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Chlorobenzyl Alcohols from Chlorobenzyl Chlorides via Corresponding Benzoate Esters: Process Development Aspects

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Abstract:

Kinetic studies in conversion of benzyl chlorides to corresponding alcohols via the benzoates are presented in this paper. The esterification reaction of 2-chlorobenzyl chloride, 4-chlorobenzyl chloride, 2,4-dichlorobenzyl chloride and benzyl chloride with aqueous sodium benzoate in the presence of phase transfer catalysts was investigated. The parameters studied are stirring speed, catalysts, the catalyst loading, temperature and the concentration of aqueous phase. The esterification reaction follows pseudo-first-order kinetics. The esters, were hydrolysed with and without a phase transfer catalyst to give corresponding benzyl alcohols without involving respective dibenzyl ethers. Material balance for the laboratory batch process of each chlorobenzyl alcohol has also been presented. A recycle strategy presented is shown to be effective in terms of alkali and benzoic acid consumption as the reactants are consumed to near stoichiometric levels.

Introduction

Chlorobenzyl alcohols have been widely used in the pharmaceutical and perfumery industries. Chlorobenzyl alcohols can be synthesized by hydrolysis of corresponding benzyl chlorides with an alkali hydroxide or carbonate. However, hydrolysis of benzyl chloride with sodium hydroxide in the presence of a phase transfer catalyst produces substantial quantities of dibenzyl ether.[1,2] Hydrolysis of benzyl chloride with sodium bicarbonate involves 10−12% dibenzyl ether.[3] Bayer A. G. has patented a process in which benzyl chloride is hydrolysed with water.[4] The formation of dibenzyl ether in this process is low, and the byproduct HCl is subjected to electrolysis to generate Cl_2 which is used to produce benzyl chloride from toluene. The process involves three separate distillation steps. This strategy may not be suitable for low-volume products because of the extensive instrumentation required and the expensive material of construction. Also the separation of benzyl chloride and benzyl alcohol is rather difficult. The possibility of formation of dibenzyl ether can be avoided if benzyl chloride is esterified and then the ester is hydrolysed. The literature has shown few practical methods regarding the manufacture of chlorobenzyl alcohols by this strategy. Also, the information regarding chlorobenzyl benzoate esters is scanty.[5] Thus, the study of the reaction of benzyl chloride and chlorobenzyl chlorides with sodium benzoate in the presence of a phase transfer catalyst is investigated. The main focus of this study was to develop a commercially viable process for the synthesis of chlorobenzyl alcohols without involving the corresponding dibenzyl ether. The substrates examined are benzyl chloride (BnCl), 4-chlorobenzyl chloride (PCBC), 2-chlorobenzyl chloride (OCBC), and 2,4-dichlorobenzyl chloride (DCBC).

Mechanism and Kinetics for the Formation of Ester. The following mechanism shows the formation of chlorobenzyl benzoate from chlorobenzyl chloride when a trialkylamine (NR_3) is used as a phase transfer catalyst. Chlorobenzyl chlorides are represented by R^1Cl where R^1 = 2-chlorobenzyl, 4-chlorobenzyl or 2,4-dichlorobenzyl and $R^1N^+R_3$ by Q^+,

$$\underset{\text{chlorobenzyl chloride}}{R^1Cl} + R_3N \rightleftharpoons \underset{\text{quaternary ammonium chloride}}{[Q^+Cl^-]} \qquad \text{(organic phase)} \quad (1)$$

In the first step, quaternisation of the tertiary amine takes place in the organic phase. This quaternary ammonium salt actually acts as the phase transfer catalyst.

$$[Q^+Cl^-]_{org} + C_6H_5COO^-_{aq} \rightleftharpoons [Q^+C_6H_5COO^-]_{org} + Cl^-_{aq} \qquad \text{(both phases)} \quad (2)$$

In the second step extraction of $C_6H_5COO^-$ ion into the organic phase takes place.

$$[Q^+C_6H_5COO^-]_{org} + R^1Cl \rightarrow \underset{\text{chlorobenzyl benzoate}}{C_6H_5COOR^1} + [Q^+Cl^-]_{org} \qquad \text{(organic phase)} \quad (3)$$

In the third step, chlorobenzyl benzoate is formed by the reaction of extracted $C_6H_5COO^-$ with chlorobenzyl chloride.

Chlorobenzyl alcohol (R^1OH) is formed by the following reaction:

$$C_6H_5COONa + H_20 \rightleftharpoons C_6H_5COOH + Na^+ + OH^- \qquad \text{(aqueous phase)} \quad (4)$$

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(1) Hwu, D. W.; Hwang, C.; Shih Y. P.; Chao, C. *Ind. Eng. Chem. Res.* **1992**, *31*, 177.

(2) Joshi, S. R.; Sawant, S. B.; Joshi, J. B. *Org. Process Res. Dev.* **1999**, *3*, 17.

(3) *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; VCH Verlagsgesellschaft mbH: Weinheim, 1985; Vol. A4.

(4) Buysch, H. J.; Jonsen, U.; Ooms, P.; Hoffmann, E. G. (Bayer A. G., Germany). German Patent EP 781,748, 1997; *Chem. Abstr.* **1997**, *127*, 81236x.

(5) Walter, H. C. R.; Abram, G.; Russel K. F. *J. Am. Chem. Soc.* **1945,** 67, 2154.

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This OH^- formed in the aqueous phase is extracted into the organic phase and reacts with benzyl chloride to give benzyl alcohol.

$$[Q^+Cl^-]_{org} + OH^-_{aq} \rightleftharpoons [Q^+OH^-]_{org} + Cl^-_{aq} \qquad (5)$$

$$[Q^+OH^-]_{org} + R^1Cl \rightarrow \underset{\text{chlorobenzyl alcohol}}{R^1OH} + [Q^+Cl^-]_{org} \text{ (organic phase)} \qquad (6)$$

Chlorobenzyl alcohol is possibly formed by hydrolysis of formed chlorobenzyl benzoate.

$$[Q^+OH^-]_{org} + C_6H_5COOR^1 \rightarrow \underset{\text{chlorobenzyl alcohol}}{R^1OH} + [Q^+C_6H_5COO^-]_{org} \quad \text{(organic phase)} \qquad (7)$$

Chlorobenzyl alcohol is possibly also formed by the following reaction which does not require any assistance of a phase transfer catalyst:

$$R^1Cl + H_2O \rightarrow [R^1O^+HH\ Cl^-] \xrightarrow{C_6H_5COONa} R^1OH + NaCl + C_6H_5COOH \qquad (8)$$

When transfer of anions to the organic phase follows extraction mechanism, first-order dependence of the rate of reaction on both the substrate concentration and catalyst concentration is observed.[6,7] In such cases, a plot $-\ln(1 - x)$ versus time is a straight line, where x is fractional conversion of the substrate, defined as:

$$x = \frac{\text{mol of the substrate consumed}}{\text{mol of the substrate charged}}$$

The slope of the line gives the observed pseudo-first-order rate constant, k_{obs}. Also a plot $\ln k_{obs}$ versus $\ln C_0$ is a straight line where C_0 is the initial concentration of the catalyst.

Experimental Section

Methods. All of the experiments were carried out in a batch manner. A borosillicate glass reactor of 75 mm i.d., 400 mL capacity, provided with a pitch-blade turbine down flow impeller (25 mm diameter), and baffles were used. Reaction temperature was maintained by using a constant-temperature bath.

A predetermined quantity of aqueous sodium benzoate was added to the reactor placed in the constant-temperature bath. A measured quantity of benzyl chloride preheated to the required temperature was then added, followed by addition of the catalyst, and then the run was started. Very small quantities of samples were withdrawn at predetermined time intervals, and the reaction in the organic layer was monitored by gas chromatography for the conversion of substrate.

Analysis. The reaction in the organic layer was monitored by gas chromatography using a 2 m, 10% OV-17 column. Nitrogen was the carrier gas, and the detector was FID. The other parameters were as follows:

injection temperature	350 °C
detector temperature	350 °C
nitrogen flow rate	30 mL/min
temperature programming	(1) 110 °C for 5 min, 110−275 °C at the rate of 30 °C/min, temperature 275 °C for 2 min (for system containing benzyl chloride, benzyl benzoate, benzyl alcohol) (2) 200 °C for 3.5 min, 200−290 °C at the rate of 30 °C/min, temperature 290 °C for 3.5 min (for system containing DCBC, corresponding ester, and alcohol) (3) 170 °C for 2.5 min, 170−275 °C at the rate of 30 °C/min, temperature 275 °C for 3 min (for system containing OCBC, PCBC, and corresponding esters and alcohols)

Results and Discussion

The conversion of substrate (%) and yield of ester (%) were determined by using following formulae:

$$\text{conversion of substrate (\%)} = \frac{\text{mol of substrate consumed}}{\text{mol of substrate charged}} \times 100$$

$$\text{yield of ester (\%)} = \frac{\text{mol of substrate consumed for the formation of ester}}{\text{mol of substrate consumed}} \times 100$$

The effect of the following variables on the conversion of substrate was studied: (1) stirring speed, (2) catalysts, (3) catalyst loading, (4) substrates, (5) temperature, (6) concentration of sodium benzoate in aqueous layer.

Effect of Change in the Stirring Speed. A phase transfer catalysed reaction is regarded as mass transfer rate-limited when the rate of anion transfer across the interface is slower compared to the rate of intrinsic reaction, while the same is intrinsic reaction rate-controlled when the rate of anion transfer across the interface is fast but the rate of intrinsic reaction is slow. At the low stirring speed, the requirement for sufficiently rapid mass transfer of the anions is not met, and mass transfer rate-limited kinetics is observed. As we increase the speed of stirring, the rate of mass transfer across the interface increases and becomes faster than the intrinsic reaction rate. Thus, at higher stirring speed, the reaction goes from being mass transfer rate-limited to intrinsic reaction rate-limited.

To investigate the effect of the speed of stirring, 4-chlorobenzyl benzoate (PCBnbzt) was synthesized by reacting PCBC with aqueous sodium benzoate using tri-*n*-butylamine as a catalyst. The experiments were performed at 100 °C. Elimination of mass transfer resistance at 100 °C also ensures that reactions at lower temperature under similar agitation

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(6) Dehmlow, E. V.; Dehmlow S. S. *Phase Transfer Catalysis*, 3rd ed.; VCH Verlagsgesellschaft mbH: Weinheim, 1993.

(7) Starks, C. M.; Liotta, C. L.; Halpern, M. *Phase Transfer Catalysis: Fundamentals, Applications & Industrial Perspectives*; Chapman & Hall, Inc.: New York, 1994.

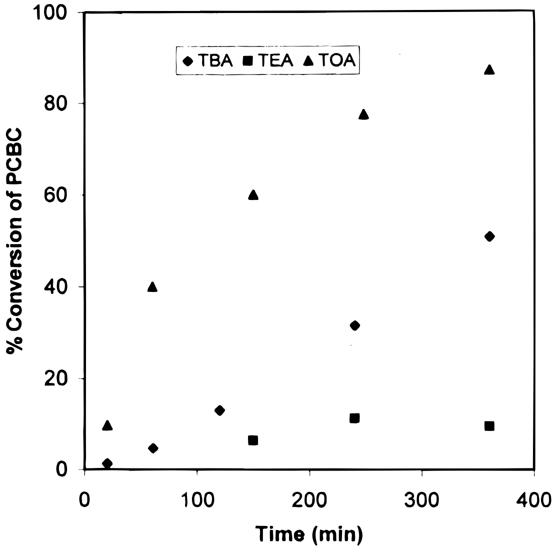

Figure 1. **Effect of different catalysts on the conversion of PCBC. PCBC = 0.3 mol. Sodium benzoate = 216 mL, 1.73 M. Temperature = 70 °C. Catalyst = 0.006 mol (2% of the organic phase). Speed of stirring = 2500 rpm.**

conditions or speed of agitation are intrinsic reaction rate-controlled. Sodium benzoate (216 mL of 1.73 M) and PCBC (0.3 mol) were taken. The molar catalyst loading was 2% of the organic phase. When experiments were performed for 1000 and 2500 rpm, there was no effect of speed of agitation on the progress of the reaction. Thus, beyond the speed of 1000 rpm the reaction becomes intrinsic reaction rate-controlled. However the further experiments were performed at 2500 rpm to ensure that the effects of various operating parameters are evaluated when the reaction is intrinsic reaction rate-controlled. If experiments are performed at low stirring speeds, the change in the reaction rate cannot be attributed to the variable under investigation alone.

Effect of Different Catalysts. Experiments were carried out at 70 °C with different catalysts. The catalysts used were triethylamine (TEA), tri-*n*-butylamine (TBA), and trioctylamine (TOA). Molar loading of all the catalysts was 2% of organic phase. PCBC (0.3 mol) and sodium benzoate (216 mL of 1.73 M) were used.

As can be seen in Figure l, whilst trioctylamine has highest catalytic activity, followed by tri-*n*-butylamine, and triethylamine has the lowest activity. The logarithm of extraction constants of homologous series of quaternary ammonium salts increased by a more or less constant factor of about 0.54 per added C atom in the quaternary molecule.[6] This result indicated the extractability of quaternary salts increases as the lipophilic nature of the quaternary cation increases. As the chain length of alkyl group in the quaternery salt increases, its lipophilicity increases. Thus lipophilicity of [$Q^+C_6H_5COO^-$] is lower when it is formed from triethylamine and higher when it is formed from trioctylamine. The concentration of the ion pair [$Q^+C_6H_5COO^-$] in the organic phase increases as the lipophilicity of Q^+ goes on increasing. This increases the rate of consumption of PCBC by reaction 3. Similar results have been reported by Hwu et al[8] for the synthesis of benzyl acetate from benzyl chloride and trialkylamine as the catalyst.

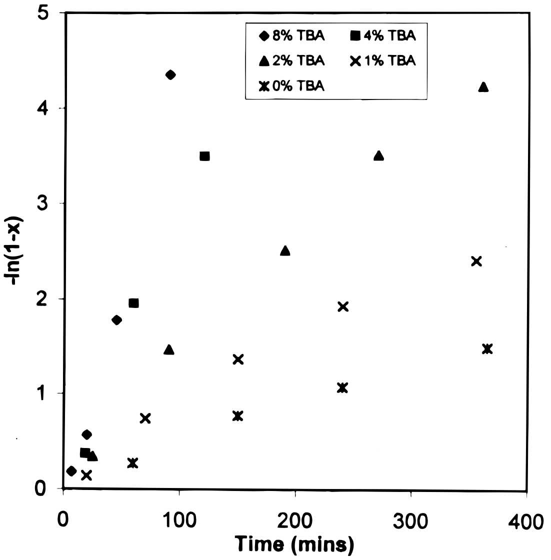

Figure 2. **Effect of catalyst concentration on the progress of the reaction. PCBC = 0.3 mol. Sodium benzoate = 216 mL, 1.73 M. Temperature = 100 °C. Catalyst = Tri-*n*-butylamine. Speed of stirring = 2500 rpm.**

Effect of Catalyst Concentration. With a view to investigate the effect of catalyst concentration the experiments were performed at 100 °C using tributylamine as a catalyst. PCBC (0.3 mol) was treated with sodium benzoate solution (216 mL of 1.73 M) at the stirring speed of 2500 rpm. These conditions represent 25% molar excess of sodium benzoate over PCBC. Further, at 2500 rpm stirring speed the reaction is intrinsic reaction rate-controlled.

When for the reaction under investigation we plotted $-\ln(1 - x)$ versus time we found that the reaction follows first-order kinetics with respect to substrate concentration. Figure 2 shows the relationship of $-\ln(1 - x)$ with time for different catalyst loadings. As can be seen in Figure 2, for the same batch time, the rate of consumption of PCBC increases as the catalyst loading increases. We determined k_{obs} for different initial catalyst concentrations (C_0). Figure 3 shows $\ln k_{obs}$ versus $\ln C_0$ plot for the experiments. A linear relationship is obtained. This result indicates that consumption of PCBC shows first-order dependence on the substrate concentration (Figure 2) and the catalyst concentration (Figure 3). In the previous sections it was shown that the reaction is independent of stirring speed above 1000 rpm and the reaction rate increases with increasing organophilicity of Q^+. All of these observations conclusively indicate an extraction mechanism for transfer of $C_6H_5COO^-$ from the aqueous to the organic phase.[7]

It is observed that in the absence of any phase transfer catalyst, the reaction does take place to a remarkable extent. Also, the yield of 4-chlorobenzyl alcohol corresponding to 77.5% conversion of PCBC was about 20%. This indicates that the presence of PTC considerably enhances the rate of formation of ester.

Effect of Change in the Substrate. Four different substrates were examined, viz., PCBC, OCBC, DCBC, and

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(8) Hwu, D. W.; Hwang, C.; Yeh, M. Y.; Jung, H. M.; Shih, Y. P. *Ind. Eng. Chem. Res.* **1990**, *29*, 2214.

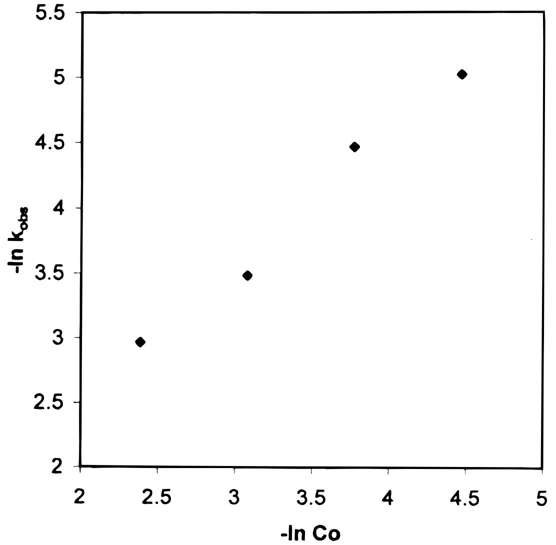

Figure 3. **Effect of catalyst concentration (ln k_{obs} vs ln C_0). PCBC = 0.3 mol. Sodium benzoate = 216 mL, 1.73 M. Temperature = 100 °C. Catalyst = Tri-*n*-butylamine. Speed of stirring = 2500 rpm.**

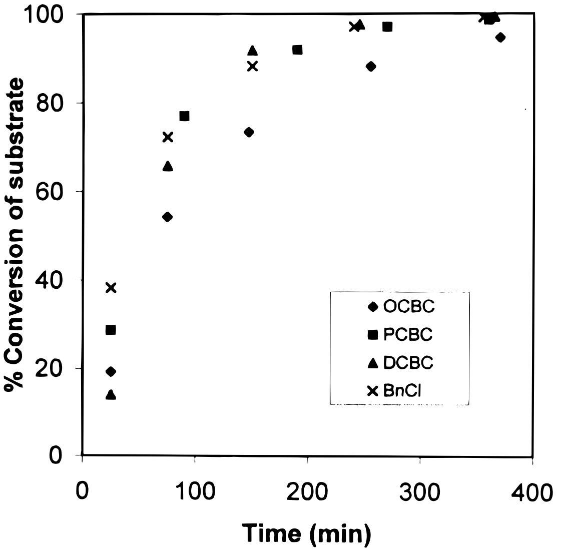

Figure 4. **Progress of the reaction of PCBC, OCBC, DCBC, and BnCl. Substrate = 38 mL. Sodium benzoate = 216 mL, 1.73 M. Temperature = 100 °C. Catalyst = Tri-*n*-butylamine, 0.006 mol. Speed of stirring = 2500 rpm.**

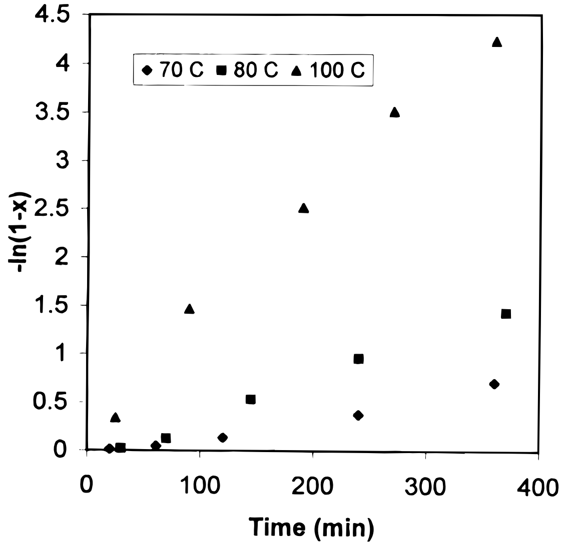

Figure 5. **Effect of temperature on the progress of the reaction. PCBC = 0.3 mol. Sodium benzoate = 216 mL, 1.73 M. Catalyst = Tri-*n*-butylamine, 0.006 mol. Speed of stirring = 2500 rpm.**

BnCl. Thirty-eight milliliters of each substrate (BnCl = 0.33 mol, PCBC = 0.3 mol, OCBC = 0.3 mol, DCBC = 0.27 mol) was treated with 216 mL of 1.73 M sodium benzoate solution at 100 °C. Tri-*n*-butylamine (0.006 mol) was used as catalyst. The volume of substrate was kept the same in all of the experiments so as to have same concentration of $[Q^+C_6H_5COO^-]$ in the organic phase. It can be seen from eq 3, that the rate of reaction depends on the concentration of $[Q^+C_6H_5COO^-]$ in the organic phase and we attempted to keep it constant by maintaining the concentration of the catalyst. Figure 4 shows the effect of change in substrate. Benzyl chloride shows the highest reactivity. PCBC and DCBC have almost the same reactivity, and OCBC has the lowest reactivity. As the substrate changes, the structure of quaternary ion changes. These quats may have different extraction coefficients in the corresponding substrates and hence $[Q^+C_6H_5COO^-]$ concentration in the organic phase may not be the same in all cases.

Effect of Temperature. Figure 5 shows the effect of temperature for the case of tri-*n*-butylamine as a catalyst and PCBC as the substrate. The experiments were carried out using 216 mL of 1.73 M aqueous sodium benzoate solution, 38 mL of substrate, and 0.006 mol tri-*n*-butylamine as a catalyst. Figure 5 indicates the pseudo-first-order kinetics for the reactions under consideration. For the experiments performed at 70 and 80 °C we can see an induction period of around 80 min, and then the reaction follows normal pseudo-first-order kinetics. This induction period is probably the outcome of low rate of quaternisation of tri-*n*-butylamine with PCBC under the experimental condition. At 100 °C, however, there is no induction period. Pseudo-first-order rate constants were determined at 70, 80, and 100 °C. Similar induction periods were also observed when OCBC and DCBC were used as the substrates. Occurrence of induction periods in the phase transfer catalysed reactions using trialkylamines and benzyl chloride has already been reported.[1] Arrhenius plots were made for all substrates (Figure 6), and the energy of activation was determined for all the substrates. The values of energies of activation are described in Table 1. The high values of energy of activation also confirm the absence of mass transfer resistance, and the progress of the reaction is governed by the intrinsic reaction in the organic phase.

Effect of Concentration of Aqueous Sodium Benzoate. The effect of change in the aqueous phase concentration was evaluated by treating 0.3 mol of PCBC with different concentrations of sodium benzoate solutions, viz., 1.39, 1.73 and 2.78 M. The volume of aqueous phase was kept constant (216 mL) in all three experiments. Tri-*n*-butylamine (0.006 mol) was used as the catalyst at 100 °C and 2500 rpm. Using aqueous-phase concentration below 1.39 M was avoided as it reduces the sodium benzoate/PCBC mole ratio below unity. After the consideration of solubility of sodium benzoate in water, the upper limit of concentration was decided. Figure

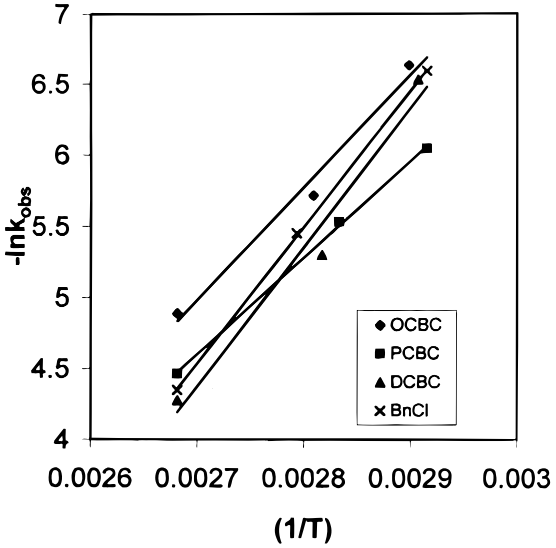

Figure 6. **Arrhenius plot. Substrate = 38 mL. Sodium benzoate = 216 mL, 1.73 M. Catalyst = Tri-*n*-butylamine, 0.006 mol. Speed of stirring = 2500 rpm.**

Table 1: **Activation energies for the reaction between chlorobenzyl chlorides and sodium benzoate in the aqueous solution**

substrate	energy of activation (kcal/mol)
PCBC	13.4
OCBC	15.6
DCBC	19.3
BnCI	18.88

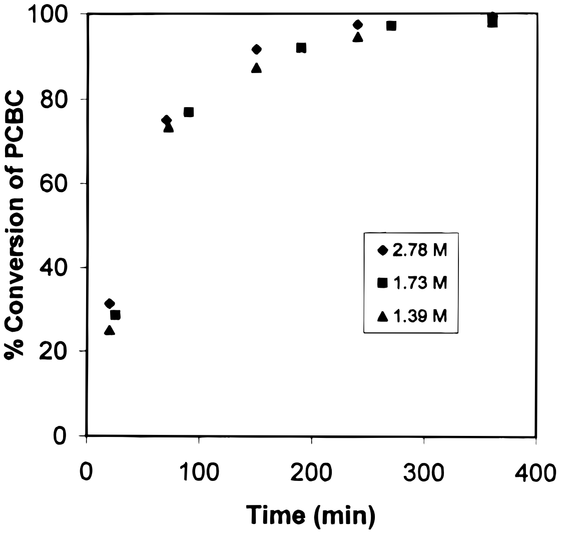

Figure 7. **Effect of aqueous phase concentration on the conversion of PCBC. PCBC = 0.3 mol, Sodium benzoate = 216 mL, Temperature = 100 °C, Catalyst = Tri-*n*-butylamine, 0.006 mol, Speed of stirring = 2500 rpm.**

7 shows the effect of aqueous phase concentration on the progress of the reaction. As can be seen from Figure 7, the progress of the reaction is not affected by the change in the aqueous-phase concentration. In the concentration range studied, it is possible that the change in the aqueous-phase concentration does not effectively change the concentration of [$Q^+C_6H_5COO^-$] in the organic phase. The intrinsic reaction between PCBC and [$Q^+C_6H_5COO^-$], (reaction 3) is the rate-determining step. Constant concentration of $C_6H_5COO^-$ in the organic phase in all cases can show the same reaction rate for all three concentrations of sodium benzoate solutions studied. A similar result has been reported by Bar et al,[9] wherein the apparent extraction constant and selectivity constant for formate and chloride in the presence of $NHex^+_4$ and a large excess of formate do not change to an appreciable extent with change in formate concentration in the aqueous phase. We also performed the experiment in the absence of sodium benzoate in the aqueous phase, other reaction parameters being the same. After 12 h, the conversion of PCBC was 60%, and the yields of corresponding alcohol and corresponding dibenzyl ether were 90 and 10%, respectively.

Table 2: **Yield of chlorobenzyl alcohols in the esterification reaction**

substrate	% conver of substrate	% yield of alcohol	temp, °C	catalyst	catalyst loading (%)	conc. of aq phase (M)
PCBC	98.54	4.23	100	TBA	2	1.73
PCBC	98.45	1.77	100	TBA	4	1.73
PCBC	99	6.7	100	TBA	8	1.73
PCBC	51	n.d[a].	70	TBA	2	1.73
PCBC	10	n.d.	70	TEA	2	1.73
PCBC	87	n.d.	70	TOA	2	1.73
PCBC	76	n.d.	80	TBA	2	1.73
PCBC	100	n.d.	100	TBA	4	2.78
PCBC	99.5	n.d.	100	TBA	4	1.39
PCBC	91	6.5	100	TBA	1	1.73
PCBC	98	4.6	100	TBA	2	1.39
PCBC	99.2	6.2	100	TBA	2	2.78
PCBC	77.5	20	100	no catalyst		1.73
OCBC	93.9	5.4	100	TBA	2	1.73
OCBC	99.7	4	100	TBA	3	1.73
DCBC	99.2	n.d.	100	TBA	2	1.73
BnCI	99	16.5	100	TBA	2	1.73

[a] n.d. = Not detected.

The yields of chlorobenzyl alcohols under various conditions are listed in Table 2.

Hydrolysis of Esters

Comparison of Purified and Unpurified Esters. The benzoates synthesized in the above study were subjected to hydrolysis with dilute sodium hydroxide solution. 4-Chlorobenzyl benzoate (PCBnbzt) and 2,4-dichlorobenzyl benzoate (DCBnbzt) formed in the above study were washed with hot distilled water and recrystallized from methanol. Their melting points were found to be 59 and 56 °C, respectively. Recrystallized ester (0.15 mol) was treated with 75 mL of 2.5 M aqueous sodium hydroxide at 80 °C and 2500 rpm. The results are presented in Figure 8. In both cases, the reaction initially proceeds sluggishly. After around 30% conversion of ester, the rate of reaction increases rapidly. As the ester is reacted, corresponding amounts of corresponding alcohol and sodium benzoate are formed. In

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(9) Bar R.; Karpuj-Bar, L.; Sasson Y.; Blum, J. *Anal. Chim. Acta.* **1983,** 154, 313; *Chem. Abstr.* **1984**, *100*, 13338z.

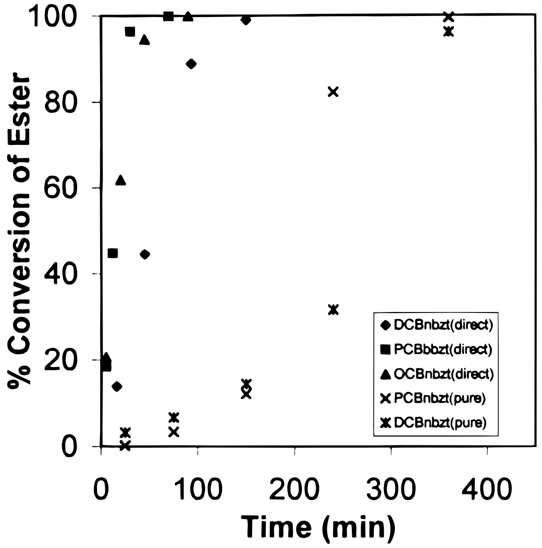
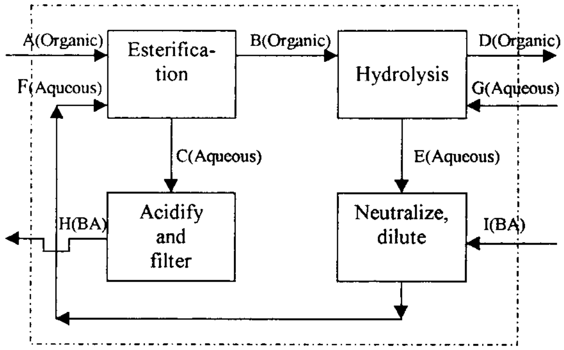


Figure 8. **Hydrolysis of esters in the presence and absence of a PTC. Ester = 0. 15 mol. NaOH = 75 mL, 2.5 M. Temperature = 80 °C. Speed of stirring = 2500 rpm.**

the presence of sodium benzoate, the solubility of benzyl alcohol in the aqueous phase increases. Due to the presence of benzyl alcohol and sodium benzoate in the aqueous phase, some ester is also solubilized in the aqueous phase. Also, it was found that the dispersion characteristics of the system changes after about 30% conversion. After 30% conversion of the ester, the time required for the phases to separate increased by about 50% over that in the initial stages, indicating finer and better dispersion of the phases. These two factors increase the contact between the OH^- ions and the ester, and the reaction proceeds smoothly. When chlorobenzyl chloride is treated with sodium benzoate in the presence of a phase transfer catalyst, there is certain quantity of $[Q^+C_6H_5COO^-]$, $[Q^+Cl^-]$ left in the organic phase after complete conversion of substrate is achieved. Experiments were performed to find out if this catalyst partitioned in the organic phase can be used to increase the rate of the hydrolysis reaction. PCBC, OCBC, and DCBC (0.15 mol) were treated separately with sodium benzoate solution (108 mL, 1.73 M) at 100 °C at 2500 rpm. Tri-*n*-butylamine (0.003 mol) is used as a catalyst in case of PCBC and DCBC. The amount of tri-n- butylamine used in case of OCBC was 0.0045 mol. After 7 h of reaction, the reaction mixture was cooled to room temperature. The aqueous phase was completely removed, the organic phase was heated to 80 °C, and hydrolysis was initiated by adding NaOH solution (75 mL, 2.5 M) preheated to 80 °C. The speed of stirring was 2500 rpm. Figure 8 also shows the results of this direct hydrolysis without purification of the product formed in the first stage. As can be seen, this strategy increases the rate of hydrolysis substantially.

Material Balance and Recyclability of the Aqueous Phase. In the esterification reaction we used 25% molar excess of sodium benzoate to ensure complete conversion of the substrate. After completion of the conversion of the substrate, excess of sodium benzoate remains in the aqueous phase. This aqueous phase, when acidified, gave benzoic acid (BA), which was then recovered by filtration of the aqueous phase. The ester formed in the first reaction is hydrolysed in the second step using 25% molar excess of sodium hydroxide. After the end of the hydrolysis reaction, the aqueous phase contains this excess sodium hydroxide together with 1 equiv of sodium benzoate formed. The excess sodium hydroxide can be reacted with corresponding amount of benzoic acid, and the aqueous phase can then be used for the esterification step after proper dilution. One mole of ester consumes one mole of sodium hydroxide, affording one mole of the corresponding alcohol. Some benzoic acid still may be lost during separation of the two phases and filtration, and it may not be completely recovered. We decided to find out the consumption of benzoic acid required for the whole process and investigated the material balance. Scheme 1 shows the reactions carried out.

Scheme 1



Substrate [A(organic) = PCBC, OCBC, DCBC] (0.15 mol) was treated with sodium benzoate [F(aqueous)] (108 mL, 1.73 M) at 100 °C. Tri-*n*-butylamine was used as the catalyst (0.003 mol in case of PCBC and DCBC, 0.0045 mol in case of OCBC). After the reaction was allowed to continue for 7 h, the reaction mixture was cooled to room temperature, and the two layers were separated. The organic phase [B(organic)] was washed with distilled water. After being washed, the organic layer was dried by evaporating water at 110 °C and weighed and analysed. The organic phase [B(organic)] was then treated with aqueous NaOH solution [G(aqueous)] (75 mL, 2.5 M) at 80 °C. After the reaction was complete, the reaction mixture was cooled to room temperature, and the solid alcohol [D(organic)] was separated by filtration, washed thoroughly with chilled distilled water, dried under vacuum, and weighed and analysed. The gas chromatographic analysis of all of the alcohols shows no presence of corresponding chlorobenzyl chloride, ester, and substituted dibenzyl ether. The melting points of crude 4-chlorobenzyl alcohol, 2-chlorobenzyl alcohol, and 2,4-dichlorobenzyl alcohol were found to be 70, 69, and 56 °C, respectively.

The aqueous phase after esterification step [C(aqueous)] was extracted with dichloroethane, and the organic solvent was evaporated. The residue was weighed and analysed to determine the amount of organics present in the aqueous phase. The aqueous phase left after the hydrolysis step [E(aqueous)] was also extracted with dichloroethane to determine the quantity of alcohol present in the aqueous phase. The results are summarised in Table 3.

Table 3: **Material balance for the esterification and hydrolysis reactions (streams corresponding to Scheme 1)**

	A (organic) moles	B (organic) moles	C (aqueous) moles	D (organic) moles	E (aqueous) moles
PCBC	0.15	–	–	–	–
ester of PCBC	–	0.14	0.0003	–	–
alcohol of PCBC	–	0.006	–	0.145	0.001
OCBC	0.15	–	–	–	–
ester of OCBC	–	0.137	0.00025	–	–
alcohol of OCBC	–	0.0081	–	0.142	0.003
DCBC	0.15	–	–	–	–
ester of DCBC	–	0.1467	0.00029	–	–
alcohol of DCBC	–	–	–	0.1455	0.001

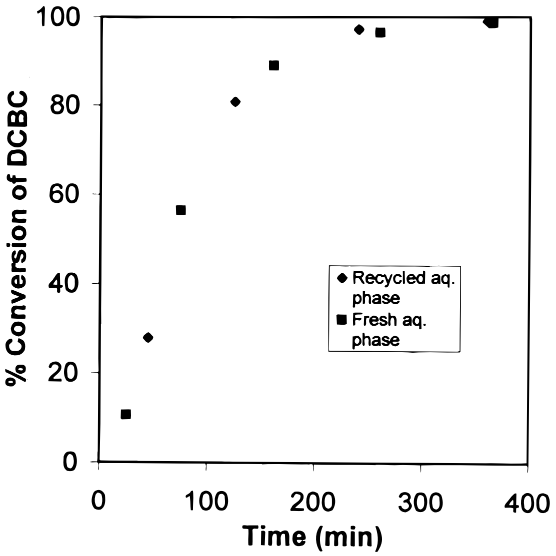


Figure 9. **Effect of recycling of the aqueous phase. DCBC = 0. 15 mol. Sodium benzoate = 108 mL, 1.73 M. Temperature= 100 °C. Catalyst = Tri-*n*-butylamine, 0.003 mol. Speed of stirring = 2500 rpm.**

To establish recyclability of the aqueous phase, the aqueous phase [E(aqueous)] of 2,4-dichlorobenzyl alcohol was extracted with dichloroethane. The aqueous layer after separating dichloroethane phase was heated to boil off traces of dissolved dichloroethane. Benzoic acid was added to this aqueous phase to neutralize excess NaOH, and the volume was adjusted to 108 mL. This was used for esterification of 0.15 mol of DCBC. The conversion profile of DCBC with this recycled aqueous phase is plotted in Figure 9 with that using fresh aqueous phase. Both the profiles match exactly.

The difference between benzoic acid recovered [H(BA)] after acidification of C(aqueous) and the amount required to neutralize E(aqueous) represented by I(BA) gives the amount of consumption of benzoic acid required per 0.15 mol of DCBC. In this case, with the net consumption of 0.0045 mol of benzoic acid together with 0.1875 mol sodium hydroxide (25% excess), DCBC has been converted to 2,4-dichlorobenzyl alcohol with complete conversion of DCBC and overall yield of 2,4-dichlorobenzyl alcohols is 97%.

In the conventional one-step process for the manufacture of benzyl alcohols from corresponding benzyl chlorides, even small fractions of unreacted benzyl chloride(s) causes problems in the subsequent separation process. The alkali is used about 20−25% in excess. The additional problem is the formation of corresponding dibenzyl ethers. This is particularly a major problem with chlorobenzyl alcohols as this represents a substantial yield loss of valuable benzyl alcohols. The present strategy is clearly beneficial in the sense that it ensures complete conversion of benzyl chlorides without involving dibenzyl ethers. This is achieved with practically the same consumption of alkali and an additional but nominal consumption of benzoic acid. Even if a small fraction of benzyl chloride(s) remains unreacted in the esterification step, it can be easily separated from the ester by distillation because of the large boiling point difference.

Conclusions

(1) A successful conversion of chlorobenzyl chlorides to corresponding alcohols via esters has been demonstrated. (2) The esterification reaction between the chlorobenzyl chlorides and sodium benzoate in the aqueous solutions, follows pseudo-first-order kinetics for the stirring speed >1000 rpm. (3) The catalyst used in the esterification reaction also enhances the hydrolysis reaction leading to the formation of chlorobenzyl alcohols. (4) The overall yield of chlorobenzyl alcohols is > 97%. (5) A recycle strategy has been established wherein the complete recovery of the benzoic acid after hydrolysis reaction has been eliminated. Because of this strategy the chlorobenzyl chloride can be successfully converted into corresponding alcohols via esterification with just 0.03 mol of benzoic acid per mol of chlorobenzyl alcohol and 1.25 mol of NaOH per mol of chlorobenzyl alcohol. (6) The present process does not produce dibenzyl ethers, which are obtained in the conventional one-step process of converting benzyl chlorides to benzyl alcohols.

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