

The preparation of ϵ -caprolactone in airlift loop sonochemical reactor

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Abstract

A facile oxidation conversion of cyclohexanone to ϵ -caprolactone using molecular oxygen in a new type reactor—the airlift loop sonochemical reactor was studied. The influences of ultrasound intensity, reaction temperature, molar ratio of benzaldehyde to cyclohexanone and oxygen gas flow rate on the conversion and selectivity of cyclohexanone were investigated and discussed. An optimized set of operating conditions was found and ϵ -caprolactone production yield of 87.7% was achieved. The reactor plays a synergistic effect of sonochemistry and higher mass transfer. Possible reaction mechanism steps were outlined and the reasons of ultrasound promoting the reaction were analyzed.

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Keywords: Ultrasound; Airlift loop reactor; Preparation; Cyclohexanone; ϵ -Caprolactone

1. Introduction

Baeyer–Villiger (B–V) oxidation is frequently used for oxidative cleavage of a carbon–carbon bond adjacent to a carbonyl, which converts ketones to esters and cyclic ketones to lactones. The oxidation of cyclohexanone to ϵ -caprolactone is of particular industrial interest since the product is extensively used in the synthesis of poly-caprolactone (PCL), which can be used as foaming materials, polyesterpolyols, biodegradable plastics, etc. Usually, B–V oxidation is carried out by the use of peracids, such as peracetic acid and mCPBA [1,2]. But the industrial application of these methods is impractical for safety and cost reasons. Molecular oxygen, on the other hand, is an ideal oxidant in the regards of economy and environment. Several procedures for preparation of ϵ -caprolactone from cyclohexanone using molecular oxygen and aldehyde catalyzed by transition metal salts or complexes had been patented [3–7]. However, the selectivity of ϵ -caprolactone described in most of these patents was not satisfactory (70–80% selectivity) and the conversions of cyclohexanone were generally low (3–30%).

Airlift loop reactor, which was characterized by a well-defined flow pattern and better dispersing effects, relatively low power consumption and a higher mass transfer coefficient, was widely used in multiphase chemical reactions [8–11]. And as

we know ultrasound-assisted chemical reactions have been carried out on many different types of organic reactions with high yields and with short reaction times compared with conventional methods [12,13]. The chemical effects of ultrasound arise out of acoustic cavitation, which is the formation, growth and implosive collapse of bubbles in a liquid. There are two regions of sonochemical reactivity, the inside zone of the collapsing bubble and the interface between the bubble and the liquid. The cavitation can generate a temperature of around 5000 K and a pressure over 1000 atm [14], which enable many chemical reactions to occur.

The airlift loop sonochemical reactor, which combines ultrasound technique with airlift loop reactor is a new sonochemical reactor. The performance of this reactor in terms of hydrodynamics and mass transfer with the gas/liquid system has previously been investigated and used in treatment of phenols wastewater by our lab [15–18]. At lower gas flow rate, the energy associated with the gas is much less and hence, the supplementary action of ultrasound results in more favorable effects. Also, the gas remains in the active zone of cavitation for a longer time resulting in a better distribution of the gas [18]. The airlift loop sonochemical reactor plays a synergistic effect of sonochemistry and higher mass transfer.

In the paper, we report a facile oxidative conversion of cyclohexanone to ϵ -caprolactone using molecular oxygen and benzaldehyde as co-reducentant in an airlift loop sonochemical reactor. The aim of the present study was both to use the airlift loop sonochemical reactor in organic reaction of the gas–liquid

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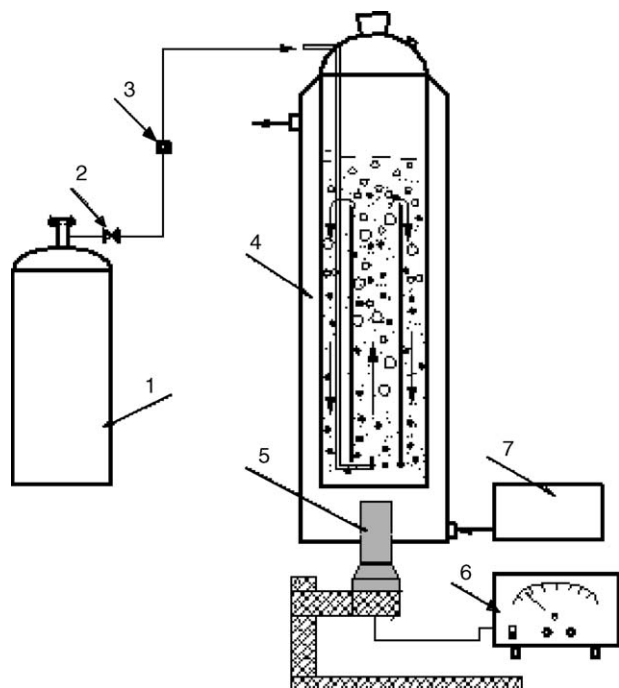


Fig. 1. Diagram of airlift loop sonochemical reactor: (1) O₂ cylinder; (2) stop valve; (3) flow meter; (4) airlift loop reactor; (5) ultrasonic probe; (6) ultrasonic generator; (7) thermostatic bath.

two-phase heterogeneous systems and to obtain the optimum operation conditions for the preparation of ϵ -caprolactone. We also investigate a synergistic effect of ultrasound and airlift loop reactor.

2. Experimental

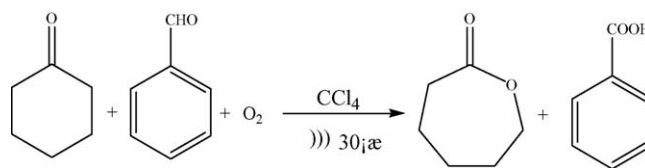
2.1. Experimental setup

The experimental setup for the preparation of ϵ -caprolactone using airlift sonochemical reactor was schematically shown in Fig. 1. The airlift loop reactor consists of two co-axial tubes with inner or outer diameters of 2.2 and 2.8 cm and the heights of these two tubes are 18 and 30 cm, respectively. The work volume of the reactor was 120 cm³. A concentric jet nozzle with a diameter of 2 mm was designed and located at the bottom part of the riser and an ultrasound probe (2.1 cm diameter) 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 in the course of reaction. Oxygen was pressurized into the riser and facilitated the circulation of solution inside of the reactor.

2.2. Synthetic protocol

The cyclohexanone and benzaldehyde were used as the starting materials, carbon tetrachloride as solvent and molecular oxygen as oxidant. The synthetic route was outlined in Scheme 1.

Co-oxidation of cyclohexanone and benzaldehyde in the investigated conditions leads to formation of two main products: ϵ -caprolactone formed as the result of the oxidation of



Scheme 1.

cyclohexanone, and benzoic acid was the product of the oxidation of benzaldehyde. Two minor products of the benzyl chloride and 2-chloro-cyclohexanone are also formed in smaller quantities. They are the result of a small quantity of chloride free radical react with benzaldehyde and cyclohexanone.

A typical ϵ -caprolactone synthesis procedure was as follows: benzaldehyde (60 mmol) and solvent of carbon tetrachloride (110 mL) were added and irradiated with ultrasound in the airlift loop sonochemical reactor. The mixtures were thoroughly mixed by continuous feeding of oxygen and the temperature was maintained at 30 °C by thermo static bath. After 10 min, cyclohexanone (30 mmol) was added and the resulting mixture was allowed to proceed for 2 h. The reaction progress was monitored by GC determination. On the completion of the reaction, benzoic acid was removed by successive treatment of the reaction mixture with Na₂SO₃ and NaHCO₃. The oxidation products in carbon tetrachloride solvent were then analyzed by GC.

2.3. Apparatus and reagents

The yields were determined by SP6800A-GC (SE-30 capillary column 0.32 mm × 25 m) and a FID detector, with bromobenzene as GC internal standard. The middle products were analyzed by Trace-DSQ and Trace-GC (Thermo Finnigan). DGC-1200 ultrasound processor (40 kHz, 0–250 W) with an ultrasonic probe ($d = 2.1$ cm). Hydrophone (CS-3) and oscillograph (SR8).

Cyclohexanone, benzaldehyde and carbon tetrachloride were reagent grade chemicals.

3. Experiment results and discussion

3.1. Effect of ultrasound

The effect of ultrasound on the oxidation of cyclohexanone was first examined. As shown in Table 1, under the influence of ultrasound the reaction completed in about 2 h yielding 87.7% of ϵ -caprolactone (Entry 1). While the silent reaction, prolonged stirring time to 5 h at elevated temperature (40 °C), the product yield was only 59.3% (Entry 2).

A possible explanation is that ultrasound can made carbon tetrachloride product free radical (Cl₃C•) and further promoted the formation of perbenzoic acid, which is an efficient oxidant for B–V oxidation. A chain reaction involving benzaldehyde and carbon tetrachloride has been setup as follows:

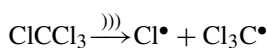
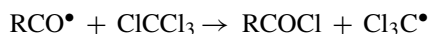
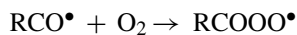
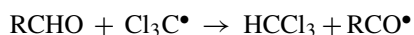
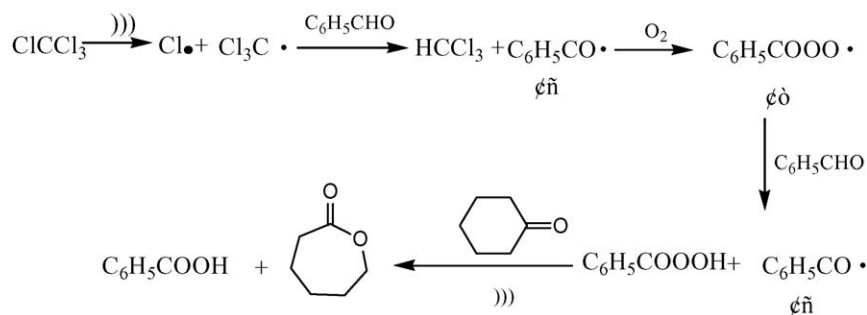


Table 1
Baeyer–Villiger oxidation of cyclohexanone in different reactor conditions^a

Entry	The form of reactor	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	Yield (%) ^b
1	Airlift sonochemical reactor	30	2	95.4	91.9	87.7
2	Airlift loop reaction	40	5	64.7	91.6	59.3

^a Reaction conditions: ketone 30 mmol, benzaldehyde 60 mmol, O₂ bubbling, carbon tetrachloride 110 mL, $U_g = 1.15 \text{ cm s}^{-1}$.

^b Yield determined by GC and based on ketones used (column temperature 140 °C, gasifying and detecting temperature are 240 °C).



Chloroform and benzoyl chloride were determined in the crude reaction mixture by GC–MS. Some authors showed that benzoyl chloride could accelerate the B–V oxidation to give high yields of lactones [20].

Scheme 2 showed a possible mechanism of oxidation of cyclohexanone to ϵ -caprolactone under ultrasound. First, ultrasound initiated carbon tetrachloride product free radical ($\text{Cl}_3\text{C}^\bullet$) and further promoted the formation of benzaldehyde to generate a benzoyl radical(I). The benzoyl radical then reacted with oxygen to give a perbenzoyl radical(II), which acted as a carrier in a chain mechanism by reacting with another benzaldehyde molecule to give perbenzoic acid, thereby generating another benzoyl radical(I). Perbenzoic acid, which is an efficient oxidant for B–V oxidation, reacted with cyclohexanone to give ϵ -caprolactone and finally, transformed into benzoic acid.

3.2. Effect of ultrasound intensity

In Fig. 2 the conversion degree and selectivity with ultrasound intensity (I) values of 0, 0.003, 0.013, 0.026, 0.041 and 0.12 W cm^{-2} were compared. The conversion and selectivity was influenced by ultrasonic intensity. When ultrasound intensity was 0.026 W cm^{-2} the conversion of cyclohexanone or selectivity of the product was the highest. However, the selectivity decreased sharply with increasing ultrasound intensity thereafter. Instead of ϵ -caprolactone, benzoic acid and caprolactone polymers were obtained. On the other hand, ultrasound

had a bigger effect on the mixing time and there was an optimal ultrasonic intensity [15].

3.3. Effect of benzaldehyde versus cyclohexanone molar ratio

The influence of n (benzaldehyde)/ n (cyclohexanone) on the conversion and selectivity of cyclohexanone at the standard reaction conditions was shown in Fig. 3. It was clear that the conversion of cyclohexanone increased with increasing n (benzaldehyde)/ n (cyclohexanone) ratio ranging from one to three, whereas the selectivity of ϵ -caprolactone dropped off accordingly. When the n (benzaldehyde)/ n (cyclohexanone) was two, the yield was 87.7%. The n (benzaldehyde)

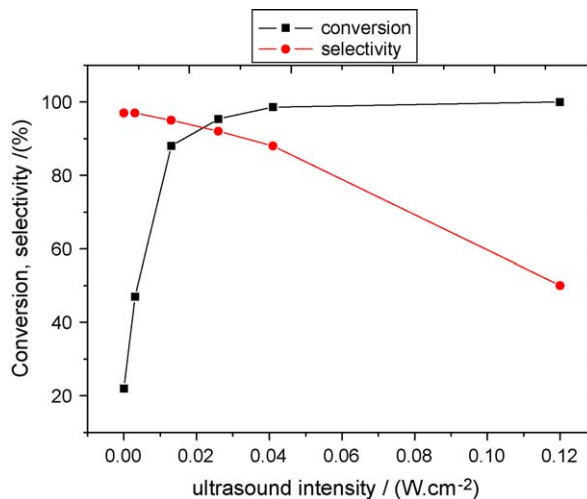


Fig. 2. Relationship between different ultrasound intensity and conversion or selectivity (conditions: $T = 30 \text{ }^\circ\text{C}$; n (benzaldehyde)/ n (cyclohexanone) = 2/1; $U_g = 1.15 \text{ cm s}^{-1}$; $t = 2 \text{ h}$).

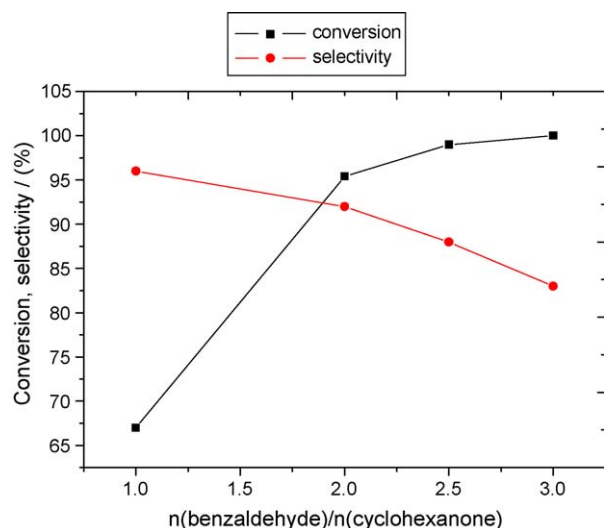


Fig. 3. Relationship between n (benzaldehyde)/ n (cyclohexanone) and conversion or selectivity (conditions: $T = 30\text{ }^{\circ}\text{C}$; $U_g = 1.15\text{ cm s}^{-1}$; $I = 0.026\text{ W cm}^{-2}$; $t = 2\text{ h}$).

hyde)/ n (cyclohexanone) is usually three in this type reaction [20–23].

3.4. Effect of oxygen flow rates

As it can be seen from Fig. 4, the conversion and selectivity of cyclohexanone increased with oxygen flow rates (U_g). It can be explained by the fact that the increase in oxygen flow rate brings about the increase of the gas holdup, the decrease of bubble diameter, the increases of the gas–liquid interfacial area and the overall gas–liquid volumetric mass transfer coefficient, and thus cause increase in conversion and selectivity of cyclohexanone. In the airlift loop reactor, when oxygen flow rate reached 2.09 cm s^{-1} , the circle liquid presented overfall phenomena. With the increase of oxygen flow rates, the conversion of cyclohexanone improved slowly. Whereas forming the overfall only

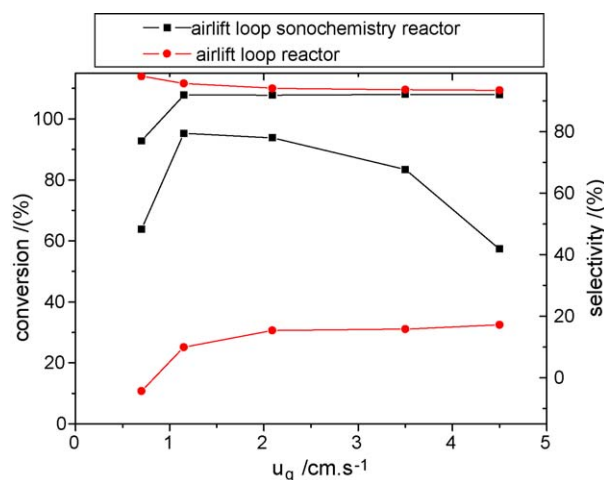


Fig. 4. Relationship between oxygen flow rate and conversion or selectivity in two sorts of reactor (conditions: $T = 30\text{ }^{\circ}\text{C}$; n (benzaldehyde)/ n (cyclohexanone) = 2/1; $I = 0.026\text{ W cm}^{-2}$, $t = 2\text{ h}$).

need oxygen flow rates of 1.15 cm s^{-1} in present of ultrasound. When the oxygen flow rates was higher than 1.15 cm s^{-1} , conversion of cyclohexanone did not depend on oxygen flow rates; the chemical regime was reached and more flow rates would result in a decrease of ultrasound effect due to the presence of gas. Because the superfluous bubbles arise the lose of ultrasonic energy. At higher flow rates, the extent of attenuation will be more leading to lower availability of the ultrasonic energy [19]. When the gas velocity increases to 6.15 cm s^{-1} , the relative effect of ultrasound is rather minor [16]. Thus, the optimal oxygen flow rates was 1.15 cm s^{-1} .

4. Conclusions

A new process for the production of ϵ -caprolactone using molecular oxygen and benzaldehyde without catalyst in airlift loop sonochemical reactor has been described. From the results, it can be seen that that ultrasound effectively promoted the reaction and intensified the rates of reactions. Under ultrasound, the amount of benzaldehyde can be reduced from 75% to 67%. The optimized operation conditions were listed as follows: the reaction temperature was $30\text{ }^{\circ}\text{C}$, the molar ratio of cyclohexanone to benzaldehyde was 1:2, the oxygen flow rate was 1.15 cm s^{-1} , and ultrasonic irradiations 2 h at 40 kHz, 0.026 W cm^{-2} . Under the optimum operation conditions, the average molar yield of ϵ -caprolactone come up to 87.7%.

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