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Novelties of liquid–liquid–liquid phase transfer catalysis Alkoxylation of *p*-chloronitrobenzene

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Abstract

Liquid–liquid–liquid phase transfer catalysis (L–L–L PTC) offers orders of magnitude intensification of rates of reaction and better selectivities than the biphasic PTC. The catalyst-rich middle phase is the main reaction phase. The etherification or alkoxylation of *p*-chloronitrobenzene (PCNB) was conducted by using alkanol and alkali instead of the metal alkoxide. A kinetic model is presented and validated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkoxylation; *p*-Chloronitrobenzene; Phase transfer catalysis; Liquid–liquid–liquid system

1. Introduction

Phase transfer catalysis (PTC) is now a mature technique for conducting multi-phase reactions. In liquid–liquid–liquid phase transfer catalysis (L–L–L PTC), the third liquid phase is the main reaction phase. The advantages of L–L–L PTC over normal PTC are: (i) increase in reaction rates by orders of magnitude; (ii) easier catalyst recovery and reuse; (iii) the catalyst need not be bound to a solid support; (iv) better selectivity. Hence the attendant difficulties of reduced activity and mechanical strength associated with liquid–liquid–solid (L–L–S) PTC can be avoided [1].

The disadvantages of L–L–L PTC are: (i) more amount of catalyst is required, which is expensive; (ii) the method is not applicable for systems where a very high temperature is required to carry out the reaction. As the temperature increases, the stability of third liquid phase decreases. However, if the catalyst is stable, then by lowering the temperature at the end of the reaction it could be easily separated into a third phase for recovery and reuse.

Synthesis of *p*-nitroanisole (PNA) and *p*-nitrophenetole (PNP) from *p*-chloronitrobenzene (PCNB), sodium hydroxide and methanol or ethanol, respectively, with tetrabutylammonium bromide (TBAB) as catalyst were chosen as the L–L–L PTC systems, because these are important precursors in organic process industry.

2. Experimental

Sodium hydroxide, toluene, methanol and ethanol of LR Grade were purchased from s.d. Fine Chemicals, Mumbai. PCNB, OCNB and MCNB were procured from Aarti Industries, Mumbai. TBAB of pure

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grade was obtained from Dishman Pharmaceuticals and Chemicals, Ahmedabad.

2.1. System 1: p-nitroanisole from PCNB, methanol and NaOH

The reactions were studied isothermally in a 5 cm i.d., fully baffled mechanically agitated glass reactor of 250 cm^3 capacity, equipped with a six bladed-turbine impeller and a reflux condenser. Typical runs consisted of 0.025 mol PCNB in 40 cm^3 toluene with 0.2 mol of NaOH in methanol (30 cm^3) and water (20 cm^3) at 80°C. The mixture was stirred with the required amount of the catalyst. Volume of the catalyst phase was measured independently by simulating the same experiment and allowing the phases to separate in the absence of any agitation.

2.2. System 2: p-nitrophenetole from PCNB, ethanol and NaOH

A standard Parr autoclave of 100 cm^3 capacity, equipped with a four bladed-turbine impeller was employed. PCNB of 0.00625 mol in 10 cm^3 toluene, with 0.05 mol of NaOH in appropriate quantities of ethanol and water and the catalyst were added and the temperature was raised to 110°C without agitation, and a 0 h sample was taken and then the stirring commenced.

Samples of the organic phase were withdrawn periodically and analysed by GC on a Chemito 8510 model using a 2.0 m × 3.2 mm i.d. stainless steel column packed with Chromosorb WHP impregnated with 10% SE-30 and FID detector. Synthetic mixtures were prepared, analysed, and used for quantification. Some amount of nitrophenol was detected in aqueous phase at the end of reaction, which was separated, purified and confirmed by measurement of physical constant. Up to 2% nitrophenol was formed after 4 h. However, for kinetic measurement up to 2 h, there was no formation of nitrophenol. Upon completion of the reaction, the mixture was filtered to remove the solids and the organic phase was washed with water. The product was separated by distillation and analysed by GC–MS.

The composition of the third phase was analysed by GC. Amount of water present in the third phase was determined by Karl-Fischer apparatus and also by gas chromatography using a TCD detector.

3. Results and discussion

3.1. Mechanism of L–L–L PTC

The reactant PCNB is present in both the organic phase and in the third but not in the aqueous phase due to its insolubility in the latter. Therefore, the reaction can be classified into three types as proposed by Yadav and Reddy [1], namely: (a) Type I — the reaction in the organic phase (L–L PTC); (b) Type II — the reaction at the interphase between an organic phase and an aqueous phase or in the bulk aqueous phase (L–L inverse PTC); (c) Type III — the reaction in the third phase.

Since the reaction rate is assumed to be proportional to the concentration of the A and the amount of the catalyst, the overall reaction rate can be expressed by the summation of respective rates for the three types I, II and III, as reported elsewhere [1,2].

$$-\frac{\mathrm{d}N_{\mathrm{A}}}{\mathrm{d}t} = (k_{\mathrm{org}}\psi_{\mathrm{org}} + k_{\mathrm{inter}}\psi_{\mathrm{aq}} + k_{\mathrm{third}}K_{\mathrm{A}}\psi_{\mathrm{third}})N_{\mathrm{Q}_0}C_{\mathrm{A-org}} \tag{1}$$

where the ψ's are the mole fractions of catalyst present in the respective phases based on the moles of catalyst N_{Q_0} added initially. When Eq. (1) is integrated, the following equation is obtained:

$$1 - X_{\mathrm{A}} = \frac{N_{\mathrm{A-org}}}{N_{\mathrm{A}_0}} = \frac{V_{\mathrm{org}}}{V_{\mathrm{org}} + K_{\mathrm{A}}V_{\mathrm{third}}}\exp(-k_{\mathrm{obs}}\omega t) \tag{2}$$

where N_{A_0} are the moles of A originally taken, $X_{\mathrm{A}} = (N_{\mathrm{A}_0} - N_{\mathrm{A}})/N_{\mathrm{A}_0}$ the fractional conversion of A and K_{A} the distribution coefficient for A in the third phase with reference to organic phase.

$$k_{\mathrm{obs}} = \frac{V_{\mathrm{org}}}{V_{\mathrm{org}} + K_{\mathrm{A}}V_{\mathrm{third}}}(k_{\mathrm{org}}\psi_{\mathrm{org}} + k_{\mathrm{inter}}\psi_{\mathrm{aq}} + k_{\mathrm{third}}K_{\mathrm{A}}\psi_{\mathrm{third}}) \tag{3}$$

$$\omega = \frac{N_{\mathrm{Q}_0}}{V_{\mathrm{org}}}, \qquad k_1 = k_{\mathrm{obs}}\omega \tag{4}$$

Depending on values of ψ, different mechanisms prevail.

3.2. Formation of third phase

In the case of reaction of PCNB in toluene with aqueous ROH ($R = CH_3, C_2H_5$) and NaOH, TBAB forms a third phase beyond a critical concentration (Table 1). Table 1 shows that TBAB is distributed between the third phase and the organic phase. The aqueous phase contains the alcohol ROH and the base sodium hydroxide.

$$[\mathrm{ROH}]_{\mathrm{aq}} + [\mathrm{OH}^-]_{\mathrm{aq}} \overset{K_\mathrm{a}}{\rightleftarrows} [\mathrm{RO}^-]_{\mathrm{aq}} + \mathrm{H_2O}_{\mathrm{aq}} \tag{5}$$

$$[\mathrm{Q}^+\mathrm{OH}^-]_{\mathrm{org}} + [\mathrm{RO}^-]_{\mathrm{aq}} \overset{K_{\mathrm{RO}}}{\rightleftarrows} [\mathrm{Q}^+\mathrm{RO}^-]_{\mathrm{org}} + [\mathrm{OH}^-]_{\mathrm{aq}} \tag{6}$$

The acidity–selectivity constant is thus defined by

$$K_{\mathrm{sel}} = K_\mathrm{a} K_{\mathrm{RO}} = \frac{[\mathrm{Q}^+\mathrm{RO}^-]_{\mathrm{org}}}{[\mathrm{ROH}]_{\mathrm{aq}}[\mathrm{Q}^+\mathrm{OH}^-]_{\mathrm{aq}}} \tag{7}$$

For methanol and ethanol, these values at 41°C are given as 70 and 420 for a chlorobenzene–aqueous sodium hydroxide system, respectively [3,4]. It would mean that $[\mathrm{Q}^+\mathrm{RO}^-]$ has a preferential distribution in organic phase in L–L system. In the current work, toluene–water–TBAB liquid phase, it is quite reasonable to assume that the distribution of $\mathrm{Q}^+\mathrm{OR}^-$, which is formed instantly occurs in the third phase and also in the organic phase.

In L–L PTC, the catalyst is mainly in the form of a $[\mathrm{Q}^+\mathrm{OR}^-]$ which gets extracted into the organic phase. Thus, it is reasonable to neglect the contribution of interfacial reaction (Type II) in L–L–L PTC. The contribution of organic phase reaction (Type I) could be found independently. $[\mathrm{Q}^+\mathrm{OH}^-]$ is difficult to extract in organic phase in comparison with $[\mathrm{Q}^+\mathrm{OR}^-]$.

Table 1
Characteristics of third phase for a standard reaction for system 1: synthesis of PNA

Organic phase volume	40 cm^3
Aqueous phase volume	46 cm^3
Third phase volume	4 cm^3
Composition of third phase (wt.%)	
Toluene	54.0
TBAB	30.0
PCNB	5.484
Water	8.60
Density	0.9736 g/cm^3
Distribution of catalyst	
Total catalyst added	0.0062 mol
ψ_{third}	0.58
ψ_{org}	0.42
K_A	0.5708
Original PCNB	0.025 mol
PCNB in third phase	0.00135 mol
PCNB in organic phase	0.02365 mol

3.3. Effect of speed of agitation

To ascertain the influence of external resistance to mass transfer of the reactants to the reaction phase, whether L–L or L–L–L system, the speed of agitation was varied in the range 500–1000 rpm. There was no effect of speed on the conversion in both systems, beyond a speed of 700 rpm. Therefore, further experiments were conducted at around 1000 rpm.

3.4. Effect of catalyst loading

The catalyst concentration was varied from 1.55×10^{-5} to 2.325×10^{-4} mol/cm^3 of organic phase for the synthesis of PNA. At a catalyst concentration of 1.55×10^{-5} mol/cm^3 there was no formation of the third phase and the usual L–L PTC was found to hold. It should be realised that since there was no resistance to mass transfer in the L–L–L system, at higher catalyst concentrations, there was obviously no mass transfer resistance for the L–L PTC at low catalyst concentration under consideration (Fig. 1). At a very low concentration, the rate of the reaction was very low due to the absence of the catalyst-rich third phase. When the catalyst loading was increased from 1.55×10^{-5} to 1.175×10^{-4} mol/cm^3, the rate of reaction increased sharply indicating that amount of TBAB had exceeded a critical value. It was also observed that there was a formation of a third phase.

In synthesis of nitrophenetole, the catalyst concentration was varied from 4.65×10^{-5} to 2.0×10^{-4} mol/cm^3 of organic phase. At a catalyst concentration of 4.65×10^{-5} mol/cm^3 there was no formation of the third phase and the usual L–L PTC was found to hold (Fig. 1). Beyond 1.5×10^{-4} mol/cm^3, there was a third phase formation.

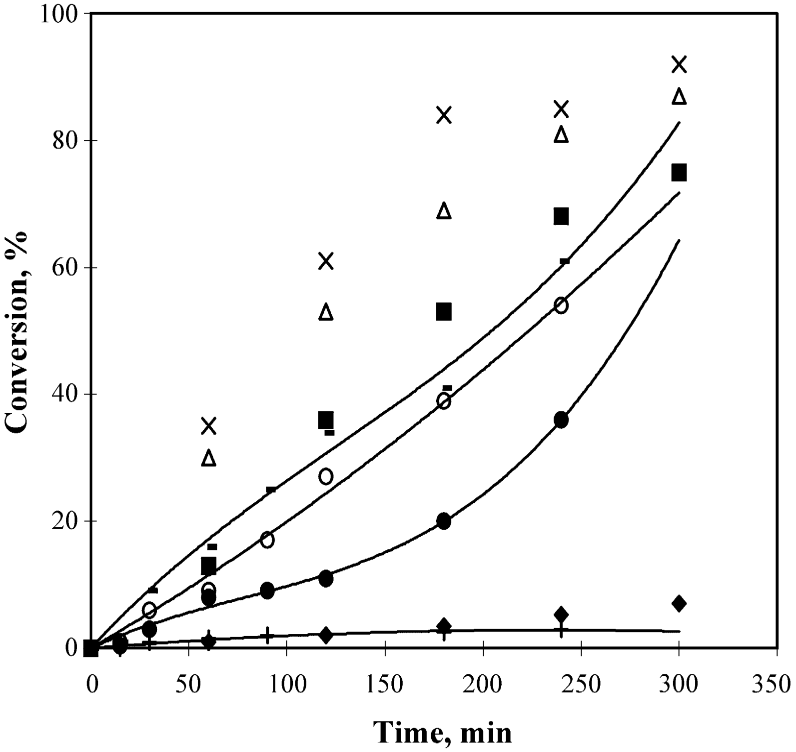

Fig. 1. Effect of catalyst concentration: (without line) PNA; (—) PNP. PNA: PCNB, 0.025 mol; toluene, 40 cm^3; TBAB, 0.0062 mol; NaOH, 0.2 mol; H_2O, 20 cm^3; CH_3OH/C_2H_5OH, 30 cm^3; temperature, 80°C; speed of agitation, 1000 rpm. PNP: PCNB, 0.0062 mol; toluene, 10 cm^3; TBAB, 0.0015 mol; NaOH, 0.05 mol; H_2O, 15 cm^3; CH_3OH/C_2H_5OH, 11 cm^3; temperature, 110°C; speed of agitation, 1000 rpm. PNA: (◆) 0.155×10^{-4} mol/cm^3, (■) 1.175×10^{-4} mol/cm^3, (△) 1.55×10^{-4} mol/cm^3, (×) 2.325×10^{-4} mol/cm^3; PNP: (+) 0.465×10^{-4} mol/cm^3, (●) 1.1×10^{-4} mol/cm^3, (○) 1.6×10^{-4} mol/cm^3, (–) 2.0×10^{-4} mol/cm^3.

3.5. Effect of concentration of sodium hydroxide

The rate of reaction increased with NaOH concentration. There are two reasons for this result. Firstly, there is a greater concentration of $[Q^+OH^-]$ and secondly, there is higher rate of generation of $[Q^+OR^-]$, which gets immediately extracted into the third phase. The volume of the third phase also increased with an increase in the concentration of NaOH up to 4.0×10^{-3} mol/cm^3 and then it decreased again. When the NaOH concentration was very less, the volume of third phase was also less because the aqueous phase was not saturated with NaOH and there was no salting out of TBAB. But as concentration of NaOH was increased, it became saturated and more and more amount of catalyst was pushed into the third phase. Any further addition of sodium hydroxide decreased the volume of third phase due to instability of the third phase in presence of excess base whereby dehydration of the catalyst phase took place leading to transfer of more and more catalyst into the organic phase. Some water is always needed in the third phase for the greater solubility of OH^- ions. Similar trend was also seen for the synthesis of PNP.

3.6. Effect of temperature

The effect of temperature was studied at 60, 80, 90 and 110°C for PNA synthesis and at 80, 110, 130°C for PNP synthesis (Fig. 2). As the temperature increased from 60 to 80°C the conversion increased for PNA system. Beyond 80°C, there was no effect of temperature, which could be due to the break-down of L–L–L system into an L–L system and also due

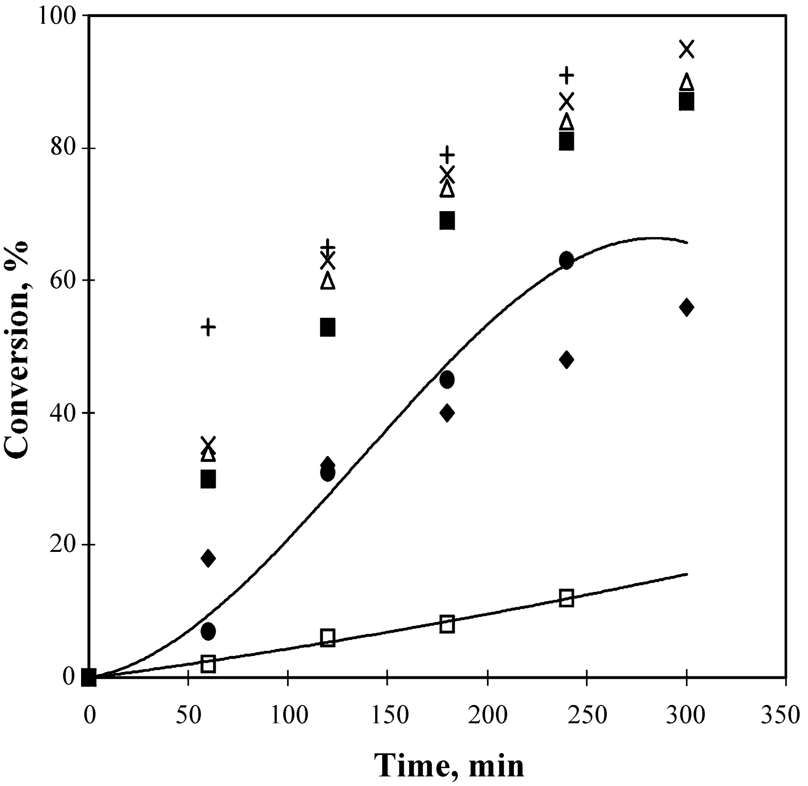

Fig. 2. Effect of temperature: (without line) PNA; (—) PNP. PNA: PCNB, 0.025 mol; toluene, 40 cm^3; TBAB, 0.0062 mol; NaOH, 0.2 mol; H_2O, 20 cm^3; CH_3OH/C_2H_5OH, 30 cm^3; speed of agitation, 1000 rpm. PNP: PCNB, 0.0062 mol; toluene, 10 cm^3; TBAB, 0.0015 mol; NaOH, 0.05 mol; H_2O, 15 cm^3; CH_3OH/C_2H_5OH, 11 cm^3; speed of agitation, 1000 rpm. PNA: (◆) 60°C, (■) 80°C, (△) 90°C, (×) 110°C; PNP: (+) 130°C, (●) 110°C, (□) 80°C.

to mass transfer limitations. In the case of PNP synthesis, as the temperature increased, the conversion increased from 80 to 130°C.

3.7. *Effect of volume ratio*

Aqueous to organic volumes chosen were 50:40, 100:40 and 50:100 cm^3 for system 1 and 25:10, 13:10 and 25:15 cm^3 for system 2. For the same volume of aqueous phase (50 cm^3), when the organic phase volume was changed from 40 to 100 cm^3, the conversion decreased due to less availability of the aqueous phase reactants, as well as decrease in the volume of the third phase. However, for the same volume of organic phase (40 cm^3), when the aqueous phase volume was changed from 50 to 100 cm^3, the conversion decreased because of unfavourable distribution of Q^+OR^- in the aqueous phase and also due to decrease in the volume of the third phase. In the above experiments, there was a marginal but critical change in the volume of the third phase. The best results were obtained with the standard aqueous to organic phase ratio of 50:40 cm^3.

For the same volume of aqueous phase (25 cm^3), in the case of PNP synthesis, when the organic phase volume was changed from 10 to 15 cm^3, the conversion decreased marginally due to less availability of the aqueous phase reactants which is similar to the observations made for the synthesis of PNA. However, for the same volume of organic phase (10 cm^3) when the aqueous phase was changed from 25 to 13 cm^3, the conversion increased due to increase in volume of the third phase. Thus, higher rates of reaction were logical.

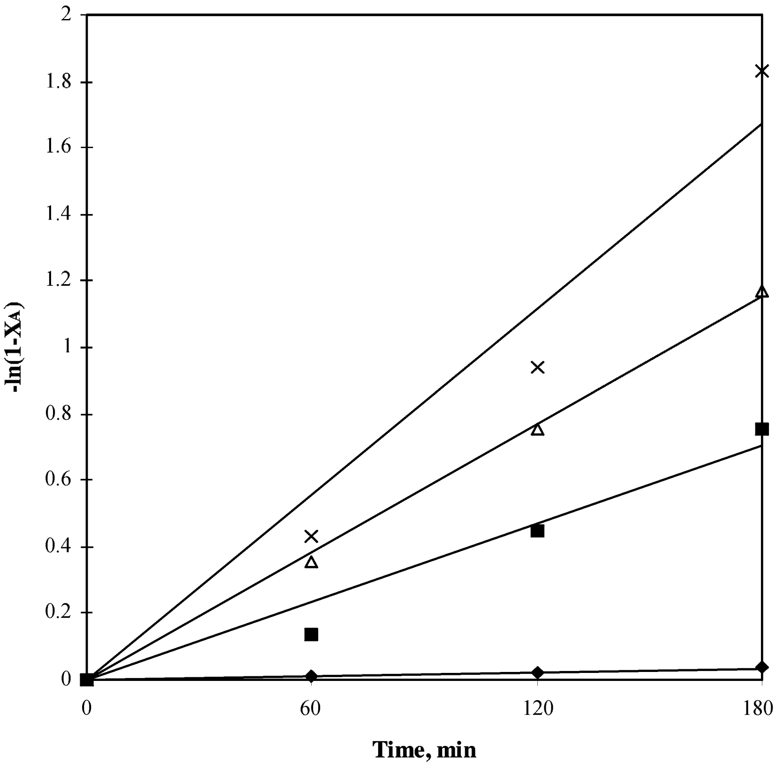

Fig. 3. Kinetic plot for the effect of catalyst concentration. PCNB, 0.025 mol; toluene, 40 cm^3; NaOH, 0.2 mol; temperature, 80°C; H_2O, 20 cm^3; CH_3OH, 30 cm^3; speed of agitation, 1000 rpm. (◆) 0.15×10^{-4} mol/cm^3, (■) 1.175×10^{-4} mol/cm^3, (△) 1.55×10^{-4} mol/cm^3, (×) 2.325×10^{-4} mol/cm^3.

3.8. *Effect of concentration of PCNB*

It was found that the rate of reaction increased with the concentration of PCNB, because of its availability into the third phase for both systems 1 and 2.

3.9. *Reusability*

After completion of the kinetic run, stirring was stopped and the reaction mixture was cooled. 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*

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 in case of system 1 and two times in case of system 2. Since both the aqueous and organic phases were freshly used, there was a loss of the catalyst with the discarded organic and aqueous phases. Therefore, there was once again 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 the reaction. The subsequent experiments with replenished aqueous and organic phases had in fact less quantity of available catalyst than the previous run and hence rates of reaction were found to decrease correspondingly.

3.9.2. *Method B: reuse of the third and aqueous phase only*

Fresh organic solvent was added along with known quantity of PCNB, for which the third phase and also the aqueous phase from the previous experiment were reused. Thus, the catalyst and the aqueous phases were reused four times and the organic phase was

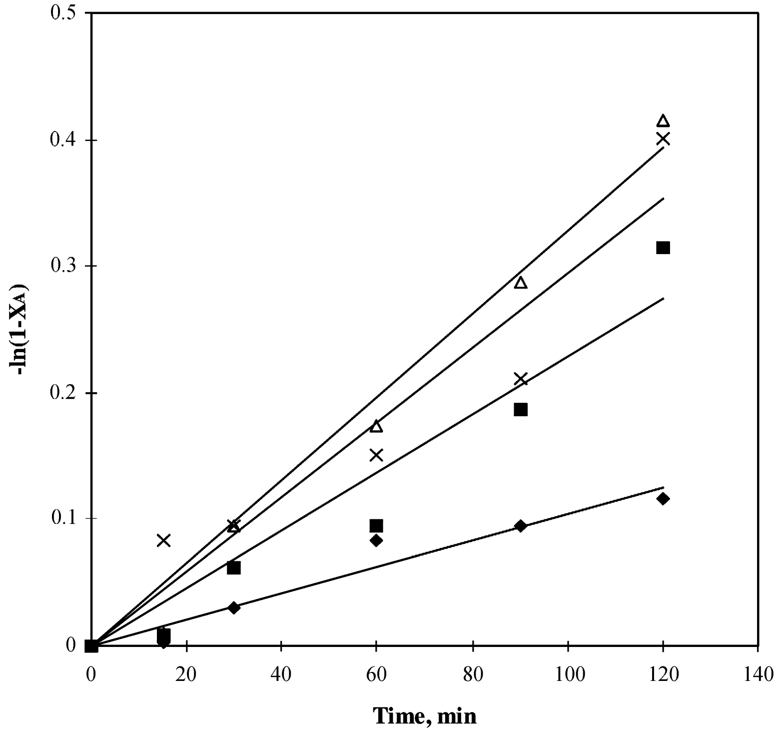

Fig. 4. Kinetic plot for the effect of catalyst concentration. PCNB, 0.0062 mol; toluene, 10 cm^3; NaOH, 0.05 mol; temperature, 110°C; H_2O, 15 cm^3; C_2H_5OH, 11 cm^3; speed of agitation, 700 rpm. (◆) 0.465 × 10^{-4} mol/cm^3, (■) 1.1 × 10^{-4} mol/cm^3, (△) 1.6 × 10^{-4} mol/cm^3, (×) 2.0 × 10^{-4} mol/cm^3.

replenished every time. It should be noted that fresh aqueous phase contained 0.75 mol of methanol and 0.2 mol of sodium hydroxide and 0.025 mol of PCNB. Theoretically, upon completion of the reaction, after the first use, 0.725 mol of methanol and 0.175 mol of sodium hydroxide were still available in the aqueous phase when the phases were allowed to separate. The top organic phase containing the product with insignificant quantity of catalyst, was removed because the catalyst in the third phase as well as in the bottom aqueous phase, was in the form of ion-pair [Q^+OH^-]. Therefore, when the second run was conducted with 0.025 mol PCNB almost all catalyst was available for reaction and therefore the loss in conversion was marginal.

3.10. Kinetics of reaction

In the present studies, as the mechanism appears to be: (i) L–L–L PTC with the middle phase as the reaction phase (Type III); (ii) L–L PTC (Type I) with organic phase as the reaction phase. The possibility that the reaction would occur at the interface by the L–L PTC mechanism (Type II) is discounted because of very high extraction constant and solubility of [Q^+OR^-] ion-pair in the third phase and to some extent in the organic droplet. Thus, Eq. (3) is written as

$$k_{\mathrm{obs}} = (k_{\mathrm{org}}\psi_{\mathrm{org}} + k_{\mathrm{third}}K_{\mathrm{A}}\psi_{\mathrm{third}}) \times \left(\frac{V_{\mathrm{org}}}{V_{\mathrm{org}} + K_{\mathrm{A}}V_{\mathrm{third}}}\right) \tag{8}$$

where k_{org} could be found independently because at low catalyst concentration there was no third phase formation. Fig. 3 shows this plot from which k_{org} is found to be 0.2 cm^3 mol^{-1} s^{-1} at 80°C at 0.00062 mol catalyst taken initially for system 1. The same figure shows three additional lines for L–L–L PTC at higher catalyst concentration. For a catalyst concentration of 0.0062 mol/cm$^3_{\mathrm{org}}$, the k_{obs} is 0.72 cm^3 mol^{-1} s^{-1}.

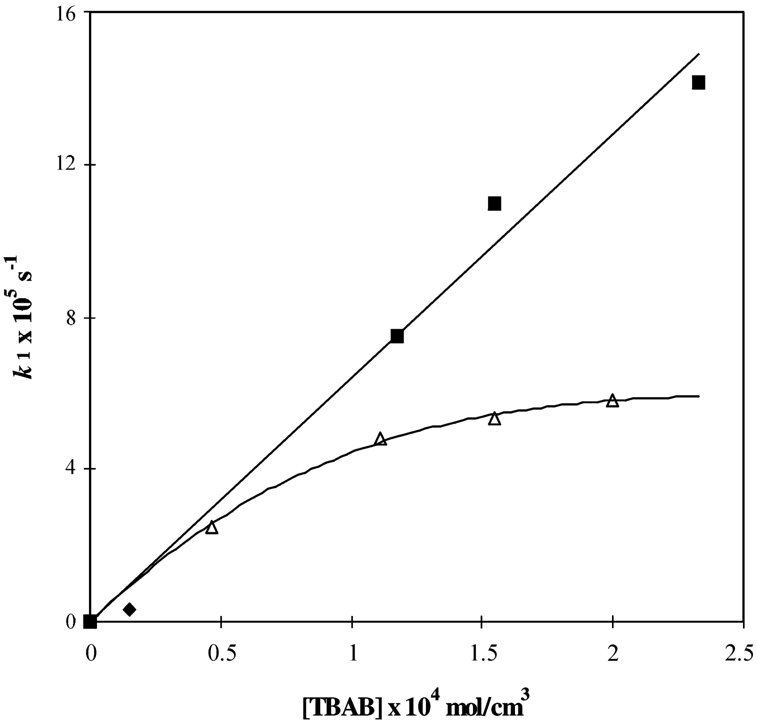

Fig. 5. Effect of concentration of TBAB on first-order rate constant: (without line) PNA; (—) PNP. PNA: PCNB, 0.025 mol; toluene, 40 cm^3; TBAB, 0.0062 mol; NaOH, 0.2 mol; H_2O, 20 cm^3; CH_3OH/C_2H_5OH, 30 cm^3; speed of agitation, 1000 rpm; temperature, 80°C. PNP: PCMB, 0.0062 mol; toluene, 10 cm^3; TBAB, 0.00155 mol; NaOH, 0.05 mol; H_2O, 15 cm^3; CH_3OH/C_2H_5OH, 11 cm^3; speed of agitation, 1000 rpm; temperature, 110°C. PNA: (◆) L–L, (■) L–L–L; PNP: (△) L–L–L.

Thus, $k_{\text{third}} = 2.04$. Thus, the contribution to the overall k_{obs} is 12.2% from organic phase reaction (Type I) under L–L PTC, and 87.8% from third liquid phase reaction under L–L–L PTC condition. Thus, the enhancement in rate due to the formation of the three phase is 7.2 times.

For other catalyst concentrations, the third phase was not analysed for the amount of PCNB, which is dependent on the catalyst quantity as shown by Ido et al. [2]. In fact, it is linearly proportional to the catalyst quantity in the third phase. As the concentration of the catalyst is lowered then the contribution to the overall rate from two phase reaction (Type I) increases but there is also contribution from the third phase reaction (Type III). k_{obs} for various catalyst concentration were calculated as 0.56, 0.6881 and 0.667 cm^3 mol^{-1} s^{-1}. The concentration from the two phase reaction diminishes as the amount of the third phase increases. In fact it can be safely assumed that the last observation is totally due to catalyst in the third phase, i.e. $\psi_{\text{third}} = 1$, because of which the rate of reaction is much higher. In other words, the pseudo-first order constant k_1, which is equal to $k_{\text{obs}}\omega$ can be plotted against catalyst concentration. It can be shown that

$$k_1 = k_{\text{org}} \frac{N_{\text{Q-org}} N_{\text{A-org}}}{N_{\text{A}_0} V_{\text{org}}} + \frac{k_{\text{third}} N_{\text{Q-third}} N_{\text{A-third}}}{N_{\text{A}_0} V_{\text{third}}} \tag{9}$$

Eq. (9) suggests that the contribution of the first term is less in comparison with the second, because $N_{\text{A-third}} > N_{\text{A-org}}$ and $N_{\text{Q-third}}/V_{\text{third}} > N_{\text{Q-org}}/V_{\text{org}}$.

It is seen that there is a substantial increase in rate if three phases are formed. Thus the data could be adequately interpreted by this method. From Fig. 4, k_{obs} was found to be 0.21 cm^3 mol^{-1} s^{-1} at 110°C at 0.000465 mol of catalyst for system 2. For a catalyst concentration of 0.000155 mol/cm^3, the k_{obs} is found

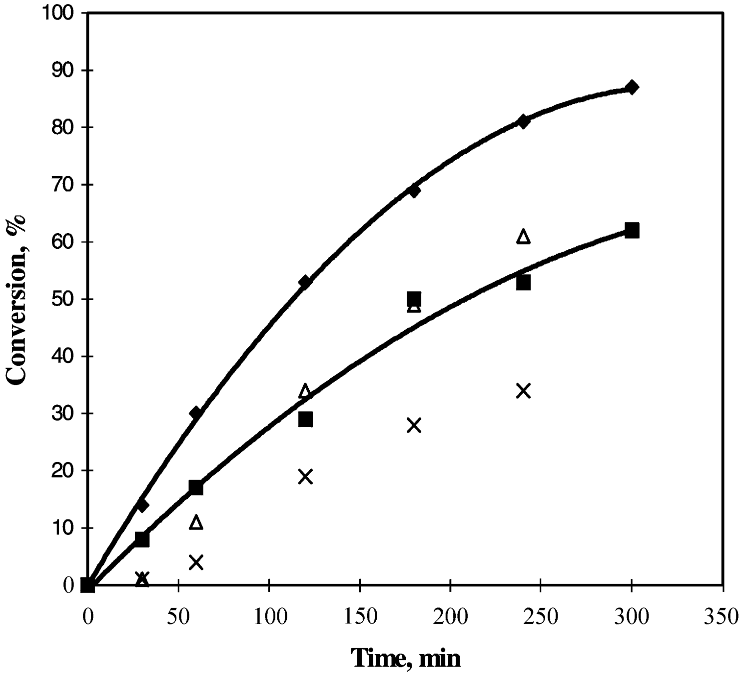

Fig. 6. Effect of isomers: (without line) PNA; (—) PNP. PNA: PCNB, OCNB, 0.025 mol; toluene, 40 cm^3; TBAB, 0.0062 mol; NaOH, 0.2 mol; H_2O, 20 cm^3; CH_3OH/C_2H_5OH, 30 cm^3; speed of agitation, 1000 rpm; temperature, 80°C. PNP: PCNB, OCNB, 0.00625 mol; toluene, 10 cm^3; TBAB, 0.00155 mol; NaOH, 0.05 mol; H_2O, 15 cm^3; CH_3OH/C_2H_5OH, 11 cm^3; speed of agitation, 1000 rpm; temperature, 110°C. PNA: (◆) PCNB, (■) OCNB; PNP: (△) PCNB, (×) OCNB.

to be 0.302 cm^3 mol^{-1} s^{-1}. But ψ_{third} is found to be one and therefore, ψ_{org} is zero, substituting the value of $K_A = 0.2901$, $V_{\text{org}} = 10\,\text{cm}^3$, $V_{\text{third}} = 2\,\text{cm}^3$, from Eq. (8) k_{third} is found to be 1.1014. Pseudo-first order rate constant k_1 was plotted against catalyst concentration (Fig. 5). Here, a clear non-linear behaviour is seen due to the complex dependence of rate on the concentration of catalyst.

3.11. Effect of potassium iodide

The effect of addition of KI was studied in the range 1.48×10^{-6}–1.2×10^{-4} mol/cm^3 of aqueous phase under otherwise similar conditions for system 1. As the concentration of KI increased the conversion increased in the beginning and then again it decreased. KI was a co-catalyst, addition of a little KI forms Q^+I^-, which was more active than Q^+Br^- and therefore the conversion was more as compared to the reaction without KI. But further addition of KI poisoned the reaction, therefore the conversion decreased.

3.12. Reactivity of other isomers

The reactivities of *o*-chloronitrobenzene (OCNB) and *m*-chloronitrobenzene (MCNB) were studied under otherwise similar conditions for both the systems and it was found that the conversion was less in case of OCNB as compared to PCNB due to less accessible *ortho* position to the incoming substituent. MCNB does not react at all due to the strong mesomeric effect which is *ortho–para* directing (Fig. 6).

4. Conclusions

The nature and concentration of catalyst and the amount of sodium hydroxide are important factors which influence the formation of the third liquid phase (catalyst-rich middle phase) and distribution of catalyst. It was observed that the third liquid phase was the main reaction phase. In the case of formation of PNA, there was some contribution (about 10%) from the reaction in the organic phase (L–L PTC) but the majority of reaction occurs in the third phase. For the synthesis of PNP, the reaction occurred entirely in the third phase. It was observed that at a certain critical concentration of the catalyst and sodium hydroxide the third phase was formed. The reuse of the third phase is important from economical point of view and it is found that the third phase can be reused effectively. The mechanism is explained properly and an appropriate kinetic model is proposed which is confirmed by experimental evidence.

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