

# A kinetic study of thioether synthesis under influence of ultrasound assisted phase-transfer catalysis conditions

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## Abstract

Alkyl bromides afford the corresponding sulfide derivatives upon treatment with aqueous sodium sulfide under phase-transfer catalysts (PTC) and ultrasound irradiation conditions. The use of phase-transfer catalysis and sonochemistry has been compared and demonstrated in these nucleophilic substitution reactions. The kinetics of the reaction depends on the effect of amount of catalyst, agitation speed, quaternary ammonium salts, amount of sodium sulfide, amount of sodium hydroxide, organic solvents, temperature and the frequency of the ultrasound waves on the conversion of alkyl bromides were investigated in detail. A kinetic model was built from which a pseudo-first order rate law is sufficient to describe the behavior of the reaction. The observed peculiar phenomena were also explained satisfactorily.

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*Keywords:* Phase-transfer catalysis; Bromobutane; Ultrasound acceleration; Sonochemistry; Thioether; Kinetic study

## 1. Introduction

Thioethers, which have been widely employed as perfume additives [1] and inverse phase-transfer catalysts [2,3] are generally synthesized in a homogeneous reaction [4]. Phase-transfer catalysis (PTC) is well-recognized as an invaluable methodology in organic syntheses in recent years [5–7]. The advantages of the PTC method for synthesizing thioethers are increased reaction rate and selectivity, hydrophilic conditions and low energy requirement. Searching for a more effective condition to enhance the reaction or to elevate the conversion is the primary purpose in phase-transfer catalysis in combination with ultrasonic waves [8–13]. Inventing selective, efficient and eco-friendly methods for applications in complex organic synthetic manipulations constitutes a major chemical research effort. In this regard, several non-conventional methods are emerging that involve reactions in aqueous media [14,15] or those that are accelerated by exposure to microwave [16–18] or ultrasound [19–22] irradiation. These methods are now recognized as viable environmentally benign alternatives [16–22]. 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. A vast majority of sonochemical applications in the synthesis deal with reactions involving metals [21,23,24] organic phase insoluble reagents, or their aqueous solutions [21,25,26].

Our interest was centered on first time evaluating the influence of ultrasound in association with phase-transfer catalyst on the rate of alkyl thioether formation. This work investigates the substitution of alkyl bromides (RBr) to sodium sulfide ( $\text{Na}_2\text{S}$ ), including linear and branched alkyl groups and the application of phase-transfer catalysts in combination with ultrasound obviously provides a more efficient synthetic approach for the preparation of thioethers. These PTC reactions were carried out in a liquid–liquid two-phase medium. In the absence of a phase-transfer catalyst and ultrasound, less than 5% conversion was detected even after 4 h of reaction. In contrast high yields of products were obtained in shorter reaction time using 4 mol% (based on the amount of alkyl bromide) of the phase-transfer catalyst, tetrabutylammonium bromide (TBAB) and ultrasound 28 kHz (200 W) conditions. Kinetics of the substitution of alkyl bromide to sodium sulfide, including the effect of amount of catalyst, agitation speed, quaternary ammonium salts, amount of sodium hydroxide, organic solvents, temperature and ultrasound frequency on the conversion were investigated in detail.

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## 2. Experimental

### 2.1. Materials

All reagents, including sodium sulfide ( $\text{Na}_2\text{S}$ ), tetrabutylammonium bromide (TBAB), tetrahexylammonium bromide (THAB), tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (BTEAB), alkyl bromides (RBr), sodium hydroxide (NaOH), biphenyl, and other reagents for synthesis were guaranteed grade (GR) chemicals, and were used as received without further purification.

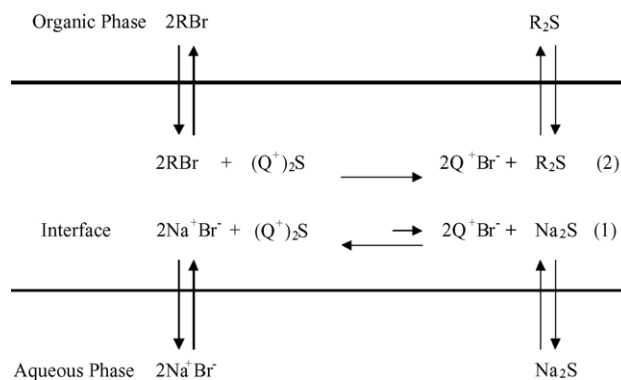
### 2.2. Instrumentation

The ultrasonic apparatus consisted of two layers stainless steel body to have safe and beauty from use. This ultrasonic apparatus (model L-400) was specially designed and constructed by a Ko Hsieh Instruments Co. Ltd., Taipei, Taiwan (<http://www.kohsieh.com.tw/>). The internal dimensions of the ultrasonic cleaner tank is 340 mm × 250 mm × 250 mm with liquid holding capacity of 22l. The external tank size is 350 mm × 355 mm × 410 mm. Two types of frequencies of ultrasound were used in these experiments, which are 28 kHz and 40 kHz with each output as 200 W. Both ultrasounds are separately produced 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 with facility of temperature controller has been also provided so as to facilitate some high and low temperature reactions.

### 2.3. Kinetics of the substitution of alkyl bromides

The reactor was a 250 ml three-necked pyrex round-bottom flask. Each neck having the purpose of agitating the solution, inserting the thermometer, taking the samples, and feeding the feed. This reaction vessel was suspended at the center of the ultrasonic cleaning bath to get the maximum ultrasound energy. Known quantities of sodium sulfide (7 g, excess agent), was put into the reactor. Ten milliliter of water was added. Then, 1-bromobutane (4 mmol, limiting reactant), and 0.5 g biphenyl (internal standard), which were dissolved in 40 ml *n*-hexane, were introduced into the reactor. The phase-transfer catalyst, tetrabutylammonium bromide (4 mol% with respect to 1-bromobutane) was added to the reactor. The reaction mixture was stirred at 500 rpm and simultaneously the ultrasonic energy 28 kHz (200 W) was passed through the reactor.

The sample (0.5 ml) was withdrawn periodically from the reactor and put into the glass vials containing 1 ml of *n*-hexane. The samples were then analyzed by Gas Chromatography (GC-Shimadzu 17 A model). The analyzing conditions were as follows: column, 30 m × 0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxane); injection temperature, 250 °C; detector, flame ionization detector (300 °C). The products formed were analysed by comparison of their retention



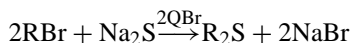
Scheme 1.

times with authentic samples. Yields were determined from standard curve and using biphenyl as internal standard.

### 2.4. Reaction mechanism and kinetic model

In this work, the substitution reaction between 1-butyl bromide (RBr) and sodium sulfide ( $\text{Na}_2\text{S}$ ) were employed in the presence of phase-transfer catalyst namely tetrabutylammonium bromide (QBr) and ultrasonic waves 28 kHz (200 W). The ultrasonic waves enhance the rate of the reaction which is discussed in Section 3. The reaction mechanism is represented in Scheme 1, which is similar to the mechanism proposed by Yadav and Bisht [27] and Hsiao et al. [28].

The overall reaction can be represented as:



when the organic and aqueous reactants are immiscible in the aqueous and organic phases, the substitution reaction (Eq. (2)) and ion-exchange (Eq. (1)), mainly take place in the phase-transfer catalyst. In addition, the hydrophilicity (or lipophilicity) of the catalyst is a crucial factor for influencing the rates of Eqs. (1) and (2).

### 2.5. Definition

The conversion ( $X$ ) of RBr is defined as follows:

$$X = 1 - \frac{[\text{RBr}]_o}{[\text{RBr}]_{o,i}} \quad (1)$$

where  $[\text{RBr}]_o$  represents the concentration of 1-butyl bromide in the organic phase at a given time,  $t$  and  $[\text{RBr}]_{o,i}$  stands for the initial concentration of 1-butyl bromide in the organic phase.

### 2.6. Rate expression

The rate expression for this reaction may be expressed as:

$$-r_{\text{RBr}} = k_{\text{app}}[\text{RBr}]_o \quad (2)$$

where  $k_{\text{app}}$  is the apparent reaction rate constant.

This reaction is carried out in a batch reactor, so the diminution rate of RBr per volume of the organic phase with time ( $t$ )

can be expressed as:

$$-\frac{d[\text{RBr}]_o}{dt} = -r_{\text{RBr}} = k_{\text{app}}[\text{RBr}]_o \quad (3)$$

on integrating the Eq. (3) yields:

$$-\ln \left( \frac{[\text{RBr}]_o}{[\text{RBr}]_{o,i}} \right) = -\ln(1 - X) = k_{\text{app}}t \quad (4)$$

Using Eq. (4), we can get the  $k_{\text{app}}$ -value experimentally by plotting  $-\ln(1 - X)$  against time ( $t$ ).

### 3. Results and discussion

#### 3.1. Effect of the agitation speed

The mass transfer as well as the chemical reaction is important in influencing the conversion or rate of the two-phase reaction. In this study, the effect of the agitation speed on the reaction rate is shown in Table 1 with the ultrasonic energy used is 28 kHz (200 W) for throughout the reaction. For agitation speed over 400 rpm, the conversion of 1-butyl bromide is insensitive to the agitation speed. This result is different from that of other reaction systems that require a high agitation speed to reach a constant value of conversion [27,29]. The main reason is that other reactions systems [27,29] need a relatively larger interfacial area to increase the mass transfer rate. However, the active intermediate of the catalyst (Q<sub>2</sub>S), which is hydrophobic, likes to stay in the organic phase, i.e., it is easy to transfer the active intermediate of the catalyst from the aqueous phase to the organic phase, in which the interfacial area is not so important. Thus, the mass transfer rate reaches a constant value when the stirring speed is larger than 400 rpm. Hence, the stirring speed was set at 500 rpm for further experiments.

In the absence of stirring speed and in the presence of the effect of ultrasonic condition at 28 kHz (200 W) the observed rate constant is  $9.8 \times 10^{-3} \text{ min}^{-1}$  in vice-versa the  $k_{\text{app}}$  value at 500 rpm is  $11.4 \times 10^{-3} \text{ min}^{-1}$ . In the presence of both condition, i.e., at 500 rpm combined with the ultrasonic wave frequency 28 kHz (200 W) the  $k_{\text{app}}$  value is  $41.7 \times 10^{-3} \text{ min}^{-1}$ . From this observation the ultrasonic effect enhances the rate 3.7 times with respect to the conventional method (stirring speed at 500 rpm only). It may be due to in the presence of ultrasonic wave increase the collision rate between the organic and aqueous phase and decrease the surface area between the two layers [30].

Table 1

Effect of the agitation speed on the apparent rate constants,  $k_{\text{app}}$ : 7 g Na<sub>2</sub>S; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml *n*-hexane, 4 mol% of TBAB; 500 rpm; 35 °C; 60 min of reaction

Agitation speed (rpm)	$k_{\text{app}} \times 10^3 \text{ (min}^{-1}\text{)}$
0	9.8
200	33.9
400	39.6
500	41.7
600	40.7
800	40.8
1000	40.6

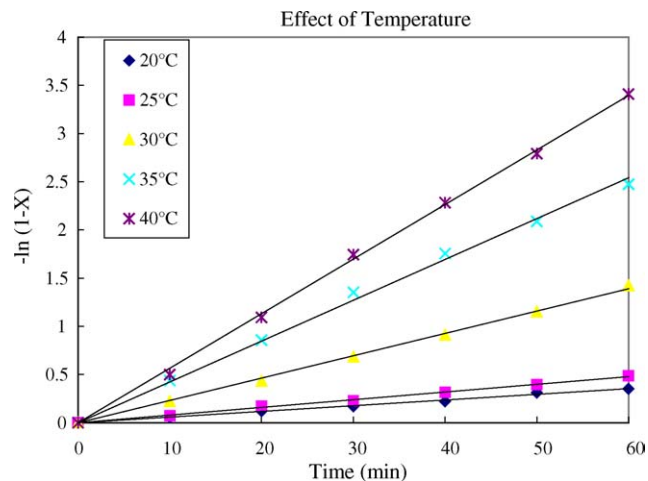


Fig. 1. Effect of the temperature on the conversion of 1-butyl bromide: 7 g Na<sub>2</sub>S; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of *n*-hexane; 4 mol% of TBAB; 0.5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

#### 3.2. Effect of temperature

The reaction was studied at five different temperature in the range of 20–40 °C. The results are shown in Fig. 1. It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect [31]. The reason 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 is increased. The other point is that the collision of the reactants at higher temperature is also increased. Hence, the reaction rate is increases with increasing temperature. Arrhenius plots were made in Fig. 2 of  $-\ln(k_{\text{app}})$  against  $1/T$  to get an activation energy of  $11.37 \text{ kcal mol}^{-1}$ .

#### 3.3. Effect of the amount of TBAB

In general, the reactivity is increased with an increase in the amount of quaternary ammonium salt. As shown in Fig. 3, the conversion of 1-butyl bromide is increased with an increase in the amount of tetrabutylammonium bromide from 25 mg to 125 mg. The rate constants are linearly dependent on the amount

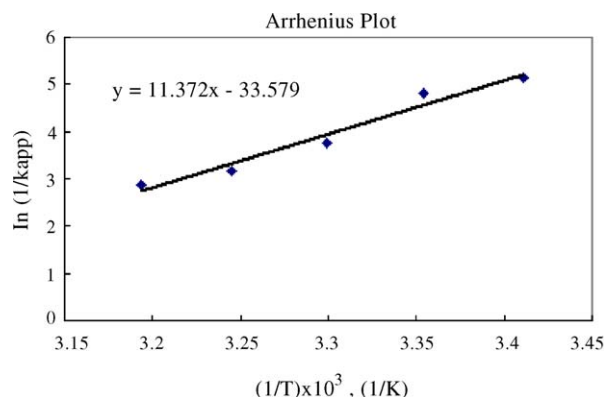


Fig. 2. Arrhenius plot: dependence of  $k_{\text{app}}$  on temperature; same reaction conditions as given in Fig. 1.

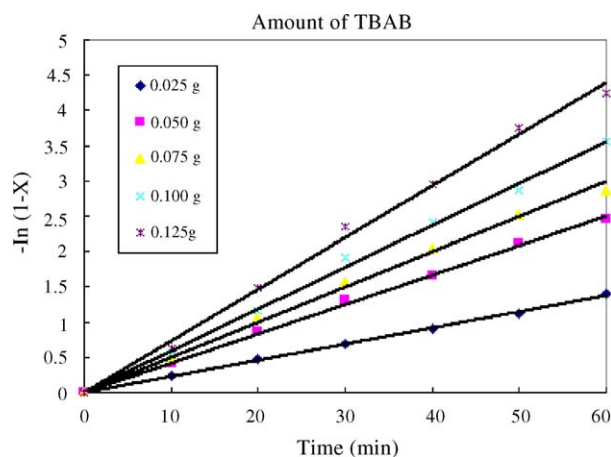


Fig. 3. Effect of the amount of TBAB on the conversion of 1-butyl bromide: 7 g  $\text{Na}_2\text{S}$ ; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of *n*-hexane; 5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

of catalyst used in each reaction (Fig. 4). So, the sonication along with phase-transfer catalyst, the  $k_{\text{app}}$  value increases which may be due to induce the surface area, change the size, and morphology of phase-transfer catalyst [32].

#### 3.4. Effect of the various phase-transfer catalysts

In principle, there is no universal rule to guide in selecting an appropriate phase-transfer catalyst except that determined from experiments. The reason is that different reactions need various catalysts to enhance the rate and to promote the yields. In this study, tetrahexylammonium bromide (THAB), tetrabutylammonium bromide, tetraethylammonium bromide (TEAB) and benzyltriethylammonium bromide (BTEAB) were employed to investigate their reactivities. The results are shown in Fig. 5. The results indicate that the reactivity of quaternary salt increases with total carbon number in the alkyl group of the cation. For example, the reaction is 100% completed within 40 min by using THAB. On comparing the catalytic activity of TEAB with BTEAB, TEAB is more reactive than BTEAB although the total number of carbon in the cation of BTEAB is larger than that of TEAB. The reason is that the benzyl group appears in the unsymmetric cation. The reaction system of the unsymmetric cation easily forms the emulsion solution, which is a retardant

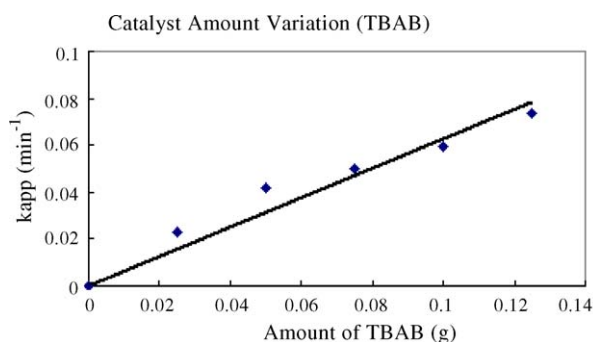


Fig. 4. Effect of catalyst amount on  $k_{\text{app}}$ : same reaction conditions as given in Fig. 3.

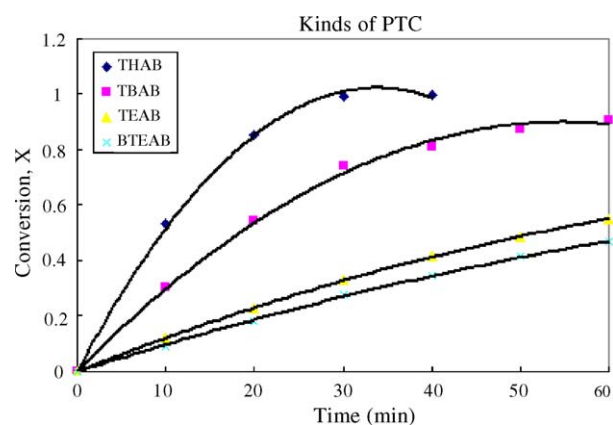


Fig. 5. Effect of the quaternary ammonium salts on the conversion of 1-butyl bromide: 7 g  $\text{Na}_2\text{S}$ ; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of *n*-hexane; 5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

state for the regeneration of catalysts and unfavorable for the attack of the nucleophilic reagent in this reaction [33].

#### 3.5. Effect of the organic solvents

In this work, hexane, cyclohexane, toluene, chloroform and 1,2-dichloroethane were employed as the organic solvents to investigate their reactivity. The results are shown in Fig. 6. Usually, the dielectric constants are used as the main index in choosing an appropriate organic solvent. However, this statement does not hold to be true in the application to a phase-transfer catalyst system. The main reason is that the effect of the organic solvent involves the solubility of the catalyst, transition state of the reaction, ion transfer, solvation, and interfacial phenomena, which are difficult to determine. Therefore, it is based on the experimental results for practical application. As shown in Fig. 6 and Table 2, toluene possesses a higher reactivity among the five organic solvents.

#### 3.6. Effect of the amount of sodium sulfide

The effect of the amount of sodium sulfide ( $\text{Na}_2\text{S}$ ) on the conversion of 1-butyl bromide is shown in Fig. 7. In principle,

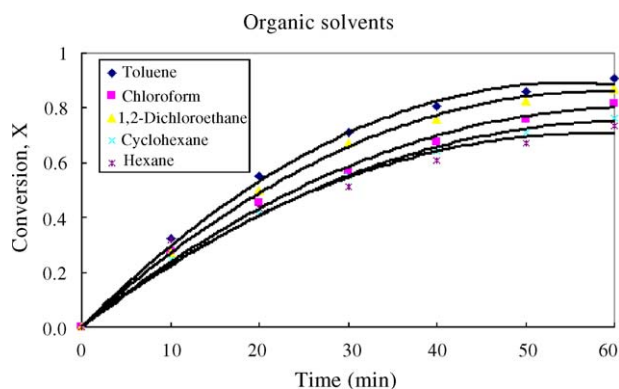


Fig. 6. Effect of the organic solvents on the conversion of 1-butyl bromide: 7 g  $\text{Na}_2\text{S}$ ; 10 ml water; 4 mmol of 1-butyl bromide; 4 mol% of TBAB; 0.5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

Table 2

Effect of the organic solvents on the conversion of 1-butyl bromide: 7 g Na<sub>2</sub>S; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of organic solvent; 4 mol% of TBAB; 500 rpm; 35 °C; 60 min of reaction

	Solvents				
	Hexane	Cyclohexane	Toluene	Chloroform	1,2-Dichloroethane
$\epsilon^a$	1.89	2.02	2.4	4.8	10.4
$k_{app} \times 10^3 (\text{min}^{-1})$	3.2	24.9	40.3	28.2	34.8

<sup>a</sup> Dielectric constant.

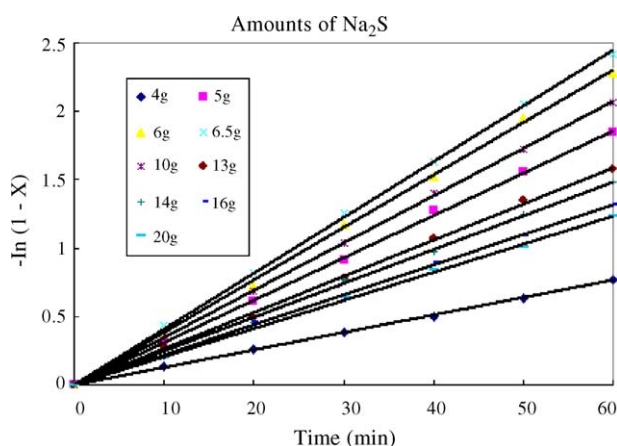


Fig. 7. Effect of the amount of sodium sulfide on the conversion of 1-butyl bromide: 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of *n*-hexane; 4 mol% of TBAB; 0.5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

the concentration of sodium sulfide affects the distribution of the catalyst between two phases. The active catalyst QS(R)<sub>2</sub>SQ in the aqueous phase is solvated to form the complex compound (QS(R)<sub>2</sub>SQ)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub>. The hydration number of QS(R)<sub>2</sub>SQ is decreased by increasing the concentration of sodium sulfide. Hence, the reaction rate is increased by increasing the amount of sodium sulfide. However, when the concentration of sodium sulfide exceeded a certain value (approximately 8 g per 10 ml water) the reaction rate decreased, it may be due to the catalyst concentration that decreased at sodium sulfide phase (salting out effect). The  $k_{app}$  value increases by increasing the sodium sulfide amount up to 7 g sodium sulfide per 10 ml water and does not increase apparently beyond this concentration (Fig. 8).

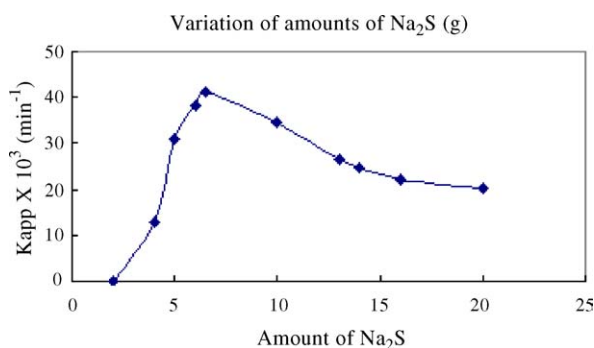


Fig. 8. Effect of sodium sulfide amount on  $k_{app}$ : same reaction conditions as given in Fig. 7.

Therefore, the conversions are obviously affected by the amount of sodium sulfide, so we choose 7 g sodium sulfide per 10 ml water for the kinetic study.

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

Fig. 9 shows the effect of sodium hydroxide amount in the aqueous phase on the thioether production. The  $k_{app}$  value increased from 0.5 g to 2.0 g of sodium hydroxide (NaOH). It may be due to increase the basicity of aqueous phase [32]. From 2.0 g to 5.0 g sodium hydroxide the  $k_{app}$  value tremendously decreased. According to Hsiao and Weng [34] adding salt (NaOH or NaBr) to the aqueous solution would inhibit the ionization of sodium sulfide, thus the rate of formation of the product is decreased and the second reason is the amount of phase-transfer catalyst salted out from the aqueous phase and thereby the reaction rate is decreased (Fig. 10).

### 3.8. Effect of alkyl bromides

Fig. 11 and Table 3 shows that the reaction follows pseudo-first order law in the presence of PTC and excess amount of sodium sulfide. The most reactive organic reactant is allyl bromide (C<sub>3</sub>H<sub>5</sub>Br). The reaction is 100% completed within 10 min for allyl bromide. It may be due to its smaller molecular size and the conjugation of pi bond. Among the alkyl bromides *sec*-propyl bromide (2-C<sub>3</sub>H<sub>7</sub>Br) is the least reactive one because of steric hindrance in its reaction. From 1-propyl bromide

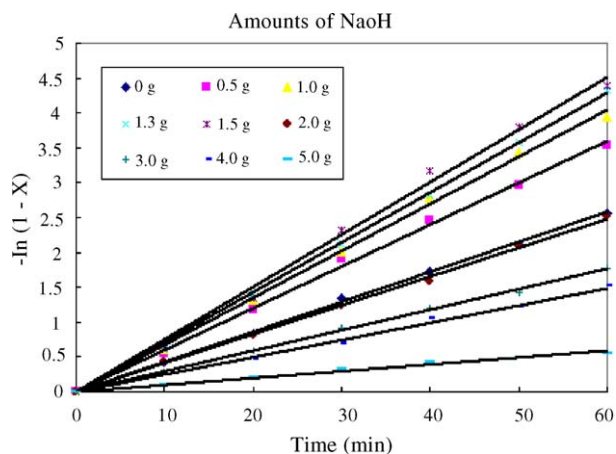


Fig. 9. Effect of the amount of sodium hydroxide on the conversion of 1-butyl bromide: 7 g Na<sub>2</sub>S; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of *n*-hexane; 4 mol% of TBAB; 0.5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

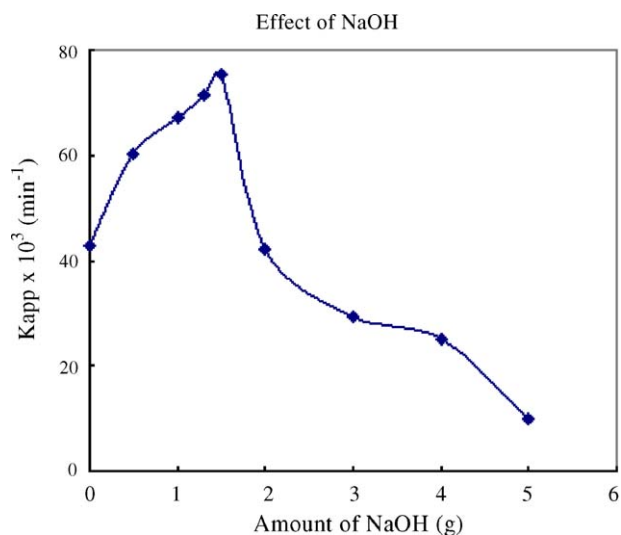


Fig. 10. Effect of sodium hydroxide amount on  $k_{app}$ : same reaction conditions as given in Fig. 9.

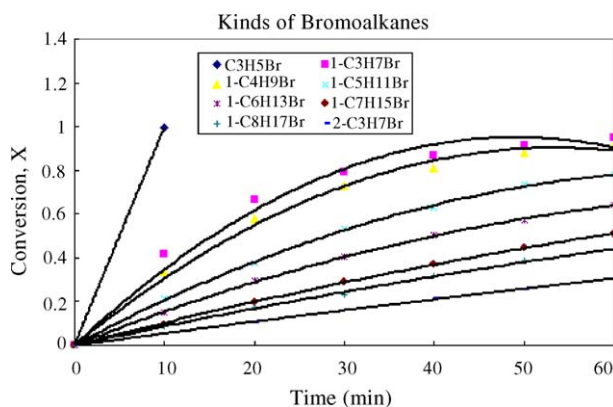


Fig. 11. Conversions of various reactants with time: 7 g  $\text{Na}_2\text{S}$ ; 10 ml water; 40 ml of *n*-hexane; 4 mol% of TBAB; 0.5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

(1- $\text{C}_3\text{H}_7\text{Br}$ ) to 1-octyl bromide (1- $\text{C}_8\text{H}_{17}\text{Br}$ ) the  $k_{app}$  value decreases due to increasing the carbon chain of the molecules and ( $\text{Q}_2\text{S}$ ) is not able to properly interact with active site of the long chain alkyl bromides.

Table 3

Conversions of various reactants vs. time: 7 g  $\text{Na}_2\text{S}$ ; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of *n*-hexane; 4 mol% of TBAB; 500 rpm; 35 °C; 60 min of reaction

Sl. no.	Alkyl bromide (molecular formula)	$k_{app} \times 10^3$ ( $\text{min}^{-1}$ )
1	Allyl bromide ( $\text{C}_3\text{H}_5\text{Br}$ ) <sup>a</sup>	
2	1-Propyl bromide (1- $\text{C}_3\text{H}_7\text{Br}$ )	49.6
3	1-Butyl bromide (1- $\text{C}_4\text{H}_9\text{Br}$ )	41.7
4	1-Pentyl bromide (1- $\text{C}_5\text{H}_{11}\text{Br}$ )	25.5
5	1-Hexyl bromide (1- $\text{C}_6\text{H}_{13}\text{Br}$ )	17.1
6	1-Heptyl bromide (1- $\text{C}_7\text{H}_{15}\text{Br}$ )	11.7
7	1-Octyl bromide (1- $\text{C}_8\text{H}_{17}\text{Br}$ )	9.5
8	2-Propyl bromide (2- $\text{C}_3\text{H}_7\text{Br}$ )	5.6

<sup>a</sup> Reaction completed within 10 min.

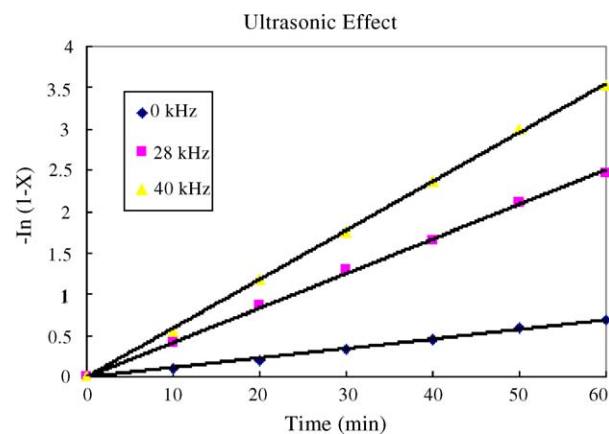


Fig. 12. Effect of ultrasonic on the conversion of 1-butyl bromide: 7 g  $\text{Na}_2\text{S}$ ; 10 ml water; 4 mmol of 1-butyl bromide; 40 ml of *n*-hexane; 4 mol% of TBAB; 0.5 g of biphenyl; 500 rpm; 35 °C; 60 min of reaction.

### 3.9. Ultrasonic effect

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 vapour or gas bubbles in the ultrasonic field [35,36]. However, in phase-transfer catalyst (PTC) reactions 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 [37]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [38,39]. 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 [40] (Fig. 12).

In our experiments the ultrasonic bath, model L-400 was used. It is consisted of two layers stainless steel body. The internal dimensions of the ultrasonic cleaner tank is 340 mm × 250 mm × 250 mm with liquid holding capacity of 22 l. The external tank size is 350 mm × 355 mm × 410 mm. We used water as a liquid in the ultrasonic cleaner. Two types of frequencies, 28 kHz and 40 kHz are available with power of ultrasound 200 W for each frequencies. Both ultrasound separately produces through a flat transducer mounted at the bottom of the sonicator. 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 with a facility of temperature controller has also been provided so as to facilitate some high and low temperature reactions. If the water level is lower than the outlet, i.e., 3 cm below from the top of the sonicator, the applied frequency is automatically cut off. So the water fill level is important. The reactor was a 250 ml three-necked pyrex round-bottom

flask. This 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 kHz and 40 kHz having same output power of 200 W. At 1 h, without ultrasonic irradiation the conversion is only 53%, but in the presence of ultrasonic the conversion is 91% and 97% for 28 kHz and 40 kHz, respectively. From this observed result ultrasonic-assisted phase-transfer catalysis significantly increased the yields. The same trend is also observed by Entezari and co-workers [31,41]. So the application of ultrasounds in organic synthesis is one of the popular areas in sonochemistry.

#### 4. Conclusion

In conclusion, the reaction rate of alkyl bromides with sodium sulfide catalyzed by phase-transfer catalyst combined with ultrasonic irradiation was investigated. The factors affecting the overall reaction rate, such as agitation speed, solvent, amount of catalyst, amount of sodium sulfide, amount of sodium hydroxide, temperature and ultrasonic effect, were studied to determine the optimal operating conditions. The reaction was not affected by stirring speeds higher than 400 rpm. The apparent reaction rates were observed to obey the pseudo-first order kinetics with respect to the organic reactant. The reaction rate increased with increasing temperature, catalyst amount and the frequency of ultrasonic wave. Nevertheless, there is an optimum value of the sodium sulfide amount to promote the yield or to enhance the reaction rate. The apparent activation energy for this two-phase reaction was determined to be 11.37 kcal mol<sup>-1</sup>.

#### Acknowledgment

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