KINETIC STUDY OF ACYLATION REACTION USING ION EXCHANGE RESIN

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ABSTRACT

The reaction of anisole with octanoic acid produces p-octanoyl anisole which is a useful intermediate in many industries. The conventional method of synthesizing ketones suffers from serious problems like corrosion, waste and safety. In this paper attempt has been made to make the process environmentally benign by using carboxylic acid as the acylating agent. An effort is made to study the kinetics of anisole with octanoic acid using Amberlyst-35 as the catalyst at reflux condition. The effect of various parameters like temperature, feed-mole ratio, catalyst loading & catalyst reusability was studied. The experimental data obtained was validated to fit pseudo-homogeneous first order reaction model.

***Keywords:* Acylation, Amberlyst 35, Anisole, Octanoic Acid, P-Octanoyl Anisole.**

I. INTRODUCTION

Friedel Craft acylation reaction is one of the most renowned reaction used in manufacturing of para-acylated ketones. The reaction accompanies a aromatic substrate along with acylating agent like an acid anhydride, an acyl halide or an ester in presence of acidic catalyst. The reaction product formed via these reactions finds wide area of application in production of various insecticides, pharmaceuticals perfumes, plasticizers, dyes which are of commercial importance[1]. The conventional processes included the use of homogeneous catalyst like metal halides which included $AlCl_3$ & BF_3, mineral acids like H_2SO_4 & HF, these catalysts result in to the formation of large corrosive waste streams and cannot be easily regenerated. The use of above catalyst has certain limitations in disposal of toxic wastes generated and difficulties in handling[2]. Thus in order to overcome these difficulties there was need urged to develop green method which is of environmental and economic concern. Carboxylic acid has potential of being used as green acylating agent because it produces water as the only byproduct. Large work has been done on application of solid acid as the catalyst especially using zeolites[3-5]. Mayadevi et.al have studied the acylation of anisole with various carboxylic acid like hexanoic, octanoic, decanoic acid and the effect of chain length of acid on wide pore zeolites[3]. Wang et.al have studied the reaction of anisole with different carboxylic acid in presence of HZSM-5 catalyst[4]. Jasra has presented a review on acylation of various aromatic compound[6]. Beers et.al have studied the acylation of anisole with octanoic acid using different catalysts like Nafion & zeolites[7,8]. Mou et.al have studied acylation of anisole with octanoyl chloride using mesoporous aluminosilicates as the catalyst. The reaction of anisole with acid chloride produced p-octanoyl anisole & hydrochloric acid as the byproduct. The drawback associated with this process is that HCl formed is corrosive & acidic in nature, it becomes difficult to handle[9].

Sartori et.al has presented a brief review on application of various solid acid like Nafion, zeolites, metal oxides, heteropoly acids in acylation reactions[10].Bai et.al have demonstrated the acylation reaction by treating zeolites with different organic acids like tartaric acid, oxalic acid and mixed organic acid[11]. Cejka et.al has presented a review on various acylation reactions using different catalyst. Also it describes acylation of anisole with carboxylic acid using different zeolites at the respective reaction temperature[12].

Beers et.al have reported the acylation of anisole with octanoic acid in presence of Amberlyst-15[5].We have attempted to use ion exchange resin Amberlyst-35, which has high temperature sustainability, of acid sites, equilibrium constant compared to that of amberlyst-15. Longer catalyst lifetime enables increase in concentration of acid sites & enhanced thermal ability. Present work demonstrates the study of kinetics of anisole with octanoic acid using ion exchange resin.

II. EXPERIMENTAL

2.1 Materials

Anisole & Octanoic acid was obtained from HPLC (India), Potassium hydroxide purified pellets & Oxalic acid dihydrate for titration & for standardisation was purchased from Merck (India). Amberlyst 35 wet was obtained from SD Fine Chemicals (India), product of m/s Dow chemicals respectively. Phenolpthalein was used as an indicator (pH range 8.2-10.0).

2.2 Catalyst Treatment

The macro-reticular ion exchange resin used in this study requires a pre-treatment before its usage. The catalyst was washed with distilled water for 2-3 times, then with acetone, followed again washing with distilled water, in order to remove the impurities. The washed catalyst was kept in vacuum oven at 363 K until water content was completely evaporated.

2.3 Apparatus and Procedure

The reaction was carried out in a three necked glass reactor having reaction mixture volume of $1.5*10^{-4}$ m^3. The reactor was equipped with a thermostat, a stirrer and a reflux condenser to measure the reaction mixture temperature. The anisole and octanoic acid was taken in 4:1 proportion, the usage of excess anisole prevents diacylation reaction. The reaction mixture of anisole & octanoic acid was first charged & allowed to attain the required temperature. Once the temperature was attained the catalyst was added. Anisole itself acted as solvent for this reaction. The reaction mixture samples were collected at different time intervals, the conversion was determined by titrating against 0.5 N standard alcoholic KOH.

III. RESULT AND DISCUSSIONS

3.1 Effect of Parameters

3.1.1 Effect of Stirring Speed

It was found that beyond the agitation speed of 1000 rpm the conversion of octanoic acid was not affected. No restriction was provided for the external mass transfer of octanoic acid from the bulk liquid phase to the outer surface of catalyst. Thus the experiments further were performed at 1000 rpm.

3.1.2 Effect of Catalyst Loading

Since the resistance to mass transfer is absent the reaction rate is directly proportional to the catalyst loading. Different experiments were performed with catalyst loading of 5%, 7%, 10% of the total weight of the reactant.

Considering feed-mole ratio of 4:1 at 398 K, it was found that with the increase in catalyst loading the reaction rate increased as shown in fig.1. But it was noticed that at 10% w/w there was limited increase in the rate, this is usually for liquid phase reaction it may be due to thermodynamic or diffusion limitation. All further experiments were performed at 7 % w/w.

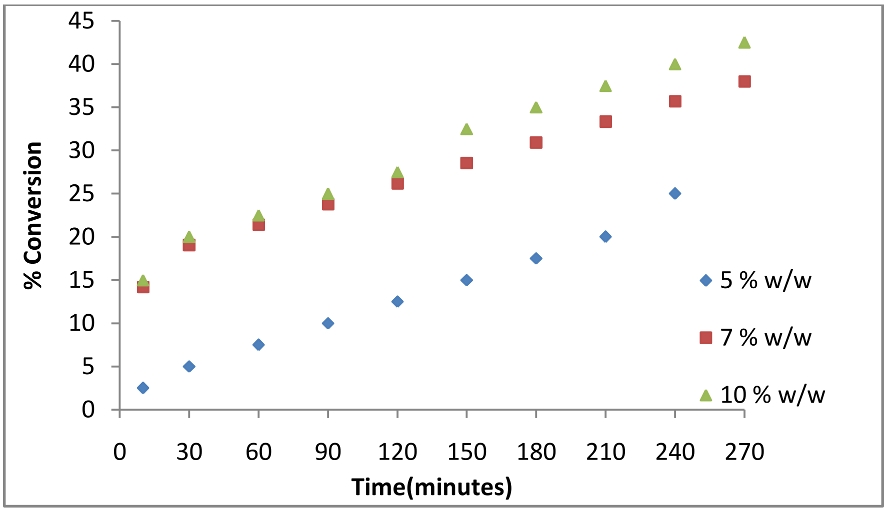

Fig 1. Effect of Catalyst loading (Temperature:398 K, mole ratio 4:1)

3.1.3 Effect of Feed-mole ratio

The reaction was carried out with different amount of anisole, the various feed mole ratio of anisole to acid that were tried was 2:1, 4:1, 6:1. These all experiments were conducted at catalyst loading of 7 % w/w at 398 K as shown in fig 2. A general increase in conversion of acid was noticed, the increase beyond anisole to acid ratio of 4 was very small. So, the further experiment were fixed to 4:1 proportion.

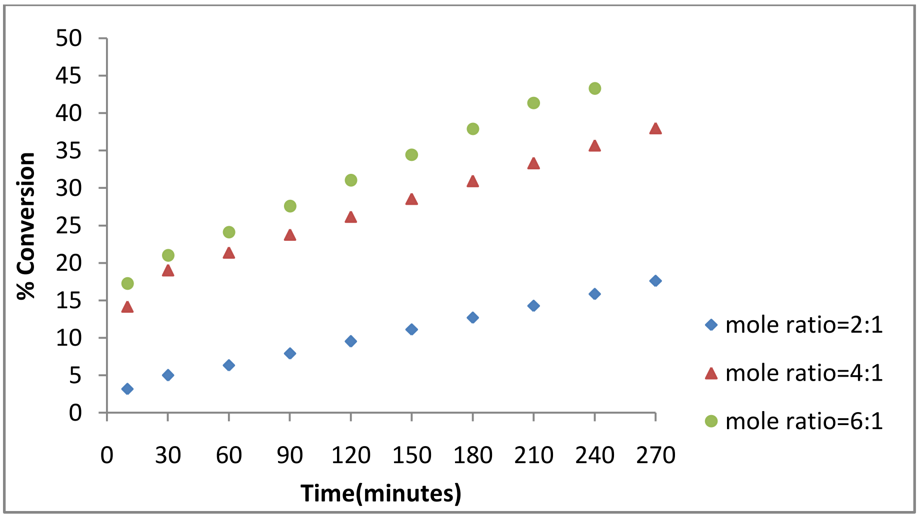

Fig 2. Effect of Mole Ratio (Temperature:398 K, Catalyst loading: 7% w/w)

3.1.4 Effect of Temperature

The study of variation of temperature is of immense importance since this data is used in calculation of activation energy for the reaction. The rate constants are basically the strong intrinsic functions of temperature. Various experiments were conducted with anisole to acid ratio of 4:1, 7 % w/w of catalyst loading comprising of temperature range of 353 K, 368 K, 383 K and 398 K as shown in fig 3. It was found that conversion rate increased with the increase in temperature. It was noticed that the conversion rate was fast at the beginning and slows down later on.

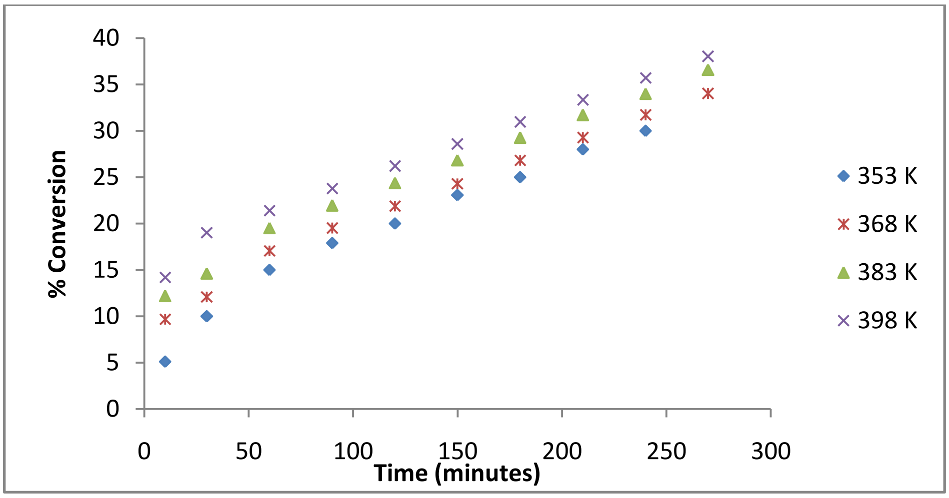

Figure 3. Effect of Temperature (Mole ratio:4:1, Catalyst loading: 7% w/w)

3.1.5 Catalyst Reusability

The reusability of catalyst was studied with fresh and used catalyst. After the completion of experiment the catalyst was filtered, washed with acetone and water. It was dried in vacuum oven at 363 K until the water was completely evaporated. The experiment was conducted with anisole to acid ratio of 4:1, 7% w/w of catalyst loading & at temperature of 398 K as shown in fig 4. It was found that there was marginal decrease in the conversion rate. Thus the catalyst can be reused repeatedly for the reaction.

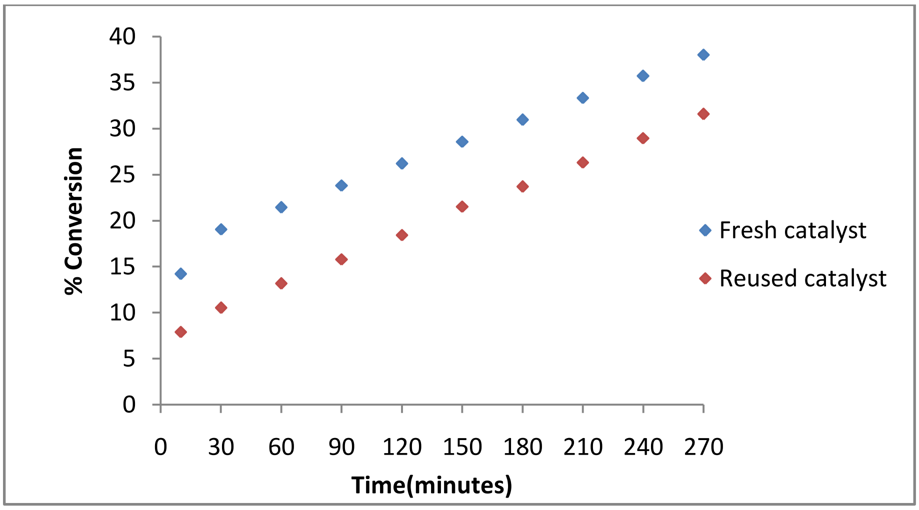

Fig 4. Catalyst Reusability(Temperature:398 K, Mole ratio:4:1,Catalyst loading: 7% w/w)

3.2 Kinetic Model

The kinetics of acylation reaction can be better explained by using a pseudo homogeneous reaction model or in absence of intraparticle diffusional limitation it can be explained by means of the more complex reaction models like Eley- Rideal mechanism or Langmuir- Hinshelwood Hougen Watson mechanism. For most of the reactions those are catalysed by means of ion exchange resin pseudo homogeneous reaction model fits the best since the reaction medium is highly polar.

3.2.1 Pseudo Homogeneous Model

Consider the reaction,

$$\text{Anisole} + \text{Octanoic Acid} \longrightarrow \text{p-Octanoyl Anisole} + \text{Water} \qquad (1)$$

There are various ways to determine the rate of reaction, the estimation of rate depends on the unit volume of the reacting fluid used for the homogeneous systems[13-15].

First order pseudo homogeneous reaction model is given by,

$$kt = -\ln(1-X) \qquad (2)$$

where k- rate constant (min^{-1})

t- time (min)

X- conversion of acid

3.2.2 Temperature and Reaction Rate

Arrhenius expression gives the variation of rate constant with temperature which is given by,

$$k = k_0\, e^{(-E/RT)} \qquad (3)$$

In order to calculate activation energy the graph of ln K v/s 1/T was plotted.

3.3 Fitting of Kinetic Data

Since the acylation reaction is kinetically controlled by external mass transfer resistance and intra-particular diffusion. The experimental data obtained was used to plot ln(1- X) verses time. It is observed from the figure that there is linear agreement between the data and pseudo homogeneous first order reaction kinetic model as shown in fig 5.

The frequency factor and energy of activation is calculated by plotting -ln k v/s 1/T as represented in figure 6. The activation energy obtained for the reaction was 19.496 KJ/mol.

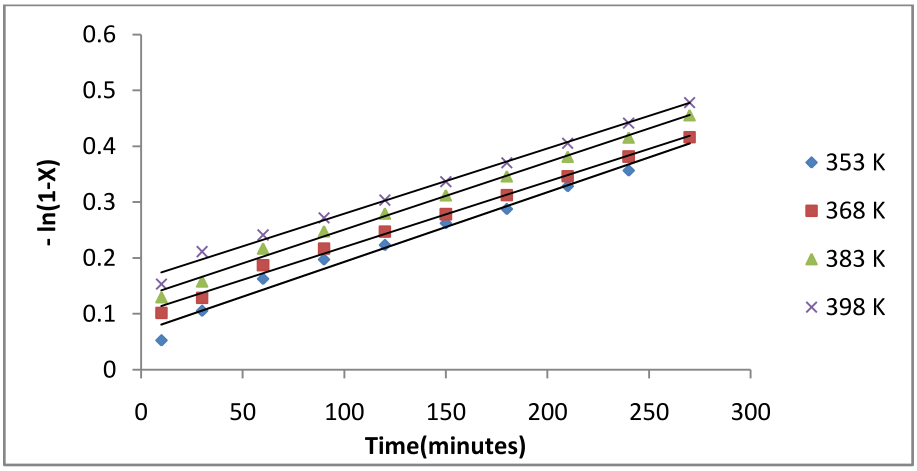

Fig 5. Pseudo First order kinetic plot (Mole ratio:4:1, Catalyst loading: 7% w/w)

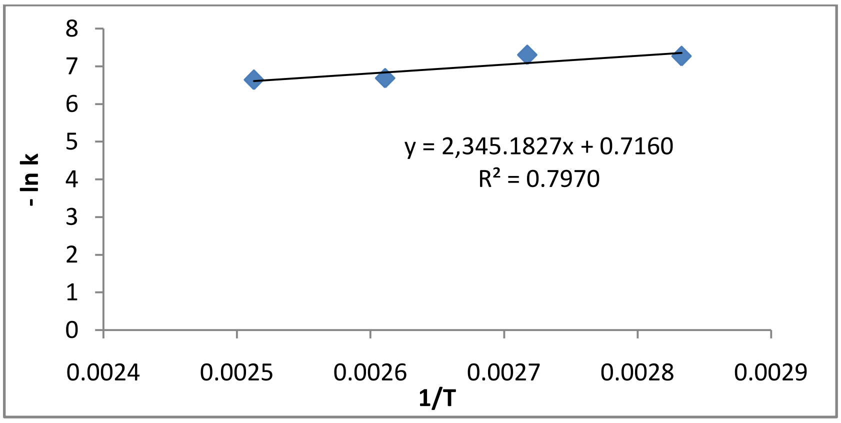

Fig 6. Arrhenius Plot

IV. CONCLUSION

The kinetics of acylation reaction of anisole with octanoic acid was studied using Amberlyst 35 as the catalyst. It was observed that with the increase in temperature, feed mole ratio and catalyst loading the conversion rate increased. There was no significant rise observed in conversion rate for feed mole ratio of 6:1.The first order pseudo-homogeneous model well fitted the experimental data. For the reaction the activation energy was found to be 19.496 KJ/mol.

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