# Articles

# Solid−Liquid Phase-Transfer-Catalysed Methoxylation of Chloronitrobenzenes to Nitroanisoles

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**Abstract:**

**Nitroanisoles are important precursors in the organic process industry and are made from chloronitrobenzenes by using sodium hydroxide and methanol under liquid−liquid phase-transfer catalysis, which requires higher temperatures, leading to loss in selectivity. Synthesis of *p*-nitroanisole was carried out from *p*-chloronitrobenzene (PCNB) and solid sodium methoxide by using tetrabutylammonium bromide as a catalyst under solid−liquid phase-transfer catalysis (S−L PTC) as opposed to the standard liquid−liquid (L−L) PTC system. The advantages of the S−L PTC are that the reaction is conducted at room temperature with 100% conversion and 100% selectivity. The kinetics and mechanism are also established for this reaction. The methoxylation of *o*-chloronitrobenzene (OCNB) was also studied. The rate of methoxylation of PCNB was much greater than that of OCNB at 30 °C. *m*-Chloronitrobenzene does not react with sodium methoxide under otherwise similar conditions. For the reaction of PCNB with sodium methoxide, the diffusional resistance was found to be unimportant. The rate of the reaction was found to be of first order with respect to both the concentration of catalyst and the substrate.**

## Introduction

Phase-transfer catalysis (PTC) has been applied to over 600 conventional processes in agrochemical, dyestuff, pharmaceutical, polymer, perfumes, flavour, and other fine chemical industries.[1−3] The sulfide and bisulfide reduction of nitroaromatics with PTC is one class of reactions. Etherification and alkoxylation reactions are another important class of reaction involving the use of PTC. Nitroanisoles are important precursors in the organic process industry. The reduction of *p*-nitroanisole leads to *p*-anisidine, which is a dye intermediate, used in the preparation of the dye Fast Bordeaux GP base. *o*-Nitroanisole can be reduced to *o*-anisidine and *o*-dianisidine, both of which are important dye intermediates for making the dyes Fast scarlet base and basic 5-nitro-*o*-anisidine (Fast red B base). The preparation of *p*-nitroanisole starting from *p*-chloronitrobenzene (PCNB) can be achieved under liquid−liquid (L−L) PTC by using aqueous sodium hydroxide, methanol, and a phase-transfer catalyst at reflux temperatures, which also gives *p*-nitrophenol as a side product. The conversion of a liquid−liquid system into a solid−liquid (S−L) system can alter the rates of reactions as well as selectivities.

Solid−liquid PTC has been employed as a useful vehicle for conducting a wide variety of organic transformations using quaternary salts and trialkylamines as well as cyclic and linear polyethers. While liquid−liquid PTC involves heterogeneous reaction processes between two liquid phases (usually an aqueous phase and an organic phase), solid−liquid PTC usually involves reaction of an anionic reagent in a solid phase (usually a salt) with a reactant located in a continuous organic phase. Several reports have appeared in which liquid−liquid (L−L) PTC fails while solid−liquid (S−L) PTC is successful. In addition, the elimination of water of hydration often increases the activity of the anion species in nonpolar, aprotic organic solvents. In some reactions, addition of a little water enhances the reaction, especially in cases where ammonium salts are used in S−L PTC.

Arrad and Sasson[4] have reported the synthesis of *p*-nitroanisole from PCNB and sodium methoxide using Amberlyst (A 27) as a catalyst to give 70% yield and 98% purity. De la Zerda et al.[5] synthesized *p*-nitroanisole using PCNB, sodium hydroxide, methanol, and tetrabutylammonium bromide (TBAB) at 80 °C to give 99% conversion, whereas Yu and Liu[6] used polystyrene-supported PEG-600 at 60−70 °C for 7 h to get 96.7% *p*-nitroanisole. Naik has reviewed some aspects of S−L PTC.[7] Recently, Yadav and Sharma[8] proposed the first model of S−L PTC for the reaction of benzyl chloride with solid sodium acetate and

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(1) Starks, C. M.; Liotta, C.; Halpern, M. *Phase Transfer Catalysis*: *Fundamentals, Applications, and Industrial Perspectives;* Chapman and Hall Publications: New York, 1994.

(2) Sasson, Y., Neumann, R., Eds. *Handbook of Phase Transfer Catalysis*; Blackie Academic and Professional: London, 1997.

(3) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 3rd ed.; VCH: New York, 1993.

(4) Arrad, O.; Sasson, Y. *J. Org Chem*. **1989**, *54*, 4993.

(5) De la Zerda, X.; Cohen, S.; Sasson, Y. *J. Chem. Soc., Perkin Trans*. **1990**, *2*, 1.

(6) Yu, S.; Liu, W. *Chem. Abstr*. **1994**, *121*, 255335x.

(7) Naik, S. S. Insights in catalysis: Novelties of multiphase transfer catalysis. Ph.D. Thesis, Mumbai University, 1998.

(8) Yadav, G. D.; Sharma, M. M. *Ind. Eng. Chem. Process Des. Dev*. **1981**, *20*, 2.

benzoate to produce the commercially important benzyl esters. Naik and Doraiswamy[9] have proposed different models of S−L PTC. There are other mechanistic aspects of S−L PTC discussed in some detail.[10,11] However, there is no information on the process development and kinetics of the preparation of nitroanisoles under S−L PTC. This paper deals with these aspects. A systematic investigation was done with PCNB as the model compound, and the results were extended to the methoxylation of *o*-chloronitrobenzene (OCNB) in comparison with the usual L−L PTC.

### Chemicals

PCNB was obtained from M/S Aarti Industries Ltd., Mumbai, India. Sodium methoxide (pure grade), tetrabutyl-ammonium bromide (TBAB), Aliquat-336, tetrabutylammonium hydrogen sulfate (TBAHS), and cetyltrimethylammonium bromide (CTAB), all of pure grade, were obtained from Loba Chemie, Mumbai, India. Toluene of LR grade was obtained from s.d. Fine Chemicals, Mumbai, India.

### Experimental Procedure

The reactions were studied in a 5-cm-i.d. fully baffled, mechanically agitated contactor of 250 cm$^3$ total capacity, equipped with a six-blade turbine impeller and a reflux condenser. Typical experiments were conducted by taking 0.025 gmol of PCNB, 0.1 gmol of sodium methoxide, the required amount of catalyst, and toluene as solvent at 30 °C. Typically, toluene was added initially to the reactor, followed by sodium methoxide addition. The mixture was stirred, and then PCNB was added to it along with the catalyst. The reaction chemistry is given below.
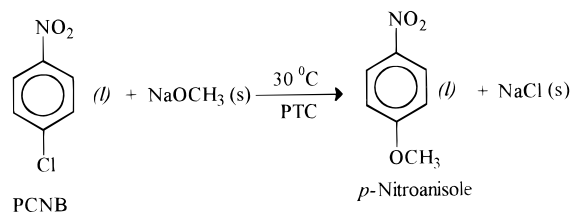


### Method of Analysis

Samples were withdrawn at particular time intervals and analyzed using gas−liquid chromatography on a Chemito model 8510 instrument. Quantitative results were obtained through calibration using synthetic mixtures of pure components. A 2.0-m × 3.2-mm-i.d. stainless steel column packed with Chromosorb WHP, which was impregnated with 10% SE-30, was used for analysis. 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 GC−MS analysis was performed.

### Results and Discussion

Preliminary experiments established that the reaction was quite facile at room temperature. To understand the enhanced

rates of reaction under milder conditions, it was thought worthwhile to study the mechanism and kinetics of this reaction. The effect of various parameters on the rates of reaction was also studied.

**Mechanism.** The usual mechanistic descriptions of S−L PTC found in the literature are not as elaborate as those forL−L PTC. In S−L PTC, the first step involves the transport of a reactant anion from the solid phase to the organic phase by a phase-transfer cation. This could be an organophilic quaternary cation or an organophilic cation derived from the complexation of a metal cation with a multidentate ligand (crown ether, cryptand, poly(ethylene oxide), etc.). The second step involves the reaction of the transferred anion with the reactant located in the organic phase. The reactant anion must be in an active form. Finally, the third step involves the transport of the product anion by the phase-transfer cation to the solid phase and the transport of another reactant anion into the organic phase. The S−L PTC mechanistic description suggests that most of the reaction takes place in anhydrous conditions and that both solid and liquid phases are dry.[8] However, if the reagents are not properly dried or freed of moisture, water is usually associated with inorganic as well as organic salts, which is called the $\omega$-phase[3]. Small amounts of water can dramatically affect the overall rate of the reaction. Very recently, Naik and Doraiswamy[9] have reviewed the S−L PTC mechanism, according to which there is both homogeneous and heterogeneous solubilisation (Figure 1).

The schematics of models of the homogeneous solubilisation are presented in Figure 2, where model A is the one developed by Yadav and Sharma.[8] Figure 3 shows the modeling approach to heterogeneous solubilisation.[9] Model A considers only the organic reaction to be controlling, with ion exchange in equilibrium and the solid dissolution and mass-transfer steps very fast in comparison to the organic reaction. Model B accounts for the ion-exchange reaction in addition to the organic reaction as contributing to the overall rate of the overall PTC cycle, with solid dissolution and mass transfer still fast. Both the ion-exchange and organic reactions are under kinetic control. Model C considers solid dissolution to contribute to the overall reaction rate in addition to the ion-exchange and organic reactions. In model D, the ion-exchange reaction occurs in the film, and then it incorporates the effects of transport of Q$^+$Y$^-$ between the film and the organic bulk phase. Here, the reaction can occur in three different ways:[12] (i) in the bulk organic phase between QY with RX in such a way that [QY] would be zero beyond the film thickness $\delta$ from the solid surface; (ii) in the film, where diffusion of QY and reaction with RX are parallel steps and no free QY exists in the bulk phase; and (iii) M$^+$Y$^-$ ion exchange with Q$^+$X$^-$ at the solid surface to form a Q$^+$Y$^-$ ion pair in such a way that Q$^+$Y$^-$ diffuses from the solid surface a small distance $\lambda$ in the liquid film ($\lambda < \delta$) in this region and then reacts with RX at that plane $\lambda$. No Q$^+$Y$^-$ diffuses into the bulk organic phase beyond that plane within the film, and no RX diffuses beyond the

(9) Naik, S. D.; Doraiswamy, L. K. *Chem. Eng. Sci.* **1997**, *52*, 4533.
(10) Esikova, I. A.; Yufit, S. S. *J. Phys. Org. Chem.* **1991**, *4*, 149, 341, 336.
(11) Halpern, M., Ed. *Phase transfer Catalysis: Mechanism and Synthesis*; ACS Symposium Series 659; American Chemical Society: Washington, DC, 1996.

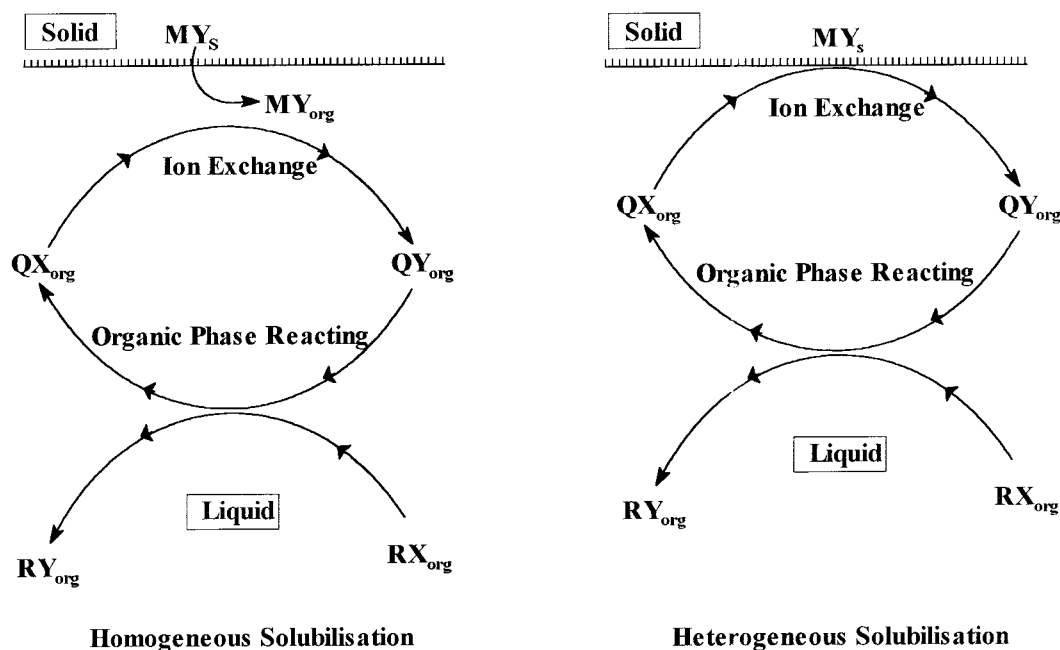(12) Yadav, G. D.; Haldavanekar, B. V. *J. Phy. Chem.* **1997**, *101*, 36.

**Figure 1.** Schematic of S−L PTC mechanism.

same plane toward the solid surface. Both have zero concentration at this plane $\lambda$.

Model A for S−L PTC, which was proposed by Yadav and Sharma,[8] was found to be appropriate for this system and is illustrated by the $S_N2$ type of reaction of the substrateRX with the nucleophile $Y^-$ of the solid reactant MY, as given below. $M^+$ is the inorganic metallic counterion of the nucleophile $Y^-$. The overall reaction is

$$RX_{(org)} + MY_{(s)} + [Q^+X^-]_{(org)} \xrightarrow{k_{obsd}}$$
$$RY_{(org)} + MX_{(s)} + [Q^+X^-]_{(org)} \quad (1)$$
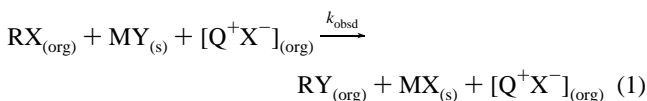
where $Q^+$ is the quaternary cation of the catalyst. $Q^+X^-$ is a loosely bound ion pair. Brackets are used to show ion pairs. The solid reactant is in equilibrium with its dissolved part in the organic phase.

$$MY_{(s)} \rightleftharpoons [M^+Y^-]_{(org)} \quad (2)$$
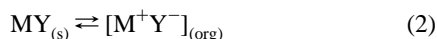
The quaternary salt ($Q^+X^-$) reacts with the dissolved part in the organic phase.

$$[Q^+X^-] + [M^+Y^-] \overset{K_e}{\rightleftharpoons} [Q^+Y^-] + [M^+X^-] \quad (3)$$

$$[M^+X^-]_{(org)} \rightleftharpoons MX_{(s)} \quad (4)$$
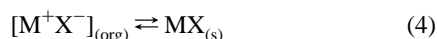
The substrate RX reacts with $[Q^+Y^-]$ according to

$$RX + [Q^+Y^-] \xrightarrow[\text{(product)}]{k_2} RY + [Q^+X^-] \quad (5)$$
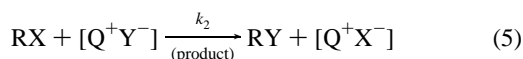
The quaternary salt is thus generated repeatedly to catalyse the reaction. However, there is no transfer of the catalyst across the interface as is normally observed in the case of liquid−liquid phase-transfer process.

The equilibrium constant for the reaction 3 is given by

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

The rate of reaction for eq 5 is given by

$$-\frac{d[RX]}{dt} = k_2[RX][Q^+Y^-] \quad (7)$$

$$= k_2 K_e \frac{[M^+Y^-]}{[M^+X^-]}[RX][Q^+X^-] \quad (8)$$

$[M^+Y^-]/[M^+X^-] = r$ can be assumed to be a constant due to the limited solubility of both the nucleophile and the leaving group in the organic phase. Then over a small range, for quaternary salt catalysis, eq 7 becomes

$$-\frac{d[RX]}{dt} = k_1[RX] \quad (9)$$

where

$$k_1 = k_2 K_e r[Q^+X^-] \quad (10)$$

Equation 9 can be integrated for fixed values of $r$, or eq 7 can be numerically solved.

Integration of eq 9 yields the following equation:

$$\ln([RX]/[RX]_0) = -k_1 t \quad (11)$$

with the boundary condition

$$\text{at } t = 0: \quad [RX] = [RX]_0 \quad (12)$$

or

## Model A
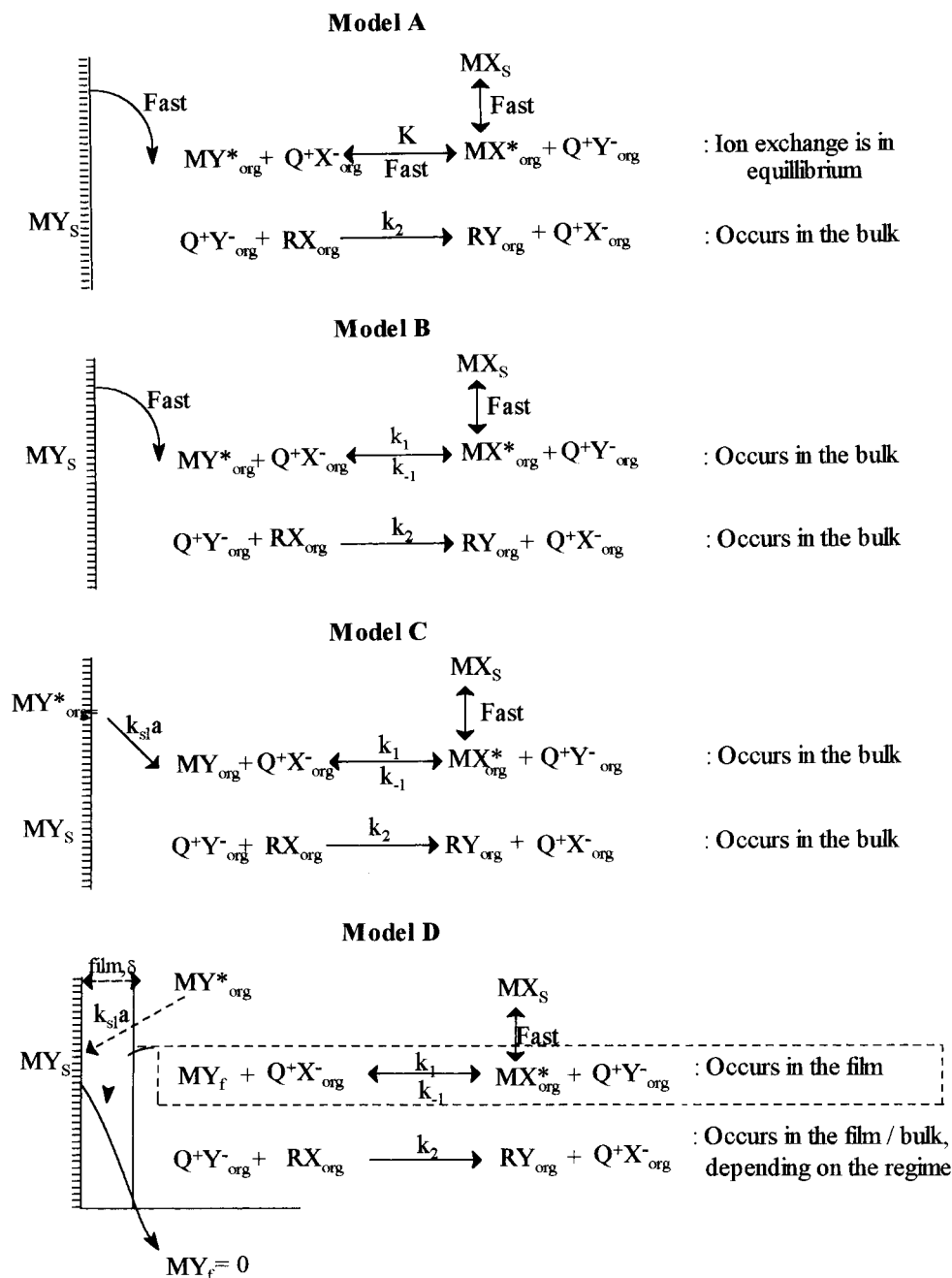


## Model B

## Model C

## Model D

**Figure 2.** Schematic models for homogeneous solubilisation.

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

where

$$X_A \text{ (fractional conversion of RX)} = ([RX]_0 - [RX])/[RX]_0 \tag{13}$$

Here, $k_1$ is a constant for a fixed catalyst concentration $[Q_0]$ added to the system. Thus a plot of $-\ln(1 - X_A)$ against $t$ will give a slope of $k_1$, the rate constant. The value of this slope can be changed by varying the catalyst concentration. A plot of $k_1$ against concentration of catalyst $[Q_o]$ will give a slope of $k_2' = k_2 K_e r$.

The above model was verified by conducting several experiments, during which the effects of different parameters on the rate of reaction were studied.

**Effect of Speed of Agitation**. Figure 4 shows that the speed of agitation had no effect on conversion in the range of 750−1200 rpm. The conversion was slightly lower at 500 rpm than that in the range 750−1200 rpm. Therefore, the speed of agitation was kept at around 1000 rpm to eliminate the external mass-transfer resistance and for assessing the effect of other variables on the rate of the reaction. This suggests that the catalyst concentration $[Q^+Y^-]_{org}$, due to anion-exchange solubilisation in organic phase, is constant, where $Y^- = CH_3O^-$.

The rate of mass transfer is given by

$$R_{MY} = k_{SL} a_p ([MY]^*_{org} - [MY]_{org}) \tag{14}$$

where $[MY]^*$ is the saturation solubility of the solid reactant in the organic phase. This rate of mass transfer should always
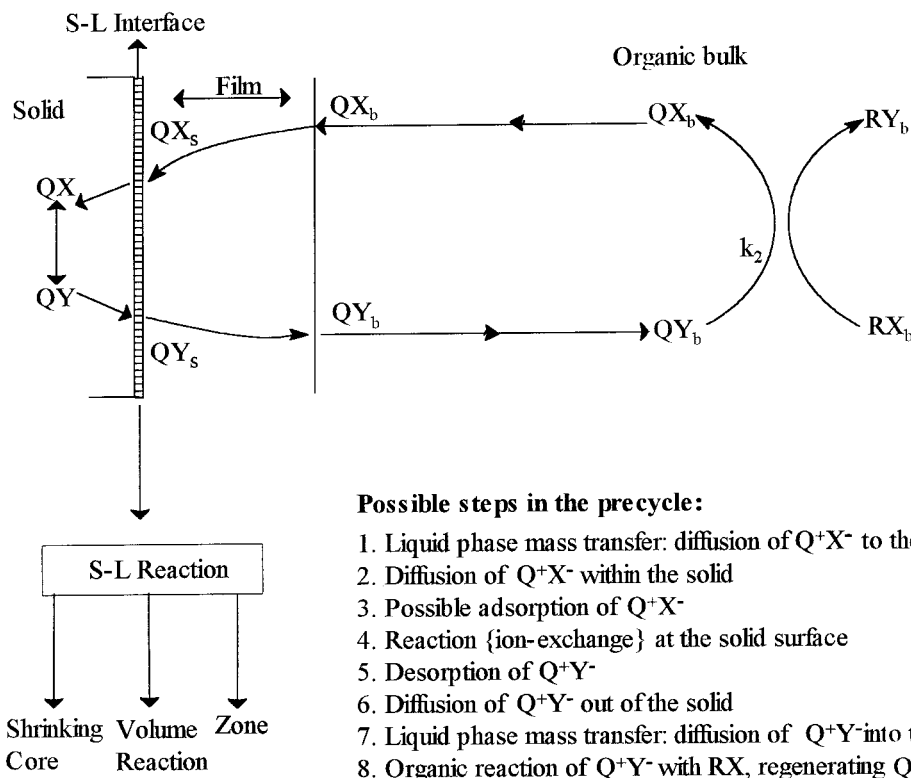
**Possible steps in the precycle:**

1. Liquid phase mass transfer: diffusion of $Q^+X^-$ to the solid surface
2. Diffusion of $Q^+X^-$ within the solid
3. Possible adsorption of $Q^+X^-$
4. Reaction {ion-exchange} at the solid surface
5. Desorption of $Q^+Y^-$
6. Diffusion of $Q^+Y^-$ out of the solid
7. Liquid phase mass transfer: diffusion of $Q^+Y^-$ into the liquid bulk
8. Organic reaction of $Q^+Y^-$ with RX, regenerating $Q^+X^-$

***Figure 3.*** Modeling approach to heterogeneous solubilisation.
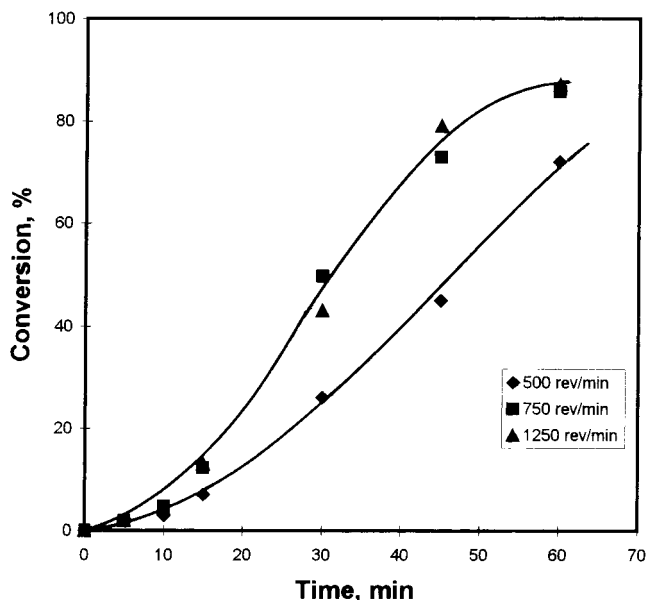


***Figure 4.*** Effect of speed of agitation. Conditions: PCNB, 0.025 gmol; NaOCH₃, 0.1 gmol; temperature, 30 °C; TBAB, 7.5 × 10⁻⁴ gmol; toluene, 45 cm³; speed of agitation, 1000 rpm.

be greater than the rate of reaction in order to eliminate mass-transfer effects. $k_{SL}$ represents the solid–liquid mass-transfer coefficient, and $a_p$ is the solid surface area per unit liquid volume. $a_p$ is dependent on solid loading, and hence it was necessary to assess the effect of solid loading on the rate of reaction.

**Effect of Sodium Methoxide Loading.** Sodium methoxide loading was varied from 0.025 to 0.125 gmol, i.e., from a mole ratio of 1:1 to 1:5 times the limiting reactant
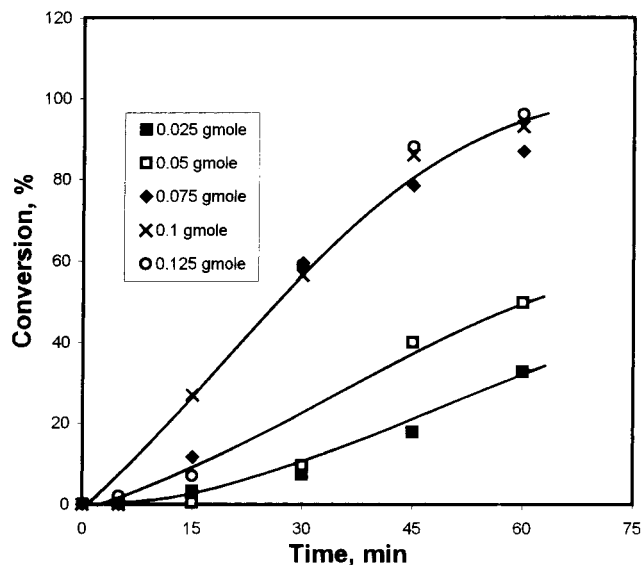


***Figure 5.*** Effect of sodium methoxide loading. Conditions: PCNB, 0.025 gmol; temperature, 30 °C; TBAB, 7.5 × 10⁻⁴ gmol; solvent, toluene; speed of agitation, 1000 rpm.

PCNB under otherwise similar conditions, where the organic phase volume was kept constant. Figure 5 shows that the reaction was independent of the loading of the solid beyond 0.05 gmol, which was twice the limiting reactant. The rate was dependent on the loading of the solid sodium methoxide up to 0.05 gmol; until then $[Q^+OCH_3^-]_{org}$ ($=[M^+Y^-]_{org}$) was not equal to the saturation concentration $[MY]^*_{org}$, and some catalyst was still in the form of $[Q^+X^-]$. Therefore, in further experiments, the solid reactant was taken four times in excess over that theoretically required for complete conversion of

**Table 1.** S−L PTC reaction of PCNB with NaOCH₃ at 30 °C

| TBAB concn, $[Q_0] \times 10^5$ gmol/cm³ | pseudo-first-order rate constant, $k_1 \times 10^4$ s⁻¹ | $k_2'$, cm³ gmol⁻¹ s⁻¹ |
|---|---|---|
| 0.55 | 0.53 | 9.63 |
| 1.66 | 4.96 | 29.87 |
| 3.30 | 7.46 | 22.60 |
| 11.1 | 14.8 | 13.33 |

**Table 2.** Efficacy of different catalysts in methoxylation of chloronitrobenzenes at 30 °C

| compound | catalyst | $[Q_0] \times 10^5$ gmol/cm³ | $k_1 \times 10^4$ s⁻¹ | $k_2'$, cm³ gmol⁻¹ s⁻¹ | relative rate wrt TBAB |
|---|---|---|---|---|---|
| PCNB | Aliquat-336 | 1.66 | 1.25 | 7.5 | 0.25 |
|  | TBAB | 1.66 | 4.9 | 29.5 | 1 |
|  | TBAHS | 1.66 | 5.6 | 33.7 | 1.142 |
| OCNB | TBAB | 1.66 | 2.01 | 12.5 | 1 |
| MCNB | TBAB | 1.66 |  |  | 0 |

PCNB. In fact, in all of these experiments, the amount of sodium methoxide was kept constant in order to have the same surface area under the dispersion. The surface area is determined on the basis of the number of particles in a given solid loading and is $a_p = 6w/(\rho_p d_p)$, where $w$ is the solid loading in g/cm³, $\rho_p$ is particle density in g/cm³, and $d_p$ is particle diameter in cm. Thus, the particle surface area $a_p$ in cm²/cm³ of liquid phase is the same in all cases. The particle surface area ($a_p$) at a loading of 5.04 g (0.1 gmol) was around 200 and 100 cm²/cm³ of the organic phase at the beginning and the end of the reaction, respectively ($\rho_p = 1.2$ g/cm³). The value of the solid−liquid mass-transfer coefficient, $k_{SL}$, assuming the limiting Sherwood number to be equal to 2, is 0.15 cm/s. The actual Sherwood number would be much greater than the limiting value of 2 when the system is under agitation. However, to demonstrate that mass-transfer effects were, indeed, absent, the lowest value was chosen. The bulk liquid-phase diffusivity was calculated as $3.5 \times 10^{-5}$ cm²/s at 30 °C. Thus, the rate of solid dissolution, represented by $k_{SL}a_p$ (30 s⁻¹), was very much greater than the apparent rate of reaction ($k_1$) under otherwise similar conditions. (Tables 1 and 2). Thus, it is clear that the diffusional resistance was unimportant.

**Effect of Catalyst Loading.** The concentration of catalyst (TBAB) was varied from $5.5 \times 10^{-6}$ to $1.1 \times 10^{-4}$ gmol/cm³. The conversion is plotted against time for different concentrations of the catalyst under otherwise similar conditions (Figure 6). As the concentration of the catalyst is increased, there is an increase in conversion. The pseudo-first-order kinetic plots are shown in Figure 7 at different catalyst concentrations, from which the pseudo-first-order constant $k_1$ values are obtained. Figure 8 shows that $k_1$ varies fairly linearly with the catalyst concentration in the range from $5.5 \times 10^{-6}$ to $1.1 \times 10^{-4}$ gmol/cm³. Thus, the solubilisation of the reactant MY is linear in catalyst concentration in the organic phase. In the absence of the catalyst, no reaction was found to take place.
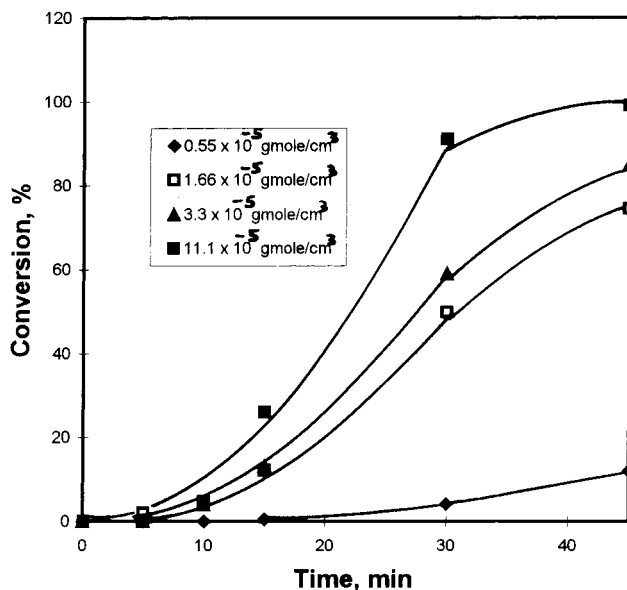
**Figure 6.** Effect of catalyst loading. Conditions: PCNB, 0.025 gmol; NaOCH₃, 0.1 gmol; temperature, 30 °C; toluene, 45 cm³; speed of agitation, 1000 rpm.
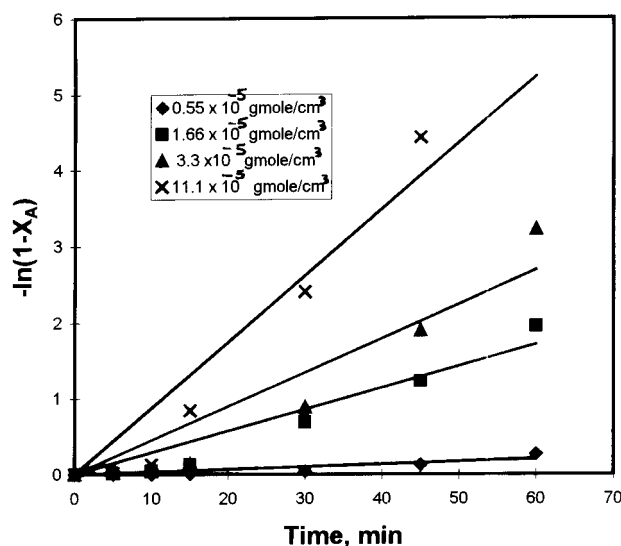


**Figure 7.** Kinetic plot for the effect of catalyst concentration. Conditions: PCNB, 0.025 gmol; NaOCH₃, 0.1 gmol; temperature, 30 °C; toluene, 45 cm³; speed of agitation, 1000 rpm.

**Effect of Concentration of PCNB.** Effect of concentration of PCNB was studied in the range from $2.78 \times 10^{-4}$ to $8.33 \times 10^{-4}$ gmol/cm³, under otherwise similar experimental conditions. Figure 9 shows that the initial rate of the reaction was proportional to the initial concentration of PCNB. This is in accordance with eq 9.

**Effect of Structure of PTC.** The different catalytic activities are mainly due to the different solubilities of the ion pair [M⁺Y⁻] in the presence of catalyst in the organic phase, which in turn can be attributed to the nature and bulkiness of Q⁺ and the property of the medium. Efficiency increases if the molecule is symmetrical. It seems that symmetrical molecules with the same number of C atoms or bulkiness distribute the charges more evenly and are, therefore, more active than the unsymmetrical molecules.[1−3]
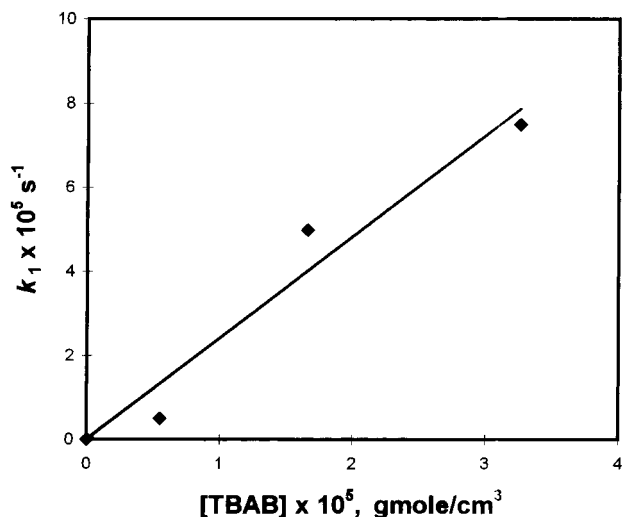
**Figure 8.** Effect of catalyst concentration on pseudo-first-order rate constant. Conditions: PCNB, 0.025 gmol; NaOCH$_3$, 0.1 gmol; temperature, 30 °C; solvent, toluene; speed of agitation, 1000 rpm.
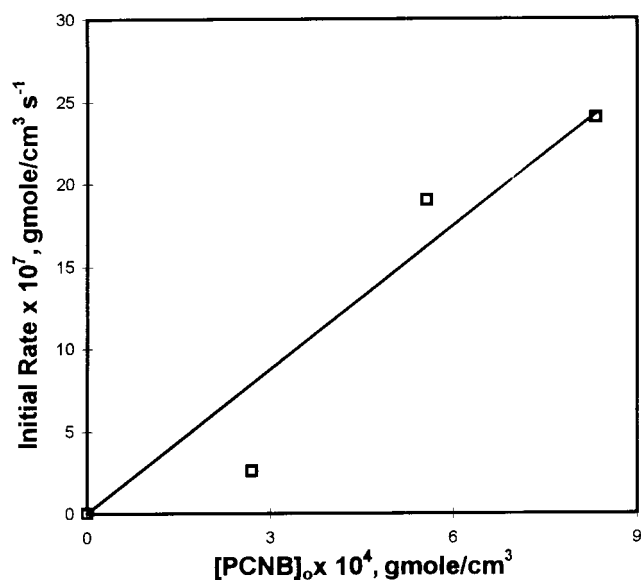


**Figure 9.** Effect of [PCNB]$_0$ on initial rate. Conditions: NaOCH$_3$, 0.1 gmol; TBAB, 7.5 × 10$^{-4}$ gmol; temperature, 30 °C; toluene, 45 cm$^3$; speed of agitation, 1000 rpm.

Tetrabutylammonium bromide (TBAB), tricaprylmethyl-ammonium chloride (Aliquat-336), cetyltrimethylammonium bromide (CTMAB), and tetrabutylammonium hydrogen sulfate (TBAHS) were used as the catalysts. There was not much difference in the efficacies due to the fact that the formation of Bu$_4$NOCH$_3$ was much faster. The different types of anion X$^-$ with the same symmetrical tetrabutylammonium ion do not matter. The bulkier catalyst Aliquat-336 gave lower conversion because the formation of (Q$^+$OCH$_3^-$) in this case was relatively slow. CTMAB did not yield any results due to nonsolubilisation of the particle. In addition, the catalyst formed a separate phase. CTMAB, being a surface-active agent, was found to be strongly bound to the solid particle (Figures 10 and 11). Table 1 gives the relevant data.
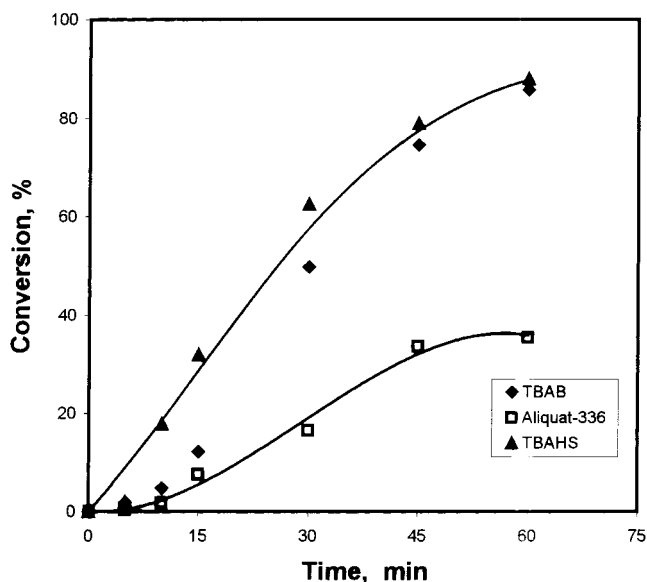


**Figure 10.** Effect of structure of PTC. Conditions: PCNB, 0.025 gmol; NaOCH$_3$, 0.1 gmol; temperature, 30 °C; toluene, 45 cm$^3$; catalyst, 7.5 × 10$^{-4}$ gmol; speed of agitation, 1000 rpm.
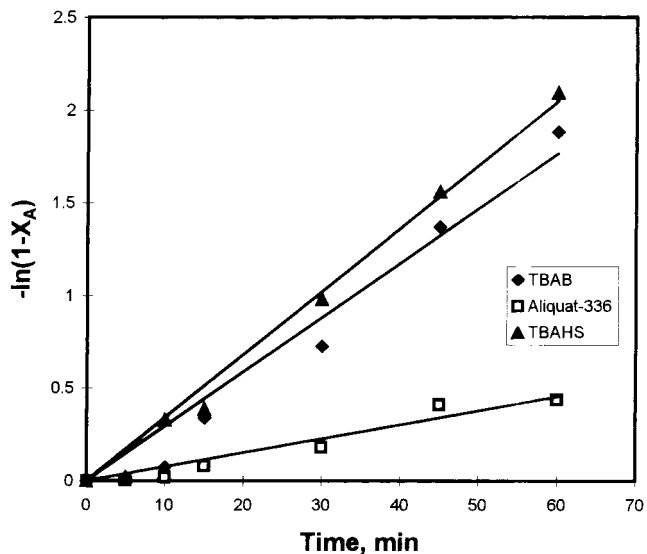


**Figure 11.** Kinetic plot for the effect of different catalysts. Conditions: PCNB, 0.025 gmol; NaOCH$_3$, 0.1 gmol; temperature, 30 °C; catalyst, 7.5 × 10$^{-4}$ gmol; toluene, 45 cm$^3$; speed of agitation, 1000 rpm.

**Effect of Solvent.** Toluene, benzene, and carbon tetrachloride were used as the solvent (Figure 12). Thus, the final conversions were found to be in the ascending order: CCl$_4$ (least) ≪ benzene < toluene (maximum). During the initial period, the increase is marginal, but as time progresses, the generation of MX salt leads to a fairly constant value of the ratio $r$ (=[MY]/[MX]). This is again due to the increase in the concentration of dissolved nucleophile Y$^-$ in these solvents, or correspondingly increased $r$ values in the same order.

**Effect of Temperature.** The reactions were studied at different temperatures under otherwise similar conditions. The conversion was found to increase with temperature. However, at 72 °C, the yield was found to decrease due to decomposition of sodium methoxide. At 100 °C, the conver-
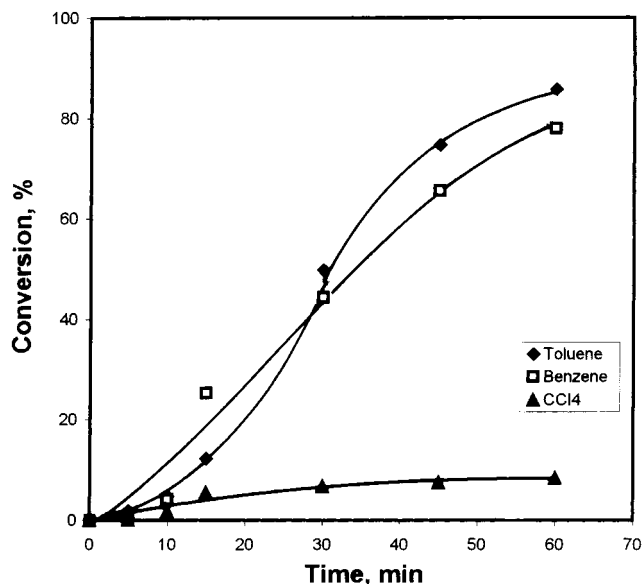
**Figure 12.** Effect of different solvents. Conditions: PCNB, 0.025 gmol; NaOCH$_3$, 0.1 gmol; temperature, 30 °C; toluene, 45 cm$^3$; catalyst, 7.5 × 10$^{-4}$ gmol; speed of agitation, 1000 rpm.



**Figure 14.** Arrhenius plot. Conditions: PCNB, 0.025 gmol; NaOCH$_3$, 0.1 gmol; TBAB, 7.5 × 10$^{-4}$ gmol; toluene, 45 cm$^3$; speed of agitation, 1000 rpm.
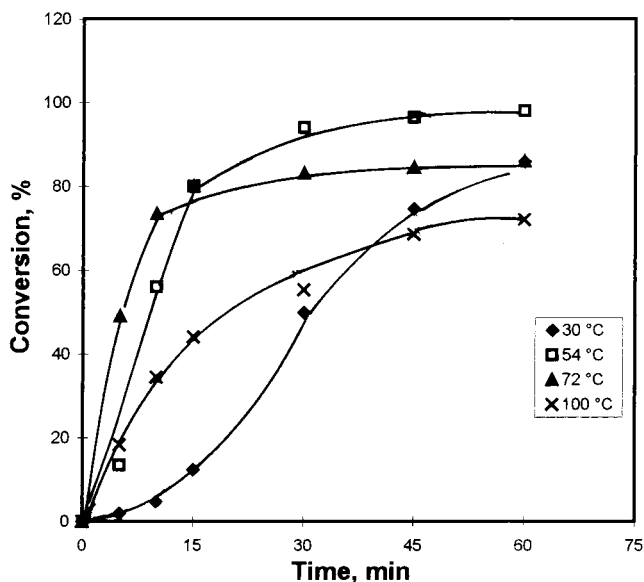


**Figure 13.** Effect of temperature. Conditions: PCNB, 0.025 gmol; NaOCH$_3$, 0.1 gmol; TBAB, 7.5 × 10$^{-4}$ gmol; toluene, 45 cm$^3$; speed of agitation, 1000 rpm.



**Figure 15.** Effect of isomer. Conditions: PCNB, 0.025 gmol; NaOCH$_3$, 0.1 gmol; temperature, 30 °C; TBAB, 7.5 × 10$^{-4}$ gmol; toluene, 45 cm$^3$; speed of agitation, 1000 rpm.

sion suffers due to extensive decomposotion of methoxide (Figure 13). Figure 14 gives the Arrhenius plot for the reaction. The energy of the activation for the reaction is 14.4 kcal/gmol. Thus, the reaction is kinetically controlled.

**Alkoxylation of OCNB and MCNB.** When under otherwise similar conditions the methoxylation was carried out with *o*-chloronitrobenzene (OCNB), the conversion was less than that with PCNB (Figure 15). The rate constant for the methoxylation of OCNB at 30 °C was found to be 12.5 cm$^3$ gmol$^{-1}$ s$^{-1}$. *m*-Chloronitrobenzene (MCNB) did not react at 30 °C. When a mixture of PCNB and OCNB (1:1 mole ratio) was reacted with 1 mol of sodium methoxide, both were found to react, with the product distribution being in the ratio of the rate constants for the respective species. Table 2 contains the pertinent data.
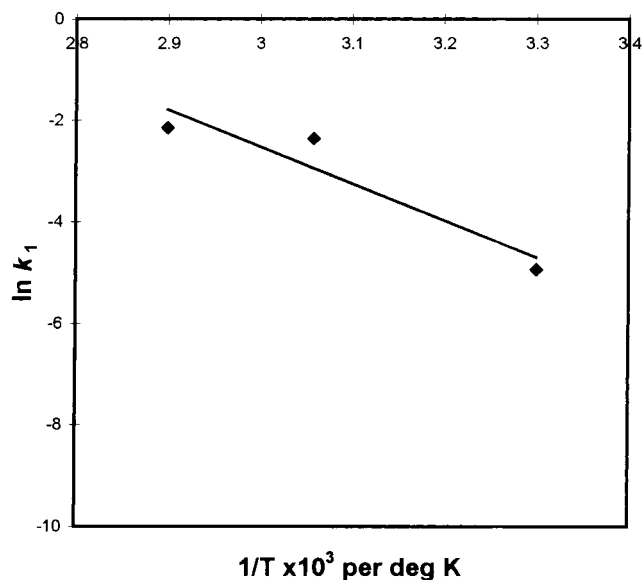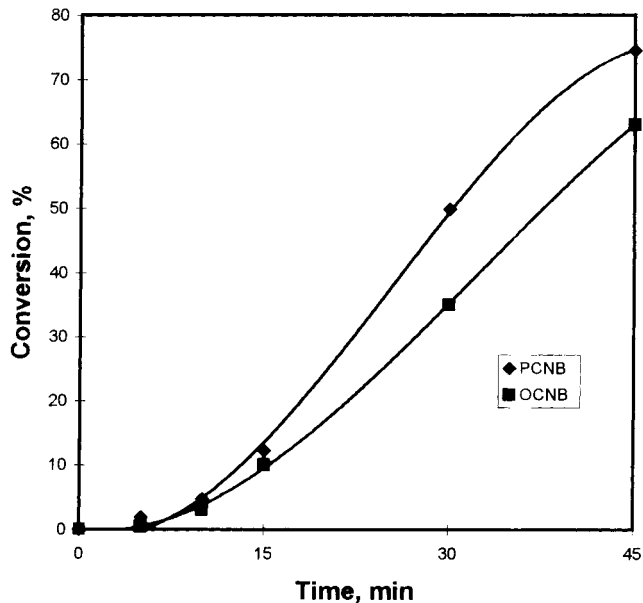
## Conclusions

Preparation of *p*-nitroanisole from PCNB and solid sodium methoxide was achieved successfully at room temperature with 100% selectivity to the alkoxylated product under solid−liquid PTC. The reaction was found to be kinetically controlled. The rate of the reaction was found to be first order with respect to both the concentrations of catalyst and the substrate. Toluene was the best solvent, and tetrabutylammonium salts were better catalysts. The type of anion in the ion pair Q$^+$X$^-$ did not affect the catalyst efficacy. The methoxylation of OCNB was much slower than that of PCNB. MCNB does not react with sodium methoxide at room temperature.

## Acknowledgment

### NOMENCLATURE

| | |
|---|---|
| $a_p$ | particle surface area, $cm^2/cm^3$ organic phase |
| $D$ | diffusivity of dissolved solid reactant in organic phase, $cm^2/s$ |
| $k_1 = k_2 K_e r[Q^+X^-]$ | pseudo-first-order rate constant, $s^{-1}$ |
| $k_2$ | second-order rate constant for reaction, $cm^3\ gmol^{-1}\ s^{-1}$ |
| $k_{obsd}$ | observed second-order rate constant of the overall reaction 1, $cm^3\ gmol^{-1}\ s^{-1}$ |
| $k_{SL}$ | solid−liquid mass-transfer coefficient, cm/s |
| $K_A$ | anion partitioning equilibrium coefficient, dimensionless |
| $K_e$ | equilibrium constant, dimensionless |
| M | metallic (inorganic) counterpart of leaving group X as well as nucleophile Y |
| MX | inorganic salt of leaving group X |
| MY | inorganic salt of nucleophile Y |
| (MY)* | saturated solubility of nucleophile in organic phase |
| $R_{MY}$ | rate of mass transfer of MY into the organic phase |
| Q | quaternary cationic part of leaving group X as well as nucleophile Y |
| QX | quaternary ammonium salt of leaving group X |
| QY | quaternary ammonium salt of nucleophile Y |
| $r = [M^+Y^-]/[M^+X^-]$ | ratio of concentrations of dissolved salts of nucleophile and leaving group |
| R | alkyl or aralkyl group of substrate RX |
| RX | substrate |
| RY | product |
| X | leaving group |
| Y | nucleophile |

*Greek Letters*

| | |
|---|---|
| $\delta$ | liquid film thickness, cm |
| $\lambda$ | distance from the solid surface in the liquid film surrounding the particle, cm |
| $\rho_p$ | density of solid reactant, MY, $g/cm^3$ |

*Abbreviations*

| | |
|---|---|
| Aliquat-336 | tricaprylmethylammonium chloride |
| CTMAB | cetyltrimethylammonium bromide |
| TBAB | tetrabutylammonium bromide |
| TBAHS | tetrabutylammonium hydrogen sulfate |
| PCNB | *p*-chloronitrobenzene |
| OCNB | *o*-chloronitrobenzene |
| MCNB | *m*-chloronitrobenzene |