

Kinetics for dichlorocyclopropanation of 1,7-octadiene under the influence of ultrasound assisted phase-transfer catalysis conditions

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Abstract

The kinetics for dichlorocyclopropanation of 1,7-octadiene with an excess of chloroform has been studied under phase-transfer catalysts and ultrasound irradiation conditions using aqueous sodium hydroxide as the base. The reaction was carried out at 30 °C and a pseudo-first order rate is used to describe the reaction rate at high alkaline concentration (>50 wt.%). Kinetics of the reaction including the effects of the reaction conditions on the conversion of 1,7-octadiene was investigated. A rational explanation was made for a peculiar phenomenon that the conversion of 1,7-octadiene was increased and then decreased with an increase in the amount of sodium hydroxide and the amount of phase-transfer catalyst, benzyltriethylammonium chloride (BTEAC).

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1. Introduction

The reaction between mutually immiscible reactants were usually difficult to conduct efficiently, even under severe operating conditions. Such problems as low reaction rate, low conversion of reactants and low yield of products can be overcome by phase-transfer catalysis (PTC). The phase-transfer catalysts, usually as quaternary onium salts, crown ethers, cryptands, etc., can be applied to give a high conversion and a high selectivity under very mild reaction conditions. Nowadays, phase-transfer catalysis is a useful tool for increasing efficiency, improving safety, and reducing environmental impact. Thousands of papers and patents have expanded the use of PTC in organic synthesis and is widely used for manufacturing pharmaceuticals, agricultural chemicals, perfumes, flavors, dyes, polymers and other import chemicals via substitution, displacement, condensation, polymerization, reduction and oxidation [1–14].

The traditional method for synthesizing 7,7-dichlorobicyclo [4,1,0] heptane is to employ the reaction of cyclohexene

and dichlorocarbene [15]. Later, the technique of generating dichlorocarbene was investigated in order to cause its reaction with olefins to produce dichlorocyclopropane [16]. However, the effect of this technique is also limited because of the low conversion of reactant even under extreme reaction conditions. Makosza and Wawrzyniewicz [17] in 1969 were perhaps the first ones to successfully prepare dichlorocyclopropane under PTC conditions. Since then, the PTC technique for generating dichlorocarbene is extensively applied by many chemists in synthesizing dichlorocyclopropane [18–22].

Ultrasound is defined as sound of frequencies above those within the hearing range of the average person, i.e., at frequencies above 16 kHz (16,000 cycles per second). Ultrasonic energy (high frequency sound waves) produces an alternating adiabatic compression and rarefaction of the liquid media being irradiated. In the rarefaction part of the ultrasonic wave (when the liquid is unduly stretched or torn apart), microbubbles form because of reduced pressure (i.e., sufficiently large negative pressures). These microbubbles contain vaporized liquid or gas that was previously dissolved in the liquid. The microbubbles can be either stable in their average size for many cycles or transient when they grow to certain size and violently collapse or implode during the compression part of the wave. The critical size depends on the liquid and the frequency of sound; at 20 kHz, for example, it is roughly 100–170 μm. The implosions are the spectacular

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part of sonochemistry. The energy put into the liquid to create the micro-voids is released in this part of the wave, creating high local pressures up to 1000 atm and high transitory temperatures up to 5000 K [23–27]. This energy-releasing phenomena of the bubble formation and collapse is simply called cavitation or cold boiling or acoustic cavitation [23,28–30]. Cavities are more readily formed when solvents with high vapor pressure (VP), low viscosity (μ), and low surface tension (σ); however, the intensity of cavitations is benefited by using solvents of opposite characteristics.

The application of ultrasound waves in chemistry was viewed as a merely convenient technique [31]. Many studies have been carried out and it is well documented that the advantages of ultrasound procedures are good yields, short reaction times and mild conditions [31–33]. No direct interaction is possible between ultrasound and matter, and so an indirect phenomenon, i.e., cavitation must be facilitated to induce a reaction. Hence, ultrasound irradiation method [23,34–37] is now recognized as viable environmentally benign alternatives [34–40]. Although sonication methods have been initially applied to homogeneous reactions in a variety of solvents, this approach has now evolved into a useful technique in heterogeneous reactions [23,41–45].

The main purpose of this work is to study the kinetics of the dichlorocyclopropanation from the reaction of olefin (1,7-octadiene) and chloroform in an alkaline solution of a NaOH/organic solvent two-phase medium under phase-transfer catalysis in combined with ultrasonic waves. The active dichlorocarbene was generated from the reaction of chloroform, sodium hydroxide, and quaternary ammonium salt at the interface between the organic and aqueous phases. High activity to obtain a high yield of dichlorocyclopropane derivatives from the generation of a high dichlorocarbene concentration was achieved. Two products, i.e., mono(dichlorocyclopropane) and bis(dichlorocyclopropane) products were obtained from PTC-ultrasound conditions. Kinetics of the reaction in synthesizing dichlorocyclopropane was investigated in detail. It was found that the reaction followed a pseudo-first order rate law only at high alkaline concentration (>50 wt.% NaOH). Peculiar phenomena observed in studying the effect of the amount of NaOH (or KOH) and the amount of benzyltriethylammonium chloride (BTEAC) catalyst on the apparent rate constants are explained satisfactorily.

2. Experimental

2.1. Materials

All reagents, including 1,7-octadiene, chloroform, tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), tetrabutylammonium hydrogensulfate (TBAHS), benzyltriethyl ammonium chloride (BTEAC), benzyltriethylammonium bromide (BTEAB), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), potassium hydroxide, and other reagents for synthesis, were guaranteed grade (GR) chemicals.

2.2. Instrumentation

The ultrasonic apparatus consisted of two layers stainless steel body to have safe and beauty in 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 \times 250 mm \times 250 mm with liquid holding capacity of 22 l. The external tank size is 350 mm \times 355 mm \times 410 mm. Two types of frequencies of ultrasound were used in these experiments which are 28 and 40 kHz with each output of 200 W. Both ultrasound separately produces through a flat transducer mounted at the bottom of the tank. In this ultrasonic instrument 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 equipped with a temperature controller has been also provided so as to conduct high and low temperature reactions.

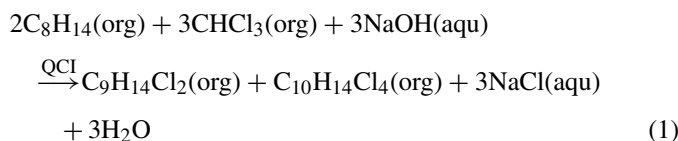
2.3. Kinetics of the two-phase reaction

The reactor was a 150 ml three-necked Pyrex flask, serving the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding the feed. A known quantity of NaOH (12 g) was dissolved in deionized water (12 ml) to prepare a 50 wt.% alkaline solution. Known quantities of 1,7-octadiene, BTEAC (0.0456 g), and nonane (internal standard, 1 g) were then dissolved in chloroform (20 ml) to form the organic solution. To start the reaction, the aqueous and organic solutions were mixed in the flask which was suspended at the center of the ultrasonic cleaning bath to get the maximum ultrasound energy. The organic-phase sample (0.05 ml), which was withdrawn from the reactor at each time interval, was put into the test tubes containing 3 ml of dichloromethane. The contents of mono(dichlorocyclopropane) and bis(dichlorocyclopropane) products and the reactant (1,7-octadiene) were measured by GC. The analyzing conditions are as follows: Shimadzu GC 17A, J&W Scientific Inc., capillary column (db-1 column); 100% poly(dimethylsiloxane) stationary phase; 15 m \times 0.525 mm column dimension; carrier gas, nitrogen (60 ml/min); flame ionization detector; injection temperature, 250 °C.

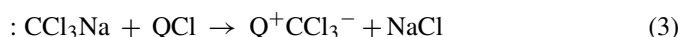
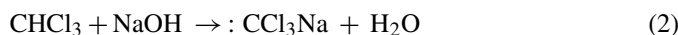
3. Reaction mechanism and kinetic model

The two main reactants in this work, 1,7-octadiene and chloroform, are insoluble in water. Therefore, in the matter of the generation of dichlorocarbene, the characteristics of a PTC reaction, which is quite different from those of Starks' extraction mechanism [1], are probably attributed to the interfacial reaction that was proposed by Makosza and Wawrzyniewicz [17]. Two sites of double bonds of 1,7-octadiene were dichlorocyclopropanated; i.e., mono(dichlorocyclopropane, C₉H₁₄Cl₂) and bis(dichlorocyclopropane, C₁₀H₁₄Cl₄) products were produced. The equation of synthesizing dichlorocyclopropane products from the reaction of 1,7-octadiene (C₈H₁₄) and chloroform (CHCl₃) in the presence of alkaline solution under PTC is

given as

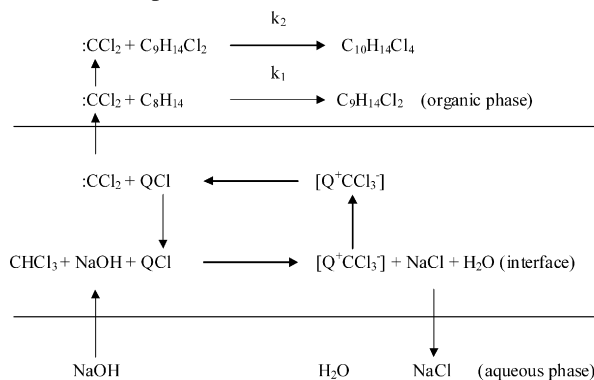


The main interfacial reactions of alkene with dichlorocarbene (:CCl₂), which is produced from chloroform and NaOH, the quaternary ammonium salt, are expressed as



where QCl is the quaternary ammonium salt and is used as the PTC.

Thus, the two-phase reaction mechanism can be described as



Based on the experimental data, the rate of C₈H₁₄ is expressed as

$$-\frac{d[\text{C}_8\text{H}_{14}]_o}{dt} = k_{\text{app},1}[\text{C}_8\text{H}_{14}]_o \quad (6)$$

where $k_{\text{app},1}$ is defined as

$$k_{\text{app},1} = k_1[\text{:CCl}_2]_o \quad (7)$$

The subscript o denotes the species in the organic phase.

Integrating Eq. (6) yields

$$-\ln(1 - X_1) = k_{\text{app},1}t \quad (8)$$

where X_1 is defined as the conversion of C₈H₁₄, i.e.,

$$X_1 = 1 - \frac{[\text{C}_8\text{H}_{14}]_o}{[\text{C}_8\text{H}_{14}]_{o,i}} \quad (9)$$

in which [C₈H₁₄]_{o,i} denotes the initial concentration of 1,7-octadiene in the organic phase. Thus, the value of $k_{\text{app},1}$ can be obtained from experimental data in conjunction with Eq. (8).

For the rate of mono(dichlorocyclopropane) product formation, we have

$$\frac{d[\text{C}_9\text{H}_{14}\text{Cl}_2]_o}{dt} = k_{\text{app},1}[\text{C}_8\text{H}_{14}]_o - k_{\text{app},2}[\text{C}_9\text{H}_{14}\text{Cl}_2]_o \quad (10)$$

where $k_{\text{app},2}$ is given as

$$k_{\text{app},2} = k_2[\text{:CCl}_2]_o \quad (11)$$

Substituting Eq. (8) into Eq. (10), we obtain

$$\frac{[\text{C}_9\text{H}_{14}\text{Cl}_2]_o}{[\text{C}_8\text{H}_{14}]_{o,i}} = \frac{k_{\text{app},1}}{k_{\text{app},2} - k_{\text{app},1}} [\exp(-k_{\text{app},1}t) - \exp(-k_{\text{app},2}t)] \quad (12)$$

Based on the experimental data of [C₉H₁₄Cl₂]_o, the value of $k_{\text{app},2}$ can be obtained from Eq. (12) with the previous knowledge of $k_{\text{app},1}$.

4. Results and discussion

4.1. Effect of the agitation speed

In this study, chloroform and 1,7-octadiene, which are insoluble in water, are the two main reactants. The interfacial reaction rate directly relates to the interfacial area between the two phases. Mass transfer and interfacial contact area between two phases in a phase-transfer catalysis system are important in affecting the conversion or the reaction rate. From the point of kinetics, changing the agitation speed can influence both the mass transfer rate, which relates to the mass transfer coefficient and the interfacial area between the two phases. In principle, a large agitation speed provides a larger interfacial area of the two phases. For such an interfacial reaction, the rate is strongly dependent on the agitation speed. The effect of the agitation speed on the conversion of 1,7-octadiene is shown in Fig. 1. The reaction follows a pseudo-first order rate law at high alkaline concentration of NaOH (50 wt.%). As shown in Fig. 1, the conversion is increased with an increase in the agitation speed from 400 to 1000 rpm. These results confirm the interfacial reaction mechanism. The dependence of $k_{\text{app},1}$ and $k_{\text{app},2}$ on the agitation speed is given in Table 1. Both of these two apparent rate constants monotonically increased with an increase in the agitation speed. For comparison, the two apparent rate constants obtained

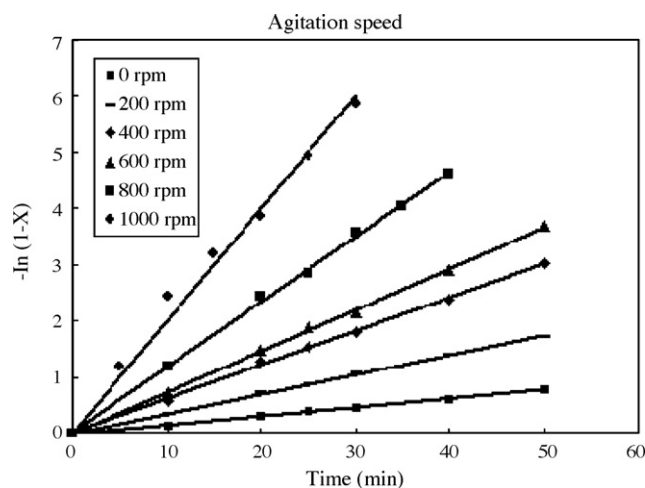


Fig. 1. Effect of the agitation speed on the apparent rate constants: 10 mmol of 1,7-octadiene, 30 ml of chloroform, 0.2 mmol of BTEAC, 15 ml of NaOH solution (50 wt.%), 30 °C, 28 kHz, 200 W.

Table 1

Effect of the agitation speed on the apparent rate constants [10 mmol of 1,7-octadiene, 30 ml of chloroform, 0.2 mmol of BTEAC, 15 ml of NaOH solution (50 wt.%), 30 °C, 28 kHz, 200 W]

	Agitation speed					
	0	200	400	600	800	1000
In the presence of ultrasonic irritation						
$k_{app,1} \times 10^2$ (min ⁻¹)	1.56	3.48	6.05	7.21	11.56	19.64
$k_{app,2} \times 10^2$ (min ⁻¹)	0.59	2.45	3.58	4.21	7.51	13.09
In the absence of ultrasonic irritation						
$k_{app,1} \times 10^2$ (min ⁻¹)	–	–	1.91	4.78	7.94	13.31
$k_{app,2} \times 10^2$ (min ⁻¹)	–	–	1.66	3.03	4.49	6.79

from the phase-transfer catalytic reaction [46] in the absence of ultrasonic irritation are also shown in Table 1. It is obvious that the ultrasonic irritation enhances the reaction.

4.2. Effect of the temperature

Fig. 2 shows the conversion of 1,7-octadiene versus time from which the first apparent rate constant $k_{app,1}$ is obtained from Eq. (8) at various temperatures. The second apparent rate constant $k_{app,2}$ is obtained from Eq. (12) via parameter estimation. The dependence of $k_{app,1}$ and $k_{app,2}$ on temperature is depicted in Table 2. For comparison, the two apparent rate constants obtained from the phase-transfer catalytic reaction [46] in the absence of ultrasonic irritation are also shown in Table 2. It is obvious that the ultrasonic irritation enhances the reaction. It is obvious that the reactivity is increased with an increase in the temperature along with the ultrasonic effect [47]. The reason is that the number of reactant molecules, which possess higher activation energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor. Thus the conversion is increased. The other point is that the collision of the reactants at higher temperature is also increased. Hence, the apparent rate constants, $k_{app,1}$ and $k_{app,2}$, are increased with an increase in the temperature. The activation energies are

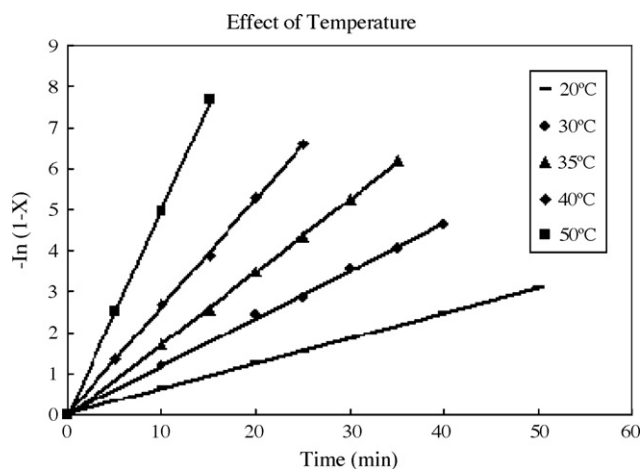


Fig. 2. Effect of the temperature on the conversion of 1,7-octadiene: 10 mmol of 1,7-octadiene, 30 ml of chloroform, 0.2 mmol of BTEAC, 15 ml of NaOH solution (50 wt.%), 800 rpm, 28 kHz, 200 W.

Table 2

Dependence of the apparent rate constants, $k_{app,1}$ and $k_{app,2}$, on the temperature [10 mmol of 1,7-octadiene, 30 ml of chloroform, 0.2 mmol of BTEAC catalyst, 15 ml of NaOH solution (50 wt.%), 800 rpm, 28 kHz, 200 W]

	Temperature				
	20	30	35	40	50
In the presence of ultrasonic irritation					
$k_{app,1} \times 10^2$ (min ⁻¹)	5.66	11.56	18.80	25.29	50.98
$k_{app,2} \times 10^2$ (min ⁻¹)	4.49	7.51	12.84	14.93	25.94
In the absence of ultrasonic irritation					
$k_{app,1} \times 10^2$ (min ⁻¹)	2.92	7.94	11.15	21.22	42.22
$k_{app,2} \times 10^2$ (min ⁻¹)	2.49	4.49	6.91	12.48	21.12

14.22 and 11.12 kcal mol⁻¹ for $k_{app,1}$ and $k_{app,2}$, respectively (Fig. 3).

4.3. Effect of the amount of catalyst

The effect of varying catalyst amounts on the rate of the dichlorocarbene addition reaction to 1,7-octadiene was studied in the range of 0.1–2 mmol of the PT catalyst. The conversion of the reaction is shown in Fig. 4. The conversion is low without adding BTEAC to the reaction solution. However, the reaction is greatly enhanced by adding a small quantity of the BTEAC catalyst. The increased rates are due to the increase in the number of catalytically active sites. An optimum value of the BTEAC catalyst corresponds to a 0.02 molar ratio of BTEAC/1,7-octadiene. A further increase in the amount of BTEAC makes the conversion of 1,7-octadiene decrease. The changes of the apparent rate constants $k_{app,1}$ and $k_{app,2}$ with the amount of BTEAC catalyst are given in Fig. 5. The reason is probably due to the fact that

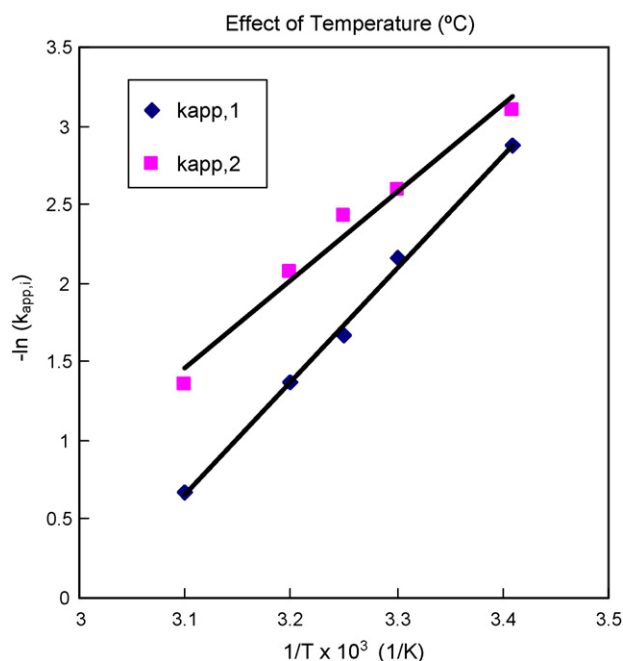


Fig. 3. Arrhenius plot: dependence of $k_{app,i}$ on temperature; same reaction conditions as given in Fig. 2.

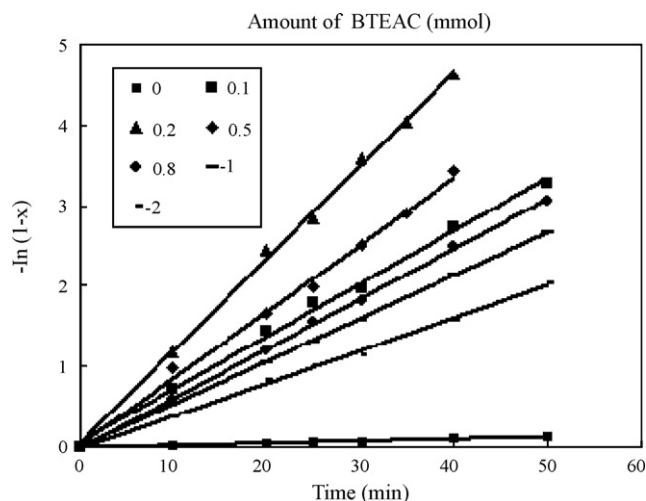


Fig. 4. Effect of the amount of BTEAC catalyst on the conversion of 1,7-octadiene: 10 mmol of 1,7-octadiene, 30 ml of chloroform, 15 ml of NaOH solution (50 wt.%), 30 °C, 28 kHz, 200 W.

the conversion of $Q^+CCl_3^-$ to QCl and $:CCl_2$ reaches a new equilibrium state. At higher concentration of QCl , the equilibrium tends to shift to the formation of $Q^+CCl_3^-$, and thus the dichlorocarbene concentration is decreased. Thus, the conversion of 1,7-octadiene is decreased with an increase in the amount of catalyst QCl at a higher concentration region.

4.4. Comparison of apparent rate constants with different phase-transfer catalysts

Dichlorocarbene addition to 1,7-octadiene has been chosen to study the comparative reactivities of eight different phase-transfer catalysts, namely, TEAC, TEAB, TBAC, TBAB, TBAI, TBAHS, BTEAC, and BTEAB. The results are shown in Fig. 6. The order of the activities for these eight quaternary ammonium salts is $TEAC > TEAB > BTEAC > TBAHS > TBAC > BTEAB > TBAB > TBAI$. The corresponding $k_{app,1}$ and $k_{app,2}$ values in using these quaternary ammonium salts are depicted in Table 3. For comparison, the two apparent rate constants obtained from the phase-transfer catalytic reaction [46] in the absence of ultrasonic irritation are also shown in Table 3. It is obvious that the ultrasonic irritation enhances the reaction.

Table 3

Effect of the quaternary ammonium salts on the apparent rate constants, $k_{app,1}$ and $k_{app,2}$ [10 mmol of 1,7-octadiene, 0.2 mmol of PTC, 30 ml of chloroform, 15 ml of NaOH (50 wt.%), 800 rpm, 30 °C, 28 kHz, 200 W]

	Catalysts							
	BTEAB	BTEAC	TBAB	TBAC	TBAI	TEAB	TEAC	TBAHS
In the presence of ultrasonic irritation								
$k_{app,1} \times 10^2 \text{ (min}^{-1}\text{)}$	9.54	11.56	5.75	6.91	4.57	15.01	23.12	11.45
$k_{app,2} \times 10^2 \text{ (min}^{-1}\text{)}$	4.01	7.51	3.65	4.01	3.43	8.94	14.11	5.25
In the absence of ultrasonic irritation								
$k_{app,1} \times 10^2 \text{ (min}^{-1}\text{)}$	5.97	7.94	4.40	5.81	3.89	11.04	14.28	6.66
$k_{app,2} \times 10^2 \text{ (min}^{-1}\text{)}$	3.61	4.49	2.54	3.47	2.31	7.57	8.86	3.79

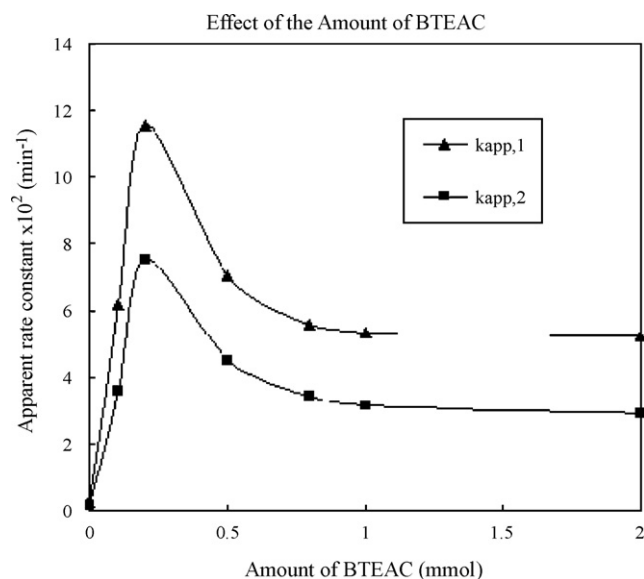


Fig. 5. Effect of the amount of BTEAC catalyst on the apparent rate constants $k_{app,1}$ and $k_{app,2}$: same reaction conditions as those given in Fig. 3.

Generally, the order of the distribution of halide ions in the organic phase is $I^- > Br^- > Cl^-$, which reflects the Starks' extraction mechanism. However, the order of the reactivities in choosing the tetrabutylammonium cation group in this work is $TBAHS > TBAC > TBAB > TBAI$. Choosing a small size of the anionic ion in the halide groups of PTCs is favorable for a high reaction rate. This phenomenon is more consistent with the interfacial reaction mechanism rather than the extraction reaction mechanism. For an interfacial reaction mechanism, the reaction rate is highly dependent on the concentration of the catalyst at the interface. For the quaternary ammonium cations with the same halide ion (chloride and bromide), the order of the activities of these PTCs is $TEA \text{ cation} > BTEA \text{ cation} > TBA \text{ cation}$. It is thus concluded that a higher reactivity is obtained for a quaternary ammonium salt of less total carbon number. As noted by Starks et al. [1], the activity of the catalyst is dependent on the structural characteristics of a quaternary ammonium cation. The yield of the product is correlated with the accessibility of the quaternary ammonium salt, q , which is a function of carbon in each chain. It is thus concluded that the order of the activities is consistent with the results indicated by Starks et al. [1].

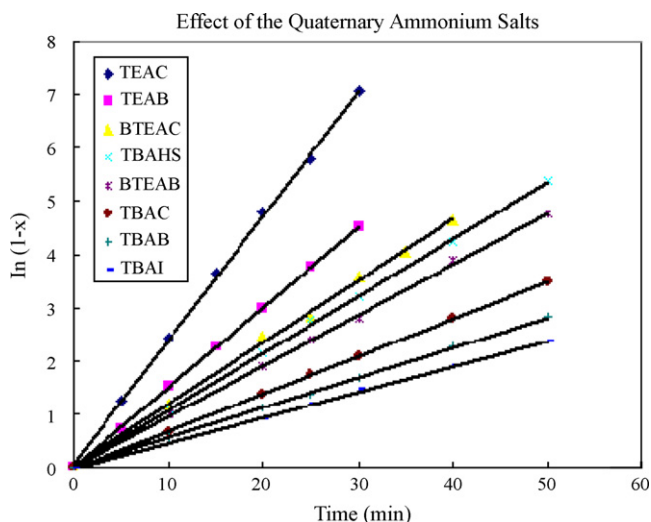


Fig. 6. Effect of the PTCs on the conversion of 1,7-octadiene: 10 mmol of 1,7-octadiene, 30 ml of chloroform, 15 ml of NaOH (50 wt.%), 0.2 mmol of catalyst, 800 rpm, 30 °C, 28 kHz, 200 W.

4.5. Effect of varying substrate amount

In the two-phase reaction, the rate and the conversion are both highly dependent on the concentration of the reactant in the organic phase. As shown in Fig. 7, the reaction rate decreases with an increase in the amount of 1,7-octadiene in the organic phase. The corresponding $k_{app,1}$ and $k_{app,2}$ values are given in Table 4. Similar results were also obtained by Jayachandran and Wang [9] in studying the cycloalkylation of phenylacetonitrile with 1,4-dibromobutane under phase-transfer catalysis conditions. This decrease in the rate constant may be attributed to the proportionate decrease in the number of catalytic active sites available. Furthermore, the ratio of 1,7-octadiene/catalyst is increased with an increase in the amount of 1,7-octadiene. Therefore, the reaction rate constant is increased with the decrease in the concentration of 1,7-octadiene because the availability of the catalyst per mole of 1,7-octadiene to catalyze the reaction

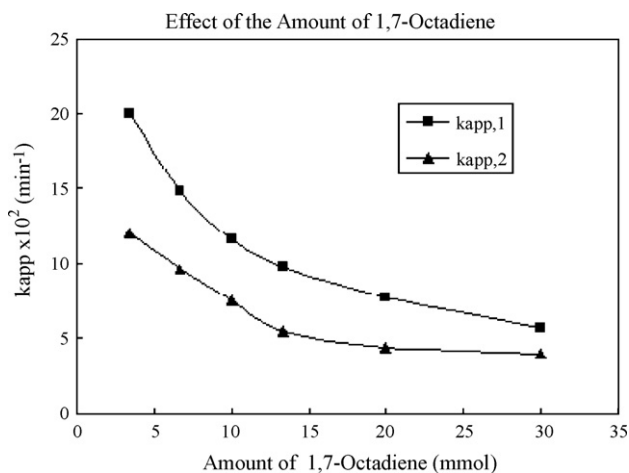


Fig. 7. Effect of the amount of 1,7-octadiene on the conversion of 1,7-octadiene: 30 ml of chloroform, 15 ml of NaOH (50 wt.%), 0.2 mmol of BTEAC catalyst, 800 rpm, 30 °C, 28 kHz, 200 W.

Table 4

Effect of the variation of the amount of 1,7-octadiene on the reaction [30 ml of chloroform, 15 ml of NaOH (50 wt.%), 0.2 mmol of BTEAC catalyst, 800 rpm, 30 °C, 28 kHz, 200 W]

1,7-octadiene (mmol)	3.39	6.67	10.00	13.34	20.00	30.00
In the presence of ultrasonic irritation						
$k_{app,1} \times 10^2$ (min ⁻¹)	19.97	14.86	11.56	9.74	7.69	5.64
$k_{app,2} \times 10^2$ (min ⁻¹)	13.34	9.46	7.51	5.43	4.36	3.95
In the absence of ultrasonic irritation						
$k_{app,1} \times 10^2$ (min ⁻¹)	12.69	11.50	7.94	6.49	5.13	3.99
$k_{app,2} \times 10^2$ (min ⁻¹)	7.15	6.75	4.49	4.13	2.95	2.05
1,7-octadiene/catalyst	16.95	33.35	50.00	66.70	100	150

is low at high 1,7-octadiene concentration. For comparison, the two apparent rate constants obtained from the phase-transfer catalytic reaction [46] in the absence of ultrasonic irritation are also shown in Table 4. It is obvious that the ultrasonic irritation enhances the reaction.

4.6. Effect of the amount of chloroform

In this work, chloroform acts both as organic solvent and as the source of dichlorocarbene. The effect of the amount of chloroform on the $k_{app,1}$ and $k_{app,2}$ values is shown in Fig. 8. Both $k_{app,1}$ and $k_{app,2}$ are decreased with an increase in the amount of chloroform. The main reason is that the concentration of dichlorocarbene decreases when the amount of chloroform is increased. In addition, the concentration of 1,7-octadiene is also lowered as the amount of chloroform is increased.

4.7. Effect of the alkaline concentration

As shown in Fig. 9, the conversion of 1,7-octadiene is increased and then decreased with an increase in the amount of NaOH. For the amount of NaOH of less than 18 g, the reaction rate is increased with an increase in the amount of NaOH.

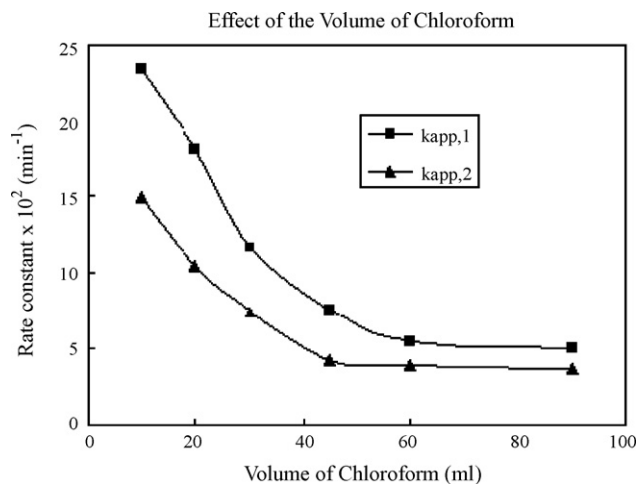


Fig. 8. Effect of the volume of chloroform on the conversion of 1,7-octadiene: 10 mmol of 1,7-octadiene, 15 ml of NaOH (50 wt.%), 0.2 mmol of catalyst, 800 rpm, 30 °C, 28 kHz, 200 W.

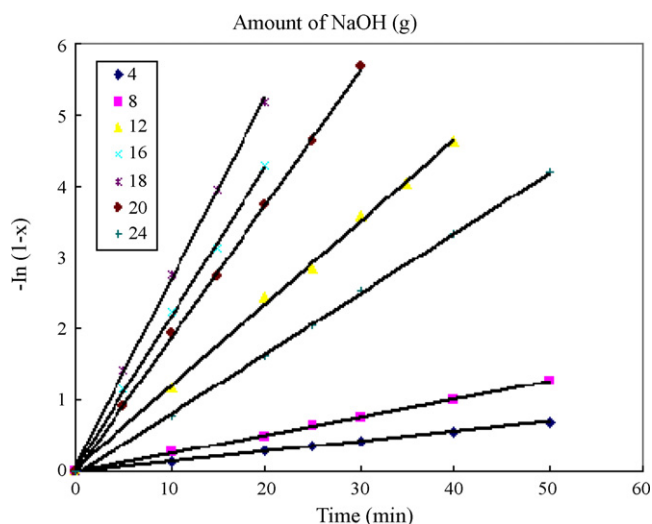


Fig. 9. Effect of the amount of NaOH on the conversion of 1,7-octadiene: 10 mmol of 1,7-octadiene, 15 ml of NaOH solution, 30 ml of chloroform, 0.2 mmol of catalyst, 800 rpm, 30 °C, 28 kHz, 200 W.

The main reason is that hydrolysis of dichlorocarbene is sluggish at low alkaline concentration. A similar trend was reported by Landini et al. [48]. In addition, the ion-exchange reaction at the interface is greatly enhanced by increasing the concentration of NaOH in the aqueous phase. It is favorable for the reaction system to generate an active intermediate product because the produced acid on the interface immediately transfers to the aqueous phase. Furthermore, hydrolysis of dichlorocarbene is prevented at higher concentration of NaOH and in the presence of a PTC. Therefore, the reaction rate is greatly enhanced at higher concentration of NaOH.

However, as shown in Fig. 10, the conversion of 1,7-octadiene is then decreased with an increase in the amount of NaOH of larger than 18 g. Under this situation, the solution is almost saturated with sodium hydroxide and becomes a slurry. With a further increase in the amount of sodium hydroxide, solid particles of sodium hydroxide are suspended in the reaction solution

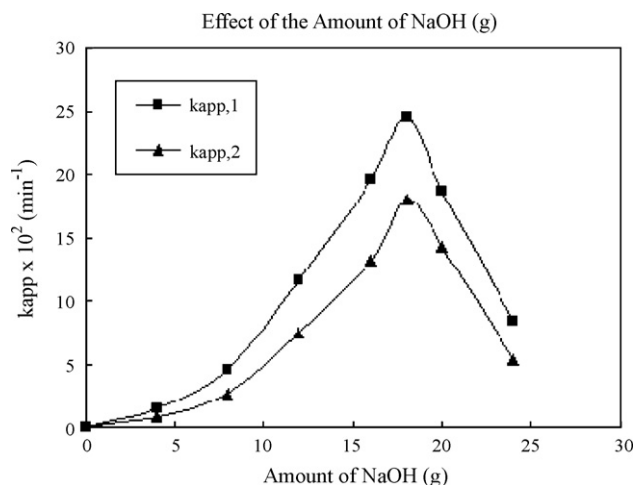


Fig. 10. Effect of the amount of NaOH on the apparent rate constants $k_{app,1}$ and $k_{app,2}$: same reaction conditions as those given in Fig. 8.

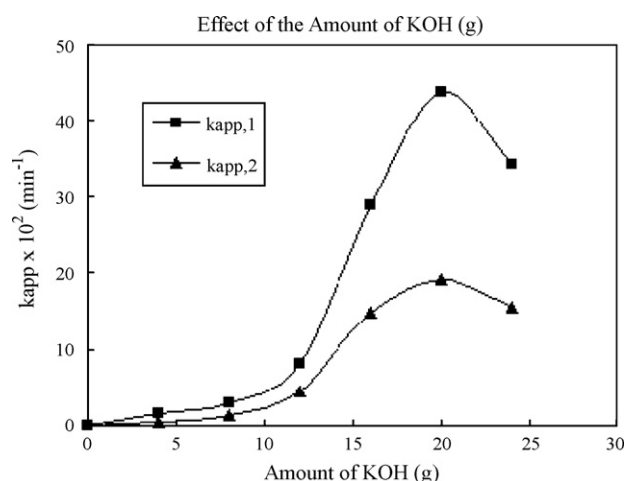


Fig. 11. Effect of the amount of KOH on the conversion of 1,7-octadiene: same reaction conditions as those given in Fig. 8.

in which the interfacial area was partly occupied by those NaOH particles. Therefore, the transfer of compounds through the interface and the reaction at the interface are decreased. Hence, the reaction is decreased at a higher amount of sodium hydroxide. The corresponding apparent rate constants $k_{app,1}$ and $k_{app,2}$ versus the amount of sodium hydroxide are shown in Fig. 10. Instead of using NaOH, several experiments are carried out in an alkaline solution of KOH. Similar results are obtained; as shown in Fig. 11, a maximum value of $k_{app,1}$ and $k_{app,2}$ were observed.

4.8. Effect of the amount of inorganic salt (NaCl)

In this study, sodium chloride was produced as a by-product from the reaction. Therefore, the addition of NaCl naturally affects the equilibrium of each component between the two phases. The results are shown in Fig. 12 and Table 5. The addition of NaCl enhances the reaction as a result of a salting-out effect in the aqueous phase and also the formed dichlorocarbene is more

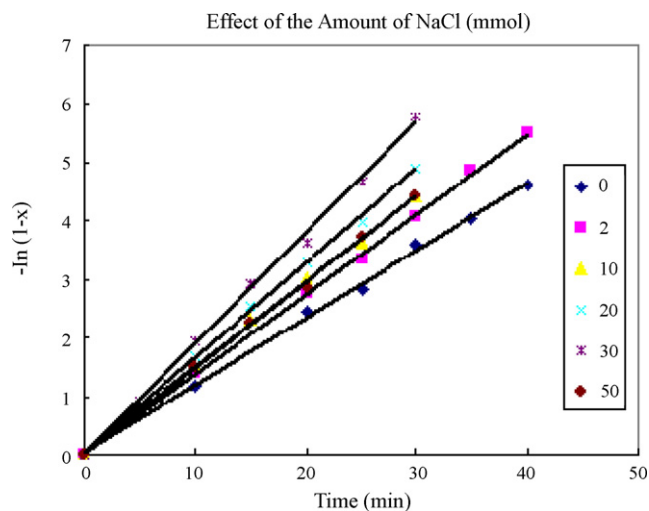


Fig. 12. Effect of the inorganic salt (NaCl) on the conversion of 1,7-octadiene: 10 mmol of 1,7-octadiene, 30 ml of chloroform, 0.2 mmol of NaOH (50 wt.%), 0.2 mmol of BTEAC catalyst, 800 rpm, 30 °C, 28 kHz, 200 W.

Table 5

Effect of sodium chloride on the conversion of 1,7-octadiene [10 mmol of 1,7-octadiene, 30 ml of chloroform, 0.2 mmol of BTEAC, 15 ml of NaOH (50 wt.%), 800 rpm, 30 °C, 28 kHz, 200 W]

NaCl (g)	0	0.117	0.585	1.170	1.755	2.925
In the presence of ultrasonic irritation						
$k_{app,1} \times 10^2$ (min ⁻¹)	11.56	13.69	15.68	15.90	16.07	14.66
$k_{app,2} \times 10^2$ (min ⁻¹)	7.51	8.41	10.11	10.42	11.01	9.12
In the absence of ultrasonic irritation						
$k_{app,1} \times 10^2$ (min ⁻¹)	7.94	11.28	12.13	14.70	14.76	13.91
$k_{app,2} \times 10^2$ (min ⁻¹)	4.49	7.33	8.02	9.14	10.46	8.92

favorable to staying in the organic phase. Meanwhile, hydrolysis of dichlorocarbene in the aqueous phase is minimized. For comparison, the two apparent rate constants obtained from the phase-transfer catalytic reaction [46] in the absence of ultrasonic irritation are also shown in Table 5. It is obvious that the ultrasonic irritation enhances the reaction.

4.9. Ultrasonic effect

The effect of ultrasound on the conversion of 1,7-octadiene is also investigated (Tables 1–5). Ultrasound has been found to enhance this reaction of liquid–liquid phase-transfer catalysts (LLPTC) bi-phase system. The chemical effects of ultrasound, attributed to intense local conditions generated due to cavitation bubble dynamics, i.e., the nucleation, formation, disappearance, and coalescence of vapor or gas bubbles in the ultrasonic field [23–31,45,49]. However, in conventional phase-transfer catalyst (PTC) reaction rate enhancements are typically due to mechanical effects, mainly through an enhancement in mass transfer. The presence of ultrasound in LLPTC systems, cavitation collapse near the liquid–liquid interface disrupts the interface and impels jets of one liquid into the other, forming fine emulsions, and leading to a dramatic increase in the interfacial contact area across which transfer of species can take place [50]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [51,52]. In such cases, the phase-transfer catalyst initiates the reaction by the transfer of species across the interface and ultrasound merely facilitates this transfer, possibly by increasing the interfacial area across which this transfer occurs [53].

In our experiments the ultrasonic bath for filling water, model L-400 was used as described in Section 2. If the water level is lower than the outlet, i.e., 3 cm below from the top of the sonicator, the applied frequency automatically cut off. So the water fill level is important. The reaction vessel was suspended at the center of the ultrasonic cleaning bath 2 cm above from the position of the transducer to get the maximum ultrasound energy. All the experimental parameters were done at 28 kHz with output power of 200 W.

The reaction rate also compared with 28 and 40 kHz having same output power of 200 W. At 40 min, without ultrasonic irritation the conversion is only 76%, but in the presence of ultrasonic the conversion is 97% and almost 100% for 28 and 40 kHz, respectively. Thus, ultrasonic-assisted phase-transfer

catalysis significantly increased the yields. The same trend is also observed by Entezari et al. [47,54]. So the application of ultrasounds in organic synthesis is one of the popular areas in sonochemistry.

5. Conclusions

In conclusion, synthesis of dichlorocyclopropane catalyzed by quaternary ammonium salt combined with ultrasonic irradiation was successfully achieved by conducting the reaction of 1,7-octadiene and chloroform in an alkaline solution of a NaOH (or KOH)/organic solvent bi-phase medium. The reaction is dramatically enhanced by adding a small amount of PTC along with ultrasonic waves. The other important factor in affecting the reaction rate is the addition of alkali. At a low alkaline concentration, hydrolysis of dichlorocarbene is slow. Hence, the conversion is low as a result of the limited contact of 1,7-octadiene and dichlorocarbene. The reaction rate is increased with an increase in the agitation speed, which is different from that of the ion-pair extraction mechanism. Among the phase-transfer catalysts, the order of the reactivities is $Cl^- > Br^- > I^-$. With the same anion (halide), a high activity is obtained using a small quaternary ammonium cation. The interfacial mechanism is well used to explain the reaction behavior. Due to a salting-out effect the addition of sodium chloride enhances the rate. The conversion is decreased with an increase in the amount of chloroform and 1,7-octadiene. The conversion is increased and then decreased with an increase in the amount of sodium hydroxide or potassium hydroxide.

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