Kinetic studies on heteropoly and mineral acids catalysed esterification of acetic acid with methanol

Purnima Singh, Rajesh Bhuiya, Anupama Mahato, Kamala Mandy Hansda, Ajit Das and Nagendranath Mahata*

Center for Adsorption and Reaction Engineering on Surface (CARES), Department of Chemistry,
Sidho-Kanho-Birsha University, Purulia-723 104, West Bengal, India

E-mail: nagendranath_mahata.chem@skbu.ac.in

Esterification of carboxylic acid is a very important class of reaction in organic synthesis. Comparative kinetic studies of esterification of acetic acid with methanol catalysed by heteropoly and mineral Bronsted acids, viz. phosphotungstic acid, hydrochloric acid, sulphuric acid, and nitric acid were carried out. The investigation was done in the temperature range of 308 to 328 K. HCl exhibited distinctively higher catalytic activity than the other three Bronsted acids. Specific reaction rate with $H_3PW_{12}O_{40}$ also was found to be excellent, particularly at higher temperature.

Keywords: Esterification, kinetics, catalysis, activation energy, phosphotungstic acid.

Introduction

Organic esters find wide and versatile day to day applications. They are essential players in the manufacture of many value added products in pharmaceutical, food, cosmetics, and fine chemical sectors[1–3]. Being green and environmentally friendly, the esters are also preferred solvent/ reaction media during organic synthesis. The esters are non-corrosive and non-toxic; in addition, they do not possess obnoxious or foul characteristics. Long chain fatty acid methyl/ethyl esters have attracted much attention recently because they are potential substitute of petroleum diesel[4–9]. Thus, esterification of carboxylic acids is of great relevance and important in organic transformations. Production and market of esters are vast. Catalysts play key role in the carboxylic acid to organic ester transformation. Sulphuric acid is being used conventionally since long back. Solid acids like ion exchange resin, supported heteropolyacid, sulphated materials, etc., are being used.

The esterification of fatty acids can be carried out applying strong Bronsted acids as catalyst. Concentrated strong acids are not preferred choice because of their corrosive nature. However, they can be used in sufficiently diluted form provided satisfactory rate of reaction is achieved. Kinetic information is very useful and essential for reactor design and process development. On the other hand, studies on kinetics of catalytic esterification of carboxylic acids are very interesting. Comparative kinetic studies of catalytic esterification of acetic acid with methanol are scanty. Further studies are worth. Kinetic studies of esterification of acetic acid with methanol catalysed by heteropoly and mineral acids viz. sulphuric acid, nitric acid, hydrochloric acid, and phosphotungstic acid are reported in the present study.

Experimental

Esterification of acetic acid with methanol was carried out in a two-necked round bottom flask reactor (500 mL capacity). The reactor was equipped with condenser, oil bath, digital temperature controller, and digital magnetic stirrer. The reaction runs were done under atmospheric pressure and in the temperature range of 308 to 328 K. Methanol was taken in large excess over acetic acid (70:1, molar ratio) in all reaction un to drive the reaction towards the ester and also to keep methanol concentration practically constant during the reaction runs and thus making the reaction effectively pseudo-first order one[10]. In a typical run, a solution of acetic acid (0.0525 mol) and methanol (3.663 mol) was taken in the reactor and heated to reaction temperature. Then, acid catalyst (0.0003 mol, in terms of H^+) in methanol (1 mL) was added and the reaction was initiated by starting stirring (600

rpm). Initial volume of reaction mixture was 150 mL. Aliquots of reaction mixture (1 mL) were pipette out periodically and analysed by conventional titrimetry using standard KOH solution[9]. KOH consumed by the catalyst acid was determined and all the titrimetry data of reaction mixtures were corrected. Reaction conditions at a glance were as follows. Initial concentration of acetic acid = 0.350 mol L^{-1}; initial concentration of methanol = 24.420 mol L^{-1}; reaction temperature = 308, 313, 318, 323, and 328 K; concentration of catalyst (H$^+$) = 0.002 mol L^{-1}; acid catalysts studied = H_2SO_4, HCl, HNO_3, and $H_3PW_{12}O_{40}$. The amount of different acid catalysts was determined keeping in mind the number of acidic protons in the particular catalyst acid molecule, i.e. two for sulphuric acid (H_2SO_4), one for hydrochloric acid (HCl) and nitric acid (HNO_3), and three for phosphotungstic acid ($H_3PW_{12}O_{40}$). Thus, H$^+$ concentration was same in the reaction runs with all catalytic species. Reaction runs in absence of external catalyst was also performed.

Results and discussion

In general, esterification reaction between carboxylic acid and alcohol follows second order kinetics with respect to the reactants[11]. However, if one reactant is taken in large excess over the other then the concentration of the reactant taken in large excess practically remains constant and the reaction effectively becomes first order one with respect to the other reactant that has been taken in smaller concentration. Such reactions are called pseudo-first order ones. In the present study, methanol (M) was taken in large excess over acetic acid (AA) and only those data corresponding to less than 20% conversion of AA were considered. Hence, concentration of M practically remained constant in the domain of study. As a result, the reaction can be considered as pseudo-first order one with respect to AA, and irreversible towards the ester.

$$AA + M + [H^+] \rightarrow Ester + H_2O$$
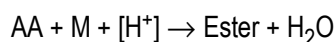
$$Rate = - dC_{AA}/dt = kC_{AA}C_M C_{H^+}$$

C terms are concentrations, t is time, and k is the rate constant. Now, C_{H^+} is constant and C_M is also practically constant.

$$Therefore, - dC_{AA}/dt = k'C_{AA}$$

where $k' = kC_M C_{H^+}$ is the pseudo-first order rate constant. Integration of the above equation results

$$\ln C_{AA} = \ln C^0_{AA} - k't \qquad (1)$$

where, $\ln C^0_{AA}$ is the initial concentration of AA.

Plot of $\ln C_{AA}$ with t gives straight line. The slope of the line gives the value of pseudo-first order rate constant, k′.

The esterification reactions between AA and M catalysed by H_2SO_4, HCl, HNO_3, and $H_3PW_{12}O_{40}$ were carried out at 308, 313, 318, 323, and 328 K. Reaction runs in absence of catalyst acid were also performed; no consumption of acetic acid was observed even at extended period of reaction time of 6 h at the highest reaction temperature (328 K). Therefore, it is obvious that transformation of acetic acid to ester was effected only by the applied external acid catalysts. The plots of $\ln C_{AA}$ vs t were made and are presented in Figs. 1, 2, 3 and 4. The data points beautifully fitted in straight lines. The results indicated that the reaction, under the applied conditions, followed first order kinetics[9,10,12].
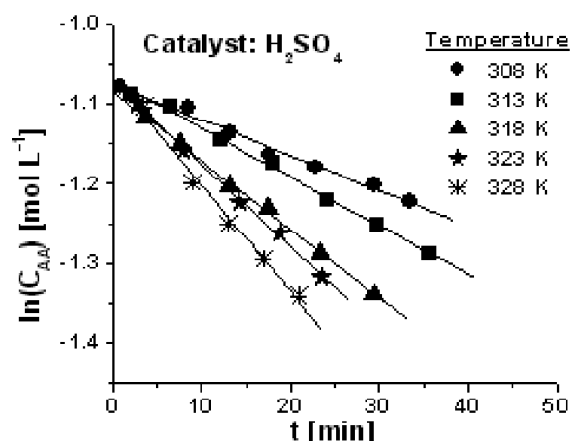

Fig. 1. First order kinetic plots of esterification of acetic acid with methanol catalysed by H_2SO_4.
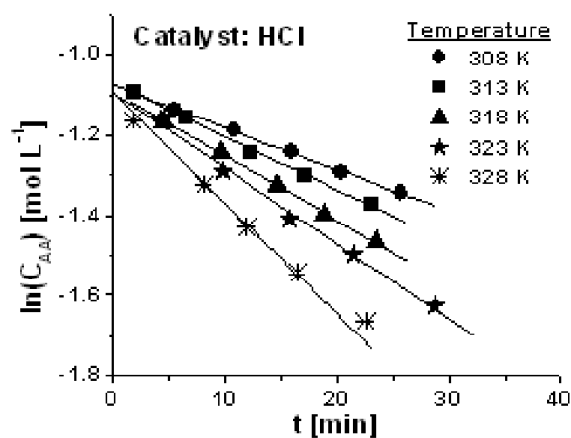

Fig. 2. First order kinetic plots of esterification of acetic acid with methanol catalysed by HCl.
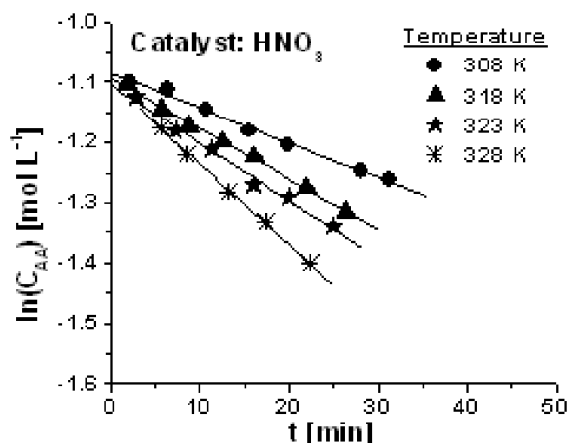
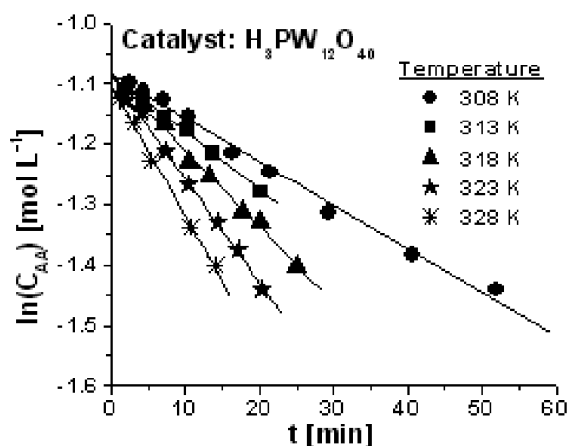**Fig. 3.** First order kinetic plots of esterification of acetic acid with methanol catalysed by HNO_3.

Fig. 4. First order kinetic plots of esterification of acetic acid with methanol catalysed by $H_3PW_{12}O_{40}$.

The reaction rate constants were determined from the slopes of the corresponding straight lines and are listed in Table 1.

The apparent activation energy was determined applying Arrhenius equation,

$$k' = A \exp(-E_a/RT) \qquad (2)$$

k' is the pseudo-first order rate constant, A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the temperature. Now, taking natural logarithm of eq. (2),

Table 1. Rate constants of the esterification of acetic acid with methanol

Temperature	Pseudo-first order rate constants, k' (min^{-1}); Esterification of acetic acid with methanol catalysed by			
(K)	H_2SO_4	HCl	HNO_3	$H_3PW_{12}O_{40}$
308	0.0044	0.0104	0.0058	0.0072
313	0.0061	0.0132	–	0.0096
318	0.0086	0.0160	0.0083	0.0127
323	0.0103	0.0187	0.0106	0.0172
328	0.0133	0.0237	0.0135	0.0216

$$\ln k' = \ln A - E_a/RT$$

Plot of ln k' vs 1/T gives straight line. Apparent activation energy (E_a) can be calculated from the slope (E_a/R) of the straight line. The pseudo-first order reaction rate constants of esterification of AA with M, catalysed by the four Bronsted acids, in the temperature range of 308 to 328 K, were determined and are listed in Table 1. Arrhenius plots (ln k vs 1/T) were constructed applying the data of Table 1 and are presented in Figs. 5, 6, 7, and 8. The data points nicely maintained linearity.

The apparent activation energies (E_a) were determined from the slopes (E_a/R) and are listed in Table 2.

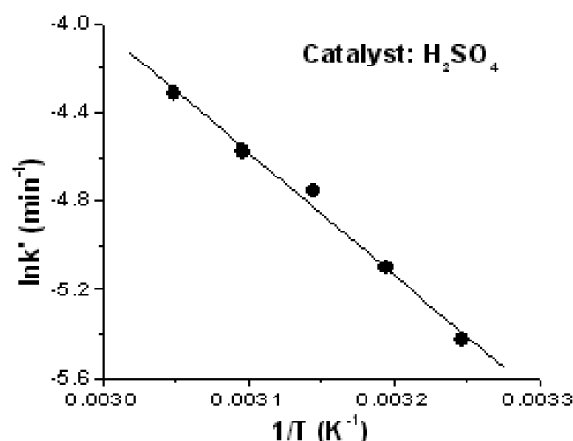The catalytic activities of the hetropoly and mineral

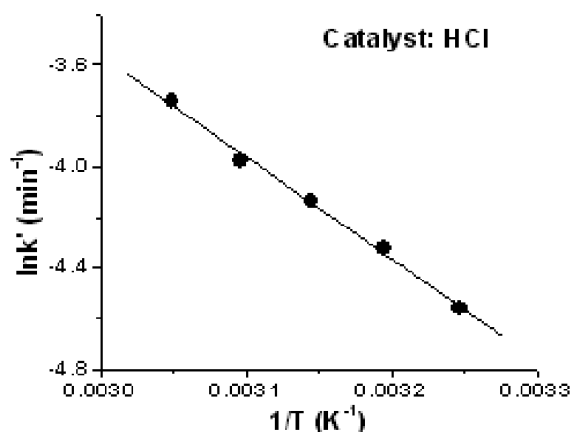**Fig. 5.** Arrhenius plot of esterification of acetic acid with methanol catalysed by H_2SO_4.

Fig. 6. Arrhenius plot of esterification of acetic acid with methanol catalysed by HCl.
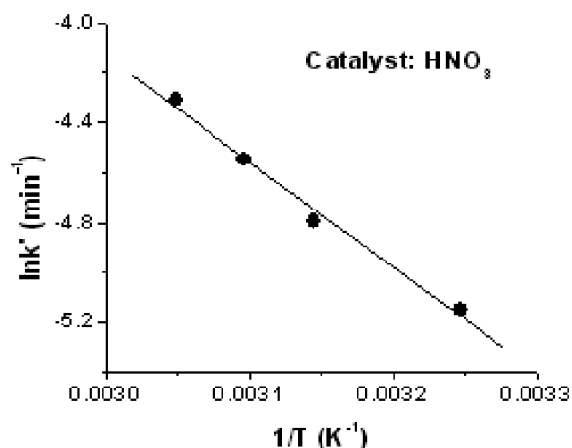

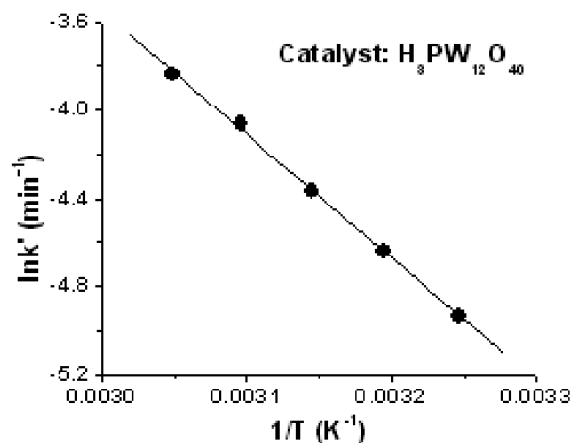**Fig. 7.** Arrhenius plot of esterification of acetic acid with methanol catalysed by HNO_3.

Fig. 8. Arrhenius plot of esterification of acetic acid with methanol catalysed by $H_3PW_{12}O_{40}$.

Table 2. Apparent activation energy of esterification of acetic acid with methanol catalysed by heteropoly and mineral Bronsted acids

Catalyst	Activation energy, E_a (kJ mol^{-1})
H_2SO_4	45.94
HCl	33.52
HNO_3	35.07
$H_3PW_{12}O_{40}$	46.63

Bronsted acids (H_2SO_4, HCl, and HNO_3, $H_3PW_{12}O_{40}$) in the esterification of acetic acid with methanol are compared at a glance in Table 1. The results clearly show that the rate of the reaction catalysed by HCl is higher than that catalysed by the other three acids at all temperature. Activity of HCl is more or less double to that of H_2SO_4, which is used frequently. The heteropoly acid, $H_3PW_{12}O_{40}$, also exhibited excellent activity. The activity of PTA is distinctively lower than that of HCl at lower temperature. However, the activity of $H_3PW_{12}O_{40}$ becomes comparable to that of HCl as the temperature is increased. Faster increase in activity of $H_3PW_{12}O_{40}$ with increase in temperature reflected in the higher value of activation energy. In spite of excellent specific activity, HCl is not a preferred catalyst in concentrated form due to its corrosive and volatile nature. However, when sufficiently diluted, as in this study (0.002 mol L^{-1}, pH ~ 2.7), HCl can be used safely. Human lower stomach experiences HCl concentration of this level or higher[13,14]. $H_3PW_{12}O_{40}$, being non-hazardous, is also a potentially good candidate[3,10–12].

Conclusions

Kinetic studies of esterification of acetic acid with methanol catalysed by heteropoly and mineral Bronsted acids ($H_3PW_{12}O_{40}$, H_2SO_4, HCl, and HNO_3) were carried out. In terms of activity, the catalysts can be graded as: HCl > $H_3PW_{12}O_{40}$ > HNO_3 > H_2SO_4. Being highly active, HCl deserves attention; it can be successfully applied in sufficiently diluted form. $H_3PW_{12}O_{40}$ also exhibited excellent activity. It is a potentially good candidate as it is environmentally friendly.

Acknowledgements

References

1. A. Q. Yaakob and S. Bhatia, *IIUM Eng. J.*, 2004, **5**, 35.

2. A. Zaidi, J. L. Gainer, G. Carta, A. Mrani, T. Kadiri, Y. Belarbi and A. Mir, *J. Biotechnol.*, 2002, **93**, 209.

3. J. C. Juan, J. Zhang and M. A. Yarmo, *J. Mol. Catal. A: Chem.*, 2007, **267**, 265.

4. F. Ma and M. A. Hanna, *Bioresource Technol.*, 1999, **70**, 1.

5. A. A. Kiss, A. C. Dimian and G. Rothenberg, *Adv. Synth. Catal.*, 2006, **348**, 75.

6. M. G. Kulkarni, R. Gopinath, L. C. Meher and A. K. Dalai, *Green Chem.*, 2006, **8**, 1056.

7. D. G. Cantrell, L. J. Gillie, A. F. Lee and K. Wilson, *Appl. Catal. A: Gen.*, 2005, **287**, 183.

8. K. Srilatha, N. Lingaiah, B. L. A. P. Devi, R. B. N. Prasad, S. Venkateswar and P. S. S. Prasad, *Appl. Catal. A: Gen.*, 2009, **365**, 28.

9. A. V. Metre and K. Nath, *Pol. J. Chem. Tech.*, 2015, **17**, 88.

10. A. L. Cardoso, R. Augusti and M. J. D. Silva, *J. Am. Oil Chem. Soc.*, 2008, **85**, 555.

11. V. Brahmkhatri and A. Patel, *Fuel*, 2012, **102**, 72.

12. A. Alsalme, E.F. Kozhevnikova and I. V. Kozhevnikov, *Appl. Catal. A: Gen.*, 2008, **349**, 170.

13. G. McLauchlan, G. M. Fullarton, G. P. Crean and K. E. L. McColl, *Gut*, 1989, **30**, 53.

14. E. M. M. Quigley and L. A. Turnberg, *Gastroenterology*, 1987, **92**, 1876.