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# Selectivity Engineering of Phase Transfer Catalyzed Alkylation of 2'-Hydroxyacetophenone: Enhancement in Rates and Selectivity by Creation of a Third Liquid Phase

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## Abstract:

Enhancements in rate of reaction and selectivity of the desired product in biphasic reactions are achieved by creating a third liquid phase, under appropriate conditions, where the third liquid phase is the locale of the main reaction, having a dramatic effect on product distribution in complex chemical reactions. Thus, in the case of phase transfer catalysis (PTC), conversion of liquid–liquid (L–L) PTC into liquid–liquid–liquid (L–L–L) PTC is of considerable techno-commercial interest resulting in waste minimization which is a major theme of green chemistry. Etherification of 2'-hydroxyacetophenone with 1-bromopentane, under traditional liquid–liquid phase transfer catalysis, results in loss of catalyst. However, the transformation of two liquid phases into three liquid phases (L–L–L) PTC leads enhancement in rates by orders of magnitude, with 100% conversion of the limiting reactant 1-bromopentane and 100% selectivity to 2'-pentyloxyacetophenone. This strategy eliminates separation problems and results in high reaction rates reducing the total reaction time. Moreover, the catalyst-rich third phase is recycled more than 7 times without loss in activity. The kinetics of the reaction are studied in great detail. There is a substantial reduction in activation energy under L–L–L PTC vis-à-vis L–L PTC, where the locale of the reaction is shifted from the organic phase to the third phase.

## 1. Introduction

Phase transfer catalysis (PTC) has fascinated many researchers and industries for the past three and half decades and is a mature discipline now.<sup>1,2</sup> The major advantages of PTC include high yield, high reaction rate, selectivity to desired product with less quantity of catalyst, mild conditions, and reduction in energy consumption. PTC has been successfully applied to economically viable synthesis of important and valuable chemicals. A large number of industrially important reactions involve the use of PTC reported under L–L phase transfer catalysis. The major disadvantage of liquid–liquid phase transfer catalysis (L–L PTC) is that the catalyst remains distributed between the two liquid phases and cannot be recovered easily. The separation of phase-

transfer catalysts from the reaction mixture can be achieved by extraction, distillation, and adsorption,<sup>1,2</sup> which are all energy intensive and uneconomical due to high dilutions. Extraction needs an additional solvent that has to be distilled off to recover the phase transfer catalyst. Distillation is possible only if the catalyst has a lower boiling point than the reactants, products, and the solvents. In the case of adsorption, the catalyst must be eluted using a solvent. Since the quantities of the catalyst used are small, they do not contribute much to the expensive product cost. Therefore, the catalyst is mostly not recovered but removed by washing the organic phase with copious quantities of water which is disposed to the effluent treatment plant as an end-of-the-pipe approach of pollution prevention. Although milder reaction conditions and use of cheap solvents in L–L PTC improve the economics, PTC needs to be practised from the green chemistry perspective such as solventless synthesis and catalyst reuse and an overall strategy of waste reduction.

Instead of conducting reactions in homogeneous media, it may be desirable to convert the reaction into a multiphase system and achieve the same objective most economically.<sup>3,4</sup> Furthermore, a third, catalyst-rich phase can be created between the aqueous and organic phases containing the reactants whereby the reaction occurs in the middle phase through a proper balance of lipophilicity, hydrophilicity, interfacial tension, solubilities, phase equilibria, and density; and this constitutes the so-called liquid–liquid–liquid (L–L–L) PTC. It was observed that when the amount of catalyst exceeds a critical value the rate of reaction increases sharply. Indeed, we have found, in a number of reactions, not only the rates of reaction but also the selectivity can be enhanced dramatically thereby reducing reaction time and separation costs.<sup>5–10</sup> The third liquid phase is the main reaction phase for the phase transfer catalyst to catalyze the reaction, and the recovery and reuse of the catalyst are easier since it forms an immiscible third liquid phase. The advantages of L–L–L PTC over L–L PTC are (i) enhanced reaction rates and milder reaction conditions such as lower temperature; (ii) easier catalyst recovery and reuse; (iii) suppression of

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byproduct and increased yields and selectivity with respect to the desired product; and (iv) the catalyst need not be bound to a solid support. Hence the attendant difficulties of reduced activity and mechanical strength associated with L–L–S PTC can be avoided. It is the major advantage of L–L–L PTC over L–L–S PTC. The L–L–L PTC requires a greater amount of catalyst (PTC), but since it is recovered, and reusable, it is an excellent way of reducing waste. The rates are very high and thus reduce the reaction times and reactor volumes, leading to an economic advantage.

When a phase transfer catalyst has limited solubility in both the aqueous and organic phases, a third liquid phase can be generated. Under these conditions, most of the reactions occur in the third liquid with both aqueous and organic reactants transferring to this phase for reaction. As the third phase is rich in catalyst, the reaction rate is increased to a great extent; since most of the catalyst is located in the third phase, it can be easily separated as catalyst phase.

Synthesis of aromatic ethers is one of the favorite reactions in organic synthesis which has been practiced using PTC, and we have studied a number of industrially relevant syntheses using different modes of PTC. 2'-Pentyloxyacetophenone is used as an intermediate in the synthesis of fungicides.<sup>11</sup> Covello and Pisepo<sup>12</sup> have reported the synthesis of 2'-pentyloxyacetophenone from 2'-hydroxyacetophenone; sodium hydroxide and 1-bromopentane in methanol at reflux temperature gives 75% conversion. Except the above-mentioned work, there is no direct report in the published literature on the details of mechanism and kinetics of alkylation of 2'-hydroxyacetophenone by using PTC. The current work deals with the synthesis of 2'-pentyloxyacetophenone from 2'-hydroxyacetophenone and 1-bromopentane, under L–L–L PTC in comparison with L–L PTC. This paper delineates the theoretical analysis and experimental details of L–L–L PTC. The method was extended to several other substrates.

## 2. Experimental Section

**2.1. Materials.** 2'-Hydroxyacetophenone, 1-bromopentane, 4-hydroxybenzaldehyde, 4'-hydroxyacetophenone, 2-methoxyphenol, 4-methoxyphenol, *m*-cresol, phenol, toluene, sodium chloride, and sodium hydroxide, all of AR grade, were obtained from Merck Pvt. Ltd. Mumbai, India. Tetraabutylammonium bromide (TBAB) was obtained as a gift sample from M/s Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India.

**2.2. Experimental Procedure.** The reactions were studied in a 7 cm i.d. fully baffled mechanically agitated contactor of 200 cm<sup>3</sup> total capacity, which was equipped with a six-blade turbine impeller. The reactor was kept in a constant temperature water bath. Typical L–L–L PTC runs were conducted by taking 0.02 mol of 2'-hydroxyacetophenone, 0.02 mol of sodium hydroxide, and 0.3 mol of sodium chloride in 50 cm<sup>3</sup> of water. This led to the formation of the third liquid phase at room temperature and at 90 °C. To this the

**Table 1. Volumes of different phases**

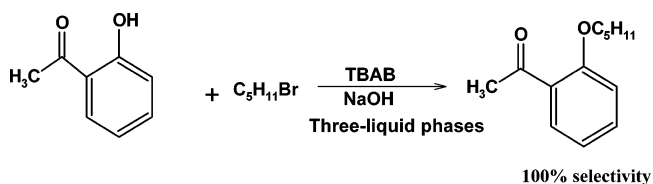
phases	volume, cm <sup>3</sup>
organic	50.0
catalyst	4.0
aqueous	55.0

required amount of TBAB catalyst was added. The organic phase comprised of 0.02 mol of 1-bromopentane in 50 cm<sup>3</sup> of toluene. All the typical reactions were carried out at 90 °C and 1000 rpm. This composition of the reaction mixture created three distinct and stable phases at the operating conditions. In the case of L–L PTC reactions, the effects of catalyst concentration and temperature were also studied to compare the enhancements in rates due to the creation of the third phase. The reactant concentrations were kept the same without any sodium chloride at the start of the reaction.

**2.3. Method of Analysis.** Samples were withdrawn periodically, and GC analyses were performed (Chemito Model 8510) by using a stainless steel column (3.25 mm × 4 m) packed with a liquid stationary phase of 10% OV-101. The conversion was based on the disappearance of 1-bromopentane in the organic phase. The products were confirmed by GC–MS.

**2.4. Determination of Composition of Third Phase.** The composition of the third phase was analyzed on gas chromatography using thermal conductivity detector (Chemito Model 8510) by using a stainless steel column (3.25 mm × 4 m) packed with a liquid stationary phase of 10% OV-17. The third phase at the end of reaction was found to contain 15.0% toluene, 30.0% TBAB, 1.5% 1-bromopentane, 0.8% 2'-hydroxyacetophenone, 1.9% 2'-pentyloxyacetophenone, and 50.36% water by weight. The amount of the water present in the third phase was analyzed by a Karl-Fisher apparatus. The appropriate details are given in Table 1. The distribution of catalyst at the end of the reaction is given in Table 2.

**2.5. Reaction Scheme.** The overall reaction is shown below. It was observed that there was no formation of any byproduct at any conversion levels in L–L–L PTC.



## 3. Results and Discussion

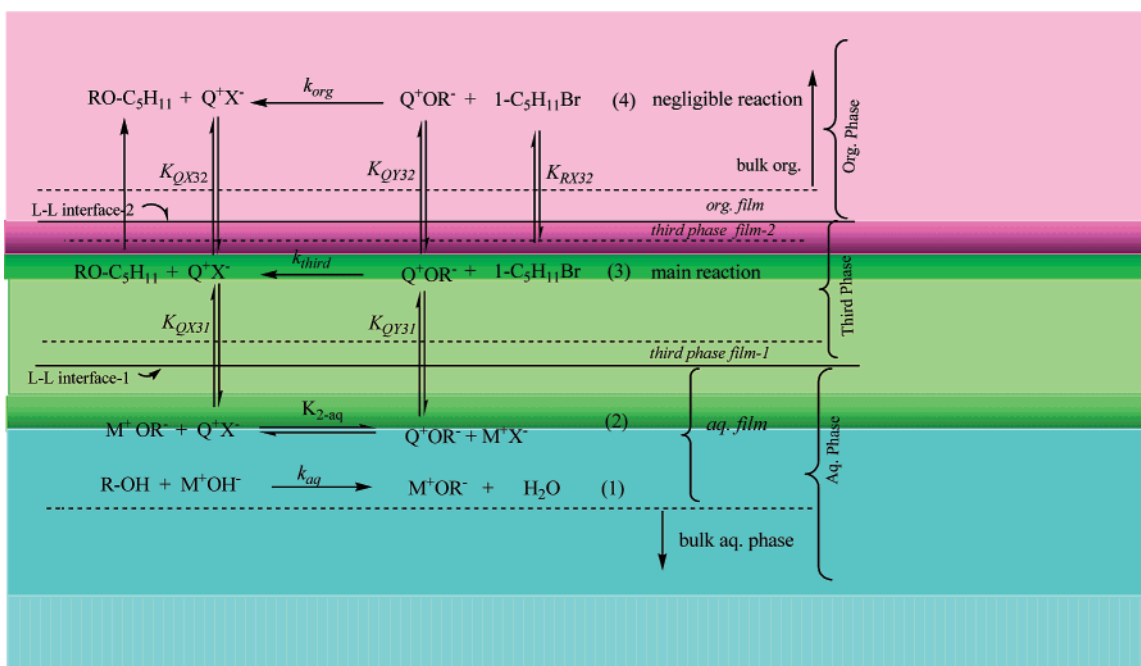
The L–L–L PTC experiments were conducted systematically to ascertain whether the reaction in the middle phase would be further enhanced and as to why there would be a 100% yield and selectivity to the desired product. In all cases, three distinct liquid phases were created.

**3.1. Reaction Mechanism.** The reaction mechanism is depicted in Scheme 1. Sodium 2-acetoxyphenate salt ( $M^+Y^-$ ) is generated in the aqueous phase by reaction 1, and then the anion exchange takes place between the quaternary salt ( $Q^+X^-$ ) and the phenate ( $M^+Y^-$ ) by reaction 2 in the aqueous phase (*phase-I*). This is an equilibrium reaction, and the

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**Scheme 1. L–L–L PTC mechanism**



Where,



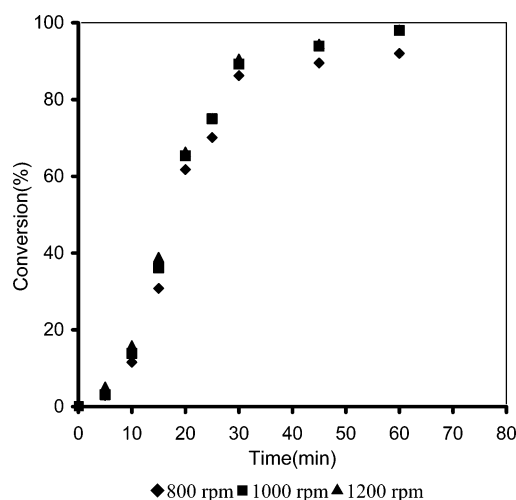
**Table 2. Distribution of catalyst<sup>a</sup>**

total catalyst added = 0.0093 mol
third phase = 0.002 79mol
aqueous phase = 0.006 51 mol
$\psi_{\text{third}}$ = mol fraction of catalyst in third phase with reference to original amount = 0.002 79/0.0093 = 0.3
$\psi_{\text{aq}}$ = mol fraction of catalyst in aqueous phase with reference to original amount = 0.006 51/0.0093 = 0.7
amount of 1-bromopentane taken = 0.02 mol
amount of 1-bromopentane in third phase = 0.000 15 mol
amount of 1-bromopentane in organic phase = 0.0198 mol

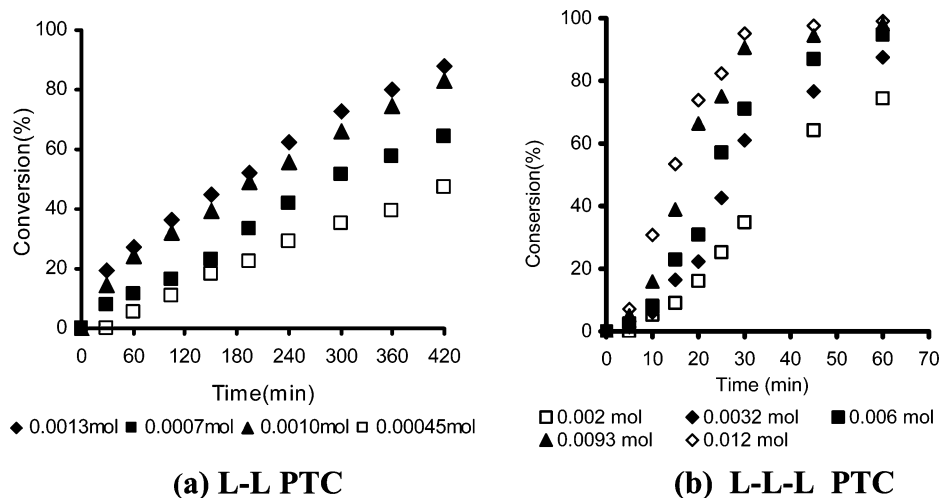
$$^a K_A = N_{\text{A-third}}V_{\text{org}}/N_{\text{A-org}}V_{\text{third}} = (0.000\ 15 \times 50)/(0.0198 \times 4) = 0.094.$$

quaternary phenate ( $\text{Q}^+\text{Y}^-$ ) formed in situ is transferred across the L–L interface-1 between aqueous phase and the third phase. There is also simultaneous transfer of 1-bromopentane from the organic phase (phase 2) to the third phase through the L–L interface-2. The main reaction takes place between  $\text{Q}^+\text{Y}^-$  and 1-bromopentane in the third phase as shown by reaction 3, and the product ether ( $\text{RO-C}_5\text{H}_{11}$ ) so generated is extracted into the organic phase. There is also distribution of  $\text{Q}^+\text{Y}^-$  in the organic phase, and thus reaction 4 can occur. However, its contribution to the overall rate is negligible. In developing the theoretical model for L–L–L PTC, thus a general approach would be to consider all three possibilities, namely, reaction in phase 1, phase 2, and phase 3 and determine their relative contributions to the overall rate of reaction. Since there was no hydrolysis of 1-bromopentane, either to 1-pentanol or condensation to form dipentyl ether, 1-bromopentane does not cross the L–L interface-1.

**3.2. Effect of Speed of Agitation.** To ascertain the influence of mass transfer resistance for the transfer of the reactants to the reaction phase, the speed of agitation was



**Figure 1. Effect of speed of agitation on conversion in L–L–L PTC. 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), NaOH (0.025 mol), NaCl (0.3 mol), TBAB (0.0093 mol), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>), temperature (90 °C).**

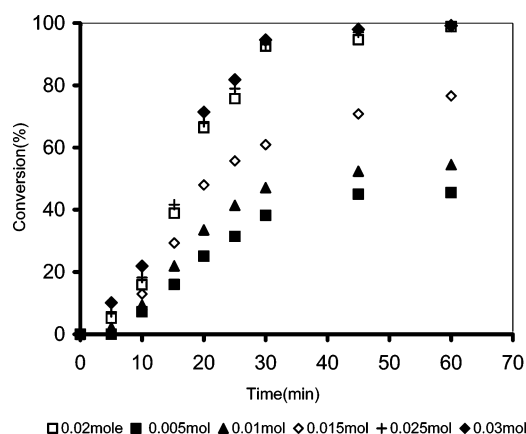


**Figure 2.** Comparison of effect of catalyst concentration in L-L versus L-L-L PTC. (a) L-L PTC: 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), sodium hydroxide (0.025 mol), water (25 cm<sup>3</sup>), toluene (25 cm<sup>3</sup>), temperature (90 °C), speed of agitation 1200 rpm. (b) L-L-L PTC: 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), NaOH (0.025 mol), NaCl (0.3 mol), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>), temperature (90 °C), speed of agitation 1200 rpm.

varied in the range 800–1200 rpm under otherwise similar conditions in the presence of TBAB as the catalyst (Figure 1). The conversion increased with increasing speed but remained practically the same at 1000 and 1200 rpm. Further increase in the speed of agitation had practically no effect on the conversion. Thus, all further experiments were carried out at 1200 rpm. This suggested that the mass transfer resistances associated with the four liquid films across the two L-L interfaces, as depicted in Scheme 1, were absent.

**3.3. Effect of Catalyst Concentration.** The comparison of rates of reactions using three liquid phases over two-liquid phases in PTC was done by conducting several experiments at different catalyst concentrations. Using the same concentrations of 2'-hydroxyacetophenone, 1-bromopentane and sodium hydroxide, the effect of catalyst concentration was studied in the range of  $4.5 \times 10^{-4}$  to  $1.3 \times 10^{-3}$  mol of TBAB at 90 °C, under L-L PTC (Figure 2 a). The rate of reaction increases with increase in catalyst concentration and the overall conversion also increased from 42.9% to 86.3% in 7 h. The initial rates of reaction were linear in catalyst concentration, which is typical of PTC. Three distinct phases appeared when the concentration of TBAB was raised to  $0.2 \times 10^{-3}$  mol with addition of 0.3 mol of NaCl. Thus, the concentration of TBAB was varied from  $2 \times 10^{-3}$  mol to  $1.2 \times 10^{-2}$  mol, keeping all other parameters constant under L-L-L PTC (Figure 2b). The rates of reaction are dramatically increased by orders of magnitude and almost complete conversions could be realized within 25 min for  $1.2 \times 10^{-2}$  mol of TBAB. Only the desired product was formed. Indeed, the rates of reaction at  $9.30 \times 10^{-3}$  mol of TBAB were almost close to those obtained with  $1.2 \times 10^{-2}$  mol, thereby suggesting the onset of mass transfer resistance. Therefore for all further experiments, the amount of TBAB was fixed at  $9.30 \times 10^{-3}$  mol.

**3.4. Effect of Sodium Hydroxide Concentration.** The sodium hydroxide amount was varied from 0.005 to 0.03 mol under otherwise similar reaction conditions (Figure 3). The rate of reaction increased with sodium hydroxide

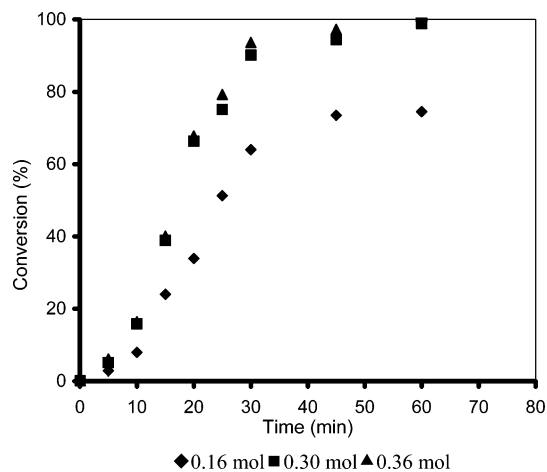


**Figure 3.** Effect of sodium hydroxide concentration in L-L-L PTC. 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), NaCl (0.3 mol), TBAB (0.0093 mol), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>), temperature (90 °C).

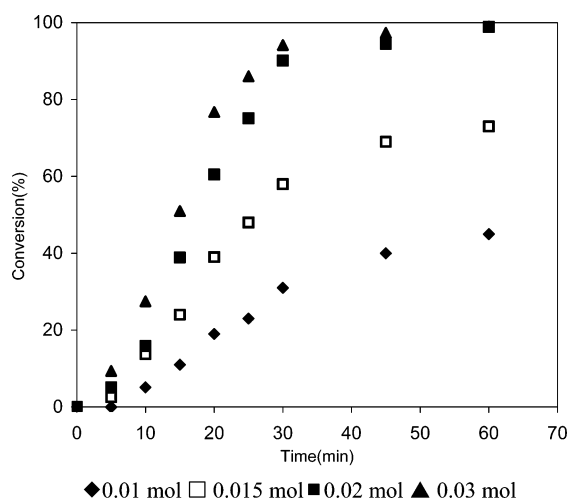
concentration because there is a higher rate of generation of  $Q^+Y^-$  which gets immediately extracted into the third phase. The best conversion was obtained with 0.025 mol of NaOH. Further increase in the NaOH concentration did not have any significant effect on the conversion, since all 2'-hydroxyacetophenone was converted.

**3.5. Effect of Sodium Chloride Concentration.** The amount of sodium chloride was varied from 0.16 to 0.36 mol under similar reaction conditions (Figure 4). As the concentration of sodium chloride was increased, the rate of the reaction increased; since the aqueous phase was saturated with NaCl, a greater amount of TBAB was driven into the third phase. Consequently the concentration of quaternary phenate,  $Q^+Y^-$  increases resulting into higher rates of reaction in the third phase. When the concentration of sodium chloride was much less, the volume of the third phase was also less because the aqueous phase was not saturated with sodium chloride and there was no salting out of TBAB. After a certain concentration of NaCl, no further increases in the rate of reaction was observed.





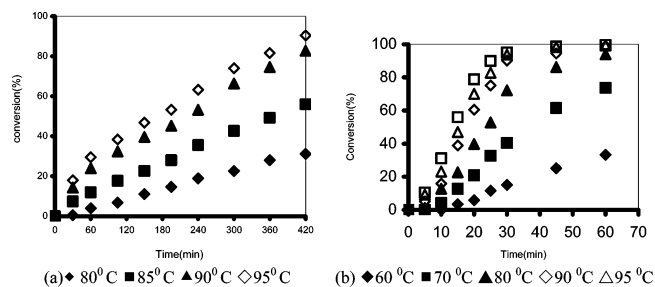
**Figure 4.** Effect of sodium chloride loading in L-L-L PTC. 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), NaOH (0.025 mol), TBAB (0.0093 mol), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>), temperature (90 °C).



**Figure 5.** Effect of mole ratio in L-L-L PTC. 2'-Hydroxyacetophenone:sodium hydroxide (1.0:1.25), 1-bromopentane (0.02 mol), NaCl (0.3 mol), TBAB (0.0093 mol), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>), temperature (90 °C).

**3.6. Effect of Mole Ratio.** The amount of sodium 2'-acetoxyphenate was varied in the range of 0.01 to 0.03 mol, which corresponded to a mole ratio of 0.5 to 1.5 of 2'-acetoxyphenate to 1-bromopentane by keeping the amount of 1-bromopentane constant (Figure 5). Increasing the concentration of sodium phenate leads to an increase in the concentration of Q<sup>+</sup>Y<sup>-</sup> which in turn increases the rates of reaction substantially.

**3.7. Effect of Temperature.** The effect of temperature on the reaction between 2'-hydroxyacetophenone and 1-bromopentane was studied under both L-L PTC and L-L-L PTC. The temperature was varied from 60 °C to 95 °C. It was observed that the rates of reaction increased with increasing temperature under L-L PTC (Figure 6 a). The L-L PTC reaction takes place in the organic phase. It was studied independently in great detail<sup>13</sup> and modeled. The apparent energy of activation was found to be 23.96 kcal/mol. In the case of L-L-L PTC, the locale of the reaction was mainly the third phase, and thus, there was always some induction period up to 5 min at lower temperature to initiate



**Figure 6.** Comparison of effect of temperature on L-L and L-L-L PTC. L-L PTC: 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), Sodium hydroxide (0.025 mol), TBAB (1.08 × 10<sup>-3</sup> mol), water (25 cm<sup>3</sup>), toluene (25 cm<sup>3</sup>), speed of agitation 1200 rpm. L-L-L PTC: 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), NaOH (0.025 mol), NaCl (0.3 mol), TBAB (0.0093 mol), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>).

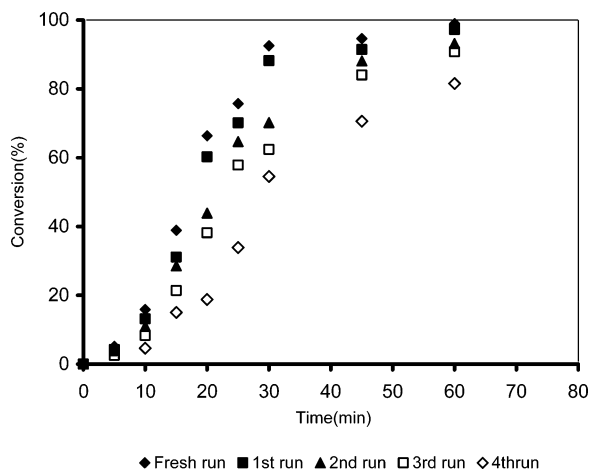
the reaction. At higher temperature, the induction period was reduced. Further, the nature of all points in Figures 1–6 show that the initial conversions are very high and, after 20 min of reaction time, the conversions start tapering. This is due to fact that the way in which the experiments were conducted required some time to form three separate phases. This will be explained further after the discussion on kinetic modeling.

**3.8. Reusability of Catalyst.** After completion of the experiment, the stirring was stopped and the reaction mixture was allowed to cool to room temperature. When phases were clearly separated, the organic phase containing the product was removed. Two strategies were adopted.

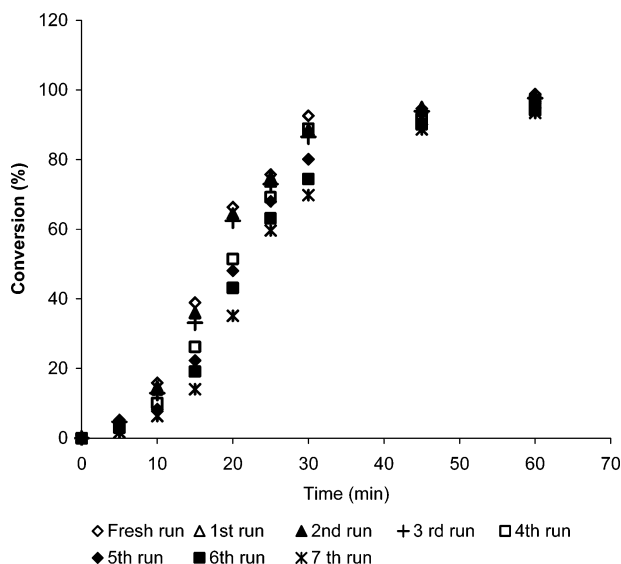
**3.9.1. Method A: Reuse of Third Phase Only.** The third phase was separated and reused by adding fresh aqueous and organic phase reactants. Thus, the third phase was used four times starting with the fresh use. Since both the aqueous and organic phases were freshly used, there was a loss of the catalyst along with the discarded organic and aqueous phases. There was again a distribution of catalyst available from the third phase to the organic phase which had reduced the volume of the third phase and hence the rates of reaction. The subsequent experiments with replenished aqueous and organic phases had a smaller quantity of available catalyst than that in the previous run, and hence rates of reaction were found to decrease correspondingly (Figure 7).

**3.9.2. Method B: Reuse of the Third and Aqueous Phase Only.** Fresh organic solvent was added along with a known amount of 1-bromopentane. The third phase and also the aqueous phase from the previous experiment were reused. Thus, the catalyst and aqueous phases were reused seven times, and the organic phase was replenished every time. The organic phase containing the product with an insignificant quantity of catalyst was removed each time. Therefore, when the second run was conducted with 0.02 mol of 1-bromopentane, almost all catalyst was available for reaction and therefore the loss in conversion is marginal (Figure 8).

**3.10. Kinetics of Reaction.** For the three-phase system, the organic reactant 1-bromopentane (A) is distributed between an organic phase and the third phase but is not in an aqueous phase due to insolubility. Scheme 1 shows this very clearly. Therefore, the reaction can be classified into three types as proposed by us,<sup>5</sup> namely: (a) Type I, the reaction in the organic phase (normal L-L PTC); (b) Type



**Figure 7.** Effect of reusability of catalyst (reusability of catalyst phase only). 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), NaOH (0.025 mol), NaCl (0.3 mol), TBAB (0.0093 mol), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>), temperature (90 °C).



**Figure 8.** Effect of reusability of catalyst in L-L-L PTC (reusability of catalyst phase with aqueous phase). 2'-Hydroxyacetophenone (0.02 mol), 1-bromopentane (0.02 mol), NaOH (0.025 mol), NaCl (0.3 mol), TBAB (0.0093 mol), temperature (90 °C), toluene (50 cm<sup>3</sup>), water (50 cm<sup>3</sup>).

II, the reaction at the interface between an organic phase and an aqueous phase or in the bulk aqueous phase (inverse L-L PTC); (c) Type III, the reaction in the third phase.

The mole balance for A is

$$N_{A0} = N_{A-org} + N_{A-third} \quad (1)$$

where  $N_{A0}$  is the total moles of A which is distributed between the organic ( $N_{A-org}$ ) and the third phase ( $N_{A-third}$ ).

When the distribution of A between an organic phase and a third phase is at equilibrium conditions, the distribution coefficient of A is defined as follows:

$$K_A = \frac{C_{A-third}}{C_{A-org}} = \frac{N_{A-third} V_{org}}{N_{A-org} V_{third}} \quad (2)$$

where  $C_A$  stands for concentration of A (1-bromopentane);

$V_{org}$  and  $V_{third}$  are the volumes of the organic and third phases, respectively.

The following equation can be obtained from eqs 1 and 2.

$$N_{A0} = N_{A-org} \left( 1 + K_A \frac{V_{third}}{V_{org}} \right) \quad (3)$$

Since the reaction rate is assumed to be proportional to the concentration of A and the amount of catalyst, the overall reaction rate can be expressed by the summation of respective rates for the three types: I, II, III.

$$\begin{aligned} -\frac{dN_A}{dt} &= k_{org} N_{Q-org} C_{A-org} + k_{inter} N_{Q-aq} C_{A-org} + k_{third} N_{Q-third} C_{Athird} \\ &= (k_{org} \psi_{org} + k_{inter} \psi_{aq} + k_{third} K_A \psi_{third}) N_{Q0} C_{A-org} \end{aligned} \quad (4)$$

where  $\psi$ 's are mole fractions of catalyst present in the respective phases, based on the mol of catalyst  $N_{Q0}$  added initially.

When eq 4 is integrated, eq 5 is obtained:

$$(1 - X_A) = \frac{N_{A-org}}{N_{A0}} = \frac{V_{org}}{V_{org} + K_A V_{third}} \exp(-k_{obs} \omega t) \quad (5)$$

where  $N_{A0}$  are the mol of A originally taken and  $X_A = (N_{A0} - N_A)/N_{A0}$  is the fractional conversion of A,

$$k_{obs} = \frac{V_{org}}{V_{org} + K_A V_{third}} (k_{org} \psi_{org} + k_{inter} \psi_{aq} + k_{third} K_A \psi_{third}) \quad (6)$$

and

$$\omega = \frac{N_{Q0}}{V_{org}} \quad (7)$$

When  $K_A V_{third}$  is negligibly small compared to  $V_{org}$ , eq 6 can be approximated as follows:

$$k_{obs} = (k_{org} \psi_{org} + k_{inter} \psi_{aq} + k_{third} K_A \psi_{third}) \quad (8)$$

Taking the logarithm of eq 5 leads to eq 9

$$-\ln(1 - X_A) = k_{obs} \omega t \quad (9)$$

For a given concentration of catalyst,  $\omega$  and  $k_{obs}$  are constant. Therefore,

$$-\ln(1 - X_A) = k_1 t \quad (10)$$

where

$$k_1 = k_{obs} \omega \quad (11)$$

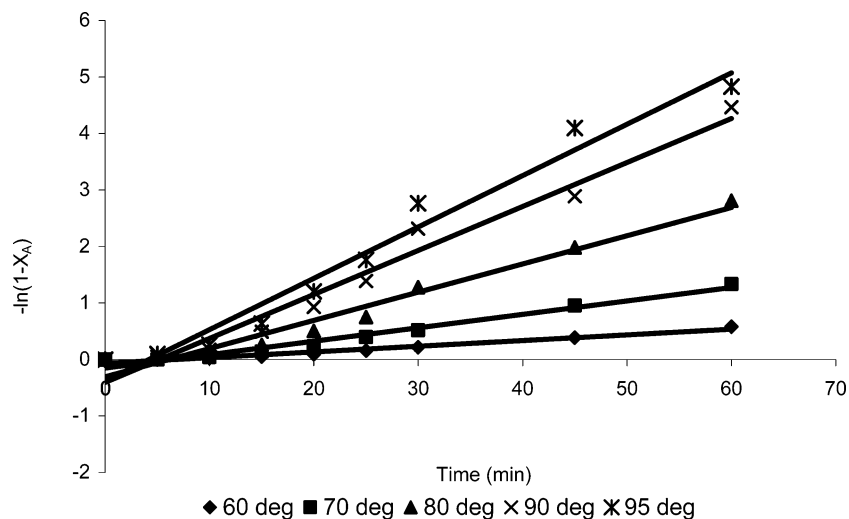
For respective types of mechanisms, the following equations are obvious:

$$k_{obs} = k_{org} \text{ for Type 1 } (\psi_{org} = 1.0); \text{ it is normal L-L PTC} \quad (12)$$

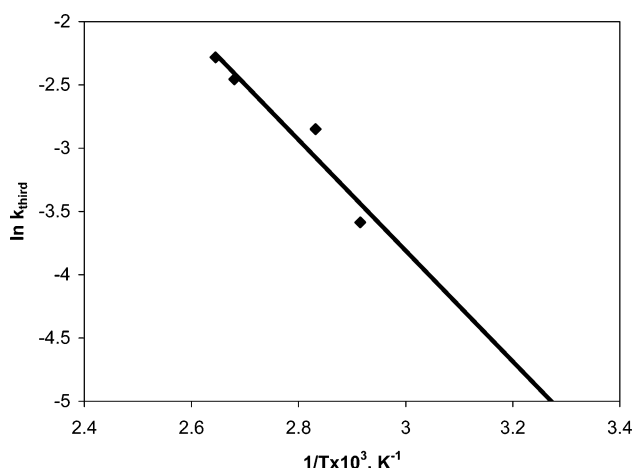
$$k_{obs} = k_{aq} \text{ for Type 2 } (\psi_{aq} = 1.0); \text{ it is inverse L-L PTC} \quad (13)$$

$$k_{obs} = k_{third} K_A \text{ for Type 3 } (\psi_{third} = 1.0); \text{ it is L-L-L PTC} \quad (14)$$

The kinetic parameters  $k_{org}$ ,  $k_{aq}$ , and  $k_{third}$ ; and  $K_A$  can be determined from experiments. A plot of  $-\ln(1 - X_A)$  against



**Figure 9.** Validity of kinetic model at various temperatures in L–L–L PTC. (Model is fitted after the induction period in each case.)



**Figure 10.** Arrhenius plot for the reaction of 2-hydroxyacetophenone with 1-bromopentane under L–L–L PTC.

time is shown at various temperatures to validate the first-order rate (Figure 9). There is an induction period in each after the organic phase reactant is added, since the third phase formation takes sometime and then the reaction takes off. As the temperature is increased, there is a reduction in the induction period. The rates of reaction are very high, and the reaction goes to almost complete conversion within 20–30 min, as the case maybe. Thus, there is a tapering of the conversion, and therefore the conversion versus time curves appear to be S-shaped. Thus, we have now excluded the induction period as well as very high conversions beyond 90% for fitting the model. The model fits very well with correlation coefficients of  $>0.98$ . The calculated rate constants were used to make the Arrhenius plot (Figure 10) from which an activation energy of 8.67 kcal/mol was obtained, which also suggests that there was no mass transfer resistance for the transfer of reactants to the middle phase and products into the respective organic and aqueous phases. This value can now be compared with an apparent activation energy of 23.96 kcal/mol obtained by using L–L PTC. The reduction in activation energy is due to the change of the locale of reaction and the microenvironment created within the third phase.

**3.11. Comparison of L–L vs L–L–L.** In the case of two-liquid phases (the normal L–L PTC), at a catalyst concentration just below the critical concentration required to generate three distinct liquid phases, the reaction reaches a maximum of 82% conversion in 7 h at 90 °C. On the contrary with the creation of the third phase, by further addition of either sodium chloride or catalyst beyond the critical value, the 2'-pentyloxyacetophenone was 100%. Thus, there is manifold increase in productivity of the same reactor with total selectivity. This third phase was reusable many times. The activation energy value is also reduced substantially in L–L–L PTC. This methodology is an excellent example of green chemistry, wherein waste minimization is desired.<sup>14</sup>

#### 4. Synthesis of Various Aromatic Ethers under L–L and L–L–L PTC

Substituted aromatic ethers are high added-value chemicals extensively used in various industries as additives of petroleum chemicals and extractants.

O-Alkylation of a variety of phenols was carried out using 1-bromopentane using tetrabutylammonium bromide (TBAB) as the phase transfer catalyst in L–L biphasic and L–L–L triphase. Compared to L–L PTC, the L–L–L PTC offers much higher rates of reaction, better selectivities, and repeated use of catalyst. The selectivities for the desired products were 100% (Table 3).

#### 5. Conclusion

L–L PTC can be elegantly modified to convert into L–L–L PTC, to recover and reuse the catalyst and also to enhance selectivity, thereby improving profitability and environmental benefits. This work has addressed the novelties of kinetics and the mechanism of the synthesis of 2'-pentyloxyacetophenone from 2'-hydroxyacetophenone and 1-bromopentane under L–L and L–L–L PTC. A detailed kinetic study has been done for the above system. The effects of different parameters such as speed of agitation, temperature, catalyst loading, reusability of catalyst rich phase, and mole

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**Table 3. Etherification of substituted phenols with 1-bromopentane under L–L PTC and L–L–L PTC**

No.	Substrate	Product	L–L PTC	L–L–L PTC
			Conversion (%) 7 h	Conversion (%) 1h
1.			82.9	100
2.			61.5	82.6
3.			89.4	99.1
4.			48.7	77.1
5.			92.7	100
6.			98.4	100
7.			98.9	100

ratio were studied. The catalyst can be reused. It was observed that the reaction rates were intensified in the L–L–L PTC vis-à-vis the L–L PTC. Different strategies could be employed to reuse the catalyst phase very effectively.

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### Nomenclature

$C_{Ao}$	feed concentration of 1-bromopentane in the organic phase, mol/cm <sup>3</sup>
$C_{A-org}$	concentration of 1-bromopentane in the organic phase, mol/cm <sup>3</sup>
$C_{A-third}$	concentration of 1-bromopentane in the third phase, mol/cm <sup>3</sup>
$K_A$	distribution coefficient of 1-bromopentane between the organic phase and the third phase, dimensionless
$k_{inter}$	rate of reaction at the interface between the organic and aqueous phases, cm <sup>3</sup> /(mol of catalysts)
$k_{obs}$	observed first-order reaction rate constant, cm <sup>3</sup> /(mol of catalysts)
$k_{org}$	rate of reaction in the organic phase, cm <sup>3</sup> /(mol of catalysts)
$k_{third}$	rate of reaction in the third phase, cm <sup>3</sup> /(mol of catalysts)
$N_{Ao}$	feed mole of 1-bromopentane, mol
$N_{A-org}$	mol of 1-bromopentane in the organic phase, mol
$N_{A-third}$	mol of 1-bromopentane in the third phase, mol
$N_{Qo}$	feed mol of catalyst, mol
$N_{Q-aq}$	mol of catalyst in the aqueous phase, mol

$N_{Q-org}$	mol of catalyst in the organic phase, mol
$N_{Q-third}$	mol of catalyst in the third phase, mol
$K_{QX31}$	distribution constant for QX between phase 3 and phase 1, dimensionless
$K_{QX32}$	distribution constant for QX between phase 3 and phase 2, dimensionless
$K_{QY31}$	distribution constant for QY between phase 3 and phase 1, dimensionless
$K_{QY32}$	distribution constant for QY between phase 3 and phase 2, dimensionless
$K_{RX32}$	distribution constant for RX between phase 3 and phase 2, dimensionless
$t$	time of reaction, min
$\nu_{third}$	volume of third phase per feed mol of catalyst, cm <sup>3</sup> /mol of catalyst
$V_{third}$	volume of the third phase, cm <sup>3</sup>
$V_{org}$	volume of organic phase, cm <sup>3</sup>
$\omega$	concentration of catalyst based on the organic phase, mol/cm <sup>3</sup> of organic
$\psi_{aq}$	mole fraction of catalyst in the aqueous phase to the feed of catalyst, dimensionless
$\psi_{org}$	mole fraction of catalyst in the organic phase to the feed of catalyst, dimensionless
$\psi_{third}$	mole fraction of catalyst in the third phase to the feed of catalyst, dimensionless

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