

Phase transfer catalysed alkylation of 2'-hydroxy acetophenone with 1-bromopentane: Kinetics and mechanism of liquid–liquid reaction

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Abstract

Studies in the preparation of aromatic ethers have proven to be quite attractive because of extensive use of these compounds in the dyestuff, perfume flavor, agriculture and pharmaceutical industries. The novelties of phase transfer catalysed alkylation of 2'-hydroxy acetophenone with 1-bromopentane were studied in detail in a biphasic system with tetrabutyl ammonium bromide (TBAB) as the catalyst. The effect of various parameters was studied systematically to understand the conversion patterns, product distribution and selectivity of desired product. A mathematical model has been proposed on the basis of the theory of mass transfer with chemical reaction in two phases. The results are novel and have industrial relevance.

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Keywords: Phase transfer catalysis; Alkylation; Liquid–liquid reactions; Selectivity; Kinetics; Mechanism; 2'-Hydroxy acetophenone; 1-Bromopentane; 2'-Pentyloxyacetophenone; 2-Acylphenol; Selectivity; Heterogeneous reactions

1. Introduction

Substituted aromatic ethers are valuable as perfume and flavor compounds, fine chemicals, solvents and precursors of a number of chemicals. These ethers can be synthesized on industrial scale by a variety of techniques including acid catalysis and phase transfer catalysis (PTC). PTC has been quite successful for C, N, O and S alkylation in fine chemical industries, apart from dehydrohalogenations [1–3]. Ethers are synthesized by alkylation reactions using liquid–liquid (PTC) [4] and liquid–liquid–liquid (L–L–L) PTC [5,6], cation-exchange resins [7], bases [8,9], clays [10] and isomerization [11]. The novelties of liquid–liquid (L–L) [12–14], solid–liquid (S–L) [15–17], solid–liquid–omega–liquid (S–L(ω)–L) [18–19] and L–L–L PTC [9,10] reactions have been studied in our laboratory for reactions of importance in perfumery, pharmaceutical and agrochemical industries. The advantages of multiple phase vis-à-vis the conventional two-liquid PTC have also been discussed [7].

The current work deals with the synthesis of 2'-pentyloxy acetophenone (or 2-acylphenyl pentyl ether) from 2'-hydroxy acetophenone (2-acylphenol) and 1-bromopentane under liquid–liquid PTC. 2'-Pentyloxy acetophenone is used as an intermediate in the synthesis of fungicides [20]. Covello and Pisepo [21] have reported the synthesis of 2'-pentyloxy acetophenone from 2'-hydroxy acetophenone, sodium hydroxide and 1-bromopentane in methanol at reflux temperature leading to 75% conversion. Except the above-mentioned work, there is no direct report in the published literature on the details of mechanism and kinetics of etherification of 2'-hydroxy acetophenone using phase transfer catalysis. Thus, the current work addresses L–L PTC catalysed reaction of 2'-hydroxy acetophenone with 1-bromopentane to produce 2'-pentyloxy acetophenone, including mechanism and kinetic modeling.

2. Experimental

2.1. Materials

2'-Hydroxy acetophenone, 1-bromopentane, toluene and sodium hydroxide, all of AR grade, were obtained from Merck Pvt. Ltd., Mumbai, India. Tetrapropyl ammonium bromide (TPAB), ethyl tripropyl phosphonium bromide (ETPB),

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Nomenclature

$[A]_{\text{org}}$	concentration of 1-bromopentane in the organic phase (mol/cm ³)
ΔG	Gibb's free energy (kcal/mol)
ΔH	enthalpy (kcal/mol)
k_{org}	second order rate constant of forward reaction in organic phase (cm ³ /(mol s))
$K_{2\text{-aq}}$	equilibrium constant for anion exchange in aqueous phase
K_e	overall ion exchange reaction equilibrium constant
K_{QX}	distribution constant for ion-pair Q^+X^- between organic and aqueous phase
K_{QY}	distribution constant for ion-pair Q^+Y^- between organic and aqueous phase
N_{Q}	total moles of catalyst added to the system at time $t = 0$ (mol)
$[N_{\text{Q}}]_{\text{org}}$	mole of catalyst in the organic phase (mol)
$[Q^+X^-]_{\text{org}}$	concentration of quaternary salt in the organic phase (mol/cm ³)
$[Q^+X^-]_{\text{aq}}$	concentration of quaternary salt in the aqueous phase (mol/cm ³)
$[Q^+OR^-]_{\text{aq}}$	concentration of nucleophile ion-pair in the aqueous phase (mol/cm ³)
$[Q^+OR^-]_{\text{org}}$	concentration of nucleophile ion-pair with quaternary salt in the organic phase (mol/cm ³)
ΔS	entropy (kcal/(mol K))
T	temperature (K)
V_{aq}	volume of the aqueous phase (cm ³)
V_{org}	volume of the organic phase (cm ³)
X^-	leaving group
X_A	fractional conversion of reactant A
Y^-	nucleophile

Greek letter

ϕ	fraction of quaternary cation in the organic phase
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tetraethyl ammonium bromide (TEAB), tetrabutyl ammonium bromide (TBAB) were obtained as gift samples from m/s Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India.

2.2. Experimental procedure

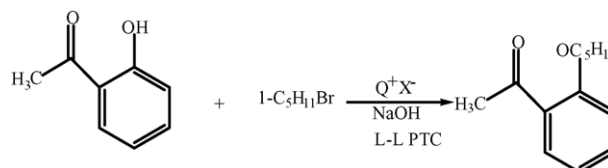
All the experiments were conducted in a 5 cm i.d. fully baffled mechanically agitated reactor of 100 cm³ capacity, equipped with four baffles and a six-bladed turbine impeller and a reflux condenser. The entire reactor assembly was immersed in a thermostatic oil bath, which was maintained at a desired temperature with an accuracy of ± 1 °C. The sodium salt of 2'-hydroxy acetophenone (also called 2-acylphenol) was prepared in situ by taking little over stoichiometric excess of NaOH and then the reactant 1-bromopentane dissolved in toluene was added to the reactor. A typical run consisted of 0.02 mol 1-bromopentane in 25 cm³ toluene and 0.02 mol of 2'-hydroxy acetophenone and

0.025 mol of sodium hydroxide in 25 cm³ water at 90 °C. The reaction mixture was agitated at 1000 rpm and a known amount of the catalyst was added at the reaction temperature. Initial sample was withdrawn, and the reaction was monitored by periodic sample.

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 \times 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 product formation was confirmed by GC-MS. As the reaction was carried out under controlled conditions, there was no formation of 1-pentanol, which is expected as reaction was carried out in the presence of a base. There was 100% selectivity to the ether. In all cases, experiments were repeated thrice and an average value was taken for fitting the model. There is an error of 3–5% in each data point.

2.4. Reaction scheme

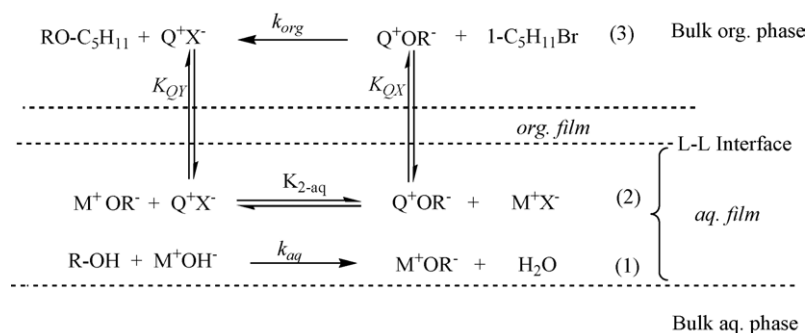


3. Results and discussion

3.1. Proposed mechanism and rate equation

The following mechanism is discussed with reference to the general L-L PTC (Scheme 1). The sodium salt of 2'-hydroxy acetophenone was formed in situ by its reaction with aqueous sodium hydroxide as shown in step (1). Indeed, as discussed in the experimental section, sodium 2-acylphenolate was formed first by taking slight excess of NaOH and then the organic reactant in toluene was added. Then the catalyst was added at the reaction temperature. Thus, there is the anion exchange reaction with sodium phenolate. The quantity of OH⁻ in the aqueous phase was not sufficient to form Q⁺OH⁻ in preference over Q⁺OR⁻. As discussed by Dehmlow et al. [22], the formation and extractability of Q⁺OH⁻ in the organic phase was difficult (Scheme 1).

2'-Hydroxy acetophenone (ROH) was converted in the presence of an aqueous alkali into the corresponding phenate (RO⁻M⁺) salt in situ and therefore no free ROH was present. The pH of the aqueous phase was always alkaline. The aqueous phase reaction produces the ion-pair (RO⁻Q⁺) (step (2)), which is instantaneously transferred to the organic phase due to high lipophilicity of the catalyst cation. It reacts with 1-bromopentane (C₅H₁₁Br) to produce the ether ROC₅H₁₁ in the organic phase (step (3)) and the regenerated catalyst Q⁺X⁻ is transferred across

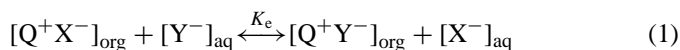


Where,



Scheme 1. *O*-Alkylation of 2'-hydroxyacetophenone with 1-bromopentane under L-L PTC.

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 equilibria across the interface can be expressed 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 equation:



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

The individual ion-pair distribution constants between organic and aqueous phases and their relationship with K_e and K_{2-aq} are given by:

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

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

$$K_e = \frac{K_{QY}[Q^+Y^-]_{aq} [X^-]_{aq}}{K_{QX}[Q^+X^-]_{aq} [Y^-]_{aq}} = \frac{K_{QY}}{K_{QX}} K_{2-aq} \quad (3)$$

$$K_e \frac{K_{QX}}{K_{QY}} = \frac{[Q^+Y^-]_{aq} [X^-]_{aq}}{[Q^+X^-]_{aq} [Y^-]_{aq}} = K_{2-aq} \quad (4)$$

Eq. (4) represents the equilibrium constant for the ion-pair exchange reaction in the aqueous phase represented by reaction (2) in Scheme 1.

If the overall reaction rate is controlled by the reaction in the organic phase, then the rate of reaction of 1-bromopentane (A) in the organic phase is given by:

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

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

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

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:

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

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

From Eq. (7):

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

Defining:

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

Eq. (9) is converted to the following:

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

Eq. (5) is rewritten with the help of Eq. (11) as:

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

and the concentrations terms $[A]_{org}$, $[X^-]_{org}$ and $[Y^-]_{aq}$ can be substituted in terms of X_A , the fractional conversion of A.

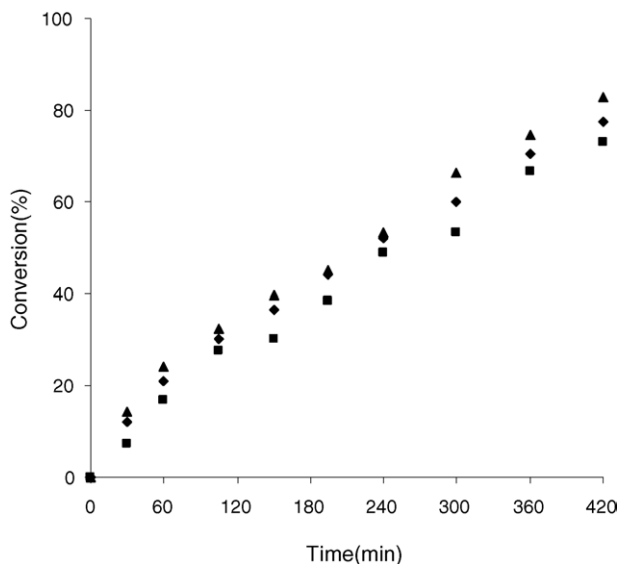


Fig. 1. Effect of speed of agitation. 2'-Hydroxy acetophenone (0.02 mol), 1-bromopentane (0.02 mol), sodium hydroxide (0.025 mol), TBAB (1.08×10^{-3} mol), water (25 cm³), toluene (25 cm³) and temperature (90 °C). (■) 800 rpm; (◆) 1200 rpm; (▲) 1400 rpm.

In terms of fractional conversion of 1-bromopentane based on initial moles, X_A , the rate equation is:

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

After separation of variables and integration, Eq. (13) leads to:

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

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

Thus, plot of $\frac{X_A}{(1 - X_A) \ln(1 - X_A)}$ versus $\frac{t}{\ln(1 - X_A)}$, can be made to get a slope of $K_e k_{\text{org}} \phi [N_Q]_{\text{org}}$ (time⁻¹) and intercept of $[K_e - 1]$. Thus, from these two quantities, the two unknowns k_{org} and K_e can be calculated.

3.2. Effect of speed of agitation

To ascertain the influence of external mass transfer resistance for the transfer of reactants to the reaction phase, the speed of agitation was varied in the range of 800–1400 rpm under otherwise similar conditions using TBAB as the catalyst (Fig. 1). Preliminary experiments have suggested that TBAB was the best catalyst, which will be discussed later. It was observed that the conversion of 1-bromopentane increased with the speed of agitation from 800 to 1200 rpm. However, there was no significant increase in the conversion of 1-bromopentane, when the speed of agitation was further increased from 1200 to 1400 rpm. In order to ensure that the reaction is kinetically controlled all sub-

sequent experiments were carried out at a speed of agitation 1200 rpm.

3.3. Efficiency of various catalysts

Various phase transfer catalysts such as TBAB, TPAB, ETTPPB and TEAB were examined to evaluate their performance. The conversion varied markedly with the type of catalyst because different types of PTC exhibit different activities due to different solubilities of the ion-pair in presence of catalyst in the organic phase, which in turn can be attributed to the nature of quaternary salt. Among these, tetrapropyl ammonium bromide, ethyl tripropyl phosphonium bromide, tetraethyl ammonium bromide showed very less activity, which was far less as compared to tetrabutyl ammonium bromide (Fig. 2). This can be attributed to the more lipophilic nature of TBAB as compared to other catalysts. TBAB facilitates the transfer of nucleophilic anions into organic phase. The experimental data were fitted to test Eq. (14) using Polymath 5.1 and the values of K_e , $K_e k_{\text{org}} \phi [N_Q]_{\text{org}}$, k_{org} were obtained. To evaluate the value of ϕ , independent experiments were performed using TBAB as the catalyst. The reaction was performed by taking the reactant as had been the case with the standard reaction, the only difference being the absence of 1-bromopentane reactant. The value of ϕ was found to be 0.75. This also demonstrates that the quaternary cation is mostly distributed in the organic phase for L–L PTC. This is also supported by comparing the value of K_e obtained by plotting Eq. (14) Polymath. The highest value of K_e obtained for TBAB, corroborated our findings that TBAB was in fact the best catalyst (Table 1). Eq. (14) can also be modified to get the plot of this model using values of K_e , $K_e k_{\text{org}} \phi [N_Q]_{\text{org}}$, k_{org} and it shows a very good fit (Fig. 3). Further, plots were also made by using Eq. (15) to get

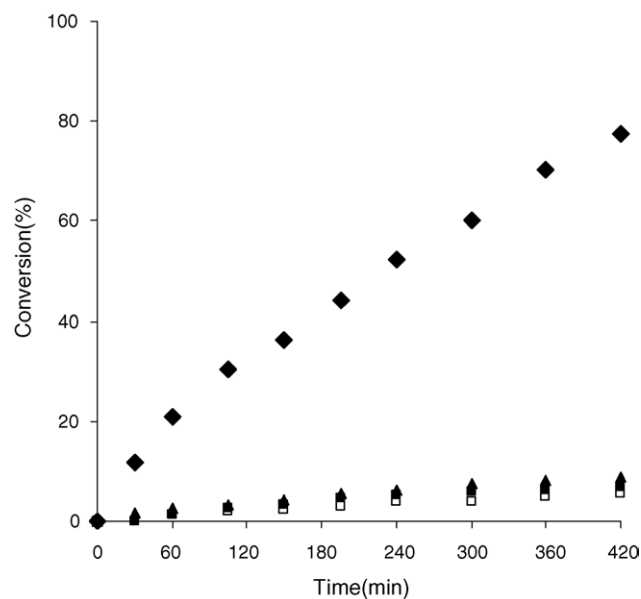


Fig. 2. Effect of type of catalyst. 2'-Hydroxy acetophenone (0.02 mol), 1-bromopentane (0.02 mol), sodium hydroxide (0.025 mol), catalyst loading (1.08×10^{-3} mol), water (25 cm³), toluene (25 cm³), temperature (90 °C) and speed of agitation (1200 rpm). (◆) TBAB; (■) TPAB; (□) TEAB; (▲) ETTPPB.

Table 1
Model fitting for etherification of 2'-pentyloxy acetophenone with 1-bromopentane for different catalysts

	TBAB	TPAB	ETPPB	TEAB
K_e	1.99	1.72	1.26	1.29
$K_e k_{org} \phi [N_Q]_{org}$	0.0045	0.0036	0.0014	0.0015
$k_{org} \phi$	52.34	49.48	26.26	27.48

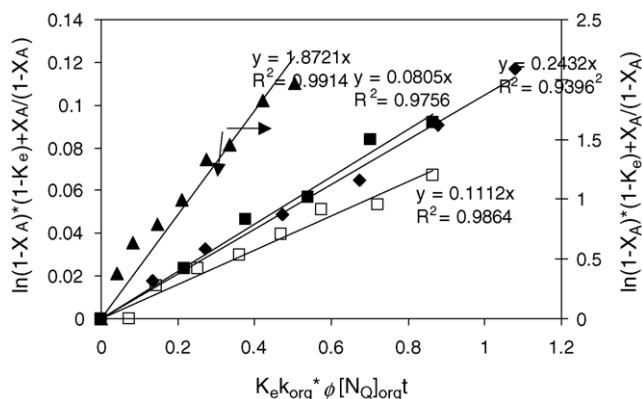


Fig. 3. Model validation for different catalysts. (■) TPAB; (▲) ETPB; (□) TEAB; (◆) TBAB.

independently the value of K_e , which was in close agreement with that formed by Polymath.

3.4. Effect of phase volume ratio

Considering the results obtained for the speed of agitation, the effect of phase volume ratio of organic to aqueous phase was studied, at 1.5:1.0, 1.0:1.0 and 1.0:1.5 under otherwise similar experimental conditions. The moles of all reactants and catalyst added were kept constant. Fig. 4 shows that when the volume

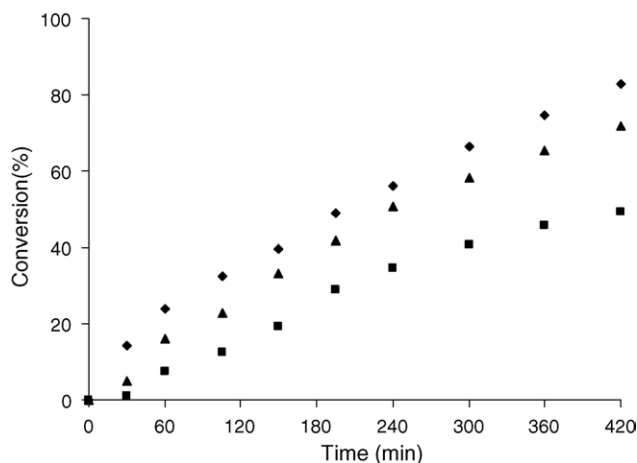


Fig. 4. Effect of phase volume ratio. 2'-Hydroxy acetophenone (0.02 mol), 1-bromopentane (0.02 mol), sodium hydroxide (0.025 mol), TBAB (1.08×10^{-3} mol), temperature (90°C), speed of agitation (1200 rpm). (◆) 1.0:1.0; (■) 1.5:1.0; (▲) 1.0:1.5.

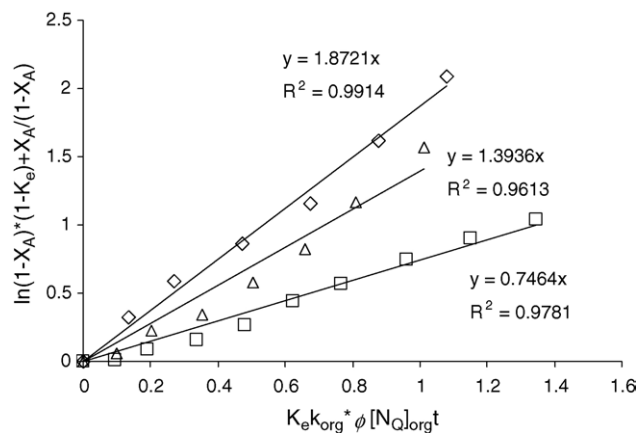


Fig. 5. Model validation for different phase volume ratio. (◆) 1.0:1.0; (□) 1.5:1.0; (△) 1.0:1.5.

ratio of organic to aqueous phase was 1.5:1, the partitioning of Q^+AcPhO^- in the organic phase was the least and hence the conversions were lowest. When the phase ratio of the organic to aqueous phase was fixed at 1:1, the best conversion values were obtained. Under these conditions, it was observed that organic phase was the dispersed phase and the aqueous phase was the continuous phase. The lower conversions for 1.5:1 and 1:1.5 volume ratios could be due to increase in dilution of the reactants in the organic and the aqueous phase, respectively, and also due to the unfavorable distribution of catalyst in the organic phase. In other words, since the rate of reaction is proportional to the available concentration of $[Q^+Y^-]_{org}$ in the organic phase, for equal volume (1:1) phases, $[Q^+Y^-]_{org}$ was the highest, followed by 1:1.5 and 1.5:1 organic to aqueous phase ratios.

So, further experiments were conducted by using equal volume phases. The model was validated against experimental data to get a very good fit (Fig. 5). The values of K_e and k_{org} for different phase volume ratio were obtained (Table 2). The K_e values for 1:1 phase volume ratio were highest and hence the highest conversions were obtained.

3.5. Effect of catalyst loading

The effect of catalyst loading was studied by using weight from 4.5678×10^{-5} to 1.397×10^{-3} mol under otherwise similar conditions. The rate of reaction increases with increase in catalyst concentration and the overall conversion also increases from 42.85 to 86.26%. A linear relationship is obtained when

Table 2
Model fitting for etherification of 2'-pentyloxy acetophenone with 1-bromopentane for different phase volume ratio

	1.5:1.0	1.0:1.5	1.0:1.0
K_e	1.10	1.19	1.99
$K_e k_{org} \phi [N_Q]_{org}$	0.0023	0.00287	0.0045
k_{org} ($\text{cm}^3/(\text{mol s})$)	65.90	76.02	70

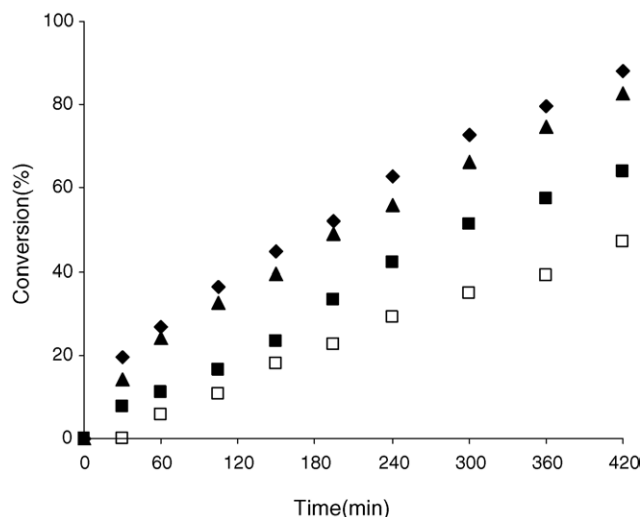


Fig. 6. Effect of catalyst loading. 2'-Hydroxy acetophenone (0.02 mol), 1-bromopentane (0.02 mol), sodium hydroxide (0.025 mol), water (25 cm³), toluene (25 cm³), temperature (90 °C), speed of agitation (1200 rpm). (◆) 0.0013 mol; (■) 0.0007 mol; (▲) 0.0010 mol; (□) 0.00045 mol.

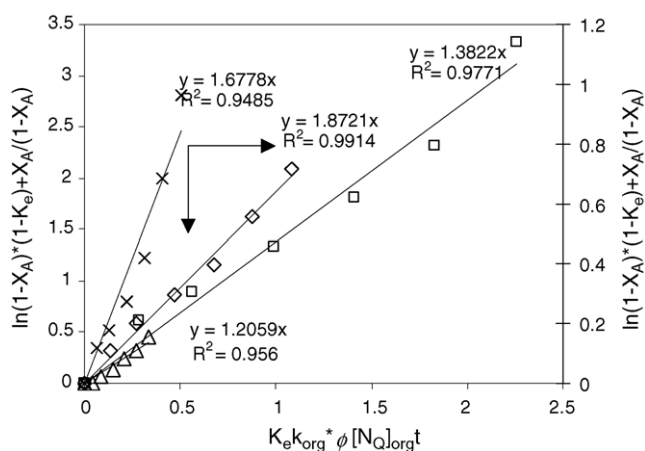


Fig. 7. Model validation for different catalyst loading. (◇) 0.001 mol; (△) 0.00045 mol; (□) 0.0013 mol; (×) 0.0007 mol.

the rates were plotted against catalyst loading, which indicate that the reaction is kinetically controlled (Fig. 6). The model was tested by invoking Eq. (14) (Fig. 7) and values of K_e and k_{org} were obtained for different catalyst loading (Table 3). The value of k_{org} can also be obtained by plotting $k_{org} [N_Q]_{org}$ versus

Table 3
Model fitting for etherification of 2'-pentyloxy acetophenone with 1-bromopentane for different catalyst loading

	Catalyst loading (mol)			
	0.0013	0.0010	0.0007	0.00045
K_e	2.68	1.99	1.44	1.12
$K_e k_{org} \phi [N_Q]_{org}$	0.0094	0.0045	0.0021	0.0014
k_{org} (cm ³ /(mol s))	80	70	69.44	66

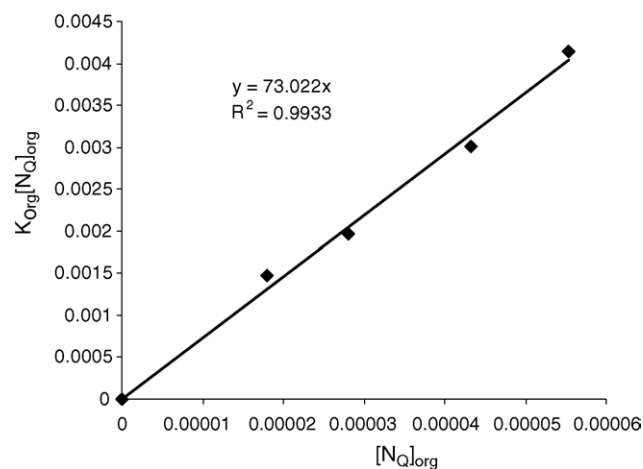


Fig. 8. Evaluation of value of k_{org} .

$[N_Q]_{org}$ which gives a straight line. The slope gives the value of k_{org} as 73.022 cm³/(mol s) (Fig. 8).

3.6. Effect of mole ratio

Different moles of $\text{AcPhO}^- \text{Na}^+$ were used in the range of 0.01–0.03 mol, holding constant the amounts of following components of the reaction mixture: 1-bromopentane (0.02 mol) and TBAB (0.00108 mol). It was found that increasing the concentration of $\text{AcPhO}^- \text{Na}^+$ increases the rate of reaction and conversion (Fig. 9). The value of $K_e k_{org}$ for different mole ratios was also obtained by solving the Eq. (14) using Polymath (Fig. 10 and Table 4). Conversion of 1-bromopentane increased for mole ratios of $\text{AcPhO}^- \text{Na}^+$ to bromopentane from 1:2, 2:2 to 3:2. At 1:2 mole ratio, 1-bromopentane was excess whereas at 3:2, excess of phenolate was available than required in which case the concentration of quaternary phenolate was constant at all

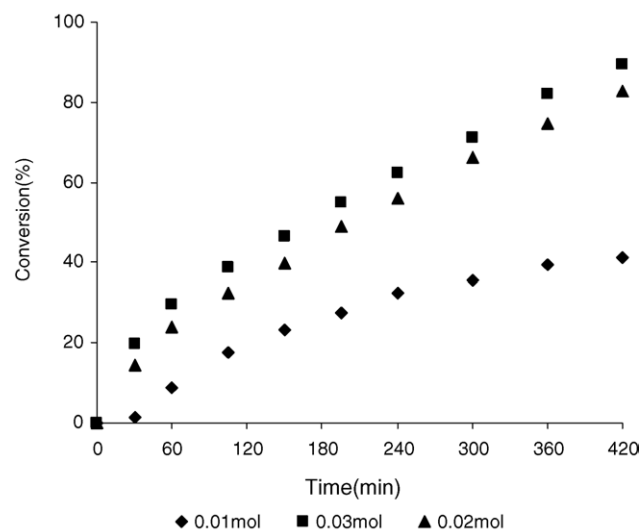


Fig. 9. Effect of mole ratio. 2'-Hydroxy acetophenone: sodium hydroxide (1:1.25), 1-bromopentane (0.02 mol), TBAB (1.08×10^{-3} mol), water (25 cm³), toluene (25 cm³), temperature (90 °C) and speed of agitation (1200 rpm). (◆) 0.01 mol; (■) 0.03 mol; (▲) 0.02 mol.

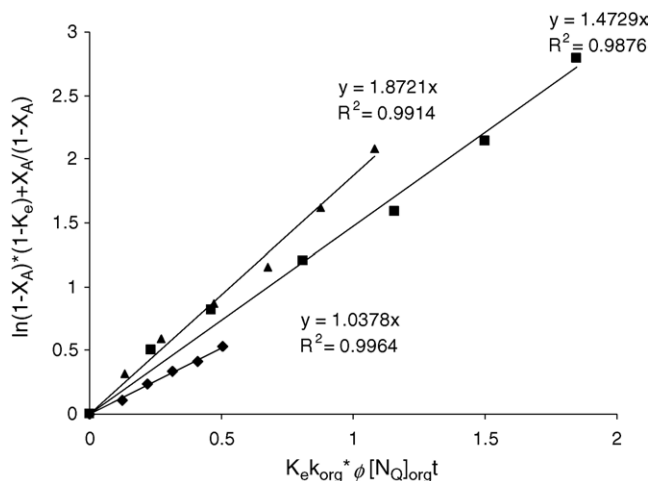


Fig. 10. Model validation for different mole ratio. (◆) 0.01 mol; (■) 0.03 mol; (▲) 0.02 mol.

Table 4
Model fitting for etherification of 2'-pentyloxy acetophenone with 1-bromopentane for different mole ratio

	Mole ratio		
	0.5:1	1:1	2:1
K_e	1.12	1.99	2.16
$K_e k_{org} \phi [N_Q]_{org}$	0.0021	0.0045	0.0077
k_{org} (cm ³ /(mol s))	68.19	70	90.81

times in comparison with other two cases. The correlation coefficient for the mole ratio of 3:2 was 0.9876 in comparison with the other two, where is 0.9914 and 0.9964. This also proves that the model is valid. In all cases, experiments were repeated thrice

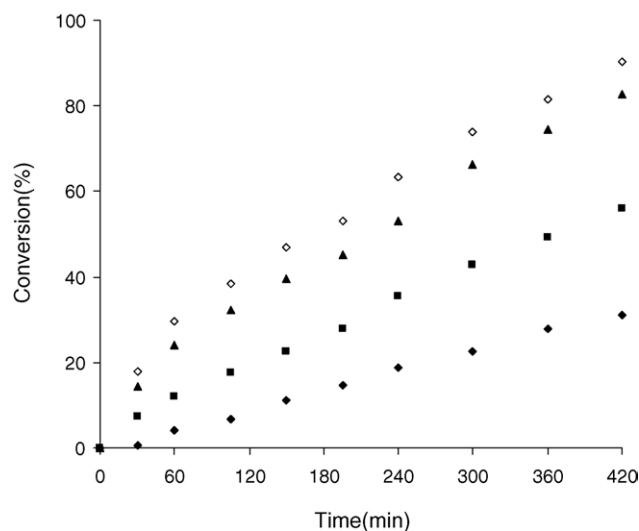


Fig. 11. Effect of different temperature. 2'-Hydroxy acetophenone (0.02 mol), 1-bromopentane (0.02 mol), sodium hydroxide (0.025 mol), TBAB (1.08×10^{-3} mol), water (25 cm³), toluene (25 cm³), speed of agitation (1200 rpm). (◆) 80 °C; (■) 85 °C; (▲) 90 °C; (◇) 95 °C.

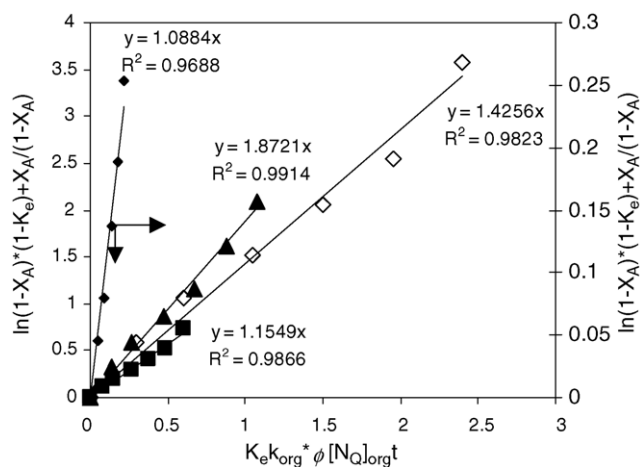


Fig. 12. Model validation for different temperature. (◆) 80 °C; (■) 85 °C; (▲) 90 °C; (◇) 95 °C.

and an average value was taken for fitting the model. There is an error of 3–5% in each data point.

3.7. Effect of temperature

To study the effect of temperature, the reaction was carried out at 80, 85, 90 and 95 °C (Fig. 11). When the temperature was increased, the conversion also increased. The validation of model was also done for each temperature, which shows a very good fit (Fig. 12). The data were fitted to Eq. (14) using Polymath and k_{org} and K_e were calculated (Table 5). These values were used to estimate Gibb's free energy for the overall exchange reaction across the interface (Fig. 13) and the activation energy (Fig. 14).

The energy of activation was been found out to be 23.96 kcal/mol. The Gibbs free energy ΔG was calculated for the overall exchange reaction at -1.198 kcal/mol ($\Delta G = \Delta H - T\Delta S = -RT \ln K_e$). The negative value shows that the overall exchange reaction is thermodynamically possible.

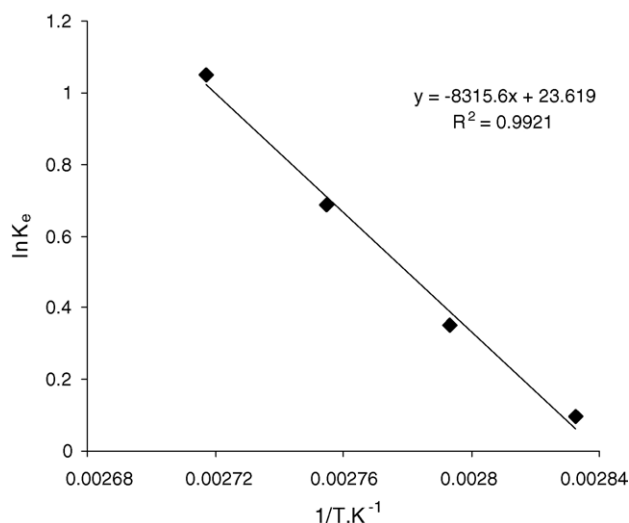


Fig. 13. Gibbs free energy plot for overall exchange reaction.

Table 5
Model validation fitting for etherification of 2'-pentyloxy acetophenone with 1-bromopentane for different temperature

	Temperature (K)			
	353	358	363	368
K_e	1.1	1.424	1.99	2.86
$K_e k_{org} \phi [N_Q]_{org}$	0.00089	0.0025	0.0045	0.01
k_{org} (cm ³ /(mol s))	25	54	70	108

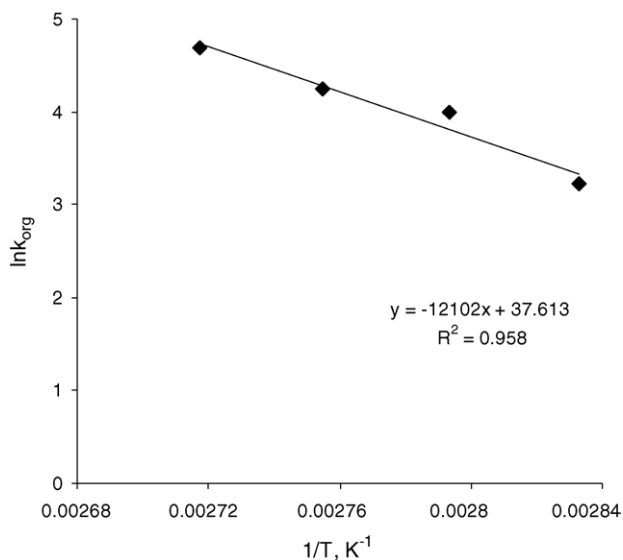


Fig. 14. Arrhenius plot.

4. Conclusions

The alkylation of 2'-hydroxy acetophenone with 1-bromopentane was studied in detail by using liquid–liquid phase transfer catalysis with a variety of catalysts such as TBAB, TPAB, TEAB and ETPB. TBAB was found to be the best catalyst. Hundred percent selectivity was obtained towards the formation of 2'-pentyloxy acetophenone. As the reaction was carried out under controlled conditions, there was no formation of 1-pentanol, which is expected as reaction was carried out in pres-

ence of a base. A complete theoretical analysis of the reaction is done to develop a model by which it was possible to calculate rate constant and overall ion exchange reaction equilibrium constant. The model was also validated for all set of experimental data.

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References

- [1] C.M. Starks, C.M. Liotta, C.M.M. Halpern, Phase Transfer Catalysis: Fundamentals, Applications and Perspectives, Chapman and Hall, New York, 1994.
- [2] Y. Sasson, R. Neumann (Eds.), Handbook of Phase Transfer Catalysis, Blackie Academic and Professional, London, 1997.
- [3] E.V. Dehmlow, S.S. Dehmlow, Phase Transfer Catalysis, third ed., VCH Weinheim, New York, 1993.
- [4] A. McKillop, C.J. Fiaud, P.R. Hug, Tetrahedron 30 (1974) 1379.
- [5] G.D. Yadav, C.A. Reddy, Ind. Eng. Chem. Res. 38 (1999) 2245.
- [6] G.D. Yadav, S.S. Naik, Catal. Today 66 (2001) 345.
- [7] M.M. Salunkhe, M.T. Thorat, M.R.B. Mane, Bull. Soc. Chim. Belg. 103 (1994) 691.
- [8] J.C. Lee, J.Y. Yuk, S.H. Cho, Synth. Commun. 25 (9) (1995) 1367.
- [9] S.L. Buchwald, J. Marcoux, S. Doye, J. Am. Chem. 119 (1997) 10539.
- [10] G.D. Yadav, M.S. Krishnan, Ind. Eng. Chem. Res. 37 (1999) 3358.
- [11] J.V. Crivello, S. Kong, J. Polym. Sci. Part A Polym. Chem. 37 (1999) 3017.
- [12] G.D. Yadav, B.V. Haldavanekar, J. Phys. Chem. A 101 (1997) 36.
- [13] G.D. Yadav, Y.B. Jadhav, J. Mol. Catal. A Chem. 192 (2003) 41.
- [14] G.D. Yadav, Y.B. Jadhav, S. Sengupta, Chem. Eng. Sci. 58 (2003) 2681.
- [15] G.D. Yadav, P.M. Bisht, J. Mol. Catal. 221 (1–2) (2004) 59.
- [16] G.D. Yadav, S.S. Naik, Org. Process Res. Dev. 3 (1999) 83.
- [17] G.D. Yadav, S. Subramanian, J. Mol. Catal. A Chem. 209 (2004) 75.
- [18] G.D. Yadav, Y.B. Jadhav, Langmuir 18 (2002) 5995.
- [19] G.D. Yadav, Y.B. Jadhav, Org. Proc. Res. Dev. 7 (2003) 588.
- [20] M. Covello, E. Pisepo, Ed. Sci. 19 (8) (1964) 675–687 (CA, 61:10619c).
- [21] M. Covello, E. Pisepo, O. Schettino, Rend. Accad. Sci. Fis. Mater. 31 (1964) 193 (CA, 64:10598a).
- [22] E.V. Dehmlow, M. Slopianka, J. Heider, Tetrahedron Lett. 27 (1977) 2361.