Organic Process Research & Development **2000**, *4,* 141–146

Articles

Clay-Supported Liquid−Liquid−Solid Phase Transfer Catalysis: Synthesis of Benzoic Anhydride

G. D. Yadav* and Suguna S. Naik

Chemical Engineering Division, University Department of Chemical Technology (UDCT), University of Mumbai, Matunga, Mumbai-400 019, India

Abstract:

Solid-supported phase transfer catalysed reactions typically involve polystyrene supports cross-linked with divinyl benzene. The use of commercially available clay as a support for the PTC reaction is attractive. This paper reports the preparation of benzoic anhydride from benzoyl chloride and sodium benzoate using clay-supported quaternary ammonium salts at 30 °C. The selectivity to the product is 100%. The mechanistic and kinetic aspects are also reported. The clay-supported catalyst was found to be more active than polymer-supported catalysts.

Introduction

The use of phase transfer catalysis (PTC) has become widespread in synthetic and commercial processes with at least 600 reported examples.[1−3] The liquid−liquid phase transfer catalysis (L−L PTC) process has been the most widely studied vis-à-vis mechanisms and kinetics. However, the drawbacks associated with the recovery and reuse of expensive phase transfer catalyst from the liquid phase were somewhat overlooked in the earlier publications perhaps due to the euphoria associated with the spectrum of reactions that could be conducted using PTC. Some techniques such as extraction of the catalyst, addition of salts for better partitioning in one phase, adsorption, or distillation were used for its recovery. The effluent treatment problems associated with soluble catalysts impose restrictions on the usefulness of PTC as an industrial tool. The applications of PTC were thus practically confined to the synthesis of low-volume and high-cost speciality chemicals, agrochemicals, and pharmaceuticals. Because of the shift in manufacturing processes towards environmentally compatible processes L−L PTC has undergone several modifications including the use of supported quaternary onium salts in bi-liquid-phase systems, and also tri-liquid-phase systems (L−L−L PTC).[4]

Supporting the phase transfer catalyst on a polymer matrix was mentioned by Regen[5] in 1975 and thereafter in his excellent review paper.[6] He reported that ammonium salts immobilised on cross-linked polystyrene resins are effective as phase transfer catalysts. Around the same time polymer-supported phosphonium salts, macrocyclic polyethers, polar solvent residues, and poly (ethylene glycol) were also reported to be efficient catalysts.[3] The technique was named as triphase catalysis containing an aqueous salt solution, an organic solution, and a swollen polymer catalyst (solid phase). The correct terminology should be liquid−liquid−solid (L−L−S) PTC. In L−L−S PTC, one of the liquid phases and the solid catalyst are dispersed in the second liquid phase, which is a continuous phase. This technique possesses some advantages such as easy recovery of the catalyst from the reaction mixture by filtration, potential use in flow reactors, and recycling. However, the disadvantages of L−L−S PTC are higher initial cost of preparation and lower catalytic activity due to diffusional limitations.

The type of support matters a great deal in L−L−S PTC. The most popular supports are microporous (gel) polystyrene resins, minimally (1−4%) cross-linked with divinylbenzene (DVB) or macroporous supports, highly cross-linked with more than 10% DVB. The microporous resins have low specific surface areas, and the polymeric chains shrink in a dry state or in poor solvents. The resins swell well in appropriate solvents to extend the polymeric chains. The macroporous resins have high specific surface areas and hardly swell in any solvent. To overcome the diffusional limitations, spacer chains are provided on the support, and this technique leads to enhanced activity.[1−3] Inorganic supports such as silica gel or alumina are also used as supports for L−L−S PTC. The inorganic supports have high surface areas and should be more useful than organic supports.

Quaternary ammonium salts immobilised on insoluble synthetic polymers and inorganic oxides, such as silica and alumina, have been widely explored in L−L−S PTC. But silica, alumina, and polymers are unstable in strong acidic

---

* Author to whom correspondence should be sent. Telephone: 91-22-410-2121, 4145616. Fax: 91-22-4145614. E-mail: gdy@udct.ernet.in or gdyadav@yahoo.com.

(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*; Chapmann and Hall publications: London, 1997.

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

(4) Yadav, G. D.; Reddy, C. A. *Ind. Eng. Chem. Res.* **1999**, *38*(6), 2245.

(5) Regen, S. L. *J. Am. Chem. Soc.* **1975**, *97*, 5956.

(6) Regen, S. L. *Angew. Chem.* **1979**, *91*, 464; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421.

10.1021/op990087c CCC: $19.00

and alkaline media and have low physical strength. In comparison, clays are cheap, have high physical strength, and possess relatively high resistance towards alkali treatment. Some work has appeared on the use of clays as supports for quaternary salts.[7−11]

Many alkylation reactions are mediated by hydroxyl ions and conducted under strong alkaline conditions with PTC. Thus, supporting the phase transfer catalyst on clays would offer certain advantages, which appear to be distinctly different due to the fact that clays are inorganic oxide surfaces with much higher surface areas and bulk densities. Typically the polymer-supported PTC have bulk densities that are bracketed between the aqueous and organic phases, and the mechanistic aspects include this fact. In the case of clays, the catalyst will be in the continuous phase, and the type of dispersed phase and the reactant within it would have a pronounced effect on the yields.

It was preferred to study the synthesis of benzoic anhydride, a reaction of commercial significance,[12] to compare the use of a clay-supported PTC with that of a polymer. The modelling aspects were also considered to be important. Benzoic anhydride is an important intermediate, which is used as a component in bleaching formulations and as an ingredient in soldering flux. It is used as a benzoylating agent in special situations where benzoyl chloride is unsatisfactory because of its excessive reactivity or the generation of hydrochloric acid. There is no report on the use of L−L−S PTC in the preparation of benzoic anhydride either with polymer or clay supports. This paper delineates our studies on the synthesis of benzoic anhydride from benzoic acid and benzoyl chloride with Tonsil clay-supported catalyst.

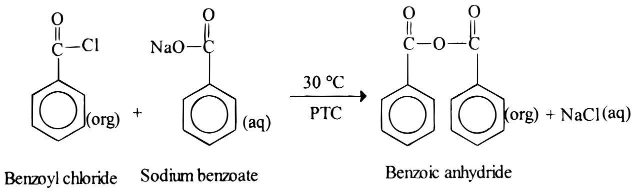
Experimental Section

Chemicals. Benzoyl chloride, sodium hydroxide, benzoic acid, methanol, and chloroform of LR grade were obtained from M/s s.d. Fine Chemicals Pvt. Ltd, Mumbai, India.

Cetyltrimethylammonium bromide (CTAB) was procured from M/s s.d. Fine Chemicals Ltd. and Tonsil clay from Sudchemie AG, Munchen, Germany. A commercial polymer-supported catalyst FF-IP was procured from M/s Ion Exchange (India) Ltd., Mumbai, India.

Catalyst Preparation. A known quantity of Tonsil clay was vaccum dried for 5 h at 80 °C. It was then transferred to a three-necked flask with a magnetic stirrer, and vacuum was applied to the system. From another neck cetyltrimethylammonium bromide (CTAB) dissolved in methanol was added dropwise from the vacuum tight addition funnel. Since the porosity of the clay was known, the quantity of methanol taken was equal to the pore volume. The amount of CTAB supported on the clay was equal to that used for the L−L PTC experiment. Typically it was 1 g of CTAB per 1 g of clay. Stirring was continued under vacuum until all of the methanol had evaporated. Then it was dried completely in a rotovac at 60 °C for 3 h. Since the incipient wetness technique was used to support the catalyst, followed by complete drying, all of the catalyst was supported on the clay. No material was discarded at any time. In addition, the supported catalyst was weighed to match the material balance. A quantity equal to 2.743×10^{-3} mol of the quaternary ammonium salt was used per g of Tonsil.

Experimental Procedure. The reactions were studied in a 4-cm i.d fully baffled mechanically agitated contactor of 250-mL capacity, which was equipped with a six-bladed turbine impeller and a reflux condenser. The reactor was immersed in a thermostatic bath whose temperature could be maintained within 0.5 °C of the desired temperature. Typical experiments were conducted by taking 0.025 mol of benzoyl chloride in chloroform (25 mL), 0.04 mol of benzoic acid and 0.04 mol of sodium hydroxide in water (20 mL), and a suitable quantity of clay-supported PTC maintained at 30 °C by using a thermostatic bath. Benzoic anhydride was the only product formed in the reaction mixture.



Method of Analysis. Samples of the organic phase were withdrawn at particular intervals of time, and benzoic anhydride and benzoyl chloride were analysed by means of gas−liquid chromatography on Chemito 8510 model. Quantitative results were obtained by comparison with synthetic standards. 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.

Results and Discussion

All experiments were done with CTAB supported on Tonsil clay as the catalyst unless mentioned otherwise.

Mechanism of Clay-Supported PTC. The mechanisms of L−L−S PTC have been evaluated in our laboratory,[13] depending on whether the support is wetted by the aqueous phase or organic phase or is of mixed-wet type, which is decided by the contact angle. Under a dynamic situation, a strongly water-wet system always retains a thin film of water around the particle. The organic phase, even though continuous, does not penetrate inside the pores of the catalyst. Thus, the catalytic action is limited to the exterior surface of the support. In the case of clay-supported catalyst, the mechanism needs to be properly understood. The clay-particles were coated with the quaternary salt. The organic phase was the continuous phase, and the aqueous phase the dispersed phase. The wettability of the clay containing quaternary salt as a solid occupying the pores is water-wet. Typically the aqueous phase droplet, upon intense agitation, would stick to the clay-

---

(7) Monsef-Mirzai, P.; McWhinnie, W. R. *Inorg. Chim. Acta* **1981**, *52*, 211.
(8) Tundo, P.; Venturello, P.; Angelletti, E. *J. Am. Chem. Soc*. **1982**, *104*, 6547.
(9) Tundo, P.; Venturello P.; Angelletti E. *J. Am. Chem. Soc*. **1982**, *104*, 6551.
(10) Choudary, B. M.; Rao, S.; Prasad, B. P. *Clays Clay Miner*. **1991**, *39*, 3, 329.
(11) Li, L. C.; Pinnavaia, T. J. *Chem. Mater*. **1991**, *3*, 213.
(12) Yeadon, A.; Turney, T. A.; Ramsay, G. *J. Chem Educ*. **1985**, *62*(6), 518.

(13) (a) Yadav, G. D.; Naik S. S. Unpublished work, 1999. (b) Naik, S. S. *Insights in Catalysis: Novelties of Multi-Phase transfer catalysis*. Ph.D. Thesis, University of Mumbai, April 1998.

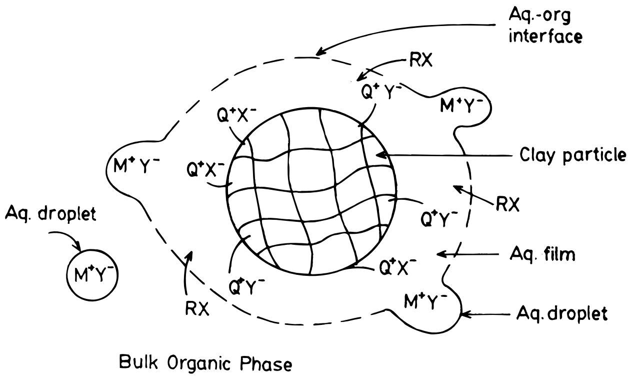


Figure 1. **Clay-supported PTC: clay surface wetted by aqueous phase, organic phase as continuous phase, and aqueous phase as dispersed phase in the reactor.**

exterior surface and exchange the nucleophile $PhCOO^-$ with the leaving group attached to the clay, $C{\sim}Q^+X^-$, where C stands for clay. Pinnavaia and co-workers have commented about the type of bonding between quaternary salts and clay supports.[11] The bonding between the quaternary salt and clay is electrostatic but strong enough, and the Q^+X^- (CTAB) has very limited solubility in either aqueous or organic phase. This is confirmed by the catalyst stability studies which are reported later in this paper. In fact, with an aqueous solution of sodium benzoate, prepared in situ, under normal L−L PTC, the catalyst accumulates at the interface. The substrate benzoyl chloride is in the vicinity of the clay particle, and hence the reaction can occur according to the mechanism[13] shown in Figure 1. There is apparently no intrusion of the L−L interface much inside the clay pores. The $C{\sim}Q^+X^-$ solid surface is water-wet, and the thin aqueous layer is sufficient for the ion-exchange and surface reaction. Upon contact with the aqueous phase, the catalyst site is regenerated.

Thus, the effect of various parameters was studied on the rate of reaction.

Effect of Speed of Agitation. The effect of the speed of agitation on the rate of reaction is depicted in Figure 2.

Initially, the rate was found to increase with an increase in the speed of agitation from 500 to 800 rev/min. However, after 800 rev/min the increase in the rate was marginal. It can be deduced from this observation that the external mass transfer, associated with the transfer of the reactant benzoyl chloride from the continuous organic phase through the aqueous film around the clay particle to its surface gets eliminated at around 800 rev/min. Furthermore, the resistance to the transfer of the nucleophile $PhCOO^-$ from the aqueous-phase droplet is eliminated. Therefore, the speed of agitation was maintained at 800 rev/min for further experiments, wherein no mass transfer resistance could be witnessed.

Effect of Catalyst Loading. Catalyst loading is the total quantity of the solid catalyst containing the quaternary salt and the clay support. The weight ratio of the quaternary salt to the clay was 1:1 in the solid catalyst. The supported amount of the catalyst was the same as that used in the L−L PTC reaction, under otherwise similar conditions for the sake of comparison. The conversion of benzoyl chloride is plotted against time under different catalyst loadings, under otherwise similar experimental conditions. It can be seen that the conversion of benzoyl chloride increased marginally when solid catalyst loading was increased from 0.1 to 0.3 g of catalyst. However, this is not proportional to the increase in external surface area based on catalyst loading. It appears that, since the reaction is very fast, the additional increase in area does not help and mass-transfer effects would have set in at higher concentrations (Figure 3).

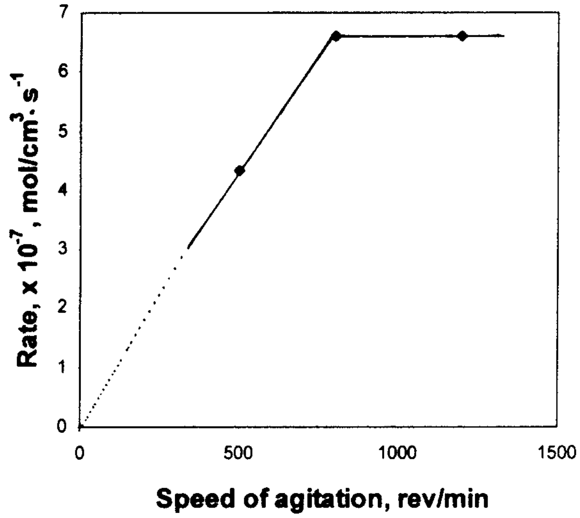


Figure 2. **Effect of speed of agitation on rate of reaction. C_6H_5COCl 0.25 mol, chloroform 25 mL, NaOH 0.0375 mol, benzoic acid 0.04 mol, CTAB/Tonsil 0.3 g, H_2O 20 mL, temperature 30 °C.**

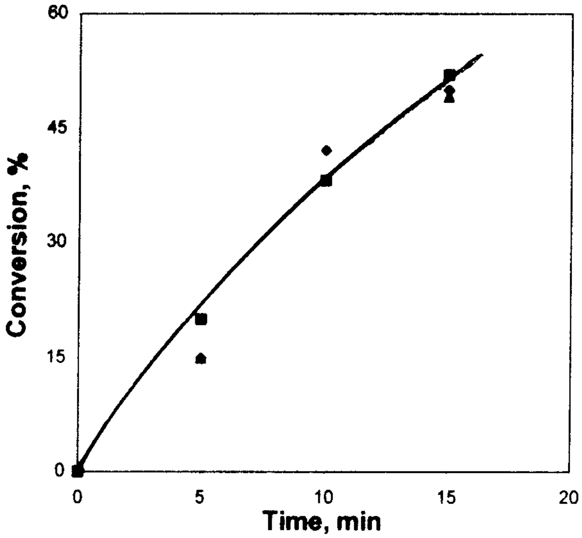


Figure 3. **Effect of catalyst loading. C_6H_5COCl 0.25 mol, chloroform 25 mL, NaOH 0.0375 mol, benzoic acid 0.04 mol, catalyst CTAB/Tonsil 0.3 g, H_2O 20 mL, temperature 30 °C, speed of agitation 800 rev/min. (◆) 0.5 g, (■) 0.3 g, (▲) 0.1 g.**

Comparison amongst L−L PTC and L−L−S with Different Catalysts. A few experiments were conducted with CTAB and TBAB under L−L PTC. A commercially available resin-supported PTC, with a trade name of FF-IP (product of Ion Exchange (India) Ltd.) was also used. FF-IP is polystyrene cross-linked with 8−9% DVB with a functional group, $-CH_2N^+Me_3Cl^-$. It has an ion-exchange capacity of 3.6 mequiv/g dry resin. The comparison amongst the two liquid-phase catalysts in L−L PTC and two L−L−S

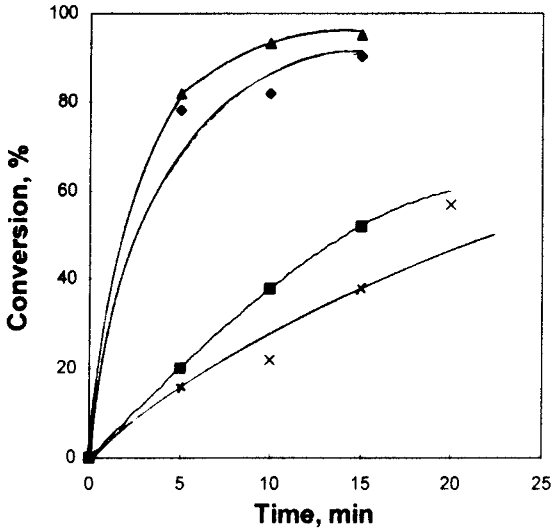


Figure 4. **Effect of different catalysts. C_6H_5COCl 0.25 mol, chloroform 25 mL, NaOH 0.0375 mol, benzoic acid 0.04 mol, H_2O 20 mL, temperature 30 °C, speed of agitation 800 rev/min. (◆) 0.15 g CTAB, (■) 0.3 g CTAB/Tonsil, (▲) 0.13 g TBAB, (×) 0.6 g FF-IP.**

PTC was made under otherwise similar conditions. It was observed that with unsupported catalysts, the conversion of benzoyl chloride was greater as compared to that with CTAB supported on Tonsil. It is due to the obvious reasons that supported catalyst is less active and not all sites are used for the reaction as explained by the model since the liquid–liquid interface cannot penetrate inside the pores and the reaction is limited to the outer surface only. When FF-IP was used as the catalyst, it was found that the conversion was less as compared to that with CTAB supported on Tonsil. It may be due to the fact that the external surface area of the FF-IP is significantly less as well as its pore size being smaller, resulting in slower diffusion of the bulky reactant molecules (Figure 4).

Effect of Concentration of Benzoyl Chloride. The effect of the concentration of benzoyl chloride was studied in the range of 6.0×10^{-4} to 1.4×10^{-3} mol/mL under otherwise similar conditions. It was found that the rate of the reaction increases linearly with an increase in the concentration of the benzoyl chloride (Figure 5). This is consistent with the observation that the reaction is overall second-order, or pseudo-first-order with respect to benzoyl chloride.

Effect of Concentration of Sodium Hydroxide. The effect of the concentration of sodium hydroxide on conversion was studied, under otherwise similar experimental conditions, at 1.25×10^{-3}, 1.875×10^{-3} and 2.5×10^{-3} mol/mL. These concentrations correspond to 1:0.625, 1:0.937 and 1:1.25 mole ratios of benzoic acid to sodium hydroxide. The conversion is plotted against time for different sodium hydroxide concentrations. Figure 6 depicts that as the concentration of sodium hydroxide increases the conversion increases due to the fact that more and more benzoic acid is converted to the sodium salt of benzoic acid. Consequently, a greater amount of nucleophile is available to react with the $P{\sim}Q^+X^-$ for the ion-exchange, and therefore X^- gets replaced with the nucleophile benzoate which subsequently reacts with benzoyl chloride. It was found that the hydrolysis of benzoyl chloride became significant at 1:1.25 mole ratio for which excess caustic was available. For other mole ratios, the hydrolysis of benzoyl chloride was insignificant (Figure 6).

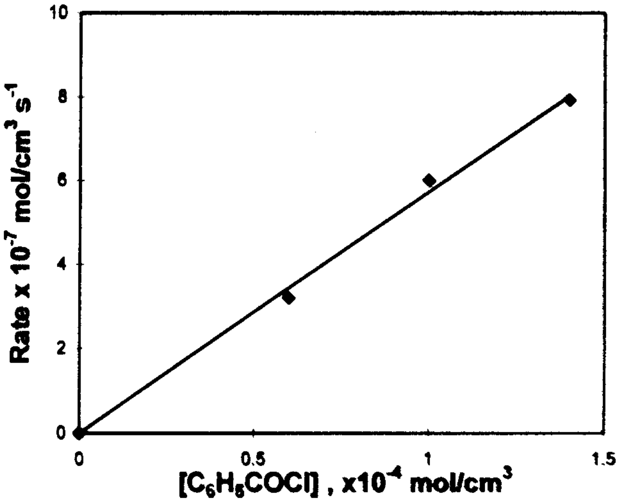


Figure 5. **Effect of concentration of benzoyl chloride on rate of reaction. NaOH 0.0375 mol, benzoic acid 0.04 mol, chloroform 25 mL, CTAB/Tonsil 0.3 g, H_2O 20 mL, temperature 30 °C, speed of agitation 800 rev/min.**

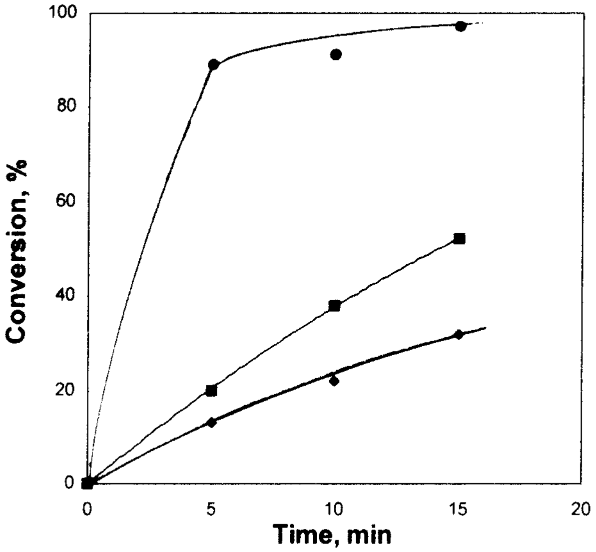


Figure 6. **Effect of concentration of sodium hydroxide. C_6H_5COCl 0.25 mol, chloroform 25 mL, benzoic acid 0.04 mol, CTAB/Tonsil 0.3 g, H_2O 20 mL, temperature 30 °C, speed of agitation 800 rev/min. (●) 1.25×10^{-3} mol/mL (■) 1.875×10^{-3} mol/mL, (◆) 2.5×10^{-3} mol/mL.**

Effect of Concentration of Benzoic Acid. The concentration of benzoic acid was varied from 1.25×10^{-3} to 2.25×10^{-3} mol/mL by keeping the same sodium hydroxide concentration. The conversion was found to decrease with an increase in the concentration of the benzoic acid from 1.25×10^{-3} to 1.75×10^{-3} mol/mL, beyond which it was independent of concentration of benzoic acid. At a lower concentration of benzoic acid, (1.25×10^{-3} mol/mL, 0.025 mol), the amount of sodium hydroxide available was 0.0375 mol, and thus all benzoic acid would be in the benzoate form. This can be easily exchanged with the clay-surface-based

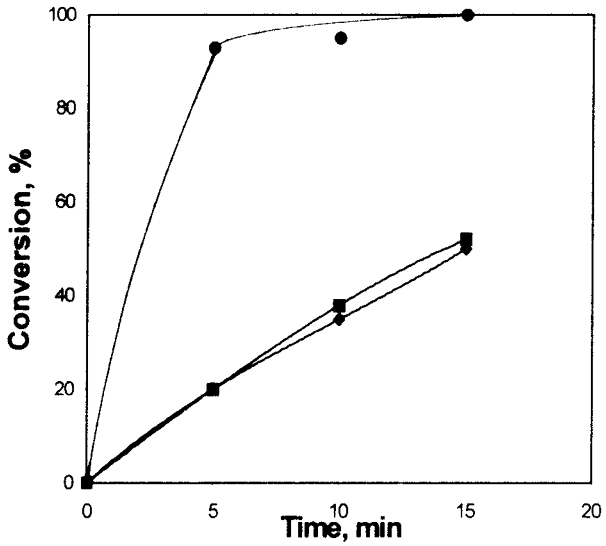


Figure 7. **Effect of concentration of benzoic acid. C_6H_5COCl 0.25 mol, chloroform 25 mL, CTAB/Tonsil 0.3 g, H_2O 20 mL, temperature 30 °C, speed of agitation 800 rev/min. (●) 1.25 × 10^{-3} mol/mL, (■) 1.75 × 10^{-3} mol/mL, (◆) 2.25 × 10^{-3} mol/mL.**

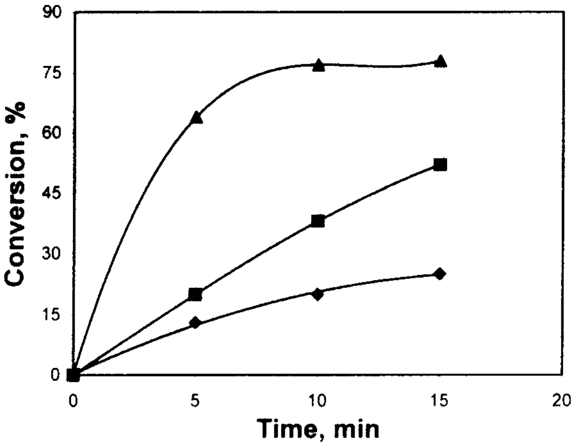


Figure 8. **Effect of temperature. C_6H_5COCl 0.25 mol, chloroform 25 mL, NaOH 0.0375 mol, benzoic acid 0.04 mol, CTAB/Tonsil 0.3 g, H_2O 20 mL, speed of agitation 800 rev/min. (◆) 10 °C, (■) 30 °C, (▲) 40 °C.**

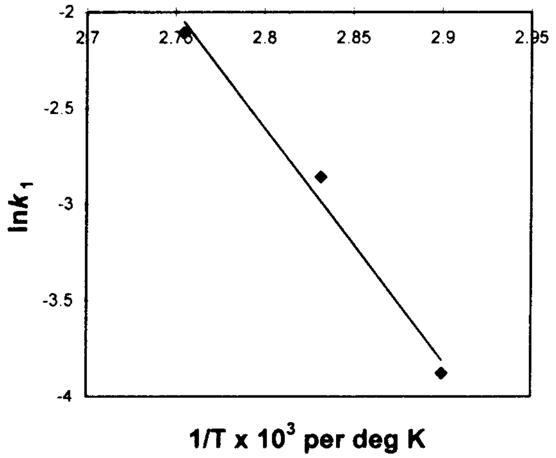


Figure 9. **Arrhenius plot. C_6H_5COCl 0.25 mol, chloroform 25 mL, NaOH 0.0375 mol, benzoic acid 0.04 mol, CTAB/Tonsil 0.3 g, H_2O 20 mL, temperature 30 °C, speed of agitation 800 rev/min.**

halide (X^-) giving a very high concentration of nucleophile on the clay. However, when the concentration of benzoic acid is increased to 0.0375 mol (1.75 × 10^{-3} mol/mL), the reaction between them may not go to completion because either the amount of benzoate formed may be less than 1.25 × 10^{-3} mol/mL or the exchange reaction may be favoured by free hydroxyl ions in the aqueous phase. Therefore, further increase in benzoic acid did not increase the rate of reaction and hence conversion. Therefore the effective concentration of the nucleophile beyond a certain concentration (beyond 1.75 × 10^{-3} mol/mL) is constant (Figure 7).

Kinetics of the Reaction. In the absence of any external and internal mass-transfer resistances, the rate of reaction can be written by true kinetic terms. Since there are three mechanisms involved in the L−L−S PTC, the concentration of $C{\sim}Q^+Y^-$ of the catalyst is the same as per the $C{\sim}Q^+X^-$ originally impregnated on the catalyst, that is, the equilibrium constant for exchange of Y^- with X^- is very high. Thus, the rate of reaction can be written as:

$$\frac{-\mathrm{d}[\mathrm{PhCOCl}]}{\mathrm{d}t} = k_2 w [\mathrm{PhCOCl}]_s [\mathrm{C}{\sim}\mathrm{Q}^+\mathrm{Y}^-] \tag{1}$$

$$= k_1\,[\mathrm{PhCOCl}] \tag{2}$$

where w is the catalyst loading, $[\mathrm{PhCOCl}]_s$ is a surface concentration of PhCOCl, where the rate constant k_1 is based on per unit weight of catalyst because $C{\sim}Q^+Y^-$ is based on per unit weight of catalyst.

Let [PhCOCl] be based on the unit organic phase volume, then a typical pseudo-first-order behaviour is obtained, in terms of the fractional conversion of benzoyl chloride X_A

$$-\ln(1 - X_A) = k_1 t \tag{3}$$

From the plot of $-\ln(1 - X_A)$ vs t, the slope k_1 was calculated as 9.56 × $10^{-4}\mathrm{s}^{-1}$, at a catalyst loading of 0.3 g CTAB supported on Tonsil clay. The plot is not shown for the sake of brevity.

Effect of Temperature. The effect of temperature on the conversion was studied in the range of 10−40 °C under otherwise similar conditions (Figure 8). The plot shows that as the temperature increases the conversion increases. The apparent activation energy of the reaction was estimated with the help of pseudo-first-order rate constant k_1 at different temperatures. The Arrhenius plot is shown in Figure 9. The apparent energy of activation for the reaction was calculated as 24.05 kcal/mol.

Catalyst Stability. Two typical blank experiments were conducted under otherwise similar conditions. One of the experiments was conducted without any catalyst as a simple liquid−liquid reaction. There was a marginal conversion of 5% in 15 min. In another experiment, the solvent chloroform was agitated with the same amount of CTAB supported on clay for the same time of 15 min. Thereafter, the solvent was then filtered off and used for a L−L reaction under otherwise similar conditions to ascertain if any CTAB had leached out from the clay support in the organic phase. This experiment showed a marginal conversion of 7%. These observations when compared with the conversion under simple L−L PTC conditions (Figure 4) show that there is insignificant loss of catalyst from clay surface. Thus, it is concluded that the catalyst is fairly stable.

Reusability of Catalyst. The catalyst was filtered off, dried, and reused under otherwise similar conditions. The catalyst was dried in order to know its exact weight before reuse. There was about 1% loss in weight during each subsequent filtration process. It was observed that the conversion of benzoyl chloride was marginally less (within 5%) and was used three times. The final conversions, after 15 min of reaction were: fresh run − 52%, first reuse − 49.7%, and second reuse − 47.5%. Thus, the catalyst is reusable within experimental error.

Conclusions

This work has addressed the utility of a clay-supported phase transfer catalyst in the synthesis of benzoic anhydride from benzoic acid and benzoyl chloride under alkaline conditions at 30 °C. Mechanistic and kinetic models are also presented. The catalyst was found to be reusable, and there was only a marginal loss of catalyst. Clay-supported catalyst was found to be more active than the polymer-supported commercial catalyst.

Acknowledgment

S.S.N. acknowledges the awards of Research Fellowships under projects by I.I.Ch.E and AICTE. G.D.Y. acknowledges the research grants from AICTE and CSIR, New Delhi, and the Darbari Seth Chair Endowment. We thank Miss Yogeeta B. Jadhav for her assistance in the preparation of the manuscript.

Received for review October 11, 1999.

OP990087C