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Extractive reaction for epoxidation of cyclohexene to cyclohexene oxide using dioxirane in ketone/Oxone® system

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Abstract

Extractive reaction for the epoxidation of cyclohexene to cyclohexene oxide using dioxirane was studied. The studies were divided into two main parts: (1) comparison of different cyclohexene oxide preparation methods and (2) effects of operating parameters such as stirring rate, type of solvent, initial solvent/aqueous ratio, temperature, pH and amount of catalyst on the performance of the extractive reaction. The results revealed that the best method was the epoxidation of cyclohexene by dioxirane in an extractive reaction system with presence of a phase transfer catalyst. A maximum conversion obtained from the system without a solvent can be exceeded with an extractive reaction process by introducing of an immiscible solvent to the system. It was found that the cyclohexene oxide yield increased with increasing stirring rate and the amount of acetone, and that the reaction system using dichloromethane showed the highest performance compared to those with toluene and benzene.

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Keywords: Extractive reaction; Epoxidation; Dioxirane; Cyclohexene oxide

1. Introduction

In recent years, single units that combine reaction and separation operations have received considerable attention. The reduction in the number of equipment units leads to investment saving, and simultaneous reaction and separation provides the possibility of bypassing the equilibrium limitation imposed by reversible reaction. The use of reactive distillation in the production of methyl acetate and methyl *tert*-butyl ether clearly demonstrates the benefits [1,2]. Similar advantages have been realized with simultaneous reaction and adsorption in a chromatographic reactor [3,4], permeation in a membrane reactor [5], and extraction in a liquid–liquid two-phase reactor [6]. A precipitator is another type of reactive separation unit in which a product precipitates out of solution, thus eliminating a crystallizer from the process flowsheet [7].

In an extractive reaction, reaction and extraction occur simultaneously. A second liquid phase containing a solvent can be deliberately imposed on the system. Frequently, the solvent selectively extracts an intermediate or a product, thereby preventing its further reaction and resulting in a higher yield and selectivity [8].

At present, an extractive reaction is mainly used in biochemical processes involving the use of enzymes [9–13]. For chemical reaction processes, there is a little research on this area and only a few reactions have been studied [9,14–18]. Because of these reasons, this work attempted to investigate the application of extractive reaction to a chemical reaction system. Epoxidation, a reaction used to generate epoxides from alkene, was chosen to study an extractive reaction process in this work.

Epoxides are important industrial organic intermediates due to their highly reactive moiety. In practice, epoxides are formed in an initial step and they are reacted further to provide industrially important products, such as pharmaceuticals, surfactants, detergents, anti-static agents, corrosion protection agents, additives for laundry detergents, lubricating oils, textiles, and cosmetics.

Generally, oxidizing agents frequently used for epoxidation of alkene are organic peracids and peroxy acids. Dioxiranes are new oxidizing agents. They are the smallest cyclic peroxide systems known as reactive and efficient oxidizing agents, usually prepared in solutions of a parent ketone. The preparation method that has received the most attention is that containing a ketone and the peracid, namely potassium

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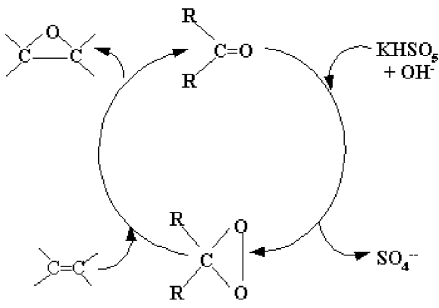


Fig. 1. Catalytic cycle of the ketone/Oxone® system [19].

peroxymonosulphate ($KHSO_5$) commercially available as Oxone® ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$). The catalytic cycle usually drawn for dioxiranes [19], as shown in Fig. 1, indicates that $KHSO_5$ is the oxidizing agent and the ketone acts as a catalyst. However, major problems encountered in this reaction system are from their low conversion and yield.

In this paper, the epoxidation of cyclohexene to cyclohexene oxide by dioxirane generated in situ from Oxone® and acetone was used as a test reaction for studying an extractive reaction. Experiments were only performed in a lab-scale batch reactor. The objectives of the study were to investigate the performance of epoxidation of cyclohexene in an extractive reaction process compared to other cyclohexene oxide preparation methods and effects of operating conditions on the yield of cyclohexene oxide in the extractive reaction.

2. Experimental section

The epoxidation of cyclohexene to cyclohexene oxide was carried out in a batch reactor. The pH of the reaction was maintained at a constant value with deviation less than 0.01 pH unit. A Radiometer Copenhagen pH stat fitted with a recorder showed base addition as a function of time. The schematic diagram of the experimental setup is given in Fig. 2.

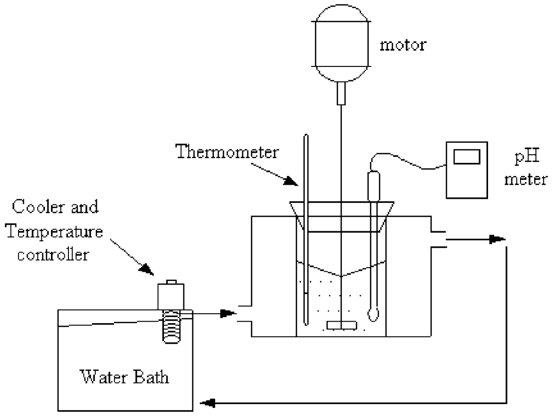


Fig. 2. Schematic diagram of the experimental setup.

2.1. Experimental procedure

Oxone®, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ (3.69 g, 11.18 mmol $KHSO_5$), was placed in the reaction vessel. Na_2EDTA (0.1 g, 0.27 mmol) was added to prevent trace metal-catalyzed decomposition of $KHSO_5$ along with the phase transfer catalyst, Bu_4NHSO_4 (0.17 g, 0.5 mmol). Phosphate buffer (10 cm^3, pH = 7.5) and distilled water were added to bring the total volume of the solution to 30 cm^3. The mixture was stirred until obtaining homogeneous phase and then an organic solvent was added. The reaction temperature was controlled at a required value. The pH of the reaction mixture at this stage was 1.7, 0.5 M KOH was added to bring the pH to the required value for the reaction (pH = 7.5 in most cases). Once the desired pH was obtained, the substrate cyclohexene (2.47 mmol, 0.255 cm^3), the internal standard *n*-octane (0.2 cm^3) and the acetone (as the catalyst) were added. As the reaction proceeded, KOH was added as required to maintain the constant pH. Samples of the reaction mixture were taken at various times for GC analysis.

2.2. Analytical method

Analysis was carried out in a SHIMADZU GC 14B gas chromatography. It was fitted with a capillary column with dimension of 30 m × 0.248 mm (0.25 μm film thickness) and a flame ionization detector. Two internal standards were used in this work. The first one was *n*-octane, which was added to the reaction system and used to measure the diluting effect of KOH addition. The second internal standard was prepared as a 1% (v/v) solution of standard substance in organic solvent and was added prior to GC analysis. A sample of 5 cm^3 was withdrawn from the reaction vessel and added with a few drops of 1 M H_2SO_4 to quench the reaction. This was allowed to settle and a set volume of the organic solvent layer (1 cm^3) was withdrawn and the internal standard (1 cm^3) was added.

3. Results and discussion

3.1. Comparison of different preparation methods

In this part, the preparation methods of cyclohexene oxide were divided into four cases: i.e. (1) epoxidation with $KHSO_5$, (2) epoxidation with $KHSO_5$ and acetone, (3) epoxidation with $KHSO_5$, acetone and a solvent, and 4) epoxidation with $KHSO_5$, acetone, a solvent and a phase transfer catalyst. It is noted that $KHSO_5$ was used as an aqueous solution throughout this study, and that a case with direct epoxidation between solid $KHSO_5$ and cyclohexene was not considered because organic-$KHSO_5$ mixtures may cause combustion [20]. Figs. 3 and 4 compare the conversion and the selectivity of cyclohexene oxide, respectively, between different methods.

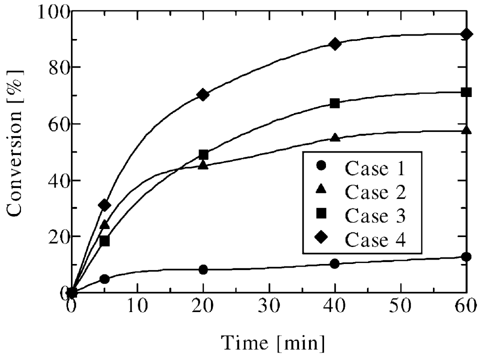


Fig. 3. The conversion of cyclohexene as a function of time (stirring rate = 2040 rpm, pH = 7.5, reaction temperature = 293 K and reaction time = 60 min). Case 1: Cyclohexene=9.7 mmol (1 cm^3), Oxone®=11.18 mmol (3.69 g). Case 2: Cyclohexene=9.7 mmol (1 cm^3), Oxone®=11.18 mmol (3.69 g), acetone = 27 mmol. Case 3: Cyclohexene = 9.7 mmol (1 cm^3), Oxone® = 11.18 mmol (3.69 g), acetone = 27 mmol, initial solvent/aqueous ratio = 0.83 using dichloromethane as a solvent. Case 4: Cyclohexene = 9.7 mmol (1 cm^3), Oxone® = 11.18 mmol (3.69 g), acetone = 27 mmol, Bu_4NHSO_4 = 0.5 mmol (0.17 g), initial solvent/aqueous ratio = 0.83 using dichloromethane as a solvent.

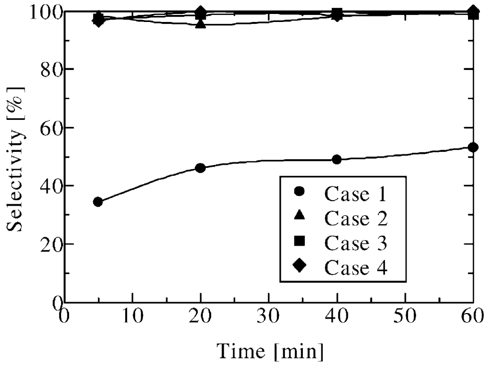
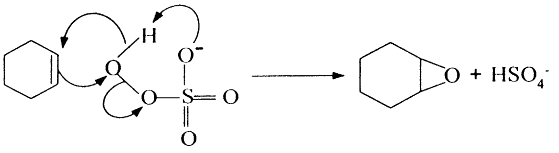


Fig. 4. The selectivity of cyclohexene oxide as a function of time.

3.1.1. Case 1: Epoxidation with $KHSO_5$ (H_2O + $KHSO_5$/cyclohexene)

In this case, cyclohexene was directly epoxidized with $KHSO_5$ to form cyclohexene oxide. The reaction mechanism was studied earlier by Zhu and Ford [21] as shown in Eq. (1).



(1)

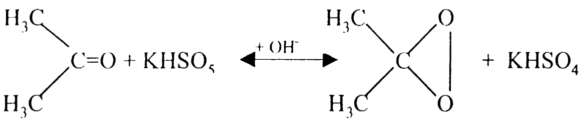
Low conversion of cyclohexene with moderate selectivity of cyclohexene oxide (approximately 50%) was obtained after a reaction time of 1 h. Because two reactants (cyclohexene and $KHSO_5$) are immiscible, the reaction takes place at an interface as illustrated by Fig. 5. Interfacial mass transfer may be a rate-determining step for the reaction system and, consequently, the low conversion was obtained. In addition, it was observed that $KHSO_5$ can further transform the product to its corresponding 1,2-diol [21]. As a result, the moderate selectivity was observed from this system.

3.1.2. Case 2: Epoxidation with $KHSO_5$ and acetone (H_2O + $KHSO_5$ + acetone/cyclohexene + acetone)

It is observed that the addition of acetone to the reaction system in Case 1 can significantly improve both conversion and selectivity, i.e. the conversion increased from 12 to 57% and the selectivity increased from 53 to 99%. This is because a dioxirane, a highly reactive and efficient oxidizing agent, was formed from acetone and $KHSO_5$ and then it selectively reacted with cyclohexene to form cyclohexene oxide and acetone as shown in Eqs. (2) and (3), respectively. The dioxirane has been successfully utilized to epoxidize other alkenes such as cyclooctane, β-methylstyrene and pyridine [22].

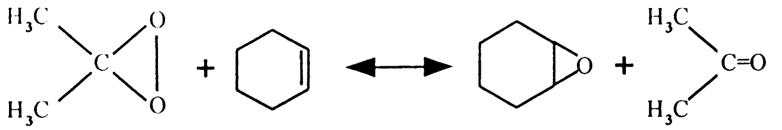
Fig. 6 shows the schematic diagram of the synthesis of cyclohexene oxide. Since the dioxirane, produced from acetone and $KHSO_5$, is miscible with the reactant, cyclohexene, the reaction can take place both readily in the organic phase and at the interface. This should be another reason for the improved conversion, compared to Case 1. In addition, it should be noted that acetone is considered to be a catalyst in this system since it is consumed to form the dioxirane, but it is subsequently generated as a co-product in the cyclohexene oxide production or it can be considered as a mediator since it mediates the oxidation of cyclohexene via an oxidation/reduction cycle.

Step 1: Formation of dioxirane (in the aqueous phase).



(2)

Step 2: Epoxidation of cyclohexene using dioxirane (in the organic phase).



(3)

3.1.3. Case 3: Epoxidation with $KHSO_5$, acetone and a solvent (H_2O + $KHSO_5$ + acetone/cyclohexene + acetone + solvent)

This system represents an extractive reaction process. The operating condition was the same as Case 2 except that dichloromethane as a solvent was added. Comparison between the cases with and without dichloromethane reveals

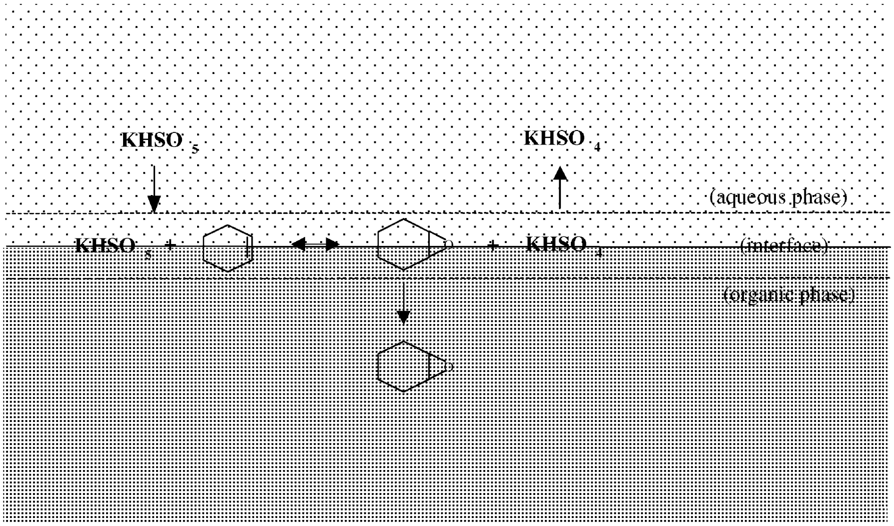


Fig. 5. The scheme for the synthesis of cyclohexene oxide in Case 1; (▦): organic phase; (⬚): aqueous phase.

that both systems offered very high selectivity of almost 100%, however, higher conversion was obtained when the solvent was introduced, i.e. the conversion at 1 h increased from 57 to 71%.

Deliberate imposition of the solvent to the reaction system alters the reaction performance via thermodynamic effects such as changing in distribution coefficient and Gibbs energy of mixing and kinetic effects such as changing in reaction rate and heat and mass transfer rates. Fig. 7 shows the reaction mechanism of this reaction system. When the solvent is added to the system, acetone can be dissolved in both the aqueous and the organic phases. As a result, the dioxirane can be formed both in the aqueous phase and at the aqueous/organic interface by the reaction between acetone and $KHSO_5$. Because the dioxirane can be preferentially extracted into the organic phase, the presence of the solvent helps transfer the reactant $KHSO_5$ (in the form of dioxirane) from the aqueous phase to the organic phase where it reacts with cyclohexene. Hence, in this study, the extractive reaction process offers significant improvement in yield over the conventional single-phase system by promoting the transfer of one reactant in the aqueous phase to react with the other reactant in the solvent phase.

3.1.4. Case 4: Epoxidation with $KHSO_5$, acetone, a solvent and a phase transfer catalyst ($H_2O + KHSO_5 + PTC$/cyclohexene + acetone + solvent)

This case is also an extractive reaction process. The operating condition was the same as Case 3, but a phase transfer catalyst, Bu_4NHSO_4 was added. The results show that

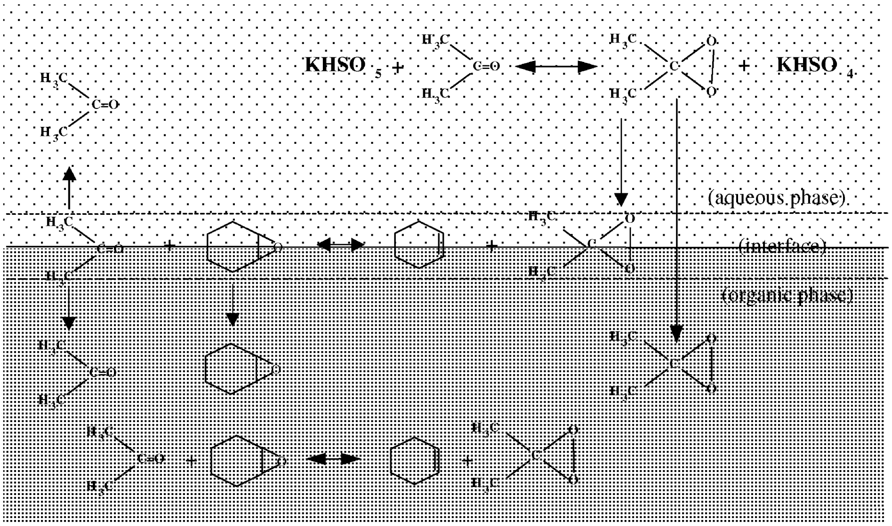


Fig. 6. The scheme for the synthesis of cyclohexene oxide in Case 2; (▦): organic phase; (⬚): aqueous phase.

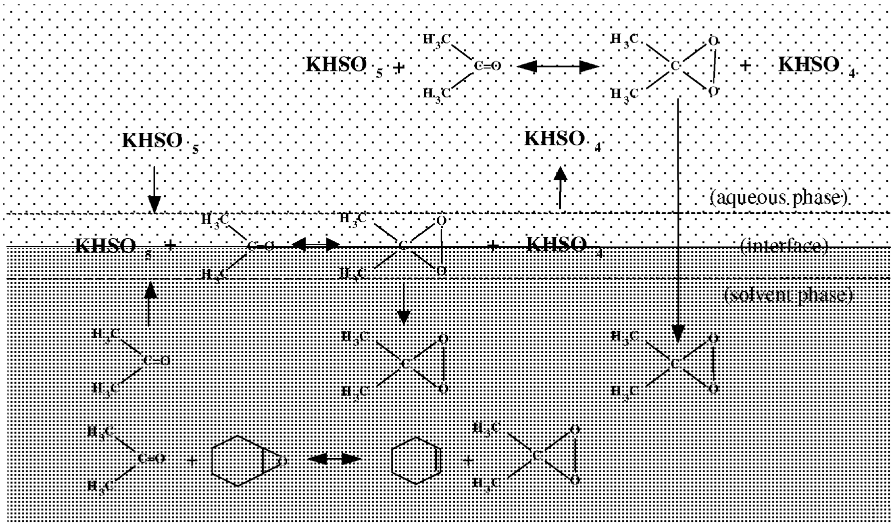


Fig. 7. The scheme for the synthesis of cyclohexene oxide in Case 3; (▦): organic phase; (⬚): aqueous phase).

almost 100% selectivity was obtained, however, when compared to Case 3 the conversion at 1 h was improved from 71 to 91%. The phase transfer catalyst helps improve the rate of formation of dioxirane and its transfer rate to the organic phase by, as illustrated by Fig. 8 [23], reacting with $KHSO_5$ in the aqueous phase to form an organic salt which is subsequently extracted to the organic phase. The organic salt reacts with acetone to form the dioxirane and returns the phase transfer catalyst back to the system. Because the dioxirane is formed and transferred to the organic phase at faster rate, the higher conversion was obtained with the use of the phase transfer catalyst. This indicates that mass transfer effect also plays an important role on the reactor performance.

It is important to note that the experimental results of all cases leveled off at approximately 1 h. In order to investigate this observation, another set of experiment was carried out. Volumes of KOH solution necessary for maintaining pH at the constant value of 7.5 were measured with time for four different cases, i.e. (1) $KHSO_5$ solution, (2) $KHSO_5$ + acetone solution, (3) $KHSO_5$ + acetone + Na_2EDTA solution and (4) $KHSO_5$ + acetone + Na_2EDTA + phase transfer catalyst solution. No solvent and cyclohexene was added in all cases. After the solution was adjusted to $pH = 7.5$ by a predetermined amount of KOH solution, the volume of KOH solution necessary for maintaining the constant pH was recorded and the results were shown in Fig. 9. Because $KHSO_5$ ($pK_a = 9.4$) can be decomposed to form $KHSO_4$ ($pK_a = 1.9$), causing the decrease of pH, a KOH solution was necessary to keep the constant pH. In Case 1, it was observed that the decomposition of $KHSO_5$ was initially

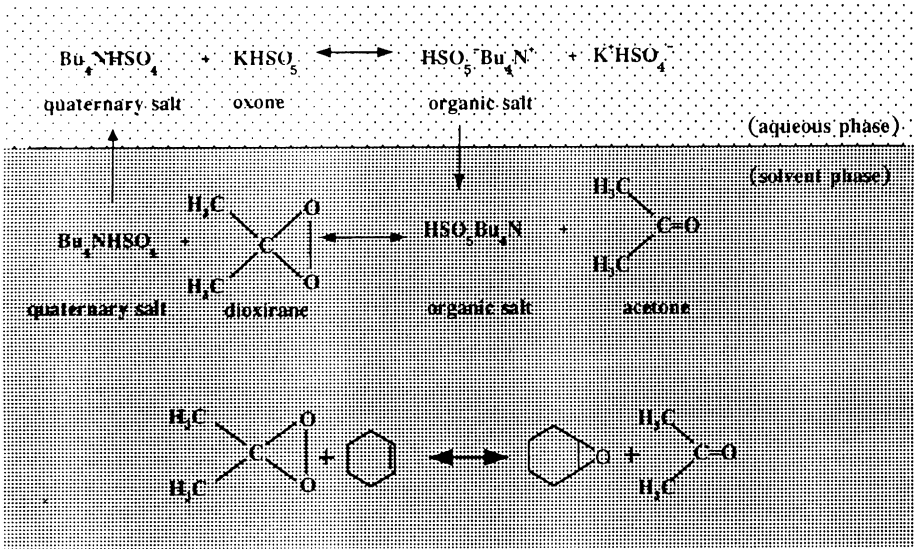


Fig. 8. The scheme for the synthesis of cyclohexene oxide in Case 4; (▦): organic phase; (⬚): aqueous phase.

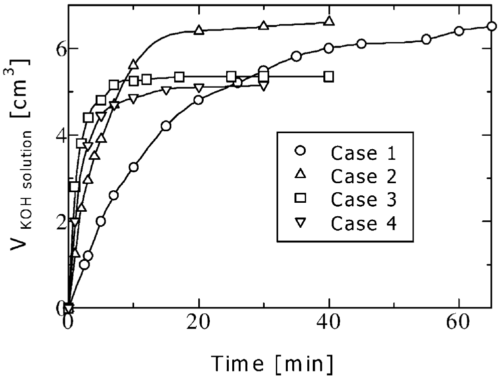


Fig. 9. Volume of KOH solution required to maintain the pH at 7.5.

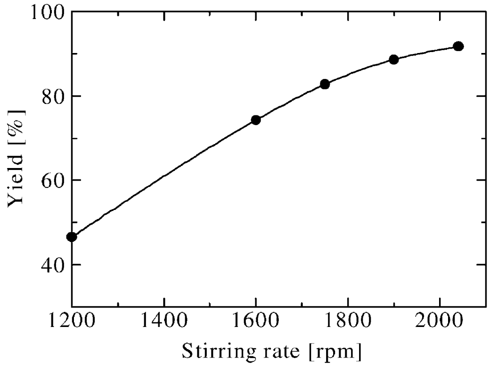


Fig. 10. Effect of stirring rate on the yields of cyclohexene oxide using dichloromethane as a solvent. Acetone = 27 mmol, cyclohexene = 2.47 mmol (0.255 cm^3), Bu_4NHSO_4 = 0.5 mmol (0.17 g), initial solvent/aqueous ratio = 0.83, pH = 7.5, reaction temperature = 293 K and reaction time = 60 min.

high and gradually leveled off after 1 h. Thus, it can be concluded that the epoxidation and $KHSO_5$ self-decomposition occur simultaneously when cyclohexene was added to the reaction system. The disappearance rate of $KHSO_5$ was higher when acetone was added to the system. This may be due to the simultaneous reactions of $KHSO_5$ decomposition and the formation of dioxirane from $KHSO_5$ and acetone. When Na_2EDTA, which was added in the reactive extraction system to prevent trace metal-catalyzed decomposition of $KHSO_5$, lower amount of KOH was observed. There was no significant change of the results of Case 4 where the phase transfer catalyst was added, compared to those of Case 3. This is because when without a solvent, the phase transfer catalyst cannot facilitate the transfer of $KHSO_5$ from the aqueous phase to the solvent phase.

By comparing the reaction performance from the different preparation methods, it could be concluded that the best performance was obtained when cyclohexene was epoxidized with dioxirane in an extractive reaction system with the presence of the phase transfer catalyst. This method was chosen for studying the effects of operating parameters on the performance of the epoxidation of cyclohexene.

3.2. Effects of operating conditions on the performance of the system

This part considers the effects of operating conditions such as stirring rate, types of reactors, type of solvent, effect of initial solvent/aqueous ratio, temperature, pH, amount of catalyst and amount of phase transfer catalyst on the performance of the epoxidation of cyclohexene. It should be noted that the experiments in this section were performed in a normal reactor without baffles.

3.2.1. Effect of stirring rate

Fig. 10 shows the effect of the stirring speed on the yield of cyclohexene oxide. The stirring speed was varied between 1200 and 2040 rpm. It was observed that the stirring rate had significant effect on the yield of cyclohexene oxide. The higher the stirring rate, the higher cyclohexene oxide yield. Because the extractive reaction system is biphasic, stirring rate is very important to ensure sufficient contact between the two phases. To promote the mass transfer, another experiment was carried out in a reactor with four baffles where coalescence and re-dispersion of a dispersed phase were promoted. At the maximum speed of 2040 rpm, the conversion at 1 h of 96% was found, compared to 91% obtained from the normal reactor without baffles. This showed that within the range of study, the mass transfer still played a role in the normal reactor without baffles even at the maximum stirring speed. However, due to the limitation of the equipment, the maximum speed of 2040 rpm was used in the following studies. It should be noted that the mass transfer in this reaction system involved the transfer of an organic salt from an aqueous phase to an organic phase and the transfer of a quaternary salt from the organic phase to the aqueous phase. Since physical properties of these components are rarely available in literature, estimations of a rate of mass transfer require a number of measurements such as interfacial surface tension, diffusivity, density, equilibrium constant of formation of salts, distribution coefficient between both phases and so on. Hence, the estimation becomes rather difficult. In addition, it is rather difficult to find reaction kinetic parameters from the experimental results obtained in this study. To study the kinetics of this reaction, it is necessary to increase the rate of mass transfer by a method such as increasing the stirring speed and/or using a baffled reactor so that the observed reaction rate is not controlled by the mass transfer step.

3.2.2. Effect of type of solvent

Three solvents, i.e. benzene, toluene and dichloromethane were used to study the effect of solvent type on the reaction performance. The solvent volume of 25 cm^3 was used for all the experiments. The conversions of cyclohexene, shown in Fig. 11, indicate that the highest conversion was obtained when dichloromethane was used as a solvent. Because of the presence of the phase transfer catalyst in the system, the polarity of the organic solvent is an important factor affecting the conversion and the reaction rate [23].

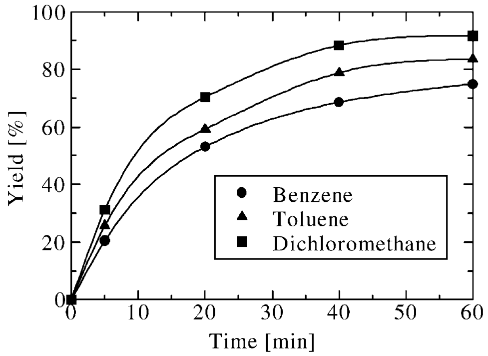


Fig. 11. The conversion of cyclohexene oxide as a function of time in biphasic system using different solvent as extractant. Acetone = 27 mmol, cyclohexene = 9.7 mmol (1 cm^3), Bu_4NHSO_4 = 0.5 mmol (0.17 g), stirring rate = 2040 rpm, initial solvent/aqueous ratio = 0.83, pH = 7.5, reaction temperature = 393 K and reaction time = 60 min.

If the organic solvent has more polarity, the quaternary organic salt will be more extracted. To investigate the effect of type of solvent quantitatively, another set of experiment was carried out by employing the similar method used for investigating the disappearance of $KHSO_5$ in an aqueous solution of Case 4. However, a solvent was also added to the system. It was observed that the amount of KOH solution required for maintaining the pH of the system at 7.5 for 1 h follows the order: dicholoromethane (6.9 cm^3) > toluene (6.3 cm^3) > benzene (4.4 cm^3). This shows that $KHSO_5$ disappeared from the aqueous phase at the highest amount when dichloromethane was used. This is corresponding to the trend observed from the results of the obtained yield.

3.2.3. *Effect of initial solvent/aqueous ratio*

The effect of initial solvent/aqueous ratio on the cyclohexene oxide yield was studied in the dichloromethane/water system. The range varied from 0.50 to 1.17 at three stirring rates of 1200, 1600 and 2040 rpm. Fig. 12 shows the yield of cyclohexene oxide at 1 h. It was found that there existed an optimum initial solvent/aqueous ratio which offered the highest yield for each stirring rate. In the range that the yield of cyclohexene oxide increased with increasing initial solvent/aqueous ratio, because the more solvent was used, the more amount of reactant was extracted. However, at higher values, the effect of the initial solvent/aqueous ratio on the observed yield was mainly due to the mass transfer effect and the dilution effect, whereas the thermodynamic effect seemed to be of minor importance. Increasing the amount of solvent while keeping the stirring rate unaltered resulted in the increased drop size of the dispersed phase. Consequently, contacting surface area and, hence, the mass transfer rate decreased, causing the decrease of the yield of cyclohexene oxide. When the stirring rate increased, the optimum performance was achieved at higher initial solvent/aqueous ratio due to the better mass transfer between the two phases. Increasing the amount of solvent also decreased the reactant concentrations and, hence, the reaction occurred at lower rate. These led to the decrease of the cyclohexene oxide yield.

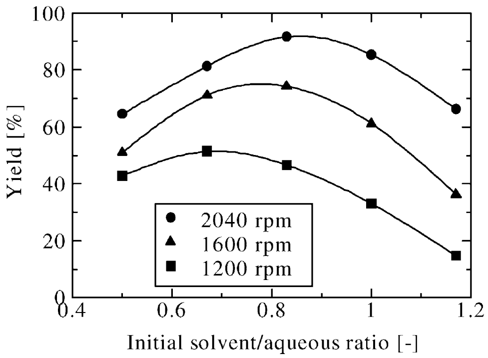


Fig. 12. Effect of initial solvent/aqueous ratio on the yields of cyclohexene oxide at various stirring rates. Using dichloromethane as a solvent. Acetone = 27 mmol, cyclohexene = 2.47 mmol (0.255 cm^3), Bu_4NHSO_4 = 0.5 mmol (0.17 g), pH = 7.5, reaction temperature = 293 K and reaction time = 60 min.

In this study, at the highest stirring rate, the optimum performance was achieved at the initial solvent/aqueous ratio of 0.83, thereby this ratio was used in following studies.

3.2.4. *Effect of temperature*

Temperature, in an extractive reaction, does not only influences the values of rates and reaction equilibrium but also the values of distribution coefficients of the reactants and products involved. Increasing the temperature resulted in the increased reaction and mass transfer rates, however, the side reactions, i.e. decomposition of $KHSO_5$ and ring expansion of epoxy group, were also greatly enhanced [24,25]. In addition, due to the exothermic nature of the reaction, the equilibrium constant decreased with the increase of operating temperature. The epoxidation experiments were carried out at different temperatures ranging between 283 and 303 K. Fig. 13 showed the effect of temperature on the cyclohexene oxide yield. Due to these competing effects, an optimum temperature of 298 K was observed, corresponding to the maximum yield of 94%.

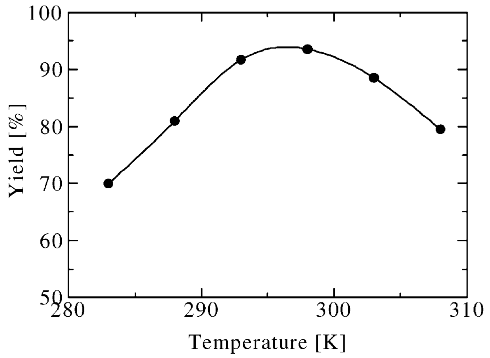


Fig. 13. Effect of temperature on the cyclohexene oxide yield. Acetone = 27 mmol, cyclohexene = 2.47 mmol (0.255 cm^3), Bu_4NHSO_4 = 0.5 mmol (0.17 g), stirring rate = 2040 rpm, initial solvent/aqueous ratio = 0.83, pH = 7.5 and reaction time = 60 min.

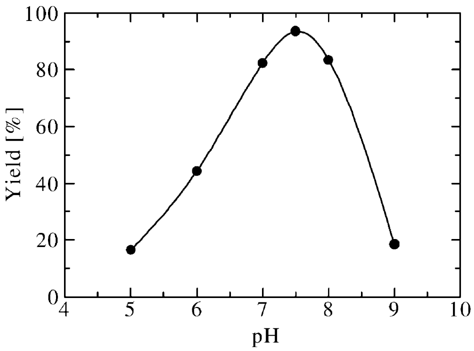


Fig. 14. Effect of pH on the cyclohexene oxide yield. Acetone = 27 mmol, cyclohexene = 2.47 mmol (0.255 cm^3), Bu_4NHSO_4 = 0.5 mmol (0.17 g), stirring rate = 2040 rpm, initial solvent/aqueous ratio = 0.83, reaction temperature = 298 K and reaction time = 60 min.

3.2.5. *Effect of pH*

To study the effect of pH on the cyclohexene oxide yield, the pH value was varied from 5 to 8. The findings are presented in Fig. 14. A maximum yield occurred at the pH of 7.5. The reaction rate increased when the pH value increased, however, at pH higher than 7.5, the rate of decomposition of $KHSO_5$ increased rapidly resulting in lower values for the cyclohexene oxide yield [26].

3.2.6. *Effect of amount of catalyst (acetone)*

The influence of the amount of catalyst on the cyclohexene oxide yield is shown in Table 1. It is clearly shown that the extent of reaction depends on the amount of acetone. The higher the amount of catalyst, the higher cyclohexene oxide yield. It should be noted that cyclohexene oxide was formed even in the absence of ketone. This was due to the direct reaction between $KHSO_5$ and cyclohexene but the yield of cyclohexene oxide at this condition was very low.

3.2.7. *Effect of amount of phase transfer catalyst*

To study the effect of phase transfer catalyst on the performance of epoxidizing cyclohexene, the amount of phase transfer catalyst was varied from 0 to 0.7 mmol. The results are shown in Table 2. It was found that the higher yield of cyclohexene oxide was achieved when the higher amount of phase transfer catalyst was used. Because the extent of generating rate of dioxirane depended on the amount of phase transfer catalyst, the increment of amount of phase transfer catalyst caused the improvement of generating rate of dioxirane and this resulted in the high yield of cyclohexene oxide.

Table 1
Effect of the acetone amount on the yields of cyclohexene oxide

Amount of acetone (mmol)	Yield (%)
0	14
6.8	43
13.6	63
27	94
68	98

Using cyclohexene = 2.47 mmol (0.255 cm^3), Bu_4NHSO_4 = 0.5 mmol (0.17 g), dichloromethane as a solvent, stirring rate = 2040 rpm, initial solvent/aqueous ratio = 0.83, pH = 7.5, reaction temperature = 298 K and reaction time = 60 min.

Table 2
Effect of the amount of phase transfer catalyst on the yields of cyclohexene oxide

Amount of Bu_4NHSO_4 (mmol)	Yield (%)
0	71
0.3	83
0.5	92
0.7	96

Using cyclohexene = 2.47 mmol (0.255 cm^3), acetone = 27 mmol, dichloromethane as a solvent, stirring rate = 2040 rpm, initial solvent/aqueous ratio = 0.83, pH = 7.5, reaction temperature = 293 K and reaction time = 60 min.

4. Conclusion

Extractive reaction for the epoxidation of cyclohexene to cyclohexene oxide using dioxirane was studied. It was found that the best cyclohexene oxide preparation method was achieved when cyclohexene was epoxidized with dioxirane in an extractive reaction system with the presence of phase transfer catalyst. In this type of extractive reaction, a solvent was added in the system to extract the reactant into the solvent phase where the reaction took place. Phase transfer catalyst was used to help improve the rate of reaction by facilitating the rate of transfer of $KHSO_5$ to the solvent phase. By investigating effects of various operating parameters, it was found that the cyclohexene oxide yield increased with increasing stirring rate and the amount of acetone. Three solvents of dichloromethane, toluene and benzene were tested and the results showed that dichloromethane provided the best performance because it preferentially extracted $KHSO_5$ from the aqueous phase to the solvent phase.

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