

Novelties in Selective Oxidation of Cinnamyl Alcohol under Liquid-Liquid Phase Transfer Catalysis with Potassium Chromate as the Oxidizing Agent

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Abstract : Cinnamyl alcohol and its derivatives find widespread use in the fragrance, pharmaceutical and agrochemical industries. In this research work the selective oxidation of cinnamyl alcohol to cinnamaldehyde was studied under liquid-liquid phase transfer conditions using potassium chromate (K_2CrO_4) as the oxidizing agent and tetrabutyl ammonium bromide (TBAB) as the phase transfer catalyst. A suitable reaction mechanism and a theoretical model have been proposed to explain the results obtained.

Keywords : Selectivity Engineering; Phase Transfer Catalysis; Cinnamyl alcohol; Cinnamaldehyde; Oxidation; Kinetic Model

1. INTRODUCTION

Oxidation of alcohols to their corresponding carbonyl compounds is a fundamental reaction in synthetic organic chemistry [1].

Selective oxidation is important in the synthesis of fine chemicals and intermediates and, in particular, the oxidation of primary alcohols to aldehydes is a fundamentally important laboratory and commercial procedure. Aldehydes are valuable both as intermediates and as high value components for the perfume industry. Many oxidations of this type are carried out using stoichiometric oxygen donors such as chromate or permanganate[2].

The known chemical methodologies for this transformation use either conventional mineral oxidants in stoichiometric amounts or environmentally benign oxidizing agents such as molecular oxygen and hydrogen peroxide catalyzed by transition metal compounds[3]. Chromium (VI) reagents represent the most widely used group of oxidation agents in organic chemistry. Using these reagents benzylic and allylic alcohols are selectively oxidized to their corresponding carbonyl compounds without any over-oxidation. There has been continued interest in the development of new chromium (VI) based oxidants for the effective oxidation of organic compounds, especially under mild and aprotic conditions[4]. In non-aqueous solutions, oxidation by Cr (VI) does not go to completion (the intermediate partially oxidized material containing Cr must be hydrolyzed for oxidation to continue); thus, under these

conditions, primary alcohols may be oxidized to aldehydes without forming carboxylic acid.

Cinnamyl alcohol and its derivatives find widespread use in the fragrance, pharmaceutical and agrochemical industries. In this research work the oxidation of cinnamyl alcohol to cinnamaldehyde was studied under liquid-liquid phase transfer conditions using potassium chromate (K_2CrO_4) as the oxidizing agent and tetrabutyl ammonium bromide (TBAB) as the phase transfer catalyst.

2. MATERIALS AND METHODS

Cinnamyl Alcohol of AR grade and Cinnamaldehyde of LR grade were obtained from M/s s.d. Fine Chemicals Pvt. Ltd, Mumbai, India. Ethyl Acetate, Sulfuric Acid (H_2SO_4) of 98% purity and Tetrabutyl Ammonium Bromide (TBAB) of 99.5% purity were procured from M/s Merck Specialities Pvt. Ltd, Mumbai, India. Potassium Chromate (K_2CrO_4) was obtained from Research-Lab Fine Chem Industries, Mumbai.

The oxidation of cinnamyl alcohol with potassium chromate were carried out batchwise in a fully baffled mechanically agitated glass reactor of capacity 500 cm³ (6.5 cm i.d.) equipped with a pitched turbine impeller and reflux condenser. The reactor was kept in a constant temperature water bath whose temperature could be controlled within $\pm 1^\circ C$.

Preliminary experiments were conducted with 13.4 g (0.1mol) of cinnamyl alcohol and adding ethyl acetate as solvent until the total volume of the organic phase was 100 ml (using a 100 ml standardization volumetric flask). Then

0.322 g (1 mol %) of the phase transfer catalyst TBAB (i.e. catalyst loading is 1 mol % based on cinnamyl alcohol) was taken and added to the organic phase. After this, 100 ml of 30% w/v H₂SO₄ (i.e. 30.622 g of concentrated (98% w/v) H₂SO₄ in 100 ml of distilled water) was prepared as the aqueous phase and 0.05 mol of potassium chromate was added to the aqueous phase by shaking well until the potassium chromate dissolves completely.

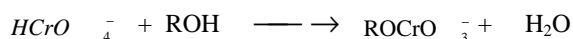
Then the aqueous phase was transferred to the 500 cm³ glass reactor and then the organic phase was transferred to the aqueous phase present in the reactor. The reactor was fitted with a reflux condenser and the reaction mixture stirred at the required temperature for 45 min. at the required speed of agitation. Samples were withdrawn at a definite interval of time from the organic phase for analysis by gas chromatography on a Chemito GC-7610 model gas chromatograph. A 1.83 m length, 3.18 mm internal diameter stainless steel column packed with 5% SE-30 on Chromosorb WHP was used for analysis in conjunction with a flame ionization detector. The preliminary experiments on the liquid-liquid phase transfer catalyzed chromate oxidation of cinnamyl alcohol with tetrabutyl ammonium bromide (TBAB) as phase transfer catalyst at 40°C showed that the reaction led to formation of only cinnamaldehyde and benzaldehyde. The conversion was based on disappearance of cinnamyl alcohol in organic phase.

3. RESULTS AND DISCUSSION

3.1. Mechanism of reaction and kinetic model

Chromium (VI) in aqueous solution exists as a pH-dependent mixture of several species, and while all the anionic species may form ion pairs and hence transfer to the organic solvent in presence of phase-transfer catalyst, the different chromium (VI) species may not be equally active for alcohol oxidation [4,5].

Indeed there is evidence that the first step in the oxidation of alcohol is



and that the chromate ester, has greater stability in organic solvents than in water.

It is observed that while cinnamaldehyde is the major product, benzaldehyde is also obtained as a by-product in this oxidation reaction. However the mechanism of its formation is not clearly understood [6].

The following theoretical model is proposed for the L-L PTC oxidation of cinnamyl alcohol with potassium chromate as the oxidizing agent :

Rate of transfer of {Q⁺ HCrO₄⁻} from the interface to the organic phase:

$$R_{c,a} = k_{LC,a} ([Q^+ HCrO_4^-]_{org,i} - [Q^+ HCrO_4^-]_{org,b}) \quad (1)$$

where R_{c,a} = Volumetric rate of transfer of {Q⁺ HCrO₄⁻} from the interface to the bulk organic phase,

k_{LC,a} = Mass transfer coefficient for transfer of {Q⁺ HCrO₄⁻} from the interface to the bulk organic phase,

a = Interfacial area per unit volume of the organic phase.

The subscripts i and b indicate the interface and bulk concentrations, respectively.

If the reaction system conforms to the Slow Reaction Regime (Regime 2), then there will be no free {Q⁺ HCrO₄⁻} present in the bulk organic phase i.e. [Q⁺ HCrO₄⁻]_{org,b} = 0 and the following rate equation will be valid:

$$R_{c,a} = k_{LC,a} [Q^+ HCrO_4^-]_{org,i} \quad (2)$$

The intrinsic rate of chemical reaction of cinnamyl alcohol to cinnamaldehyde in the organic phase may be represented by the equation:

$$R_{c,a} = k_R [Q^+ HCrO_4^-]_{org,b} [C_6H_5CH=CHCH_2OH]_{org} \quad (3)$$

Rearranging and adding Equations 2 and 3 gives:

$$R_{c,a} = \frac{k_{LC,a} k_R [Q^+ HCrO_4^-]_{org,i} [C_6H_5CH=CHCH_2OH]_{org}}{k_{LC,a} + k_R [C_6H_5CH=CHCH_2OH]_{org}} \quad (4)$$

When the concentration of cinnamyl alcohol is high, then k_R [C₆H₅CH=CHCH₂OH]_{org} >>> k_{LC,a} and the term k_{LC,a} can be neglected in the denominator of Equation 4. Then, Equation 4 becomes in this case:

$$R_{c,a} = k_{LC,a} [Q^+ HCrO_4^-]_{org,i} \quad (5)$$

and the rate of reaction is independent of the concentration of cinnamyl alcohol and the reaction is of zero order.

When the concentration of cinnamyl alcohol is low, then k_R [C₆H₅CH=CHCH₂OH]_{org} <<< k_{LC,a} and the term k_R [C₆H₅CH=CHCH₂OH]_{org} can be neglected in the denominator of Equation 4. Then, Equation 4 becomes in this case:

$$R_{c,a} = k_R [Q^+ HCrO_4^-]_{org,i} [C_6H_5CH=CHCH_2OH]_{org} \quad (6)$$

and the rate of reaction is linearly dependent on the concentration of cinnamyl alcohol and the reaction is of first order.

3.2 Effect of different parameters

To validate the proposed mechanism, the effects of various parameters on rate of reaction were studied and are described in the following sections :

3.2.1 Effect of speed of agitation:

The speed of agitation was varied in the range of 500–1200 rpm under otherwise similar conditions (namely, 0.1 mol cinnamyl alcohol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H₂SO₄) volume = 100 ml, 0.05 mol of potassium chromate, 1 mol % of PTC (TBAB) loading, temperature = 313K) as shown in Figure 1. The conversion was found to gradually increase with the speed of agitation from 500 to 1200 rpm during the initial stages of the reaction which suggests that mass transfer effects are important in this oxidation reaction. Further experiments to study the effect of other reaction parameters were carried out at 1200 rpm.

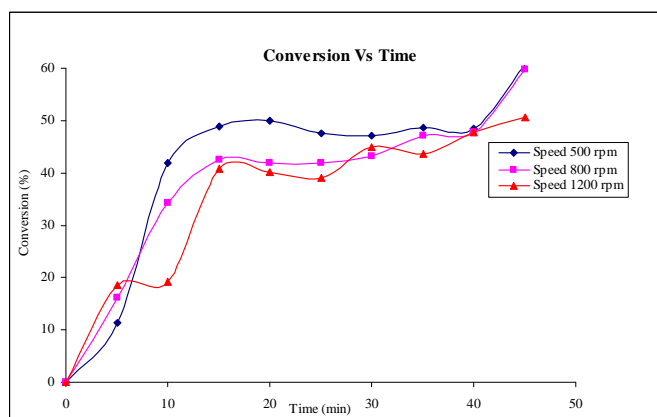


Figure 1 : Effect of Speed of Agitation

3.2.2 Effect of temperature:

The effect of temperature on the oxidation of cinnamyl alcohol was studied by carrying out the reaction at various temperatures, viz. 40^oC (313K) to 70^oC (343K) under otherwise similar conditions (namely, 0.1 mol cinnamyl alcohol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H₂SO₄) volume = 100 ml, 0.05 mol of potassium chromate, 1 mol % of PTC (TBAB) loading, speed of agitation = 1200 rpm) as shown in Figure 2. When the reaction temperature was increased from 40^oC (313K) to 70^oC (343K) it was observed that the conversion of cinnamyl alcohol

increased. From the slope of the Arrhenius plot for the initial stages of the reaction shown in Figure 3 the activation energy was calculated to be ≈ 1.1 kcal/mol which indicates that the reaction may be mass transfer controlled.

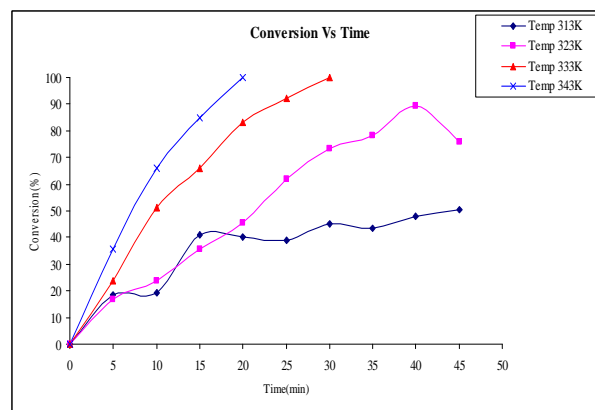


Figure 2: Effect of Temperature

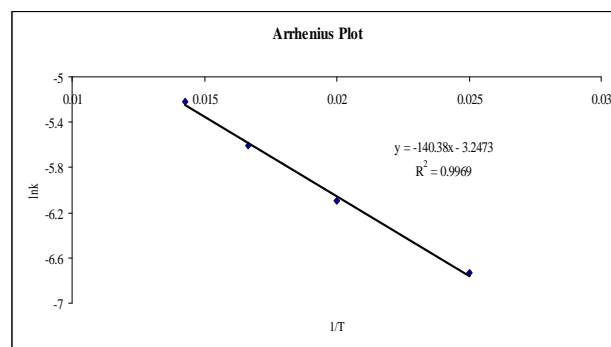


Figure 3: Arrhenius Plot

3.2.3 Effect of concentration of cinnamyl alcohol:

The effect of concentration of cinnamyl alcohol in the organic phase on the oxidation reaction was studied by varying the concentration cinnamyl alcohol from 5 x 10⁻⁴ to 2.0 x 10⁻³ gmol/cm³ under otherwise similar conditions (namely, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H₂SO₄) volume = 100 ml, 0.05 mol of potassium chromate, 1 mol % of PTC (TBAB) loading, speed of agitation = 1200 rpm, temperature = 313K). As shown in Figure 4 it was observed that the initial rate of reaction was independent of the concentration of cinnamyl alcohol in the organic phase and this suggests that the reaction may be mass transfer controlled.

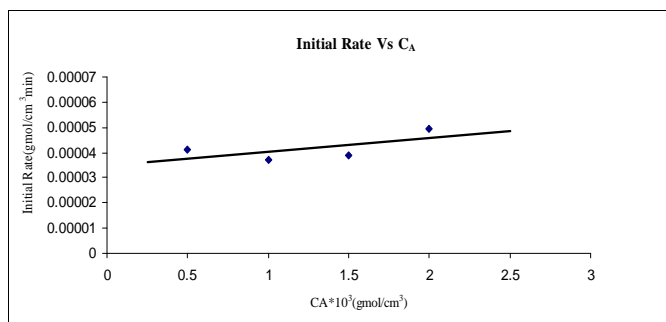


Figure 4 : Initial Rate of Reaction vs. Concentration of Cinnamyl Alcohol

3.2.4 Effect of concentration of potassium chromate:

The effect of concentration of the oxidizing agent, namely potassium chromate (K_2CrO_4), in the aqueous phase on oxidation reaction was studied by varying the concentration of potassium chromate in the aqueous phase from 2.5×10^{-4} gmol/cm³ to 1.0×10^{-3} gmol/cm³ under otherwise similar conditions (namely, 0.1 gmol cinnamyl alcohol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H_2SO_4) volume = 100 ml, 1 mol % of PTC (TBAB) loading, speed of agitation = 1200 rpm, temperature = 313K). As shown in Figure 5 it was observed that the initial rate of reaction increased linearly with the concentration of potassium chromate.

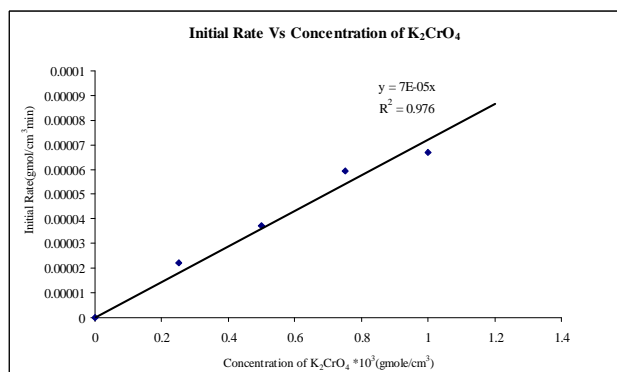


Figure 5 : Initial Rate of Reaction vs. Concentration of K_2CrO_4

3.2.5 Effect of phase transfer catalyst loading:

The effect of phase transfer catalyst loading on the oxidation of cinnamyl alcohol was studied by varying the phase transfer catalyst (tetrabutyl ammonium bromide, TBAB) loading from 1 mol% to 3 mol% (based on cinnamyl alcohol) under otherwise similar conditions (namely, 0.1 gmol cinnamyl alcohol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H_2SO_4) volume = 100 ml, 0.05 gmol of potassium chromate, speed of agitation = 1200 rpm, temperature =

313K). As shown in Figure 6 it was observed that the initial rate of reaction increased linearly with the total concentration of phase transfer catalyst in the organic phase for the concentration range studied.

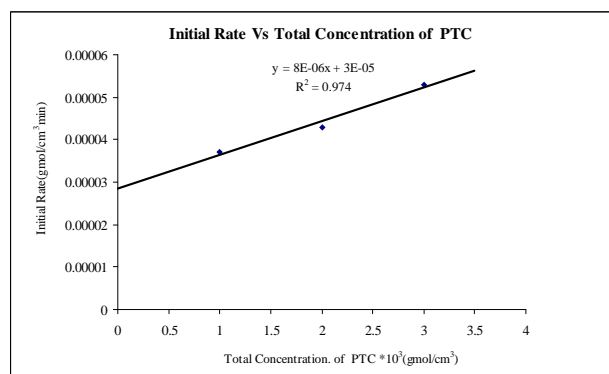


Figure 6 : Initial Rate of Reaction Vs. Total Concentration of PTC

4. CONCLUSION

The oxidation of cinnamyl alcohol to cinnamaldehyde was successfully carried out with potassium chromate as an oxidizing agent under liquid-liquid phase transfer catalysis with TBAB as the phase transfer catalyst. It was observed that the initial rate of reaction increases with concentration of potassium chromate and phase transfer catalyst concentration but is independent of the concentration of cinnamyl alcohol. A suitable reaction mechanism and a theoretical model have been proposed to explain the results obtained.

REFERENCES

- [1] Starks, C.M. (1971): *J. Am. Chem. Soc.*, **93**, 195.
- [2] Starks, C.M.; Liotta, C.L. (1978): *Phase Transfer Catalysis* Academic, New York.
- [3] Dehmlow, E.V.; Dehmlow, S.S. (1983): *Phase Transfer Catalysis*, **2nd ed.**, Verlag Chemie Weinheim..
- [4] Pletcher, Derek and Tait, Stephen J.D. (July 1978) : *Journal of Chemical Society Perkin-II*, 788-791.
- [5] Yadav, Ganapati D. and Haldavanekar, Bhagyashree V. (1997): *Journal of Phys. Chem.*, **101** (1), 36-48.
- [6] Carlsen, Per H.J; Husbyn, Mette; Braenden, Jon E. and Eliason, Robert (1989) : *Acta Chemica Scandinavica*, **43**485-488.