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Selective oxidation of methyl mandelate to methyl phenyl glyoxylate using liquid–liquid–liquid phase transfer catalysis

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ABSTRACT

The conversion of the traditional liquid–liquid (L–L) phase transfer catalysis (PTC) into liquid–liquid–liquid (L–L–L) PTC offers several advantages. L–L–L PTC is a novel strategy which offers catalyst recovery, waste reduction including better selectivity and improving profitability. The middle catalyst-rich phase formed between the other two phases is the locale of main reaction and it intensifies the rates of reaction by order of magnitude. In the current work, oxidation of methyl mandelate to methyl phenyl glyoxylate has been studied by using L–L–L PTC with tetra-butyl ammonium bromide as a catalyst at 45 °C. It leads to 100% selectivity towards methyl phenyl glyoxylate within very short reaction time. The method offers several advantages including catalyst separation and reusability. The effects of different parameters were studied in detail. A mathematical model is developed and validated with the observed reaction data.

1. Introduction

Phase transfer catalysis (PTC) is one of the most widely used synthetic techniques and it finds more than 700 industrial applications [1,2]. Major advantages of PTC are its simplicity, use of inexpensive reagents under mild conditions, high reaction rates, and high selectivity to the desired product [3]. A large number of industrially important reactions have been reported by using liquid–liquid (L–L) phase transfer catalysis wherein recovery and reuse of the catalyst is not usually practised. Also, L–L PTC is not preferred for systems in which the presence of water leads to side reactions such as hydrolysis. It would be possible to achieve the same objective most economically by converting a biphasic reaction into a triphasic system such as liquid–liquid–solid (L–L–S) and liquid–liquid–liquid (L–L–L) PTC. In L–L–S PTC, the expensive catalyst is bound to a solid support like polymeric resin [4–5] or inorganic oxides [6] or polymeric capsule membrane (CM) [7–9]. In L–L–L PTC, the third-liquid phase (catalyst-rich phase) is an immiscible middle-liquid phase which is the locale of reaction. The rates are very high, thereby reducing the reaction times and reactor volumes. The advantages of L–L–L PTC over forms of PTC include enhanced reaction rates, absence of intra-particle diffusion resistance prevalent in L–L–S PTC, milder reaction conditions, ease of catalyst recovery and reuse, suppression of by-product formation, high selectivity with respect to the desired product [9–22]. L–L–L PTC requires more amount of catalyst but the catalyst-rich phase is recovered and reused. Hence it is an excellent way of waste reduction from the Green Chemistry point of view.

Oxidation is an important class of reaction from both industrial and academic perspectives. Several oxidizing agents have been employed for a variety of industrial reactions, but many of them are polluting and result into poor yields. PTC offers many excellent opportunities for conducting oxidation reactions by using inexpensive primary oxididizing agents such as oxygen, sodium hypochlorite and hydrogen peroxide [23–25]. Aqueous hypochlorites such as NaOCl and $Ca(OCl)_2$ are mild and used for the oxidation of various organic substrates at 20–40 °C by using PTC [26].

This paper deals with an insight into the selective oxidation of methyl mandelate to methyl phenyl glyoxylate by using sodium hypochlorite under L–L–L PTC and delineates kinetics and mechanism of the reaction. Mandelates have played an important role in organic synthesis and are used in artificial flavoring and perfumes. Methyl phenyl glyoxylate, which contains two carbonyl groups, is an important intermediate used in fine chemical industry [27–35].

2. Experimental

2.1. Materials

Methyl mandelate and aqueous sodium hypochlorite (4%, w/w) were obtained from M/s Merck India ltd. and used without further

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purification. Tetra-butyl ammonium bromide (TBAB) was obtained as a gift sample from Dishman Pharmaceuticals and Chemicals Ltd., Ahmadabad, India. All other chemicals were procured from M/s S.D. Fine Chemicals, Mumbai, India and were analytical grade reagents.

2.2. Procedure

The reaction was studied in a 5 cm internal diameter, fully baffled mechanically agitated glass reactor of 100 cm^3 total capacity. It was equipped with a 6 bladed-turbine impeller and equi-spaced baffles. The reactor was kept in an isothermal oil bath whose temperature could be maintained at a desired value. The reaction mixture was agitated mechanically with the help of an electric motor.

A typical three phase reaction mixture contained 0.03 mol methyl mandelate in toluene (made up to 10 cm^3), 0.03 mol 4% sodium hypochlorite in aqueous phase, 0.0046 mol TBAB and 0.0375 mol NaCl in aqueous phase (made up to 10 cm^3) at 45 °C. Upon mixing these two mixtures, the third phase would appear and its volume was 1.3 cm^3 with a density of 0.84 g/cm^3. The experiments were repeated and an average of three data points was taken in each case.

2.3. Method of analysis

The samples were periodically withdrawn at regular time intervals. The stirring was stopped momentarily and the phases were allowed to separate. The samples of a predetermined quantity were collected from the respective phases and then analyzed. The volume of third phase does not change as the aqueous phase is saturated with sodium chloride. The volume of third phase practically remains the same till the reaction goes to completion. This has been brought out in different systems involving tri-liquid PTC [36–40]. Analysis of the reaction mixture was performed by HPLC (A Knauer, model K-501: 63614) with a UV detector (Knauer, model K-501: 62964) by using acetonitrile/water (60: 40) as a mobile phase with a flow rate of 1 ml/min at λ_{max} of 261 nm. The quantification of the data was done by a standard calibration method.

The composition of the third phase was analyzed on GC (Chemito model 8510) by using a 4 m × 3.8 mm stainless steel column packed with 10% OV 17 on Chromosorb WHP, coupled with a thermal conductivity detector. The injector and detector temperatures were kept at 300 °C. Synthetic mixtures of the reactant and internal standard were used to calibrate the chromatograms and quantify the data.

The amount of the water present in the third phase was analyzed by Karl-Fisher apparatus.

2.4. Determination of third phase composition

The formation and stability of the third phase was verified independently at the reaction temperature by a trial and error procedure. In a typical experiment, the composition of the third phase was analyzed by gas chromatography. The third phase volume was 1.3 cm^3 with a density of 0.84 g/cm^3 containing 31.13% toluene, 51.37% TBAB, 0.04% methyl mandelate, 2.38% methyl phenyl glyoxylate and 15.08% water by weight.

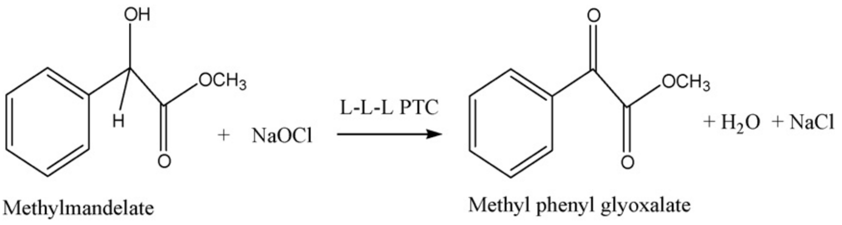
2.5. Reaction mechanism

The overall reaction is represented in Scheme 1 and the mechanism is depicted in Scheme 2, which is as follows:

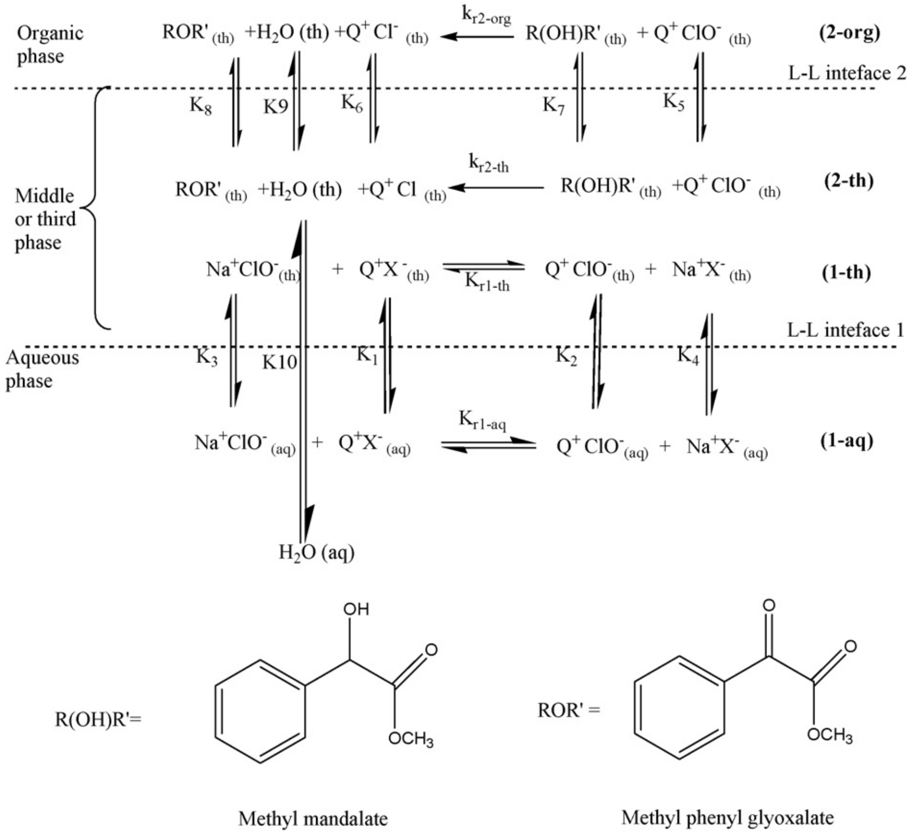
- Firstly the quaternary ammonium salt reacts with sodium hypochlorite to form the quaternary ammonium hypochlorite

Nomenclature

A	methyl mandelate
C_A^{org}	concentration of methyl mandelate in the organic phase (mol/cm^3 of organic phase)
C_A^{th}	concentration of methyl mandelate in the third phase (mol/cm^3 of third phase)
C_{QClO}^{aq}	concentration of QClO in aqueous phase (mol/cm^3 aqueous phase)
C_{QX}^{aq}	concentration of QX in aqueous phase (mol/cm^3 aqueous phase)
C_{QClO}^{th}	Concentration of QClO in third phase (mol/cm^3 third phase)
C_{QX}^{th}	concentration of QX in third phase (mol/cm^3 third phase)
C_{QClO}^{org}	concentration of QClO in organic phase (mol/cm^3 organic phase)
C_{QX}^{org}	concentration of QX in organic phase (mol/cm^3 organic phase)
K_i	distribution constants, as given as follows: $K_1 = \frac{C_{QX}^{th}}{C_{QX}^{aq}}, K_2 = \frac{C_{QClO}^{th}}{C_{QClO}^{aq}}, K_3 = \frac{C_{ClONa}^{th}}{C_{ClONa}^{aq}}, K_4 = \frac{C_{NaX}^{aq}}{C_{NaX}^{th}},$ $K_5 = \frac{C_{QClO}^{org}}{C_{QClO}^{th}},\ K_6 = \frac{C_{QX}^{org}}{C_{QX}^{th}},\ K_7 = \frac{C_{R(OH)R'}^{th}}{C_{R(OH)R'}^{org}},\ K_8 = \frac{C_{ROR'}^{th}}{C_{ROR'}^{org}},$ $K_9 = \frac{C_{H_2O}^{th}}{C_{H_2O}^{org}}, K_9 = \frac{C_{H_2O}^{aq}}{C_{H_2O}^{th}}, K_{r1-aq} = \frac{k_{r1-aq}}{k'_{r1-aq}},$ $K_{r1-th} = \frac{k_{r1-th}}{k'_{r1-th}}$
k_{app}	apparent first order rate constant, cm^3/(mol of catalyst s)
k_{org}	organic phase reaction rate constant, cm^3/(mol of catalyst s)
k_{r1-aq}	rate of exchange in the aqueous phase, cm^3/(mol of catalyst s)
$k_{r1\text{-}th}$	rate of exchange reaction in the third phase, cm^3/(mol of catalyst s)
$k_{r2\text{-}th}$	rate of main reaction in the third phase, cm^3/(mol of catalyst s)
$k_{r1\text{-}org}$	rate of reaction in the organic phase, cm^3/(mol of catalyst s)
N_{Qtot}	total moles of catalyst added to the system (mol)
N_A^{th}	moles of A in third phase (mol)
N_A^{org}	moles of A in organic phase (mol)
N_{QClO}^{th}	moles of QClO in third phase (mol)
QX	quaternary salt
R(OH)R′	methyl mandelate
NaClO	sodium hypochlorite
ROR′	methyl phenyl glyoxylate (or benzyl formate)
t	time of reaction (s)
V^{aq}	volume of aqueous phase (cm^3)
V^{org}	volume of organic phase (cm^3)
V^{th}	volume of the third phase (cm^3)
	$X_A = \frac{N_{A0} - N_A}{N_{A0}}$, fractional conversion
$\alpha = \frac{V^{th}}{V^{aq}}$	ratio of third to aqueous phase volumes
$\beta = \frac{V^{th}}{V^{org}}$	ratio of third to organic phase volumes
$\eta = \frac{C_{QClO}^{th}}{C_{QClO}^{th} + C_{QX}^{th}}$	molar ratio of Q^+ in the form of QClO at any time in the third phase.



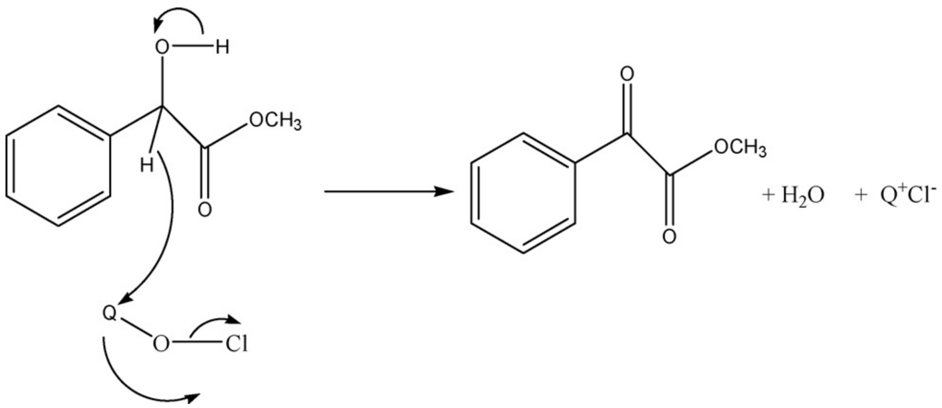
Scheme 1. Overall reaction scheme of oxidation of methyl mandelate to methyl phenyl glyoxalate.



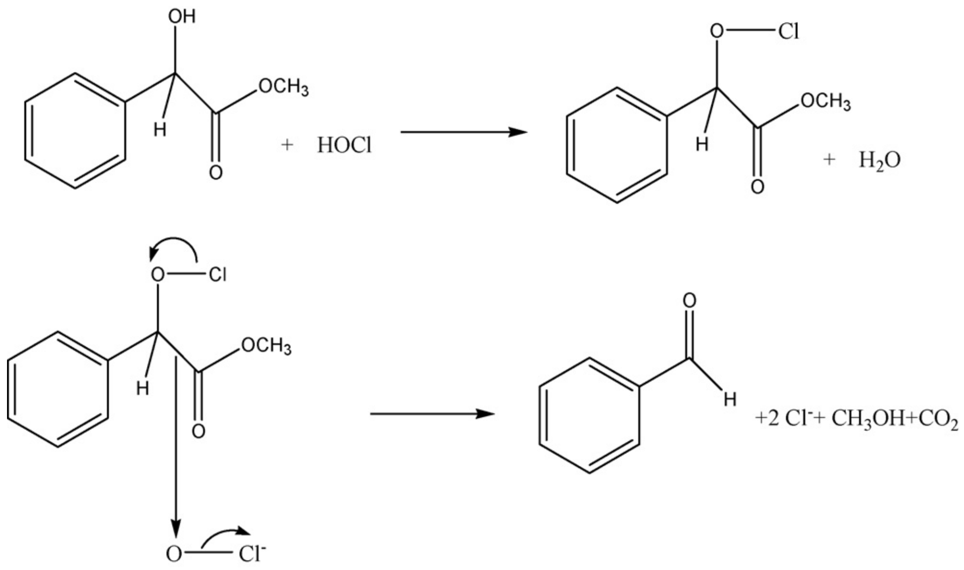
Scheme 2. L–L–L PTC mechanism for oxidation of methyl mandalate to methyl phenyl glyoxalate.

ion-pair (Q^+ClO^-). This reaction takes place in the aqueous phase (reaction 1-aq). There is a distribution of all these species into the middle (third) phase (1-th).

- The reactant methyl mandalate R(OH)R′ is transferred across the interface between third phase and organic phase at the top.
- This quaternary ammonium hypochlorite ion-pair is being strongly lipophilic reacts with methyl mandelate to form the product in the third phase (2-th). Since there is distribution of Q^+ClO^-) in the organic phase, part of the reaction can also take place in the organic phase (2-org) but its contribution is insignif-



Scheme 3. Mechanism of oxidation of methyl mandelate by hydride transfer.



Scheme 4. Mechanism of oxidation of methyl mandelate by C–C bond cleavage: this side reaction is suppressed under L–L–L PTC.

icant. The rate of reaction 2-th is far greater than that of 2-org. The actual mechanism of formation of the product methyl phenyl glyoxalate is given in Scheme 3. It abstracts hydride ion from the intermediate to give the product (Scheme 2).

- If any by-product is formed it can be due to free HClO, which is shown in Scheme 4. It will substitute OH group by OCl and in a subsequent step it can lead to a carbon–carbon bond cleavage to form benzaldehyde.

As the carbon–carbon bond formation requires more energy than the hydride abstraction, the formation of methyl phenyl glyoxylate is favorable. It was observed that there was no formation of any by-product at any conversion levels in L–L–L PTC. Hence, the selectivity towards methyl phenyl glyoxylate was 100%.

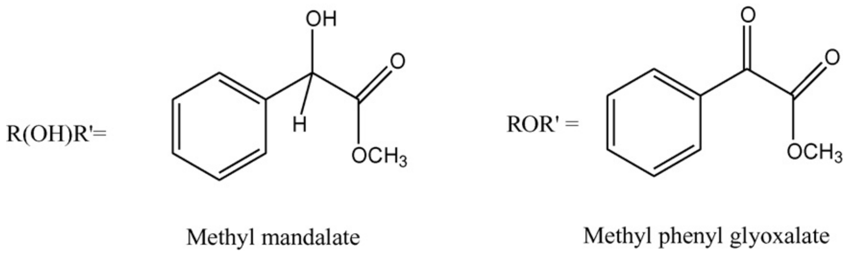
3. Results and discussion

3.1. Kinetics of L–L–L PTC

The overall reaction given in Scheme 1 can be depicted as:

$$\mathrm{NaOCl}_{(aq)} + \mathrm{R(OH)R'}_{(org)} \overset{\text{L–L–LPTC}}{\longrightarrow} \mathrm{ROR'}_{(org)} + \mathrm{NaCl}_{(aq)} + \mathrm{H_2O}_{(aq)}$$

where R(OH)R′ = methyl mandelate, and ROR′ = methyl phenyl glyoxalate (or methyl benzoylformate)



The steps involved in the overall reaction are:

(1) Ion exchange reaction of $\mathrm{ClO^-Na^+}$ and $\mathrm{Q^+X^-}$ in the aqueous phase to form the ion-pair with the nucleophile $\mathrm{Q^+ClO^-}$

$$\mathrm{Na^+ClO^-} + \mathrm{Q^+X^-} \overset{K_{r1-aq}}{\rightleftarrows} \mathrm{Q^+ClO^-} + \mathrm{Na^+X^-} \tag{1}$$

(2) Transport of $\mathrm{Q^+X^-}$, $\mathrm{ClO^-Na^+}$ and $\mathrm{Q^+ClO^-}$ from the aqueous phase into the third-liquid phase with equilibrium constants K_1, K_2, and K_3 respectively:

$$\mathrm{Q^+X^-} \rightleftarrows \mathrm{Q^+X^-} \qquad K_1 = \frac{C_{\mathrm{QX}}^{\mathrm{th}}}{C_{\mathrm{QX}}^{\mathrm{aq}}} \tag{2}$$

$$\mathrm{Q^+ClO^-} \rightleftarrows \mathrm{Q^+ClO^-} \qquad K_2 = \frac{C_{\mathrm{QClO}}^{\mathrm{th}}}{C_{\mathrm{QClO}}^{\mathrm{aq}}} \tag{3}$$

$$\mathrm{Na^+ClO^-} \rightleftarrows \mathrm{Na^+ClO^-} \qquad K_3 = \frac{C_{\mathrm{NaClO}}^{\mathrm{th}}}{C_{\mathrm{NaClO}}^{\mathrm{aq}}} \tag{4}$$

(3) Ion exchange reaction of $\mathrm{Na^+ClO^-}$ and $\mathrm{Q^+X^-}$ can also take place in the third-liquid phase to form $\mathrm{Q^+ClO^-}$ and $\mathrm{Na^+X^-}$.

$$\mathrm{Na^+ClO^-} + \mathrm{Q^+X^-} \overset{K_{r1-th}}{\rightleftarrows} \mathrm{ClO^-Q^+} + \mathrm{Na^+X^-} \tag{5}$$

Here the halide $\mathrm{X^-}$ is $\mathrm{Br^-}$. There is a very insignificant contribution by the reaction in organic phase but is shown for sake of completeness.

$$\mathrm{Na^+X^-} \rightleftarrows \mathrm{Na^+X^-} \qquad K_4 = \frac{C_{\mathrm{NaX}}^{\mathrm{aq}}}{C_{\mathrm{NaX}}^{\mathrm{th}}} \tag{6}$$

$$\mathrm{Q^+ClO^-} \rightleftarrows \mathrm{Q^+ClO^-} \qquad K_5 = \frac{C_{\mathrm{QClO}}^{\mathrm{org}}}{C_{\mathrm{QClO}}^{\mathrm{th}}} \tag{7}$$

$$\mathrm{Na^+Cl^-} \rightleftarrows \mathrm{Na^+Cl^-} \qquad K_6 = \frac{C_{\mathrm{NaCl}}^{\mathrm{aq}}}{C_{\mathrm{NaCl}}^{\mathrm{th}}} \tag{8}$$

(4) Reaction of Q^+ClO^- with $R(OH)R'$ in the third-liquid phase:

$$Q^+ClO^- + R(OH)R'_{(th)} \xrightarrow{k_{r2-th}} ROR'_{(th)} + Q^+Cl^- + H_2O_{(th)} \tag{9}$$

The critical analysis of rate data suggested that the conversions of methyl mandelate were linear in time suggesting zero order reaction up to a certain time and then it followed an exponential pattern indicating apparent first order. It was neither first order nor zero order over the entire range of concentrations in L–L–L PTC.

The rate of formation of ROR′ can be written from Eq. (9). The stoichiometry of the reaction suggests that for every one mol of R(OH)R′, one mol of product ROR′ is formed. Thus, the rate of formation of the product per unit volume of the third phase is given by:

$$\frac{dC^{th}_{R(OH)R'}}{dt} = k_{th} C^{th}_{QOCl} C^{th}_{R(OH)R'} \tag{10}$$

Further,

$$K_7 = \frac{C^{th}_{R(OH)R'}}{C^{org}_{R(OH)R'}} \quad \text{and} \quad K_8 = \frac{C^{th}_{R(OH)R'}}{C^{org}_{R(OH)R'}} \tag{11}$$

The fractional conversion of ROR′ (designated as A) is given by:

$$X_A = \frac{N_{A_0} - N_A}{N_{A_0}} \tag{12}$$

where ‘0’ denotes the zero time or initial condition.

The rate of formation of ROH in mol/time is equal to that of reaction of RHOH as shown below.

$$\frac{dN_{R(OH)R'}}{dt} = V^{th} \frac{dC^{th}_{R(OH)R'}}{dt} = V^{th} k_{th} C^{th}_{QClO} C^{th}_{R(OH)R'} = \frac{-dN_A}{dt} \tag{13}$$

$$\frac{-dN_A}{dt} = V^{th} k_{th} C^{th}_{QClO} K_7 C^{org}_A \tag{14}$$

The volumes of the aqueous, third and organic phases are given by V^{aq}, V^{th} and V^S respectively. The total numbers of moles of A at any time are distributed between the organic and third phase and none in the aqueous phase, $N_A = N^{th}_A + N^{org}_A$and

$$K_7 = \frac{C^{th}_{R(OH)R'}}{C^{org}_{R(OH)R'}} = \frac{C^{th}_A}{C^{org}_A} = \frac{N^{th}_A V^{org}}{N^{org}_A V^{th}}, \tag{15}$$

and therefore the following can be derived:

$$C^{org}_A = \frac{N_A}{(V^{org} + K_7 V^{th})} \tag{16}$$

$$\frac{-dN_A}{dt} = \frac{V^{th} k_{th} K_7 C^{th}_{QClO} N_A}{(V^{org} + K_7 V^{th})} = \frac{k_{th} K_7 N^{th}_{QClO} N_A}{(V^{org} + K_7 V^{th})} \tag{17}$$

Taking mass balance for the catalyst (N_{Qtot}, the total moles of catalyst added initially) which is distributed in six different species in the three phases,

$$N_{Qtot} = V^{aq}(C^{aq}_{QClO} + C^{aq}_{QCl}) + V^{th}(C^{th}_{QClO} + C^{th}_{QCl}) + V^{org}(C^{org}_{QClO} + C^{org}_{QCl}) \tag{18}$$

As stated earlier, the contribution of the organic phase reaction is negligible since the amount of Q in the organic phase is negligible and thus Eq. (18) becomes:

$$N_{Qtot} = V^{aq}(C^{aq}_{QClO} + C^{aq}_{QCl}) + V^{th}(C^{th}_{QClO} + C^{th}_{QCl}) \tag{19}$$

Let the amount of catalyst in the third phase be denoted by

$$C^{th}_Q = C^{th}_{QClO} + C^{th}_{QCl}, \quad C^{th}_{QClO} = \eta C^{th}_Q \tag{20}$$

In Eq. (20), η is the molar ratio of Q^+ in the form of QClO at any time in the third phase.

Substituting Eqs. (2,3,20) into (19) the following is obtained.

$$\begin{aligned} N_{Qtot} &= \left[\left(\frac{1}{K_2} + \frac{V^{th}}{V^{aq}}\right) + \left(\frac{1}{K_1} + \frac{V^{th}}{V^{aq}}\right)\left(\frac{1-\eta}{\eta}\right)\right] C^{th}_{QClO} V^{aq} C^{th}_{QClO} \\ &= \frac{N^{th}_{QClO}}{V^{th}} \\ &= \frac{N_{Q_{tot}}/V^{aq}}{\left[((1/K_2) + (V^{th}/V^{aq})) + ((1/K_1) + (V^{th}/V^{aq}))((1-\eta)/\eta)\right]} \end{aligned} \tag{21}$$

$$\begin{aligned} \frac{-dN_A}{dt} &= \frac{k_{th} K_7 N^{th}_{QClO} N_A}{(V^{org} + K_7 V^{th})} \\ &= \frac{k_{th} K_7 N_A}{(V^{org} + K_7 V^{th})} \\ &\quad \times \frac{N_{Qtot} V^{th}/V^{aq}}{[((1/K_2) + (V^{th}/V^{aq})) + ((1/K_1)) + (V^{th}/V^{aq}))((1-\eta)/\eta)]} \end{aligned} \tag{22}$$

$$\frac{-dN_A}{dt} = \frac{\alpha k_{th} K_7 N_A N_{Qtot}}{V^{org}(1 + K_7 \beta)\left[((1/K_2) + \alpha) + ((1/K_1) + \alpha)((1-\eta)/\eta)\right]} \tag{23}$$

where

$$\alpha = \frac{V^{th}}{V^{aq}} \quad \text{and} \quad \beta = \frac{V^{th}}{V^{org}} \tag{24}$$

In Eq. (23) above, α, β, K_7 and k_{th} are constants and hence can be suitably combined as an apparent rate constant k_{app}. The catalysts quantity added, $N_{Qtot,}$ is also constant.

In terms of fractional conversion, now Eq. (24) is written as follows,

$$\frac{dX_A}{dt} = k_{app}(1 - X_A) N_{Qtot} \tag{25}$$

By integrating Eq. (24) gives,

$$-\ln(1 - X_A) = k_{app} N_{Qtot} t \tag{26}$$

The above model can be fitted to the collected data.

3.2. Effect of speed of agitation

To ascertain the influence of mass transfer resistance, the speed of agitation was varied in the range of 200–800 rpm under otherwise constant reaction conditions in presence of TBAB as the catalyst. The conversion is plotted as a function of time against agitation speed. The conversion was found to be practically the same at 500 and 800 rpm. Further increase in the speed of agitation to 500 rpm had practically no effect on the conversion (Fig. 1). This implies that there was no mass transfer resistance beyond a speed of 500 rpm. To be on safer side, further experiments were conducted at 800 rpm.

3.3. Effect of catalyst loading

Three distinct phases appeared when 3.1×10^{-4} mol/cm^3 of TBAB was added in aqueous layer saturated with 0.0032 mol/cm^3 of NaCl. The concentration of catalyst (TBAB) was varied from 3.1×10^{-4} to 6.2×10^{-4} mol/cm^3, keeping all other parameters constant under L–L–L PTC. The conversion is plotted against time for different concentrations of catalyst (Fig. 2). It was observed

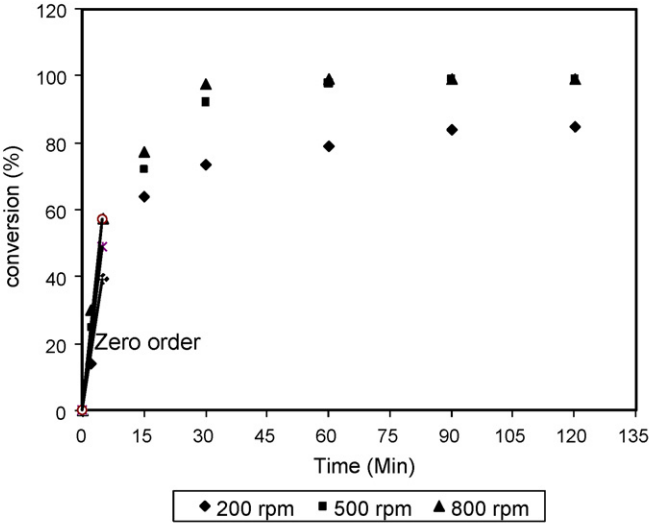


Fig. 1. Effect of speed of agitation on conversion of methyl mandelate. Methyl mandelate 0.03 mol, TBAB 0.0046 mol, sodium chloride 0.05 mol, sodium hypochlorite, 0.03 mol, temperature, 45 °C.

that as the concentration of the catalyst is increased up to 5.59×10^{-4} mol/cm^3, the conversion increased, beyond which there was no substantial increase. It appears that the reaction becomes mass transfer resistance limited. The rates of reaction are dramatically increased by orders of magnitude and almost complete conversions within short time could be realized, when a two-phase system (below 3.1×10^{-4} mol/cm^3) is converted into a three-phase system. Besides, there was 100% selectivity to desired product. This shows that the locale of the reaction is the middle catalyst-rich or the third phase.

Not only higher conversions were obtained due to more amount of catalyst present but also intensification of the rate had occurred. There was a total suppression of side reactions leading to 100% selectivity of the product. The linearity of concentration with time up to 60% conversion suggests a zero order kinetics which proves the validity of the kinetic model discussed before.

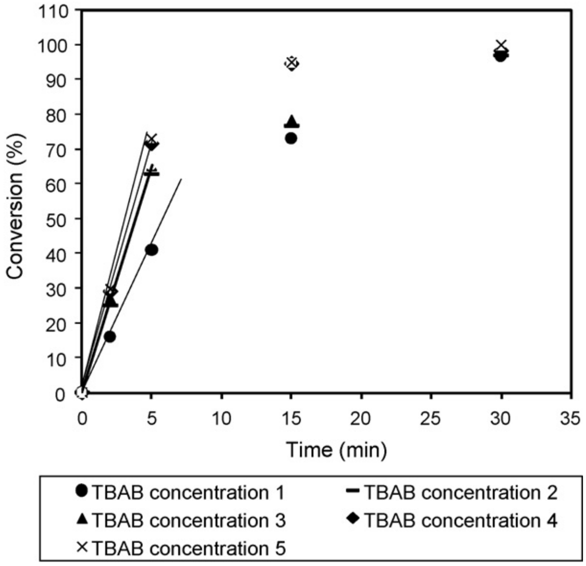


Fig. 2. Effect of catalyst loading on conversion of methyl mandelate. TBAB concentration 1 = 3.11×10^{-4} mol/cm^3, TBAB concentration 2 = 3.73×10^{-4} mol/cm^3, TBAB concentration 3 = 4.66×10^{-4} mol/cm^3, TBAB concentration 4 = 5.59×10^{-4} mol/cm^3, TBAB concentration 5 = 6.21×10^{-4} mol/cm^3. Methyl mandelate, 0.03 mol; sodium chloride, 0.05 mol; sodium hypochlorite, 0.03 mol; temperature, 45 °C; speed of agitation 800 rpm.

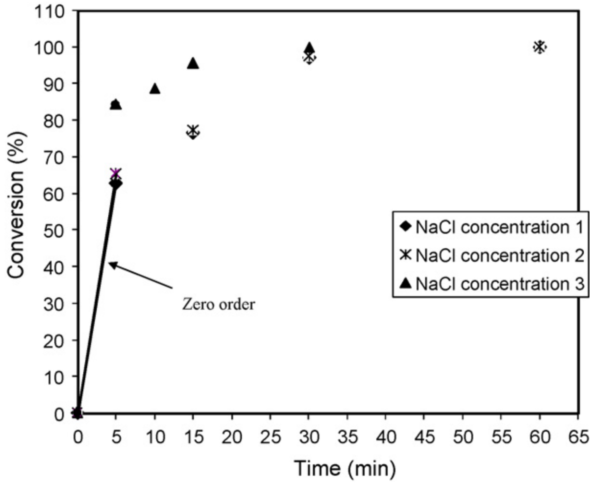


Fig. 3. Effect of sodium chloride concentration on conversion of methyl mandelate. NaCl concentration 1 = 6.25×10^{-3} mol/cm^3, NaCl concentration 2 = 5×10^{-3} mol/cm^3, NaCl concentration 3 = 3.75×10^{-3} mol/cm^3. Methyl mandelate, 0.03 mol; TBAB, 4.66×10^{-3} mol; sodium hypochlorite, 0.03 mol; temperature, 45 °C; speed of agitation 800 rpm.

3.4. *Effect of sodium chloride concentration*

The concentration of sodium chloride loading was varied from 0.037 to 0.062 mol under similar reaction conditions. As the concentration of sodium chloride was increased, the rate of the reaction increased (Fig. 3). There is a greater concentration of $[Q^{+}ClO^{-}]$ which gets immediately extracted. When the concentration of sodium chloride is very less, the volume of third phase is also less because the aqueous phase is not saturated with sodium chloride and there is no salting out of TBAB. But as the concentration of sodium chloride is increased aqueous phase becomes saturated and more and more amount of catalyst is pushed into the catalyst phase. After saturation concentration addition of NaCl has no significant effect on the rate of reaction. This is in consonance with the theory.

3.5. *Effect of mole ratio sodium hypochlorite to methyl mandelate*

Effect of mol ratio of sodium hypochlorite to methyl mandelate was studied in the range of 1:0.7–1:3. Fig. 4 shows the conversion of methyl mandelate as a function of time. With an increase in the mol ratio, the initial rate was observed to increase. It was also observed that beyond a certain limit there was no effect of increased concentration of sodium hypochlorite on reaction rate since the reaction becomes zero order as will be discussed in the following section. At 1:2, excess of methyl mandelate was available than required hence the concentration of quaternary methyl mandelate ion-pair was constant at all times in comparison with other two cases. This also proves that the model is valid.

3.6. *Effect of temperature*

To study this effect reactions were carried out in the range of 20–55 °C. It was observed that at lower temperature reaction rate was slow. Reaction rate was intensified with increase in the temperature from 20 to 50 °C (Fig. 5). There was no increase in rate when the temperature was further raised to 55 °C. This also suggests that there is a mass transfer limitation.

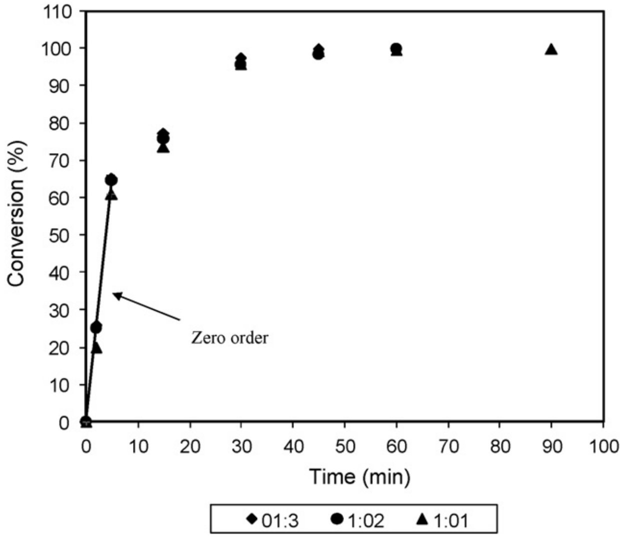


Fig. 4. Effect of mol ratio on conversion of methyl mandelate. Mole ratio, methyl mandelate: sodium hypochlorite; TBAB, 4.66×10^{-3} mol; sodium chloride, 0.05 mol; temperature, 45 °C; speed of agitation, 800 rpm.

3.7. L–L–L PTC kinetics

The determination of equilibrium constants in a reacting system is difficult. And therefore an order of magnitude estimate can be done. The creation of three phases in the absence of reaction requires a totally non-reacting equivalent system. This is also then an approximation. It could be done having two-phase systems each involving middle phase-organic phase and middle phase-aqueous phase systems. Since equilibrium constants in such case would depend on ionic strength, it creates further complications. Therefore it was not tried.

For a control experiment, both zero order and first order kinetic plots are given in Figs. 6 and 7. These data fit very well. The zero order behavior for which conversion is linear with time is shown by straight lines for initial periods in Fig. 1 (for 500 and 800 rpm), Fig. 2 (for 4.66×10^{-4} mol/cm^3 of TBAB), Fig. 3 (for 5×10^{-3} mol/cm^3 of NaCl), Fig. 4 (for 1:1 mole ratio of methyl mandelate: sodium hypochlorite), and Fig. 5 (all temperatures). The zero order rate constants were used to make the Arrhenius plot (Fig. 8) from which the apparent activation energy of 7.84 kcal/mol is obtained.

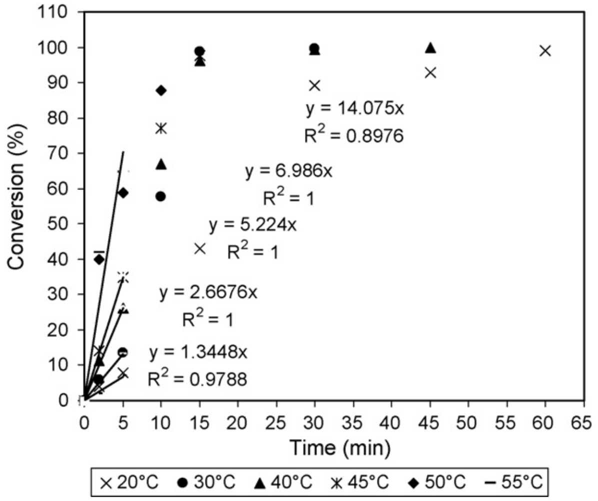


Fig. 5. Effect of temperature on conversion of methyl mandelate. Methyl mandelate, 0.03 mol; TBAB, 4.66×10^{-3} mol; sodium chloride, 0.05 mol; sodium hypochlorite, 0.06 mol; speed of agitation, 800 rpm.

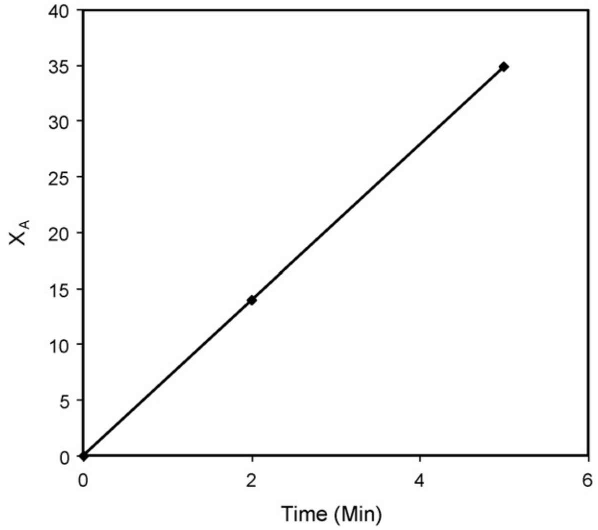


Fig. 6. L–L–L PTC zero order kinetics upto 5 min. Methyl mandelate, 0.03 mol; TBAB, 4.66×10^{-3} mol; sodium chloride, 0.05 mol; sodium hypochlorite, 0.06 mol; speed of agitation, 800 rpm, temperature, 45 °C.

3.8. Reusability study

After completion of the kinetic run, the stirring was stopped and the reaction mixture was cooled. The third phase was separated and reused by adding fresh aqueous and organic phase reactants. In this method the third phase was used three times starting with the fresh use. There is a distribution of catalyst in catalyst-rich third phase and organic phase and the aqueous phase. Since both the aqueous and organic phases were freshly used, there was some loss of the catalyst with discarded organic and aqueous phases. Therefore, there is once again distribution of catalyst available from the third phase to the organic phase which reduces the volume of the third phase and hence the rates of reaction. The

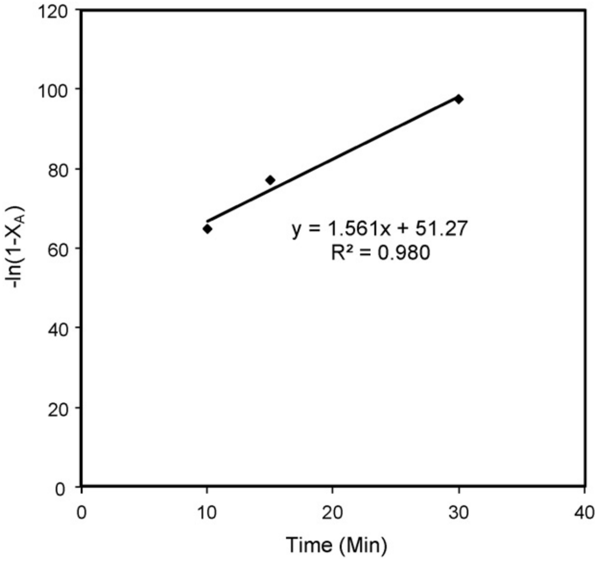


Fig. 7. L–L–L PTC first order kinetics after 5 min. Methyl mandelate, 0.03 mol; TBAB, 4.66×10^{-3} mol;, sodium chloride, 0.05 mol; sodium hypochlorite, 0.06 mol; speed of agitation, 800 rpm, temperature, 45 °C.

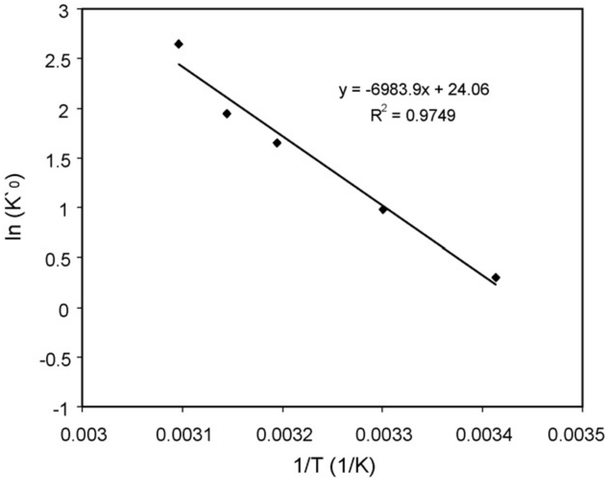


Fig. 8. Arrhenius plot for oxidation of methyl mandelate under L–L–L PTC. Methyl mandelate, 0.03 mol; TBAB, 4.66×10^{-3} mol; sodium chloride, 0.05 mol; sodium hypochlorite, 0.06 mol; speed of agitation, 800 rpm.

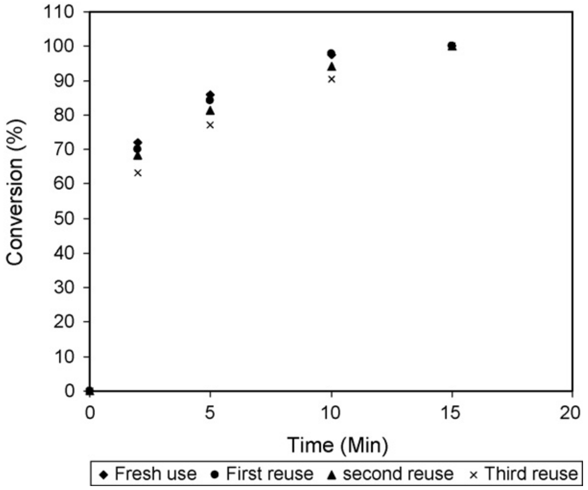


Fig. 9. Catalyst reusability study. Methyl mandelate, 0.03 mol; TBAB, 4.66×10^{-3} mol; sodium chloride, 0.05 mol; sodium hypochlorite, 0.06 mol; speed of agitation, 800 rpm, temperature, 45 °C.

subsequent experiments with replenished aqueous and organic phases had in fact less quantity of available catalyst than previous run and hence rates of reaction had decreased correspondingly (Fig. 9).

4. Conclusion

In this work, the novelties of liquid–liquid–liquid phase transfer catalysis in the oxidation of methyl mandelate to methyl phenyl glyoxylate under milder conditions have been brought out using sodium hypochlorite, thereby eliminating the need for expensive metallic catalysts, high temperatures and extreme pressures. The combination of high yields and 100% selectivity with low cost and ease of product isolation makes this method economically attractive. Conversion and selectivity have been shown to be high in comparison to established oxidation processes. A mechanistic model has also been proposed. Effects of different parameters such as speed of agitation, temperature, catalyst loading, reusability of catalyst-rich phase, salt concentration and mole ratio have been studied to arrive at the reaction kinetics. The amount of catalyst, sodium chloride and sodium hypochlorite are important factors, which influence the formation of the third-liquid (catalyst-rich) phase and distribution of catalyst.

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