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Ultrasound assisted phase-transfer catalytic epoxidation of 1,7-octadiene – A kinetic study

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Abstract

An ultrasound assisted phase-transfer catalyzed epoxidation of 1,7-octadiene is greatly enhanced by using a cocatalyst of phosphotungstic acid in the presence of hydrogen peroxide in an organic solvent/aqueous solution two-phase medium. An active intermediate of the catalyst ($Q_3PW_{12}(O)_nO_{40}$, where $Q = R_4N^+$) produced from the reaction of phosphotungstic acid, hydrogen peroxide, and Aliquat 336. A rational mechanism of epoxidation is proposed to account for the reaction from the experimental evidence. The organic-phase reactions, including two series reactions, are the rate-controlling steps to produce two products, viz., 1,2-epoxy-7-octene and 1,2,7,8-diepoxyoctane. The kinetics of epoxidation, including the characteristics of the catalyst and the effect of the amount of cocatalyst, agitation speed, quaternary ammonium salts, amount of Aliquat 336, amount of hydrogen peroxide, amount of chloroform, pH value, organic solvents, and temperature on the conversion of 1,7-octadiene were investigated in detail. A kinetic model was built, from which a pseudo-first-order rate law is sufficient to describe the behavior of the reaction.

Keywords: Phase-transfer catalysis; Ultrasound acceleration; Sonochemistry; 1,7-Octadiene; Epoxidation; Phosphotungstic acid; Kinetic study

1. Introduction

The rate of reacting two immiscible reactants is low because of a shortage of molecule collisions. To increase the reaction rate, the common way to solve this problem is to carry out the reaction at extreme conditions or in a cosolvent. However, this effort is limited. Also, the byproducts, from which the side reactions frequently occur at extreme reaction conditions, were produced. The characteristics of phase-transfer catalysis (PTC) meet the requirement to produce a high reaction rate [1–5].

The high-additive-value epoxides are extensively used in insulating materials, adhesives, coating materials, construction materials, and electronic parts, in recent years. The conventional methods to synthesize epoxides include the oxidation of olefins by organic peroxycarboxylic acids and peroxides [6–13]. However, the organic insoluble oxidant restricts the oxidation of hydrophobic olefins. In addition, the epoxidation of a water-insoluble substance by oxidant and cocatalyst was carried out to some extent under PTC conditions. Nevertheless, this application is still restricted to the oxidation of cycloolefins. For example, the yield obtained from the epoxidation of long-chain olefins under PTC and cocatalyst is low. Quaternary ammonium salts, in general, are used as the phase-transfer catalysts [14]. Conventionally, the active oxidation catalyst was prepared from the reaction of sodium tungstate, phosphoric acid, and hydrogen peroxide and quaternary ammonium salts [12,15,16].

The use of ultrasound in promotion of phase-transfer catalysis reactions has met with success in some reactions [17,18]. This ultrasonic method (non-conventional method) is now recognized as viable environmentally benign alternatives [19–22]. Although, sonication methods have been initially applied to homogeneous reactions in a variety of

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solvents, this approach has now evolved into a useful technique in heterogeneous reactions [21–25].

The primary purpose of this work is to improve the epoxidation of 1,7-octadiene (long-chain olefin) under ultrasound condition (28 kHz; 200 W) along with phosphotungstic acid ($H_3PW_{12}O_{40}$), hydrogen peroxide, and Aliquat 336 (trioctylmethylammonium chloride), in an organic solvent/aqueous solution two phase medium. An active intermediate of the catalyst ($Q_3PW_{12}(O)_nO_{40}$) produced from the reaction of phosphotungstic acid, hydrogen peroxide, and Aliquat 336. A rational reaction mechanism is proposed. Satisfactory explanations were made in using phosphotungstic acid as the cocatalyst. Two products, 1,2-epoxy-7-octene and 1,2,7,8-diepoxyoctane, were obtained from the series of reactions in the organic solution. The kinetics of reaction, such as the characteristics of the catalyst, agitation speed, quaternary ammonium salts, amount of Aliquat 336, pH value, amount of cocatalyst, amount of hydrogen peroxide, organic solvents, the amount of chloroform, and temperature, were investigated in detail. A kinetic model using the pseudo-steady-state hypothesis (PSSH) was built up to obtain the two apparent rate constants of the series of reactions in the organic phase.

2. Experimental

2.1. Materials

All reagents including 1,7-octadiene, phosphotungstic acid ($H_3PW_{12}O_{40}$), hydrogen peroxide, trioctylmethylammonium chloride [Aliquat 336, Q^+Cl^-, where $Q^+ = (C_8H_{17})_3N^+CH_3$] and other reagents for synthesis were guaranteed (GR) grade chemicals, and were used as received without further purification.

2.2. Instrumentation

The ultrasonic apparatus consisted of two layers stainless steel body to have safe to use. This ultrasonic apparatus (model L-400) was specially designed and constructed by a Ko Hsieh Instruments Co. Ltd., Taipei, Taiwan. The internal dimensions of the ultrasonic cleaner tank is 340 mm × 250 mm × 250 mm with liquid holding capacity of 22 l. The external tank size is 350 mm × 355 mm × 410 mm. Two types of frequencies of ultrasound were used in these experiments which are 28 kHz and 40 kHz with each output is 200 W. Both ultrasound separately produces through a flat transducer mounted at the bottom of the tank. In this ultrasonic instruments there is a provision for a drain as well as an outlet at the top, which gives facility of continuous operation of work. An additional heater with a facility of temperature controller has been also provided so as to facilitate some high and low temperature reactions.

2.3. Kinetics of the epoxidation of 1,7-octadiene

The reactor was a 150 ml three-necked Pyrex round-bottom flask. Each neck having the purpose of agitating the solution, inserting the thermometer, taking the samples, and feeding the feed. This reaction vessel was suspended at the center of the ultrasonic cleaning bath to get the maximum ultrasound energy. A known quantity of phosphotungstic acid (1.92×10^{-4} mol) was completely dissolved in a hydrogen peroxide aqueous solution (9.23×10^{-2} mol, 8%). The solution was put into the reactor, which was submerged into a well-controlled temperature ultrasonic water bath. Then, Aliquat 336 (5.77×10^{-4} mol) was first dissolved in chloroform (16 ml) and then added to the solution, and the resulting mixture was agitated for one min. 1,7-octadiene (A) (9.09×10^{-3} mol) dissolved in chloroform (16 ml) and biphenyl (3.24×10^{-3} mol; internal standard) were then introduced to the reactor to start the reaction. The sample (0.1 ml) was withdrawn periodically from the reactor and put into the test tubes containing 1 ml of chloroform. The samples were analyzed for the two products, mono-substituted product (1,2-epoxy-7-octene) and bi-substituted product (1,2,7,8-diepoxyoctane). The content of the reactant (1,7-octadiene, A) and the two products (B and C) were measured by Gas Chromatography (GC-Shimadzu 17A model). The analyzing conditions were as follows: Column, 30 m × 0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxane); injection temperature, 250 °C; detector, flame ionization detector (300 °C). The product formed were analysed by comparison of their retention times with authentic samples. Yields were determined from standard curve and using biphenyl as internal standard. We used 28 kHz (200 W) ultrasonic wave for the kinetic study of this reaction.

3. Reaction mechanism and kinetic model

A total reaction for the present system is

$$\underset{(C_8H_{14},A)}{\text{1,7-Octadiene}} \xrightarrow[\text{Hydrogen peroxide}]{\substack{\text{Phosphotungstic acid} \\ \text{Aliquat 336}}} \underset{(C_8H_{14}O,B)}{\text{1,2-Epoxy-7-octene}} + \underset{(C_8H_{14}O_2,C)}{\text{1,2,7,8-Diepoxyoctane}}$$