

Selective Oxidation of Lauryl Alcohol to Lauraldehyde under Liquid-Liquid Phase Transfer Catalysis (LL-PTC) with Potassium Chromate as the Oxidizing Agent

Ranveer, Anil C.; Ranade, Suresh V.; Mistry, Cyrus Keki*⁺

Department of Chemical Engineering, Mahatma Gandhi Mission's College of Engineering and Technology, Kamothe, Navi Mumbai, Maharashtra, 410 209 INDIA

ABSTRACT: *In the present research, the selective oxidation of lauryl alcohol to lauraldehyde was studied under liquid-liquid phase transfer conditions using potassium chromate (K_2CrO_4) as an oxidizing agent and tetrabutyl ammonium bromide (TBAB) as the phase transfer catalyst. Chromium (VI) reagents are used in these oxidations since the alcohols are selectively oxidized to the aldehydes without any over-oxidation. In non-aqueous solutions the oxidation by chromium (VI) does not go to completion as the intermediate partially oxidized material containing chromium must be hydrolysed for oxidation to continue. Liquid-Liquid Phase Transfer Catalysis (LL-PTC) involves the transfer of one reactant from the aqueous phase to the organic phase with the help of small quantities of a phase transfer catalyst which is usually quaternary ammonium or phosphonium salt. It was observed that no over-oxidation products such as lauric acid and high molecular weight esters of lauryl alcohol were formed under the reaction conditions used. The effect of various reaction parameters such as the speed of agitation, temperature, the concentration of lauryl alcohol, the concentration of potassium chromate and phase transfer catalyst loading were studied. A reaction mechanism involving the formation of chromate ester in the organic phase has been proposed and a kinetic model has been developed based on the experimental results obtained.*

KEYWORDS: *Selective Oxidation; Perfumery and Aroma Chemicals; Lauraldehyde; Phase Transfer Catalysis; Kinetic Model.*

INTRODUCTION

The oxidation of primary and secondary alcohols to aldehydes and ketones is one of the most important transformations in organic chemistry both at a laboratory and industrial scale [1]. The oxidation of alcohols particularly the oxidation of octanol, decanol, and dodecanol plays an important role in organic synthesis and aldehydes (Octanal, decanal and dodecanal)

are widely used in the perfume industry and the synthesis of citrus oil. The catalytic oxidation for the manufacture of organic compounds (octanal, decanal, and dodecanal) is an interesting area of research and forms the subject of this work.

The transformation of alcohols into aldehydes or ketones is a fundamental reaction in organic synthesis [2], a number of methods are known for alcohol oxidation,

* To whom correspondence should be addressed.

+ E-mail: cyruskmistry@gmail.com

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and however, the development of newer methods and methodologies is gaining much attention currently due to the significance of this reaction. In the last four years some fine articles have appeared, describing manganese [3], copper [4, 5], ruthenium [6, 7], iron [8], palladium [9, 10], gold [11, 12] catalyzed reactions with dioxygen or hydrogen peroxide.

While there is a general trend to use environmentally friendly oxidizing agents such as air or hydrogen peroxide in industrial oxidations there is also a renewed interest in the use of chromates as oxidizing agents for those reactions where air or hydrogen peroxide lead to the formation of over-oxidation products and low selectivity to the desired product.

In this research work the selective oxidation of lauryl alcohol (1-dodecanol) to lauraldehyde (1-dodecanal) 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.

EXPERIMENTAL SECTION

Materials

1-Dodecanol (Lauryl Alcohol) of AR grade was obtained from M/s S. d. Fine Chemicals Pvt. Ltd, Mumbai, India. Ethyl Acetate, Potassium Chromate (K_2CrO_4), Sulfuric Acid (H_2SO_4) and Tetrabutyl Ammonium Bromide (TBAB) of 99.5% purity were obtained from M/s Merck Specialities Pvt. Ltd, Mumbai, India.

Methods

The oxidations of 1-dodecanol 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 pitched turbine impeller and a reflux condenser. The reactor was kept in a constant temperature water bath whose temperature could be controlled within $\pm 1^\circ C$.

Typical L-L PTC runs were conducted by taking 0.1 gmol 1-dodecanol and adding ethyl acetate as solvent until the total volume of the organic phase was 100 mL (using a 100mL standardization volumetric flask). Then 5 mol % (1.61 gm) of the phase transfer catalyst TBAB (i.e. catalyst loading is 5 mol % based on 1-dodecanol) was taken and added to the organic phase. After this, 100 mL of 30% w/v H_2SO_4 (i.e. 31.25 gm of concentrated

(98% w/v) H_2SO_4 in 100 ml of distilled water) was prepared as the aqueous phase and 0.05 gmol 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. While handling potassium chromate all necessary precautions were taken such as wearing hand gloves and avoiding direct contact with skin.

The reactor was fitted with a reflux condenser and the reaction mixture stirred at the required temperature for 1 hour (60 min.) at the required speed of agitation. The samples were taken at regular intervals from the organic phase for analysis by gas chromatography on a ChemitoGC-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. In liquid-liquid phase transfer catalytic reaction system, only 1-dodecanal was produced with a negligible amount of 1-dodecanoic acid. The conversion was based on the disappearance of 1-dodecanol in the organic phase.

RESULTS AND DISCUSSION

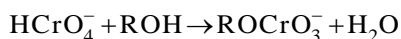
Preliminary experiments were carried out using hydrogen peroxide as the oxidizing agent for the liquid-liquid phase transfer catalysed the oxidation of lauryl alcohol. However, the yield of lauraldehyde obtained was very low and there was also a possibility of the formation of over-oxidation products if greater than stoichiometric amounts of the oxidizing agent were used. Therefore, in order to obtain lauraldehyde in high selectivity and to prevent the formation of over-oxidation products it was decided to study the liquid-liquid phase transfer catalysed the oxidation of lauryl alcohol to lauraldehyde using potassium chromate as the oxidizing agent. Chromium (VI) reagents are used in these oxidations since the alcohols are selectively oxidized to the aldehydes without any over-oxidation. Furthermore, potassium chromate solutions are not harmful if handled properly and proper treatment methods are used for the effluent aqueous waste stream in industrial oxidations.

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.

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



and that the chromate ester, ROCrO_3^- , has greater stability in organic solvents than in water. Hence, the following theoretical model is proposed for the L-L PTC oxidation of 1-dodecanol with potassium chromate as the oxidizing agent:

Rate of transfer of $\{ \text{Q}^+\text{HCrO}_4^- \}$ from the interface to the organic phase:

$$R_{c,a} = k_{LC,a} \left(\left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},i} - \left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},b} \right) \quad (1)$$

Where $R_{c,a}$ = Volumetric rate of transfer of $\{ \text{Q}^+\text{HCrO}_4^- \}$ from the interface to the bulk organic phase,

$k_{LC,a}$ = Mass transfer coefficient for transfer of $\{ \text{Q}^+\text{HCrO}_4^- \}$ 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 $\{ \text{Q}^+\text{HCrO}_4^- \}$ present in the bulk organic phase i.e.

$\left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},b} = 0$ and the following rate equation will be valid:

$$R_{c,a} = k_{LC,a} \left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},i} \quad (2)$$

The intrinsic rate of the chemical reaction of 1-dodecanol to 1-dodecanal in the organic phase may be represented by the equation:

$$R_{c,a} = k_R \left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},i} \left[\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \right]_{\text{org}} \quad (3)$$

Rearranging and adding Equations (2) and (3) gives:

$$R_{c,a} = \frac{k_{CL,a} k_R \left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},i} \left[\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \right]_{\text{org}}}{k_{LC,a} + k_R \left[\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \right]_{\text{org}}} \quad (4)$$

When the concentration of 1-dodecanol is high, then $k_R \left[\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \right]_{\text{org}} \gg k_{LC,a}$ and the term $k_{LC,a}$ can be neglected in the denominator of Eq. (4). Then, Eq. (4) becomes in this case:

$$R_{c,a} = k_R \left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},i} \quad (5)$$

and the rate of reaction is independent of the concentration of 1-dodecanol and the reaction is of zero order.

When the concentration of 1-dodecanol is low, then

$k_R \left[\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \right]_{\text{org}} \ll k_{LC,a}$ and the term $k_R \left[\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \right]_{\text{org}}$ can be neglected in the denominator of Equation 4. Then, Equation 4 becomes in this case:

$$R_{c,a} = k_R \left[\text{Q}^+\text{HCrO}_4^- \right]_{\text{org},i} \left[\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \right]_{\text{org}} \quad (6)$$

and the rate of reaction is linearly dependent on the concentration of 1-dodecanol and the reaction is of the first order.

Effect of different parameters

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

Effect of Speed of Agitation

To ascertain the influence of mass transfer limitations in the L-L PTC oxidation of 1-dodecanol with K_2CrO_4 , the speed of agitation was varied in the range of 900–1800 rpm under otherwise similar conditions (namely, 0.1 gmol 1-dodecanol, 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, 5 mol % of PTC (TBAB) loading, temperature = 313K) as shown in Fig. 1. The conversion was found to gradually increase with the speed of agitation from 900 to 1800 rpm thus mass transfer effects are important in this oxidation reaction. Further experiments to study the effect of other reaction parameters were carried out at 900 rpm.

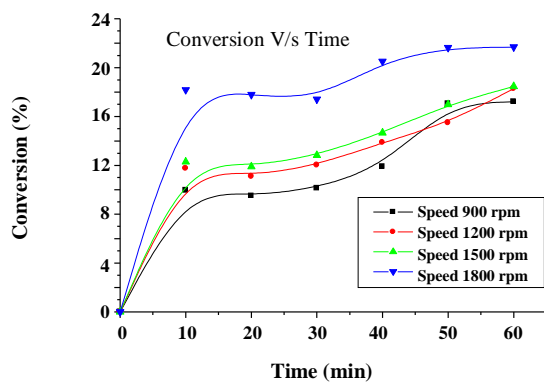


Fig. 1: Effect of Speed of Agitation.

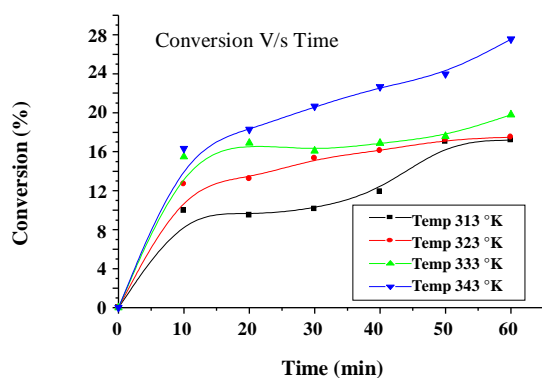


Fig. 2: Effect of Temperature.

Effect of Temperature

The effect of temperature on the oxidation of 1-dodecanol was studied by varying the temperature from 40°C (313K) to 70°C (343K) under otherwise similar conditions (namely, 0.1 gmol 1-dodecanol, organic phase made up to 100 mL with ethyl acetate as solvent, aqueous phase (30% w/v H₂SO₄) volume = 100 mL, 0.05 gmol of potassium chromate, 5 mol % of PTC (TBAB) loading, speed of agitation = 900 rpm) as shown in Fig. 2. The conversion of 1-dodecanol was observed to increase with the increase in reaction temperature. From the slope of the Arrhenius plot for the initial stages of the reaction shown in Fig. 3 is the activation energy which was calculated to be ≈ 5 kcal/mol. This indicates that the reaction may be mass transfer controlled.

Effect of Concentration of 1-Dodecanol

The effect of concentration of 1-dodecanol in the organic phase on the oxidation reaction was studied

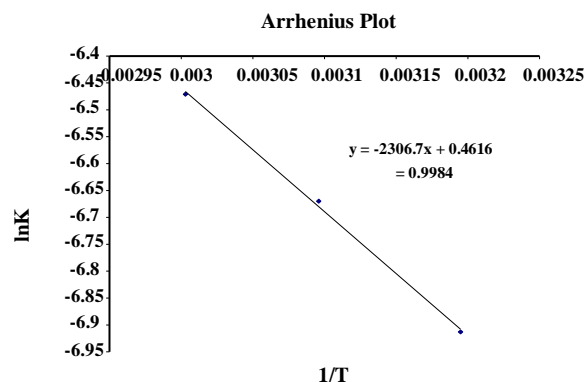


Fig. 3: Arrhenius Plot for Initial Stages of Reaction.

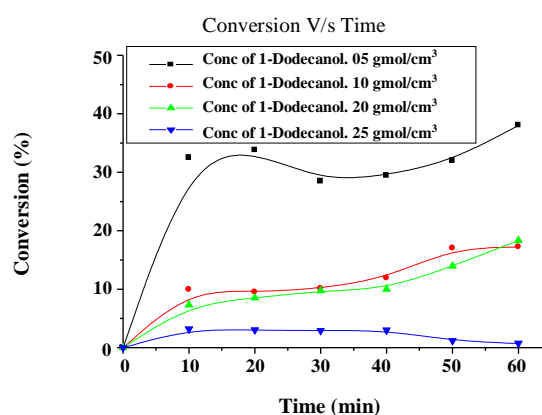


Fig. 4: Effect of Concentration of 1-Dodecanol.

by varying the concentration of 1-dodecanol in the organic phase from 5×10^{-4} gmol/cm³ to 2.5×10^{-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 gmol of potassium chromate, 5 mol % of PTC (TBAB) loading, speed of agitation = 900 rpm, Temperature = 313K) as shown in Fig. 4. The conversion of 1-dodecanol was observed to decrease with increase in the concentration of 1-dodecanol in the organic phase since the mole ratio of oxidizing agent to 1-dodecanol was higher at lower concentrations of 1-dodecanol. A plot of $\ln \left(\frac{[C_{11}H_{23}CH_2OH]_t}{[C_{11}H_{23}CH_2OH]_0} \right) / \left(\frac{[C_{11}H_{23}CH_2OH]_t - [C_{11}H_{23}CH_2OH]_0}{[C_{11}H_{23}CH_2OH]_0} \right)$ versus $t / ([C_{11}H_{23}CH_2OH]_0 - [C_{11}H_{23}CH_2OH]_t)$ was prepared which was linear and the values of k_R and k_{LCa} were determined from the slope and intercept of this plot and found to be 1.0 cm³/gmol.min and 9.59×10^{-4} min⁻¹, respectively.

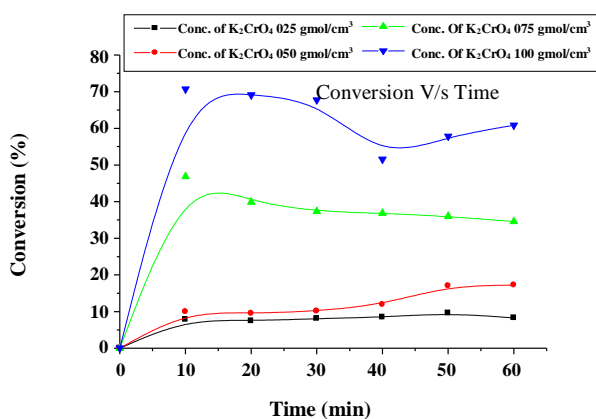


Fig. 5: Effect of Concentration of Potassium Chromate.

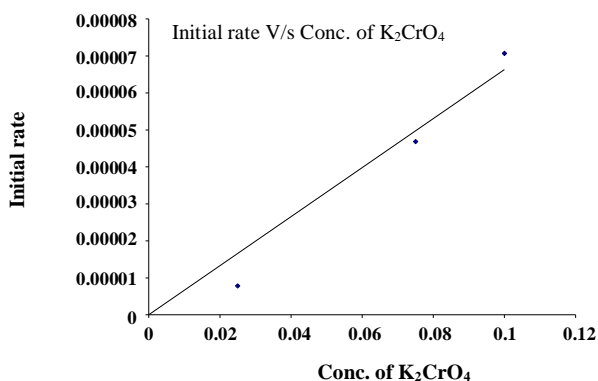


Fig. 6: Initial Rate of Reaction V/s Concentration of K_2CrO_4 .

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 $2.5 \times 10^{-4} \text{ gmol/cm}^3$ to $1.0 \times 10^{-3} \text{ gmol/cm}^3$ under otherwise similar conditions (namely, 0.1 gmol 1-dodecanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H_2SO_4) volume = 100 ml, 5 mol % of PTC (TBAB) loading, speed of agitation = 900 rpm, temperature = 313K) as shown in Fig. 5. The conversion of 1-dodecanol was observed to increase with the increase in the concentration of potassium chromate in the aqueous phase. As shown in Fig. 6 it was observed that the initial rate of reaction was linearly dependent on the concentration of potassium chromate in the aqueous phase.

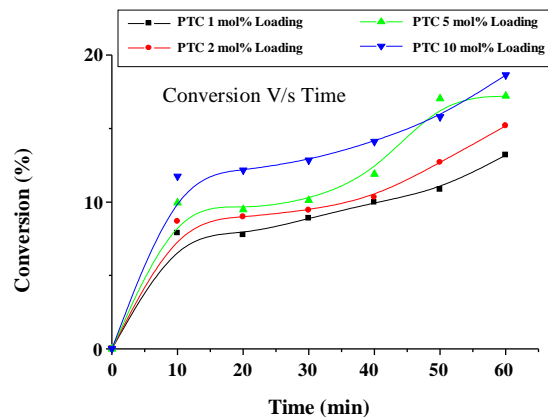


Fig. 7: Effect of Phase Transfer Catalyst Loading.

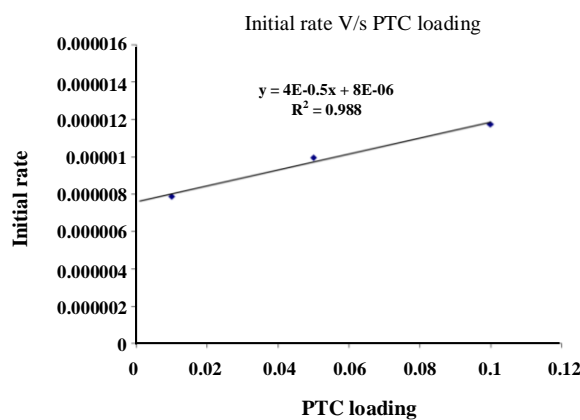


Fig. 8: Initial Rate of Reaction V/s Phase transfer catalyst loading.

Effect of Phase Transfer Catalyst Loading

The effect of phase transfer catalyst loading on the oxidation of 1-dodecanol was studied by varying the phase transfer catalyst (tetrabutyl ammonium bromide, TBAB) loading from 1 mol% to 10 mol% (based on 1-dodecanol) under otherwise similar condition (namely, 0.1 gmol 1-dodecanol, 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 = 900 rpm, temperature = 313K) as shown in Fig. 7. The conversion of 1-dodecanol was observed in general to increase with the increase in the phase transfer catalyst loading for the range of catalyst, loadings studied. A plot of the initial rate of reaction versus total concentration of the phase transfer catalyst in the organic phase was prepared as shown in Fig. 8 and it was observed that the initial rate

of the reaction was linearly dependent on the total concentration of phase transfer catalyst in the organic phase for the concentration range studied and the reaction took place to some extent even in the absence of phase transfer catalyst.

CONCLUSIONS

The oxidation of 1-dodecanol to 1-dodecanal was successfully carried out with potassium chromate as an oxidizing agent under liquid-liquid phase transfer catalysis with tetrabutyl ammonium bromide as the phase transfer catalyst. It was observed that the conversion of 1-dodecanol increases with the speed of agitation, temperature, and phase transfer catalyst loading. A suitable reaction mechanism and a theoretical model have been proposed to explain the experimental results obtained.

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