CHAPTER 3

ESTERIFICATION

3.1 INTRODUCTION

Esters are carboxylic acid derivatives with the general formula R-COOR' (R,R'=H, alkyl or aryl). When a carboxylic acid is treated with a large excess of an alcohol, in presence of an acid catalyst, an ester is formed. The reaction is called acid catalysed esterification or sometimes Fischer esterification after the great German chemist Emil Fischer. The esterification process introduced by E.Fischer and A. Speier(1895) consists in refluxing acid and excess methanol or ethanol in presence of about 3% hydrogen chloride. The reaction is represented in (1):

$$\mathrm{RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O} \qquad \text{..........}(1)$$

Esterification is a widely employed reaction in the organic process industry. Esters fall under a very wide category, ranging from aliphatic to aromatic with various substitutions and multifunctional groups, organic esters being valuable intermediates in the chemical industry. Esters are mostly used as plasticizers, solvents, perfumery and flavour chemicals and also as precursors to many pharmaceuticals, agrochemicals and fine chemicals.

The conventional esterification is an equilibrium reaction. For the stoichiometric mixture of acid and alcohol, equilibrium generally reaches ~68% [1] of conversion for the straight chain saturated alcohol. In order to obtain maximum yields Le Chatlier's principle, is followed and the reaction is driven to the right hand side/forward direction, as follows:

Addition of one of the reactants in excess: The reaction usually reaches a point of equilibrium at ~60% conversion, but in a small scale experiment a conversion of 60-80% can be achieved by use of a large excess of either acid or alcohol.

Removal of one of the products: Either ester or water formed is removed as soon as it is formed. Generally, suitable organic solvents are employed to remove the water formed during the reaction as a binary azeotrope or by employment of dehydrating agent such as anhydrous magnesium sulfate or molecular sieves [2].

3.2 SYNTHETIC ROUTES TO ESTERIFICATION

To avoid equilibrium reaction, various precursors are used to achieve irreversible reaction, which involves the use of acyl halides (2) or anhydrides (3) in place of parent carboxylic acids. With acid halides though the reactions are rapid and irreversible, HCl produced as a byproduct is difficult to remove. Further, an additional step is involved, where pyridine is used to remove HCl. Also such reactions are efficient for primary alcohols only. With secondary alcohols the yields are lower and no reaction occurs with tertiary alcohols. Further, the aromatic acid chlorides are considerably less reactive when compared to aliphatic acid chlorides.

$$\mathrm{RCOCl + R'OH \longrightarrow RCOOR' + HCl} \qquad \text{.........(2)}$$

When acid anhydrides are used, the reaction is slow and produces one mole of carboxylic acid in place of HCl. This process is widely accepted in industry for the esterification of polyhydroxy compounds such as carbohydrates, cellulose etc.

$$\mathrm{(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH} \qquad \text{.........(3)}$$

Other methods include the use of alkyl tert-butyl ether or by alkylation of salts of carboxylic acids with alkyl halides, transesterification, carbonylation of olefins, alcoholysis of nitriles etc.

The conventional catalyst used in esterification reactions is sulphuric acid, cited as a potential environmentally hazardous chemical, posing several disadvantages in industrial processes, which include wasting large amount of catalyst, corroding reactors, causing an acidic waste water, difficulty of catalyst recovery, and often lead to colouration of the product. In view of the deficiencies encountered, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids. Some of the solid acids used in esterification reactions are zeolites, niobic acid, solid super acids, heteropolyacids, pillared clays etc [3-18]. They possess high catalytic activity and selectivity, do not corrode reaction vessels or reactors and finally, repeated use of solid acid catalyst from reaction mixture is easy and the product is free from colour and acid contamination.

3.3 MONOESTERS

Monoesters are very important industrially and find a wide range of applications in perfumery, flavours, pharmaceuticals and as solvents. They are typically synthesized by [19,20] (1) Solvolytic reactions (2) Condensation reactions(3) Free radical processes (4) miscellaneous processes.

Solvolytic Reactions: Conversion of carboxylic acids and acid derivatives into esters by reaction with hydroxylic compounds are solvolytic reactions, which include (a) direct esterification of acids (b) alkylation of carboxylic salts(c) alcoholyses of acyl halides (d) alcoholyses of anhydrides(e) alcoholyses of nitriles and amides (f) alcoholyses of ketenes (g) transesterification.

Condensation Reactions: Reactions involving carbanion intermediates can be used to prepare carboxylic acid esters. Some well-known reactions of this category are (a) Knovengel reaction (b) Darzens reaction (c) Wittig reaction (d) Reformatsky reaction (e) Acetoacetic ester synthesis (f) malonic ester synthesis (g) derivatives of α-anions of esters (h) Michael reaction and related conjugate addition (i) Claisen condensation.

Free-Radical Processes include (a) radical additions and substitution reaction (b) acyloxylation reaction (c) anodic dimerization.

Miscellaneous processes include (a) from organoboranes (b) from acetylenes (c) from diazo esters (d) by carbonylation of alcohol (e) by phase transfer catalyzed reaction of alkyl or aryl halide with inorganic salt of the carboxylic acid (both liquid-liquid and solid-liquid).

For the preparation of perfumery and flavour grade esters, only a few of the above mentioned routes can be considered, due to the stringent specifications of the final product. The most widely employed and supposedly cleaner production technique for such esters, involves the reaction of the appropriate carboxylic acid with an alcohol in the presence of a mineral acid catalyst or a heterogeneous catalyst under reflux conditions, followed by separation of the ester by distillation. Research is being focussed on the use solid acids to meet the requirements.

3.4 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

Esterification has been widely investigated using several solid acids. Cation exchange resins Dowex 50 Wx2 and Amberlite IR-120 [21,22] have been used as solid acid catalysts for kinetic study of esterification of acetic acid with isobutanol. Esterification of acrylic and lactic acids with butanol using Amberlyst-15 [23,24] and lactic and salicylic acids with methanol using Dowex 50W resin as solid acid catalysts [25,26] has been reported.

Jiang et al [27] have studied catalytic activity of mesoporous TiO_2 solid super acid for esterification of iso amyl alcohol and salicylic acid. Salmi et al [28] have studied methyl acetate formation on polyolefin supported sulfonic acid catalysts. These catalysts were found to be highly stable and active in esterification reaction.

Manohar et al [29] have reported esterification of acetic acid and benzoic acid using ZrO_2 and Mo-ZrO_2 as solid acid catalysts and found that Mo-ZrO_2 exhibits better catalytic activity than ZrO_2. Valdeilson et al [30] have studied esterification of acetic acid with alcohols using supported niobium pentoxide on silica–alumina catalysts.

Silicotungstic acid supported zirconia is reported as an effective catalyst for esterification reactions using formic, acetic, propionic, *n*-butyric acid and *n*-butyl alcohol, isobutyl alcohol and *sec*-butyl alcohol [31]. Chu et al [32] have reported the vapor phase synthesis of ethyl and butyl acetate by immobilized dodecatungstosilicic acid on activated carbon. The rate of esterification was found to be dependent on the partial pressure of the reactants. Also the structure of the alcohol was found to show a profound effect on the esterification rate as well as on the mechanism involved. Dupont et al [33] have reported heteropolyacids supported on activated carbon as catalysts for the esterification of acrylic acid by butanol. Deactivation of the catalyst was observed under flow conditions (from 43 to 32% conversion) and was due to the dissolution of the supported heteropoly acid in the reaction medium (25%). Timofeeva et al [34] have reported esterification of acetic acid and *n*-butyl alcohol using Keggin and Dawson type heteropoly acids and found that the reaction rate depends on the acidity, as well as on the structure and composition of heteropoly acids. The Dawson type heteropoly acids exhibited higher activity compared to the Keggin type heteropoly acids. Sharath et al studied benzyl acetate formation in the presence of zeolites and their ion exchanged forms. They reported reasonably good yield with 100% selectivity [35].

Blanchard and Brennecke have reported that the equilibrium conversion of acetic acid for esterification with ethanol can be shifted from 63 to 72% by applying CO_2 pressure[36].

Ma et al have reported the use of zeolites for the synthesis of ethyl, butyl and benzyl acetates with high yields and 100% selectivity [3].

As mentioned in the above quoted literature, esterification reactions have been widely investigated using several solid acids such as sulphated metal oxides, zeolites, ion exchange resins, heteropoly acids, metal oxides etc. However, it has been observed that though sulphated metal oxide is a very good esterification catalyst, it gets easily deactivated by losing the sulphate ions and thereby recycling of the catalyst is restricted. In case of heteropoly acids, the separation is difficult and when supported on carbon the activity decreases. Ion exchange resins have also been found to be unsatisfactory due to their low operating temperature.

Inorganic ion exchangers of the class of tetravalent metal acid (TMA) salts indicate good potential for application as solid acid catalysts. They behave as cation exchangers due to the presence of exchangeable protons contained in the structural hydroxyl groups. Earlier, esterification reactions have been reported from this laboratory using TMA salts as catalysts [37-42].

In the present endeavor, the potential use of M(IV) phospahates and tungstates of the class of TMA salts have been investigated as solid acid catalysts by studying esterification as a model reaction wherein monoesters Ethyl Acetate (EA), Propyl acetate (PA), Butyl acetate (BA) and Benzyl acetate (BzA) have been synthesized. Further in order to see the effect of crystallinity on the catalytic performance, crystalline M(IV)phosphates have been explored for synthesis of monoesters.The catalytic activity of amorphous and crystalline materials as well as phosphates and tungstates have been compared and correlated with surface properties of the materials.

3.5 EXPERIMENTAL

Catalyst Synthesis and Characterisation

Discussed in Chapter II.

Materials

Acetic acid, ethanol, propanol, butanol, benzyl alcohol, cyclohexane and toluene were procured from Merck India.

Experimental Setup

Esterification reactions were carried out varying different parameters such as reaction time, mole ratio of reactants, amount of catalyst used and these parameters optimized using ZrP (Table 3.1). In a typical reaction, a 100 ml round bottomed flask equipped with a Dean and Stark apparatus, attached to a reflux condenser was used and charged with acetic acid (0.075 mol),alcohol (0.05 mol), catalyst (0.1 g) and 10-15 mL of a suitable solvent. Cyclohexane was used as solvent for synthesis of EA and toluene for PA, BA and BzA. The reaction mixture was refluxed for 8 h. All esters have been synthesized at a fixed temperature – EA (80^{O}C), PA (110^{O}C), BA (115^{O}C) and BzA (115^{O}C). The yields of the ester formed (Table 3.2) were determined by titrating the combined liquid with 0.1 M KOH- EtOH solution. The yield of the esters were calculated using the formula: % yield= [(A-B)/A]x M x 100 where A=acid value of the sample before reaction, B=acid value of sample withdrawn after reaction and M=mole ratio of acid :alcohol. The yields of ester formed were also determined using GC. After completion of reaction, the catalyst was separated by decantation and reaction mixture was distilled to obtain the product. The catalyst was regenerated by refluxing in ethanol followed by drying and acid treated as described in Chapter 2, section 2.5.

3.6 RESULTS AND DISCUSSION

Equilibrium constants of the esterification reactions are low. As in any equilibrium reaction, the reaction may be driven to the product side by controlling the concentration of one of the reactants (Le Chatlier's Principle). When concentration of one of the reactant relative to the other is increased, the reaction is driven to the product side. In order to obtain higher yield of esters, Le Chatlier's Principle has been followed. Solvents cyclohexane and toluene have been employed to remove the water formed during the reaction as a binary azeotrope. Monoesters EA, PA, BA and BzA were synthesized as described in experimental section. Esterification reactions were carried out varying the amount of catalyst, mole ratio of the alcohol to acid and reaction time. The parameters have been optimized in case of ZrP (Table 3.1) and optimum results obtained for all catalysts have been presented in Table 3.2. It was observed that in all the cases the % yield increased with increasing amount of catalyst, which is due to proportional increase in the number of active sites. The % yield of ester increases with increase in mole ratio of acid. Apart from driving the equilibrium towards product side, the excess acid catalyses the reaction. The temperature parameter has not been varied. This is due to the fact that the reaction temperature is sensitive to boiling points of reactants as well as solvents used as azeotrope. During optimization of reaction time, it was observed that the conversion rate was very high initially, indicating that the reaction obeys first order kinetics.

Esterification of monoesters EA, PA and BA has been reported [3] in absence of catalyst and exhibit poor yields. Therefore catalyst is a must for these reactions. In case of BzA however, it is observed that with an excess of acetic acid and in the absence of any catalyst the yield is as high as 90.6 % which is attributed to auto catalysis. In another report [35] high yields of BzA were obtained with small amount of the catalyst but the reaction time was relatively high. Amongst mono esters, catalytic activity/TON increases with increasing chain length of alcohol and the trend in TON is BzA>BA>PA>EA. Higher yields of benzyl acetate could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. It is observed that the catalytic activity/TON is higher for ZrP compared to SnP and TiP which could be attributed to surface acidity values of ZrP(2.34 mmol/g), SnP(1.81 mmol/g) and TiP(0.59 mmol/g). Amongst crystalline and amorphous M(IV) phosphates, though crystalline materials exhibit lower surface area and surface acidity, the catalytic activity/TONs do not decrease much which could be attributed to higher desorption temperatures in ammonia TPD curves indicating presence of strong acidity. Amongst M(IV) tungstates TiW exhibits highest activity/TON for BA and BzA formation attributed to higher surface acidity and surface area values of TiW compared to SnW and ZrW.

In the present work, relatively higher amount of catalyst is required to get optimum yield in the case of EA. Equilibrium constant of lower magnitude, for the reaction of ethyl alcohol with acetic acid can explain this. For PA, BA and BzA the amount of catalyst used per mole of alcohol is 2 g which is lower as compared to zeolites[3] used to carry out the same reaction (3 g per mol of alcohol).

Reaction mechanism:

The mechanism of esterification can be different for the various solid acid catalysts and also depends on gas- or liquid-phase operation as well as the substrate. Chu *et al.* [32] claim that the esterification mechanism of acetic acid with butanol over carbon-supported HPA catalysts proceeds via a protonated alcohol intermediate, but most authors [43-45] proposed a protonated carboxylic acid as the reaction intermediate. The two possible intermediates, protonated ethanol and protonated acetic acid, are shown in Figure 1.

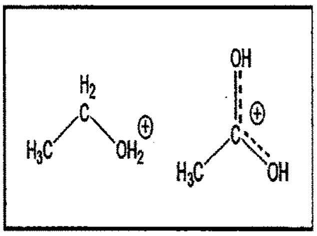

Figure1 Possible protonated Intermediates in esterification reaction

Based on the classical mechanism for acid catalysed esterification reaction, we propose a mechanism(Figure 2) for esterification of ethanol with acetic acid as a typical case, involving a protonated acetic acid intermediate.

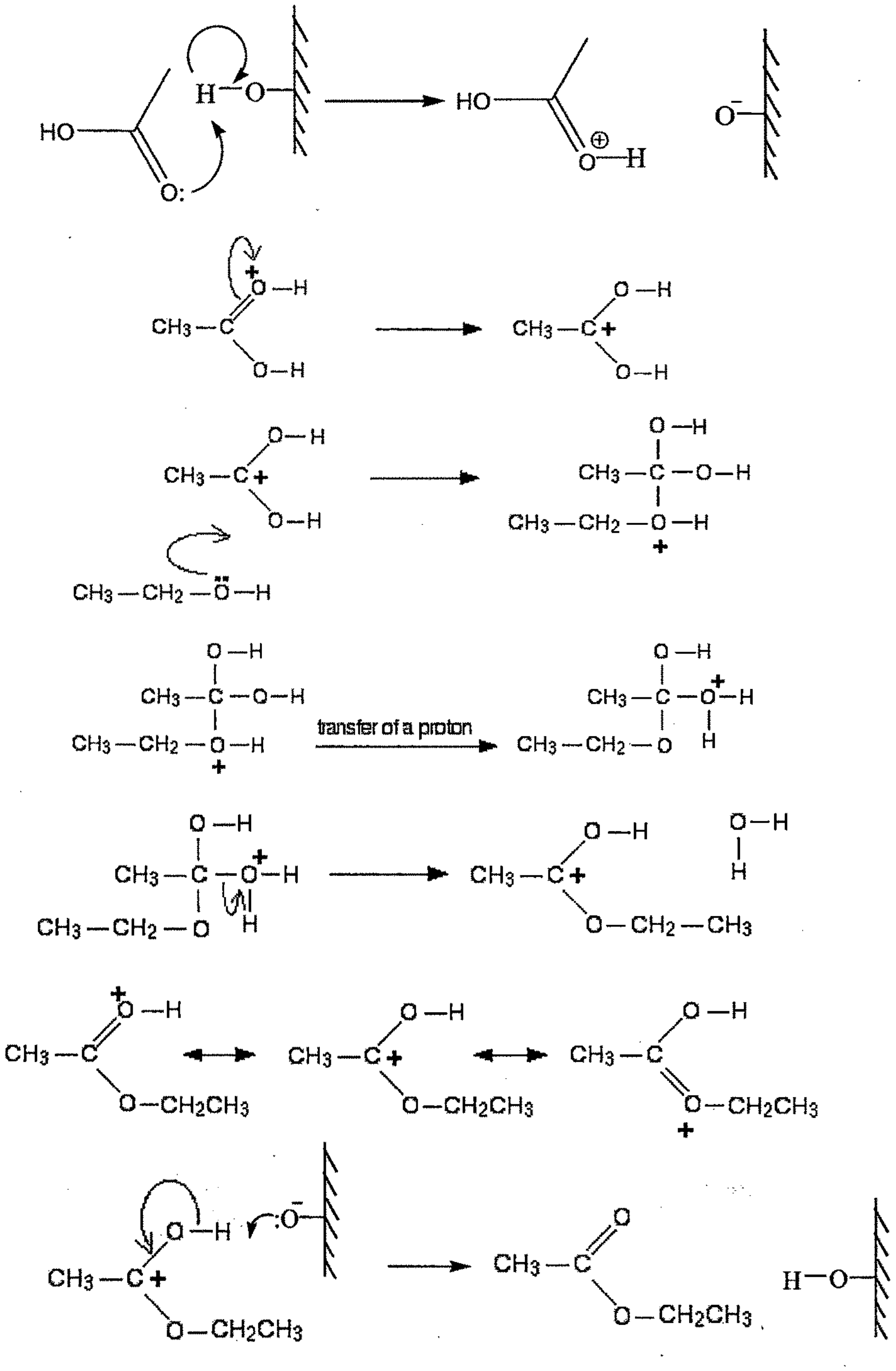

Figure 2 Reaction mechanism for esterification

The activity of the regenerated catalyst was reduced by ~10%. During the course of the reaction, the catalyst colour changes from white to light grey. This is probably due to the reacting molecules getting adsorbed onto the surface of the catalyst. The catalyst however regains its original colour when treated with alcohol for regeneration. The possibility of molecules entering the interstices of the catalyst cannot be ruled out, which is observed from the fact that yields go down after regeneration. The study shows that M(IV) phosphates and tungstates are insoluble during the reaction, are recoverable by simple filtration, and can be reused without significant loss in catalytic activity.

HANSA MEHTA LIBRARY
The University of Baroda

Table 3.1. Optimisation of reaction conditions for mono esters using ZrP:

Substrates (Mole ratio)	**Product**	**A**	**B**	**C**	**% Yield**
ethanol+acetic acid(1:1)	EA	0.05	1	80	15.4
ethanol+acetic acid(1:1)	EA	0.05	2	80	22.7
ethanol+acetic acid(1:1)	EA	0.05	3	80	29.1
ethanol+acetic acid(1:1)	EA	0.05	4	80	34.1
ethanol+acetic acid(1:1)	EA	0.05	5	80	36.2
ethanol+acetic acid(1:1)	EA	0.05	6	80	38.1
ethanol+acetic acid(1:1)	EA	0.05	7	80	39.2
ethanol+acetic acid(1:1)	EA	0.05	8	80	40.1
ethanol+acetic acid(1:1)	EA	0.1	8	80	60.2
ethanol+acetic acid(1:1.5)	EA	0.1	8	80	70.3
ethanol+acetic acid(1:1.5)	EA	0.15	8	80	78.3
ethanol+acetic acid(1.5:1)	EA	0.15	8	80	68.2
ethanol+acetic acid(1:1.5)	EA	0.15	8	110	77.4
propanol+acetic acid(1:1)	PA	0.1	8	110	64.1
propanol+acetic acid(1:1.5)	PA	0.1	8	110	81.3
propanol+acetic acid(1.5:1)	PA	0.1	8	110	60.8
propanol+acetic acid(1:1.5)	PA	0.1	8	130	77.4
butanol+acetic acid(1:1)	BA	0.1	8	110	65.1
butanol+acetic acid(1:1.5)	BA	0.1	8	110	94.1
butanol+acetic acid(1.5:1)	BA	0.1	8	110	62.1
butanol+acetic acid(1:1.5)	BA	0.1	8	130	85.1
butanol+acetic acid(1:1.5)	BA	0.15	8	110	92.7
benzy alcohol+acetic acid(1:1.5)	BzA	0.1	8	110	95.2
benzy alcohol+acetic acid(1:1.5)	BzA	0.1	8	115	100
benzy alcohol+acetic acid(1:1.5)	BzA	0.15	8	130	98.2

A= catalyst amount(g) B= reaction time(h), C= reaction temperature(°C)

Table 3.2. % Yield of monoesters using M(IV)phosphates and tungstates

Ester	ZrP	TiP	SnP	ZrW	TiW	SnW	ZrPcry	TiPcry	SnPcry
EA	78.3	76.1	89.5	93.6	71.9	96.7	76.4	75.5	85.4
TON	27.70	26.9	31.7	33.1	25.4	34.2	27.0	26.7	30.2
PA	81.3	70.0	79.9	72.8	71.5	93.5	80.4	69.2	78.1
TON	48.8	42.0	48.0	43.7	42.9	56.1	48.2	41.5	46.8
BA	94.1	63.1	83.8	72.9	98.6	83.7	92.4	65.1	78.7
TON	63.1	42.3	56.2	48.9	66.1	56.1	61.9	43.6	52.8
BzA	100	82.3	100	67.4	93.8	100	98.5	81.3	98.4
TON	84.1	69.2	84.1	56.6	78.8	84.1	82.8	68.3	82.7

EA=3 g catalyst per mol of alcohol, 80°C

BA=2 g catalyst per mol of alcohol, 110° C

BzA=2 g catalyst per mol of alcohol, 115 °C

3.7 DIESTERS

Diesters dioctyl phthalate (DOP), dibutyl phthalate (DBP) and diethyl malonate (DEM) are important bulk chemicals. DOP and DBP are used as additives in the form of plasticizer, to the important plastic polyvinyl chloride. In western Europe it accounts for about 50% of all plasticizer usage and considered as an industrial standard. DEM occurs naturally in grapes and strawberries as a colourless liquid with an apple-like odour, and is used in perfumes. It is also used to synthesize other compounds such as barbiturates, artificial flavourings and as intermediates for synthesis of vitamin B_1, and vitamin B_6.

Diesters of phthalic anhydride with alcohol can be prepared in two stages (Figure 3) [46].

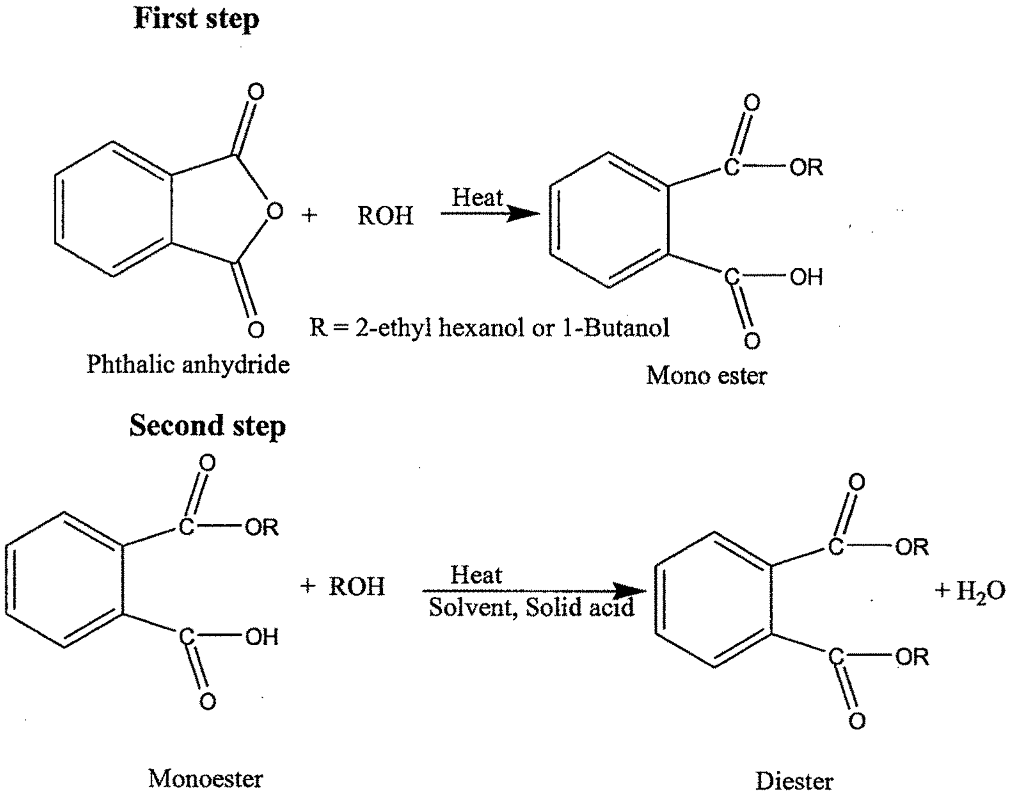

Figure 3 Schematic presentation of diester formation

The first stage is very rapid and can be carried out in the absence of a catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by an acid catalyst, resulting in the formation of water as a by product. The reaction is an equilibrium one and hence to facilitate it in the forward direction the water molecule must be removed by azeotrope formation. The current commercial process is a batch method which is very efficient with respect to its feed stocks. Conversion (based on phthalic anhydride) and selectivity can reach 99.2 and 99.8%, respectively. To reach this high conversion, a 20% excess of alcohol is used. The excess is recovered after reaction by a steam stripping process. Hardly any purification is required after synthesis, because of the high selectivity, usually only a decolourization is carried out. A typical byproduct is the dialkyl ether formed by the condensation of two molecules of alcohol.

For the diester formation, a large number of catalysts have been reported. Normally, liquid phase catalysts such as sulphuric acid, p-toluene sulfonic acid (PTSA), methanesulfonic acid (MSA), hydrochloric acid, phosphoric acid etc. have been used. The kinetics of esterification reaction have been studied by Bhutada and Pangarkar [47] by using homogeneous catalysts such as tetrabutyl titanate (TBT), tetra butyl zirconate (TBZ) and p-toluene sulfonic acid (PTSA). The alkyl titanates have the advantage of very low byproduct formation when compared with PTSA or sulphuric acid. However, their very low activity as compared to the bronsted acids, necessitates reaction temperatures as high as $200^{O}C$. Further, homogeneous catalysts are known to colour the product and cannot be reused. As already mentioned, liquid acids have several disadvantages. Due to these problems accompanied by the increasing environmental awareness, lot of efforts are being focused for replacement of these conventional liquid acids by suitable solid acids.

3.8 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

Nozawa [48] was the first to report the use of complexed metal oxide (or hydrate) catalysts such as $MgO.Al_2O_3$, $Na_2O.Al_2O_3$ for diesterification.

Bhagiyalakshmi et al [49] have studied effect of hydrophobic and hydrophilic properties of Al-MCM-41 (Si/Al = 50,100 and 150) and Hβ zeolite on the esterification of maleic anhydride with ethanol. Wang et al studied the synthesis of n-butyl, isopentyl and benzyl acetates, ethyl and n-butyl benzoates and DOP using ZSM-5 and HY zeolites [3]. HY was found to be an excellent catalyst for the synthesis of phthalates and benzoates compared to ZSM-5.

Suter [50] has reported a noncatalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs.

Bekkum and Schwegler investigated the use of heteropolyacids (homogeneous and carbon supported) for phthalate diester formation [8]. They obtained a superior activity at low temperatures in both homogeneous and supported form. Amini et al [46] have recently reported the use of heteropoly acids for the production of DOP and DBP. They have reported 100% conversion of phthalic anhydride to DOP and DBP over a molybdenum substituted Preyssler heteropolyacid .

Yadav et al have reported the use of solid super acids (sulfated and heteropolyacid supported onto oxides) for the synthesis of DOP [12]. They have reported a selectivity >99% and demonstrated that selection of optimum calcination temperature is a must for the optimum yield. G Lu [51] also investigated DOP synthesis over solid superacids SO_4^{2-}/Ti-M-O (M=Al, Fe, Sn). They obtained superior activity in case of SO_4^{2-}/Ti-Al-Sn-O system and found that acid strength, surface area and catalytic activity of the system is affected by the preparation conditions.

Z H Zhao [52] has also reported the use of aluminophosphate and silicoaluminophosphate molecular sieves as solid acid catalyst for the synthesis of DOP.

DEM synthesis has been reported by Reddy et al [53] using montmirillonite clay, but the yield is low (41 %) and relatively high amount of catalyst (0.5 g) was used. In another report, DEM was synthesized by Jiag et al [54] using the reaction of CO with $ClCH_2COOC_2H_5$. In this case high yield was observed but the reaction was carried out at high pressure.

In the present endeavour, the potential use of M(IV) phospahates and tungstates of the class of TMA salts have been investigated as solid acid catalysts by studying esterification as a model reaction wherein diesters DOP, DBP and DEM have been synthesized. Further, in order to see the effect of crystallinity on the catalytic performance, crystalline M(IV)phosphates have been explored for synthesis of diesters. The catalytic activity of amorphous and crystalline materials as well as phosphates and tungstates have been compared and correlated with surface properties of the materials.

3.9 EXPERIMENTAL

Catalyst Synthesis and Characterisation

Discussed in Chapter II.

Materials

Phthalic anhydride, 2-ethyl 1-hexanol, 1-butanol, malonic acid, cyclohexane and xylene were obtained from Merck. Phthalic anhydride was subjected to sublimation prior to its use. Ethanol was dehydrated using calcium oxide and distilled prior to use.

Experimental Setup

The diesters were synthesized in two steps. In the first step, equimolar proportion (0.025 mole) of acid and alcohol (malonic acid and ethanol for DEM, phthalic anhydride and 2-ethyl 1-hexanol for DOP, phthalic anhydride and 1-butanol for DBP) were taken in a round bottomed flask and the reaction mixture stirred at ~ 85 °C for DEM, ~ 140 °C for DOP, and ~110 °C for DBP for about 10-15 min in absence of any catalyst and solvent. The dicarboxylic acid and anhydride gets completely converted to the monoester, so that the acid concentration at this stage is taken as the initial concentration. The obtained product (monoester) was then subjected to esterification reaction by addition of a second mole (0.025 mole) of respective alcohol, catalyst (0.10 - 0.20 g) and 15 mL solvent (cyclohexane for DEM and DBP and xylene for DOP). The reactions were carried out varying several parameters such as amount of catalyst, mole ratio of reactants, reaction time and these parameters optimized using ZrP (Table 3.3). In all cases the round bottomed flask was fitted with Dean and Stark apparatus, with a condenser to remove water formed during the reaction.

After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product. The catalyst was regenerated by refluxing in ethanol followed by drying and acid treated as described in Chapter 2, section 2.5.

The yields of the diesters formed were determined by titrating the reaction mixture with 0.1 M alcoholic KOH solution. The yield of the esters were calculated using the formula, % yield = [(A - B) / A] × M × 100, where A and B are acid values of the sample withdrawn before and after reaction and M is mole ratio of acid : alcohol. The yield of ester formed was also determined using GC.

3.10 RESULTS AND DISCUSSION

The reaction parameters have been optimized in case of ZrP (Table 3.3) and optimum results obtained for all catalysts have been presented in Table 3.4.

It is observed that yield/TON of esters increases with an increase in the amount of anhydride. The mole ratio of alcohol to anhydride was varied in the range of 1.8 to 2.5 and maximum yields were obtained for the mole ratio of 1.8.

The yield increases with an increase in the catalyst amount due to increased number of active sites per g of the substrate.

It was observed that the initial conversion is very high and then the conversion increases slowly with further increase in time. Maximum yields were obtained at a reaction time of 10 h.

In the present work the yields/ TON for DOP are higher than DBP which could be attributed to higher boiling point of 2 ethyl 1 hexanol compared to 1-butanol. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapour phase and not be available in the liquid phase. This is the reason why the heavier alcohols react more than the lighter ones. Also the stability of carbocation is higher for an intermediate containing branched alcohol (2-ethyl 1-hexanol) compared to straight chain alcohol(n-butanol).

In general, it is observed that diester formation depends on several factors, acidity of the catalyst being the predominant one. However, the effect of nature and amount of alcohol should not be ignored. Esterification yields using 2-ethyl 1-hexanol in the present work is higher than that of 1-butanol due to higher boiling point of the former alcohol and consequently higher reaction rate [43]. Further, high yields in case of DEM, compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step.

It is observed that the catalytic activity/TON is higher for ZrP compared to SnP and TiP which could be attributed to surface acidity values of ZrP(2.34 mmol/g), SnP(1.81 mmol/g) and TiP(0.59 mmol/g). Amongst crystalline and amorphous M(IV) phosphates, though crystalline materials exhibit lower surface area and surface acidity, the catalytic activity/TON do not decrease much which could be attributed to higher desorption temperatures in ammonia TPD curves indicating presence of strong acidity.

The mechanism of diester formation over solid acid catalyst is similar to that of conventional mechanism involving the formation of protonated dicarboxylic acid, using proton donated by the catalyst, followed by nucleophilic attack of alcoholic group to yield the respective monoester (Figure 2). The second carboxylic group present in monoester gets further esterified by the same mechanism in a repeat reaction, which ultimately results in the diester formation [52].

DOP formation has been catalysed by zeolites[3], metallic oxides[49], solid super acids[12,54] and heteropoly acids[8]. Suter[50] has reported a non-catalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs.

In the present work, it is observed that yields of DOP and DBP are low as compared to those obtained when zeolites [3] and solid super acids [55,56] were used as catalysts. When homogeneous liquid acids are used as catalysts for synthesis of DOP and DBP, the result is a product that is coloured and of a poor quality. In the present work though the yields of diesters obtained are low, the advantage is that the diester is the unique product and colourless.

The activity of the regenerated catalyst was reduced by ~10%. During the course of the reaction, the catalyst colour changes from white to light grey. This is probably due to the reacting molecules getting adsorbed on to the surface of the catalyst. The catalyst however regains its original colour when treated with alcohol for regeneration. The possibility of molecules entering the interstices of the catalyst cannot be ruled out, which is observed from the fact that yields go down after regeneration. The study shows that M(IV) phosphates and tungstates are insoluble during the reaction, are recoverable by simple filtration, and can be reused without significant loss in catalytic activity.

Table 3.3. Optimisation of reaction conditions for synthesis of DOP using ZrP:

Substrates (Mole ratio)	**A**	**B**	**C**	**% Yield**
PhA+EH (1:2.5)	0.5	1	115	56.7
PhA+EH (1:2.5)	0.5	3	115	66.4
PhA+EH (1:2.5)	0.5	5	115	73.4
PhA+EH (1:2.5)	0.5	10	115	85.2
PhA+EH (1:2.5)	0.5	10	95	65.1
PhA+EH (1:2.5)	0.3	10	95	62.8
PhA+EH (1:2.5)	0.1	10	95	62.1
PhA+EH (1:2)	0.1	10	95	49.6
PhA+EH (1:2.1)	0.1	10	95	57.6
PhA+EH (1:2.2)	0.1	10	95	58.9
PhA+EH (1:2.3)	0.1	10	95	59.1
PhA+EH (1:2.4)	0.1	10	95	59.1
PhA+EH (1:2.5)	1	10	95	68.2
PhA+EH (1:2.5)	0.5	10	105	66.4
PhA+EH (1:2.5)	0.5	10	115	85.2
PhA+EH (1:1.8)	0.1	10	155	64.3

PhA=phthalic anhydride,EH=2-ethyl 1-hexanol,

A= catalyst amount(g) B= reaction time(h), C= reaction temperature(°C)

Table 3.4. % Yield of DOP using M(IV) phosphates and tungstates at 155°C

Catalyst	Catalyst amount (g)	Mole ratio (Acid/alcohol)	% Yield	TON
ZrP[b]	0.15	0.55	64.3	65.65
SnP[a]	0.15	0.45	65.2	44.38
TiP[b]	0.15	0.55	51.7	35.19
ZrW[b]	0.15	0.55	60.6	41.25
SnW[a]	0.10	0.55	58.2	59.43
TiW[b]	0.10	0.42	30.7	31.35
ZrPcry[a]	0.10	0.55	61.8	63.10
SnPcry[a]	0.10	0.45	62.9	64.22
TiPcry[b]	0.10	0.55	51.9	52.99

Reaction time [a] =8h, [b]=10h

Table 3.5 % Yield of DBP using M(IV) phosphates and tungstates at 155°C

Catalyst	Catalyst amount (g)	Mole ratio (Acid/alcohol)	% Yield	TON
ZrP[b]	0.10	0.55	54.2	40.14
SnP[a]	0.10	0.55	56.1	41.55
TiP[b]	0.10	0.55	42.3	31.33
ZrW[b]	0.10	0.55	19.6	14.52
SnW[a]	0.20	0.55	24.6	9.11
TiW[a]	0.20	0.55	19.5	7.22
ZrPcry[a]	0.10	0.55	51.5	38.14
SnPcry[a]	0.10	0.55	55.8	41.33
TiPcry[b]	0.10	0.55	43.1	31.92

Reaction time [a] =8h, [b]=10h

Table 3.6 % Yield of DEM using M(IV) phosphates and tungstates at 85°C

Catalyst	Catalyst amount (g)	Mole ratio (Acid/alcohol)	% Yield	TON
ZrP	0.25	0.5	61.1	11.99
SnP	0.25	0.5	63.2	12.40
TiP	0.25	0.5	67.3	13.20
ZrW	0.25	0.5	53.7	10.54
SnW	0.25	0.5	58.6	11.50
TiW	0.25	0.5	60.5	11.87
ZrPcry	0.25	0.5	59.2	11.62
SnPcry	0.25	0.5	61.2	12.01
TiPcry	0.25	0.5	64.5	12.65

Reaction time =8h

REFERENCES

[1] Lowenheim F A, Moran M K 1975 *Industrial Chemicals* Wiley-Interscience, NewYork

[2] Harrison H R, Haynes W M and Edmund J 1965 *Chem Ind* **45** 1568

[3] Ma Y, Wang Q L, Yan H, Ji X and Qin Q 1996 *Appl Catal* **139** 51

[4] Lasperas M, Graffin P and Geneste P 1993 *J Catal* **139** 362

[5] Okazaki S and Wada N 1993 *Catal Today* **16** 349

[6] Izuka T and Tanabe K 1984 *Chem Lett* **13** 1085

[7] Baba T and Ono Y 1986 *Appl Catal* **22** 321

[8] Schwegler M A and van Bekkkum H 1991 *Appl Catal* **74** 191

[9] Meuzellar G J, Maat L, Sheldon R A and Kozhenikov I V 1997 *Catal Lett* **45** 249

[10] Verhoef M J, Kooyman P J, Peters J A and van Bekkum H 1999 *Microporous and Mesoporous Mat* **27** 365

[11] D'Souza J and Nagaraju N 2001 *Ind J Chem* **40B** 266

[12] Thorat T S, Yadav V M and Yadav G D 1992 *Appl Catal* **90** 73

[13] Choudhary B M, Bhaskar V, Laxminathan M L, Rao K K and RAghavan K V 2000 *Green Chem* **2** 67

[14] Yadav G D and Goel P K 2000 *Green Chem* **2** 71

[15] Tanaka K, Yoshikawa R, Ying C, Kita H and Okamoto K 2001 *Catal Today* **67** 121

[16] Beers A E W, Spruijt R A, Nijhuis T A, Kaptteijn F and Moulijn J A 2001 *Catal Today* **66** 175

[17] Altıokka M R and Çıtak A 2003 *Appl Catal A: General* **229** 141

[18] Kirumakki S R, Nagaraju N, Chary V R and Narayanan S 2003 *Appl Catal A:General* **248** 161

[19] Ogliaruso M A and Wolfe J. F 1991 *Synthesis of Carboxylic Acids, Esters and their Derivatives*, John Wiley, New York

[20] Yadav G D and Mehta P H, 1994 *Ind Eng Chem Res* **33** 2198

[21] Izci A and Bodur F 2007 *React and Func Poly* 67 **12** 1458

[22] Altiokka M R and Çıtak A 2003 *Appl Catal A: General* **239** 141

[23] Chen X, Xu Z and Okuhara T 1999 *Appl Catal A: General* **180** 261

[24] Darge O and Thyrion F C 1993 *J Chem Tech Biotechnol* **58** 351

[25] Dassy S, Wiame H and Thyrion F C 1994 *J Chem Tech Biotechnol* **59** 149

[26] Choi J I, Hong W H and Chang H N 1996 *Int J Chem Kinet* **28** 37

[27] Jiang T, Zhao Q, Li M and Yin H 2008 *J Hazard Mat* In Press

[28] Maki-Arvela P, Salmi T, Sundell M, Ekman K, Peltonen R and Lehtonen J 1999 *Appl Catal A: General* **184** 25

[29] Manohar B, Reddy V R and Reddy B M 1998 *Synth Comm* **28** 3183

[30] Valdeilson S B, Ivoneide C L,Garcia F, Sílvia D and Dias J 2008 *Catal Today* **133** 106

[31] Parida K and Mallick S 2007*J Mol Catal A: Chemical* **275** 77

[32] Chu W, Yang X, Ye X and Wu Y 1996 *Appl Catal A: General* **145** 125

[33] Dupont P, Jacques C, Vedrine J, Paumard E, Hecquet G and Lefebvre F 1995 *Appl Catal A:General* **129** 217

[34] Timofeeva M N, Matrosova M M, Maksimov G M, Likholobov V A, Golovin A V, Maksimovskaya R I and Paukshtis E A 2001 *Kinet Catal* **42** 868

[35] Sharath K R, Vijayshree S and Nagaraju N 2001 *Ind J Chem Tech* **8** 362

[36] Blanchard L A and Brennecke J F 2001 *Green Chem* **3** 17

[37] Patel P, Shivanekar A and Chudasama U 1992 *Ind J Chem* **31A** 803

[38] Shivanekar A and Chudasama U 1990 *Recent Trends in Catalysis* (Eds.) Vishwanathan B and Pillai C N Narosa Publishing House, New Delhi **489**

[39] Parikh A, Patel A and Chudasama U 1999 *Recent Trends in Catalysis* (Eds.) Murugesan V, Arbindoo B and Palanichamy M. Narosa Publishing House, New Delhi **421**

[40] Beena B and Chudasama U 1995 *Ind J Chem Tech* **2** 339

[41] Patel S and Chudasama U 2002 *Ind J Chem (Sec A)* **41A** 1864

[42] Parikh A and Chudasama U 2003 *Ind J Chem Tech* **10** 44

[43] Corma A, Garcia, H, Iborra, S and Primo J 1989 *J Catal* **120**, 78–87

[44] Santacesaria E, Gelosa D, Danise P and Carra S 1983 *J Catal* **80** 427.

[45] Mochida I, Anju Y, Kato A and Seiyama T 1971 *J Catal* **21** 263.

[46] Arabi M, Amini M M, Abedini M, Nemati A and Alizadeh M 2003 *J Mol Catal A:Chemical* **200** 105

[47] Bhutada S R and Pangarkar V G 1986 *J Chem Tech Biotech* **36** 61

[48] Nozawa R 1975 *Chem Economy Engg Rev* **7(10)** 26

[49] Bhagiyalakshmi M. Vishnu P S, Mabel J H, Murugesan V 2008 *Catal Comm* **9** 2007.

[50] Suter H 1967*Chem Engg Tech* **41** 971

[51] Lu G 1995 *Appl Catal* **133** 11

[52] Zhao Z H 2001 *J Mol Catal* **168** 147

[53] Reddy C R, Iyengar P, Nagendrappa G, Jai Prakash B S 2005 *Catal Lett* **101** 87

[54] Thorat T S, Yadav V M and Yadav G D 1992 *Appl Catal* **90** 73

[55] Song W H, Jiang X Z 2000*Chinese Chem Lett* **11** 1035

[56] Guan Zhong L 1995 *Appl Catal* **133** 11