



REGULAR ARTICLE

Special Issue on Recent Trends in the Design and Development of Catalysts and their Applications

# Insight into solid-liquid phase transfer catalyzed synthesis of Mecoprop ester using $K_2CO_3$ as base and development of new kinetic model involving liquid product and two solid co-products

GANAPATI D YADAV\* and GUNJAN P DESHMUKH

Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai, Maharashtra 400 019, India  
E-mail: gdyadav@yahoo.com; gd.yadav@ictmumbai.edu.in

MS received 15 April 2017; revised 2 August 2017; accepted 5 August 2017; published online 16 November 2017

**Abstract.** 2-Methyl-4-chlorophenoxy propionic acid (Mecoprop) is a widely used household herbicide. In the current work, a simple synthetic method is developed for Mecoprop methyl ester using solid-liquid phase transfer catalysis (S-L PTC) with  $K_2CO_3$  as mild base and toluene as solvent. Conversion of 95% was achieved with 100% selectivity for Mecoprop ester at 100 °C. Simple isolation process was employed to recover the product from the reaction mixture. A reaction mechanism was proposed and new kinetic model developed involving one liquid and two solid co-products. The activation energy for the reaction was calculated. This is the first example of its kind being reported vis-à-vis kinetics and mechanism.

**Keywords.** Phase transfer catalysis; O-alkylation; mecoprop ester; kinetic modelling; solid-liquid reaction.

## 1. Introduction

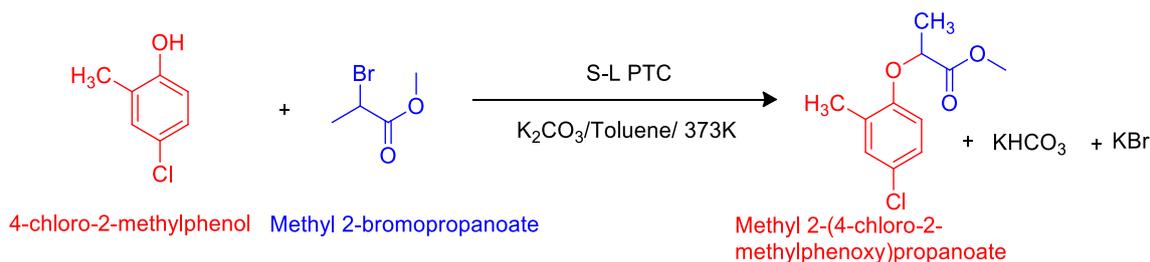
2-Methyl-4-chloro phenoxy propionic acid (Mecoprop) is one of the widely used herbicides of the phenoxy acid family.<sup>1</sup> Several salts and esters of Mecoprop are used as active agents in herbicidal formulations. It is also utilized as an intermediate in the synthesis of natural products and pesticides. Methyl-2-(4-chloro-2-methylphenoxy) propionate (Mecoprop ester) is one of the esters, employed as an intermediate in the synthesis of Mecoprop. Several methods are reported for synthesis of chloro phenoxy acid derivatives using alkali as base.<sup>2–6</sup> In almost all processes, strong aqueous bases are used which are neutralized using mineral acids generating waste and are difficult to handle.

Phase transfer catalysis (PTC) is a widespread technique with continuous developments and new applications in the current age of synthetic chemistry. Different types of phase transfer catalytic techniques are known with several applications. During last few years, our laboratory has developed different concepts and applications of PTC such as process intensification in liquid-liquid-liquid (L-L-L) PTC,<sup>7</sup> microwave irradiated L-L-L PTC (MILL-PTC)<sup>8,9</sup> ionic liquid as PTC and pseudo-PFC.<sup>10</sup> Among these studies, solid-liquid PTC

is a well-known technique for different reactions. Alkalis such as NaOH and KOH are widely used as bases in phase transfer catalyzed reactions. These strong bases sometimes portray several disadvantages. The reactions with alkali as base involve multi-step synthesis and isolation of product, which is a tedious process reported in a couple of patents.<sup>11,12</sup> In the case of water sensitive reactants, carbonates can be used as bases to avoid side reactions and hydrolysis of reactants. Thus, carbonates can be a good option to explore them as non-nucleophilic bases. Non-nucleophilic alkali carbonates such as  $K_2CO_3$  and  $Na_2CO_3$  can provide an efficient substitution for these alkali bases.<sup>13</sup> Carbonates provide mild conditions for reaction, can suppress the side reactions and provide minimum corrosion of reactor and auxiliary equipment. A variety of PTC reactions are reported, wherein carbonates are employed as bases such as reactions of phosphorous and sulphur based compounds,<sup>14</sup> oxidation,<sup>15</sup> N-alkylation,<sup>13</sup> O-alkylation<sup>16</sup> and synthesis of amino acids,<sup>17</sup> etc. A variety of multiphasic reactions involving PTC have been modeled by us.<sup>18,19</sup>

In the present work, a novel route for the synthesis of Mecoprop ester was established. Several phase transfer catalysts such as tetrabutylammonium bromide (TBAB), ethyltriphenyl phosphonium bromide (ETPPB), tetrabutylphosphonium bromide (TBPB),

\*For correspondence



**Scheme 1.** Synthesis of Mecoprop ester from 4-chloro-2-methyl phenol under S-L PTC.

tetrabutyl ammonium hydrogen sulfate (TBAHS) and triethylammonium bromide (TEAB) were screened for the reaction. Among these  $\text{K}_2\text{CO}_3$ –TBAB: base-catalyst pair in solid-liquid PTC was found the best. In relatively milder conditions, >95% conversion and 100% selectivity for the product was achieved. Kinetics for the reaction was established and the activation energy was also calculated. The product was recovered by simple isolation process.

## 2. Experimental

### 2.1 Chemicals and catalysts

4-Chloro-2-methyl phenol (CMP) and ethyl-2-chloro propionate (ECP) were obtained from Sigma Aldrich. All PTC reagents were obtained from Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India as gift samples. NaOH and toluene were obtained from M/s S.D. Fine Chemicals, Mumbai, India. All the chemicals were used as received without purification.

### 2.2 Experimental procedure

All the reactions were studied in a glass reactor. The details of the reactor are mentioned in previous work done in our lab.<sup>18</sup> The impeller of the reactor was kept 2 cm above the bottom to ensure complete mixing of solid–liquid suspension to achieve maximum mass transfer rates. The reactor was placed in an isothermal oil bath at the temperature required to perform the reaction. The quantities of chemicals and reagents were weighed, added to the reactor and then the temperature raised. The catalyst quantity was added in reactor once it reached the desired temperature. Typical experimental runs were conducted by preparing reaction mixture of CMP (0.0028 mol), ECP (0.003 mol),  $\text{K}_2\text{CO}_3$  (0.0032 mol), toluene (20 cm<sup>3</sup>) and TBAB ( $3 \times 10^{-4}$  mol) at 100 °C.

### 2.3 Analysis

Samples were withdrawn periodically. Agitation was stopped and the solid suspension allowed to settle. The sample was centrifuged after withdrawal and further analyzed by GC (Chemito model 1000) using capillary column (BPX- 50).

The products were confirmed by GCMS (Perkin Elmer, Clarus Model 500 on Elite 1 capillary column of length 30 m and inner diameter 0.25 mm).

### 2.4 Reaction scheme

2.4a Overall reaction: See Scheme 1.

2.4b Reaction mechanism: See Scheme 2.

### 2.5 Isolation of the product

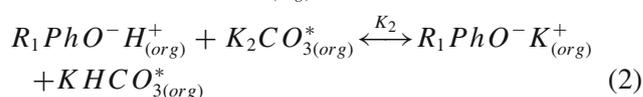
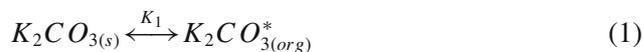
At the end of the experiment, the reaction mass was filtered to remove solid  $\text{KHCO}_3$ , unreacted  $\text{K}_2\text{CO}_3$  and KBr. The solid was washed with 5 mL toluene to collect the adsorbed product on the surface of solid particles. The collected filtrate was washed with 2% NaOH. Further, toluene was distilled out to obtain the pure product.

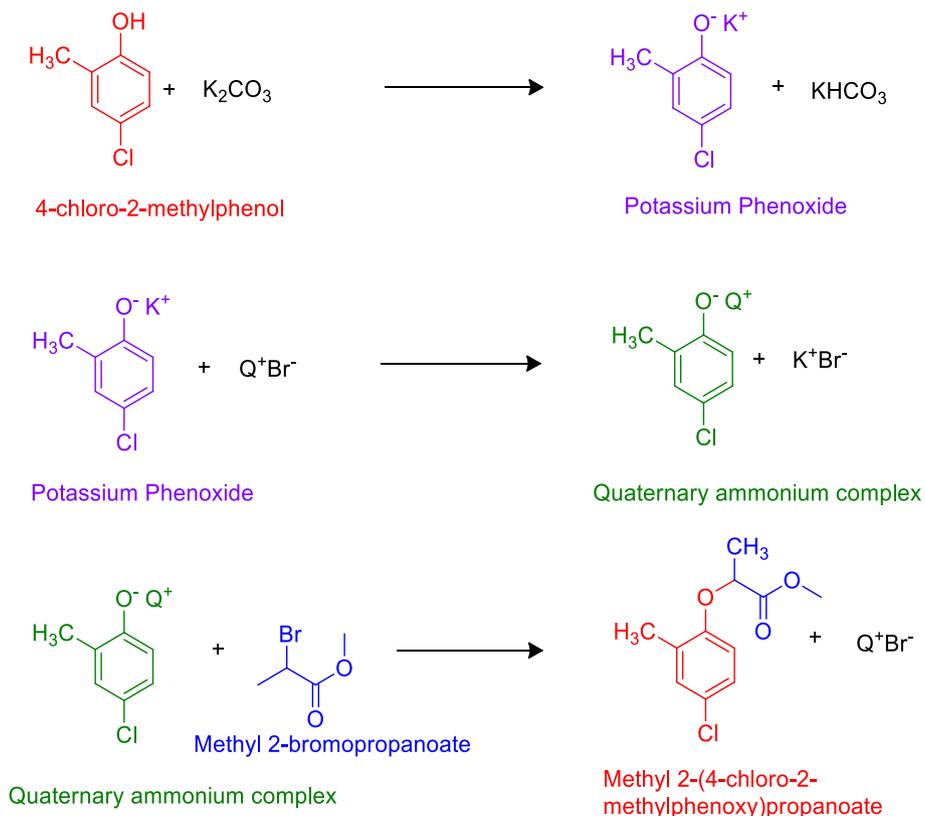
## 3. Results and Discussion

### 3.1 Mechanism and kinetic model

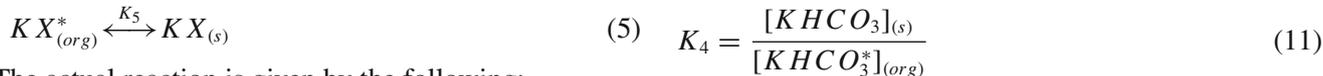
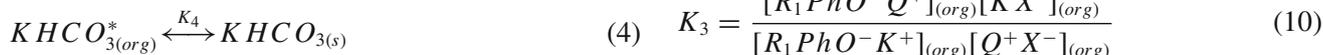
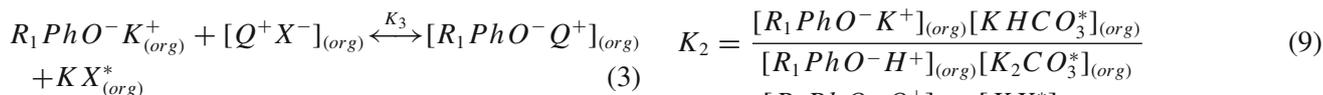
In the usual mechanism of S-L PTC, an ion-pair is formed between the quaternary phase transfer cation and the reactive anion (ion-exchange reaction) as discussed in our previous work.<sup>18,19</sup> However, in this case, a different model is developed due to the specific nature of reaction forming two solid products. The complete reaction sequence can be illustrated as given below.

In this overall reaction, the first reaction step is an abstraction of a proton from the phenolic compound ( $R_1PhO^-H^+$ ) by  $\text{K}_2\text{CO}_3$  in organic phase. All inorganic salts are sparingly soluble in organic medium and thus there is a saturation solubility denoted by an asterisk with an equilibrium. The various equilibria and reactions are also depicted as given below:

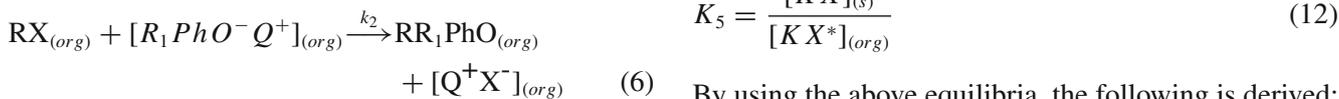




**Scheme 2.** The reaction mechanism for the synthesis of Mecoprop ester under S-L PTC.



The actual reaction is given by the following:



By using the above equilibria, the following is derived:

$$[R_1PhO^-Q^+]_{(org)} = \frac{K_1K_2K_3K_4K_5[R_1PhO^-H^+]_{(org)}[K_2CO_3]_{(s)}[Q^+X^-]_{(org)}}{[KHCO_3]_{(s)}[KX]_{(s)}} \quad (13)$$

The rate of reaction of RX is given by:

$$-\frac{d[RX]_{(org)}}{dt} = k_2[RX]_{(org)}[R_1PhO^-Q^+]_{(org)} \quad (7) \quad K_1K_2K_3K_4K_5 = K_e \quad (14)$$

In Equation (7), it is necessary to substitute for  $[R_1PhO^-Q^+]_{(org)}$  in terms of known variables.

The following equilibria hold:

$$K_1 = \frac{[K_2CO_3^*]_{(org)}}{[K_2CO_3]_{(s)}} \quad (8)$$

The phenolic  $R_1PhOH$  is taken in stoichiometric excess over the substrate RX and also the conversion of  $R_1PhOH$  is complete in the  $R_1PhOK$  form since  $K_2CO_3$  is taken in excess over  $R_1PhOH$ . Thus, the following could be written:

$$[R_1PhO^-Q^+]_{(org)} = \frac{K_1K_2K_3K_4K_5[R_1PhO^-H^+]_{(org)}[K_2CO_3]_{(s)}[Q^+X^-]_{(org)}}{[KHC O_3]_{(s)}[KX]_{(s)}} \quad (15)$$

$$= K_e[Q^+X^-]_{(org)} \quad (16)$$

Now, in the organic phase the total catalyst  $Q_0$  exists in the form of two ion-pairs in S-L PTC, unlike the L-L PTC where it is in four different ion-pairs. The material balance on total catalyst added to the system gives the following:

$Q_0$  = total concentration of catalyst in organic phase, mol/cm<sup>3</sup>

$$\begin{aligned} &= [R_1PhO^-Q^+]_{(org)} + [Q^+X^-]_{(org)} \\ &= [R_1PhO^-Q^+]_{(org)} \left(1 + \frac{1}{K_e}\right) \\ &= \left(\frac{K_e + 1}{K_e}\right) [R_1PhO^-Q^+]_{(org)} \quad (17) \end{aligned}$$

$$[R_1PhO^-Q^+]_{(org)} = \frac{K_e Q_0}{(K_e + 1)} \quad (18)$$

$$-\frac{d[RX]_{(org)}}{dt} = \frac{k_2 K_e Q_0}{(K_e + 1)} [RX]_{(org)} \quad (19)$$

The above equation is a typical pseudo-first order rate equation.

Let  $X_A = \frac{[RX]_0 - [RX]}{[RX]_0}$ , the fractional conversion of RX. Then on integration, it leads to:

$$-\ln(1 - X_A) = \frac{k_2 K_e Q_0}{(K_e + 1)} t = k Q_0 t = k_1 t \quad (20)$$

Where

$$k_1 = k Q_0 \quad (21)$$

and

$$\frac{k_2 K_e}{(K_e + 1)} = k \quad (22)$$

Thus, a plot of  $-\ln(1 - X_A)$  against  $t$  will give a slope equal to  $k_1$ . From the knowledge of the initial quantity of catalyst, the rate constant  $k$  can be calculated. Order of magnitude analysis suggests that the catalyst is mostly in the  $[R_1PhO^-Q^+]_{(org)}$  form and thus  $K_e \gg 1$  leading to  $[R_1PhO^-Q^+]_{(org)} \simeq Q_0$ . It was thus planned to test the above model.

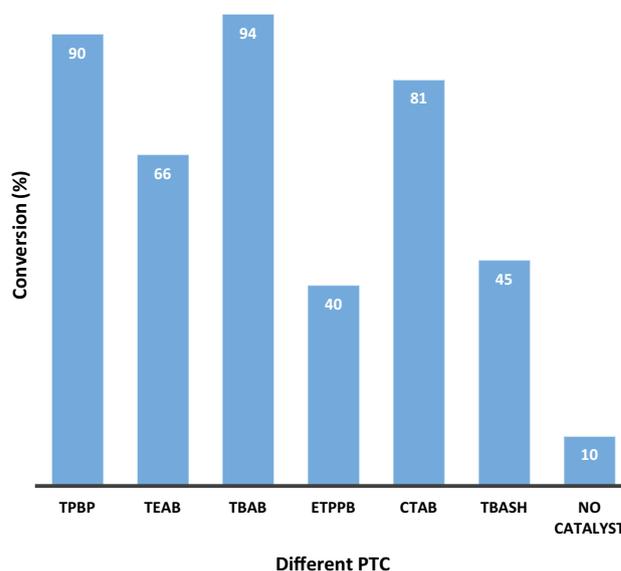
### 3.2 Effect of different phase transfer catalysts

Various nitrogen, phosphorous and sulphur based PTC were screened for O-alkylation of CMP. Catalysts such as TBAB, ETPPB, TBPB, TBAHS and TEAB were used (Figure 1). In S-L PTC the entire quantity of the catalyst is present in bulk organic phase (toluene) to form active  $[R_1PhO^-Q^+]_{(org)}$  unlike the L-L PTC wherein

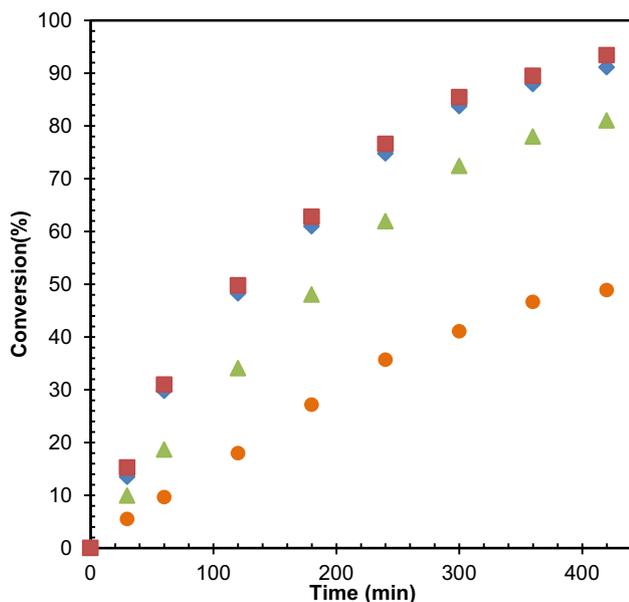
it remains distributed across the aqueous and organic phases in four ion-pairs. The ion exchange reaction for TBAB is very fast with  $K_2CO_3$  as compared with other catalysts such as CTAB, TEAB and ETPPB.<sup>20</sup> Tetrabutyl cation is more reactive as compared with tetraethyl cations, when exchanged with large anions of  $[R_1PhO^-Q^+]_{(org)}$ . Further, in the case of ethyltriphenyl cation, it shows less activity due to the formation of strong ion pairs with bromides.<sup>21</sup> The order of the catalyst for the conversion of phenol can be given in the following sequence:

$$\begin{aligned} \text{TBAB(max)} &> \text{TBPB} > \text{TBAHS} > \text{CTAB} \\ &> \text{TEAB} > \text{ETPPB}. \end{aligned}$$

From the reactivity trend obtained, it is concluded that TBAB gives the perfect balance between its lipophilicity and structure size. A catalyst such as TEAB lacks the lipophilic character to allow the ion pair to dissolve in toluene and further react with the substrate. On the contrary catalysts with bulkier alkyl group show steric hindrance to form ion pair with the phenol. The reaction was also studied without catalyst which showed marginal conversion.



**Figure 1.** Effect of different PTC used for reaction of 4-chloro-2-methyl phenol (CMP). 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.003 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; agitation speed – 1200 rpm; solvent (toluene) – 20 ml; temperature – 100 °C.



**Figure 2.** Effect of the speed of agitation on conversion of CMP. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.003 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; solvent (Toluene) – 20 mL; temperature – 100 °C. (●) 800, (▲) 1000, (◆) 1200, (■) 1400.

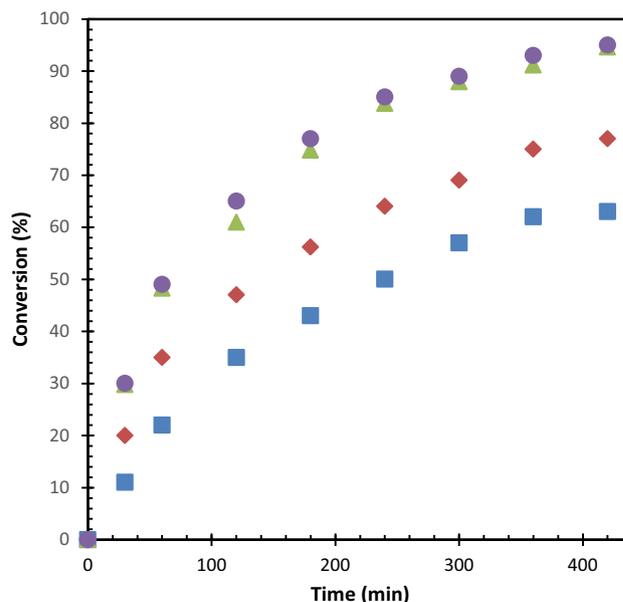
Thus, all further reactions were studied using TBAB as a catalyst as it showed enhanced activity, is inexpensive and commercially available with high purity.

### 3.3 Effect of speed of agitation

Influence of mass transfer was determined by varying the stirring speed from 800 to 1400 rpm. The rate of the reaction dramatically increases when stirring speed is increased from 800 to 1200 rpm (Figure 2). This might be due to increase in interfacial area per unit volume of dispersion which increases linearly with increase in speed of agitation. However, there is a marginal difference in conversion between 1200 and 1400. Thus, S-L mass transfer resistance at and above 1200 rpm is overcome and further experiments were studied at 1200 rpm.

### 3.4 Effect of $K_2CO_3$ quantity and particle size

The effect of quantity of  $K_2CO_3$  was studied for the conversion of CMP to form the product. As the solid base was added to the reaction, its concentration in organic phase could not be varied. The quantity of  $K_2CO_3$  to CMP was varied in the ratio of 0.9 to 1.2. As stated earlier, more quantity of  $K_2CO_3$  helps in saturation of organic phase as given by equations 1 and 3, and then exchange with the quaternary cation leading to maximum of  $[R_1PhO^-Q^+]_{(org)}$  occurs. Conversion of CMP



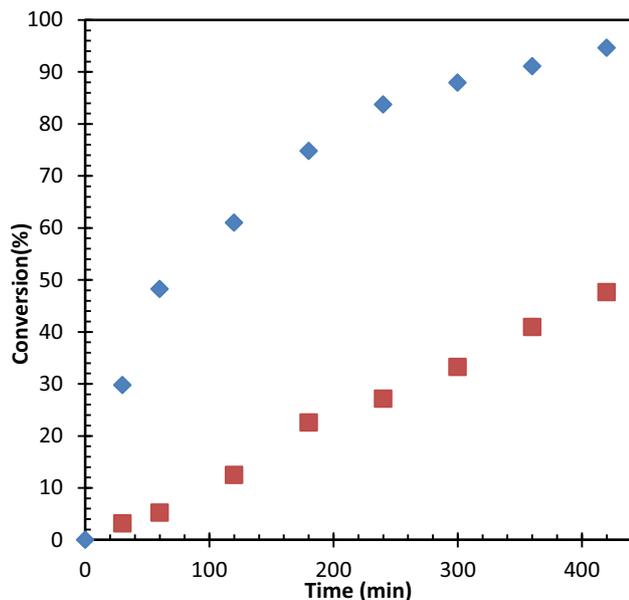
**Figure 3.** Effect of quantity of  $K_2CO_3$  on conversion of CMP. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.003 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; solvent (Toluene) – 20 mL; temperature – 100 °C (■) 1:0.9, (◆) 1: 1, (▲) 1: 1, (●) 1: 2.

goes on increasing with increase in the quantity of base. At lower mole ratio less conversion was observed and this might be due to the insufficient quantity of  $K_2CO_3$  which is available for reaction. From Figure 3, one can note that a little more quantity of  $K_2CO_3$  than stoichiometry is enough to achieve the best conversion. Further, the reaction was studied with fine powder and granular  $K_2CO_3$ . The fine powder gave a good rate and conversion for the reaction which is explained later (Figure 4).

The rate of solid-liquid mass transfer is dependent upon the surface area provided by the number of particles and will be maximum if fine particles instead of granular ones are used. In the current case the surface area per unit volume of the particle is:

$$n_p \left( \frac{6}{d_p} \right)$$

where  $n_p$  and  $d_p$  are a number of particles and particle diameter, respectively. Thus, with finer the particles more surface area is provided. Thus, the solid-liquid mass transfer coefficient can be given by the limiting Sherwood number,  $Sh = \frac{k_{SL}d_p}{D_A} = 2$ , which is far greater than 2 in agitated vessels.  $D_A$  is the diffusivity of dissolved  $K_2CO_3$  in the liquid phase. The value of particle surface area per unit liquid volume is  $a_p = \frac{6W}{\rho_p d_p}$  where  $W$ ,  $\rho_p$  and  $d_p$  are solid loading (g/cm<sup>3</sup>), particle density (g/cm<sup>3</sup>) and particle diameter respectively. Thus,

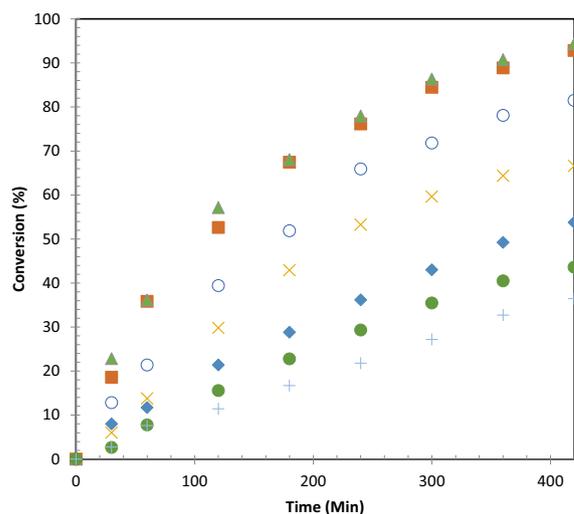


**Figure 4.** Effect of size of  $K_2CO_3$  on conversion of CMP. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.003 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; solvent (Toluene) – 20 mL; temperature – 100 °C. (■) Granular  $K_2CO_3$  (◆) Fine powder of  $K_2CO_3$ .

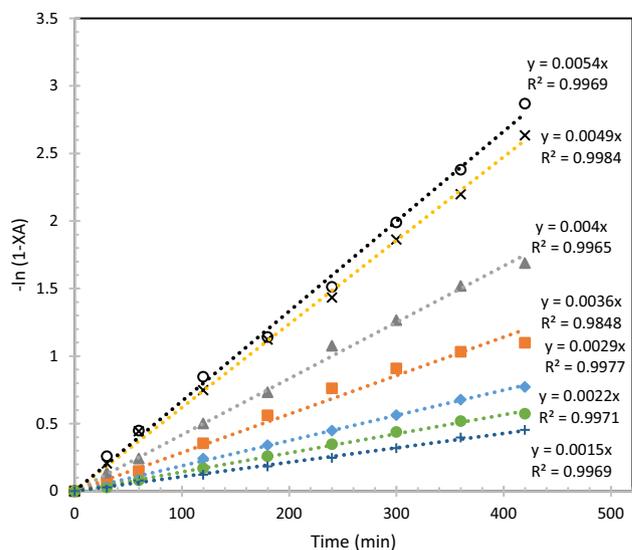
the solid-liquid mass transfer rate is given by  $k_{SL}a_p[B_S]$  where  $[B_S]$  is the solid saturation concentration wherein B forms an ion-pair with phenoxide species leading to the formation of potassium salt with K and  $KHCO_3$ . The  $K^+$  is then exchanged with  $Q^+X^-$  (org) species to form quaternary ion-pair and  $K^+X^-$  (solid). The concentration of the phenoxide ion will always be at its saturation value for fine particles and the rate of solid-liquid mass transfer will be far greater than reaction rate in the liquid phase. Thus, after certain particle size, the rate of reaction or conversion will be independent of particle size as given in Figure 4.

### 3.5 Effect of catalyst loading

Catalyst concentration plays an important role in S-L PTC because the catalyst is a medium between reaction between solid and organic phase. Increase in catalyst concentration increases the rate of reaction. The catalyst concentration was varied from  $6.2 \times 10^{-6}$  to  $1.5 \times 10^{-5}$  mol/cm<sup>3</sup> (Figure 5). Even though the concentration of the catalyst is increased the concentration of  $Q^+PhO^-$  is the saturation value and therefore, the rate of conversion remains the same. Thus,  $1.4 \times 10^{-5}$  mol/cm<sup>3</sup> was considered as optimum catalyst concentration. The experimental data were validated with the model (Figure 6).

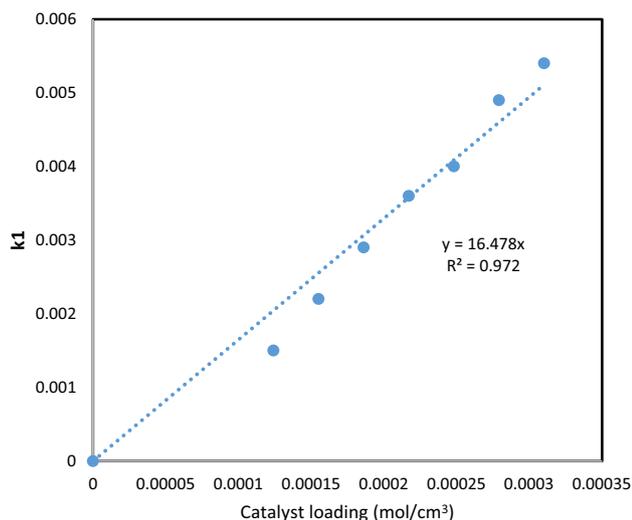


**Figure 5.** Effect of catalyst loading on conversion of CMP. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl chloro propionate – 0.0032 mol;  $K_2CO_3$  – 0.0032 mol; agitation speed – 1200 rpm; solvent (Toluene) – 20 mL; temperature – 100 °C. (+)  $6.2 \times 10^{-6}$  mol/cm<sup>3</sup>; (●)  $7.8 \times 10^{-6}$  mol/cm<sup>3</sup>; (◆)  $9.31 \times 10^{-6}$  mol/cm<sup>3</sup>; (×)  $1.1 \times 10^{-5}$  mol/cm<sup>3</sup>; (○)  $1.24 \times 10^{-5}$  mol/cm<sup>3</sup>; (■)  $1.39 \times 10^{-5}$  mol/cm<sup>3</sup>; (▲)  $1.55 \times 10^{-5}$  mol/cm<sup>3</sup>.

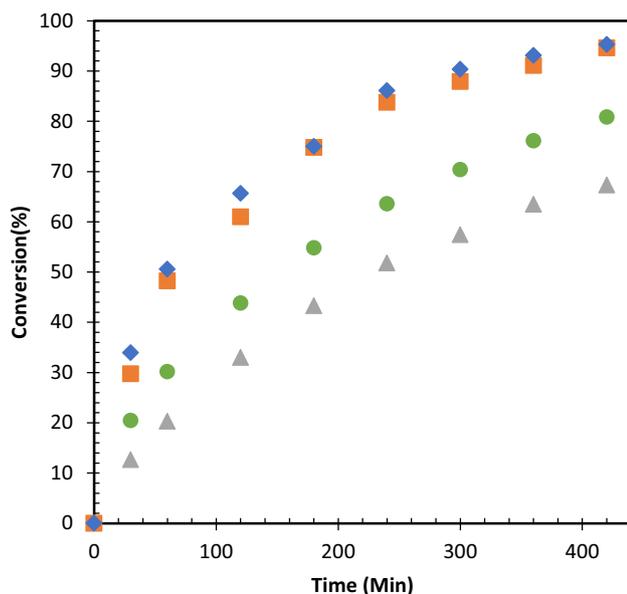


**Figure 6.** Validation of model at different catalyst loadings. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.0032 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; agitation speed – 1200 rpm; solvent (Toluene) – 20 mL; temperature – 100 °C. (+)  $6.2 \times 10^{-6}$  mol/cm<sup>3</sup>; (●)  $7.8 \times 10^{-6}$  mol/cm<sup>3</sup>; (◆)  $9.31 \times 10^{-6}$  mol/cm<sup>3</sup>; (■)  $1.1 \times 10^{-5}$  mol/cm<sup>3</sup>; (▲)  $1.24 \times 10^{-5}$  mol/cm<sup>3</sup>; (×)  $1.39 \times 10^{-5}$  mol/cm<sup>3</sup>; (○)  $1.55 \times 10^{-5}$  mol/cm<sup>3</sup>.

Figure 7 demonstrates the effect of catalyst concentration of the pseudo-rate constant  $k_1$ . It gives a very good fit suggesting that as stated earlier  $K_e \gg 1$  and hence  $[R_1PhO^-Q^+]_{(org)} \approx Q_o$ .



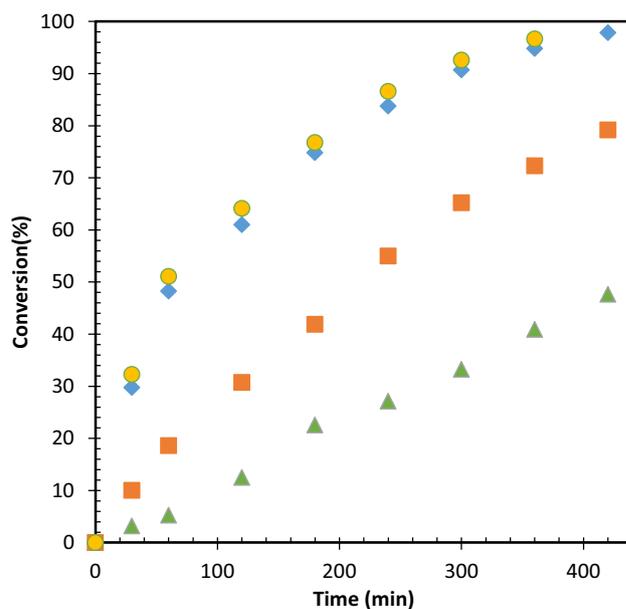
**Figure 7.** Effect catalyst concentration in organic phase on pseudo-rate constant  $k_1$  (see Eq. 21).



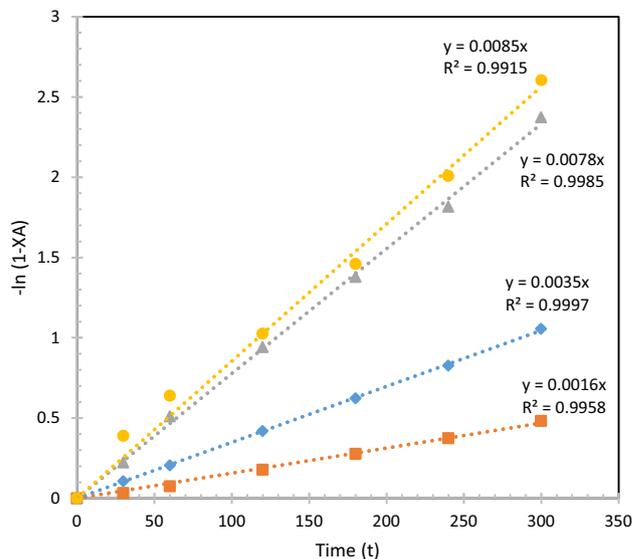
**Figure 8.** Effect of mole ratio on conversion of CMP. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.0032 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; agitation speed – 1200 rpm; solvent (Toluene) – 20 mL; temperature – 100 °C; (▲) 1: 0.9 (●) 1:1, (■) 1:1.1, (◆) 1:1.2.

### 3.6 Effect of mole ratio

The effect of variation in mole ratio was studied to find out optimum concentration to achieve maximum conversion and selectivity towards the product. Mole ratio was studied from 1: 0.9 to 1.2 with reference to CMP (Figure 8). The catalyst loading was kept  $1.4 \times 10^{-5}$  mol/cm<sup>3</sup>. It is concluded that the conversion goes on increasing with increase in the concentration of CMP.



**Figure 9.** Effect of temperature on conversion of CMP. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.0032 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; agitation speed – 1200 rpm; solvent (Toluene) – 20 mL. (▲) 70 °C, (■) 80 °C, (◆) 90 °C (●) 100 °C.



**Figure 10.** Validation of model at different temperatures. 4-Chloro-2-methyl phenol – 0.0028 mol; Ethyl-2-chloropropionate – 0.0032 mol;  $K_2CO_3$  – 0.0032 mol; catalyst – 0.000014 mol/cm<sup>3</sup>; agitation speed – 1200 rpm; solvent (Toluene) – 20 mL. (■) 70 °C, (◆) 80 °C, (▲) 90 °C (●) 100 °C.

### 3.7 Effect of temperature

The effect of temperature on conversion of CMP was studied at different temperatures from 80 to 110 °C under otherwise similar experimental conditions (Figure 9). Increase in temperature results in an increase in

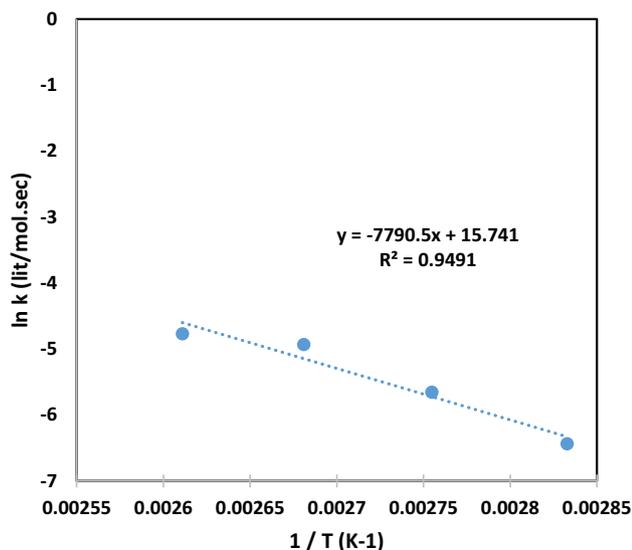


Figure 11. Arrhenius plot.

the initial rate of reaction. The conversion also increased subsequently.

However, only marginal difference was observed. The model for each temperature was also tested to get good statistical fit (Figure 10). Thus, the Arrhenius plot was made and activation energy for the reaction was found as 15.4 kcal/mol (Figure 11).

#### 4. Conclusion

A simple process was developed for the synthesis of mecoprop ester from 4-chloro-2-methyl phenol (CMP) and ethyl-2-chloropropionate using  $K_2CO_3$  as a mild base with >95% conversion under solid-liquid phase transfer catalysis. Tetrabutylammonium bromide was found as an excellent catalyst among all the catalysts screened. A simple isolation process for the product was developed. A new insight was provided into the reaction mechanism and kinetics of the reaction. A complete theoretical analysis of the process involving one liquid and two solid co-products was carried out to describe the observed rate data for the first time in published literature on S-L PTC. The apparent activation energy for the reaction is 15.4 kcal/mol.

#### Acknowledgements

G D Yadav acknowledges support from R T Mody Distinguished Professor Endowment and J C Bose National Fellowship of Department of Science And Technology, Government of India. G P Deshmukh acknowledges University Grant Commission (UGC) for award of SRF under its UGC-SAP green technology programme.

#### References

- White A H 1980 (+)-2-(4-Chloro-2-methylphenoxy) propionic acid *Acta Cryst.* **B36** 992
- Hayashi M, Wada K and Munakata K 1983 Synthesis and Nematicidal Activity of Phenoxypropionic Acid Derivatives *Agric. Biol. Chem.* **47** 2653
- Hassaneen H M, Elwan N M and Hassaneen H M 2002 Novel synthesis of 4,5-dihydrospiropyrazole-5,2'-indane-1',3'-diones *Synth. Commun.* **32** 3047
- Camps P, Pérez F and Soldevilla N 1998 (R)- and (S)-3-Hydroxy-4,4-dimethyl-1-phenyl-2-pyrrolidinone as chiral auxiliaries in the enantioselective preparation of  $\alpha$ -aryloxypropanoic acid herbicides and  $\alpha$ -chlorocarboxylic acids *Tetrahedron: Asymmetr.* **9** 2065
- Carbonara G, Fracchiolla G, Loiodice F, Tortorella P, Conte-Camerino D, De Luca A and Liantonio A 2001 Carboxylic acids and skeletal muscle chloride channel conductance: Effects on the biological activity induced by the introduction of an aryloxyalkyl group? to the carboxylic function of 4-chloro-phenoxyacetic acid *Farmaco* **56** 749
- Thirupathi G, Venkatanarayana M, Dubey P K and Kumari Y B 2013 Facile and Green syntheses of 2-(N-methylindole-3-carbonyl)-3-(N-methylpyrrol-2-yl)acrylonitriles and a study of their antimicrobial activities *Synth. Commun.* **43** 2967
- Yadav G D and Sowbna P R 2012 Process intensification and waste minimization in liquid-liquid-liquid phase transfer catalyzed selective synthesis of mandelic acid *Chem. Eng. Res. Des.* **90** 1281
- Yadav G D and Sowbna P R 2012 Modeling of microwave irradiated liquid-liquid-liquid (MILLL) phase transfer catalyzed green synthesis of benzyl thiocyanate *Chem. Eng. J.* **179** 221
- Yadav G D and Jain S S 2012 Novelties of low energy microwave-irradiated tri-liquid phase transfer catalysis (MILLL-PTC): halo-exchange of benzyl chloride with sodium bromide *Clean Technol. Environ. Policy* **14** 709
- (a) Yadav G D and Tekale S P Selective 2010 O - Alkylation of 2-Naphthol using Phosphonium-Based Ionic Liquid as the Phase Transfer Catalyst *Org. Process Res. Dev.* **14** 722; (b) Yadav G D and Kadam A A Atom-Efficient Benzoin Condensation in Liquid-Liquid System Using Quaternary Ammonium Salts: Pseudo-Phase Transfer Catalysis *Org. Process Res. Dev.* **16** 755-763
- Loewenthal H J E and Loewenthal B 2002 Conversion of hydroxy group in certain alcohols into a fluoro-sulphone ester or a trimethanesulphonate ester United States Patent 6395918 B1
- Soula G and Michelet D 1982 Preparations of aliphatic/aromatic ETHERS United States Patent 4314086
- Sasson Y and Bilman N 1989 Mechanism of solid/liquid phase-transfer catalysis in the presence of potassium carbonate: alkylation of pyrrolidin-2-one *J. Chem. Soc., Perkin Trans. 2* **12** 2029
- Jászay Z M, Petneházy I and Töke L 2004 Reaction of chlorides of phosphoric, sulfonic, and carboxylic acids

- on solid potassium carbonate surface under PTC circumstances *Heteroatom Chem.* **15** 447
15. Sasson Y, Wiener H and Bashir S 1987 Ruthenium-catalysed oxidation of benzyl alcohols to benzaldehydes by carbon tetrachloride under phase-transfer conditions *J. Chem. Soc. D* **20** 1574
  16. Ouk S, Thiebaud S, Borredon E, Le Gars P and Lecomte L 2002 O-Methylation of phenolic compounds with dimethyl carbonate under solid/liquid phase transfer system *Tetrahedron Lett.* **43** 2661
  17. Kotha S and Brahmachary E 2000 Synthesis of indan-based unusual alpha-amino acid derivatives under phase-transfer catalysis conditions *J. Org. Chem.* **65** 1359
  18. (a) Yadav G D and Sharma M M 1981 Kinetics of reaction of benzyl chloride with sodium acetate/benzoate: Phase transfer catalysis in solid-liquid system *Ind. Eng. Chem. Proc. Des. Dev.* **20** 385; (b) Yadav G D and Motirale B G 2008 Novelities of solid-liquid phase transfer catalyzed synthesis of triclosan from potassium 2,4-dichlorophenolate and 2,5-dichlorophenol *Ind. Eng. Chem. Res.* **47** 9055; (c) Yadav G D and Haldavanekar B V 1997 Mechanistic and kinetic investigation of liquid-liquid phase transfer catalyzed oxidation of benzyl chloride to benzaldehyde *J. Phys. Chem. A* **101** 36; (d) Yadav G D and Lande S V 2005 Liquid-liquid-liquid phase transfer catalysis: a novel and green concept for selective reduction of substituted nitroaromatics *Adv. Synth. Catal.* **347** 1235; (e) Yadav G D and Naik S S 2001 Novelities of liquid-liquid-liquid phase transfer catalysis: Alkoxylation of p-chloronitrobenzene *Catal. Today* **66** 345; (f) Yadav G D and Paranjape P M 2005 Novelities of solid-liquid phase transfer catalysed synthesis of p-toluenesulfonyl fluoride from p-toluenesulfonyl chloride *J. Fluor. Chem.* **126** 289; (g) Yadav G D and Badure O P 2009 Liquid-liquid-liquid phase-transfer catalysis for cleaner and selective etherification of p-hydroxy-biphenyl with benzyl chloride to 1, 1'-biphenyl-4-(phenylmethoxy) *Clean Technol. Environ. Policy* **11** 163
  19. (a) Yadav G D and Bisht P M 2004 Novelities of microwave irradiated solid-liquid phase transfer catalysis (MISL-PTC) in synthesis of 2-benzyloxyacetophenone *J. Mol. Catal. A: Chem.* **221** 59; (b) Yadav G D and Bisht P M 2004 Synergism of low energy microwave irradiation and solid-liquid phase transfer catalysis for selective alkylation of phenols to phenolic ethers *Synth. Commun.* **24** 2285
  20. Zhao Q, Sun J, Li J and He J 2013 Kinetics and mechanism of Horner – Wadsworth – Emmons reaction of weakly acidic phosphonate in solid – liquid phase-transfer catalysis system *CATCOM* 36 98
  21. Stark C M, Loitta C L and Halpern M 1994 In *Phase transfer catalysis: Fundamentals, Applications and Industrial prospectives* (London: Chapman & Hall) pp. XIV 668