Novelties of kinetics of chemoselective reduction of citronellal to citronellol by sodium borohydride under liquid–liquid phase transfer catalysis

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Abstract

Borohydride reductions, although common, have not been studied from kinetic and mechanistic view points due to complex chemistry and more so, there is no report on kinetics and mechanism of such reductions under phase transfer catalysis. The novelties of phase transfer catalysed chemoselective reduction of citronellal to citronellol using sodium borohydride were studied in detail in liquid–liquid phase transfer catalysis using tetrabutylammonium bromide (TBAB), tetrapropylammonium bromide (TPAB), tetraethyl ammonium bromide (TEAB) and tetrabutylammonium hydrogen sulfate (TBAHS). TBAB was the best catalyst at 30 °C. Citronellol is very extensively used in a number of perfume compositions. The effects of different parameters such as speed of agitation, phase volume ratio, catalyst concentration, sodium borohydride concentration, citronellal concentration and temperature have been studied. The reaction was found to be 100% selective towards the formation of the desired product. The kinetics and mechanism are presented to account for the effects of various parameters on conversion and rates. It was possible to establish both rate constant and distribution constant from the same set of data. The results are novel.
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1. Introduction

Many organic reactions in pharmaceutical, agrochemical, perfumery and flavor industries involve molecules containing multifunctional groups in which selective reduction of only one group is desired. The nature of the reducing agent obviously affects the selectivity of such reductions depending on the complexity of the molecule and number of phases involved in the process. Selective hydrogenation of unsaturated aldehydes to alcohols poses challenges; for instance, citronellal hydrogenation to citronellol is such an example [1,2]. Citronellal (3,7-dimethyl-6-octen-l-al) is a precursor for the preparation of several fine chemicals. Synthesis of citronellol (3,7-dimethyl-6-octen-l-ol) from citronellal is very widely studied due to its use as a low cost and rosy fragrance in many formulations and soaps [3–5]. A lot of work has been done on the hydrogenation of citronellal using monometallic, bimetallic and multimetallic supported catalysts. However, these heterogeneous catalysts do not lead to 100% selectivity to citronellol and the selectivity is affected greatly by the nature of catalyst, type of support, solvent, temperature and pressure. Besides, these processes are beset with cumbersome separation problems. Biotechnological routes for preparation of citronellol from citrenellal including using free and immobilized *Rhodotorula minuta* [6], and baker's yeast [7] are also explored but are of limited commercial utility.

Borohydrides are very routinely used for selective reduction in preparatory synthesis and also on commercial scale in fine chemical industries. Water, alcohol or aqueous alkali are used in conjunction with borohydride to improve selectivity [8–12]. Reduction of aldehydes, ketones, acyloins, α-diketones and conjugated enones to corresponding alcohols has been studied using $NaBH_4$, $NaBH_4$–$MoCl_5$, [13] $NaBH_4$–$lnCl_3$ [14], sulfurated barium borohydride [$Ba(BH_2S_3)_2$] in dry THF [15], organosamarium(III)hydride [16], potassium borohydride [17], bis(triphenylphosphine) (tetrahydroborato) zinc complex [18], methyl triphenylphosphonium tetrahydrobo-

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rate [19], polymethylhydrosiloxane with metal hydride, [20] polyvinylpyridine chloroaluminum borohydride [21] and cross-linked polyvinylpyridine supported zinc borohydride [22]. Among these, sodium borohydride is found to be highly efficient and selective under mild conditions [8–12]. The use of quaternary ammonium borohydrides as stoichiometric agents was also reported as highly efficient and selective [23]. Like borohydrides, phase transfer catalysed sulfide reduction is also industrially relevant in liquid–liquid, liquid–liquid–liquid, solid–(ω)liquid–liquid and liquid–liquid–solid PTC is reported [24–28]. The rates of biphasic borohydride reductions can be intensified elegantly using phase transfer catalysis (PTC) [29,30]. The usefulness of dilute aqueous sodium borohydride as a reducing agent in L–L PTC has been highlighted in a number of reactions practised in fine chemical industry [31,32]. However, the mechanism and kinetics of the borohydride reduction of carbonyl compounds under PTC have not appeared so far. The genesis of the current work lies in these lacunae. Citronellal was taken as a model compound apart from its commercial significance.

2. Experimental

2.1. Chemicals and catalysts

Citronellal, sodium borohydride, toluene, all of AR grade were obtained from M/s E (Merck) India Ltd. Tetrabutylammonium bromide (TBAB), tetrapropylammonium bromide (TPAB), tetraethylammonium bromide (TEAB) and tetrabutylammonium hydrogen sulfate (TBAHS), of pure grade were procured as gift samples from M/s. Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India. All other chemicals were of analytical reagents obtained from M/s s.d. Fine Chemicals Pvt. Ltd. Mumbai.

2.2. Experimental procedure

The experimental set-up consisted of a 4 cm i.d. fully baffled mechanically agitated reactor of 50 ml capacity, equipped with four baffles and a six-bladed turbine impeller. The entire reactor assembly was immersed in a thermostatic water bath, which was maintained at the desired temperature with an accuracy of $\pm 1\,^\circ C$. Typical biphasic runs were conducted by taking 2.5×10^{-3} mol citronellal in 10 ml toluene to create the organic phase. The aqueous phase comprised of 2.5×10^{-3} mol sodium borohydride and 1.5×10^{-3} mol sodium hydroxide in 10 ml water. Both the organic and aqueous phases were added in the reactor and appropriate quantity of the catalyst was then added. All control reactions were carried out at $30\,^\circ C$ and 1200 rpm. Clear liquid samples were withdrawn periodically over 2 h for analysis.

2.3. Analysis and isolation of product

Samples were analysed by GC (Chemito Model 8610). A stainless steel column (3.25 mm × 2 m) packed with a liquid stationary phase of 10% SE-30 and a FID were used for analysis. The quantification was done by calibration using synthetic
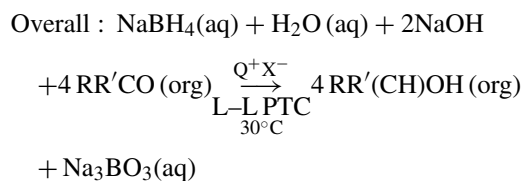
mixtures. Initial rates of reactions were also evaluated from the disappearance of the limiting reactant. Typical reaction time was 2 h. At the end of the reaction, the organic phase was washed with copious quantities of water to remove any traces of catalyst, sodium borohydride and the organic phase was distilled under vacuum to get a pure product. It was also confirmed by GC–MS and IR. Only a single product was formed. Following is the overall reaction:
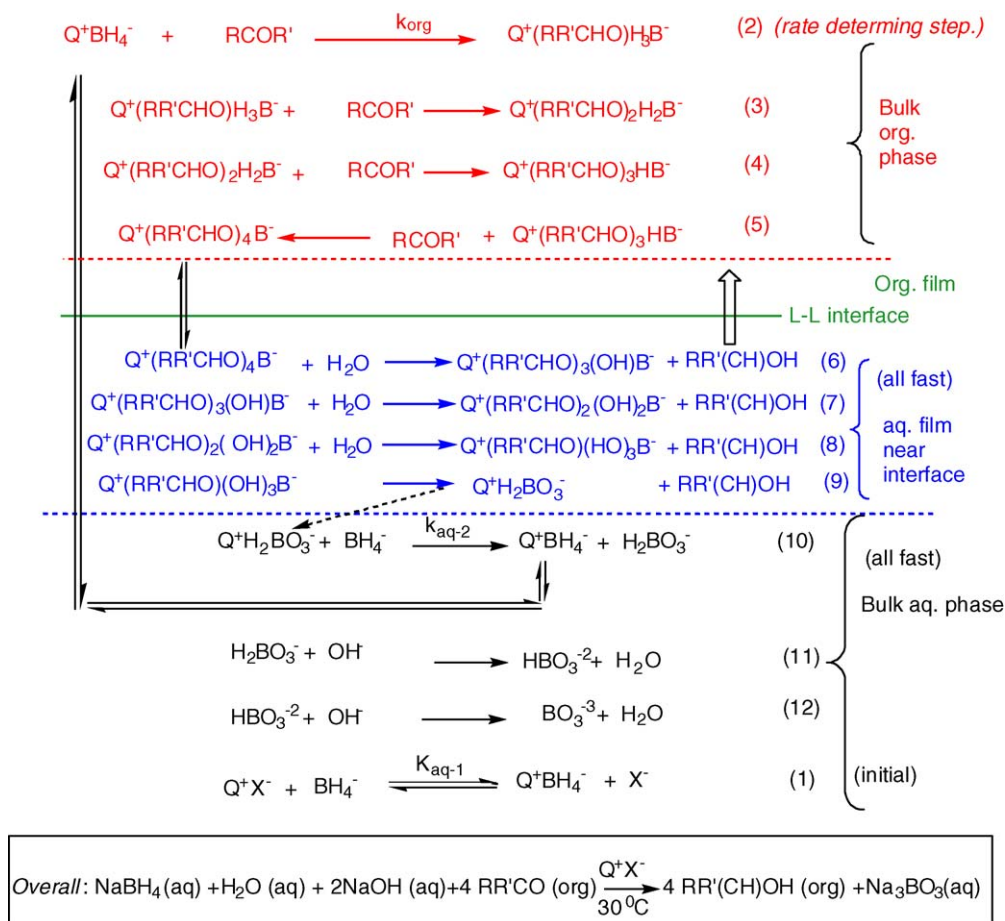

Citronellal   Citronellol
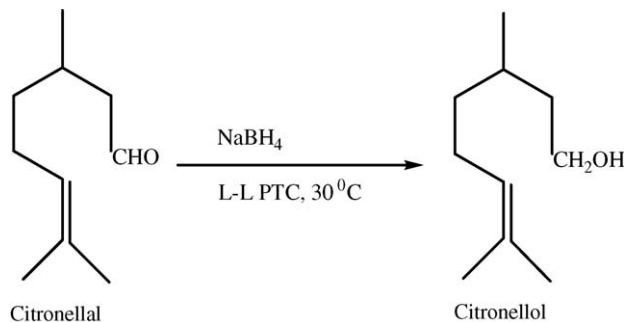
3. Results and discussion

3.1. Mechanism of L–L PTC reduction

The reaction of borohydride ion with aldehyde or ketones in aqueous or alcoholic solution is considered to proceed stepwise with successive replacement of each of the four hydride with alkoxide groups generated by reduction of carbonyl compound [23]. In the case of borohydrides used as reducing agents, it is essential to add water or alkali at the end of the reaction to complete the final step which breaks that ion-pair to liberate the product. With L–L PTC, using aqueous phase containing sodium borohydride and organic phase containing the carbonyl compound, the overall stoichiometry is as follows.

Overall : $NaBH_4(aq) + H_2O(aq) + 2NaOH$

$$+ 4\,RR'CO\,(org) \underset{\substack{L-L\,PTC \\ 30\,^\circ C}}{\overset{Q^+X^-}{\longrightarrow}} 4\,RR'(CH)OH\,(org)$$

$$+ Na_3BO_3(aq)$$

The borohydride reduction presents an interesting case of L–L PTC, which is rather uncommon. The stoichiometry of the above reaction suggests a complex mechanism. Raber and Guida [23] used tetrabutylammonium borohydride in dichloromethane as the reagent in the reduction of a variety of ketones and aldehydes at room temperature in the absence of protic solvents. It was the subsequent addition of water to the reaction medium which led to formation of the product. The selectivity was similar to that exhibited by sodium borohydride in aqueous or alcoholic media. However, the literature is silent about exact details of mechanism. Their studies show that although four molecules of substrate are reduced by each mole of borohydride, the reaction is first order in the substrate, indicating a stepwise reduction in a homogeneous reaction and therefore the first step should be rate determining even in a heterogeneous biphasic reaction. Thus, Scheme 1 is proposed and discussed. It is obvious that step (2)

$$Q^+BH_4^- \;+\; RCOR' \xrightarrow{\;k_{org}\;} Q^+(RR'CHO)H_3B^- \qquad (2)\ (rate\ determing\ step.)$$

$$Q^+(RR'CHO)H_3B^- \;+\; RCOR' \longrightarrow Q^+(RR'CHO)_2H_2B^- \qquad (3)$$

$$Q^+(RR'CHO)_2H_2B^- \;+\; RCOR' \longrightarrow Q^+(RR'CHO)_3HB^- \qquad (4)$$

$$Q^+(RR'CHO)_4B^- \longleftarrow RCOR' \;+\; Q^+(RR'CHO)_3HB^- \qquad (5)$$

Bulk org. phase

---- Org. film

L-L interface

$$Q^+(RR'CHO)_4B^- \;+\; H_2O \longrightarrow Q^+(RR'CHO)_3(OH)B^- \;+\; RR'(CH)OH \qquad (6)$$

$$Q^+(RR'CHO)_3(OH)B^- \;+\; H_2O \longrightarrow Q^+(RR'CHO)_2(OH)_2B^- \;+\; RR'(CH)OH \qquad (7)$$

$$Q^+(RR'CHO)_2(OH)_2B^- \;+\; H_2O \longrightarrow Q^+(RR'CHO)(HO)_3B^- \;+\; RR'(CH)OH \qquad (8)$$

$$Q^+(RR'CHO)(OH)_3B^- \longrightarrow Q^+H_2BO_3^- \;+\; RR'(CH)OH \qquad (9)$$

(all fast) aq. film near interface

$$Q^+H_2BO_3^- + BH_4^- \xrightarrow{\;k_{aq-2}\;} Q^+BH_4^- + H_2BO_3^- \qquad (10)$$

(all fast) Bulk aq. phase

$$H_2BO_3^- + OH^- \longrightarrow HBO_3^{-2} + H_2O \qquad (11)$$

$$HBO_3^{-2} + OH^- \longrightarrow BO_3^{-3} + H_2O \qquad (12)$$

$$Q^+X^- \;+\; BH_4^- \underset{\;K_{aq-1}\;}{\rightleftharpoons} Q^+BH_4^- \;+\; X^- \qquad (1)$$ (initial)

$$Overall:\ NaBH_4\,(aq) + H_2O\,(aq) + 2NaOH\,(aq) + 4\,RR'CO\,(org) \xrightarrow[30\,^0C]{Q^+X^-} 4\,RR'(CH)OH\,(org) + Na_3BO_3\,(aq)$$

Scheme 1. Reaction mechanism for PTC catalysed borohydride reduction of carbonyl compounds.

in Scheme 1 is the rate determining step (RDS) and controls the overall rate of reaction.

It is clear that as shown by step (1) in aqueous phase in Scheme 1, in the beginning of the reaction, there is an in situ generation quaternary ammonium borohydride ion-pair, $[Q^+BH_4^-]_{aq}$, by the reaction of quaternary ammonium salt $[Q^+X^-]_{aq}$ and sodium borohydride. $[Q^+BH_4^-]_{aq}$ formed in the aqueous phase is transferred to the organic phase where it reacts with one mole of aldehyde leading to the formation of $[Q(RR'CHO)H_3B]_{org}$. This step is slow and rate determining (step 2). This ion-pair $[Q^+(RR'CHO)H_3B^-]_{org}$ subsequently reacts with another molecule of the substrate and forms ultimately a complex $[Q^+(RR'CHO)_4B^-]_{org}$ through steps 2–5 which are fast steps. $[Q^+(RR'CHO)_4B^-]_{org}$ formed in step 5 is transferred from organic phase to aqueous phase across the interface and this complex is broken due to its consecutive reaction with water in aqueous phase to give the desired alcohol through steps 6–9 in the aqueous film in the vicinity of interface. The alcohol formed in aqueous phase is transferred to organic phase. Here also steps 6–9 are very fast. Step 10 in aqueous phase shows that the salt $[Q^+H_2BO_3^-]_{aq}$ exchanges the anion with $[BH_4^-]_{aq}$ which is available in large excess to form ion-pair, $[Q^+BH_4^-]_{aq}$, which is transferred to the organic phase and the catalytic cycle is completed. The $H_2BO_3^-$ in the aqueous phase is neutralized successively with OH^- ions as shown in steps 11 and 12 to give

the borate BO_3^{-3} species due to the alkaline pH of the aqueous phase. Since steps 11 and 12 are fast and irreversible, the formation of $[Q^+BH_4^-]_{aq}$ by step 10 is irreversible and all quaternary cation Q^+ in the aqueous phase is associated with BH_4^-.

If V_{org} and V_{aq} are the volumes of organic and aqueous phases, and N_Q is the quantity of catalyst added initially to the reaction mixture, it is distributed in the organic phase in moles and the following material balance is valid.

$$[Q^+BH_4^-]_{org} V_{org} + [Q^+BH_4^-]_{aq} = N_Q \qquad (1)$$

Let $K_{BH_4} = \dfrac{[Q^+BH_4^-]_{org}}{[Q^+BH_4^-]_{aq}} =$ the distribution constant for $[Q^+BH_4^-]$ between organic and aqueous phases.

$$[Q^+BH_4^-]_{org} V_{org} = N_Q - [Q^+BH_4^-]_{aq} V_{aq}$$

$$= N_Q - \frac{[Q^+BH_4^-]_{org} V_{aq}}{K_{BH_4}} \qquad (2)$$

Which on simplification leads to the following:

$$[Q^+BH_4^-]_{org} = \frac{N_Q}{V_{org}(1 + (V_{aq}/K_{BH_4}V_{org}))}$$

$$= \frac{[Q_{tot}]_{org}}{(1 + (\beta/K_{BH_4}))} \qquad (3)$$

where, $[Q_{tot}]_{org} = \frac{N_Q}{V_{org}}$ is the concentration of the total catalyst added to the organic phase at time $t = 0 =$ phase volume ratio.

The rate of reduction of RCOR′ is given by the following equation, when step 2 is the rate determining step.

$$\frac{-d[RCOR']_{org}}{dt} = k_{org}[RCOR']_{org}[Q^+BH_4^-]_{org}$$
$$= k_{org}[RCOR']_{org}\frac{[Q_{tot}]_{org}}{(1 + \beta/K_{BH_4})} \quad (4)$$

Let:

$$A = RCOR'$$
$$X_A = \frac{N_{A_0} - N_A}{N_{A_0}} = \frac{[A_0]_{org} - [A]_{org}}{[A_0]_{org}} \quad (5)$$

X_A is the fractional conversion of A based on initial moles of A_o in the organic phase and if the reaction occurs.

$$-\ln(1 - X_A) = k_{org}\frac{[Q_{tot}]_{org}t}{(1 + (\beta/K_{BH_4}))} \quad (6)$$

Thus, a plot of $-\ln(1 - X_A)$ against t will be a straight line with a slope of $\alpha = k_{org}([Q_{tot}]_{org}/(1 + \beta/K_{BH_4}))$ If $[Q_{tot}]_{org}$ and/or β are changed to change values of α, it is possible to get both rate constant and equilibrium constant from the same set of data.

3.2. Efficiency of various catalysts

Various phase transfer catalysts like TBAB, TPAB, TEAB and TBAHS were examined to evaluate their performance. The conversion varied markedly with the type of catalyst due to different distribution constant K_{BH_4} of the ion-pairs in the presence of the catalyst in the organic phase, which in turn can be attributed to the nature of quaternary salt. Among these, TPAB and TEAB showed very less activity, which was far less as compared to both TBAB and TBAHS (Fig. 1). TBAB was found as the best catalyst and used for further studies.

3.3. Effect of speed of agitation

Since the reaction mechanism involves complex steps, it was essential to ascertain the influence of mass transfer resistance for the transfer of ion-pairs across the interface. The speed of agitation was varied in the range of 800–1500 rpm under otherwise similar conditions (Fig. 2). From 800 to 1200 rpm, there was an increase in the rate of reaction and final conversion. There was no further increase in the conversion of reactant when the speed was further increased from 1200 to 1500 rpm. In order to ensure that the reaction is kinetically controlled, all subsequent experiments were carried out at a speed of 1200 rpm.

Scheme 1 suggests that the reaction of the Q (RR′CHO)$_4$B$^-$ species with water (step 6) must occur in the aqueous film near the interface, followed by the next three steps 7 to 9 to liberate the alcohol, which has no solubility in the aqueous phase. The alcohol is transferred back into the organic phase. In this case, aqueous alkali was used to enhance this transfer and neutralization of H$_2$BO$_3^-$ with OH$^-$ as BO$_3^{3-}$ (steps 11 and 12)
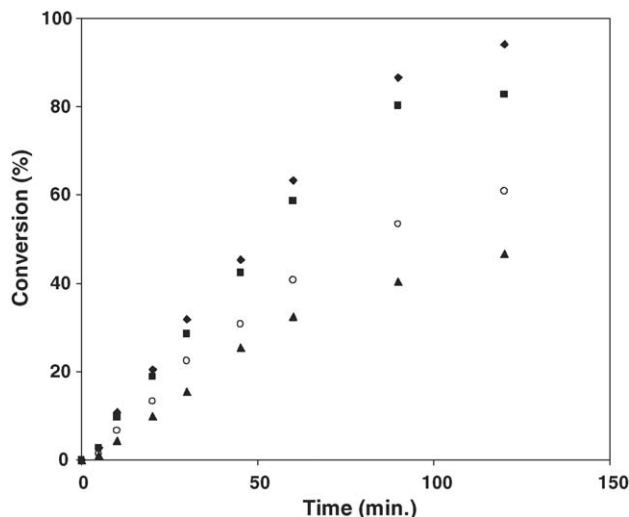

Fig. 1. Effect of different catalysts. Citronellal 2.5×10^{-3} mol; sodium borohydride 2.5×10^{-3} mol; PTC 2.5×10^{-4} mol; sodium hydroxide 1.5×10^{-3} mol; water 10 cm^3; toluene 10 cm^3; speed of agitation 1200 rpm; temperature 300C. ((♦) TBAB, (■) ETPB, (▲) TEAB, (○) TPAB).

which are irreversible reactions. All further experiments were done above 1200 rpm.

3.4. Effect of aqueous to organic phase volume ratio (β)

Effect of phase volume ratio was studied for 0.5:1 1:1, 1:0.5 ratios of aqueous to organic phase volume under otherwise similar experimental conditions. The moles of all reactants and catalyst added were kept constant (Fig. 3). The theory was validated by using these data for different values of phase volume ratio β (Fig. 4). There is an excellent fit. Table 1 values give pertinent data.
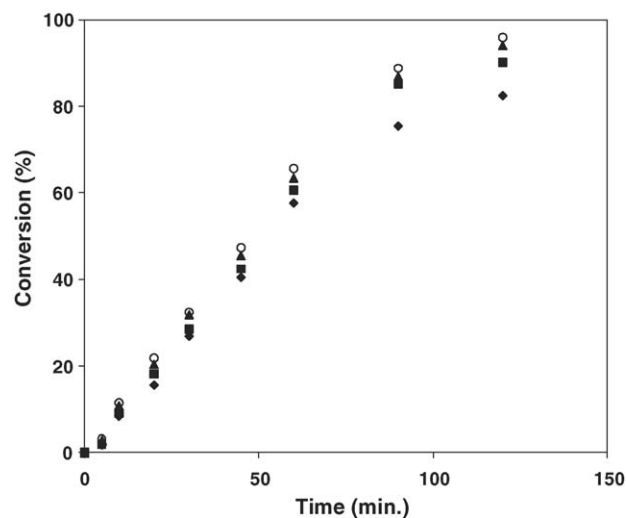

Fig. 2. Effect of speed of agitation. Citronellal 2.5×10^{-3} mol; sodium borohydride 2.5×10^{-3} mol; TBAB 2.5×10^{-4} mol; sodium hydroxide 1.5×10^{-3} mol; water 10 cm^3; toluene 10 cm^3, temperature 30 °C. ((♦) 800 rpm, (■) 1000 rpm, (▲) 1200 rpm, (○) 1500 rpm).
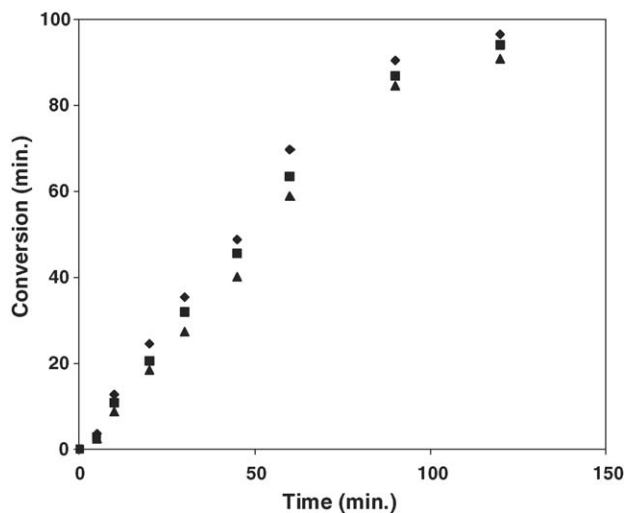
Fig. 3. Effect of aqueous to organic phase volume ratio. Citronellal 2.5×10^{-3} mol; sodium borohydride 2.5×10^{-3} mol; TBAB 2.5×10^{-4} mol; sodium hydroxide 1.5×10^{-3} mol; water 10 cm³; toluene 10 cm³; speed of agitation 1200 rpm; temperature 30 °C. ((♦) 0.5:1, (■) 1:1, (▲) 1:0.5).
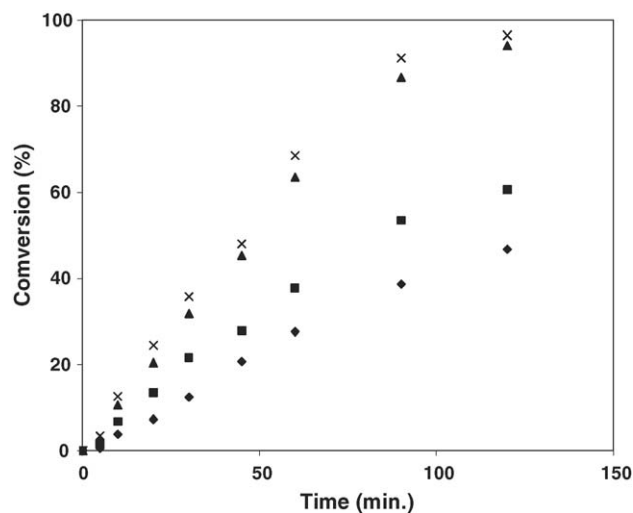

Fig. 5. Effect of catalyst loading. Citronellal 2.5×10^{-3} mol; sodium borohydride 2.5×10^{-3} mol; sodium hydroxide 1.5×10^{-3} mol; water 10 cm³; toluene 10 cm³; speed of agitation 1200 rpm; temperature 30 °C. ((♦) 1×10^{-4} mol, (■) 1.5×10^{-4} mol, (▲) 2.5×10^{-4} mol, (○) 3×10^{-4} mol).

So, further experiments were conducted by using equal volumes of both phases.

3.5. Effect of catalysts quantity

The effect of catalysts quantity was studied from 1×10^{-4} to 3×10^{-4} mol under otherwise similar conditions (Fig. 5). The initial rate of reaction increased with increasing concentration of the catalyst. The model was tested by invoking Eq. (6) and the various values of slopes α were obtained and plotted against $[Q_{tot}]$ (Fig. 6). It is a straight line passing through origin. This also shows that the rate of reaction is linearly proportional to catalyst concentration.

3.6. Effect of sodium borohydride

Different moles sodium borohydride were used in the range of 1×10^{-3} to 5×10^{-3} mol, holding constant the amounts
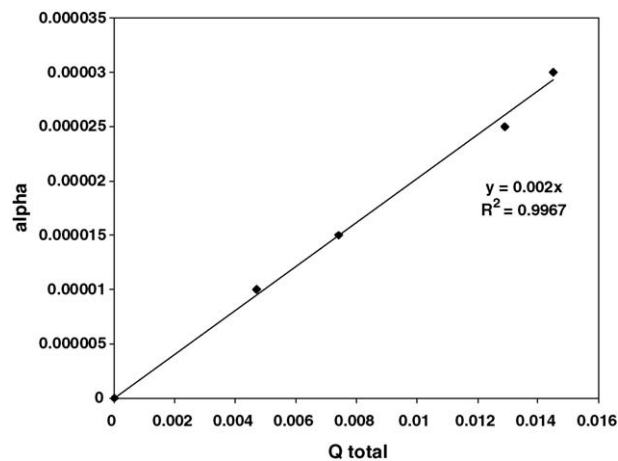

Fig. 4. Model validation—evaluation of rate constant. ((♦) 0.5:1, (■) 1:1, (▲) 1:0.5).

Thus, it was possible to obtain both k_{org} and K_{BH_4} as 11.21 cm³ mol⁻¹ s⁻¹ and 3.294, respectively. The measurements of distribution constant for the borohydride ion-pair between toluene and aqueous phase lies in the same range. The following order is observed for the conversion values as 0.5:1 > 1:1 > 1:0.5. But there was no much significant change in the rate when aqueous to organic phase ratio were 0.5:1 and 1:1.

Table 1
Estimation of rate constant and distribution constant from kinetic experiments

No.	V_{aq} (cm³)	V_{org} (cm³)	β	Slope = α (min⁻¹)	N_Q (mol)	$[Q_{tot}]$ (mol/cm³)
1	5	10	0.5	0.0146	2.5×10^{-4}	2.5×10^{-5}
2	10	10	1	0.0129	2.5×10^{-4}	2.5×10^{-5}
3	10	5	2	0.011	2.5×10^{-4}	5.0×10^{-5}

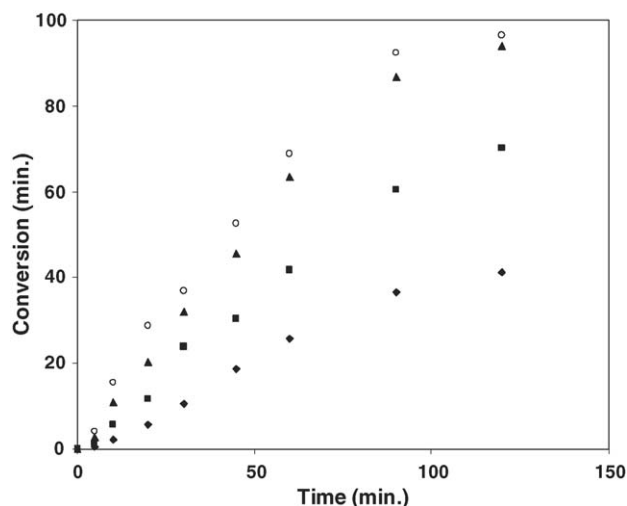Fig. 6. Model validation for different catalyst loading—plot of slope against $[Q_{tot}]$.

Fig. 7. Effect of sodium borohydride. Citronellal 2.5×10^{-3} mol; TBAB 2.5×10^{-4} mol; sodium hydroxide 1.5×10^{-3} mol; water $10\,cm^3$; toluene $10\,cm^3$; speed of agitation 1200 rpm; temperature 30 °C. ((♦) 1×10^{-3} mol, (■) 1.5×10^{-3} mol, (▲) 2.5×10^{-3} mol, (○) 5×10^{-3} mol).
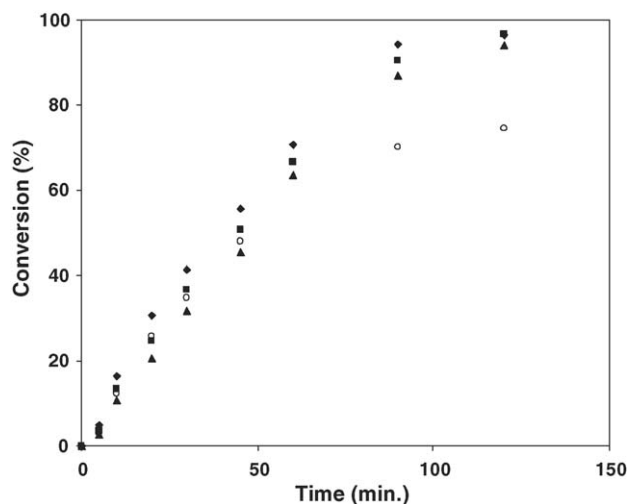

Fig. 8. Effect of concentration of citronellal. Sodium borohydride 2.5×10^{-3} mol; TBAB 2.5×10^{-4} mol; sodium hydroxide 1.5×10^{-3} mol; water $10\,cm^3$; toluene $10\,cm^3$; speed of agitation 1200 rpm; temperature 30 °C. ((♦) 1×10^{-3} mol, (■) 1.5×10^{-3} mol, (▲) 2.5×10^{-3} mol, (○) 5×10^{-3} mol).

of following components of the reaction mixture: citronellal (2.5×10^{-3} mol), and TBAB (2.5×10^{-4} mol). It was found that increasing the concentration of sodium borohydride increases the rate of reaction and conversion (Fig. 7). The formation of $[Q^+BH_4{}^-]_{aq}$ occurs by step 10 in the catalytic cycle and when the concentration of sodium borohydride is very high, this reaction leads to maximum formation of $[Q^+BH_4{}^-]_{aq}$ which is then extracted in organic phase. Normally this step 7 is an equilibrium step, being anion exchange, and when the amount of borohydride is doubled to 5×10^{-3} from the standard 2.5×10^{-3} mol, the conversions are little higher. Step 10 could be reversible to an extent at lower amounts below 2.5×10^{-3} mol, which is the amount of borohydride initially which was thrice that required stoichiometrically in control experiments.

3.7. Effect of concentration of citronellal

The effect of citronellal was studied in the range of 1×10^{-3} to 5×10^{-3} mol. It was observed that as the concentration increases the rate as well as conversion increases. However, for 5×10^{-3} mol, the rate of reaction decreased due to less availability of hydride ion (Fig. 8). The initial rate of reaction is linear in the concentration of the substrate in organic phase and not to the fourth power which could have been the case, according to the stoichiometry of the reaction. This also validates the fact that the rate determining step is step 2 in organic phase (Scheme 1). Thus, the model was once again validated and figure is not shown for sake of brevity.

3.8. Effect of sodium hydroxide

The effect of sodium hydroxide concentration was studied by changing the amount from 0.001 to 0.002 mol. It was observed that as the concentration increased, there was a slight change in the rate of the reaction (Fig. 9). Stoichiometrically, 2 mol of

NaOH are required per mole of aldehyde and basic medium is required to complete steps 11 and 12. Thus, quantity of NaOH required was always kept more than this in the current study.

3.9. Effect of temperature

To study the effect of temperature, experiments were carried out at 20, 30, 35 and 45 °C (Fig. 10). Beyond 35 °C, the rate of the reaction and conversion were found to decrease because of the decomposition of sodium borohydride with increasing temperature. Thus, 30 °C was found an optimum temperature.
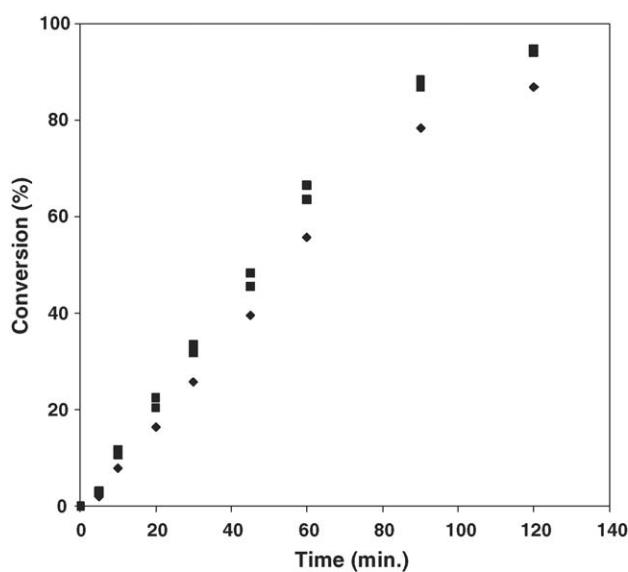

Fig. 9. Effect of sodium hydroxide. Citronellal 2.5×10^{-3} mol; sodium borohydride 2.5×10^{-3} mol; TBAB 2.5×10^{-4} mol; water $10\,cm^3$; toluene $10\,cm^3$; speed of agitation 1200 rpm; temperature 30 °C. ((♦) 0.001 mol, (■) 0.0015 mol, (▲) 0.002 mol).
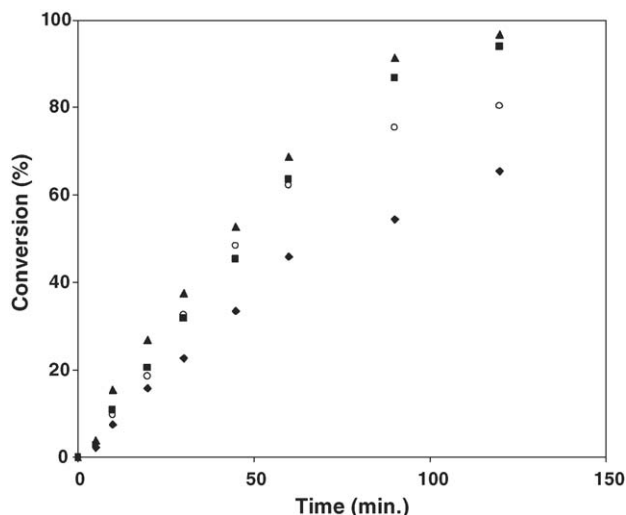
Fig. 10. Effect of temperature. Citronellal 2.5×10^{-3} mol; sodium borohydride 2.5×10^{-3} mol; TBAB 2.5×10^{-4} mol; sodium hydroxide 1.5×10^{-3} mol; water $10\,cm^3$; toluene $10\,cm^3$; speed of agitation $1200\,rpm$; temperature $30\,°C$. (($\blacklozenge$) $20\,°C$, ($\blacksquare$) $30\,°C$, ($\blacktriangle$) $35\,°C$, ($\bigcirc$) $45\,°C$).

4. Conclusions

The novelties of phase transfer catalysed chemoselective reduction of citronellal to citronellol using sodium borohydride were studied in detail in L–L PTC system with TBAB as the catalyst. Citronellol is very extensively used in a number of perfume compositions. The effect of different parameters such as speed of agitation, phase volume ratio, catalyst concentration, sodium borohydride concentration, citronellal concentration and temperature have been studied. A mechanistic and kinetic model is developed. It was possible to establish both rate constant and distribution constant from the same set of data.

Acknowledgements

References

[1] P.N. Rylander, H. Greenfield, R.L. Augustine, Catalysis of Organic Reactions, Marcel Dekker, New York, 1988.

[2] S. Arctender, Perfumery and Flavor Chemicals, vols. I and II, Allured Publishing Co, New York, 1969.

[3] U.K. Singh, M.A. Vannice, Stud. Surf. Sci. Catal. 130 (2000) 497.

[4] F.V. Wells, M. Billot, Perfumery Technology, E. Horwood Publishers, Chichester, UK, 1981, p. 149.

[5] C. Milone, C. Gangemi, R. Ingoglia, G. Neri, S. Galvagno, Appl. Catal. A: Gen. 184 (1999) 89.

[6] H.R. Velankar, M.R. Heble, E. J. Biotechnol. 6 (2) (2003).

[7] S.D. Doig, A.T. Boam, D.J. Leak, A.G. Livingston, D.C. Stuckey, Biocat. Biotrans. 16 (1) (1998) 27.

[8] R.H. Tale, K.M. Patil, S.E. Dapurkar, Tetrahedron Lett. 44 (2003) 3427.

[9] N. Boechat, J.C.S. da Costa, J. de Souza Mendonca, P.M. de Oliveira, M.V.N. De Souza, Tetrahedron Lett. 45 (2004) 6021.

[10] H.I. Schlesinger, H.C. Brown, H.R. Hoekstra, L.R. Rapp, J. Am. Chem. Soc. (1953) 75199.

[11] H.C. Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca, 1972.

[12] H.C. Brown, R. Krishnamurthy, Tetrahedron (1979) 35567.

[13] B. Zeynizadeh, S. Yahyaei, Bull. Korean Chem. Soc. 24 (11) (2003) 1664.

[14] B.C. Ranu, S. Samanta, Tetrahedron 59 (40) (2003) 7901.

[15] H. Firouzabadi, M. Ghadami, Phosphorus, Sulfur Silicon Relat. Elem. 166 (2000) 83.

[16] Z.-y. Yue, T. Gao, X. Xie, H. Sun, J. Gao, Peop. Rep. China. Chem. Res. Chin. Univ. 20 (3) (2004) 308.

[17] V.A. Darin, N.A. Federman, A.D.L. Borges, J. Miller, Main Group Metal Chem. 22 (8) (1999) 505.

[18] H. Firouzabadi, M. Adibi, M. Ghadami, Phosphorus, Sulfur Silicon Relat. Elem. 142 (1998) 191.

[19] F. Habib, M. Adibi, Phosphorus, Sulfur Silicon Relat. Elem. 142 (1998) 125.

[20] H. Mimoun, S.A. Firmenich, La P. Switz, J. Org. Chem. 64 (7) (1999) 2582.

[21] B. Tamami, M.M. Lakoraj, H. Yeganeh, Iran. Polym. J. 6 (3) (1997) 159.

[22] H. Firouzabadi, B. Tamami, N. Goudarzian, Synth. Commun. 21 (22) (1991) 2275.

[23] D.J. Raber, W.C. Guida, J. Org. Chem. 41 (4) (1976) 690.

[24] G.D. Yadav, Chim. Ind. 6 (2000) 1.

[25] G.D. Yadav, Top. Catal. 29 (3–4) (2004) 145.

[26] G.D. Yadav, Y.B. Jadhav, S. Sengupta, Chem. Eng. Sci. 58 (2003) 2681.

[27] G.D. Yadav, Y.B. Jadhav, S. Sengupta, J. Mol. Catal. A: Chem. 200 (2003) 117.

[28] G.D. Yadav, S.V. Lande, Adv. Synth. Catal. 347 (9) (2005) 1235.

[29] E.V. Dehmlow, S.S. Dehmlow, Phase Transfer Catalysis, Monographs in Modern Chemistry, vol. II, Verlag Chemie, Weinheim, Germany, 1983.

[30] C.M. Starks, C.L. Liotta, M. Halpern, Phase Transfer Catalysis, Fundamentals, Applications and Industrial Perspectives, Chapman & Hall, New York, 1994.

[31] V.G. Yadav, G.D. Yadav, J.R. Vyas, Chimica Oggi 18 (6) (2000) 39.

[32] V.G. Yadav, G.D. Yadav, J.R. Vyas, Chimica Oggi 18 (7/8) (2000) 3.