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Propargylation of indole under a new dual-site phase-transfer catalyst: A kinetic study

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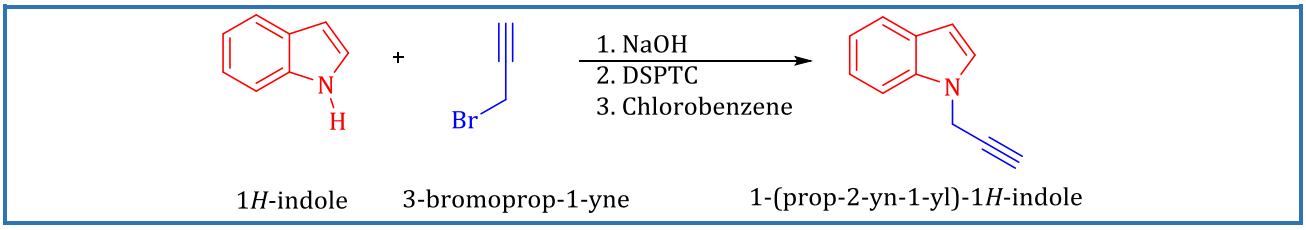
ABSTRACT

A new multi-site phase-transfer catalyst viz., *N,N'*-dihexyl-4,4'-bipyridinium dibromide (DSPTC) was synthesized from the low cost starting materials. The structures of the synthesized DSPTC and 1-(prop-2-ynyl)-1*H*-indole were evidenced by ^{1}H NMR and ^{13}C NMR. The potentiality of the new multi-site phase transfer catalyst was demonstrated by following the kinetics propargylation of the indole under pseudo-first order conditions by using the aqueous sodium hydroxide and indole in excess, and the reaction was monitored by gas chromatography. Moreover, the catalytic efficiency of the DSPTC was compared with the single-site phase-transfers catalysts.

Graphical Abstract



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Introduction

As the environmental and economic concerns have intensified over the last few years, it would be essential for the chemists to find out as many environmentally benign catalytic reactions as possible. For a successful completion of a reaction, involving the lipophilic and hydrophilic reactant, it is imperative that the reactants collide with each other as often as possible. One must notice that the use of protic solvent in reactions involving immiscible reactants may enhance the reaction rate. However, this is accompanied by the unfavorable reaction [1, 2]. As a consequence, these techniques are not favorable for the industries.

A plausible technique known as phase-transfer catalysis (PTC) was developed to overcome the hindrance due to the mutual insolubility of the aqueous phase with organic phase [3–22]. In this approach, the PTC has the ability to carry one of the reactants, residing in immiscible phase, as highly reactive species, penetrate into the other phase for reaction take place. The main advantages of using the PTC technique include obtaining a large conversion, high reaction rate, and good selectivity at the moderate reaction conditions.

Idoux et al. [22] first reported the soluble and the insoluble phosphonium ion containing the multi-site PTCs, which have three active sites. In resent years, *Wang* and *Lee* reported the efficiency of the catalytic capabilities of quaternary ammonium ions having two active sites used in the investigation of ethoxylation reaction [23, 24]. However, not all the quaternary salts serve effectively as PTCs [25]. Alkylation reactions have been widely studied and the results contribute significantly to understanding the nucleophilic properties of the amide and amine moiety. *N*-alkylation of the primary and secondary amide and amine has been practiced for decades, both in the presence of stoichiometric amounts of strong bases and under phase-transfer conditions [26–29]. Cycloalkylations are important reactions in organic synthesis, and often in the pharmaceutical syntheses [30–32].

Amines are widely used as the intermediate in the preparation of solvents, fine chemicals, agrochemicals, pharmaceuticals and catalysts for polymerizations. The nucleophilic attack of the alkyl halides by the primary and secondary amines is useful for the preparation of the tertiary amines but the reactions is invariably slow and gives rise to a mixture of the secondary and tertiary amines [33]. The thermal reaction between the alkyl halides and the amines in the presence of a base requires a longer reaction time periods and affords lower yield of the desired product. Therefore, these methods are limited in view of the harsh reaction conditions.

The genesis of the current work lies in these lacunae. As part of an ongoing program, we have decided to design a novel multi-site phase transfer catalyst containing the maximum possible number of the active sites. Herein we report, for the first time, synthesis of the tetra quaternary ammonium

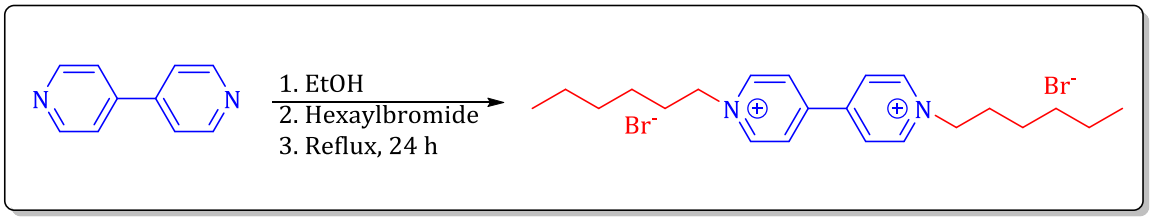
bromide viz., *N*,*N*'-dihexyl-4,4'-bipyridinium dibromide, multi-site phase transfer catalyst (DSPTC) by a only one step process using inexpensive starting materials (Scheme 1). The obtained product has been well characterized by the spectroscopic techniques such as FT-IR, ^{1}H NMR, and ^{13}C NMR. Having successfully designed and synthesized the novel DSPTC, we decided to examine its efficiency by evaluating the kinetics of propargylation of indole under the pseudo-first order reaction conditions (Scheme 2).

This study reports for the first time a thorough kinetic study of the same by evaluating the various experimental parameters. We have also compared the catalytic efficiency of is newly prepared DSPTC with the various single-site phase-transfer catalysts.

Experimental

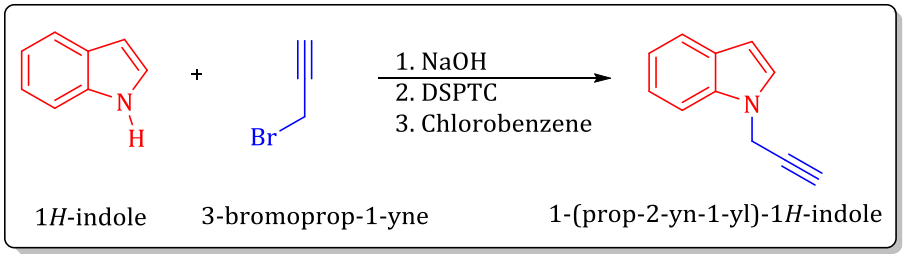
Materials and methods

Ethanol, sodium hydroxide, Propargyl bromide, indole, 4,4' bipyridene, tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium hydrogen sulphate (TBAHS), tetraethylammonium bromide (TEAB), and trioctylmethylammonium chloride, Aliqate 336 and other reagents were all guaranteed grade (GR) chemicals were purchased from Aldrich companies.



Scheme 1. Preparation of *N, N'*-dihexyl-4,4'-bipyridinium dibromide (DSPTC)

Scheme 2. Propargylation of indole in the presence of DSPTC



Synthesis of N,N'-dihexyl-4,4'-bipyridinium dibromide (DSPTC)

A mixture of 4,4'-bipyridine (1.56 g, 10 mmol), 15 mL of *n*-hexylbromide, and 60 mL of ethanol was placed in a 250 mL three necked round bottomed pyrex flask. The reaction was carried out at 60 °C for 24 h and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, *N,N'*-dihexyl-4,4'-bipyridinium dibromide (DSPTC) was washed with *n*-hexane (3×20 mL). The white solid DSPTC was stored in $CaCl_2$ desiccator. Yield 90%, mp 199 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82-0.85 (t, 6H), 1.26-1.34 (m, 12H), 1.99-2.11 (m, 4H), 4.63-4.67 (t, 4H), 8.52-8.59 (dd, 4H), 8.95-9.15 (dd, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7, 24.8, 27.4, 32.8, 33.0 64.2, 124.6, 144.7, 147.2. Anal. Calcd. For $C_{20}H_{26}Cl_2N_2$: C, 54.33; H, 7.05; N, 5.76; Found: C, 54.30; H, 7.01; N, 5.72.

Synthesis of 1-(prop-2-ynyl)-1-indole

The reaction of the indole (13.20 mmol) with sodium hydroxide (10.71 M), chlorobenzene (30 mL), DSPTC (5 mmol%) with respect to limiting reagent, propargyl bromide (11.69 mmol), was prepared at 40 °C. The mixture was stirred using a mechanical mixer at 700 rpm for 3 h. Then, the two-phase solution was separated and the portion of the organic solution was washed five times with distilled water to remove the NaOH and DSPTC. The organic solvent was removed using a vacuum evaporator. Furnished the 1-(prop-2-ynyl)-1-indole colorless solid after silica-gel purification (*n*-Hexane/ethyl acetate, 9:1). Then, the mixture was separated by column chromatography. Yield 90%, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, J = 7.8Hz,1H), 7.40 (d, J = 8.1Hz, 1H), 7.23 (m, 2H), 7.11 (m, 1H), 6.52 (d, J = 3.3Hz, 1H), 4.85 (d, J = 2.4Hz, 1H), 2.38 (t, J = 2.55Hz, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 35.8, 73.5, 77.7, 102.1, 109.3, 119.9, 121.1, 121.9, 127.2, 128.9, 135.8. Anal. Calcd. For $C_{11}H_9N$: C, 85.13; H, 5.85; N, 9.03; Found: C, 85.10; H, 5.81; N, 8.97.

Kinetics of the propargylation of indole

The reaction was conducted on a 150 mL three-necked pyrex round-bottom flask which permits agitating the solution, inserting the water condenser to recover the organic reactant and taking samples and feeding the reactants. This reaction vessel was suspended at the center of the thermo state. A known quantity of the chlorobenzene (30 mL, solvent), sodium hydroxide (10.71 M), 0.5 g biphenyl IS (Internal standard) were introduced into the reactor. Then, 13.2 mmol of indole and 11.69 mmol of propargyl bromide, 5 mol% of DSPTC (With respect to propargyl bromide, limiting reagent) were introduced to the reactor to start the reaction. The reaction mixture was stirred at 700 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 seconds 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 followed by estimating the amount of propargyl bromide (Limiting reagent) that disappeared using a gas chromatography. The analyzing conditions were as follows; Column, 30 m × 0.525 mm i.d. capillary column containing 100% poly(Dimethl siloxanen); injection temperature, 250 °C; FID detector (300 °C). Yields were determined from standard curve and using biphenyl as internal standard.

Reaction and mechanism

This study discusses the non-benzonoid aromatic nucleophilic substitution reactions between the indole and propargyl bromide in the presence of the DSPTC (QBr). The rate of the reaction is discussed in Section 3. The reaction mechanism is represented in Scheme 2.

Definition

The conversion (X) of propargyl bromide (PyBr) is defined as follows:

$$X = 1 - [PyBr]_o/[PyBr]_{o,t} \quad (1)$$

where $[PyBr]_o$ and $[PyBr]_{o,t}$ represent the concentration of benzylation at time (t), t = 0 and t > 0, respectively.

Rate expression

The rate expression for this reaction may be expressed as:

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

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

$$-d\,[PyBr]_o / dt = -r(PyBr) = kapp\,[PyBr]o \quad (3)$$

This reaction is carried out in a batch reactor, so the diminution rate of [PyBr] with time (t) can be expressed on integrating the Eq. 3:

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

Using the Eq. 4, we can get kapp value experimentally by plotting –ln (l–X) against time, t.

Results and discussion

A new multi-site phase transfer catalyst, DSPTC, was successfully synthesized. The effect of several experimental parameters that control the catalytic activity of the DSPTC was evaluated by choosing the propargylation of indole with propargyl bromide as a model reaction (Scheme 2).

The kinetic experiments were conducted under pseudo-first order conditions with excesses of aqueous sodium hydroxide and imidazole. The kinetics of the propargylation was followed by estimating the amount of the propargyl bromide that disappeared using the gas chromatography analysis. The pseudo-first order constants were evaluated from the plots of -In (1–X) versus time, where X is the concentration of propargyl bromide at any time.

Effect of change of agitation speed

The essential condition for a reaction to occur is the effective collision of the reactant molecules, even in the phase-transfer catalysis system. To ascertain the influence of the stirring speed on rate of the reaction, we varied the speed of agitation from 200 rpm to 1000 rpm in the presence of the DSPTC as the catalyst under pseudo-first order reaction conditions at 40 °C (As seen in Figure 1). The apparent rate constants were evaluated using the linear plots of -In (1–X) versus time. The results indicated that the rate of the reaction increased linearly as the agitation speed raised from 200 to 700 rpm. This is attributed to the interfacial area per unit volume of the dispersion increases with the corresponding increase in the stirring speed. The increase of the stirring speed changed the particle size of the dispersed phase. Therefore, to study the other kinetic variables of the propargylation of indole we kept the stirring speed at 700 rpm. Above 700 rpm, there is no significant change in the apparent rate constant. Hence, Figure 1 is an indicative of the interfacial reaction mechanism [34, 35] rather than of a starks extraction mechanism. *Chiellini* et al. [36] reported that the continuous increase in the rate of the ethylation with stirring speeds up to 2000 rpm; proceed through an interfacial mechanism. *Wang* et al. [37] and *Murugan* et al. [38] observed a continuous increase in the rate of ethylation of phenylaceto nitrile (PAN), for which an interfacial mechanism was proposed.

Effect of varying substrate concentration

The amount of propargyl bromide was varied from 11.69 mmol to 18.31 mmol while keeping indole at 13.2 mmol and NaOH at 10.3142 M. The apparent rate constant increases as the amount of the PyBr increases (As shown in Table 1). The increase in the rate may be attributed to the proportionate increase in the number of catalytic active sites available in the DSPTC. When the PyBr concentration was increased, the probability of finding the substrate along with active-site of the

catalyst is enhanced and thereby the rates of reaction increased. This result suggests that the concentration of PyBr in the organic phase is higher and that the concentration of the substrate at the interface may be essential. Recently, *Wang* et al. [39] observed a similar trend for the *N*-alkylation of succinimide with 1-bromo-3-phenyl propane using TOAB as PTC.

Effect of amount of catalyst

The effect of the amount of DSPTC catalyst on the reaction was studied by conducting six experiments. As show in Figure 2 the apparent rate constant (k_{app}) is plotted against the DSPTC amount ranging from 2.5 to 30 mol%. With respect to PyBr. It is obvious that the apparent rate constant (k_{app}) increased linearly with the amount of DSPTC. In the absence of DSPTC 6% of the conversion of 1-(prop-2-ynyl)-1-indole was obtained after 3hr. Nevertheless, 40% of the conversion was obtained only within 15 min of reaction when 5 mol% of (DSPTC) catalyst was added to the solution. It shows that the phase-transfer catalyst is indeed capable of promoting the of indole effectively. In the kinetics study of the ethylation of p-chlorobenzene under PTC condition, *Wang* and *Rajendran* [40] observed a similar dependence of pseudo-first order constant on the amount of catalysts.

Effect of quaternary ammonium salts

Quaternary ammonium salts are generally used as phase-transfer catalysts to promote reaction rate. In addition to DSPTC, six other single site quaternary ammonium salts, such as tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium hydrogensulphate (TBAHS), tetraethylammonium bromide (TEAB), and trioctylmethylammonium chloride, Aliqate 336, were investigated to test their reactivities. The experimental results are listed in Table 2. The reactivity of the indole anion depends on its degree of hydration and on the structure of its counter cation. A comparison among the TEAB, TBAB, and TBAB reveals that the more lipophilic of the quaternary ammonium cation, the greater the effectiveness in transferring nucleophilic anion into the organic media. In other words, the catalytic activities are mainly due to the solubilities of their ion-pair $Q^+ N^-$ in the organic phase, which turn can be attributed to the nature and bulkiness of Q^+ and the medium. As shown in Table 2, the reactivities of TBAB, TBAC, and TBAHS are not affected significantly by the anions X^-, with the symmetric tetrabutyl ammonium cation (Q^+). However, the sulfate ion of TBAHS catalyst is relatively weaker in basicity than those of Br^- and Cl^- of TBAB and TBAC catalysts. Therefore, the dissociation of HSO_4^- from TBAHS is more difficult than those of the TBAB and TBAC catalysts. The reactivity of the TBAHS is less than those of the TBAB and TBAC catalysts. The activity of the lipoph ilic cation Q^+ is determined mainly by two factors: its extractability

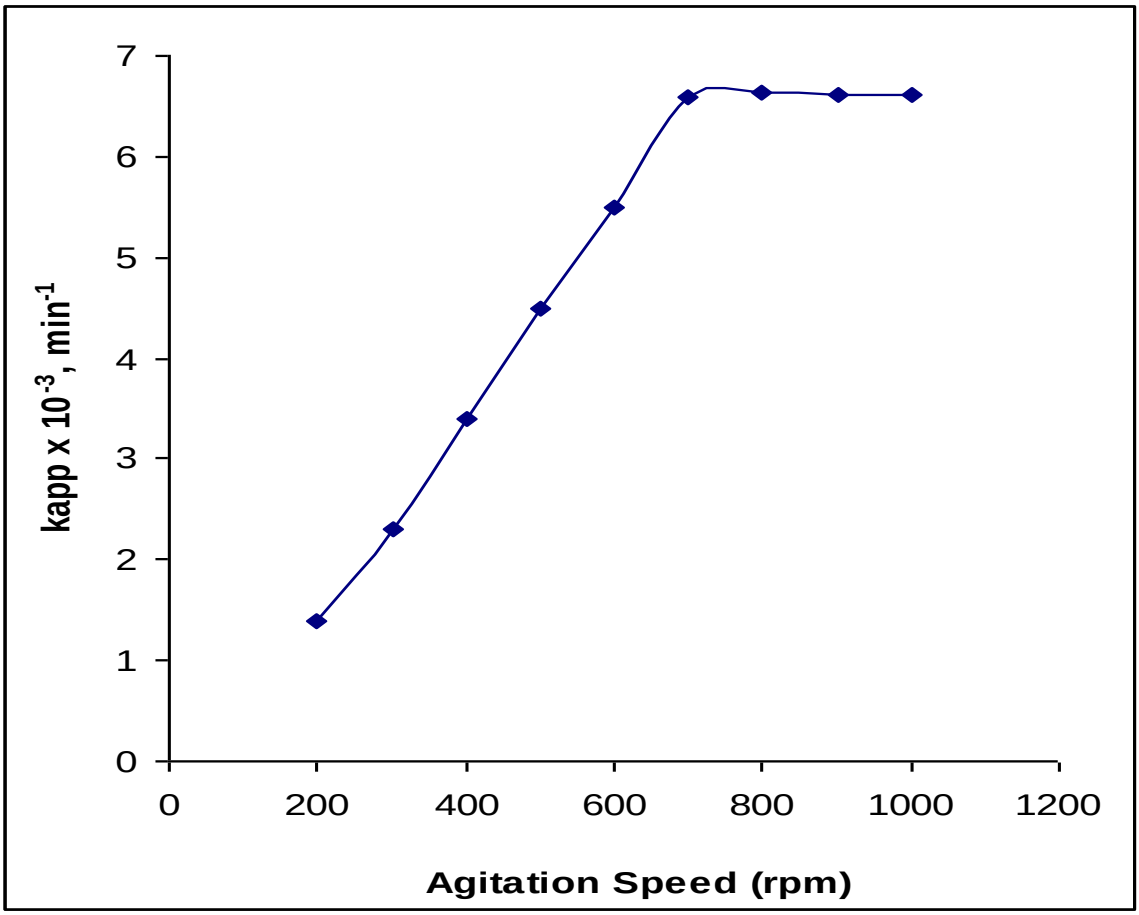


Figure 1. Dependence of k_{app} on agitation speed: Indole (13.20 mmol), propargyl bromide (11.69 mmol), sodium hydroxide (10.71 M), DSPTC (5 mol%), chlorobenzene (30 mL), at 40 °C

Table 1. Effect of the variation of substrate amount on the apparent rate constant (k_{app})

Propargyl bromide (mmol)	k_{app} x 10^3, min^{-1}
1.69	3.56
5.01	4.32
8.35	5.76
11.69	6.59
15.03	7.88
18.31	9.04

[a] Reaction conditions: 13.20 mmol of imidazole, 10.71 M sodium hydroxide, 5 mol% of DSPTC, 30 mL of chlorobenzene, 700 rpm, and 40 °C

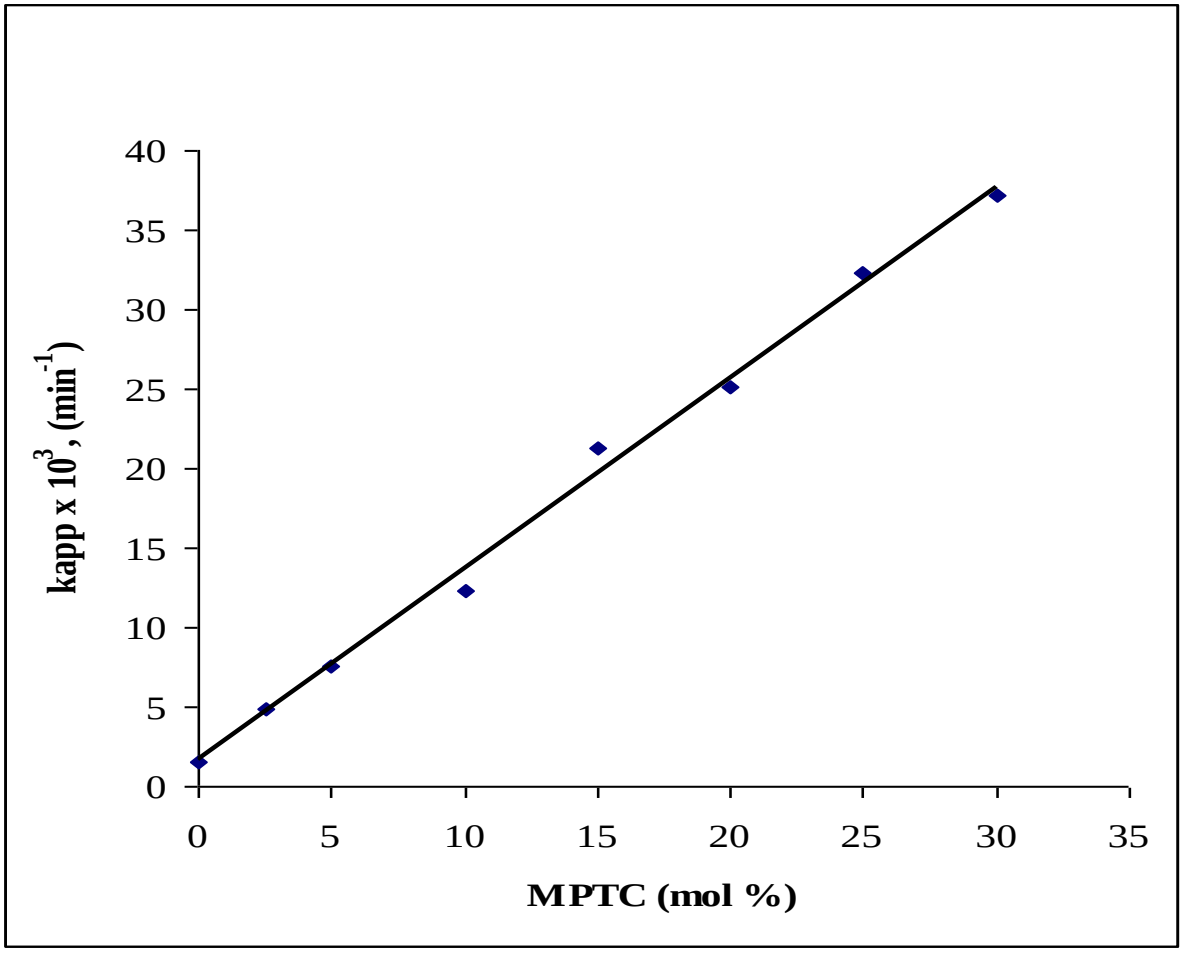


Figure 2. Effect of the amount of DSPTC catalyst on the apparent rate constant, k_{app}; Indole (13.20 mmol), propargyl bromide (11.69 mmol), sodium hydroxide (10.71 M), chlorobenzene (30 mL), 40 °C, at 700 rpm

Table 2. Effect of the phase-transfer catalysts (PTC) on the apparent rate constant (k_{app})

PTC	k_{app} x 10^3, min^{-1}
TEAB	3.32
TBAHS	4.49
TBAC	4.65
TBAB	4.77
Aliquat 336	5.04
DSPTC	6.59

[a] Reaction conditions: 11.69 mmol of propargyl bromide, 13.20 mmol of indole, 10.71 M sodium hydroxide, 30 mL of chlorobenzene, 700 rpm, and 40 °C

and the anion activation ability, Structural factors affect the formation of active catalyst cation-anion pairs between the organic phase and aqueous phase. Based on the above argument, the order of the reactivities of these quaternary ammonium salts are in the order DSPTC > aliquat 336 > TBAB > TBAC > TBAHS > TEAB. Therefore, the reaction rate of TBASH is less then these of TBAI, TBAB and TBAC catalysts [41].

Effect of varying sodium hydroxide concentrations

In phase-transfer catalytic reaction by quaternary ammonium salt, it is seen that the reaction rate was highly affected by alkaline concentration. The rate of the propargylation of indole strongly depends on the strength of the sodium hydroxide. Kinetic experiments were carried out, employing arrange of 8.25–25.00 M aqueous sodium hydroxide under similar reaction conditions. The kinetic profile of the reaction is obtained by plotting –ln (1–X) vs time. The observed rate constants tremendously increased with increase in basicity of hydroxide ion, the apparent rate constants were found to increase with an increase in sodium hydroxide concentration (As seen in Figure 3). The main reason is that on increasing the concentration of alkali, the hydroxide ion is less solvated by water molecules i.e. the hydration of OH^- is minimized and as result the activity of OH^- increased. Therefore, at higher alkaline concentration the rate of propargylation is much higher than that at low concentration of NaOH. *Chillni* et al. [36] reported that the rate of ethylation of phenyl acetonitrile (PAN) with TBAB increased at higher concentration of hydroxide ion and have proposed an interfacial mechanism. In the study of phenoxide allylation in a phase transfer catalytic system *Wu* and *Lai* [42, 43] observed that the extraction of phenol (Using PTC) is more effective if the base concentration is higher.

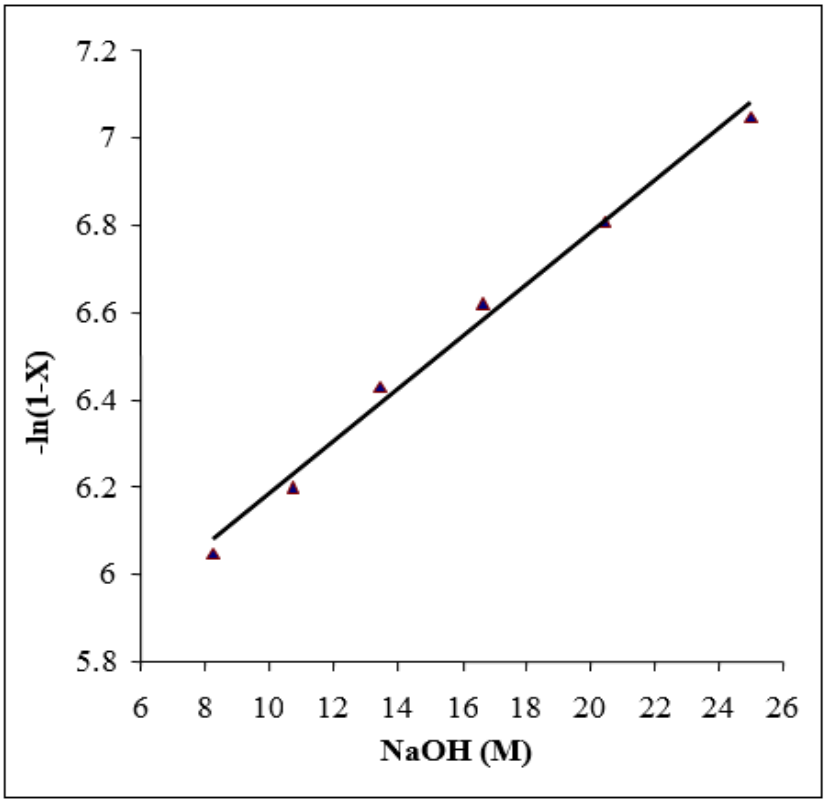


Figure 3. Effect of the Sodium hydroxide on the conversion of propargyl bromide; Indole (13.20 mmol), propargyl bromide (11.69 mmol), DSPTC (5 mol%), chlorobenzene (30 mL), 40 °C at 700 rpm

Effect of temperature

The effect of temperature on rate of the reaction between the indole and propargyl bromide was studied under otherwise similar conditions. The temperature was varied from 30 to 50 °C. The conversion of propargyl bromide was observed to increase with increase in reaction temperature. The effect of temperature on conversion of propargyl bromide is given in Figure 4. The arrhenius plot was made to determine the apparent energy of activation (E_a). It was found to be 48.09 kJ. mol^{-1}. K^{-1} (Figure 5). The other thermodynamic parameters namely entropy of activation (ΔS), enthalpy of activation (ΔH), and free energy of activation (ΔG) were calculated from Eyring's equation and the obtained values were -104.69 kJ. K^{-1}. mol^{-1}, 50.98 kJ. K^{-1}. mol^{-1}, 93.75 kJ. K^{-1}. mol^{-1}. Respectively. A higher E_a value of 88.58 kJ. mol^{-1}. K^{-1} has been reported for the polystyrene bound trimethylammonium ion catalysed reaction, which was controlled by strict intrinsic reactivity under triphase conditions [44]. *Ford* et al. [45] also reported that the activation energy for heterogeneous ethylation of polyacetonitrile was 82.4 kJ. K^{-1}. mol^{-1} and proposed an interfacial mechanism. The E_a value for the alkylation of pyrrolidine-2-one under solid/liquid PTC in presence of potassium carbonate was reported to be 51.08 kJ. K^{-1}. mol^{-1} and an interfacial mechanism was proposed [46]. In a comprehensive study of the synthesis of 4-bromophenyl allyl ether [44], it has been observed that the conversion of allyl bromide increases with increase of temperature and the value of E_a was found at 51.5 kJ. K^{-1}. mol^{-1}. *Yadav* et al. [47] reported an E_a value of 57.68 kJ. K^{-1}. mol^{-1}, for the etherification reaction between β-napthol and benzyl chloride in the presence of NaOH and tetrabutylammonium bromide (TBAB). In the present investigation, it is proposed that the reaction proceeds through the interfacial mechanism.

Effect of the organic solvents

In the phase-transfer catalytic reaction, the solvent dramatically influences the reactivity. Dibutly ether, toluene, benzene, chlorobenzene, 1,4-dioxane, cyclohexane, were used to investigate the influence of organic solvent on reactivity. The results are shown in Table 3. The order of the reactivities for theses organic solvent was; cyclohexane < 1,4-dioxane < Benzene < Toluene < dibutyl ether < chlorobenzene. In the reaction system, organic solvent is used to dissolve the catalyst and benzyl bromide. Howere, the active catalyst and the reacting molecules in the solution often become inactive because they are always surrounded by a number of solvent molecule. In general, the more polar the solvent, the more it can strip the bound water away from the catalyst. High solvation to the active catalyst and reacting molecules often has a negative effect on the acceleration of benzylation. Furthermore, organic solvent also affect the distribution of the active c atalyst between the two phases and the chemical environment of the reaction system. The effect of organic solvents on the

reaction is complicated. It is not simple to predict their effects simply by using dielectric constant values only.

Phase-transfer mechanism study

Generally in the interfacial mechanism [45] of hydroxide ion initiated propargylation under PTC conditions, the hydroxide ion deprotonates the organic substrate N–H at the interface forming an ion-pair, ($Na^+ N^-$), on the addition of the phase-transfer catalyst ($Q^+ X^-$), ion exchange takes place at the interface there by facilitating the migration of the newly formed ion-pair ($Q^+ N^-$) easily into the organic phase.

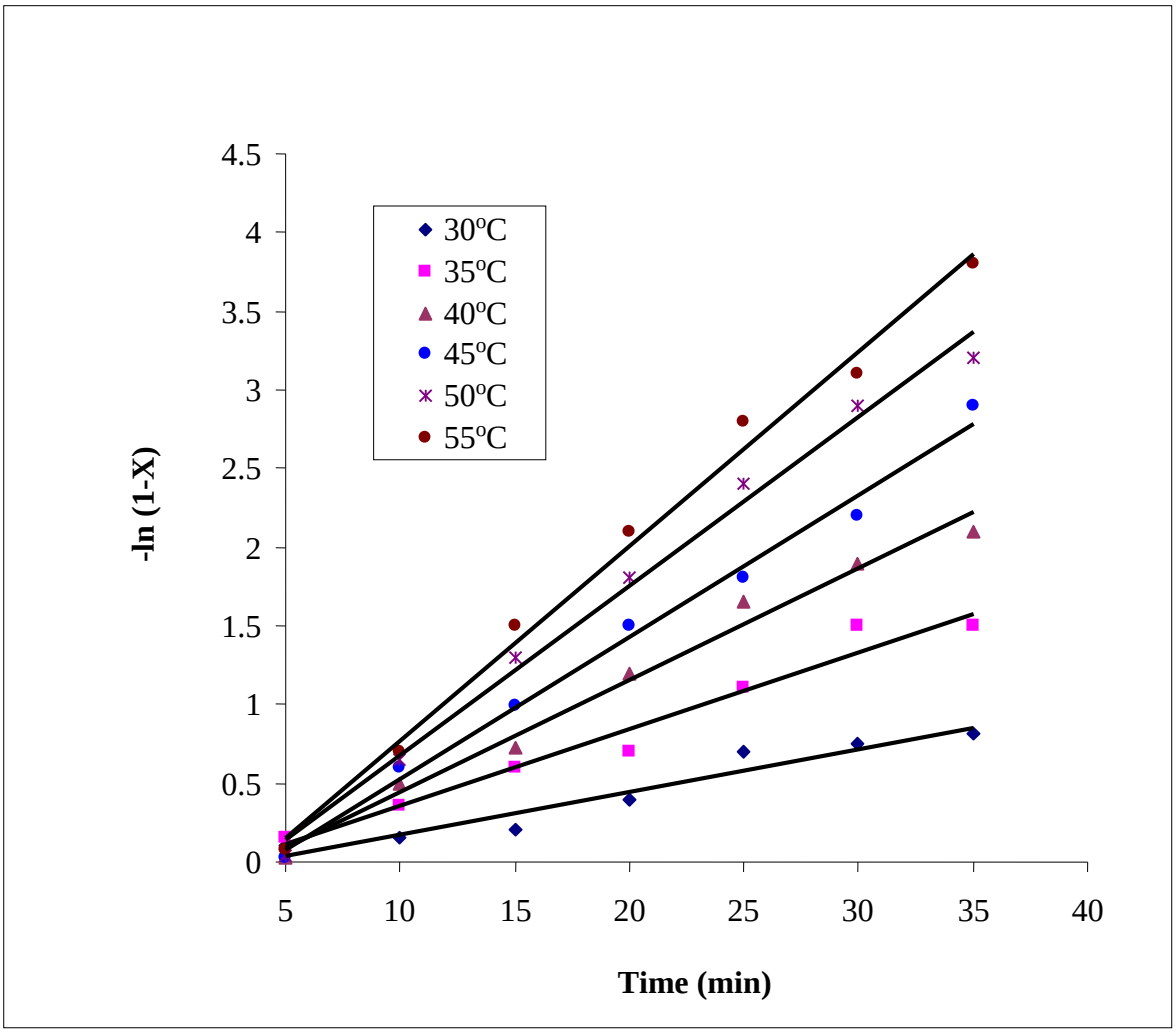


Figure 4. Effect of the temperature on the conversion of propargyl bromide; Indole (13.20 mmol), propargyl bromide (11.69 mmol), sodium hydroxide (10.71 M), DSPTC (5 mol%), chlorobenzene (30 mL), at 700 rpm

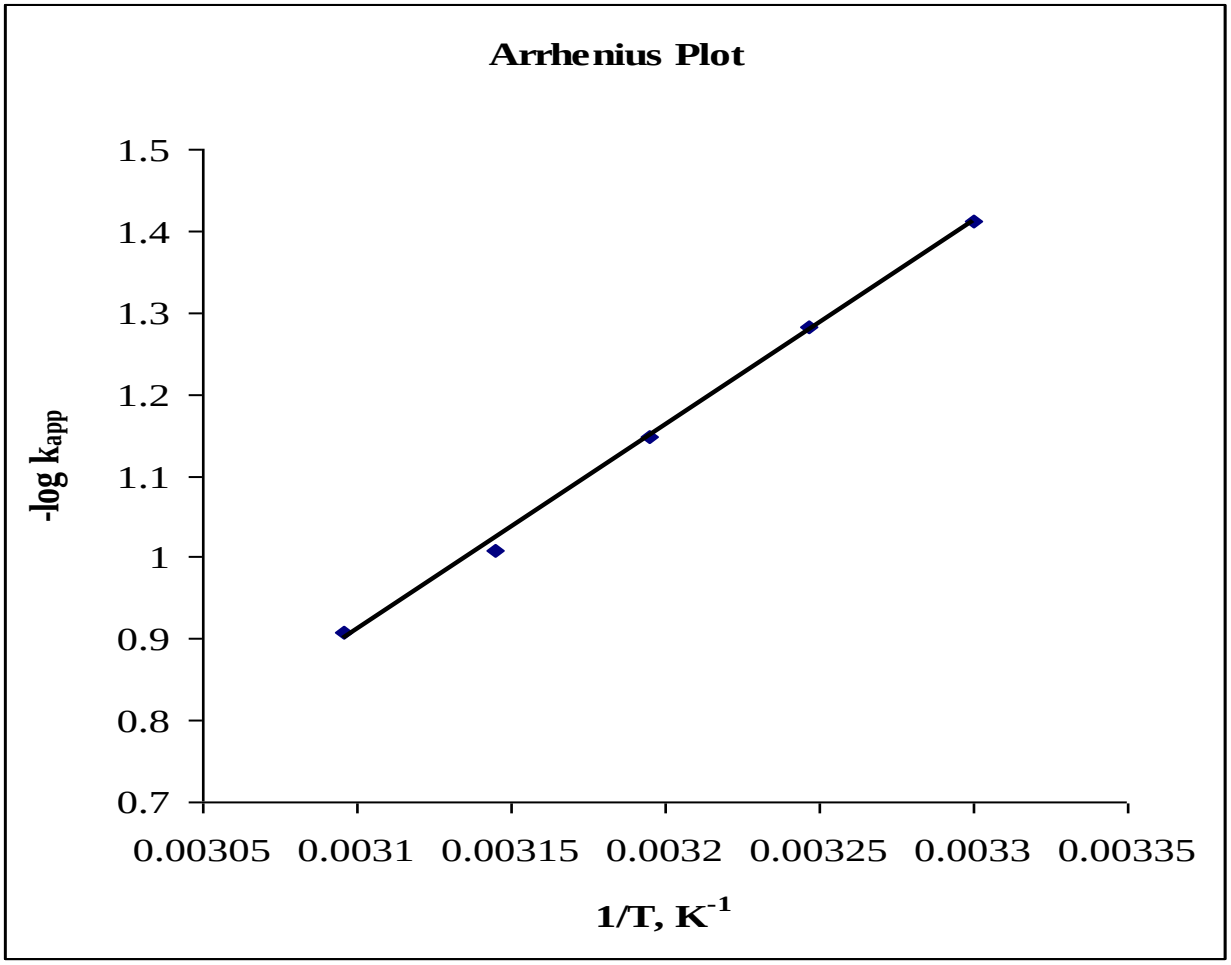


Figure 5. Effect of the Arrhenius Plot on the conversion of propargyl bromide; Indole (13.20 mmol), propargyl bromide (11.69 mmol), sodium hydroxide (10.71 M), DSPTC (5 mol%), chlorobenzene (30 mL of)

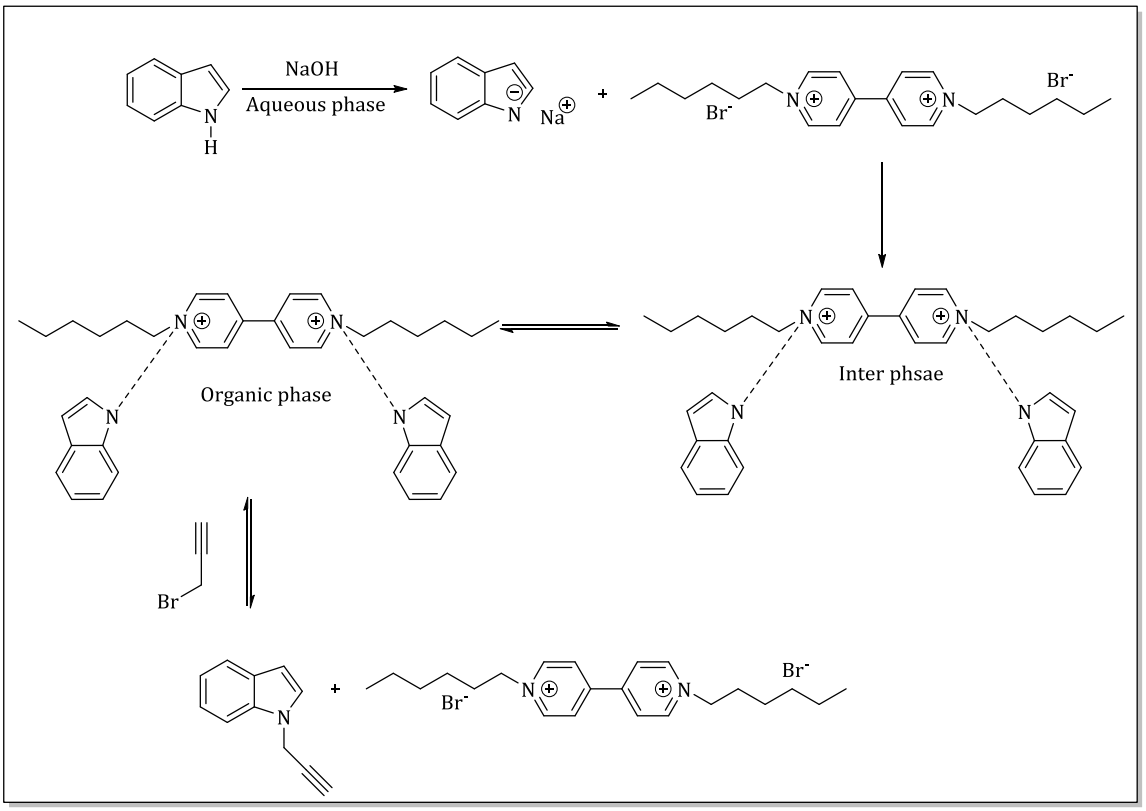
Table 3. Effects of the organic solvents on the apparent rate constant (k_{app})[a]

Organic solvent	Polarity (ε)[b]	k_{app} x 10^3, min^{-1}
Cyclohexane	2.1	2.76
1,4-Dioxane	2.3	2.69
Benzene	2.4	2.98
Toluene	2.5	3.26
Dibutyl ether	2.9	3.58
Chlorobenzene	5.7	6.59

[a] Reaction conditions: 11.69 mmol of propargyl bromide, 13.20 mmol of indole, 10.71 M sodium hydroxide, 5 mol% of DSPTC 700 rpm, and 40 °C

[b] ε Is polarity of the solvent

This ion-pair reacts with the propargylation agent in the organic phase affording *N*-propargylation of indole (Scheme 2). The role of phase transfer catalyst in the *N*-propargylation is to enhance the *N*-formation at the interface. In a systematic kinetic study [36] of ethylation of PAN, it was reported that the chemical reaction is not the sole rate determining steps. From the observed experimental results, it is apparent that the dependencies of the kinetic data on the entire stirring speed range, concentrations of the catalyst, aqueous hydroxide ions, temperature and higher E_a value are consistent with the interfacial mechanism. The mechanism of the propargylation of indole with propargyl bromide, under DSPTC conditions is presented in Scheme 3.



Scheme 3. Reaction mechanism

Conclusion

For the first time, we have synthesized and characterized a new dual-site phase transfer catalyst containing the two-active-sites (DSPTC) and its catalytic ability has been proved thoroughly based on the enhanced pseudo-first order rate constant of propargylation of indole with propargyl bromide in the presence of a aqueous sodium hydroxide (30%, w/w). It is further confirmed that this DSPTC is found to be more active than the corresponding soluble di-site DSPTC and single-site PTCs owing to higher degree of organophilicity. The change of various experimental parameters, viz., stirring

speed, substrate, catalyst, hydroxide ion have found to influence the observed rate constants in the propargylation reaction even under lower (DSPTC) and (NaOH) conditions. In addition, we evaluated E_a and other thermodynamic parameters such as E_a = 48.97 kJ. mol^{-1}. K^{-1}, ΔG = 93.85 kJ. mol^{-1}. K^{-1}, ΔS = -104.09 e.u and ΔH = 50.18 kJ. mol^{-1}. K^{-1}, the observed higher E_a value has confirmed that propargylation reaction should proceed via an interfacial mechanism.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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