

Rate intensive and selective etherification of vanillin with benzyl chloride under solid–liquid phase transfer catalysis by aqueous omega phase

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Received 29 July 2005; received in revised form 13 September 2005; accepted 13 September 2005

Available online 19 October 2005

Abstract

The alkylation of vanillin, containing three reactive groups, with benzyl chloride is challenging and can lead to both C- and O-alkylated products, particularly when liquid–liquid (L–L) phase transfer catalysis (PTC) is used. In the current studies, solid–liquid (S–L) PTC has been employed in the reaction of solid sodium salt of vanillin and benzyl chloride in toluene at 90 °C to make 4-benzyloxy vanillin, an ether, which is used as a perfume and also as a starting material for the synthesis of thalifoline, ephedradine as alkaloids and in synthesis of flavonoid compounds. The selectivity towards the desired product under S–L PTC is 100%. The rates of reaction are enhanced greatly by using trace quantities of water (the so-called omega phase (ω)) with 100% selectivity to the ether. Efficacy of various phase transfer agents such as TBAB (tetra-*n*-butyl ammonium bromide), TBAHS (tetra-*n*-butyl ammonium hydrogen sulfate), TPAB (tetra-*n*-propyl ammonium bromide), TEAB (tetraethyl ammonium bromide) and ETPB (ethyl triphenyl phosphonium bromide) was evaluated under otherwise similar conditions at 90 °C and explained. The order of activity was as follows: TBAB (maximum) > TBHS > TPAB > TEAB > ETPB (minimum). A theoretical model is developed to account for the enhancements in rates of reaction and selectivity to the ether. The kinetic constants have been evaluated and the apparent activation energy is determined as 9.64 kcal/mol. The results are novel.

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Keywords: Solid–liquid phase transfer catalysis; Aqueous omega phase; Vanillin; Benzyl chloride; 4-Benzyloxy vanillin; Etherification; Kinetics; Selectivity

1. Introduction

Phase transfer catalysis (PTC) has matured into a beneficial industrial practice for the past three and half decades [1,2]. A repertoire of reactions with complex mechanisms and kinetics has been pursued and over 600 odd examples are cited, amongst which alkylation and polymerization constitute a majority. The major advantages of PTC include high yield, high reaction rate, and selectivity to the desired product with less quantity of catalyst, mild conditions and reduction in energy consumption. Various strategies by which PTC can be converted into a green concept have been recently highlighted [3]. Alkylation reactions present a challenging selectivity problem in PTC, wherein different functional groups such as OH, SH, NH₂ and CH₂ are present in the same substrate leading to different products having several applications. Preparation of substituted aromatic ethers is one such example, which is amenable to PTC.

Williamson synthesis is the most widely used route for the synthesis of substituted aromatic ethers. Although the normal method involves treatment of a halide with an alkoxide, it is also possible to mix the halide and alcohol directly with solid KOH and DMSO [4] or with HgO and tetrafluoroboric acid in CH₂Cl₂ [5]. Yadav et al. [6–13] have developed several new beneficial PTC procedures for Williamson synthesis in terms of mildness of conditions, yield, and convenience including liquid–liquid (L–L), solid–liquid (S–L) and liquid–liquid–liquid (L–L–L) PTC in the presence of microwave irradiation, named as MILL-PTC, MISL-PTC and MILLL-PTC, respectively [14–18].

A large number of industrially important reactions involve the use of PTC under liquid–liquid conditions [1,2]. The major disadvantage of L–L PTC is that the catalyst remains distributed between the two-liquid phases and it cannot be recovered easily and due to presence of water it can lead to side reactions such as hydrolysis and oxidation in substituted phenolic compounds. To overcome this problem the conversion of an L–L PTC reaction in to a solid–organic liquid reaction proves to be favourable from the perspective of not only suppression of different types of side reaction but also the intensification of rates and selectivity to the

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Nomenclature

$[Y^-]_{\omega}$	concentration of Y^- in the ω phase (mol/cm^3)
$[QX]_{\omega}$	concentration of QX in ω phase (mol/cm^3)
$[QX]_{\text{org}}$	concentration of QX in organic phase (mol/cm^3)
$[X^-]_{\omega}$	concentration of X^- in ω phase (mol/cm^3)
$[QY]_{\omega}$	concentration of QY in ω phase (mol/cm^3)
$[RX]_{\text{org}}$	concentration of RX in the organic phase (mol/cm^3)
$N_{Q\text{total}}$	feed mole of catalyst (mol)
$N_{Q-\omega}$	moles of catalyst in omega phase (mol)
$N_{Q-\text{org}}$	moles of catalyst in organic phase (mol)
$N_{QX-\omega}$	moles of QX in omega phase (mol)
$N_{QY-\text{org}}$	moles of QY in organic phase (mol)
$N_{QX-\text{org}}$	moles of QX in organic phase
$N_{QY-\omega}$	moles of QY in omega phase (mol)
k_{R2}	second order rate constant ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)

desired product. The rates are enhanced due to the increase in particle surface area by orders of magnitude in comparison to that offered in liquid–liquid dispersion. Furthermore, in a S–L PTC process, addition of a third aqueous phase in trace amounts to form the so-called omega phase (ω) enhances the rates and selectivity to a great extent [19–23]. While several papers have been written on the advantages of S–L PTC in several types of reactions [1–3,24–27], there is a dearth of studies on the modeling aspects [28–30].

The current work focuses on the novelties of etherification of vanillin with benzyl chloride under S (reagent)–L (aqueous ω phase) and L (organic reagent) PTC process over L–L PTC to get 4-benzyloxy vanillin selectively which is an important product in perfumery industries. The product is also used as a starting material for synthesis of thalifoline, ephedradine as alkaloids and in synthesis of flavonoid compounds [31,32]. Besides, vanillin is an ideal substrate containing hydroxyl, aldehyde and ether groups, in which only the O-alkylation without attacking any other groups is targeted. The current paper covers the determination of process parameters such as catalyst structure, catalyst loading, substrate loading, and temperature on the conversion and rates of reaction. The role of omega (ω) phase, in the intensification of rate and selectivity is investigated.

2. Experimental

2.1. Chemicals and catalysts

Benzyl chloride, vanillin, toluene and sodium hydroxide all of AR grade were obtained from M/s s.d. Fine Chemicals Pvt. Ltd. Mumbai, India. TBAB (tetra-*n*-butyl ammonium bromide), TEAB (tetraethyl ammonium bromide), TPAB (tetra-*n*-propyl ammonium bromide), ETPB (ethyl triphenyl phosphonium bromide) and TBAHS (tetra-*n*-butyl ammonium hydrogen sulfate) of pure grade were procured as gift samples from M/s. Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India. These

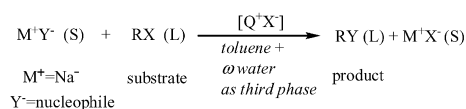
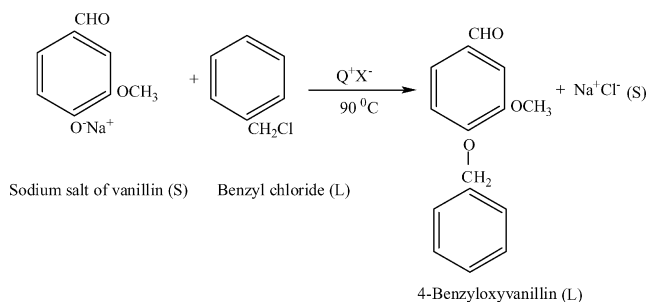
were used as received without any further purification. All other chemicals were of analytical grade.

2.2. Experimental set-up

The reactions were studied in a 5.0 cm i.d. fully baffled mechanically agitated contactor of 100 cm^3 total capacity, which was equipped with a six-blade-turbine impeller (1.7 cm diameter) and a reflux condenser. The reactor was kept in an isothermal bath whose temperature could be maintained at the desired value using a temperature indicator controller. Typical runs were conducted by taking 3 g vanillin as fine solid particles (0.02 mol), 0.97 g dry NaOH (0.02425 mol) and 30 ml toluene. It was agitated at 1200 rpm at 110 °C for 1 h to ensure complete formation of the sodium salt of vanillin. Then the temperature was reduced to 90 °C. The reaction mass contained 0.36 ml water, which was miscible in the toluene phase. The reaction mass contained fine slurry of sodium vanillinate. To this slurry, 0.02 mol benzyl chloride and 1 ml of water (ω phase) and 0.002 mol phase transfer catalyst were added. A zero time sample was withdrawn. All the typical reactions were carried out at 90 °C and 1200 rpm. The reaction scheme is as given below.

2.3. Analysis and isolation of product

Samples were withdrawn periodically and analyzed by GC (Chemito Model 8610) by using a stainless steel column (3.25 mm \times 4 m) packed with a liquid stationary phase of 10% OV-17. The conversion was based on the disappearance of benzyl chloride in the organic phase. At the end of the reaction, the reaction mass which contained 4-benzyloxy vanillin was washed with water to remove any traces of catalyst, sodium salt of vanillin, and the solvent was distilled under vacuum to get pure solid product. The melting point of isolated 4-benzyloxy vanillin (99.0% purity) was found to be 63–64 °C (literature value 61–64 °C). It was also confirmed by GC–MS. A complete material balance was also done. There was no side product in this reaction.



A general mechanism for the reaction and mode of operation is shown in Fig. 1, which involves the dissolution of solid M^+Y^- (sodium vanillate) in to the aqueous ω phase, followed by anion-exchange reaction with the catalyst to form the

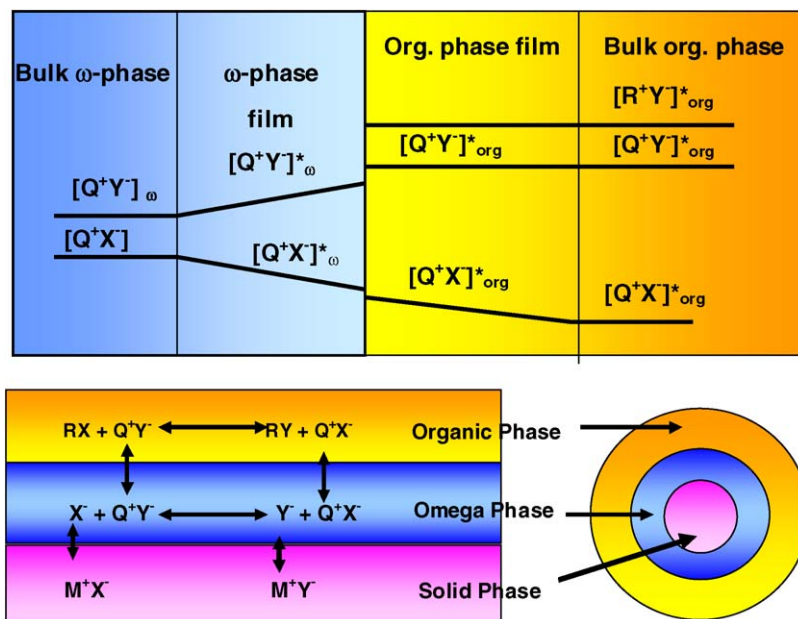


Fig. 1. General mechanism for S–L PTC in the presence of ω phase.

active ion-pair Q^+Y^- in the ω phase. There should be enough quantity of water to form a thin layer of aqueous phase surrounding the sodium salt of vanillin. Q^+Y^- is then transferred to the organic phase where the nucleophilic substitution reaction takes place. Addition of small quantities of water, thus, facilitates the distribution of the salt between the organic and solid phases. To determine the actual mechanism of the reaction, the effects of various parameters on the rate of reaction were studied.

3. Results

3.1. Effect of different catalysts

Various catalysts with different cationic as well as anionic structures, such as TBAB, TBAHS, TPAB, TEAB and ETPB were employed under otherwise similar concentration of the catalysts at 90 °C and 1200 rpm (Fig. 2). The order of activity of these catalysts was as follows:

TBAB (maximum) > TBHS

> TPAB > TEAB > ETPB (minimum).

Tetrabutyl cation forms an ion-pair more readily with the vanillin counter anion which is better distributed in the omega phase leading to higher conversion, in comparison with tetrapropyl, tetraethyl and ethyltriphenyl cations. Among symmetric cations, higher the molecular weight better is the partition in the organic phase. Br^- seems to be a better counter anion than hydrogen sulfate anion when trace amounts of water are present. Also for low temperature reactions, quaternary ammonium salts are better than phosphonium salts. Thus, TBAB was the most active catalyst and employed as the catalyst for all further experiments. Further, It is easily available

in the market and cheap. The selectivity to the ether was 100%.

3.2. Effect of speed of agitation

To ascertain the influence of resistance for the transfer of reactants to the reaction phase, the speed of agitation was varied in the range of 800–1500 rpm under otherwise similar conditions. The conversion was found to be practically the same at 1200 and 1500 rpm (Fig. 3). Further increase in the speed of agitation had practically no effect on the conversion. Thus, a speed of agitation of 1200 rpm was employed to get a maximum

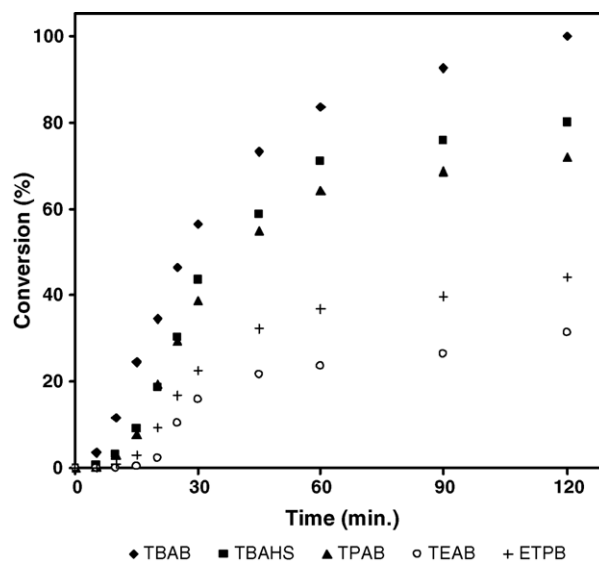


Fig. 2. Effect of different catalysts—vanillin: 0.02 mol, NaOH: 0.025 mol, benzyl chloride: 0.02 mol, water: 1 cm³, toluene: 30 cm³, speed of agitation: 1200 rpm and temperature: 90 °C.

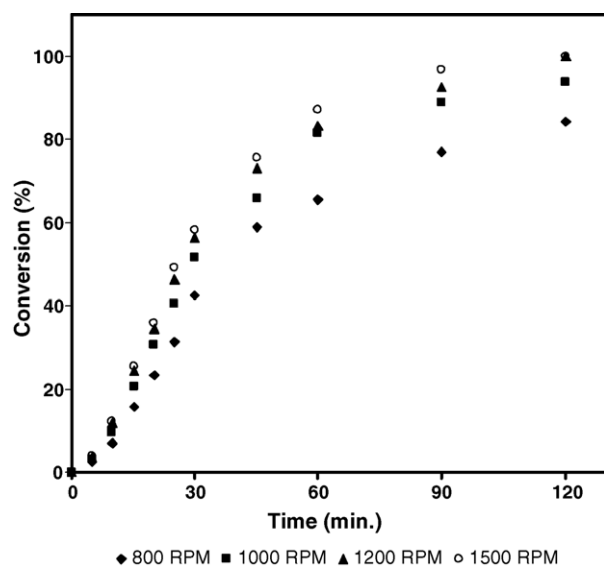


Fig. 3. Effect of speed of agitation—vanillin: 0.02 mol, NaOH: 0.025 mol, benzyl chloride: 0.02 mol, water: 1 cm³, TBAB: 0.002 mol, toluene: 30 cm³ and temperature: 90 °C.

rate and for assessing the effect of other variables on the rate of reaction.

3.3. Effect of catalyst quantity

The catalyst amount was varied from 1×10^{-3} to 6×10^{-3} mol under otherwise similar conditions. It was observed that as the concentration was increased, the conversion increased (Fig. 4). The initial rate of reaction was directly proportional to the amount of catalyst. This will be further explained later.

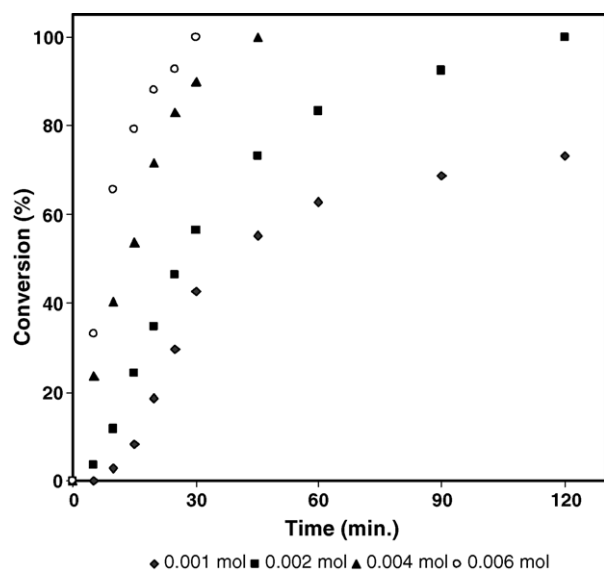


Fig. 4. Effect of catalyst loading—vanillin: 0.02 mol, NaOH: 0.025 mol, benzyl chloride: 0.02 mol, water: 1 cm³, toluene: 30 cm³, temperature: 90 °C and speed of agitation: 1200 rpm.

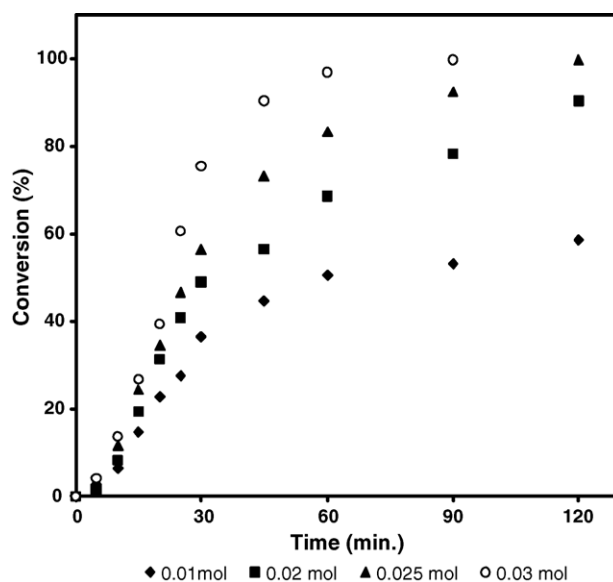


Fig. 5. Effect of concentration of sodium hydroxide—vanillin: 0.02 mol, benzyl chloride: 0.02 mol, water: 1 cm³, TBAB: 0.002 mol, toluene: 30 cm³, temperature: 90 °C and speed of agitation: 1200 rpm.

3.4. Effect of NaOH quantity

Sodium hydroxide amount was varied from 0.01 to 0.03 mol under similar reaction conditions by taking 0.02 mol of vanillin. The sodium salt of vanillin was formed in-situ corresponding to the amount of NaOH taken initially. Fig. 5 shows that the conversion was low at low concentrations of NaOH because stoichiometrically less quantity of NaOH was used. So the maximum amount of Y⁻ nucleophile and hence the conversion would be was equivalent to the NaOH taken. The best conversion was obtained with 0.025 mol of NaOH. Further increase in the NaOH concentration increases the side reaction such as Cannizzaro reaction due to active aldehyde group in vanillin. Therefore, 0.025 mol NaOH was taken as the optimum quantity for further experiments, all other quantities remaining the same.

3.5. Effect of amount of water as ω phase

It was desirable to know whether the 'ω' phase retains its identity by forming a third aqueous film around the particle. If the particle solubility increases substantially with temperature, then it is also important to ascertain the fate of the 'ω' phase. It is known that the 'ω' phase enhances the rate in S-L PTC in certain cases, and there is an optimum quantity beyond which the rate falls dramatically [21,28]. Thus, careful experiments were done by adding trace quantities of water in the range of 0.5–2 cm³ per g solid in 30 cm³ of organic phase. A model reaction was also conducted in the absence of water under nearly anhydrous conditions. The average particle size was 120 μm, and thus, for a given solid loading, the number of particles could be calculated from the knowledge of solid density. An average of 10 μm thickness of aqueous

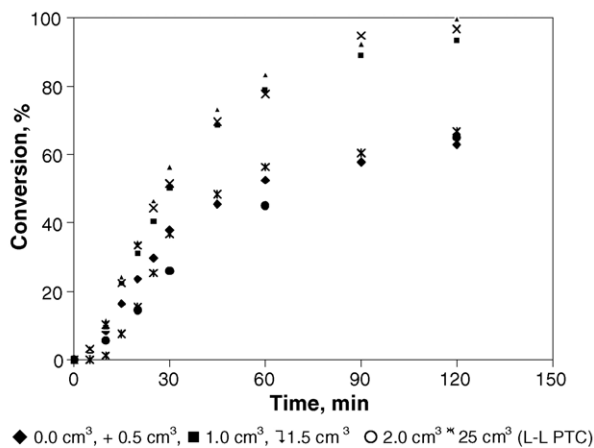


Fig. 6. Effect of volume of water (ω phase)—vanillin: 0.02 mol, NaOH: 0.025 mol, benzyl chloride: 0.02 mol, TBAB: 0.002 mol, toluene: 30 ml, speed of agitation: 1200 rpm and temperature: 90 °C.

film surrounding the particle leads to 0.53 ml water requirement for the ω phase formation for the control experiment. As the amount of water is increased, the mode of operation could change from solid–liquid (org) to solid–liquid (aq. ω)–liquid (org) to liquid (aq.)–liquid (org). It was observed that small amounts of water substantially increase the rates of reaction compared to those under anhydrous conditions, and a sudden rate enhancement was observed (Fig. 6). In all further experiments, 1 cm³ of water was added to the reaction mixture for the ' ω ' phase formation. The role of the ' ω ' phase is to enhance the local concentration of the nucleophile for the ion-exchange reaction with Q⁺X⁻, which is also partitioned in the ' ω ' phase.

In the case of two-liquid phases (the normal L–L PTC), when the amount of water was increased to 25 cm³, the reaction reaches a maximum of 65% conversion with 85% selectivity to 4-benzyloxy-vanillin in 2 h at 90 °C and the conversion went to 93% in 8 h with a selectivity of 83%.

3.6. Effect of mole ratio

The effect of mole ratio of vanillin to benzyl chloride was studied from 0.5:1 to 2:1, keeping the total volume of the reaction mass constant with toluene. In these experiments initially the sodium salt of vanillin was prepared by using 1:1.25 mol ratio of vanillin to NaOH. It was found that increasing the concentration of vanillin increases the rate of reaction and conversion (Fig. 7).

3.7. Effect of temperature

The effect of temperature was studied under otherwise similar reaction conditions from 75 to 95 °C (Fig. 8). It was found that the conversion increased substantially with increase in temperature from 75 to 95 °C. However, there was a marginal increase in conversion at 95 °C than that at 90 °C, bringing into play the mass transfer effects.

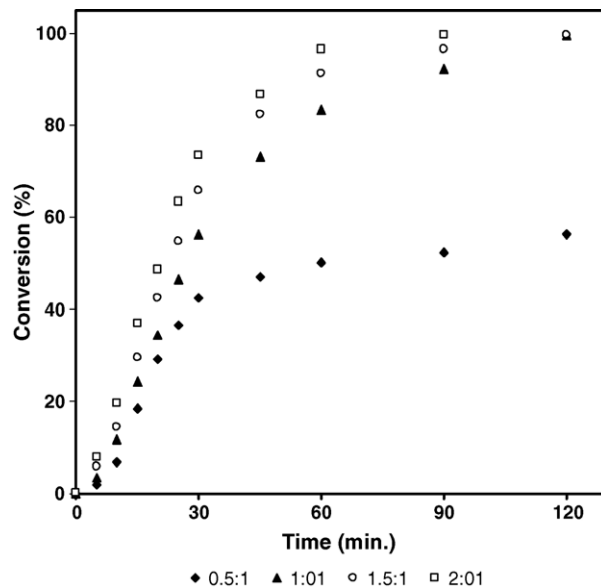


Fig. 7. Effect of mole ratio—vanillin, benzyl chloride and water: 1 cm³, TBAB: 0.002 mol; toluene: 30 cm³, speed of agitation: 1200 rpm and temperature: 90 °C.

3.8. Kinetics of reaction

3.8.1. Model describing instantaneous phase saturation with shrunk particle

This model is valid for solids which are soluble in the aqueous phase or in ω phase in the presence of other dissolved species. Since the quantity of ω phase used is small, that phase is saturated with the nucleophile, with the core of particle retaining its identity and also there is quaternary salt distributed in the ω phase.

The solubility of MY, the solid substrate, is very high and increases with temperature substantially. It would mean that on

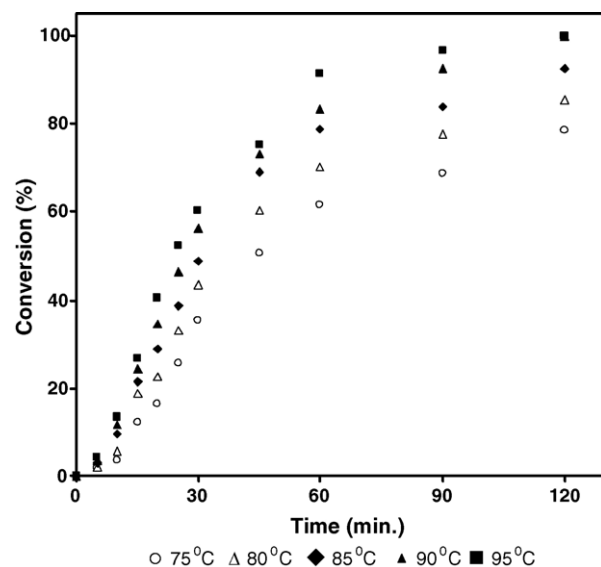


Fig. 8. Effect of temperature—vanillin: 0.02 mol, NaOH: 0.025 mol, benzyl chloride: 0.02 mol, water: 1 cm³, TBAB: 0.002 mol, toluene: 30 cm³ and speed of agitation: 1200 rpm.

addition of trace quantities of water which forms the ω phase, instantaneous dissolution of particles should occur thereby saturating the ω phase with interior core of the particle retaining its identity for sometime. Besides NaCl (MX) which is generated in-situ as the reaction proceeds will also be dissolved within the ω phase. This would suggest that $[Q^+Y^-]$ ion-pair which is formed in the ω phase is immediately distributed in the organic phase and the reaction proceeds there. This would be a typical L(ω)–L (org) PTC reaction, which occurs in the organic phase, either near the aqueous(ω)–organic interface in the liquid film on organic side or in the bulk organic phase.



Mass transfer to and from and reaction in organic phase:



Equilibrium constants:

$$K_{QX} = \frac{[QX]_{\omega}}{[QX]_{org}} \quad \text{and} \quad K_{QY} = \frac{[QY]_{org}}{[QY]_{\omega}} \quad (6)$$

Rate equations:

$$\frac{d[QX]_{\omega}}{dt} = k_{L\omega} a \{ [QX]_{\omega}^* - [QX]_{\omega} \} - k_{R1} [QX]_{\omega} [Y^{-}]_{\omega} + k'_{R1} [QY]_{\omega} [X^{-}]_{\omega} \quad (7)$$

$$-\frac{d[RX]_{org}}{dt} = k_{R2} [QY]_{org} [RX]_{org} \quad (8)$$

$$\frac{d[QY]_{\omega}}{dt} = k_{R1} [QX]_{\omega} [Y^{-}]_{\omega} - k'_{R1} [QY]_{\omega} [X^{-}]_{\omega} + k_{LO} a_{\omega} \{ [QY]_{\omega} - [QY]_{\omega}^* \} \quad (9)$$

$$\frac{d[QY]_{org}}{dt} = k_{LO} a_{\omega} \{ [QY]_{org}^* [QX]_{org} \} - k_{R2} [QY]_{org} [RX]_{org} \quad (10)$$

The total quantity of catalyst added $N_{Qtotal} = N_{Q-\omega} + N_{Q-org}$, which is distributed in four-ion pairs.

$$N_{QX-\omega} + N_{QY-\omega} + N_{QX-org} + N_{QY-org} \quad (11)$$

$$\{ [QX]_{\omega} + [QY]_{\omega} \} V_{\omega} + \{ [QX]_{org} + [QY]_{org} \} V_{org} \quad (12)$$

$$\{ [QX]_{org} K_{QX} V_{\omega} + [QX]_{org} V_{org} \} + \left\{ \frac{[QY]_{org}}{K_{QY}} V_{\omega} + [QY]_{org} V_{org} \right\} \quad (13)$$

$$[QX]_{org} \left\{ K_{QX} + \frac{V_{org}}{V_{\omega}} \right\} + [QY]_{org} \left\{ \frac{1}{K_{QY}} + \frac{V_{org}}{V_{\omega}} \right\} \quad (14)$$

Let $V_{org}/V_{\omega} = \gamma$

$$N_{Qtotal} = [QX]_{org} \{ K_{QX} + \gamma \} + [QY]_{org} \left\{ \frac{1}{K_{QY}} + \gamma \right\} \quad (15)$$

$$\{ K_{QX} + \gamma \} = \alpha \quad \text{and} \quad \left\{ \frac{1}{K_{QY}} + \gamma \right\} = \beta \quad (16)$$

$$N_{Qtotal} = \alpha [QX]_{org} + \beta [QY]_{org} \quad (17)$$

$$[QY]_{org} = \frac{N_{Qtotal} - \alpha [QX]_{org}}{\beta} \quad (18)$$

$$\frac{d[RX]_{org}}{dt} = k_{R2} [RX]_{org} \left[\frac{N_{Qtotal} - \alpha [QX]_{org}}{\beta} \right] \quad (19)$$

If $[QX]_{org} = \text{constant}$, then the above equation can be integrated to get

$$-\ln(1 - X_A) = k_{R2} \left[\frac{N_{Qtotal} - \alpha [QX]_{org}}{\beta} \right] t \quad (20)$$

Eq. (20) was fitted to the experimental data using Polymath 5.1 and the constant K_{QX} , $[QX]_{org}$ and k_{R2} were obtained (Table 1). The parity plot of $-\ln(1 - X_A)$ calculated with these values was made against the experimental data and it shows a good fit (Fig. 9). It also shows that as the temperature is increased, the distribution of the active ion-pair in the organic phase increases substantially. The rate constants obtained at different temperature were used to make the Arrhenius plot (Fig. 10). The frequency factor and activation energy were obtained from the Arrhenius plot as $2.92 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ and 9.64 kcal/mol , respectively. This activation energy also supported the fact that the overall rate of reaction is not influenced by mass transfer resistance and it is an intrinsically kinetically controlled reaction.

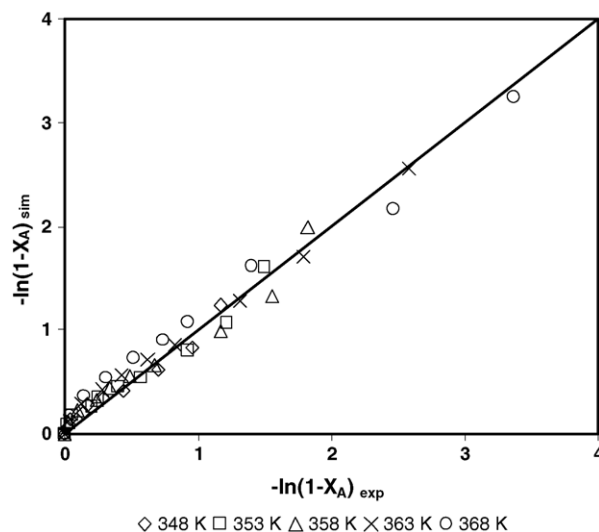


Fig. 9. Parity plot of experimental and simulated values of $-\ln(1 - X_A)$.

Table 1
Model fitting for O-alkylation of vanillin with benzyl chloride

Temperature	348 K	353 K	358 K	363 K	368 K
k_{R2} ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)	265.55	304.95	358.60	444.08	569
β	32.79	32.104	30.89	30.068	30.01
$[\text{QX}]_{\text{org}}$ (mol/cm^3)	9.68×10^{-6}	3.97×10^{-6}	3.05×10^{-6}	2.55×10^{-6}	2.66×10^{-6}
K_{QY}	0.35	0.47	1.12	14.70	100

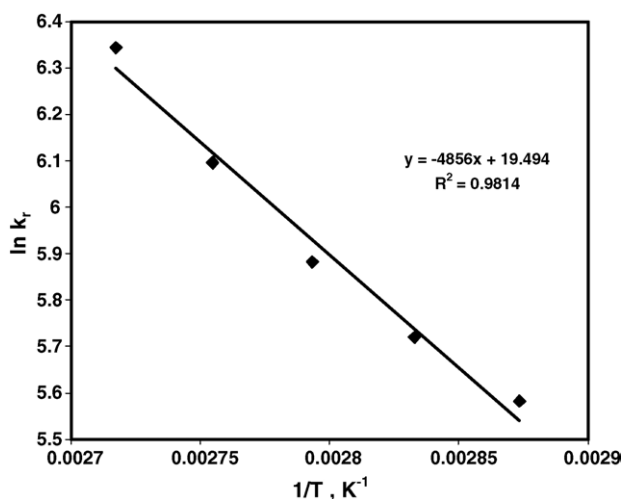


Fig. 10. Arrhenius plot.

4. Conclusion

Phase transfer catalysis often provides an attractive alternative for organic synthesis since PTC reactions generally proceed under relatively mild conditions. The intensification of rates and selectivity to O-alkylation of sodium salt of vanillin with benzyl chloride to 4-benzyloxy vanillin was studied by using solid–liquid PTC with aqueous omega phase at 90 °C. The product is a very valuable fine chemical. The effects of structure and chain length of various catalysts such as TBAB, TBAHS, TPAB, TEAB and ETPB were studied; among which TBAB was found to be the best. A complete theoretical model is developed to account for the enhancements in rates of reaction and selectivity to the ether. The kinetic constants have been determined and the apparent activation energy is found as 9.64 kcal/mol.

Acknowledgment

G.D. Yadav acknowledges Darbari Seth Endowment for supporting the Chair and also CSIR-NMITLI for a research grant under which SVL earned his JRF.

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