

Synthesis of Diallyl Thioether under the Influence of Ultrasound Assisted Multi-Site Phase-Transfer Catalysis Condition – A Kinetic Study.

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Abstract: Allyl bromides afford the corresponding sulfide derivatives upon treatment with aqueous sodium sulfide under multi-site phase-transfer catalysts (MPTC) 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 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 frequency of the ultrasound waves on the conversion of allyl bromide was 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.

Keywords: Phase-transfer catalysis; Allyl bromide; ultrasound acceleration; Thioether.

I. 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. Phase-transfer catalysis (PTC) is well-recognized as an invaluable methodology in organic syntheses in recent years [4-7]. The advantageous 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 combined 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 [16,17] or ultrasound [8-13] irradiation. These methods are now recognized as viable environmentally benign alternatives [10,11,16-18]. 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.

First time, we evaluate the influence of ultrasound in association with phase-transfer catalyst on the rate of allyl thioether formation. This work investigates the substitution of allyl bromide (RBr) to sodium sulfide (Na_2S), under liquid-liquid bi-phase reaction using phase-transfer catalysts in combination with ultrasound. In the absence of a phase-transfer catalyst and ultrasound, less than 4% conversion was detected even after 4h of reaction. In contrast high yields of products were obtained in shorter reaction time using 16 mol% (based on the amount of allyl bromide, limiting reagent) of a multi-site phase-transfer catalyst, viz., 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrabromide (MPTC) and ultrasound 28 kHz (300 W) conditions. Kinetics of the substitution of allyl bromide to sodium sulfide, including the effect of amount of multi-site phase-transfer catalyst, agitation speed, quaternary ammonium salts, amount of sodium hydroxide, organic solvents, temperature and ultrasound frequency on the conversion were investigated in detail.

II. EXPERIMENTAL

2.1 Materials

All reagents, including sodium sulfide (Na_2S), tetrabutylammonium bromide (TBAB), tetrahexylammonium bromide (THAB), tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (BTEAB), allyl bromide (RBr), sodium hydroxide (NaOH), biphenyl, and were used as received without further purification.

2.2. Synthesis of Mptc

A mixture of 7g of hexamethylenetetramine, 40 mL of benzyl bromide, and 60 mL of ethanol was placed in a 250 mL three necked round – bottomed Pyrex flask. The reaction was carried out at 40°C for 24

hours and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, ie, 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetra bromide (MPTC) was washed with n- hexane (3 x 20 mL). The white solid MPTC was stored in a CaCl₂ desiccator (scheme 1). m.p 199°C; Yield: 90%; ¹H NMR (100 MHz, DMSO); δ 4.06 (s, 8H, Ar-CH₂), 5.30 (s, 12H, N-CH₂), 7.44-7.77 (m, 5H, ArH); ¹³C NMR (400 MHz, DMSO): δ 69.48 (Ar-CH₂), 78.77 (N-CH₂), 128.53, 128.76, 128.90, 129.90. (Ar-C) for hexamethylenetetramine (HMTA) ¹H NMR (400MHz, DMSO): δ 4.71 (s, 12H, N-CH₂); ¹³C NMR (100 MHz, DMSO): δ 76.13 (N-CH₂); MS (EI, 70 Ev, %): M/Z 824; Elemental analysis Calc.: C, 49.51; H, 4.85; N, 6.79; Found, C, 49.47; H, 4.79; N, 6.81.

2.3 Instrumentation

Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers stainless steel body. The sonochemical reactor configuration used in the present work is basically an ultrasonic cleaner tank with internal dimension of 48 cm x 28 cm x 20 cm with liquid holding capacity of 5 litres. Two types of frequencies of ultrasound were used in these experiments, which are 28 kHz and 40 kHz with each output as 300 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.

2.4 Kinetics of the substitution of allyl bromide

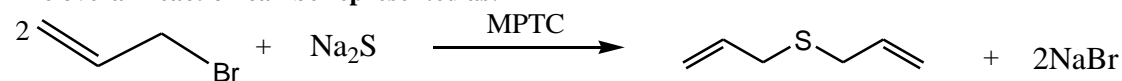
The reactor was a 250 mL three-necked Pyrex round-bottom flask. Each neck having the purpose of agitation the bi-phase solution, inserting the thermometer, taking the samples, and feeding the feed. This reaction vessel was suspended at the center of the ultrasonic cleaning bath to get the maximum ultrasound energy. Known quantities of sodium sulfide (7g, excess agent), was put into the reactor. Ten milliliter of water was added. Then, allyl bromide (10 mmol, limiting reactant), and 0.5g biphenyl (internal standard), which were dissolved in 40 mL of hexane were introduced into the reactor. The multi-site phase transfer catalyst i.e., 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrabromide (16 mol% with respect to allyl bromide) was added to the reactor. The reaction mixture was stirred at 500 rpm and simultaneously the ultrasonic energy 28 kHz (300 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-(GC-Varian 3700 model). The analyzing conditions were as follows; Column, 30 m x 0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxanen); injection temperature, 200°C; FID detector (250°C). Yields were determined from standard curve and using biphenyl as internal standard.

2.5 Reaction mechanism and kinetic model

In this study, the substitution reaction between allyl bromide (RBr) and sodium sulfide (Na₂S) were employed in the presence of multi-site phase-transfer catalyst namely 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrabromide (MPTC, QBr) and ultrasonic waves 28 kHz (300 W). The ultrasonic waves enhance the rate of the reaction which is discussed in Section 3, and the reaction mechanism is represented in (Scheme 2).

The overall reaction can be represented as:



When the organic and aqueous reactants are immiscible in the aqueous and organic phases, the substitution reaction, mainly take place in the presence of multi-site phase-transfer catalyst. In addition, the lipophilicity of the catalyst is a crucial factor for influencing the rates.

2.6. Definition

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

$$X = 1 - \left\{ \frac{[\text{RBr}]_t}{[\text{RBr}]_{0,i}} \right\} \quad (1)$$

Where [RBr]_t represents the concentration of allyl bromide in the organic phase at a given time, t and [RBr]_{0,i} stands for the initial concentration of allyl bromide in the organic phase.

2.7 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_{app} is the apparent reaction rate constant. This reaction is carried out in a batch reactor, so the diminution rate of RBr volume of organic phase with time (t) can be expressed as:

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

on integrating the Eq. (3) yields:

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

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

III. 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 of 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 28 kHz (300 W) used for throughout the reaction. For agitation speed over 400 rpm, the conversion of allyl bromide is insensitive to the agitation speed. The main reason is that the reaction systems need a relatively larger interfacial area to increase the mass transfer rate. However, the active intermediate of the catalyst Q_2S_4 , (MPTC having 4 active site i.e., 4N^+) which is more organophilicity, therefore it 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 (300 W) the observed rate constant is $9.8 \times 10^{-3} \text{ min}^{-1}$ vice-versa the k_{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 (300W) the k_{app} value is $41.7 \times 10^{-3} \text{ min}^{-1}$. From this observation the ultrasonic effect enhances the rate 3.6 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 [19].

3.2 Effect of temperature

The reaction was studied at four different temperatures in the range 30 - 45°C. The results are show in (Fig. 1). It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect [8]. 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 points that the collision of the reactants at higher temperature is also increased. Hence, the reaction rate increases with increasing temperature. For the system, the energy of activation is $9.28 \text{ kcal mol}^{-1}$, which is calculated from Arrhenius equation.

3.3 Effect of the amount of MPTC

In general, the reactivity is increased with an increase in the amount of quaternary onium salts. As shown in (Fig. 2), the conversion of allyl bromide is increased with an increase in the amount of MPTC 0.08 g to 0.16 g. The rate constants are linearly dependent on the amount of catalyst used in each reaction. So, the sonication along with multi-site phase-transfer catalyst, the k_{app} value increases which may be due to induce the surface area, change the size, and morphology of multi-site phase-transfer catalyst [20].

3.4 Effect of the various phase-transfer catalysts

In principle, there is no universal rule to guide in selection of 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, 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrabromide (MPTC), tetrahexylammonium bromide (THAB), tetrabutylammonium bromide (TBAB), tetraethylammonium bromides (TEAB) and benzyltriethylammonium bromide (BTEAB) were employed to investigate their reactivities. The observed results show that the reactivity of quaternary salt increases with total carbon number as well as active sites of the PTC. On comparing the catalytic activity of MPTC, THAB, TBAB, TEAB and BTEAB, among them MPTC having more reactivity due to its more organophilicity as well as more active site (4N^+) present in the catalyst [6].

3.5 Effect of the organic solvents

In this work, hexane, cyclohexane, benzene, toluene and chlorobenzene were employed as the organic solvents to investigate their reactivity. 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. From our experimental results (Table 2), toluene possesses a higher reactivity among the five organic solvents.

3.6 Effect of the amount of sodium sulfide

In principle, the concentration of sodium sulfide affects the distribution of the catalyst between two phases. The multi-site phase-transfer catalyst in the aqueous phase is solvated to form the complex compound $(Q_2S_4)_m(H_2O)_n$. The hydration number of Q_2S_4 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 exceed a certain value (approximately 8 g per 10 mL water), the k_{app} value decreases (Fig. 3). Therefore, the conversions are obviously by the amount of sodium sulfide, so we choose 7g sodium sulfide per 10 mL water for the kinetic study.

3.7 Effect of the amount of sodium hydroxide

(Fig. 4) shows the effect of sodium hydroxide amount in the aqueous phase on the allyl 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 [20]. From 2.0 g to 4.0 g sodium hydroxide the k_{app} value tremendously decreased. According to Hsiao and Weng [21] 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 MPTC salted out from the aqueous phase and thereby the reaction rate is decreased.

3.8 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 cavitations bubble dynamics, i.e., the nucleation, formation, disappearance, and coalescence of vapour or gas bubbles in the ultrasonic field [22,23]. However, in phase-transfer catalyst (PTC) reactions rate enhancements are in phase-transfer 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 [24]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [25, 26]. In such cases, the phase-transfer catalyst initiates the reaction [27] 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 (Fig. 5).

The reaction rate also compared with 28 kHz and 40 kHz having same output power of 300 W. At 1 h, without ultrasonic irradiation the conversion only 53%, but in the presence of ultrasonic conversion is 87 % and 94 % for 28 KHz and 40 KHz, respectively. From this observed result ultrasonic assisted phase-transfer catalysis significantly increase the yields. The same trend is also observed by Entezari and co-workers [27]. So the application of ultrasounds in organic synthesis is one of the popular areas in sonochemistry.

IV. CONCLUSION

In conclusion the reaction rate of allyl bromide with sodium sulfide catalyzed by multi-site phase-transfer catalyst combined with ultrasonic irradiation was investigated. The factors affecting the over all 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 speed higher than 500 rpm. The apparent reaction rates were observed to obey pseudo-first order kinetics with respect to the organic reactant. The reaction rate increased with increasing temperature, catalyst amount and 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 9.28, kcal mol⁻¹.

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Figures

Fig: 1 Effect of the temperature on the conversion of allyl bromide: 7 g Na 2 S; 10 mL H 2 O; 10 mmol of allyl bromide; 40 mL of hexane; 16 mol% of MPTC; 0.5 g of biphenyl; 500 rpm; 30 min; Ultrasound 40 kHz (300 W).

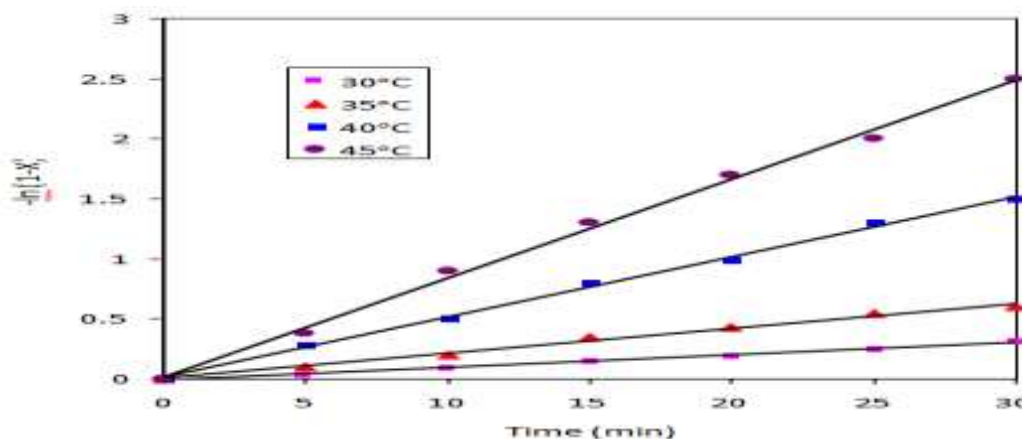


Fig: 2 Effect of the amount of MPTC on the conversion of allyl bromide: 7 g Na 2 S; 10 mL H 2 O; 10 mmol of allyl bromide; 40 mL of hexane; 0.5 g of biphenyl; 500 rpm; at 35 o C; time 30 min; Ultrasound 40 kHz (300 W).

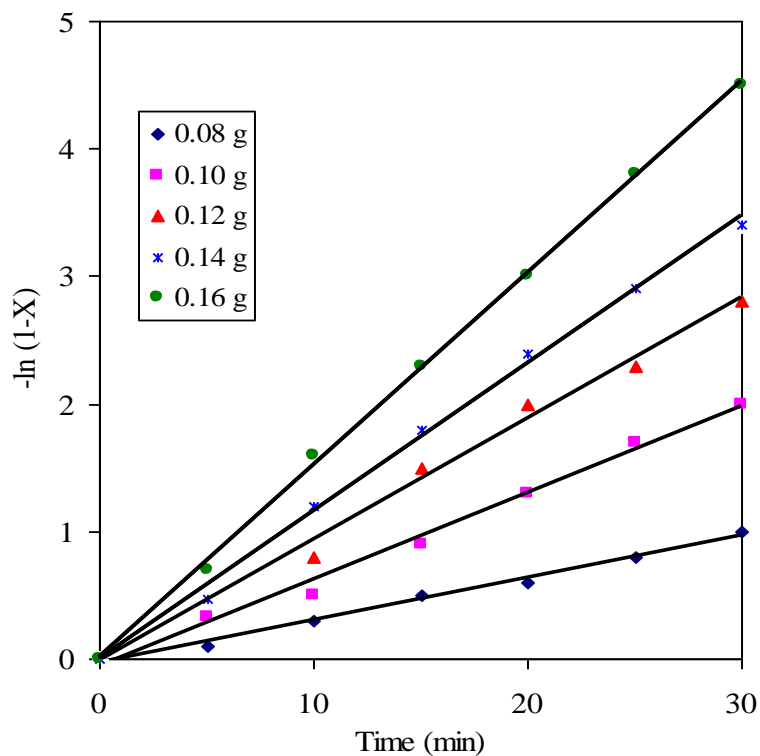


Fig: 3 Effect of the amount of sodium sulfide on k_{app} : 10 mmol of allyl bromide; 40 mL of hexane; 16 mol% of MPTC; 0.5 g of biphenyl; 500 rpm; at 35 o C; time 30 min; Ultrasound 40 kHz (300 W).

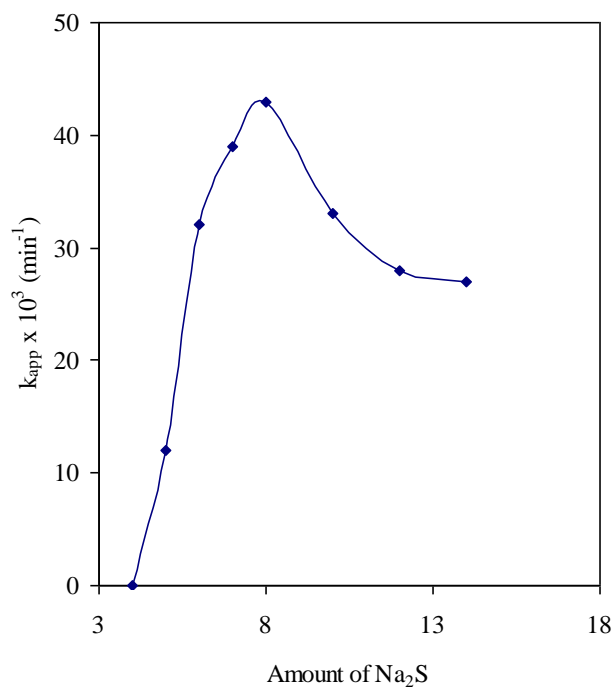


Fig: 4 Effect of sodium hydroxide amount on k_{app} : 7 g Na₂S; 10 mL H₂O; 10 mmol of allyl bromide; 40 mL of hexane; 16 mol% of MPTC; 0.5 g of biphenyl; 500 rpm; at 35 o C; time 30 min; Ultrasound 40 kHz (300 W).

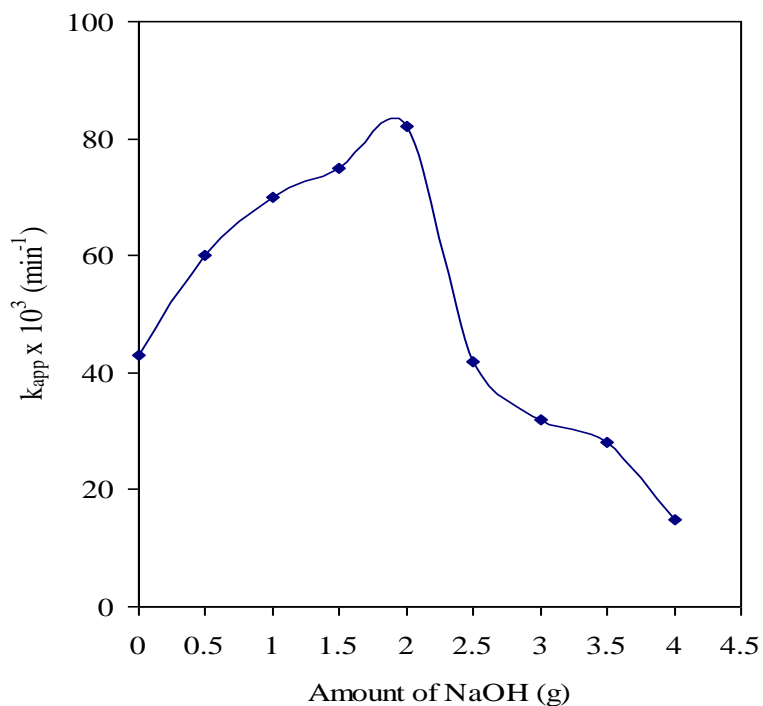
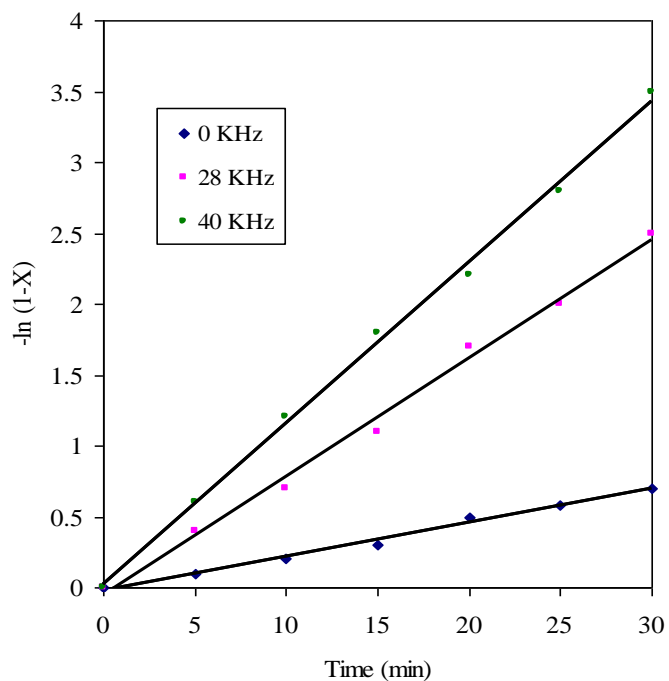
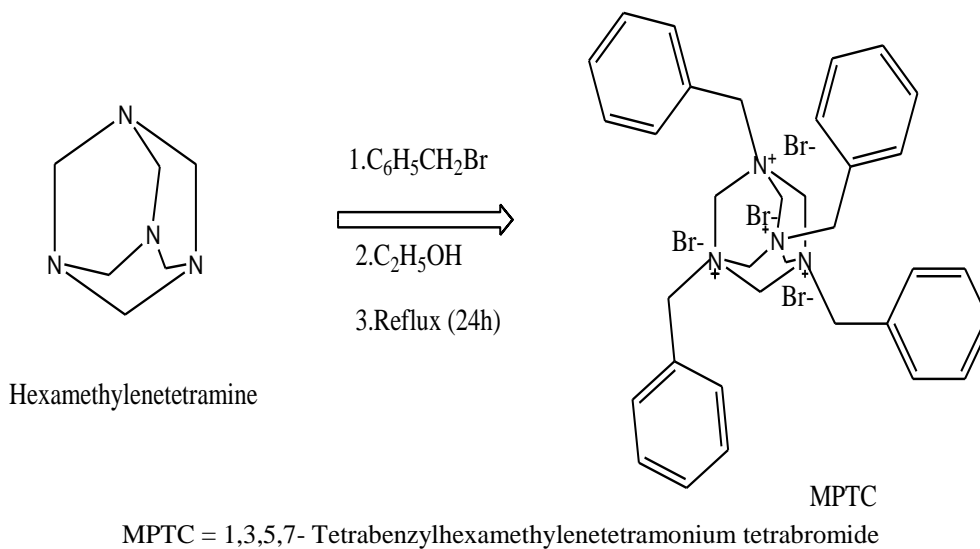


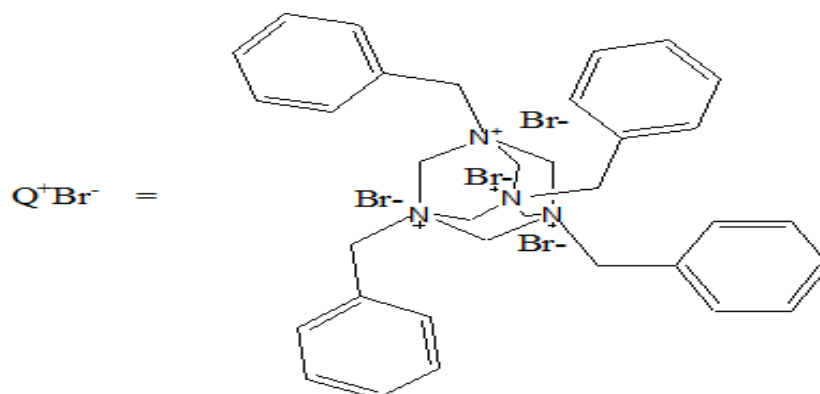
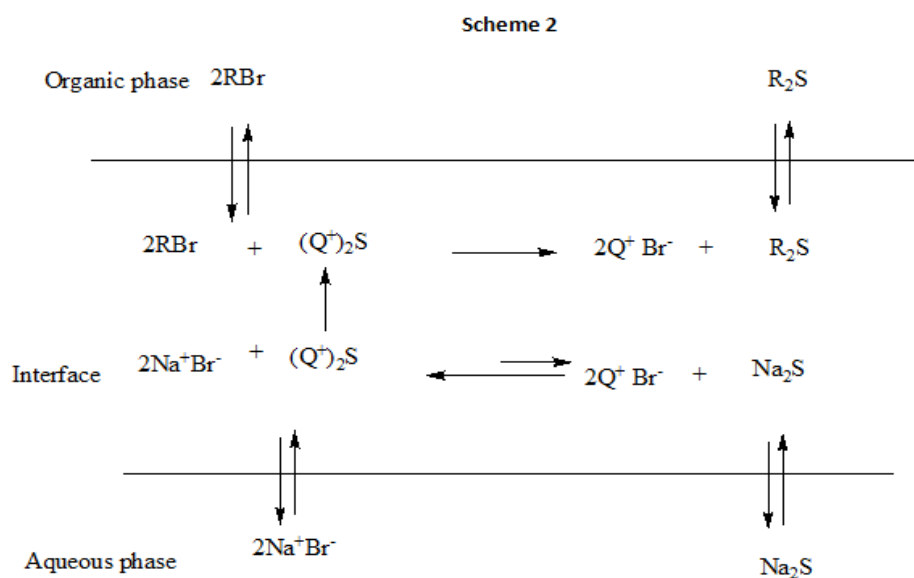
Fig: 5 Ultrasonic effect on the conversion of allyl bromide: 7 g Na₂S; 10 mL H₂O; 10 mmol of allyl bromide; 40 mL of hexane; 16 mol% of MPTC; 0.5 g of biphenyl; 500 rpm; at 35 °C; time 30 min.



Scheme - 1



Scheme 2



Tables
Table 1

| Agitation speed (rpm) | $k_{app} \times 10^3$ (min^{-1}) |
|-----------------------|---|
| 0 | 4.28 |
| 200 | 28.72 |
| 400 | 35.61 |
| 500 | 43.44 |
| 600 | 41.62 |
| 800 | 41.71 |
| 900 | 41.56 |

Effect of the stirring speed on the conversion of allyl bromide: 7 g Na_2S ; 10 mL H_2O ; 10 mmol of allyl bromide; 40 mL of hexane; 16 mol% of MPTC; 0.5 g of biphenyl; at 35°C; time 30 min; Ultrasound 40 kHz (300 W).

Table 2

| | Solvent | | | | |
|--|---------|-------------|---------|---------|---------------|
| | Hexane | Cyclohexane | Toluene | Benzene | Chlorobenzene |
| ϵ^a (Dielectric constant) | 1.89 | 2.02 | 2.5 | 2.4 | 5.60 |
| $k_{app} \times 10^3, \text{min}^{-1}$ | 3.5 | 30.2 | 43.5 | 31.4 | 28.7 |

Effect of the solvent on the conversion of allyl bromide: 7 g Na_2S ; 10 mL H_2O ; 10 mmol of allyl bromide; 16 mol% of MPTC; 0.5 g of biphenyl; 500 rpm at 35°C; time 30 min; Ultrasound 40 kHz (300 W).