



Kinetic study of dichlorocyclopropanation of 1,7-octadiene under two-phase phase-transfer catalysis at low alkaline concentration

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Abstract

This work investigates the phase-transfer catalytic (PTC) reaction of dichlorocyclopropanation of 1,7-octadiene in an alkaline solution/organic solvent two-phase medium. The reaction is dramatically enhanced in the presence of quaternary ammonium salt. The reaction mechanism proposed is that the active dichlorocarbene (:CCl₂) is first generated from the interfacial reaction of chloroform, sodium hydroxide and quaternary ammonium salt to form an active complex (QCCl₃) of the dichlorocarbene (:CCl₂) precursor. Then, this active complex QCCl₃ (or dichlorocarbene :CCl₂), which transfers from the aqueous phase to the organic phase, further reacts with 1,7-octadiene to produce mono-dichlorocyclopropane and bi-dichlorocyclopropane in the organic phase. No other byproducts were detected during or after the reaction. The conversion of 1,7-octadiene is increased with the increase in the amount of NaOH in the aqueous phase. At lower alkaline concentration (30% NaOH or less), the reaction obeys a third-order rate law. However, a pseudo first-order rate law is sufficient to describe the kinetic behavior at higher alkaline concentration (>50% NaOH). Explanations are made for this discrepancy. The effects of the reaction conditions, such as quaternary ammonium salts, amount of catalyst, agitation, concentration of 1,7-octadiene, temperature, amount of chloroform, and amount of NaOH on the conversion were investigated in detail.

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1. Introduction

The technique of phase-transfer catalysis is a promising method for synthesizing specialty chemicals from two immiscible reactants. The primary advantages of using phase-transfer catalysis are to obtain a large conversion, high reaction rate and selectivity at moderate reaction conditions. It has been extensively applied to synthesize medical drugs, polymers and other important chemicals via substi-

tution, displacement, condensation, polymerization, reduction and oxidation [1–4].

Doering and Hoffmann [5] were the first ones to report synthesis of dichlorocyclopropane, which is usually difficult to produce. They employed the reaction of cyclohexene and dichlorocarbene, which was produced from chloroform and potassium *t*-butanoxide, to produce 7,7-dichlorobicyclo[4.1.0]heptane. Later, William and Edward [6] developed the technique for the generation of dichlorocarbene by reaction with olefins to produce dichlorocyclopropane. However, the application of these techniques are limited due to low conversion of reactant, even at extreme reaction conditions. Makosza and Wawrzyniewicz [7] then

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successfully prepared dichlorocyclopropane under phase-transfer catalytic (PTC) conditions, finding no reaction between chloroform and cyclohexene in an alkaline solution of KOH or NaOH [7]. However, the reaction rate is dramatically increased by adding a small quantity of benzyltriethylammonium chloride (BTEAC), yielding about 70% of dichlorocyclopropane. Since then, the PTC technique for generation of dichlorocarbene has been extensively applied by many chemists [8–14].

As stated, the production of dichlorocyclopropane was very difficult before the technique of phase-transfer catalysis was developed for synthesizing dichlorocarbene. The main purpose of this study is to synthesize dichlorocyclopropane from the reaction of olefins (1,7-octadiene) and chloroform in an alkaline solution of NaOH/organic solvent two-phase medium under phase-transfer catalysis conditions. The active dichlorocarbene was generated from the reaction of chloroform, quaternary ammonium salt and sodium hydroxide at the interface between organic and aqueous phases. In this work, reaction conditions to generate a high concentration of dichlorocarbene in such a way to obtain a high yield of dichlorocyclopropane, were investigated. Kinetics of the reaction in synthesizing dichlorocyclopropane, such as quaternary ammonium salts, amount of catalyst, agitation speed, concentration of 1,7-octadiene, temperature, amount of chloroform and amount of NaOH were investigated in detail. Two products, i.e. mono-dichlorocyclopropane and bi-dichlorocyclopropane were obtained from the phase-transfer catalytic reaction. One peculiar phenomenon found was that the reaction follows a third-order rate law at lower alkaline concentration (30% NaOH or less), but it obeys a pseudo first-order rate law at higher alkaline concentration (>50% NaOH). Explanations of the difference in reaction rate at different levels of alkaline concentration are provided.

2. Experimental section

2.1. Materials

All reagents, including 1,7-octadiene, chloroform, tetrabutylammonium chloride (TBAC), benzyltriethylammonium chloride, tetrabutylammonium bromide (TBAB), tetraethylammonium chloride (TEAC), tetra-

butylammonium hydrogensulfate (TBAHS), tetraoctylammonium bromide (TOAB), potassium hydroxide and other reagents for synthesis were guaranteed grade (GR) chemicals.

2.2. Procedures

2.2.1. Synthesis of products

Measured quantities of NaOH (10 g) and TBAHS (0.2 g) were dissolved in 10 ml of water. The mixed solution was introduced to a 150 ml flask and uniformly agitated at isothermal condition for 20 min. Then, 1,7-octadiene (organic reactant; 2.2 g) was added to the mixed solution. To start the reaction, chloroform (20 ml) was gradually added dropwise over 30 min to complete the reaction. After reaction, the solution was separated and the portion of aqueous solution was extracted twice by ether. Magnesium sulfate was also added to adsorb the residual water. Organic solvent (chloroform) and other residues were stripped in an vacuum evaporator. Chromatography method was employed to separate mono-dichlorocyclopropane and bi-dichlorocyclopropane products through an adsorption column (75 cm glass tube filled with 70–230 mesh silica gel powder, eluent: *n*-hexane). The mono-dichlorocyclopropane and bi-dichlorocyclopropane products were collected from the sample cell and concentrated by vacuum evaporation. Products of mono-dichlorocyclopropane and bi-dichlorocyclopropane of 98% purity were obtained. The products and the reactant were identified by gas chromatography (GC) mass for molecular weight, FT-IR and NMR (^1H NMR and ^{13}C NMR) for functional groups and elements for components. The contents of the components obtained from experiments are consistent with the theoretical values.

2.2.2. Kinetics of the two-phase reaction

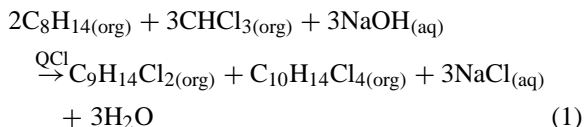
The reactor was a 150 ml three-necked Pyrex flask, used for agitating the solution, inserting the thermometer, taking samples, and feeding the feed. A known quantity of NaOH (6 g) was dissolved in deionized water (14 ml) to prepare a 30% alkaline solution. Known quantities of 1,7-octadiene, tetrabutylammonium chloride (0.056 g), 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 a 150 ml flask immersed in an isothermal water bath. The organic-phase

sample (0.05 ml), which was withdrawn from the reactor at each time interval, and put into test tubes containing 3 ml dichloromethane. The content of mono-dichlorocyclopropane and bi-dichlorocyclopropane products, and the reactant (1,7-octadiene) were measured by gas chromatography (GC). The analysis conditions were: Shimadzu GC17A, J&W Scientific Inc., capillary column (db-1 column), 100% poly(dimethylsiloxane) stationary phase, 15 m × 0.525 m column dimension, carrier gas: nitrogen (60 ml/min), FID detector, 250 °C injection temperature.

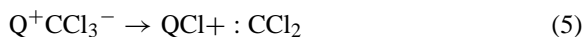
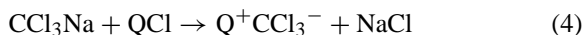
3. Reaction mechanism and kinetic model

In general, the most acceptable mechanism of a phase-transfer catalytic reaction is the extraction mechanism proposed by Starks et al. [1], using the so-called Starks' phase-transfer catalyst. Many experimental data and phenomena of phase-transfer catalytic reactions are well explained by the Starks' extraction mechanism, in which the active catalyst (or intermediate) transfers to the organic phase from the aqueous phase. However, the reaction of dichlorocyclopropanation, except sodium hydroxide, chloroform and 1,7-octadiene of the two main reactants are both insoluble in water, and only soluble in most organic solvents in this work. Transfer of the active catalyst

chloroform in the presence of alkaline solution under phase-transfer catalysis conditions is given as

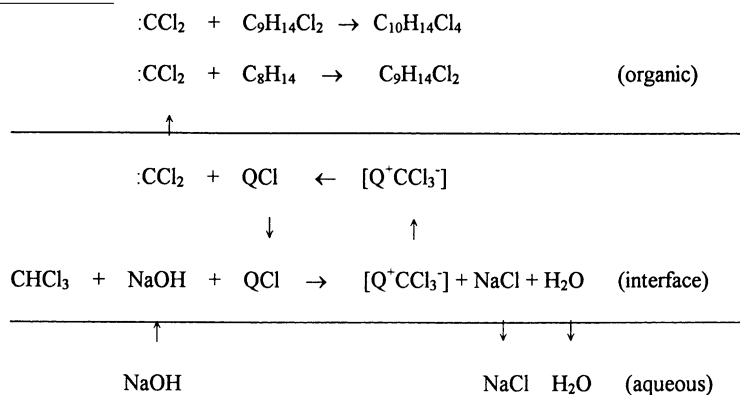


The mainly interfacial reactions of alkene with dichlorocarbene (:CCl₂), which is produced from chloroform and NaOH, are expressed as



where QCl is the quaternary ammonium salt and is used as the phase-transfer catalyst. It is reasonable to assume that the deprotonation of chloroform (CHCl₃) by hydroxide ion (OH⁻) takes place on the interface of aqueous-organic to produce :CCl₃Na. Then, quaternary salt (Q⁺) bring ⁻CCl₃ to the organic phase to generate dichlorocarbene (:CCl₂) for further reaction [15].

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



(or intermediate) from one phase to another phase is difficult from such characteristics of species solubility. Thus, the mechanism of dichlorocyclopropanation is best explained by Makosza's interfacial mechanism [1] rather than by Starks' extraction mechanism. From a stoichiometric quantity, the equation of synthesizing dichlorocyclopropane from the reaction of olefin and

In this work, both 1,7-octadiene and chloroform are soluble only in organic solvents, not in water. The experimental data are fitted well by a third-order rate law at low alkaline solution (30% NaOH or less), rather than a pseudo first-order rate law, i.e.

$$\frac{d[\text{C}_8\text{H}_{14}]_o}{dt} = -k_{\text{app},3}[\text{C}_8\text{H}_{14}]_o^3 \quad (6)$$

where the subscript “o” denotes the species in the organic phase, and $k_{app,3}$ the defined as the apparent rate constant of the third rate law. The $k_{app,3}$ -value is a product of the intrinsic rate constant (k_{int}) and the concentration of dichlorocarbene ($[:\text{CCl}_2]$).

Integrating Eq. (6), we obtain

$$\frac{1}{2} \left\{ \frac{1}{[\text{C}_8\text{H}_{14}]_0^2} - \frac{1}{[\text{C}_8\text{H}_{14}]_{0,0}^2} \right\} = k_{app,3}t \quad (7)$$

The subscript “0” denotes the initial concentration of the species at time $t = 0$. By plotting the term on the left hand side of Eq. (7) versus t , the apparent rate constant $k_{app,3}$ for a third-order rate kinetics is obtained. The reason that the reaction obeys the third-order rate kinetics is probably because the capability of deprotonation is low at low alkalinity concentration (30% NaOH or less). This is due to the fact that the low concentration of NaOH at 30% or less is insufficient to de-hydrogen from chloroform. So, the formation of Q^+CCl_3^- is correspondingly decreased at low alkaline concentration. Therefore, the rate is both controlled in the organic-phase reaction and the interfacial reaction. Such a complicated reaction mechanism probably leads to a third-order rate kinetics rather than a simple pseudo order rate kinetics. By plotting the term on the left hand side of Eq. (7) versus time, the apparent rate constant $k_{app,3}$ for a third-order kinetics is obtained.

In general, most conventional two-phase phase-transfer catalytic reactions can be described by a pseudo first-order rate law when the concentration of aqueous-phase reactant is larger than that of the organic-phase reactant [16]. Based on the proposed reaction mechanism, the apparent rate constant ($k_{app,1}$) is equal to the intrinsic rate constant multiplied by the concentration of dichlorocarbene ($[\text{:CCl}_2]$) in the organic phase. The concentration of dichlorocarbene should be kept at a constant value for the reaction to obey pseudo first-order rate kinetics. Based on the experimental data, the reaction is best described by the pseudo first-order rate law at high alkaline solution (>50% NaOH), i.e.

$$\frac{d[\text{C}_8\text{H}_{14}]_o}{dt} = -k_{app,1}[\text{C}_8\text{H}_{14}]_o \quad (8)$$

where the subscript “o” also denotes the species in the organic phase, and $k_{app,1}$, which is a product of the intrinsic rate constant (k_{int}) and the concentration of

dichlorocarbene ($[\text{:CCl}_2]$), is defined as the apparent rate constant of the pseudo first-order rate law.

Integrating Eq. (8), we obtain

$$\ln \left(\frac{[\text{C}_8\text{H}_{14}]_o}{[\text{C}_8\text{H}_{14}]_{0,0}} \right) = -k_{app,1}t \quad (9)$$

By plotting the term on the left hand side of Eq. (9) versus t , the apparent rate constant $k_{app,1}$ for a pseudo first-order kinetics is obtained.

The conversion of 1,7-octadiene is defined as X , i.e.

$$X = 1 - \frac{[\text{C}_8\text{H}_{14}]_o}{[\text{C}_8\text{H}_{14}]_{0,0}} \quad (10)$$

4. Result and discussion

In this work, the phase-transfer catalyzed reaction of dichlorocyclopropanation of 1,7-octadiene yields both mono-dichlorocyclopropane and bi-dichlorocyclopropane. For a typical reaction, the distributions of the mono-adduct and di-adduct are shown in Fig. 1. At earlier stage of reaction, mono-adduct is first generated and then the di-adduct is generated for a sequential addition of dichlorocarbene. In Fig. 1, the results follow material balance from which the sum of the concentration of mono-adduct, di-adduct and 1,7-octadiene (reactant) at any time equals to the initial concentration of 1,7-octadiene.

The kinetic behaviors of the reaction were studied. Therefore, the data obtained from experiments (e.g. Fig. 1) were transformed to the conversion of 1,7-octadiene by employing Eq. (10). The effects of the reaction conditions on the conversion or the reaction rate (i.e. the apparent rate constant) are discussed in the following.

4.1. Effect of the quaternary ammonium salts

In this study, special quaternary ammonium salts, such as: tetraethylammonium chloride; tetrabutylammonium chloride; tetrabutylammonium bromide; tetrabutylammonium hydrogensulfate; tetraoctylammonium bromide and benzyltriethylammonium chloride, were used as the phase-transfer catalysts to investigate their reactivities. As shown in Fig. 2, the order of the reactivities for these quaternary ammonium salts for the reaction carried out at low alkaline

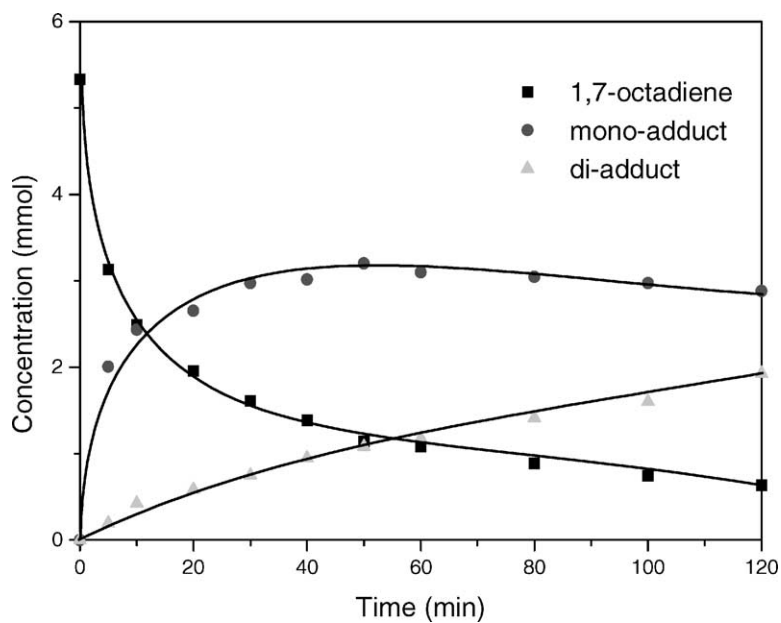


Fig. 1. Distributions of reactant, mono-adduct and di-adduct during the reaction period: 5.33 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C.

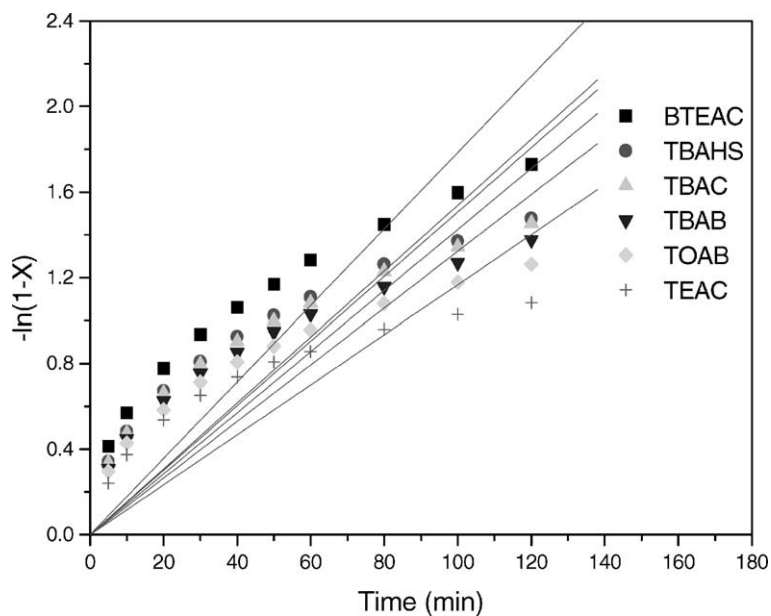


Fig. 2. Effects of the quaternary ammonium salts on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH) (pseudo first-order rate law approach): 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of quaternary ammonium salt, 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C.

Table 1

Effect of the quaternary ammonium salts on the $k_{app,3}$ -value at low NaOH concentration: 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of quaternary ammonium salt, 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C

PTC	$k_{app,3} \times 10 \text{ (min}^{-1} \text{ M}^{-2}\text{)}$
BTEAC	5.14
TBAHS	3.50
TBAC	3.29
TBAB	2.82
TOAB	2.34
TEAC	1.65

concentration (30% NaOH or less) are: BTEAC > TBAHS > TBAC > TBAB > TOAB > TEAC. It can be seen that neither quaternary ammonium salts of total high carbon number (e.g. TOAB) nor those of total low carbon number (e.g. TEAC) do not possess high reactivities. Larger conversion was obtained in using quaternary ammonium salt of appropriate total carbon number (e.g. BTEAC, TBAHS, TBAC and TBAB). The corresponding $k_{app,3}$ -values for these different quaternary ammonium salts are given in Table 1. These results are reasonably explained by viewing the characteristics of the interfacial reaction mechanism. That is, those quaternary ammonium salts of total low carbon number which are hydrophilic, such as TEAC, are not adequate to enhance the reaction. However, those quaternary ammonium salts of total high carbon number which possess large alkyl groups are hydrophobic such as TOAB, do not produce the effective intermediate on the interface between two phases.

The effect of the anions of the quaternary ammonium salts on the reaction rate can also be obtained using tetrabutylammonium cation with various anions, such as Cl^- , Br^- and HSO_4^- . As indicated in the above, the order of the reactivities are: TBAHS > TBAC > TBAB. These results are different from those explained by Starks' extraction mechanism, in which TBAB exhibits high reactivity. From the point view of the Starks' extraction mechanism based on the total carbon number of quaternary ammonium salts, the reactivity of BTEAC should be less than that of TBAC by counting the total carbon number of the catalyst. However, the reactivity of BTEAC is clearly higher than that of TBAC. The aromatic compound is more favorable to generate dichlorocyclopropane than that

of alkyl compound by viewing the structure of quaternary ammonium salts. Therefore, instead of the extraction reaction mechanism, we infer that the present reaction system is the interfacial reaction mechanism.

In general, most conventional phase-transfer catalytic reactions can be described by a pseudo first-order rate law when the concentration of the aqueous-phase reactant is larger than that of the organic-phase reactant [16]. Under this circumstance, the data were fitted well when a pseudo first-order rate law was applied. However, as shown in Figs. 2 and 3, only a third-order rate law rather than a pseudo first-order rate law can be used to describe the data successfully for the reaction carried out at low alkaline concentration (30% NaOH or less). Based on the experimental results, we can infer that Starks' extraction mechanism [1] cannot be applied to explain the complicated reaction on the interface, even though the effect of mass transfer is not neglected. Otherwise, the reaction follows the interfacial mechanism.

In this work, chloroform and 1,7-octadiene are the two main reactants both of which are organic soluble. However, the aqueous soluble NaOH participates in the generation of dichlorocarbene. Therefore, it is reasonable to assume that the interfacial reaction is the main mechanism in this work. Fig. 4 shows the conversion of 1,7-octadiene versus t when the reaction was carried out at a relative high alkaline concentration (>50% NaOH). A pseudo first-order rate law is sufficient to describe these reaction kinetics.

4.2. Effect of agitation speed

Mass transfer between two phases in a phase-transfer catalysis system is 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 two phases, and the reaction rate. Increasing the agitation speed leads to increase both the mass transfer coefficient and the interfacial area, thus enhancing the mass transfer rate. In this work, the effect of agitation speed on the conversion for the reaction carried out at low alkaline concentration (30% NaOH) is shown in Fig. 5. No other byproducts were obtained during or after the reaction. The conversion is highly dependent on agitation speeds less than 800 rpm, above which

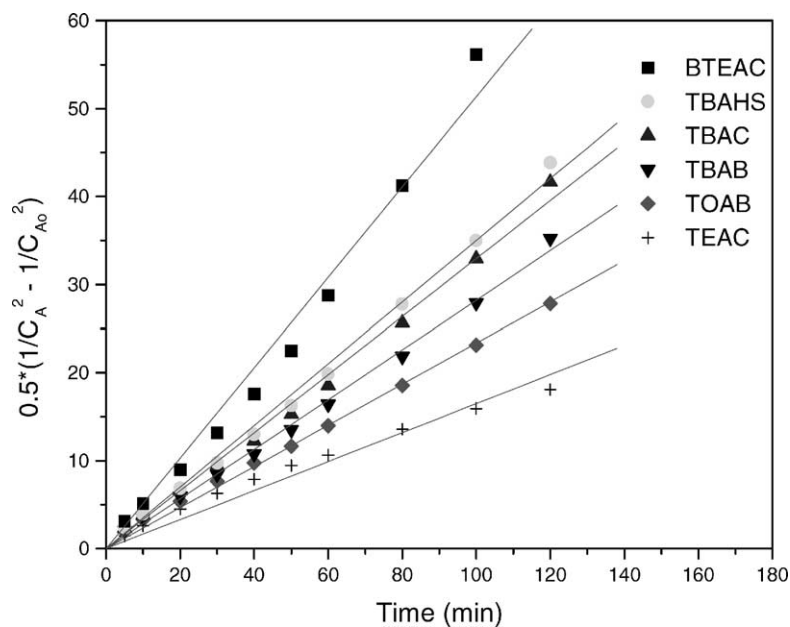


Fig. 3. Effects of quaternary ammonium salts on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH) (third-order rate law approach): 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of quaternary ammonium salt, 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C.

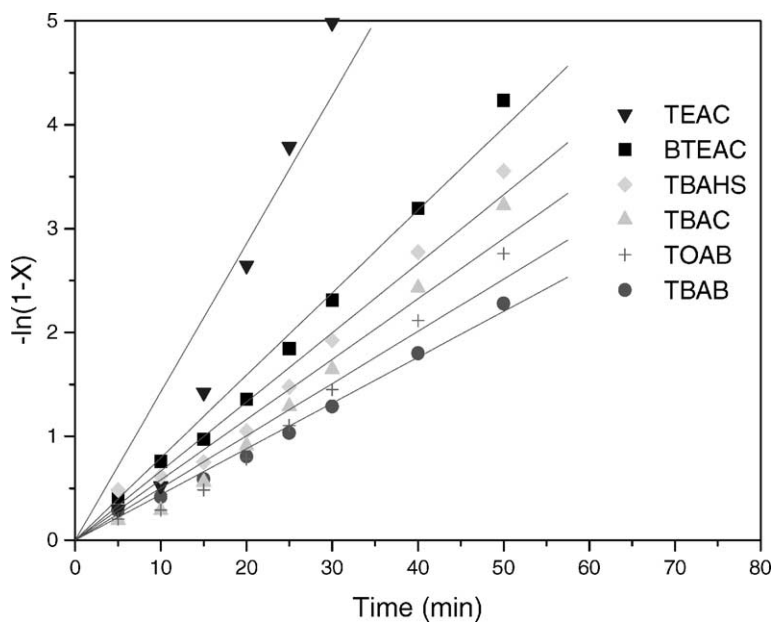


Fig. 4. Effects of quaternary ammonium salts on the conversion of 1,7-octadiene at low alkaline concentration (50% NaOH) (pseudo first-order rate law approach): 10 mmol of 1,7-octadiene, 30 ml of chloroform, 0.2 mmol of quaternary ammonium salt, 50% of NaOH, 14 ml of water, 800 rpm, 30 °C.

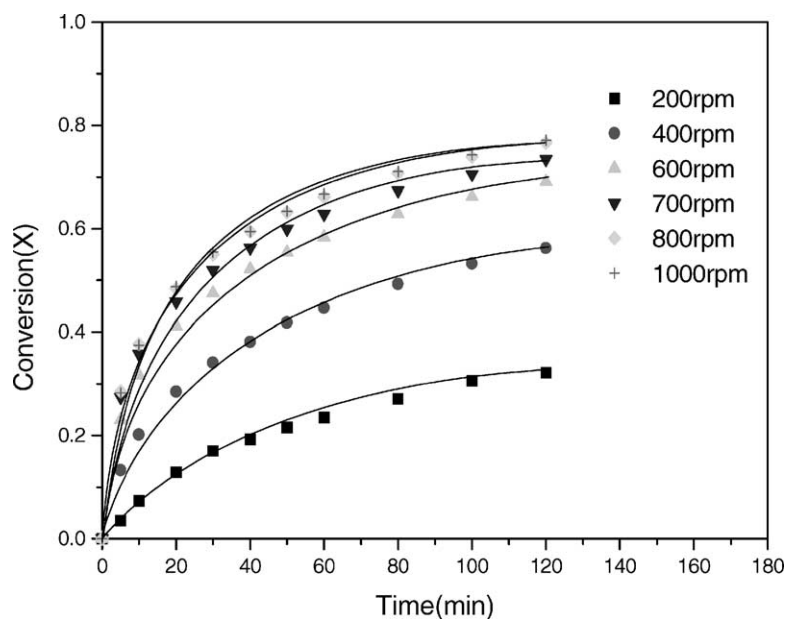


Fig. 5. Effect of the agitation speed on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH): 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 40 °C.

the conversion is not influenced by increasing the agitation speed. The corresponding $k_{app,3}$ -values with various agitation speeds are given in Table 2.

4.3. Effect of the amount of catalyst

This work also investigates the effect of the amount of tetrabutylammonium chloride on the conversion of 1,7-octadiene. As shown in Fig. 6, the conversion is low when the reaction was carried out in the absence of TBAC. However, the reaction rate is dramatically enhanced when TBAC of a small quantity was added

to the reaction solution. Furthermore, the conversion is increased with an increase in the amount of TBAC, up to a 0.02 molar ratio of TBAC/1,7-octadiene. Further increase in the amount of TBAC catalyst does not make the conversion increase at low alkaline concentration (30% NaOH or less). This result confirms that TBAC reacts with chloroform to form an intermediate of the constant value. Similarly, the experimental data follows a third-order rate law at low alkaline concentration (30% NaOH or less). The corresponding $k_{app,3}$ -values with various amounts of TBAC catalyst are given in Table 3.

Table 2

Effect of the agitation speed on the $k_{app,3}$ -value at low NaOH concentration: 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 40 °C

Agitation speed (rpm)	$k_{app,3} \times 10 \text{ (min}^{-1} \text{ M}^{-2}\text{)}$
200	0.26
400	0.88
600	1.90
700	2.58
800	3.29
1000	3.41

Table 3

Effect of the amount of TBAC catalyst on the $k_{app,3}$ -value at low NaOH concentration: 10 mmol of 1,7-octadiene, 20 ml of chloroform, 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C

TBAC (g)	$k_{app,3} \times 10 \text{ (min}^{-1} \text{ M}^{-2}\text{)}$
0.014	1.11
0.028	2.05
0.042	3.07
0.056	3.29
0.112	3.23
0.278	3.38

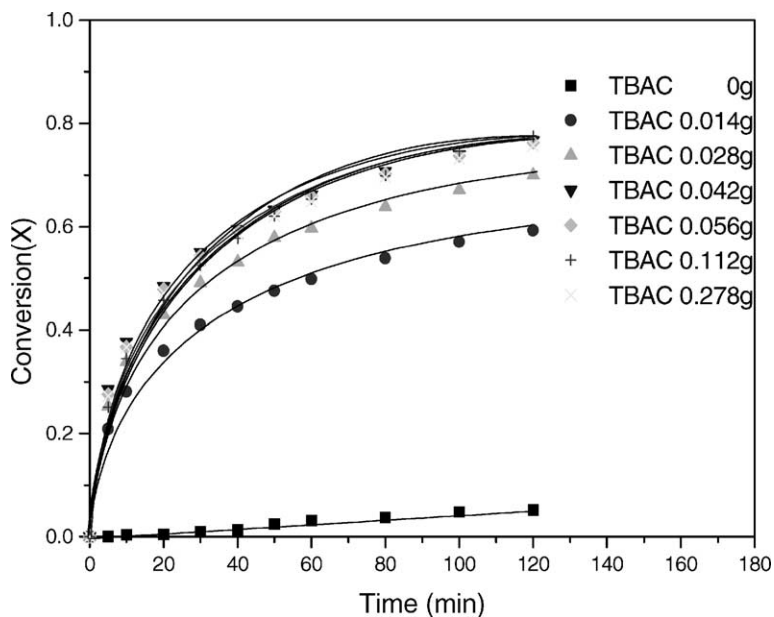


Fig. 6. Effects of the amount of tetrabutylammonium chloride (TBAC) on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH): 10 mmol of 1,7-octadiene, 20 ml of chloroform, 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C.

4.4. Effect of temperature

As shown in Fig. 7, the conversion of 1,7-octadiene is increased with the increase in temperature. A plot for the Arrhenius equation of $k_{app,3}$, which is obtained from the third-order rate law, is given in Fig. 8. The activation energy for this reaction system is 13.42 kcal/mol.

4.5. Effect of the alkaline concentration

In a phase-transfer catalytic reaction by quaternary ammonium salt, the reaction rate is highly affected by the alkaline concentration. The main reason is that the distribution of the active catalyst between two phases and the solubility of the inorganic salt are both dependent on the alkaline content in the aqueous phase. Kinetic data for the effect of low alkaline concentration on the conversion of 1,7-octadiene are shown in Fig. 9. Similar to the results above, the data obtained at a low alkaline concentration are well described by a third-order rate law. The corresponding $k_{app,3}$ -values with various alkaline concentrations are given in Table 4. The reaction rate is substantially

increased with the increase in the alkali concentration. This phenomenon is well explained by the interfacial reaction mechanism, i.e. the reaction of chloroform, quaternary ammonium salt and sodium hydroxide on the interface between organic and aqueous phases. By increasing the concentration of alkaline, the rate of ion-exchange, which occurs on the interface, accelerated. Meanwhile, the inorganic salt produced from the interfacial region then transfers to the aqueous phase, so it is favorable for the reaction being carried out and generating intermediate species.

Table 4

Effect of the NaOH concentration of the $k_{app,3}$ -value: 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 14 ml of water, 800 rpm, 40 °C

Concentration of NaOH (%)	$k_{app,3} \times 10$ ($\text{min}^{-1} \text{M}^{-2}$)
0	0
10	0.41
20	1.01
30	3.29
40	6.01
50	20.49

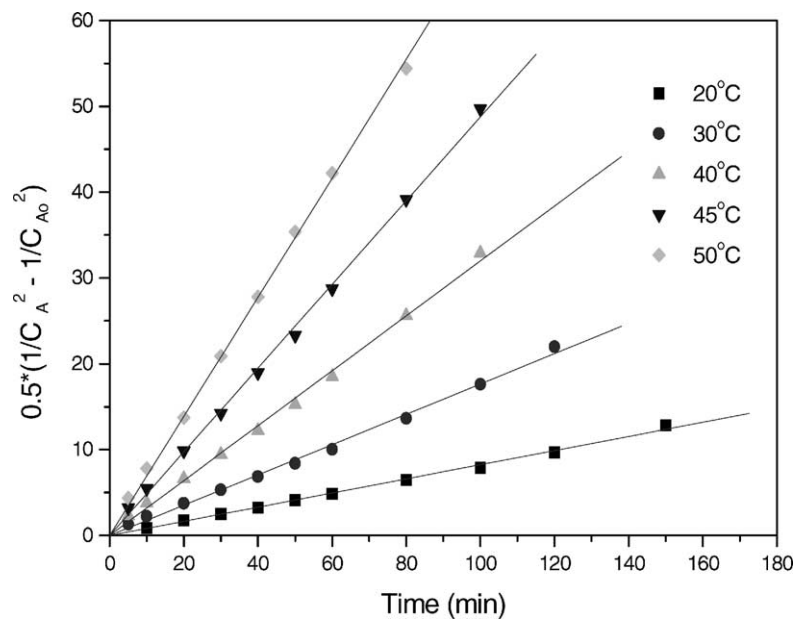


Fig. 7. Effects of the temperature on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH) (third-order rate law approach): 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 800 rpm.

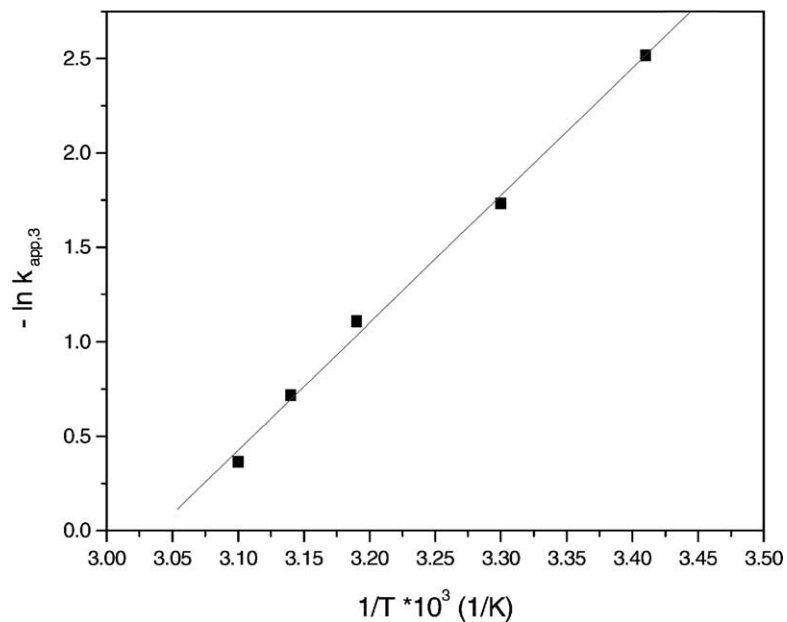


Fig. 8. Arrhenius plot of $k_{app,3}$ vs. $1/T$ for third-order rate law approach (same reaction conditions as given in Fig. 7).

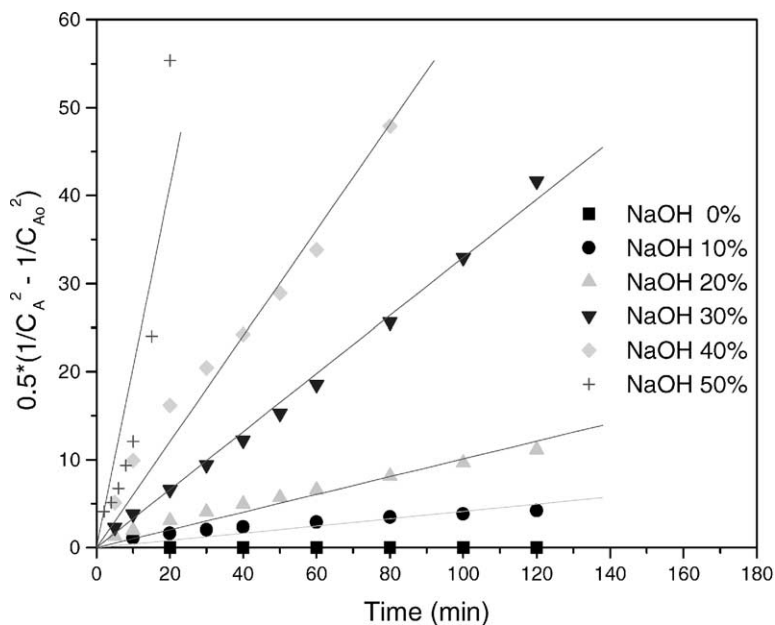


Fig. 9. Effects of the concentration of NaOH on the conversion of 1,7-octadiene (third-order rate law approach): 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 14 ml of water, 800 rpm, 40 °C.

4.6. Effect of the amount of 1,7-octadiene

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. 10, the reaction rate decreases with the increase in the amount of 1,7-octadiene in the organic phase. The corresponding $k_{app,3}$ -values with various amounts of 1,7-octadiene are given in Table 5. The same results were also obtained by Jayachandran and Wang [17] in studying the cycloalkylation of phenylacetonitrile with 1,4-dibromobutane under phase-transfer catalysis conditions. This decrease in rate may be attributed to

Table 5
Effect of the amount of 1,7-octadiene on the $k_{app,3}$ -value at low NaOH concentration: 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C

1,7-Octadiene (g)	$k_{app,3} \times 10 \text{ (min}^{-1} \text{ M}^{-2}\text{)}$
0.5866	28.80
1.1040	3.29
2.0059	0.48
4.0002	0.06

the proportionate decrease in the number of catalytic active sites available. The results suggest that the concentration of 1,7-octadiene in the organic phase is not important, whereas the concentration of 1,7-octadiene at the interface may be vital. Similar characteristics are obtained from the interfacial reaction.

Keeping the same other conditions, the reactions were carried out at different concentrations of 1,7-octadiene. The results for using 5.33 and 36.36 mmol of 1,7-octadiene are shown in Figs. 1 and 11, respectively. It is obvious that the yield of mono-adduct at high 1,7-octadiene concentration (36.36 mmol) is larger than that at low 1,7-octadiene concentration (5.33 mmol). Nevertheless, the yield of the di-adduct is insensitive to the initial concentration of 1,7-octadiene. A much more plausible interpretation is that, as the reaction proceeds, a higher fraction of the dichlorocarbene generated is consumed by reaction with 1,7-octadiene. For this, less instantaneous dichlorocarbene exist under the condition of high 1,7-octadiene concentration. Therefore, the corresponding $k_{app,3}$, which is a product of the intrinsic rate constant (k_{int}) and the concentration of dichlorocarbene [$:CCl_2$], is low at high 1,7-octadiene concentration, as shown in Fig. 10.

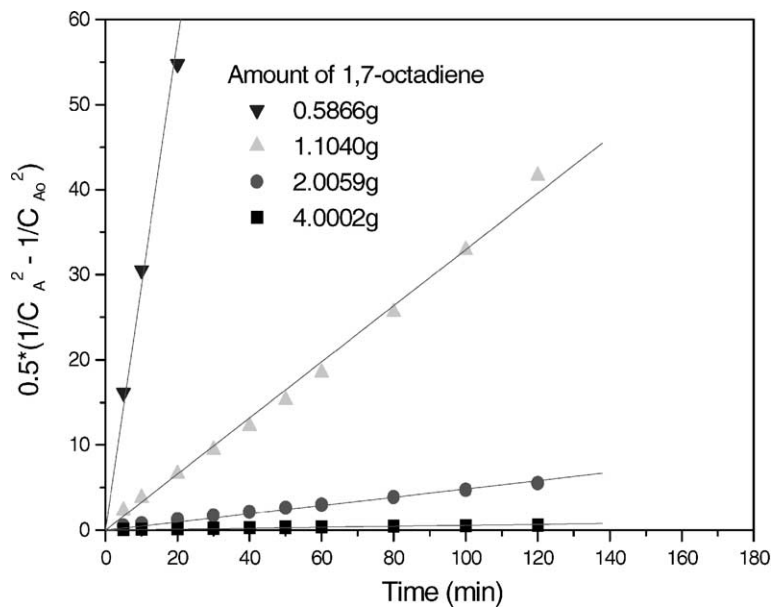


Fig. 10. Effects of the amount of 1,7-octadiene on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH) (third-order rate law approach): 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C.

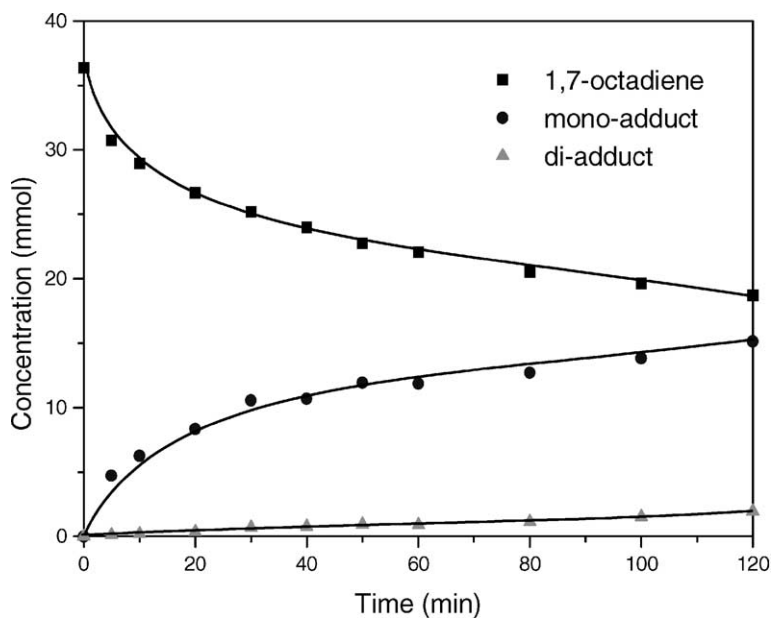


Fig. 11. Distribution of reactant, mono-adduct and di-adduct during the reaction period: 36.36 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C.

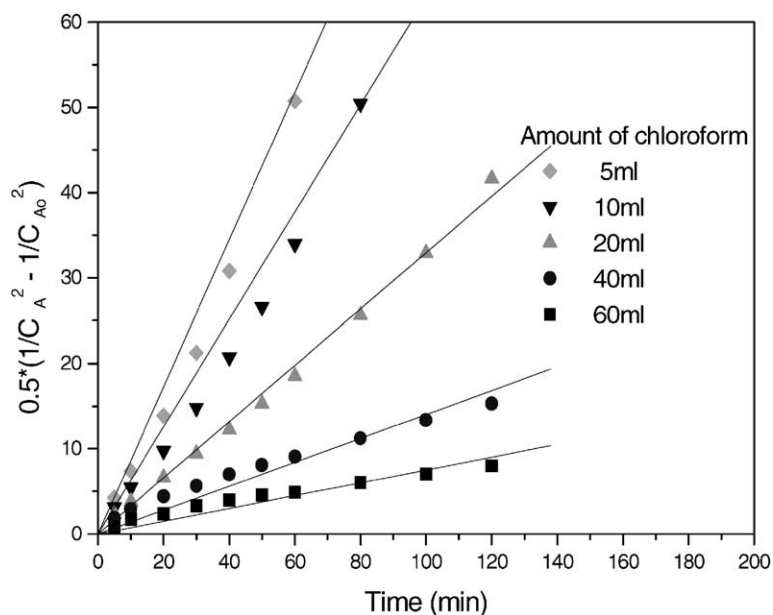


Fig. 12. Effects of the amount of chloroform on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH) (third-order rate law approach): 10 mmol of 1,7-octadiene, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C.

Furthermore, the ratio of 1,7-octadiene/catalyst is increased with the increase in the concentration of 1,7-octadiene. Therefore, the reaction rate 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 is low at high 1,7-octadiene concentration.

4.7. Effect of the amount of chloroform

In this work, chloroform acts both as organic solvent and the source of dichlorocarbene. The effect of the amount of chloroform on the conversion of 1,7-octadiene is shown in Fig. 12. The conversion is reduced with the increase in the amount of chloroform. The corresponding $k_{app,3}$ -values with various amounts of chloroform are given in Table 6. In principle, the generation of dichlorocarbene, which is favorable to enhance the reaction, is increased with the increase in the amount of chloroform. However, the generation of dichlorocarbene occurs at the interface of the two phases. The interfacial area remains at a constant value for a constant agitation speed. Furthermore, the generation of dichlorocarbene is also limited due to the limited amount of phase-transfer catalyst added and

Table 6

Effect of the amount of chloroform on the $k_{app,3}$ -value at low NaOH concentration: 10 mmol of 1,7-octadiene, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 800 rpm, 40 °C

Chloroform (ml)	$k_{app,3} \times 10$ ($\text{min}^{-1} \text{M}^{-2}$)
5	8.62
10	6.29
20	3.29
40	1.40
60	0.75

the amount of water. The dichlorocarbene generated is diluted by increasing the amount of chloroform in the organic phase. Thus, the concentration of dichlorocarbene in the organic phase (chloroform) is decreased with the increase in the amount of chloroform. In this way, the conversion is decreased by increasing in the amount of chloroform.

5. Conclusions

In this work, dichlorocyclopropanation of 1,7-octadiene was successfully catalyzed by quaternary

ammonium salt in an alkaline solution of NaOH/organic solvent two-phase medium. It is believed that the reaction was carried out by first synthesizing the active dichlorocarbene from the reaction of sodium hydroxide, chloroform and quaternary ammonium salt at the interface. Both mono-dichlorocyclopropane and bi-dichlorocyclopropane products were obtained from the reaction of dichlorocarbene and 1,7-octadiene in the organic phase. Effects of the quaternary ammonium salts, the amount of catalyst, the agitation speed, alkaline concentration, temperature, amount of 1,7-octadiene and amount of chloroform on the reaction rate were investigated in detail. At relatively low alkaline concentration (30% NaOH or less), the experimental kinetic data are described by a third-order rate law. Up to a certain molar ratio of catalyst/1,7-octadiene ($=0.02$), the rate of reaction is not further increased by the increase in the amount of catalyst. One interesting result obtained is that the quaternary ammonium salts having extreme hydrophilic or hydrophobic characteristics do not have high reactivities. The reason for this is that the reaction occurs at the interface between organic and aqueous phases as shown by experimental evidence and it is difficult for those hydrophilic or hydrophobic quaternary ammonium salts to form the active intermediate on the interface.

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