cyclohexene oxide were investigated and discussed, and the optimal operation condition was found, under which 95.2% conversion of cyclohexene and 90.7% selectivity of cyclohexene oxide were achieved. The ultrasonic airlift loop reactor utilizes the synergistic effect of sonochemistry and higher oxygen transfer rate. Possible reaction mechanisms were outlined and the reason of ultrasound promotion of epoxidation reaction was analyzed.

Keywords airlift loop reactor, ultrasound, epoxidation, cyclohexene, oxygen

1 INTRODUCTION

Epoxidation of alkenes has attracted much attention both in industrial processes and in organic syntheses. Epoxides are among the most useful intermediates for the synthesis of oxygen-containing natural products or the production of epoxy resins, *etc.* The use of molecular oxygen as an oxidant for such processes was particularly attractive from both economic and environmental standpoints. Much effort has been made to develop the epoxidation reaction of olefins by use of molecular oxygen in recent years[1—6]. However, the metal catalysts are usually needed.

The airlift loop reactors, characterized by a well-defined flow pattern, better dispersing effects, relatively low power consumption and a higher mass transfer coefficient, were widely used in multiphase chemical reactions[7—9]. And ultrasound-assisted chemical reactions have been carried out on many different types of organic reactions with high yield and short reaction time compared with conventional methods. Ultrasound airlift loop reactor is a new type of reactor that combines the advantages of airlift loop reactor and sonochemical reactor. So far, very few studies about this reactor were conducted. Tang *et al.*[10,11] had investigated in terms of hydrodynamics and mass transfer with the gas/liquid system. Kong *et al.*[12] and Xu *et al.*[13] used it in treatment of phenol wastewater. Yasuda *et al.*[14] decomposed tetraphenylporphine tetrasulfonic acid by ultrasonic irradiation using a stirring/circulation type reactor and an airlift loop reactor. The reaction did not proceed without ultrasound.

Recently, the oxidation of cyclohexanone to ϵ -caprolactone with dioxygen and benzaldehyde in ultrasound airlift loop reactor was reported[15]. It was found that this reactor is also efficient for the epoxidation of cyclohexene with dioxygen and *iso*-butyraldehyde in absent of metal catalyst. In this article, the facile oxidative conversion of cyclohexene to yield cyclohexene oxide using molecular oxygen in the ultrasound airlift

loop reactor and the optimum operation conditions of this reaction were proposed. A synergistic effect of sonochemistry and higher oxygen transfer rate in the reactor, the reaction mechanism and the possible reason of ultrasound promoting the epoxidation reaction were explored as well.

2 EXPERIMENTAL

2.1 Material and equipment

The yield was determined by SP6800A-GC (SE-30 capillary column ϕ 0.32mm \times 25m). The intermediate products were analyzed by Trace-DSQ and Trace-GC (Thermo Finnigan). DGC-1200 ultrasound processor (40kHz, 0—250W) with an ultrasonic probe (d = 2.1cm), hydrophone (CS-3) and oscillograph (SR8) were also used.

Cyclohexene, *iso*-butyraldehyde, 1,2-dichloroethane, *m*-perbenzoic acid (*m*-CPBA) (purity 85.6%) were obtained in AR grade.

2.2 Experimental setup

The experimental setup for the preparation of cyclohexene oxide using ultrasound airlift loop reactor was schematically shown in Fig.1.

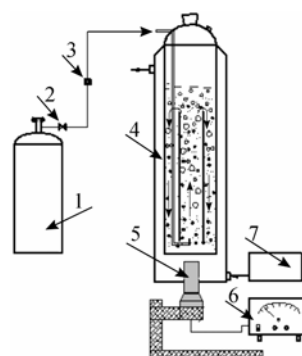


Figure 1 Diagram of experimental device

1—O₂ cylinder; 2—valve; 3—flowmeter; 4—airlift loop reactor; 5—ultrasonic probe; 6—ultrasonic generator; 7—thermostatic bath

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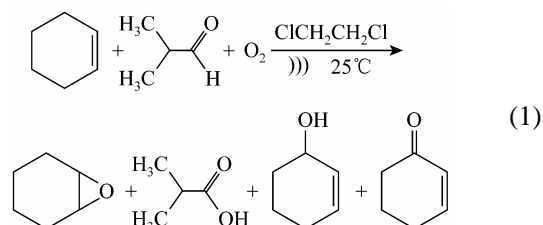
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The airlift loop reactor consists of two co-axial tubes with inner or outer diameters of 2.2 and 2.8cm and the heights of these two tubes are 18 and 30cm, respectively. The working volume of the reactor was 120cm³. A central jet nozzle with a diameter of 2.1 mm was designed and located at the bottom part of the riser and an ultrasound probe (40kHz, 0–250W) was inserted into the central column of the reactor from bottom. The gas flow rate was regulated by a calibrated rotameter and constant temperature was maintained using a temperature controlling system. Oxygen was bubbled into the riser and facilitated the circulation of solution inside the reactor.

2.3 Synthetic process

Co-oxidation of cyclohexene and isobutyraldehyde under the investigated conditions leads to formation of two main products: cyclohexene oxide formed as the result of the oxidation of cyclohexene, and butyric acid was the product of the oxidation of isobutyraldehyde. Two minor products of the oxidation cyclohexene: cyclohexenol and cyclohexenone are also formed in smaller quantities [Reaction (1)].



A typical procedure for synthesis of cyclohexene oxide was as follows: Cyclohexene (30mmol) isobutyraldehyde (75mmol) and 1,2-dichloroethane (110ml) were added and irradiated in the ultrasound airlift loop reactor. The mixture was stirred thoroughly by continuously feeding oxygen gas, while maintained at the temperature of 25°C by the thermostatic bath. The resultant mixture was allowed to react for 3h. The reaction progress was monitored by gas chromatograph (GC) determination. On the completion of the reaction, isobutyric acid was removed by successive treatment of the reaction mixture with Na₂SO₃ and NaHCO₃. The oxidation products in the solvent of dichloroethane were then identified by Trace-DSQ GC/MS system and quantified by SP 6800A GC, equipped with a capillary column (SE30-30m×0.25mm×0.25μm) and a flame ionization detector (FID), with bromobenzene as GC internal standard.

3 RESULTS AND DISCUSSION

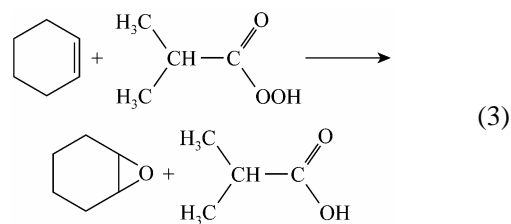
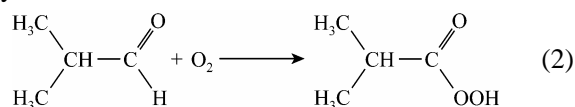
3.1 Comparison of different reactors

Our work was started with examination of different reactors. Results of epoxidation of cyclohexene at 25°C under 0.1MPa of O₂ with isobutyraldehyde were shown in Table 1. High yields of cyclohexene oxide were obtained as the predominant product, with small amounts of the allylic oxidation products: cyclohexenol and cyclohexenone. Under the influence of ultrasound, 88.7% and 95.2% conversions were attained at 3 h, yielding 77.5 % and 86.3% of cyclohexene oxide, respectively (Entries 3,4). While the silent reaction (magnetically stirred) only 52.5% conversion of cyclohexene was obtained (Entry 1).

The conversion of cyclohexene was found to be 5.6% higher in airlift loop reactor than that in common flask with stirring (Entries 1, 2). It was well known that the dispersion of oxygen in the liquid medium was very important in this reaction, especially in the absence of catalysts. The airlift loop reactor with better dispersing effect and higher mass transfer coefficient was superior to the magnetical stir. From the result it is found that the reaction is enhanced in ultrasound airlift reactor than that in ultrasound reactor or airlift loop reactor due to the synergistic effect of ultrasound and airlift loop reactor.

3.2 Effect of ultrasound

Acceleration of the epoxidation reaction given in Table 1 can be explained from the mechanism of co-oxidation cyclohexene and isobutyraldehyde. The reaction process consists of two steps: Reaction (2) isobutyraldehyde with O₂ to perisobutyric acid, and Reaction (3) oxygen transfer from perbutyric acid to cyclohexene:



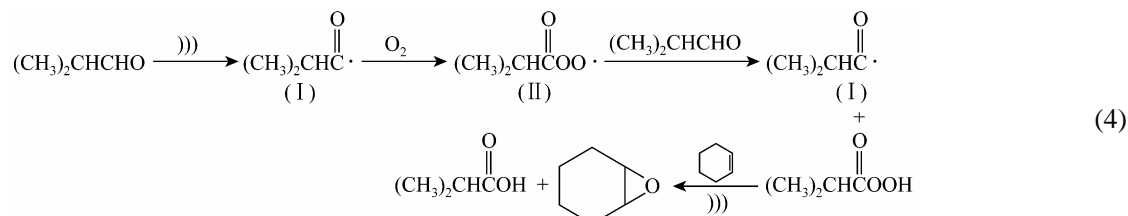
To ensure the role of ultrasound in each step the epoxidation of cyclohexene was carried out using

Table 1 Epoxidation of cyclohexene in different reactor conditions[ⓐ]

Entry	Reactor	Conversion [ⓑ] , %	Selectivity of products [Ⓒ] , %		
			Cyclohexene oxide	Cyclohexenol	Cyclohexenone
1	stirred reactor [Ⓓ]	52.5	92.3	3.4	4.3
2	airlift loop reactor [Ⓔ]	58.1	92.9	3.1	4.0
3	ultrasound reactor [Ⓕ]	88.7	87.4	3.7	5.9
4	ultrasound airlift reactor [Ⓖ]	95.2	90.7	3.0	5.5

ⓐ Reaction conditions: *n*(isobutyraldehyde)/*n*(cyclohexene)=2.5:1, 3h, 25°C; ⓑ 100ml three-necked round flask, cyclohexene (10mmol); Ⓒ *U_g* (2.09 cm·s⁻¹); Ⓓ 100ml three-necked round flask, cyclohexene (10mmol), *I* (0.65W·cm⁻²); Ⓔ *I* (0.65W·cm⁻²), *U_g* (1.15 cm·s⁻¹); Ⓕ determined by GC and based on cyclohexene used.

m-CPBA instead of O₂/isobutyraldehyde as an oxidant with and without ultrasound. A typical procedure of epoxidation of cyclohexene is as follows: cyclohexene (1mmol), *m*-CPBA (1.2mmol), and 1,2-dichloroethane (7ml) were added into a 25ml flat-bottom flask. The mixture was stirred at 0°C for 15min with or without ultrasound irradiation. The products were analyzed by GC. The oxidation in the presence of ultrasound gave a higher yield of cyclohexene oxide than without ultrasound. Yield of cyclohexene oxide is 87% and 54% with and without ultrasound, respectively. The fact



Equation (4) showed a possible mechanism of co-oxidation cyclohexene and isobutyraldehyde in the presence of ultrasound. First, ultrasound initiated some radicals in the solution, which in turn promoted converting isobutyraldehyde isobutyric acyl radical (I). The isobutyric acyl radical then reacted with dioxygen to give an isobutyric acylperoxy radical (II), which acted as a carrier in a chain mechanism by reacting with another isobutyraldehyde molecule to give the peroxy isobutyric acid, thereby generating another isobutyric acyl radical (I) and perisobutyric acid. Perisobutyric acid reacted with cyclohexene to give cyclohexene oxide and finally converted into isobutyric acid.

3.3 Effect of ultrasound intensity

In Fig.2 the conversion and selectivity with ultrasound intensity at 0, 0.27, 0.5, 0.65, 1.38, 2.88W·cm⁻² were compared. The conversion and selectivity was influenced by ultrasonic intensity. When ultrasound intensity was 0.65W·cm⁻² the conversion of cyclohexene was 95.2% and selectivity of the product was 90.7% giving the highest yield of cyclohexene oxide. However, the selectivity decreased sharply with increasing ultrasound intensity thereafter. Besides cyclohexene oxide, other side products such as cyclohexanone and polymers were also obtained.

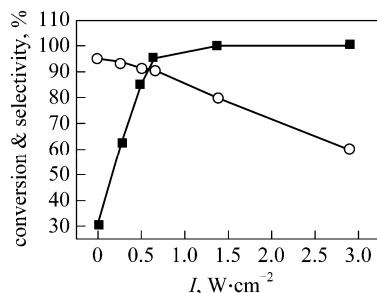


Figure 2 Effect of ultrasound intensities on conversion of cyclohexene and selectivity of cyclohexene oxide
 [Reaction conditions: cyclohexene (30mmol), isobutyraldehyde (75mmol), 1,2-dichloroethane (110ml), oxygen velocity (1.15cm·s⁻¹), 25°C]
 ■ conversion; ○ selectivity

support that ultrasound strongly promote the step of oxygen transfer from perisobutyric acid to cyclohexene.

In order to examine whether ultrasound promoted formation of perisobutyric acid, the amount of perisobutyric acid was measured by the iodometric titration method in both autoxidation of isobutyraldehyde with and without ultrasound. It was found that ultrasound speeded up the formation of perisobutyric acid but could not increase the yield of perisobutyric acid. Therefore, it suggested that ultrasound accelerate the two steps.

3.4 Effect of molar ratio of isobutyraldehyde and cyclohexene

The influence of $n(\text{isobutyraldehyde})/n(\text{cyclohexene})$ molar ratio on the conversion of cyclohexene and selectivity of cyclohexene oxide at the standard reaction conditions was shown in Fig.3. It was clear that when the ratio was varied from 1.5 to 3.0, the conversion of cyclohexene increased, whereas the selectivity of cyclohexene oxide reached a maximum at an intermediate ratio. When the ratio was 2.5 the selectivity was the highest up to 90.7 %.

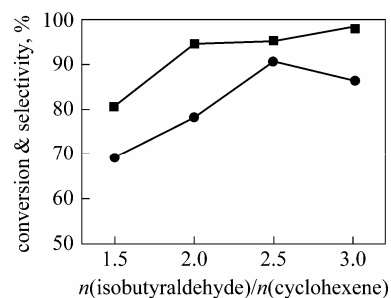


Figure 3 Effect of $n(\text{isobutyraldehyde})/n(\text{cyclohexene})$ on conversion of cyclohexene and selectivity of cyclohexene oxide
 [Reaction conditions: I (0.65W·cm⁻²), U_g (1.15cm·s⁻¹), 25°C]
 ■ conversion; ● selectivity

3.5 Effect of oxygen gas flow rate

As it can be seen from Fig.4, the conversion of cyclohexene and selectivity of cyclohexene oxide increased with oxygen flow rates when the oxygen flow rates less than 1.15cm·s⁻¹. It was mainly explained by the fact, as well known, that the increasing in oxygen gas flow rate brings about the increased gas holdup, smaller bubble diameter, larger gas-liquid interfacial area and the overall gas-liquid volumetric mass transfer coefficient, and thus causing the increase in the yield of cyclohexene oxide. However, when the oxygen flow rate was higher than 1.15cm·s⁻¹, conversion of cyclohexene decreased with the oxygen flow rate, because the superfluous bubble caused the loss of ultrasonic energy[10] and decreased ultrasound effect. When the oxygen flow rate was higher than 4.5cm·s⁻¹,

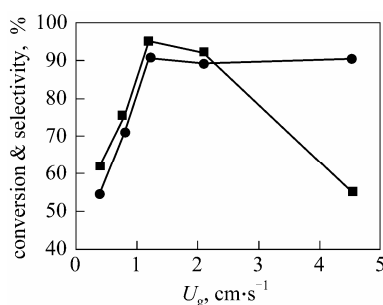


Figure 4 Effect of oxygen velocity on conversion of cyclohexene and selectivity of cyclohexene oxide

[Reaction conditions: cyclohexene (30mmol), isobutyraldehyde (75mmol), 1,2-dichloroethene (110ml), I ($0.65\text{W}\cdot\text{cm}^{-2}$), 25°C]

■ conversion; ● selectivity

the ultrasound had little effect on the selectivity of cyclohexene oxide. Therefore, the optimal oxygen flow rate was $1.15\text{cm}\cdot\text{s}^{-1}$, which is in accord with our previous research[15].

4 CONCLUSIONS

A new process for the production of cyclohexene oxide using molecular oxygen and isobutyraldehyde in ultrasonic airlift reactor has been described. From the experimental results, it can be seen that ultrasound effectively promotes the reaction. Ultrasound not only intensifies the rate of reaction but also increases the yield of cyclohexene oxide. The optimal operation conditions are determined as follows: the reaction temperature is 25°C , the molar ratio of cyclohexene to isobutyraldehyde is 1 : 2.5, the superficial oxygen gas velocity is $1.15\text{cm}\cdot\text{s}^{-1}$, and ultrasound irradiates 3h at 40kHz , $0.65\text{W}\cdot\text{cm}^{-2}$.

Under the optimal operation conditions, the average molar yield of cyclohexene oxide reaches up to 86.3%.

NOMENCLATURE

I ultrasound intensity, $\text{W}\cdot\text{m}^{-2}$
 n mole number of species
 U_g oxygen flow rate, $\text{cm}\cdot\text{s}^{-1}$

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