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Sonocatalyzed synthesis of 2-phenylvaleronitrile under controlled reaction conditions – A kinetic study

P.A. Vivekanand, Maw-Ling Wang *

Department of Environmental Engineering, Safety and Health, Hungkuang University, Shalu, Taichung County, Taiwan 43302, Taiwan, ROC

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ABSTRACT

In the current study, kinetics of synthesis of 2-phenylvaleronitrile (PVN) was successfully carried out by selective C-alkylation of benzyl cyanide (BC) with *n*-bromopropane (BP) using aqueous KOH and catalyzed by TBAB under ultrasonic (300 W) assisted organic solvent-free conditions. Selective monoalkylation of benzyl cyanide has been achieved by controlling the reaction conditions and has been followed using gas chromatogram. The effects of various parameters such as agitation speed, catalyst concentration, KOH concentration, benzyl cyanide concentration, volume of water, ultrasonic frequency and temperature were studied systematically to understand their influence on the rate of the reaction. The experimental observations are consistent with an interfacial-type process. Further the kinetic results demonstrate clearly, that ultrasonic assisted phase-transfer catalysis significantly increased the reaction rate when compared to silent reactions.

1. Introduction

Application of traditional techniques [1] in reaction systems involving immiscible reactants (lipophilic and hydrophilic reactants), for removing the constraints of mutual insolubility of aqueous phase with organic phase, are industrially unattractive and polluting. Mutual insolubility of such reaction systems can be alleviated by an environmentally benign technique known as “phase transfer catalysis” (PTC). This technology has emerged as a broadly useful tool [2–6] in solving the heterogeneity of the reaction medium. In this key green approach [7,8], involving a substrate (in the organic layer) and an anionic reagent or a nucleophile (in the aqueous layer), reacting anions are continuously introduced into the organic phase by the phase transfer agent. Currently, PTC is an important choice in organic synthesis and is widely applied in the manufacturing processes of specialty chemicals, such as pharmaceuticals, perfumes, dyes, additives, pesticides and monomers [6]. One of the most important applications of PTC is in the alkylation of benzyl cyanaide and its derivatives, because many pharmaceuticals contain the phenylacetic framework [9–11].

We reported [1] the synthesis of *N*-butylphthalimide, from the reaction of 1-bromobutane and potassium salt of phthalimide, under solid–liquid phase-transfer catalytic condition (SL-PTC) instead of carrying out the reaction in a liquid–liquid two-phase medium i.e., the reaction was followed under non-aqueous PTC condition. The salient feature of this study is the serious hydration of potassium salt of phthalimide from the reaction of 1-bromobutane and potassium salt of phthalimide can be avoided compared to liquid–liquid two-phase system.

Currently, ingenious new analytical and process experimental techniques which are environmentally benign techniques viz., ultrasound and microwave irradiation have become immensely popular in promoting various organic reactions [12–16]. Ultrasound irradiation is a transmission of a sound wave through a medium and is regarded as a form of energy for the excitation of reactants consequently enhancing the rate of diffusion [17–19].

Richards and Loomis [20] reported, on the chemical effects of high-power ultrasound, two types of chemical reaction: (i) the acceleration of conventional reactions by ultrasound and (ii) redox processes in aqueous solutions. In a liquid medium, the effects of ultrasound are produced due to the phenomenon called cavitation. When a liquid is irradiated by ultrasound, microbubbles can appear, grow and oscillate extremely quickly and even collapse violently if the acoustic pressure is high enough. The occurrence of these collapses near a solid surface will generate microjets and shock waves [21]. Moreover, in the liquid phase surrounding the particles, high micromixing will increase the heat and mass transfer and even the diffusion of species inside the pores of the solid [22].

Application of ultrasonic waves in organic synthesis (homogeneous and heterogeneous reactions) has been boosted in recent years [23–29]. Sonification of multiphase systems accelerates the reaction by ensuring a better contact between the different phases [30,31]. Further, they also increase the reaction rate and avoid the

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* Corresponding author. Tel.: +886 426 318652; fax: +886 426 529226.
E-mail address: chmmlw@sunrise.hk.edu.tw (M.-L. Wang).

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use of high reaction temperatures [32]. These days this environmental benign technology is combined with PTC with primary objective of optimizing reaction conditions [33–35]. Palladium catalysts along with PTC proved to be excellent catalytic systems for Heck reactions involving several aryl bromides with styrene and acrylic compounds under ultrasonic conditions [36]. Yang and Peng [37] investigated the green synthesis of butyl salicylate by an efficient process of ultrasound-assisted third-liquid phase transfer catalysis in a countercurrent two-phase-flow reactor. Recently, we reported the synthesis of 1-(3-phenylpropyl)-pyrrolidine-2,5-dione, which is a biologically and industrially useful imide derivative, from the reaction of succinimide with 1-bromo-3-phenylpropane under ultrasound assisted solid-liquid phase-transfer catalytic almost water-free conditions [38].

The genesis of the current work lies in these lacunae. Our interest was centered on first time evaluating the influence of ultrasound in association with phase-transfer catalyst on the synthesis of 2-phenylvaleronitrile by monoalkylation of benzyl cyanide (BC, **1**) using *n*-bromoprpoane (BP, **2**) as an alkylating agent. One of the interesting results of the current study is that we were able to get exclusive mono-alkylated product (2-phenylpentanenitrile, **3**) when we utilize BP as a limiting agent (Scheme 1). However, when benzyl cyanide was employed as a limiting agent, both *mono* as well as *bis*-alkylated products (2-phenyl-2-propylpentanenitrile) were observed. Since, the kinetic study of mono-alkylation of BC using 1-bromopropane under controlled PTC reaction conditions will be interesting and challenging, we followed the kinetic study of monoalkyaltion using tetrbutylammonium bromide (TBAB) as a catalyst under ultrasonic condition (50 kHz; 300 W). Further, to best of our knowledge, there are no literature reports regarding monoalkylation of BC with BP under PTC-ultrasonic condition.

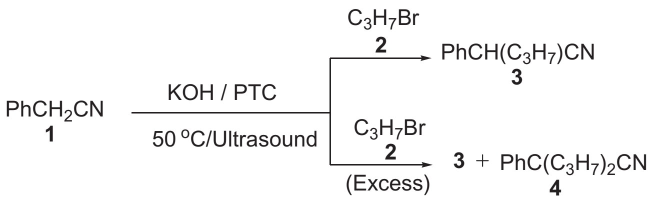
2. Experimental

2.1. Materials

All reagents, including benzyl cyanide (Fluka), 1-bromopropane (Acros), tetrabutylammonium bromide (TBAB, Acros), tetraethylammonium chloride (TEAC, Acros), tetraethylammonium bromide (TEAB, Acros), benzyltriethylammonium bromide (BTEAB, Acros), benzyltriethylammonium chloride (BTEAC, Acros), potassium hydroxide (Acros), toluene (TEDIA), chlorobenzene (TEDIA) and other reagents for synthesis were guaranteed grade (GR) chemicals and were used as received without further purification.

2.2. General

FTIR spectra were recorded on a Perkin–Elmer Spectrum 1000 on KBr pellets. ^{1}H NMR and ^{13}C spectra were recorded on a Bruker DRX 400 spectrometer. Chemical shifts (δ) are given in ppm and coupling constants (J) in hertz (Hz). Multiplicities of NMR signals are designed as *t* (triplet) and *m* (multiplet). Attribution of ^{13}C signals are based on the J-modulated spin-echo sequence and/or heteronuclear two-dimensional techniques. ^{13}C NMR spectra were recorded with complete proton decoupling. Gas chromatography was carried out using a GC–Shimadzu 17 A model.



Scheme 1. C-alkylation of benzyl cyanide under controlled PTC assisted ultrasonic condition.

3. Ultrasonic process equipment

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 bath (model L-600) equipped with flat transducer, procured from Ko Hsieh Instruments Co. Ltd., Taipei, Taiwan (http://www.kohsieh.com.tw/). The internal dimension of the ultrasonic cleaner tank is 250 mm × 250 mm × 380 mm with liquid holding capacity of 23 liters. The external tank size is 420 mm × 520 mm × 600 mm. The reactor has an operating frequency of 25 kHz and 50 kHz with a output of 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. Further, in order to carry out high and low temperature reactions, an additional heater (Thermo Haake) with facility of temperature controller has been provided. The process vessel is immersed in the water present in the tank.

4. General procedure for the synthesis of 2-phenylvaleronitrile under sonocatalyzed condition

To the mixture of KOH (6 g, 0.10 mol) in water (10 mL) and TBAB (0.17 g, 5.27×10^{-4} mol), benzyl cyanide (12.86 g, 0.10 mmol) was added under overhead stirring to generate the carbanion. Then *n*-bromoprpoane (1.35 g, 0.010 mol) was added slowly. The reaction mixture was heated at 50 ^{0}C for 2 hours with vigorous stirring. The monoalkylation was followed by GC monitoring. The crude product was isolated by simple extraction with diethyl ether (2 × 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was chromotographed (SiO_2) employing hexane: ethylacetate (10:1) as eluent to obtain pure monoderivative. The identity of the product was confirmed by IR, ^{1}H NMR and ^{13}C NMR spectra of the product. IR (KBr, cm^{-1}): 655, 798, 1455, 1581, 2238, 2935; ^{1}H NMR ($CDCl_3$): δ 0.92 (*t*, *J* = 7.6 Hz, 3H), 1.44–1.56 (*m*, 2H), 1.78–1.94 (m, 2H,-CH_2), 3.76 (*t*, *J* = 8.0 Hz, 1H), 7.73–7.80 (*m*, 5H, –C_6H_5).^{13}C NMR ($CDCl_3$): δ 13.25, 20.14, 36.97, 37.71, 120.77,127.089,127.81,128.87 and 135.92.

5. Sonicated kinetics of the bi-phase reaction system

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 KOH (10 g, 0.17 mol) was dissolved in deionized water (20 ml) to prepare a aqueous alkaline solution. Known quantities of TBAB (0.30 g, 9.3×10^{-4} mol), benzyl cyanide (25.73 g, 0.21 moles) and toluene (internal standard, 0.1 g) were added to reaction vessel, which was suspended in the middle of ultrasonic bath to get the maximum ultrasound energy, to form the organic solution. After stirring at 600 rpm for ten minutes at 50 °C, *n*-bromopropane (2.7 g, 0.021) was added. To start the reaction, the aqueous and organic solutions were mixed in the flask. The organic-phase sample (0.05 ml) was withdrawn from the reactor at each time interval and was put into the glass vials containing 2 mL of chlorobenzene. The contents of the reaction sample (2-phenylvaleronitrile, *n*-bromopropane and benzyl cyanide) were measured by GC. The analyzing conditions are as follows: Shimadzu GC 17A, J&W Scientific Inc., capillary column (db-1 column); 100% poly(dimethylsiloxane) stationary phase; 15 m × 0.525 m column dimension; carrier gas, nitrogen (60 ml/min); flame ionization detector; injection temperature, 250 °C. The product formed was analyzed by comparison of their retention times with authentic samples. Yields were determined from standard curve and using toluene as internal standard. Ultrasonic frequency and power employed in the current study is 50 kHz and 300 W respectively.

6. Reaction mechanism and kinetic model

For synthesizing 2-phenylvaleronitrile compound, the overall reaction of benzyl cyanide (BC) and *n*-bromopropane (RBr) was catalyzed by TBAB (QBr) in the aqueous alkaline (KOH) bi-phase medium and is represented in Scheme 1. The reaction is carried out under PTC assisted ultrasonic condition. Main reason for investigating the reaction in presence of ultrasonic irradiation is to enhance rate of the reaction. In the current investigation the kinetics was followed in presence of excess benzyl cyanide by fixing the *n*-bromopropane as limiting agent.

6.1. Definition

The conversion (*X*) of *n*-bromopropane, (BP) is defined as follows:

$$X = 1 - \frac{[\mathrm{BP}]_0}{[\mathrm{BP}]_{0,i}} \qquad (1)$$

where $[\mathrm{BP}]_{0,\mathrm{i}}$ and $[\mathrm{BP}]_0$ represent the concentration of *n*-bromopropane at time (*t*) *t* = 0 and *t* > 0, respectively.

6.2. Rate expression

The rate expression for this reaction may be expressed as

$$-r_{BP} = k_{app}[BP]_0 \qquad (2)$$

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

$$-\frac{d[\mathrm{BP}]_0}{dt} = -r_{ArCl} = k_{app}[\mathrm{BP}]_0 \qquad (3)$$

on integrating the Eq. (3) yields:

$$-\ln\frac{[\mathrm{BP}]_0}{[\mathrm{BP}]_{0,i}} = -\ln(1-X) = k_{app} \qquad (4)$$

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

7. Results and discussion

The monoalkylation of benzyl cyanide with *n*-bromopropane was performed using potassium hydroxide as a base and tetrabutylammonium bromide as a phase transfer catalyst at 50 °C under ultrasonic condition (Scheme 1). The kinetic results show a material balance between reactant and products, i.e., the consumption of the amount of reactant (*n*-bromopropane, BP) equals to the sum of the generation of the amount of the product (2-phenylvaleronitrile) from the reactant *n*-bromopropane (**2**) under ultrasonic conditions, as shown in Fig. 1. Further, no byproducts were observed during or after reaction. Thus, rate of the decrease of *n*-bromopropane is consistent with the rate of production of 2-phenylvaleronitrile. Pseudo-first order kinetics was indicated by the linearity of the plot of $-\ln(1-\mathrm{X})$ versus time. The reaction mixture was analyzed by GC. The effects of the reaction conditions on the conversion (*X*) of the limited reactant RBr and the apparent rate constant (k_{app}) are discussed below.

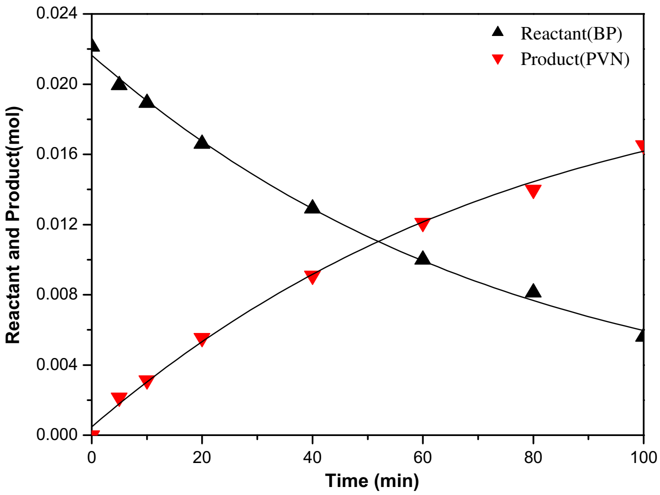


Fig. 1. Distribution of reactant and product during the reaction period (mass balance plot); 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 50 °C, 600 rpm; under ultrasound conditions (50 kHz, 300 W).

7.1. Effect of Stirring Speed

To ascertain the influence of agitation speed on the rate of monoalkyation of benzyl cyanide, the speed of agitation was varied in the range of 100-1000 rpm under otherwise similar conditions using TBAB as the catalyst. Apparent rate constants are evaluated from the linear plot of $-\ln(1-\mathrm{X})$ versus time. The results indicate that the rate of the reaction increases linearly as the agitation speed increases from 100 to 600 rpm (Fig. 2). 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 the stirring speed till 600 rpm is reached, where 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

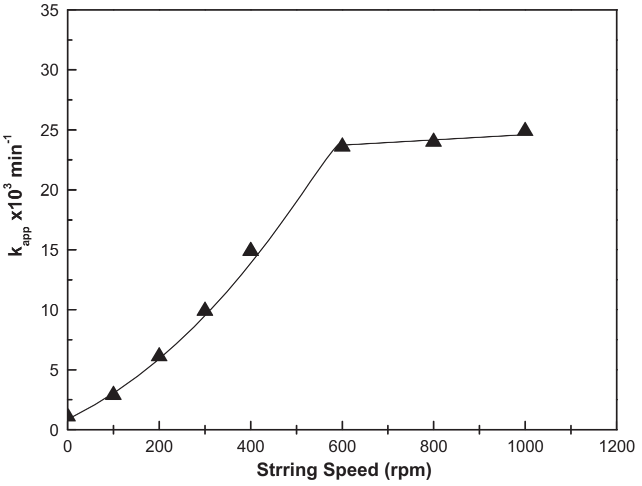


Fig. 2. Plot of the apparent rate constants versus various agitation speeds; 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 50 °C; under ultrasound conditions (50 kHz, 300 W).

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. Generally in the two-phase reaction system, the effect of stirring speed on the rate of the reaction can be explained by (i) Starks' extraction mechanism and (ii) Makosza's interfacial reaction mechanism. Kinetic studies into effects of variation in stirring speed reveal that the interfacial mechanisms [3,5,39–42] are transfer rate-limited below a given stirring speed (600–800 rpm) and are intrinsic reaction rate-limited above this stirring speed. Our lab reported [43] an interfacial mechanism in the synthesis of dichlorocyclopropane catalyzed by quaternary ammonium salt from the reaction of 1,7-octadiene and chloroform in an alkaline solution of a NaOH/organic solvent two-phase medium. Vivekanand and Balakrishnan [44] observed a linear dependence of rate constant on stirring speed up to 500 rpm for C-alkylation of indene using the new onium salt for which an interfacial mechanism was proposed. Reactions involving extraction mechanism, proposed by Starks and Owens [45], display analogous performance but with a smaller limit of agitation speed between physical and chemical control (100–300 rpm).

7.2. Effect of the amount of TBAB

Experiments were conducted by varying the amount of catalyst quantity but keeping other experimental parameters constant under pseudo-first order condition. Influence of amount of TBAB on the monoalkyaltion of benzyl cyanide has been studied by varying amount of catalyst from 0.1 g to 0.5 g under ultrasound activation. Apparent rate constants were evaluated from the plot of $-\ln(1-X)$ versus Time (Fig. 3). In general, the reactivity is increased with an increase in the amount of quaternary ammonium salt. As shown in Fig. 4, the rate of the reaction increased with the increase in the amount of tetrabutylammonium bromide. The rate constants are linearly dependent on the amount of catalyst used (Table 1). The increase in the k_{app} value is attributed to the change in the size, surface area and morphology of phase-transfer catalyst [46]. Further, the opportunity of collision between intermediates is increased by increasing catalyst concentration. Therefore, the opportunity of forming a complex between them is largely increased. Hence, the apparent rate constant values increased with the increase in the amount of catalyst.

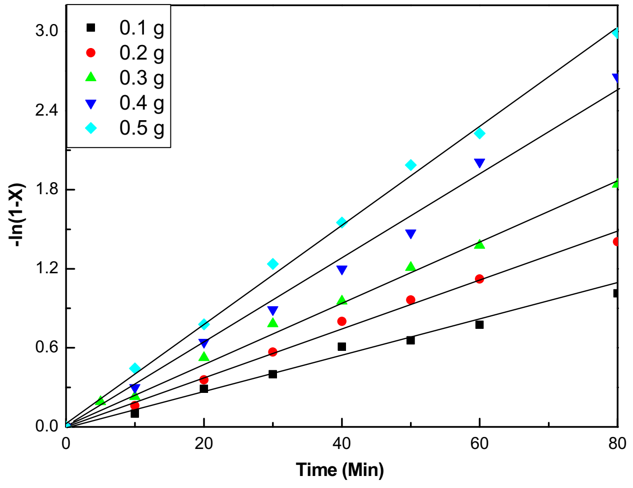


Fig. 3. Plot of $-\ln(1-X)$ versus time with various amounts of phase-transfer catalysts; 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 600 rpm, 50 °C; under ultrasound conditions (50 kHz, 300 W).

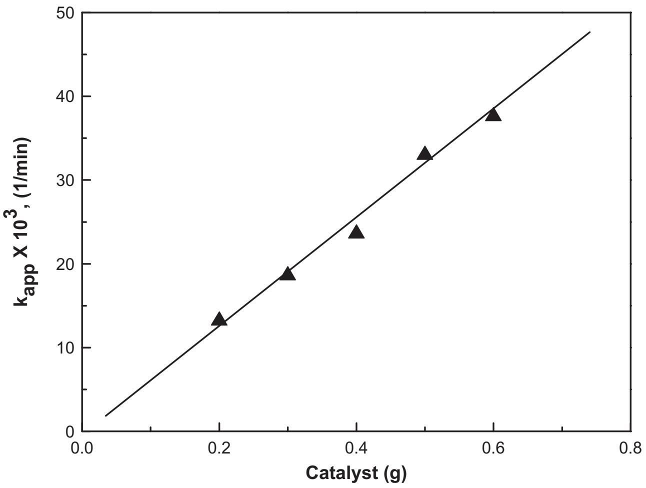


Fig. 4. Effect of the amount of catalyst on the apparent rate constant: 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 600 rpm,50 °C; under ultrasound conditions (50 kHz, 300 W).

Table 1
Effect of amount of BC on the rate of C-alkylation under ultrasonic condition: 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 600 rpm, 50 °C; under ultrasound conditions (50 kHz, 300 W).

Entry. no.	Amount of BC (g)	k_{app} ($\times 10^{-3}$, min^{-1})
1	12.8	28.8
2	19.3	25.4
3	25.7	23.6
4	32.1	18.5
5	38.5	12.9

7.3. Effect of volume of BC

To investigate the influence of benzyl cyanide (BC) on the kinetics of synthesis of 2-phenylvaleronitrile under sonocatalyzed reaction condition, the amount of BC was varied from 0.109 mol to 0.328 mol. Apparent rate constants are calculated from the plot $-\ln(1-X)$ versus time. The results are shown in Fig. 4. The reaction rate is decreased with an increase in the amount of BC. The reason is that the concentration of the reactants is diluted using a larger volume of BC. Hence, the k_{app} value decreases with increasing the amount of BC. Similar decrease in the rate of the reaction is reported [46] on increasing the amount of ethanol in the ethoxylation of *p*-chloronitrobenzene using benzyltriethylammonium chloride as a phase-transfer catalyst under ultrasound irradiation conditions. In the dicholorcarbene addition to styrene under PTC condition [47], the rate was found decrease with increase in concentrateion of styrene.

7.4. Effect of variation of temperature

The effect of temperature on the reaction between BC and *n*-bromopropane was studied under otherwise similar conditions. The temperature was varied from 40 to 60 °C. The kinetic profile of the reaction is obtained by plotting $-\ln(1-X)$ versus time. The rate constant increased with the increase in temperature. The energy of activation was also calculated from the Arrhenius plot; $E_a = 16.20$ (Fig. 5). The result is consistent with results obtained previously in studies of different reaction systems [48,49]. It is evident that the rate of C-alkylation increases with an increase in the temperature along with ultrasonic effect [46]. We attribute this

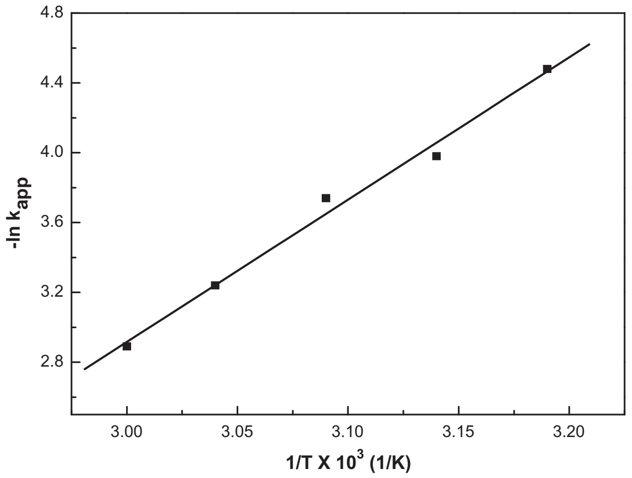


Fig. 5. Arrhenius plot for $-\ln(k_{app})$ versus $1/T$; 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 600 rpm; under ultrasound conditions (50 kHz, 300 W).

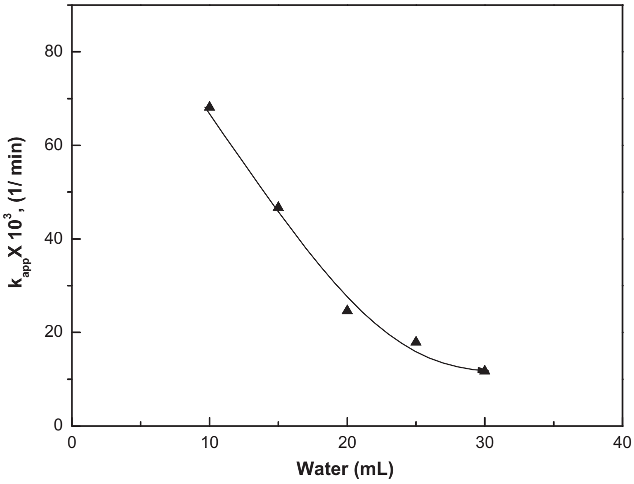


Fig. 6. Plot of the apparent rate constants versus various different volumes of water; 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 600 rpm, 50 °C; under ultrasound conditions (50 kHz, 300 W).

phenomenon to the increase in collision of the reactants molecules at higher temperature. Hence, the reaction rate is increased at higher temperature. The activation energy of intraparticle diffusion of anion exchange resins in aqueous solutions is of the order of 5-10 kcal mol^{-1} [50]. The energy of activation was reported to be 8 kcal mol^{-1} in the dehydrobromination of (2-bromoethyl)benzene catalyzed by tetraoctylammonium bromide. For this process, an extraction mechanism was proposed [51]. In general, a higher activation energy suggest that a contribution of intrinsic reactivity limitations is more than that of intraparticle diffusion limitations [47,52]. The activation energy for the heterogeneous ethylation of phenylacetonitrile was reported to be 20 kcal mol^{-1} and for this an interfacial mechanism was proposed [53]. In the alkylation of pyrrolidine-2-one under solid/liquid PTC in presence of potassium carbonate, Sasson and Bilman reported [54] a higher E_a value (12.4 kcal mol^{-1}) and for this reaction they proposed 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 of the organic phase. The rate-determining step in the process is the anion exchange at the interphase. In our study, the observed higher E_a value, i.e. 16.20 kcal mol^{-1}, indicates that the contribution of intrinsic reactivity limitations is more than that of intraparticle diffusion limitations and hence we propose an interfacial mechanism [6,44,47,55,56].

7.5. Influence of amount of water

C-alkylation of benzyl cyanide with *n*-bromopropane as a limiting agent under sonocatalysis conditions was examined by varying the amount of water from 10 to 30 mL under standard reaction conditions. Apparent rate constants were obtained from the plot of $-\ln(1 - X)$ versus time. Generally, the volume of water directly affects both the concentration of KOH in the aqueous phase and also generation of anions. Therefore, the conversion (or the reaction rate) will be affected by the volume of water. Fig. 6 shows the effect of the amount of water on the rate of the reaction. In principle, the conversion of RBr (*n*-bromopropane) is decreased with greater volume of water. The decreased rate constant is attributed to the decrease in the active catalyst, Ph $[CH^{-}Q^{+}]$ CN, at higher volume of water. Further on increasing the volume of water, the concentration of alkali compound in aqueous solution is decreases. This situation would dramatically reveal the hydration effect of the active catalyst as the volume of water changed from 15 to 30 mL. Thus, concentration of the alkali compound in aqueous solution would also affect the distribution of the active catalysts between two phases. Thus, less active catalyst exists in the organic phase. In the kinetic study [57] of the phase-transfer catalyzed etherification of 4,4-*bis*(chloromethyl)-1,1-biphenyl with phenol in an alkaline solution of KOH/organic solvent two-phase medium, similar decrease in rate of the reaction on corresponding increase in volume of water was reported.

7.6. Effect of Ultrasonic Power

Ultrasonic irradiation is defined as acoustic waves with frequencies in the 20 kHz -100 MHz range [26,58]. Their energy create cavities generating locally high temperatures and pressures [59–62] or strong electric fields [60,62–64]. Ultrasound is known to accelerate diverse types of organic reactions and it is established as an important technique in organic synthesis [58,60,62]. Heterogeneous reactions, which are otherwise slow due to poor mass transfer are accelerated by sonication due to cavitation [61]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [62]. 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.

To ascertain the influence of various ultrasonic frequencies on the rate of monoalkyaltion of benzyl cyanide with same output power of 300 W, the ultrasonic frequency was varied in the range of 40-120 kHz under otherwise similar conditions using TBAB as the catalyst. Also we followed the reaction under silent condition. The kinetic profile of the reaction is obtained by plotting $-\ln(1 - X)$ versus time. 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 are 250 mm × 250 mm × 380 mm with liquid holding capacity of 23 l. The external tank size is 420 mm × 520 mm × 600 mm. We used water as a liquid in the ultrasonic cleaner. Further details are presented in experimental section. At 80 minutes, without ultrasonic irradiation the rate constant is only 8.5×10^{-3} min^{-1}, but in the presence of ultrasonic the rate constants are

Table 2
Influence of ultrasonic frequencies on the on the rate of C-alkylation of benzyl cyanide: 21.93×10^{-2} mol of benzyl cyanide,10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane,0.3 g of TBAB, 600 rpm, 50 °C; under ultrasound conditions (300 W).

Ultrasonic frequency (kHz)	0	28	40	50	120
k_{app} ($\times 10^3$, min^{-1})	8.5	17.7	20.8	23.6	33.4

17.7×10^{-3} min^{-1}, 20.8×10^{-3} min^{-1}, 23.6×10^{-3} min^{-1} and 33.4×10^{-3} min^{-1} for 28 kHz, 40 kHz, 50 kHz, and 120 kHz, respectively (Table 2). From these observed results, it can be inferred that ultrasonic assisted phase-transfer catalysis significantly increased the rate of the reaction. Similar trend was observed by Entezari and coworkers [65,66]. Hence, the application of ultrasounds in organic synthesis is one of the popular areas in sonochemistry.

7.7. Effect of organic solvents

In this work, the influence of various organic solvents on the rate of monoalkylation of BC was followed under otherwise standard reaction conditions. Five organic solvents employed in this study are cyclohexanone, anisole, cyclohexene, chlorobenzene, and benzene. From the plot of $-\ln(1-X)$ versus time, the rate constants are obtained. The order of the reactivity for these five organic solvents is: cyclohexanone($C_6H_{12}O_1$) > chlorobenzene(C_6H_5Cl) > anisole($C_7H_{16}O_1$) > benzene (C_6H_6) > cyclohexene (C_6H_{10}). The effect of the organic solvents on the apparent rate constant (k_{app}) is shown in Table 3. The increased rate constant is attributed to the increase in the dielectric constant of the organic solvent. As the dielectric constant values of solvents increases, the activity of the nucleophilic reagent and also the distance between the bromide atom and the propyl group is increased. Hence the rate of the reaction increases [67].

7.8. Effect of different catalysts

Comprehensive comparative kinetic studies for the propanation of benzyl cyanide by *n*-bromopropane (alkylating agent) were carried out using various onium salts viz., benzyltriethylammounium chloride (BTEAC), benzyltriethylammounium bromide (BTEAB), tetrabutylammounium bromide (TBAB), tetraethylammonium bromide(TEAB) and tetraethylammonium chloride(TEAC).The reaction was carried out under ultrasonic condition at standard reaction conditions. The pseudo-first order rate constants were evaluated for all the catalysts from the plot of the plot of $-\ln(1-X)$ versus time and are presented in Table 4 (entries 1–5). According to Stark's extraction mechanism, the order of the distribution of halide ions in the organic phase is $I^- > Br^- > Cl^-$. Conversely, in the current study, the order of the reactivities in choosing the TEA cation group in this work is TEAC > TEAB. Thus, highier reaction rate is obtained by choosing a small size of the anionic ion in the halide groups of PTC's. Hence, this phenomenon is more consistent with the interfacial reaction mechanism rather than the extraction reaction mechanism. For an interfacial reaction mechanism, the reaction rate is highly dependent on the concentration of the catalyst at the interface. By comparing the catalytic activity of the quaternary ammonium cations with that of the same halide ion, the order of the reactivities of these PTCs is TEA cation > BTEA cation > TBA cation. We attribute the higher reactivity obtained for TEA cation to lower total carbon number. In general, the activity of the catalyst is dependent on the structural characteristics of a quaternary ammonium cation [5]. For this, the yield of the product is correlated with the accessibility of the quaternary ammonium salt, *q*, which is a function of carbon in each chain. It is thus concluded that the order of the reactivity is TEA cation > BTEA cation > TBA cation, which is consistent with the results indicated by Starks et al. In an interfacial mechanicsm driven dichlorocarbene addition to 1,7-octadiene under PTC conditions a similar trend was observed [43].

Table 4
Effect of various PTC's on the rate of C-alkylation of benzyl cyanide under ultrasonic condition: 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 9.30×10^{-4} mol of PTC, 600 rpm, 50 °C; under ultrasound conditions (50 kHz, 300 W).

Entry. no.	PTC	k_{app} ($\times 10^{-3}$, min^{-1})
1	TEAC	36.1
2	TEAB	33.5
3	BTEAC	30.4
4	BTEAB	28.2
5	TBAB	23.6

Table 5
Influence of alkalinity on k_{app} in the C-alkylation of benzyl cyanide with *n*-bromopropane catalyzed by TBAB under ultrasonic condition; 21.93×10^{-2} mol of benzyl cyanide, 20 mL of H_2O, 0.1 g of internal standard (toluene), 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 600 rpm, 50 °C; under ultrasound conditions (50 kHz, 300 W).

Entry. no.	Amount of KOH (g)	k_{app} ($\times 10^{-3}$, min^{-1})
1	5.0	10.30
2	7.5	15.30
3	10	23.60
4	15	32.10
5	20	41.20

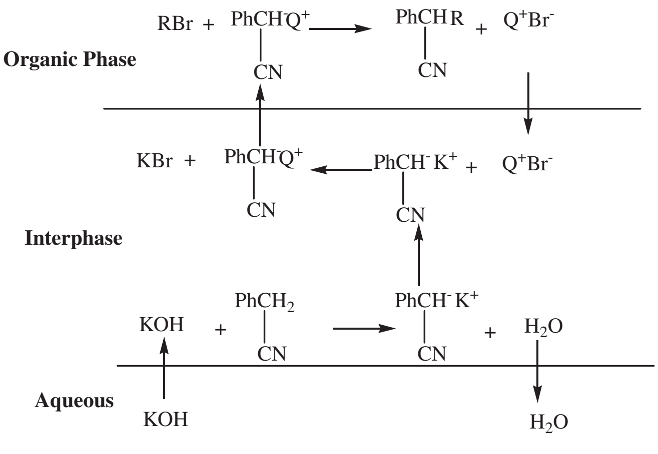
7.9. Effect of varying potassium hydroxide concentrations

In the PTC/OH catalyzed reaction, the reaction rate is known to be greatly affected by the concentration of the alkaline compound. The rate of monoalkylation of benzyl cyanide strongly depends on the strength of the potassium hydroxide. Kinetic experiments were carried out, employing 5-20 g under similar reaction conditions. The kinetic profile of the reaction is obtained by plotting $-\ln(1-X)$ versus time. The rate constants tremendously increased with increase in basicity of hydroxide ion i.e., the rate constants were found to increase with an increase in potassium hydroxide concentration (Table 5). This suggests that the hydroxide ions are less solvated by water molecules and thereby the activity of the hydroxide

Table 3
Influence of organic solvents on the rate of C-alkylation of benzyl cyanide under ultrasonic condition: 21.93×10^{-2} mol of benzyl cyanide, 10 g of KOH, 20 mL of H_2O, 0.1 g of internal standard (toluene), 20 mL of solvent, 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 600 rpm, 50 °C; under ultrasound conditions (50 kHz, 300 W).

	Solvents				
	Cyclohexane	Benzene	Anisole	Chlorobenzene	Cyclohexanone
ε^a	2.02	2.28	4.3	5.6	8.2
k_{app} ($\times 10^{-3}$, min^{-1})	2.2	2.9	5.7	7.0	9.8

[a] Dielectric constant.



Where, RBr = C_3H_7Br ; Q^+Br^- = PTC

Scheme 2. Interfacial mechanism of monoalkylation of benzyl cyanide under PTC condition.

ion increases. Landini et al. [68] observed that, on increasing the alkalinity concentration of, the quantity of hydroxide extracted decreases. The overall activity of the hydroxide actually increases due to the dependence of hydroxide basicity on hydration. In the kinetic study [44] of C-alkylation of indene with 1,4-dibromobutane under PTC condition, the observed rate constants tremendously increased with increase in basicity of hydroxide ion. In the case of phenoxide allylation [49], the extraction of phenol using is more effective if the base concentration is higher.

8. Mechanism

Generally, mechanism [3,5,44,43,69] for hydroxide ion initiated PTC reactions are classified into two types viz, (i) Starks extraction mechanism and (ii) Maksosza Interfacial mechanism. The extraction-like mechanism is more likely to be part of reactions when they depend agitation speed only upto certain level (300 rpm) and there after the rate will be constant factor. Also the energy of activation calculated from the Arrhenius plot will be below 10 kcal mol^{-1}. On the other hand, if the reaction is interfacial driven reaction the rate of the reaction keep on increasing even after 300 rpm and energy of activation will be above 10 kcal mol^{-1}.

The experimental results from the present kinetic studies indicate the dependencies of the kinetic data on the entire stirring speed, concentration of the catalyst, aqueous potassium hydroxide, temperature and higher E_a value are indicative of an interfacial mechanism. Hence we propose interfacial mechanism for the current study (Scheme 2). Initially, the hydroxide ion deprotonates the organic substrate R–H at the interface, forming an ion pair $[K^+R^-]$. This ion pair at the phase boundary cannot migrate into either phase (aqueous or organic) because it is insoluble in both phases. Upon addition of the catalyst, Q^+X^-, ion exchange takes place at the interface and the newly formed ion pair Q^+R^- easily migrates into the organic phase. This ion pair reacts with the alkylating agent in the organic phase resulting in the formation of the required mono-alkylated product (2-phenylvaleronitrile). The function of onium salt in this reaction is to enhance the carbanion formation at the interface and transfer it to organic phase.

9. Conclusions

In the present study, the reaction was controlled to study the kinetic aspects of the formation of the 2-phenylvaleronitrile (mono-product) from benzyl cyanide and *n*-bromopropane under ultrasonic-PTC controlled condition. The apparent reaction rates were observed to obey the pseudo-first order kinetics. Performing the reaction in sonicatalysis condition resulted in shorter reaction time, 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., [catalyst], [KOH], ultrasonic frequency, stirring speed and temperature. However it decreases with increase in volume of water and benzyl cyanide. Five different ammonium salts were compared under ultrasonic conditions and TEAC was found to be more efficient under given experimental conditions. Energy of activation was calculated from the Arrhenius plot. Based on the experimental evidence, an interfacial mechanism has been proposed. Combination of ultrasound and PTC resulted in better efficacy as compared to the individual operations.

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