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Ultrasonically promoted synthesis of N-benzylmorpholine under polymer-supported phase-transfer catalysis – a kinetic study

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Kinetics of synthesis of N-benzylmorpholine has been studied by carrying out the reaction of morpholine with benzyl bromide using aqueous potassium hydroxide and catalyzed by a newly synthesized polymer supported mono-site phase transfer catalyst viz., polymer supported N-benzyl-N-ethyl-N-isopropylpropan-2-aminium bromide (PSPTC) under ultrasonic (40 kHz, 300 W) assisted organic solvent conditions. The pseudo first-order kinetic equation has been applied to describe the overall reaction. Under ultrasonication (40 kHz, 300 W) in a batch reactor, the overall reaction rate has been observed to be greatly enhanced than that without ultrasound. The phenomenon for the dependence of the reaction rate on the amount of PSPTC and ultrasonication have been explained.

Keywords: Polymer-supported phase transfer catalysts, Ultrasonication, Morpholine, Benzyl bromide, Solid-liquid reactions, Kinetics

Phase transfer catalysis (PTC) is an effective tool for the synthesis of organic chemicals from two immiscible reactants[1]. As the chemical reactants reside in immiscible phases, phase transfer catalysts have the ability to carry one of the reactants as a highly active species for penetrating the interface, into the other phase where the reaction takes place, and to give a high conversion and selectivity for the desired product under mild reaction conditions. The first reaction scheme addressed by Starks in 1971 was for the reaction of aqueous sodium cyanide and organic 1-chlorooctane. This cyanide displacement reaction takes place rapidly by the addition of 1% tetrahexylammonium chloride to achieve near 100% of product yield in 2–3 h, which is in contrast to the result observed, i.e., that of no reaction observed after 24 h in the absence of any catalyst[2]. Phase transfer catalyst facilitates the migration of a reactant in a heterogeneous system from one phase into another phase where the reaction takes place. A phase transfer catalyst typically acts as a carrier for the anions of inorganic salts into organic solvents and also returns them into aqueous phase. Reactions usually progress under mild conditions with easy work-up procedures in the presence of PTC and hence these catalysts are commercially very important. Nowadays, synthetic methods including alkylation, oxidation, reduction, addition, hydrolysis, etherification, chiral reaction, polymerization, and biochemical reactions, are confirmed to have promising results by applying phase transfer catalysis techniques[2-11].

Currently, ingenious new analytical and process experimental techniques which are environmentally benign techniques viz., ultrasonication and microwave irradiation have become immensely popular in promoting various organic reactions[12-20]. Ultrasound has been used to accelerate the chemical reactions proceeding via the formation and adiabatic collapse of transient cavitation bubbles. The ultrasonic effect induces very high local pressure and temperatures inside the bubbles and enhances mass transfer and turbulent flow in the liquid. Ultrasound has been utilized to accelerate a number of synthetically useful reactions, especially in heterocyclic chemistry. The ultrasound approach decreases time and increases yields of products by providing the activation energy

in the form of sound energy in micro surroundings. The ultrasound approach offers several advantages such as higher yields, enhanced organic reaction rates, milder reaction conditions and waste minimization compared with traditional methods, thus saving energy and being economic. Ultrasonication is the transmission of a sound wave through a medium and is regarded as a form of energy which enhances the rate of the reaction due to mass transfer and effective mixing[18-25].

Herein, the PSPTC reactions were carried out in a solid-liquid two-phase medium. In the absence of a phase-transfer catalyst and ultrasound, less than 5% conversion was detected even after 2 h of reaction. In contrast, high yields of products were obtained in shorter reaction time using 4 mol% (based on the amount of aryl bromide) of the phase-transfer catalyst, polymer supported N-benzyl-N-ethyl-N-isopropylpropan-2-aminium bromide (PSPTC) and ultrasound 40 kHz (300 W) conditions. Kinetics of the substitution of morpholine with benzyl bromide, including the effect of amount of catalyst, agitation speed, quaternary ammonium salts, amount of potassium hydroxide, organic solvents used, temperature and ultrasound frequency on the conversion were investigated in detail.

Materials and Methods

All the reagents, including, morpholine (Merck), benzyl bromide (Merck), diisopropylethylamine (Merk), polymer-supported benzyl bromide (Aldrich), biphenyl (Aldrich), tetrabutylammonium chloride (TBAC) (CDH), tetrabutylammonium bromide (TBAB) (CDH), benzyltriethylammonium chloride (BTEAC) (CDH), tetraethylammonium chloride (TEAC) (CDH), tetraethylammonium bromide (TEAB) (CDH), potassium hydroxide (CDH), *n*-hexane (CDH), chlorobenzene (CDH), diethyl ether (CDH) and other reagents for synthesis were guaranteed grade (GR) chemicals and were used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz and 75 MHz respectivly using TMS as an internal standard. Ultrasonic water bath (40 kHz) (Equitron, Media Instrument Manufacturing Company, Chennai 600 004, India). The ultrasonic generator was a thermostatic bath (40 kHz) of electric power 300 W with 0.0126 W/mL of power density.

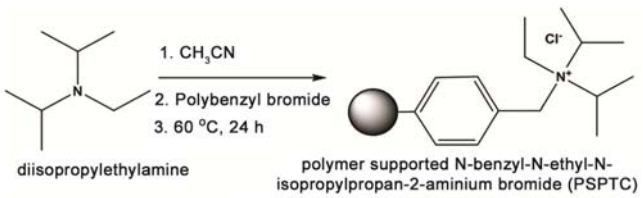
Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers of stainless steel body. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath. The internal dimension of the ultrasonic cleaner tank is 48 cm×28 cm×20 cm with liquid holding capacity of 5 L. 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 were separately produced through a flat transducer mounted at the bottom of the sonicator. A 250 mL three-necked pyrex round-bottom flask was used as the reactor. This reaction vessel was supported at the centre of the ultrasonic cleaning bath 2 cm above from the position of the transducer to get the maximum ultrasound energy. Experiments were performed at 40 kHz with output power of 300W[26-30].

Preparation of a new polymer supported N-benzyl-N-ethyl-N-isopropylpropan-2-aminium bromide (PSPTC)

The polymer-supported benzyl bromide (2 g) was soaked in acetonitrile (150 mL) for about 24 h and then transferred into a 500 mL three-necked round bottomed flask with excess diisopropylethylamine (20 mL). The reaction mixture was stirred continuously using a mechanical stirrer equipped with a poly(tetrafluoroethylene) (PTFE) half-moon blade agitating at 600 rpm under a nitrogen atmosphere. The reaction was carried out at reflux condition for 60 °C. The solvent was then completely removed under vacuo and the onium salt viz., polymer supported N-benzyl-N-ethyl-N-isopropylpropan-2-aminium bromide (PSPTC) was washed with diethyl ether, methanol and acetone (Scheme 1) and was stored in a $CaCl_2$ desiccator. The SEM image of polymer supported N-benzyl-N-ethyl-N-isopropylpropan-2-aminium bromide is shown in Fig. 1. The extent of quaternization, the amount of chloride ion present in the PSPTC was quantitatively estimated by Volhard's method and found to be 1.1 mequiv^{-1}. FT-IR (KBr), cm^{-1}: 1152 (C–N+), 1443 (C–C), 1605(aromatic C=C), 2931(alkyl stretching) (Supplementary Data, Fig. S1).

Synthesis of N-benzylmorpholine

To the well powdered KOH (30 g), 40 mL water was added under overhead stirring for few minutes.



PSPTC synthesis
Scheme 1

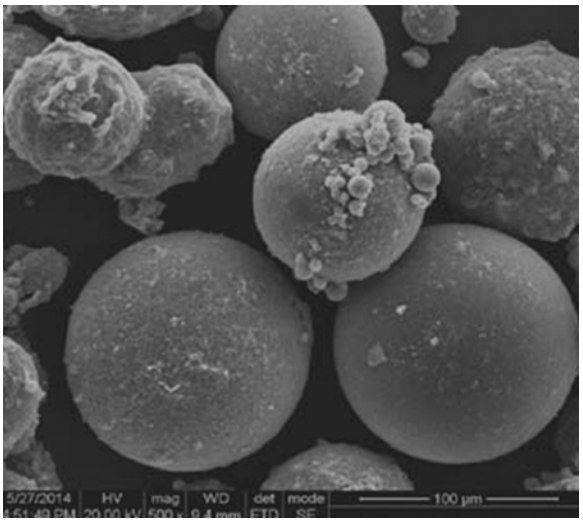


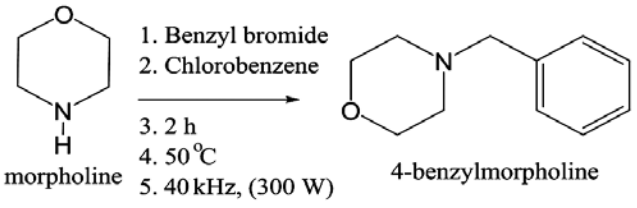
Fig. 1 — SEM image of polymer supported phase transfer catalyst.

Then morpholine (1g) and 1.0 g of the newly synthesized PSPTC was added under overhead stirring to generate the anion. Then benzyl bromide (2.22 g, 1.5 mL) in chlorobenzene (30 mL) was added slowly. The reaction mixture was heated at 50 °C for 2 h with vigorous stirring. The progress of the reaction and reaction completion were evidenced by thin layer chromatography (TLC). The crude product was isolated by simple extraction with water (3×25 mL) and ether (3×25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The product was obtained as a pure derivative (N-benzylmorpholine; Scheme 2) in the form of a yellow liquid after being subjected to column chromatography (SiO_2) employing hexane: ethyl acetate (9:2) as an eluent.

The identity of the product was confirmed by IR (cm^{-1}) 3027, 1493, 1350, 1070, 736, 693 and ^1H NMR and ^{13}C NMR spectra. ^1H NMR (300 MHz, $CDCl_3$): δ 2.3 (4H, N-CH_2), δ 3.6 (4H, O-CH_2), δ 3.4 (2H, Ar-CH_2), δ 7.14 -7.26 (5H, Ar-CH) ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.65 (N-CH_2), δ 67.01 (O-CH_2), δ 65.39 (Ar-CH_2), δ 137.76 (Ar-C), δ 129.22, 128.28, 127.61 (Ar-CH) (Supplementary Data, Figs S2-S4).

Reaction mechanism and kinetic model

The reaction was conducted in a 250 mL three-necked pyrex round-bottom flask which permits agitating the solution, inserting the water condenser to recover organic reactant and taking samples and feeding the reactants. This reaction vessel was supported at the centre of the sonicator. Known quantities of chlorobenzene (30 mL, solvent),



Synthesis of N-benzylmorpholine

Scheme 2

morpholine (1g in 40 mL water) and 0.2 g biphenyl (IS-internal standard) were introduced into the reactor. Then, benzyl bromide (2.22 g) and 1.0 g of the newly synthesized PSPTC were introduced to the reactor to start the reaction. The reaction mixture was stirred at 600 rpm. The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer of the mixture (by stopping the stirring for 20–30 each time) at regular time intervals. A pinch of anhydrous $CaCl_2$ was placed in the sample vials to absorb any moisture present in the organic layer. Each run consisted of six samples taken over the period ranging from 5 to 30 min. The kinetics was studied by estimating the amount of benzyl bromide that disappeared and was measured by gas chromatography (GC-Varian 3700 model). The GC conditions were as follows: metal column, 30 m×0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxanen); injection part temperature, 250 °C; FID detector (300 °C). Yields were determined from standard curve using biphenyl as an internal standard.

Results and Discussion

For the synthesis of N-benzylmorpholine compound, the overall reaction of morpholine and benzyl bromide (BB) was catalyzed by the newly synthesized polymer supported N-benzyl-N-ethyl-N-isopropylpropan-2-aminium bromide (PSPTC) (Q^+Br^-) in the aqueous alkaline (KOH) bi-phase medium (Scheme 1). The reaction is carried out under PSPTC assisted ultrasonic irradiation condition. In the current investigation, the kinetics was studied in the presence of an excess amount of morpholine and by fixing benzyl bromide as the limiting agent. The main reason for investigating this reaction is to study the effect of low frequency ultrasound irradiation (40 kHz, 300 W) and agitation speed (600 rpm) to find out the change in k_{app} value of this system.

The conversion (X) of benzyl bromide (BB) is defined as follows:

$$X=1-\{[\,BB]_0/[\,BB]_{0,i}\} \quad \ldots(1)$$

where $[BB]_0$ and $[BB]_{0,i}$ represent the concentration of benzyl bromide at time (t) t = 0 and t > 0, respectively.

The rate expression for this reaction may be given as;

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

where k_{app} is the apparent reaction rate constant. This reaction is carried out in a batch reactor, so the diminution rate of BB with time (t) can be expressed as:

$$-d[BB]_0 / dt = -r_{BB} = k_{app}[BB]_0 \quad \ldots (3)$$

integrating eqn (3) yields:

$$-\ln\{[BB]_0/[BB]_{0,i}\} = -\ln(1-X) = k_{app} \quad \ldots (4)$$

Using Eqn 4, we can get the k_{app} value experimentally by plotting –ln(1−X) against time, (t). This pseudo first-order equation was used to calculate the k_{app} value for the present study.

Combined effect of ultrasound and stirring on the reaction

To ascertain the influence of agitation speed on the rate of morpholine consumption, the speed of agitation was varied in the range of 100–1000 rpm along with ultrasonication (40 kHz, 300 W) using polymer supported N-benzyl-N-ethyl-N-isopropylpropan-2-aminium bromide (PSPTC) as the phase transfer catalyst. The result indicates that the rate of reaction increases linearly as the agitation speed increases from 100 to 600 rpm (Supplementary Data, Fig. S5). However, on further increasing the agitation speed from 600 to 1000 rpm, there is no significant improvement in the reaction rate constant. This is because the interfacial area per unit volume of dispersion increased linearly with increasing stirring speed till 600 rpm is reached, thereafter, there is no significant increase in the interfacial area per unit volume of dispersion with the corresponding increase in the speed. Thus, increasing the stirring speed changes the particle size of the dispersed phase. Therefore, the agitation speed was set at 600 rpm for studying the reaction phenomena from which the resistance of mass transfer stays at a constant value[28-30]. The k_{app} values are evaluated from the linear plot of –ln(1–X) versus time. The results indicate that the mechanical effects brought up by the use of ultrasounds are responsible for the enhancement of kinetics by rapid mixing, enhancement of mass transfer and so on. Further, when the same reaction was carried out in the absence of ultrasound, the observed k_{app} value ($k_{app} = 4.22\times10^3$, min^{-1}, silent condition) was found to be almost four fold lesser than that in the presence of ultrasonication ($k_{app} = 22.82\times10^3$, min^{-1}, 40 kHz, 300 W).

Effect of amount of PSPTC

Experiments were conducted by varying the amounts of the newly prepared PSPTC by keeping other experimental parameters constant. The influence of the amount of PSPTC on the N-benzyl morpholine has been studied by varying the amount of PSPTC from 0.1 g to 1 g under ultrasound irradiation (40 kHz, 300 W). Apparent rate constants were evaluated from the plot of –ln(1–X) versus time, which follows pseudo first-order kinetics. The rate of the reaction increased with increasing amount of PSPTC under ultrasonication (40 kHz, 300 W) (Supplementary Data, Fig. S6). The k_{app} values are linearly dependent on the amount of phase-transfer catalyst. The increase in the k_{app} value is attributed to the positive effect of ultrasound which might enhace the rate[31] along with stirring speed (600 rpm).

Effect of benzyl bromide concentration

To investigate the influence of benzyl bromide (BB) on the kinetics of synthesis of N-benzyl morpholine under ultrasonic irradiation condition (40 kHz, 300 W), the amount of benzyl bromide was varied from 0.5 mL to 2.5 mL. Results the presence and absence of ultrasound, are shown in Table 1. The data clearly indicates that the k_{app} value increases with increasing amount of benzyl bromide. When the benzyl bromide concentration increases, the probability of finding the substrate with active-site of the catalyst is enhanced and thereby the rate of the reaction increased[31-32]. The results also indicate an additional increase when the reaction was carried out under ultrasound condition at 40 kHz, 300 W. It may be due to the reduction in the surface area between the aqueous and organic phases, and hence more reactants

Table 1 — Effect of amount of benzyl bromide on the rate of N-benzylmorpholine synthesis

benzyl bromide (BB) (mL)	$k_{app}\times10^3$ (min^{-1}) (with ultrasound, 40 kHz, 300 W)	$k_{app}\times10^3$ (min^{-1}) (without ultrasound)
0.5	16.91	7.01
1.0	21.82	9.02
1.5	23.82	11.33
2.0	26.42	12.14
2.5	27.82	13.97

reaction condition: 30g of KOH, 40 mL of H_2O, 0.2 g of internal standard (biphenyl), 1 g of PSPTC, 30 mL of chlorobenzene, 600 rpm, 50 °C; ultrasound conditions (40 kHz, 300 W).

collide with each other simultaneously, yielding higher k_{app} values.

Effect of temperature

The effect of temperature on the reaction between morpholine and benzyl bromide was studied, keeping other conditions same. The temperature was varied from 30 to 55 °C. The kinetic profile of the reaction is obtained by plotting the pseudo first-order relation i.e., –ln(1–X) versus time. It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect[33]. The reason is that the number of reactant molecules which possess higher kinetic energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor [34]. Also, the collision of the reactants at higher temperature increased. Hence, the apparent rate constant is increased at higher temperature. Therefore, the apparent rate constants are increased with an increase in temperature under ultrasonic condition viz., 40 kHz, 300 W. Arrhenius plots of $-\ln I_{app}$ against $1/T$ were plotted to obtained an activation energy of 49.46 kJ mol^{-1} (Supplementary Data, Fig. S7).

For the dehydrobromination of (2-bromoethyl) benzene catalyzed by tetraoctylammonium bromide (TOAB), an extraction mechanism was proposed[35], in coherence with a lower E_a value (< 43 kJ mol^{-1}). In general, a higher activation energy (more than 43 kJ mol^{-1}) suggests an interfacial mechanism. The activation energy for the heterogeneous ethylation of phenylacetonitrile was reported to be 53.64 kJ mol^{-1} and based on this, an interfacial mechanism was proposed[36]. Further, in the N-alkylation of pyrrolidine-2-one, based on the E_a (51.35 kJ mol^{-1}) reported by Sasson and Bilman[37] an interfacial mechanism was proposed. They concluded that the deprotonation of the substrate takes place at the interphase and consequently the organic anion is extracted and reacts in the bulk or the organic phase. The rate determining step in the process is the anion exchange at the interphase. In our study, the observed E_a value is 48.36 kJ mol^{-1}. Hence, we proposed an interfacial mechanism for our present study[38,39].

Effect of Ultrasonic Power

Ultrasonic waves are defined as acoustic waves with frequencies in the range of 20 kHz –100 MHz. They create cavities generating locally high temperatures and pressures or strong electric fields[40-42]. Ultrasound is known to accelerate diverse types of organic reactions and it is established that many organic reactions, which are otherwise slow due to poor mass transfers, are accelerated by sonication due to cavitation[43,44]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone[45-47]. In such transfer of species across the interface and ultrasound merely facilitates this transfer, possibly by increasing the interfacial area across which this transfer occurs.

In the present study two different ultrasonic frequencies i.e., 28 kHz and 40 kHz were used for 4-benzylmorpholine with same output power of 300 W, under otherwise similar conditions using PSPTC as the catalyst. The pseudo first-order kinetic profile of the reaction is obtained by plotting –ln(1–X) against time. Under the experimental condition at 30 min, without ultrasonication (silent condition) the k_{app} values is 4.22×10^3 min^{-1} but in the presence of ultrasonic irradiation the k_{app} values are 15.85×10^3 min^{-1} and 22.82×10^3 min^{-1} for 28 kHz (300 W) and 40 kHz (300 W), respectively (Table 2). The applied ultrasonic frequency induces various degrees of 'cavity factor'. The cavity factor otherwise called cavitational effect is the propagation of ultrasound through a liquid solution in the reactor which induces both physical and chemical processes by acoustic cavitation: the formation, growth and adiabatically implosive collapse of bubbles in the liquid solution. The final collapse of the bubbles produces extremely high temperatures (> 5000 °C) and pressures (> 100 Mpa), which accelerats the reaction.

At lower frequencies (under 100 kHz) the formation of bubble has more time to grow and therefore the cavitational collapse is more violent. Consequently, studies aim at looking for mass transfer improvement generally for the lower frequency range. At higher frequencies more bubbles are produced which collapse, producing more products[28]. Mason *et al*. demonstrated the inverse dependence of mechanical and chemical effects on frequency in their treatment of polyphenylene ether[48]. Additionally, increased sonochemical activity at high frequencies was shown in a comparative study by Entezari and Kruus[49]. Hence, at higher frequencies, higher reaction rates are observed[50]. The exact maximum frequency for cavitation to occur is also dependent on the geometry, temperature, ambient pressure, viscosity and the gas composition of the reactor solution. There is general agreement for chemical processes that are

Table 2 — Effect of ultrasonic frequency on the rate of N-benzylmorpholine synthesis

Ultrasonic frequency (kHz, 300W)	0	28	40
k_{app} x 10^3 (min^{-1})	5.22	15.85	23.82

maximised at high frequencies and mechanical effects which are maximised at low frequencies[51-53]. However, the experimental conditions employed in our study indicated that the overall k_{app} increased upon increasing the ultrasonic frequency in the order: silent condition (without ultrasonication) < 28 kHz (300 W) < 40 kHz (300 W).

Effect of organic solvents

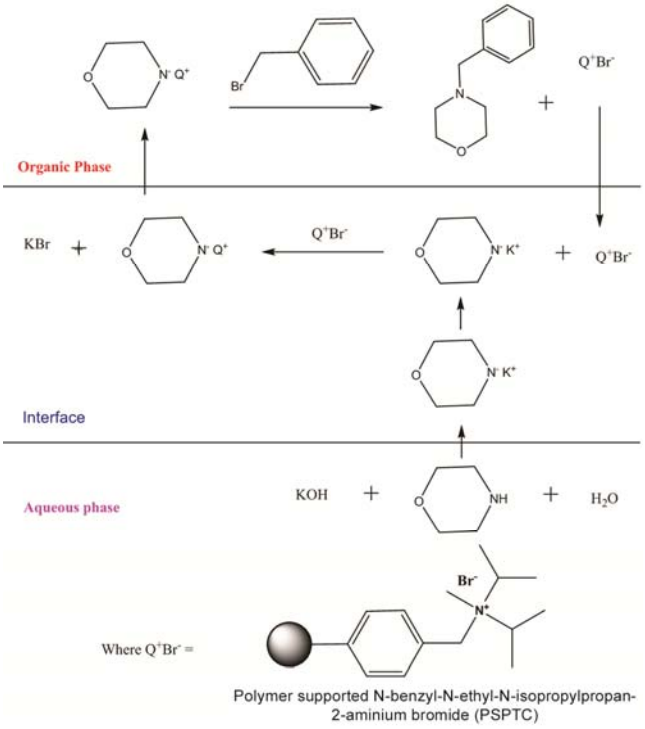
In this work, the influence of various organic solvents on the rate of N-benzyl morpholine was analysed under otherwise standard reaction conditions. Five organic solvents employed in this study are toluene, anisole, cyclohexane, chlorobenzene, and n-hexane. From the pseudo first-order plot of –ln(1–X) against time, the k_{app} values are shown in (Table 3). It is observed that chlorobenzene possesses a higher k_{app} value among the five organic solvents due to its higher dielectric constant. It may be due to the effect of ultrasonication that enhances the rate in the presence of more polar solvents due to the passing of greater number of ultrasonic waves to the reactor that causes effective collisions between the reactants, and hence we get higher k_{app} value for chlorobenzene solvent of this heterogeneous reaction[43].

Effect of potassium hydroxide concentrations

In the PSPTC/ OH^- catalyzed reaction, the reaction rate is known to be greatly affected by the concentration of the alkaline compound. The rate of N-benzylmorpholine synthesis strongly depends on the strength of potassium hydroxide. The pseudo first-order kinetic experiments were carried out, employing 20 to 40 g of KOH under similar reaction conditions. The kinetic profile of the reaction is obtained by plotting –ln(1–X) against time. The k_{app} values increase to a great extent with an increase in the basicity of hydroxide ion (Table 4). It suggests that the hydroxide ions are less solvated by water molecules at higher concentration of KOH and hence the activity of the hydroxide ion increases. In the kinetic study of C–alkylation of benzyl cyanide with *n*-bromopropane under PTC condition[33-35], the observed rate constant tremendously increased with increase in basicity of hydroxide ion. In the present case extraction of morpholine is more effective when the reaction is carried out in the presence of ultrasonicatiom at a higher concentration of potassium hydroxide.

Mechanism

The experimental results from the present kinetic study show that the dependency of the kinetic data on factors including stirring speed, concentration of the catalyst, aqueous potassium hydroxide, temperature and higher E_a value are indicative of an interfacial mechanism. Hence, we proposed an interfacial mechanism for the current study (Scheme 3). Initially,



Reaction and mechanism

Scheme 3

Table 4 — Effect of potassium hydroxide on k_{app} of N-benzylmorpholine synthesis

Amount of KOH (g)	$k_{app}\times10^3$ (min^{-1}) (with ultrasound, 40 kHz, 300 W)	$k_{app}\times10^3$ (min^{-1}) (without ultrasound)
20	14.22	7.82
25	18.93	9.91
30	23.82	11.21
35	31.84	15.34
40	40.34	19.44

Table 3 — Effect of organic solvents on the rate of N-benzylmorpholine synthesis

	Cyclohexane	n-hexane	Toluene	Toluene	Chlorobenzene
ε^a (Dielectric constant)	2.02	2.28	2.31	4.30	5.60
k_{app} x 10^3 (min^{-1}) (With ultrasound, 40 kHz, 300 W)	10.02	11.24	18.92	21.61	23.82
k_{app} x 10^3 (min^{-1}) (Without ultrasound, 40 kHz, 300 W)	4.98	5.92	7.82	10.21	11.43

the hydroxide ion deprotonates morpholine at the interface, forming an ion-pair (InN^-K^+). Upon addition of the catalyst, Q^+X^-, ion exchange takes place at the interface (InN^-Q^+) and the new formed ion pair InN^-Q^+ with more organophilicity easily migrates into the organic phase. This ion-pair reacts with the N-aryllating agent (BB) in the organic phase resulting in the formation of the required N-arylated product i.e., N-benzyl morpholine.

Conclusions

In the present study, the reaction was controlled to study the kinetic aspects of the formation of N-benzylmorpholine from morpholine and benzyl bromide under ultrasonic phase-transfer catalysis condition. The apparent reaction rates were observed to obey pseudo-first order kinetics. Performing the reaction in ultrasonic condition resulted in shorter reaction time, high selectivity, high yield, etc. The reaction mechanism and the apparent rate constants were obtained from the experimental results, the apparent rate constants are found to be directly dependent on each kinetic variable, viz., [PSPTC], [KOH], ultrasonic frequency, stirring speed, nature of organic solvent and temperature. The energy of activation was calculated from the Arrhenius plot. Based on the experimental evidence, an interfacial mechanism has been proposed. Combination of ultrasound and PSPTC resulted in better efficacy as compared to the individual operations.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http:// www.niscair.res.in/jinfo/ijca/IJCA_58A(01)45-52_SupplData.pdf.

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