Ultrasonics Sonochemistry 19 (2012) 1139-1143

Contents lists available at SciVerse ScienceDirect

# Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

### Short Communication

# Phase-transfer catalytic dichlorocyclopropanation of styrene under the influence of ultrasound conditions – A kinetic study

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#### ARTICLE INFO

Article history: Received 3 May 2010 Received in revised form 16 February 2012 Accepted 24 February 2012 Available online 7 March 2012

Keywords: Reaction kinetics Phase-transfer catalysis Dichlorocarbene Styrene Dichlorocyclopropanation Ultrasound condition

#### ABSTRACT

The kinetics for dichlorocyclopropanation of styrene with an excess of chloroform were studied under phase-transfer catalysis and ultrasound irradiation conditions using aqueous sodium hydroxide as the base and benzyltriethylammonium bromide as a catalyst. The reaction was carried out at 35 °C under pseudo-first order conditions by keeping aqueous sodium hydroxide and chloroform in excess and was monitored by gas chromatography (GC). The effects of agitation speed, quaternary ammonium salts, amount of catalyst, amount of sodium hydroxide and temperature on the kinetics of the conversion were investigated.

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#### 1. Introduction

Phase-transfer catalysis (PTC) supports catalytic processes in both homogeneous and heterogeneous reaction systems [1–3]. PTC is a versatile, well-established synthetic technique, applied with several advantages to a number of organic reactions [4–12]. Phase-transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers, polyethylene glycols and cryptands, have been used to carry out reactions between reactants which exist in the same or different phase(s) [1–12]. Presently, PTC has extensively been applied in the synthesis of organic chemicals via condensation, elimination, substitution, redox and polymerization. The advantage of using PTC can be carried out under moderate conditions to obtain a high reaction rate. High selectivity of the main product and high conversion of the reactant were obtained [12–15].

The main purpose of this work is to study the kinetics of dichlorocyclopropanation for the reaction of an olefin (styrene) and chloroform in a two-phase alkaline solution of NaOH/organic solvent medium under the influence of ultrasound assisted phase-transfer catalysis conditions. Dihalocyclopropanes are very useful compounds that can be reduced to cyclopropane derivatives, treated with magnesium or sodium to give allenes and can be converted to a number of other products.

The application of ultrasound waves in chemistry is a convenient technique for the facilitation of chemical reactions [16]. Many studies have been carried out and it is well documented that the advantages of ultrasound procedures give good yields, short reaction times and mild conditions [16-18]. No direct interaction is possible between ultrasound and matter, and so it is an indirect phenomenon, i.e., cavitation must be facilitated to induce a reaction. Hence, the use of ultrasound to enhance chemical reactivity [19–22] is now recognized as a viable environmentally benign alternative technology [20-24]. 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 [25-28]. Kinetics of the reaction in synthesizing dichlorocyclopropane, such as agitation speed, quaternary ammonium salts, amount of catalyst, amount of sodium hydroxide and temperature on the conversion were investigated in detail.

#### 2. Experimental

#### 2.1. Materials

All reagents, including styrene, chloroform, tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (BTEAB),



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<sup>1350-4177/\$ -</sup> see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ultsonch.2012.02.010

tetrabutylammonium bromide (TBAB), tetrahexylammonium bromide (THAB), tetraoctlyammonium bromide (TOAB), sodium hydroxide and other reagents for synthesis were guaranteed grade (GR) chemicals.

#### 2.2. Instrumentation

This ultrasonic apparatus (model L-400) was specially designed and constructed by a Ko Hsieh Instruments Co. Ltd., Taipei, Taiwan, The internal dimension of the ultrasonic cleaner tank was  $340 \times 250 \times 250$  mm with liquid holding capacity of 221. The external tank size was  $350 \times 355 \times 410$  mm. Two frequencies of ultrasound were used in these experiments (28 and 50 kHz), each with an electrical output of 200 W. Ultrasound was produced through a flat transduce mounted at the bottom of the tank. In this ultrasonic instrument there was a provision for a drain as well as an outlet at the top, which gave facility of continuous operation of work. An additional heater equipped with a temperature controller was also provided so as to conduct high and low temperature reactions.

#### 2.3. Kinetics measurements

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 (10 g) was dissolved in deionized water (15 ml) to prepare a 40 wt.% alkaline solution. Known quantities of styrene, BTEAB (0.046 g), and nonane (internal standard, 1 g) were then dissolved in chloroform (35 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 (0.5 ml), which was withdrawn from the reactor at each time interval, was put into the test tubes containing 3 ml of dichloromethane. The contents were measured by GC. The analyzing conditions were as follows: Shimadzu GC 17A, J&W Scientific Inc., capillary column (db-1 column); 100% poly(dimethylsiloxane) stationary phase;  $15 \times 0.525 \text{ m}$  column dimension; carrier gas, nitrogen (60 ml/min); flame ionization detector; injection temperature, 250 °C.

#### 3. Results and discussion

The kinetic experiments (followed by GC) of the dichlorocyclopropanation of styrene were carried out under pseudo-first-order conditions, taking chloroform and 40% aqueous NaOH in excess, at 35 °C (Scheme 1).

#### 3.1. Effect of varying stirring speed

The effect of varying the stirring speed on the rate of dichlorocyclopropanation of styrene reaction using BTEAB was studied in the range of 0–1000 rpm. The interfacial reaction rate directly relates to the interfacial area between the two phases. The mass



Fig. 1. Effect of agitation speed on the conversion of styrene: 35 ml of chloroform: 15 ml of NaOH solution (40 wt.%); 35 °C; 0.2 mmol of BTEAB; 60 min of reaction; 28 kHz: 200 W.

Table 1
Effect of agitation speed on the apparent rate constants,
kapp: 20 mmol of styrene; 35 ml of chloroform; 15 ml of
NaOH solution (40 wt.%); 35 °C; 0.2 mmol of BTEAB;
60 min of reaction; 28 kHz; 200 W.

Agitation speed	$k_{\mathrm{app}}  imes 10^3  (\mathrm{min}^{-1})$
0	4.53
200	11.87
400	12.38
600	16.26
800	17.52
1000	21.46

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 styrene is shown in Fig. 1. The reaction follows a pseudo-first order rate law at 40 wt.% alkaline concentration of NaOH. The conversion was increased with an increase in the agitation speed from 0 to 1000 rpm. These results confirm the interfacial reaction mechanism. The dependence of  $k_{app}$  on the agitation speed is given in Table 1. The apparent rate constant increased with an increase in the agitation speed.



(2,2-Dichlorocyclopropyl)benzene

Table 2

Effect of phase-transfer catalysts on the apparent rate constants,  $k_{\rm app}$ : 20 mmol of styrene; 35 ml of chloroform; 15 ml of NaOH solution (40 wt%); 35 °C; 800 rpm; 60 min of reaction; 28 kHz; 200 W.

Catalysts (g)	$k_{ m app}  imes 10^3 \ ({ m min}^{-1})$
TEAB	21.31
BTEAB	17.52
TBAB	14.21
THAB	13.91
TOAB	11.40

#### 3.2. Effect of different phase-transfer catalysts

Quaternary ammonium salts are generally used as phase-transfer catalysts to promote reaction rate. In addition to BTEAB, four other quaternary ammonium salts, such as TEAB, TBAB, THAB and TOAB were investigated to test their reactivities. The experimental results are listed in Table 2. Based on the experimental results, the order of the reactivities of these quaternary ammonium salts are TBAB > BTEAB > TEAB > TOAB > THAB. The higher reactivity is obtained for a quaternary ammonium salt of less total carbon number. The activity of the catalyst is dependent on the structural characteristics of a quaternary ammonium cation [12].

#### 3.3. Effect of the amount of BTEAB

The conversion of styrene was low without adding BTEAB to the reaction solution. However, the reaction is greatly enhanced by adding a small quantity of the BTEAB catalyst. The increased rates are due to the increase in the number of catalytically active sites. An optimum value of the BTEAB catalyst corresponds to a 0.15 g of BTEAB. A further increase in the amount of BTEAB made the conversion of styrene to decrease. The changes of the apparent rate constants  $k_{app}$  with the amount of BTEAB catalyst are shown in Fig. 2. The reason is probably due to the fact that the conversion of Q<sup>+</sup>CCl<sub>3</sub><sup>-</sup> to QCl and :CCl<sub>2</sub> reaches a new equilibrium state. At higher concentration of QCl, the equilibrium tends to shift to the formation of Q<sup>+</sup>CCl<sub>3</sub><sup>-</sup>, and thus the dichlorocarbene concentration is decreased. Thus, the conversion of styrene decreased with increase in the amount of catalyst QCl at a higher concentration region.



**Fig. 2.** Effect of the amount of BTEAB on the apparent rate constants,  $k_{app}$ : 20 mmol of styrene; 35 ml of chloroform; 15 ml of NaOH solution (40 wt.%); 35 °C; 800 rpm; 60 min of reaction; 28 kHz; 200 W.

#### 3.4. Effect of the amount of sodium hydroxide

The dichlorocyclopropanation is highly dependent on the alkali compound. Dichlorocarbene (:CCl<sub>2</sub>) which can be generated from chloroform in the presence of alkaline solution, reacts with organic-phase reactant (e.g., styrene) to produce the desired products. Therefore, the rate of dichlorocyclopropanation is highly influenced by the concentration of alkali in aqueous solution. Kinetic experiments were carried out employing 5–20 g sodium hydroxide. The reaction rate increased with increasing amount of sodium hydroxide. However, when the concentration of sodium hydroxide exceeded a certain value (approximately 10 g of NaOH per 15 ml of water and 35 ml of chloroform) the reaction rate decreased as shown in Fig. 3. It may be due to the catalytic decomposition at higher NaOH concentration as well as a salting out effect [10,11].

#### 3.5. Effect of temperature

The conversion of styrene was studied at different temperatures in the range of 35–50 °C. The results are shown in Table 3. It is obvious that the reactivity increased with increase in the temperature along with ultrasonic effect. The reaction is that the number of reactant molecules, which possess larger activated energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor. Thus the conversion was increased. The other point is that the collision of the reactants at higher temperature is also increased. Hence, the reaction rate increased at higher temperature. Therefore, as shown in Table 3, the apparent rate constant



**Fig. 3.** Effect of the amount of sodium hydroxide on the apparent rate constants,  $k_{app}$ : 20 mmol of styrene; 35 ml of chloroform; 35 °C; 0.2 mmol of BTEAB; 800 rpm; 60 min of reaction; 28 kHz; 200 W.

Table 3

Effect of the temperature on the apparent rate constants,  $k_{app}$ : 20 mmol of styrene; 35 ml of chloroform; 15 ml of NaOH solution (40 wt.%); 0.2 mmol of BTEAB; 800 rpm; 60 min of reaction; 28 kHz; 200 W.

Temperature (°C)	$k_{\rm app}  imes 10^3 \ ({ m min}^{-1})$
30	13.06
35	17.52
40	18.69
45	20.36



**Fig. 4.** Arrhenius plot: dependence of  $k_{app}$  on temperature.

increased with increase in the temperature. The energy of activation  $(E_a)$  is calculated from the Arrhenius plot (Fig. 4) which is 5.51 kcal/mol.

#### 3.6. Ultrasonic effect

Ultrasound was 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 [16,19,29,30]. However, conventional PTC reaction rate enhancements are typically due to mechanical effects, mainly through an enhancement in mass transfer. The presence of ultrasound in LLPTC systems, cavitational 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 [31]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [32,33]. 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 [34]. In our experiments the ultrasonic bath for filling water, model L-400 was used as described in Section 2.2. 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 50 kHz having same output power of 200 W. At 60 min, without ultrasonic irritation the conversion is only 56%, but in the presence of ultrasonic the conversion is 73% and 82% for 28 and 50 kHz, respectively. Thus, ultrasonic-assisted phase-transfer catalysis significantly increased the yields. The same trend is also observed by Entezari and co-workers [35]. So the application of ultrasounds in organic synthesis is one of the popular areas in sonochemistry.

#### 3.7. Mechanism

The generation and reaction of carbene with styrene may be represented in Scheme 2. According to Starks' extraction mechanism [12], it was thought that the hydroxide ion may be extracted from an aqueous reservoir into an organic phase with the help of quaternary ammonium cations. Makosza and Bialecka [36] proposed an alternative mechanism for dichlorocarbene addition reactions in which deprotonation of the organic substrate by the hydroxide ion occurs at the interface. According to this mechanism, the role of catalyst is to remove the resulting organic anion from the interface into the bulk organic phase for subsequent reaction. Several studies [37,38] have provided support for various aspects of Makosza's mechanism.

It has been established by Makosza and Fedorynski [39] that the slowest reaction is the addition of  $CCl_2$  (dichlorocarbene) to alkenes, considering the other steps as fast equilibrium processes. In our study, a fractional order with respect to catalyst concentration suggests that the step (2) is not the sole rate-determining one and that of the chemical reaction in the organic phase is also rate-determining. The effects of other experimental results such as stirring speed, sodium hydroxide concentration and temperature over the observed rate of the reaction support the interfacial mechanism proposed by Makosza for the PTC/OH<sup>-</sup> systems rather than Starks' extraction mechanism.



Scheme 2. Mechanism for phase-transfer catalytic dichlorocyclopropanation of styrene under the influence of ultrasound conditions.

#### 4. Conclusions

In conclusion, the reaction rate dichlorocyclopropanation of styrene catalyzed by phase-transfer catalyst combined with ultrasonic irradiation was investigated. The factors affecting the overall reaction rate, such as the effect of stirring speed, quaternary ammonium salts, amount of catalyst, amount of sodium hydroxide and temperature were studied to determine the optimal operating conditions. The apparent reaction rates were observed to obey the pseudo-first order kinetics with respect to the styrene. The reaction rate increased with increasing temperature and catalyst amount. Nevertheless, there is an optimum value of the sodium hydroxide amount to promote the yield or to enhance the rate of the reaction.

#### Acknowledgment

The authors would like to thank The National Science Council. Taiwan, Republic of China for financial support under the Grant No. NSC 95-2221-E-241-022-MY3.

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