Organic Process Research & Development **2010,** *14,* 722–727

Selective *O*-Alkylation of 2-Naphthol using Phosphonium-Based Ionic Liquid as the Phase Transfer Catalyst†

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Abstract:

The selective preparation of *O*-alkylated aromatic products from substituted phenol and naphthols is challenging. The *O*-alkylation of 2-naphthol with benzyl chloride has been studied in this work using phosphonium-based ionic liquids as catalysts such as trihexyl(tetradecyl)phosphonium chloride (THTDPC), trihexyl(tetradecyl)phosphonium bromide (THTDPB), trihexyl(tetradecyl)phosphonium decanoate (THTDPD), and trihexyl(tetradecyl)phosphonium hexafluorophosphate (THTDPH). This is a liquid−liquid phase-transfer-catalysed reaction with reuse of catalyst. The effects of various parameters such as agitation speed, various phosphonium-based ionic liquids, phase volume ratio, catalyst concentration, NaOH concentration, mole ratio of starting materials, and temperature were studied systematically to understand the conversion patterns and the selectivity of the desired product. A mechanism of the reaction and a kinetic model are proposed.

1. Introduction

Ionic liquids have added to the repertoire of chemists for the development of benign routes to synthetic targets. Ionic liquids have been used in a variety of areas such electrochemistry (electrolytes for batteries and fuel cells),[1] heavy metal ion extraction,[2−4] phase transfer catalysis, polymerization,[5] and as *green* solvents, mainly as a replacement for conventional volatile organic compounds (VOC).[6,7] Ambient temperature ionic liquids encompassing 1,3-dialkylimidazolium cations have shown great promise as attractive alternatives to conventional solvents.[8−10] The important properties of these ionic liquids are low volatility, negligible vapor pressure, ease of handling, accelerated reaction rates, potential for recycling, and compatibility with various organic compounds and organometallic catalysts.[11] The ease of separation of the products from reactions conducted in ionic liquids by using various organic solvents adds to their advantages.

Because of the near absence of any vapor pressure, distillation of unreacted reagents and products facilitates product separation by distillation. This is a great advantage from a process engineering viewpoint, since separation by distillation is an effective means for product isolation.[11]

A new promising class of ionic liquids is based on the phosphonium ion, such as the halide ions Cl^-, Br^-, etc., as well as more complex counterions such as PF_6^-, etc.[12] These phosphonium-based ionic liquids, when compared with some other routine ionic liquids such as imidazolium-based salts[13] exhibit a relatively wide electrochemically stable window, high ion mobility, a broad range of room temperature liquid composition, and negligible vapor pressure.[13] They can be used both as green solvents and phase transfer catalysts in multiphase reactions.[6] The hydrophobic nature of certain ionic liquids allows for formation of two-phase systems with water, due to their immiscibility with polar phases.[6] This work is concerned with the catalytic properties of phosphonium-based ionic liquids in biphasic systems in *O*-alkylations.

The majority of reported phase transfer-catalysed reactions, such as nucleophilic substitution, elimination, and polymerisation reactions are reported under liquid−liquid phase transfer catalysis (L−L PTC) conditions. One of the drawbacks of the L−L PTC processes from environmental aspects is that the catalyst distributed between the two phases is normally not recovered and reused. The organic phase is washed with copious quantities of water to remove the catalyst, and the aqueous phase is discarded. This is because the cost of the catalyst per kilogram of product is very low, and many PTC processes involve high-value low-volume products. This is where the phosphonium-based ionic liquids will promote ‘green’ practices in L−L PTC reactions.[15]

Synthesis of aromatic ethers is an industrially important process because of their extensive use in the dyestuff, perfume, flavor, agriculture, and pharmaceutical industries, and we have reported the synthesis of aromatic ethers by phase transfer catalysis (PTC).[16−25] Benzyl-2-naphthyl ether is one of the

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10.1021/op100052g

industrially important products as it is used as an additive in preparation of thermographic recording materials, as an aromatic sensitizer in heat-sensitive recording material for excellent color and printed-image stability.[26] We here report a potentially viable *O*-alkylation of β-naphthol with benzyl chloride using ionic liquids as phase transfer catalysts.

2. Experimental Section

2.1. Chemicals. Phosphonium-based ionic liquids were supplied by Cytec Industries, Canada ($([R_3PR']_3)X^-$, where $R = C_6H_{13}$; $R' = C_{14}H_{27}$; $X^- = Cl^-$, Br^-, CH_3^-, $(CH_2)_n^-$, COO^-), and included trihexyl(tetradecyl)phosphonium chloride (THTDPC), trihexyl(tetradecyl)phosphonium bromide (THTDPB), trihexyl(tetradecyl)phosphonium decanoate (THTDPD), and trihexyl(tetradecyl)phosphonium hexafluorophosphate (THTDPH). These chemicals were of commercial grade and used as such without any purification. All other chemicals and solvents were procured from M/s SD. Fine Chemicals, Mumbai.

2.2. Experimental Setup. The experimental setup consisted of a fully baffled mechanically agitated glass reactor of 5 cm i.d. and 100-mL capacity equipped with a six-bladed turbine impeller and a reflux condenser. The entire reactor assembly was immersed in a thermostatic oil bath, which was maintained at a desired temperature with an accuracy of ±1 °C.

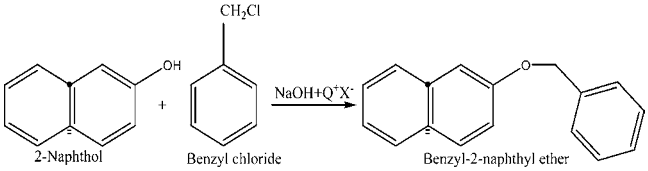
A typical reaction mixture consisted of 0.01 mol of 2-naphthol, 0.02 mol of NaOH in 25 mL of aqueous phase, and 0.01 mol of benzyl chloride and 1.5×10^{-3} mol of the catalyst in 25 mL of toluene. All reactions were carried out at 90 °C and 1000 rpm except where effects of temperature and speed were studied. Samples were withdrawn periodically and analyzed by HPLC (Knaeur model D14163). For the isolation of the product, the organic phase from the reaction mixture was separated and vacuum distilled further.The product distillate was analyzed via GC−MS (Perkin-Elmer Claurus 500), and the ionic liquid catalyst was recycled.

2.3. Method of Analysis and Isolation of Product. The analysis was carried out on HPLC using the following: Column: Merck: RP 8, Eurospher 100, 5 μm, Mobile phase: MeOH/water (70:30), Flow rate: 0.5 cm^3/min, Detector: Knauer K-2501 UV detector set at 245 nm. The product identity was confirmed by using Perkin-Elmer GC−MS (Perkin-Elmer Claurus 500).

3. Results and Discussion

3.1. Reaction Scheme. Benzyl-2-naphthyl ether was prepared selectively by the *O*-alkylation of 2-napthol in the presence of a phosphonium-based ionic liquid and NaOH. Below, we detail the impact of varying certain parameters (Scheme 1).

Scheme 1. **Etherification of 2-naphthol with benzyl chloride**



3.2. Effect of Different Ionic Liquids. Since this is a liquid−liquid reaction catalysed by the ionic liquid as a phase transfer agent, the efficacy of different catalysts and their reuse was of importance. Different ionic liquids such as trihexyl(tetradecyl)phosphonium chloride (THTDPC), trihexyl(tetradecyl)phosphonium bromide (THTDPB), trihexyl(tetradecyl)phosphonium decanoate (THTDPD), and trihexyl(tetradecyl)phosphonium hexafluorophosphate (THTDPH) were employed as catalysts to assess their efficacy in this reaction (Figure 1). All reactions were carried out at 90 °C and at a speed of 1000 rpm using 1.5×10^{-3} mol of ionic liquid. The comparison of different ionic liquids was done by considering the percent conversion of benzyl chloride. The reactivities of the phosphonium-based ionic liquids differ because of the anion attached to the phosphonium cation and are in the following order:

$$\text{THTDPB} > \text{THTDPC} > \text{THTDPH} > \text{THTDPD}$$

The reactivity trends of these ionic liquids were dependent on the anion attached to phosphonium cation in the order Br^- > Cl^-> hexafluorophosphate > decanoate which is the same order as nucleophilicity for the anions used in this study.[27,28] The anion-exchange reactions with the nucleophile is more rapid with Br^- than others.[29,30] Further studies were carried out with trihexyl(tetradecyl)phosphonium bromide (THTDPB), as a catalyst on the basis of these results.

3.3. Effect of Speed of Agitation. The speed of agitation was varied in the range of 600−1000 rpm with THTDPB under

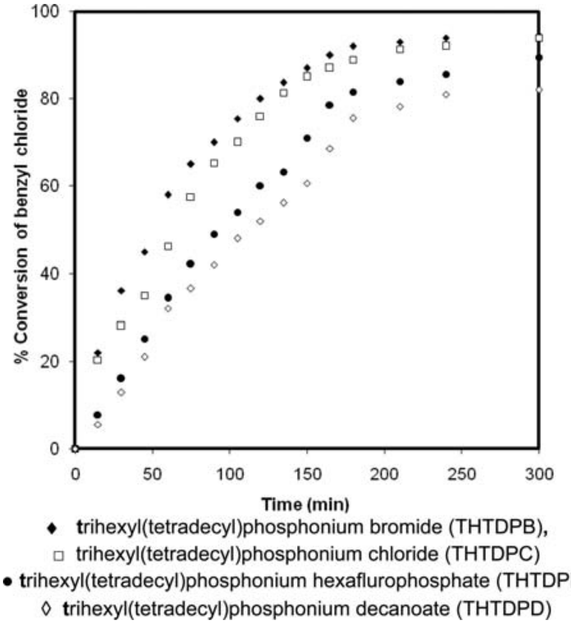


Figure 1. **Effect of different ionic liquids as catalysts. Reaction conditions: 2-naphthol (0.01 mol), NaOH (0.02 mol), benzyl chloride (0.01 mol), catalyst (1.5×10^{-3} mol), toluene/water (25 cm^3:25 cm^3), speed of agitation (1000 rpm), temperature (90 °C).**

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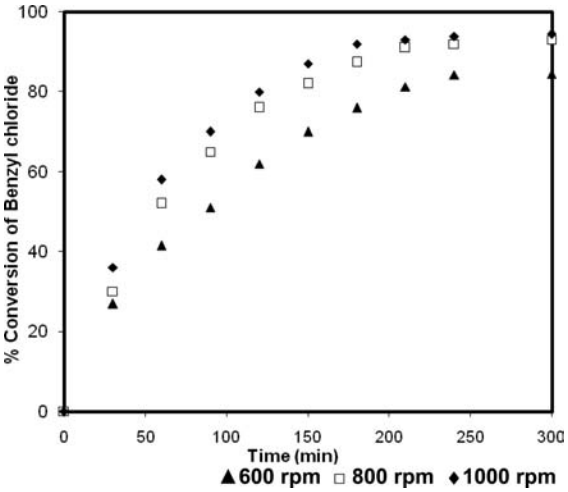

Figure 2. **Effect of speed of agitation. Reaction conditions: 2-naphthol (0.01 mol), NaOH (0.02 mol), benzyl chloride (0.01 mol), THTDPB (1.5 × 10^{-3} mol), toluene/water (25 cm^3:25 cm^3), temperature (90 °C).**

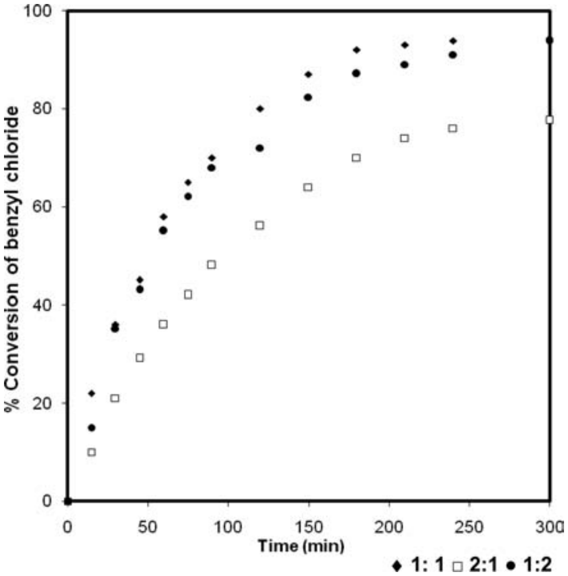

Figure 3. **Effect of phase volume ratio (organic/aqueous). Reaction conditions: 2 -naphthol (0.01 mol), NaOH (0.02 mol), benzyl chloride (0.01 mol), THTDPB (1.5 × 10^{-3} mol), speed of agitation (1000 rpm), temperature (90 °C).**

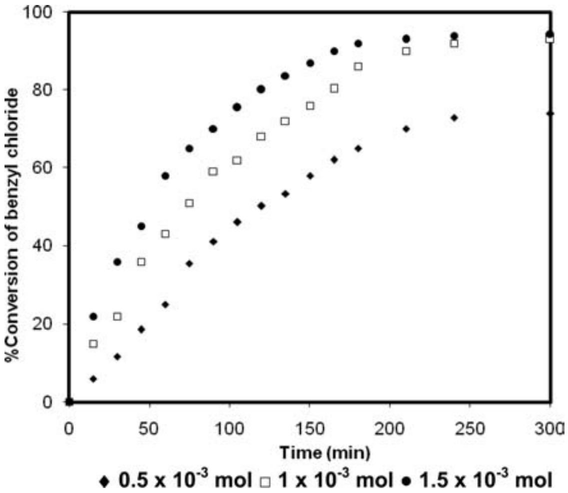

Figure 4. **Effect of concentration of catalyst. Reaction conditions: 2-naphthol (0.01 mol), NaOH (0.02 mol), benzyl chloride (0.01 mol), catalyst (THTDPB), toluene/water (25 cm^3:25 cm^3), speed of agitation (1000 rpm), temperature (90 °C).**

otherwise similar conditions (Figure 2). The conversion increased with an increase in the speed of agitation from 600 to 1000 rpm There was a marginal increase in conversions at 800 and 1000 rpm. There was no increase in conversion beyond 1000 rpm; hence, all further experiments were carried out at 1000 rpm.

3.4. Effect of Phase Volume Ratio. The effect of the ratio of organic phase volume to aqueous phase volume was studied at 1:2, 1:1, and 2:1 under otherwise similar reaction conditions (Figure 3.). When the volume ratio of organic to aqueous phases was fixed at 1:1, the best conversion values were obtained. Under these conditions, it was observed that the organic phase was the dispersed phase and the aqueous phase was the continuous phase. When the phase volume ratio was 2:1 (organic/aqueous), lower conversion levels were obtained, due to the dilution of both the limiting reactant (benzyl chloride) and the concentration of the catalyst in the organic phase.

When organic to aqueous phase volume ratio was 1:2, there was no significant change in conversion. This could be due to the partitioning of THTDPB in the organic phase, remaining practically the same at 1:1. Therefore, further experiments were conducted by using equal phase volume ratio.

3.5. Effect of Concentration of Catalyst. The concentration of catalyst THTDPB was varied from 0.5 × 10^{-3} to 1.5 × 10^{-3} mol (Figure 4). The rate of reaction is directly proportional to catalyst concentration, which is a typical characteristic of PTC reactions.[29] The maximum conversion was obtained at 1.5 × 10^{-3} mol THTDPB. Hence, all further experiments were carried out at 1.5 × 10^{-3} mol.

3.6. Effect of NaOH Concentration. The concentration of NaOH was varied from 0.01 to 0.02 mol (Figure 5). 2-Naphthol was completely converted into the sodium salt at 0.02 mol of NaOH, leading to the best conversion, which in turn results in more $[Q^+Y^-]_{org}$ going into the organic phase, where Y^- is the nucleophile. Hence 0.02 mol of NaOH was used for all reactions, which ensures the complete formation of the sodium salt of 2-naphthol.

3.7. Effect of Mole Ratio. The mole ratio of benzyl chloride/2-naphthol was varied from 0.5:1 to 1:1 mols under similar operating conditions (Figure 6). The best results were obtained using 1:1 mol ratio. Thus, all the subsequent reactions were carried out with 1:1 mol ratio of benzyl chloride/2-naphthol.

3.8. Effect of Temperature. The effect of temperature was studied by conducting the reactions at 70, 80, and 90 °C under otherwise similar conditions (Figure 7.). As the temperature was increased, conversion of benzyl chloride also increased with

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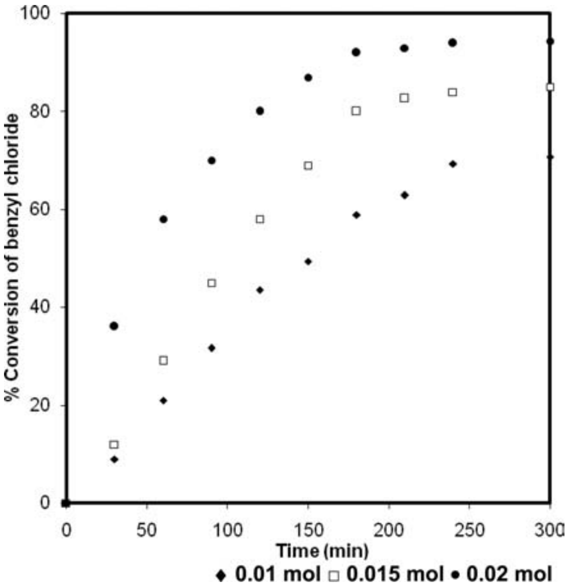


Figure 5. **Effect of NaOH concentration. Reaction conditions: 2-naphthol (0.01 mol), benzyl chloride (0.01 mol), THTDPB (1.5 × 10^{-3} mol), toluene/water: (25 cm^3: 25 cm^3), speed of agitation (1000 rpm), temperature (90 °C).**

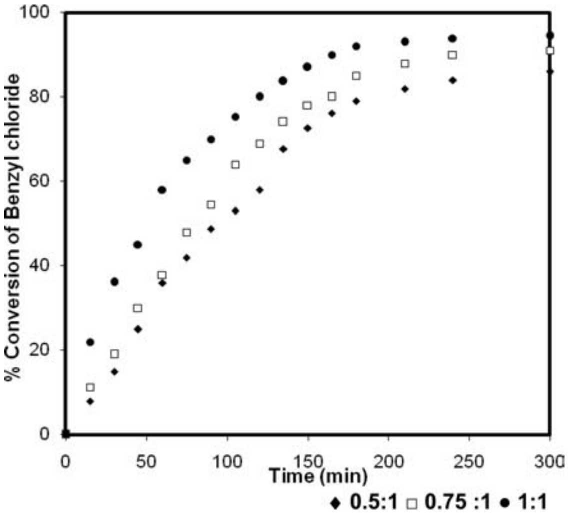


Figure 6. **Effect of mole ratio. Reaction conditions: *β*-naphthol (0.01 mol), NaOH (0.02 mol), THTDPB (1.5 × 10^{-3} mol), toluene/water: (25 cm^3: 25 cm^3), speed of agitation (1000 rpm), temperature (90 °C).**

maximum conversion at 90 °C. This suggested that the reaction would be kinetically controlled and is discussed later.

3.9. Reusability of Ionic Liquid (IL). In this study, the catalyst was separated from organic layer by vacuum distillation. After the first attempt, IL was used directly for the subsequent attempt without further purification or adding any fresh catalyst (Figure 8). After the second run, the conversion began to decrease, suggesting catalyst loss (because the ionic liquid has finite solubility in the aqueous phase) and also due to handling. Hence, one recycling of THTDPB is possible at its original activity.

3.10. Kinetics of Reaction. 2-Naphthol (ROH) was converted in the presence of an aqueous alkali into the corresponding phenate (RO^-M^+) salt in situ, and no free ROH was present.

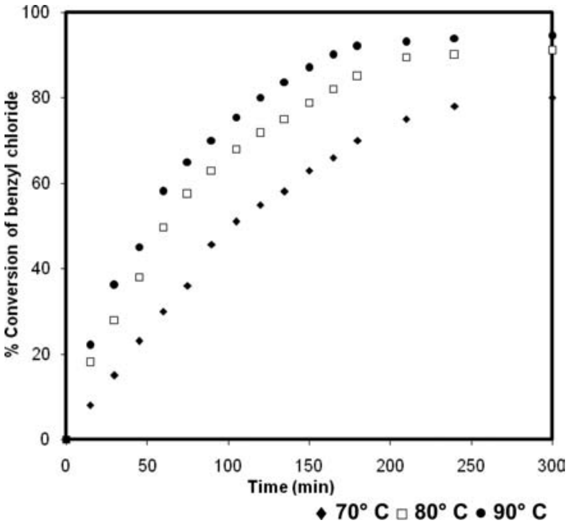


Figure 7. **Effect of temperature. Reaction conditions: 2-naphthol (0.01 mol), NaOH (0.02 mol), benzyl chloride (0.01 mol), THTDPB (1.5 × 10^{-3} mol), toluene/water (25 cm^3:25 cm^3), speed of agitation (1000 rpm).**

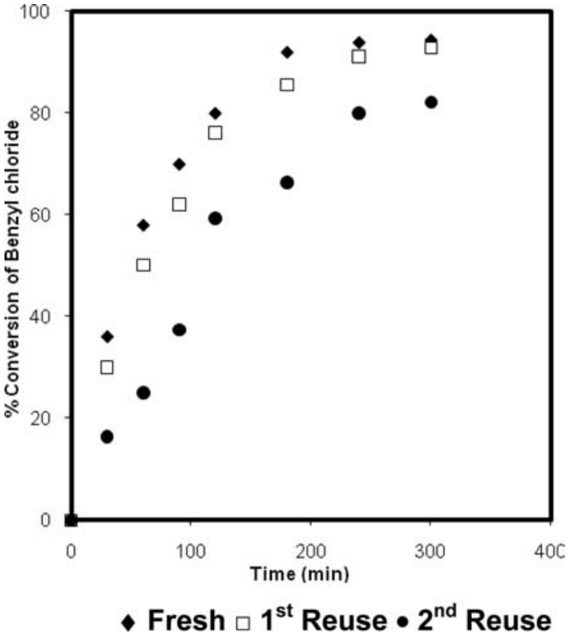
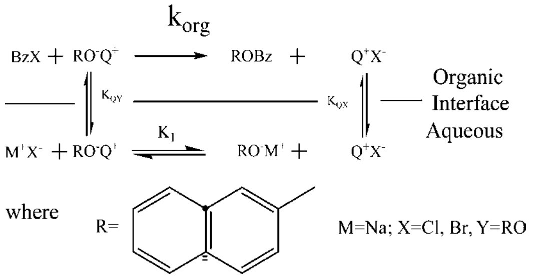


Figure 8. **Reusability of catalyst. Reaction conditions: 2-naphthol (0.01 mol), NaOH (0.02 mol), benzyl chloride (0.01 mol), THTDPB (1.5 × 10^{-3} mol), toluene/water (25 cm^3:25 cm^3), speed of agitation (1000 rpm), temperature (90 °C).**

The pH of the aqueous phase was always alkaline. The aqueous phase reaction produces the ion-pair (RO^-Q^+) which is instantaneously transferred to the organic phase due to high lipophilicity of the catalyst cation. It reacts with benzyl chloride (BzCl) to produce the ether ROBz in the organic phase, and the regenerated catalyst Q^+X^- is transferred across the interface to the aqueous phase. The quaternary cation Q is distributed as four ion-pairs when the selectivity is 100% to *O*-alkylation. The ion-exchange equilibrium across the interface can be written in terms of an overall exchange reaction equilibrium constant (K_e), which is also called selectivity equilibrium constant, for exchange of $[X^-]_{aq}$ by $[Y^-]_{aq}$ and its transfer to the organic phase, by the following equations:



$$[Q^+X^-]_{org} + [Y^-]_{aq} \overset{K_e}{\longleftrightarrow} [Q^+Y^-]_{org} + [X^-]_{aq} \qquad (1)$$

$$K_e = \frac{[Q^+Y^-]_{org}}{[Q^+X^-]_{org}} \cdot \frac{[X^-]_{aq}}{[Y^-]_{aq}} \qquad (2)$$

The individual ion-pair distribution constants between organic and aqueous phases and their relationship with K_e and K_1 are given by:

$$K_{QX} = \frac{[Q^+Y^-]_{org}}{[Q^+Y^-]_{aq}}, \quad K_{QY} = \frac{[Q^+Y^-]_{org}}{[Q^+Y^-]_{aq}}$$

$$K_e = \frac{K_{QY}[Q^+Y^-]_{aq}}{K_{QX}[Q^+X^-]_{aq}} \cdot \frac{[X^-]_{aq}}{[Y^-]_{aq}} = \frac{K_{QY}}{K_{QX}} K_1 \qquad (3)$$

$$K_e \frac{K_{QX}}{K_{QY}} = \frac{[Q^+Y^-]_{aq}}{[Q^+X^-]_{aq}} \cdot \frac{[X^-]_{aq}}{[Y^-]_{aq}} = K_1 \qquad (4)$$

Equation 4 represents the equilibrium constant for the ion-pair exchange reaction in the aqueous phase. If the overall reaction rate is controlled by the reaction in the organic phase, then the rate of reaction of benzyl chloride (A) in the organic phase is given by:

$$\frac{-d[A]_{org}}{dt} = k_{org}[A]_{org}[Q^+Y^-]_{org} \qquad (5)$$

The concentration of the active catalyst in the organic phase needs to be substituted in terms of known concentrations.

$$[Q^+Y^-]_{org} = \frac{K_e[Q^+X^-]_{org}[Y^-]_{aq}}{[X^-]_{aq}} \qquad (6)$$

The catalyst is distributed as two ion-pairs in each of the organic and aqueous phases. If N_Q is total amount of catalyst (mol) added to the reaction mixture initially and ϕ is the fraction of the catalyst cation Q^+ distributed in the organic (reaction) phase, then:

$$[Q^+X^-]_{org}V_{org} + [Q^+Y^-]_{org}V_{org} = \phi N_Q \quad \text{(organic phase)} \qquad (7)$$

$$[Q^+X^-]_{aq}V_{aq} + [Q^+Y^-]_{aq}V_{aq} = (1-\phi)N_Q \quad \text{(aqueous phase)} \qquad (8)$$

From eq 7,

$$[Q^+Y^-]_{org} = \phi\frac{N_Q}{V_{org}} - [Q^+X^-]_{org} \qquad (9)$$

Defining,

$$[N_Q]_{org} = \frac{N_Q}{V_{org}} = \text{total catalyst mol/unit organic phase volume} \qquad (10)$$

Equation 9 is converted to the following:

$$[Q^+Y^-]_{org} = \frac{\phi[N_Q]_{org}}{\left(1 + \frac{1}{K_e}\frac{[X^-]_{aq}}{[Y^-]_{aq}}\right)} \qquad (11)$$

Equation 5 is rewritten with the help of eq 11 as:

$$\frac{-d[A]_{org}}{dt} = k_{org}[A]_{org}\frac{\phi[N_Q]_{org}}{\left(1 + \frac{1}{K_e}\frac{[X^-]_{aq}}{[Y^-]_{aq}}\right)} \qquad (12)$$

and the concentrations terms $[A]_{org}$, $[X^-]_{aq}$, and $[Y^-]_{aq}$ can be substituted in terms of X_A, the fractional conversion of A. For equimolar concentrations of the reactants, the rate equation is:

$$\frac{dX_A}{dt} = k_{org}\frac{\phi[N_Q]_{org}(1-X_A)}{\left(1 + \frac{1}{K_e}\frac{X_A}{(1-X_A)}\right)} \qquad (13)$$

After separation of variables and integration, eq 13 leads to:

$$\ln(1-X_A)[1-K_e] + \frac{X_A}{(1-X_A)} = K_e k_{org}\phi[N_Q]_{org}t \qquad (14)$$

It is possible to determine the rate constant (k_{org}) and the equilibrium constant (K_e) by further manipulation of eq 14 as given below:

$$\frac{X_A}{(1-X_A)\ln(1-X_A)} = K_e k_{org}\phi[N_Q]_{org}\frac{t}{\ln(1-X_A)} + [K_e - 1] \qquad (15)$$

Equation 15 is that of a straight line. When $(X_A)/((1-X_A)\ln(1-X_A))$ is plotted against $(t)/(\ln(1-X_A))$, it should give a slope of $K_e k_{org}\phi[N_Q]_{org}$ (time^{-1}) and intercept of $[K_e - 1]$ from which the equilibrium constant K_e and the rate constant $k' = k_{org}\phi$ are obtained.

Since the ionic liquid used as a phase transfer catalyst can be separated without much loss, it is clear that the value of the value of ϕ should be close to 1. This indicates the distribution constant is almost constant.

3.10. Validation of the Model. In order to verify the proposed mechanism of the reaction and validate the model, the following plots are drawn. Figure 9 shows the plot of $(X_A)/((1-X_A)\ln(1-X_A))$ is plotted against $(t)/(\ln(1-X_A))$, which gives a straight line with a slope of $K_e k_{org}\phi[N_Q]_{org}$ (time^{-1}) and

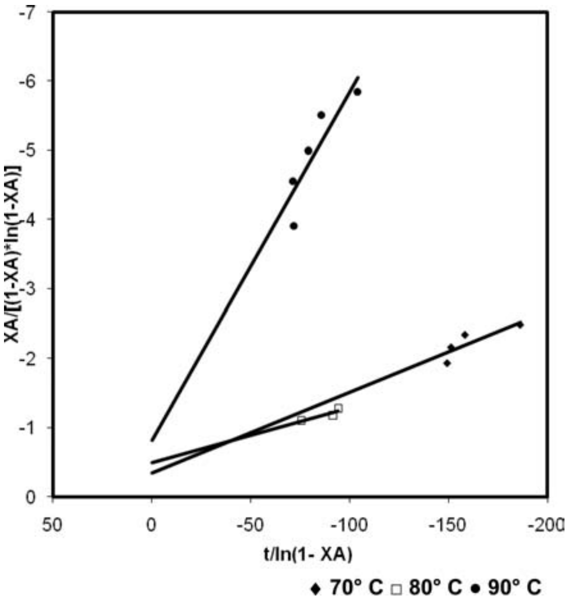


Figure 9. **Validity of kinetic model at various temperatures.**

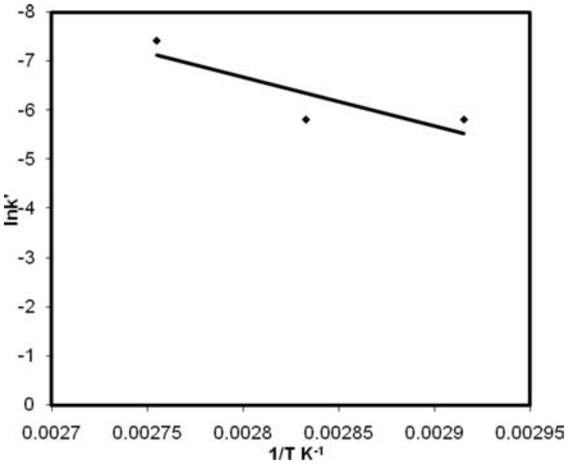


Figure 10. **Arrhenius plot.**

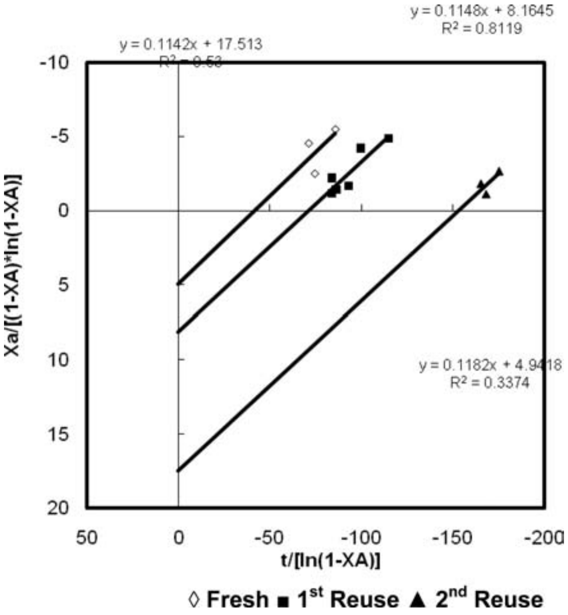


Figure 11. **Reusability of catalyst for finding rate constant for constant concentration of catalyst (THTDPB) (1.5×10^{-3} mol).**

intercept of $[K_e - 1]$ from which the equilibrium constant K_e and the rate constant $k' = k_{org}\phi$ are obtained. Since $\phi \cong 1$, $k' \cong k_{org}$.

The calculated rate constants were used to derive the Arrhenius plot (Figure 10) from which an activation energy of 19.74 kcal/mol was obtained, which also suggests that there was no mass transfer resistance.

The third reuse data are also plotted in the same figure (Figure 11) to see that the slopes are the same when divided by the catalyst concentration. It would mean the ionic liquid used does not degrade as a catalyst.

4. Conclusions

The effects of various kinetic parameters such as speed of agitation, different phosphonium-based ionic liquids, phase volume ratio, and catalyst concentration were studied for the *O*-alkylation of 2-naphthol with benzyl chloride as in a L−L PTC system. A kinetic model was built, and the analysis demonstrated that both rate constant and equilibrium constant could be obtained from the same set of data.

Acknowledgment

G.D.Y. acknowledges financial support for personal chair from the Darbari Seth Endowment.

Nomenclature

$[A]_{org}$	Concentration of benzyl chloride in the organic phase, mol/cm^3
k_{org}	Second-order rate constant of forward reaction in organic phase, cm^3/mol·s
K_e	Overall ion-exchange reaction equilibrium constant
N_Q	Total moles of catalyst added to the system at time $t = 0$, mol
$[N_Q]_{org}$	Moles of catalyst in the organic phase, mol/cm^3
$[Q^+X^-]_{org}$	Concentration of catalyst in the organic phase, mol/cm^3
$[Q^+X^-]_{aq}$	Concentration of catalyst in the aqueous phase, mol/cm^3
$[RO^-Q^+]_{aq}$	Concentration of nucleophile ion-pair in the aqueous phase, mol/cm^3
$[RO^-Q^+]_{org}$	Concentration of nucleophile ion-pair with catalyst in the organic phase, mol/cm^3
THTDPC	trihexyl(tetradecyl)phosphonium chloride
THTDPB	trihexyl(tetradecyl)phosphonium bromide
THTDPD	trihexyl(tetradecyl)phosphonium decanoate
THTDPH	trihexyl(tetradecyl)phosphonium hexaflurophosphate
T	Temperature, K
V_{org}	Volume of the organic phase, cm^3
X^-	Leaving group
X_A	Fractional conversion of reactant A
Y^-	Nucleophile
ϕ	Fraction of quaternary cation in the organic phase

Received for review February 16, 2010.

OP100052G