



Kinetics of methyl esterification of lauric acid catalysed by Bronsted acids

Anupama Mahato, Purnima Singh, 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

Manuscript received online 04 December 2020, accepted 24 December 2020

Methyl/ethyl esters of long chain fatty acids are potential fuels for diesel engines. Kinetics of esterification of lauric acid with methanol catalysed by four Bronsted acids, viz. hydrochloric acid, sulphuric acid, nitric acid, and phosphotungstic acid are investigated in the present study. The reaction was investigated in the temperature range of 308–328 K. Catalytic activity of HCl was found to be much higher than that of the other three Bronsted acids. Specific reaction rate with HCl was more than double to that with H_2SO_4 , which is used frequently. Specific reaction rate with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ also was found to be excellent.

Keywords: Esterification, biodiesel, kinetics, lauric acid, activation energy.

Introduction

Esterification of carboxylic acids is highly important in organic transformation. Organic esters are extensively used as intermediates/building blocks in food, cosmetics, pharmaceutical and fine chemical industries^{1–3}. They also enjoy the credibility of preference as solvent because they are green and environmentally friendly. They are non-toxic and non-corrosive; and do not possess any foul characteristics. Recently, mono-alkyl long chain fatty esters have attracted much attention because they can be substitute of petroleum diesel^{4–9}. Fossil liquid fuel/petroleum stock is limited and is depleting day by day. Also, consumption of fossil fuel results severe damage to the environment by discharging obnoxious sulphur and nitrogen oxides in addition to excessive pumping of CO_2 , a major culprit responsible for global warming, into the atmosphere. Thus, search for alternate liquid fuel is inevitable. The mono-alkyl long chain fatty esters, the so called bio-diesel, might be the right answer. They are renewable; carbon balance is zero. Also, they are extremely clean; they do not contain sulphur or nitrogen compound^{5,9}. Currently, most of bio-diesel is produced by trans-esterification of vegetable oils and animal fats⁹. Because of short crop cycle, vegetable oils can be potentially good resource. In addition, production of bio-diesel from vegetable oil creates

a positive social impact by uplifting rural economy⁸. However, vegetable oils contain significant amount of free fatty acids⁹. Hence, utilisation of the free fatty acids must be done to make the process more viable economically. The free fatty acids are generally esterified with short chain alcohols like methanol or ethanol. Thus, methyl esterification of long chain fatty acids is of immense importance. The esterification can be carried out using Bronsted acid as catalyst. Even though concentrated strong mineral acids are not preferred because of their corrosive nature, they can be applied in sufficiently diluted form provided acceptable rate of reaction is achieved. Also, academic interest demands studies on this line. Till date there is no report in the literature on the direct comparison of kinetic studies of esterification of lauric acid with methanol catalysed by mineral Bronsted acids and heteropoly acid. In the present study, kinetics of esterification of lauric acid with methanol catalysed by four Bronsted acids viz. phosphotungstic acid, sulphuric acid, hydrochloric acid and nitric acid is reported.

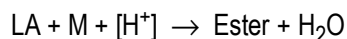
Experimental

Esterification of lauric acid with methanol was carried out in a glass reactor (500 mL capacity). The reactor was equipped with ice-water condenser, digital magnetic stirrer,

oil bath, and digital temperature controller. The reaction runs were performed in the temperature range of 308 to 328 K. Methanol was taken in large excess over the lauric acid (68:1, molar ratio). Large excess of methanol was taken to drive the reaction towards the ester and also to keep methanol concentration practically constant during the reaction and thus making the reaction pseudo-first order one¹⁰. In a typical reaction run, a solution of lauric acid (0.051 mol) and methanol (3.465 mol) was heated to reaction temperature. Then, 0.0003 mol acid catalyst (in terms of H⁺) in methanol (1 mL) was added and the reaction was initiated immediately by starting stirring (700 rpm). Initial total volume of reaction mixture was 150 mL. Periodically 1 mL aliquots of reaction mixture were pipette out and analysed by conventional titrimetry using standard KOH solution⁹. KOH consumed by the catalyst acid was determined and all titrimetry data of reaction mixtures were corrected. Reaction conditions at a glance are as follows. Initial concentration of lauric acid = 0.340 mol L⁻¹; initial concentration of methanol = 23.100 mol L⁻¹; reaction temperature = 308, 313, 318, 323, and 328 K; concentration of catalyst (H⁺) = 0.002 mol L⁻¹; acid catalysts = H₃PW₁₂O₄₀, H₂SO₄, HCl, HNO₃. The amount of different acid catalysts was determined keeping in mind the number of acidic protons in the particular acid molecule, i.e. three for phosphotungstic acid (H₃PW₁₂O₄₀), two for sulphuric acid (H₂SO₄), one for hydrochloric acid (HCl), and one for nitric acid (HNO₃). Thus, H⁺ concentration was same in all the reaction runs. Reaction runs in absence of external catalyst was also performed.

Results and discussion

The esterification of lauric acid (LA) with methanol (M) follows second order kinetics with respect to the reactants¹¹. However, M was taken in large excess compared to LA and only those data corresponding to less than 20% conversion of LA were considered in the present study. Hence, concentration of M practically remained constant. Thus, the reaction can be considered as pseudo-first order one and irreversible towards the ester.



$$\text{Rate} = -dC_{\text{LA}}/dt = kC_{\text{LA}}C_{\text{M}}C_{\text{H}^+}$$

C terms are concentrations, t is time, and k is the rate con-

stant. Now, C_{H⁺} is constant and C_M is also practically constant.

$$\text{Therefore, } -dC_{\text{LA}}/dt = k'C_{\text{LA}}$$

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

$$\ln C_{\text{LA}} = \ln C_{\text{LA}}^0 - k't \quad (1)$$

where, ln C_{LA}⁰ is the initial concentration of LA.

Plot of ln C_{LA} with t gives straight line; the slope of the line gives the value of pseudo-first order rate constant, k'.

The esterification of LA with M was carried out at 308, 313, 318, 323, and 328 K, catalysed by H₃PW₁₂O₄₀, H₂SO₄, HCl, and HNO₃. Reaction run in absence of external acid was also carried out; no consumption of lauric acid was detected even at extended period of time of 5 h. Hence, it is clear that conversion of lauric acid was effected only by the external acid catalysts applied. The plots of ln C_{LA} vs t were made and shown in Figs. 1, 2, 3, and 4. The data points nicely fitted in straight lines, indicating that the reaction followed pseudo-first order kinetic pathway^{9,10,12}.

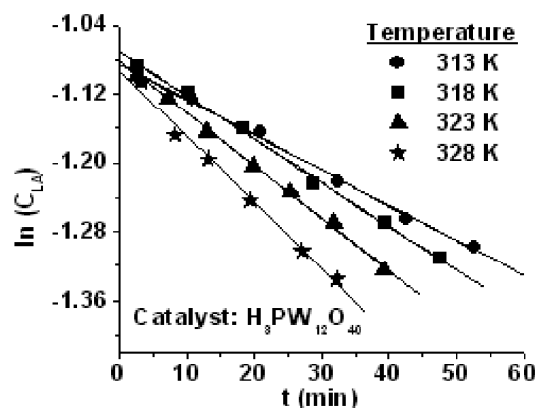


Fig. 1. First order kinetic plots of esterification of lauric acid with methanol catalysed by H₃PW₁₂O₄₀.

The rate constants were determined from the slopes and are shown in Table 1.

Apparent activation energy was determined applying Arrhenius equation,

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

k' is the pseudo-first order rate constant, A is pre-exponen-

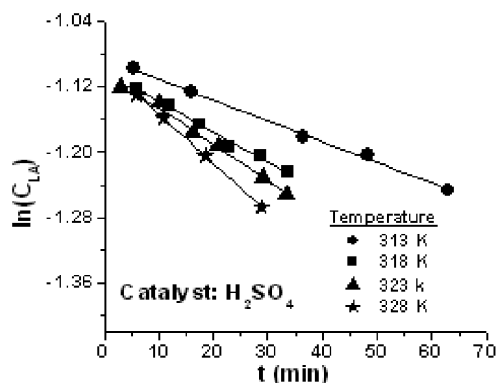


Fig. 2. First order kinetic plots of esterification of lauric acid with methanol catalysed by H_2SO_4 .

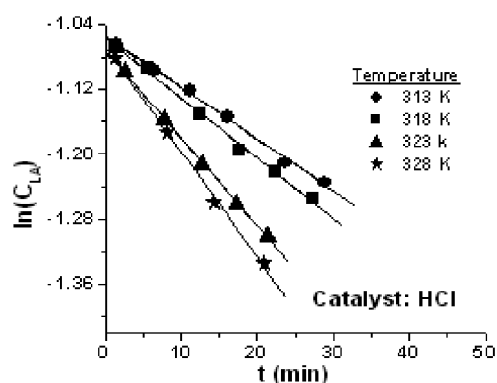


Fig. 3. First order kinetic plots of esterification of lauric acid with methanol catalysed by HCl.

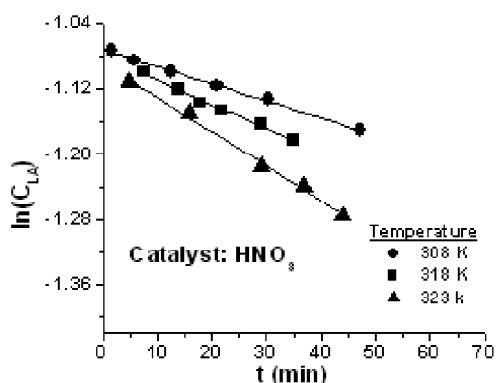


Fig. 4. First order kinetic plots of esterification of lauric acid with methanol catalysed by HNO_3 .

tial factor, E_a is apparent activation energy, R is the universal gas constant, and T is temperature. Now, taking natural

Table 1. Rate constants of the esterification of lauric acid with methanol catalysed by some Bronsted acids

Temperature (K)	Pseudo-first order rate constants, k' (min^{-1}); Esterification of lauric acid with methanol catalysed by			
	$H_3PW_{12}O_{40}$	H_2SO_4	HCl	HNO_3
308	–	–	–	0.00207
313	0.00409	0.00253	0.00636	–
318	0.00507	0.00372	0.00741	0.00294
323	0.00607	0.00443	0.0108	0.00419
328	0.00771	0.00599	0.01251	–

logarithm of eq. (2),

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

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 rate constants of the esterification of LA with M, catalysed by four Bronsted acids, at the temperature range of 308 to 328 K, were determined and are shown in Table 1. Arrhenius plots ($\ln k'$ vs $1/T$) were constructed utilizing the data of Table 1 and shown in Fig. 5, 6, 7, and 8.

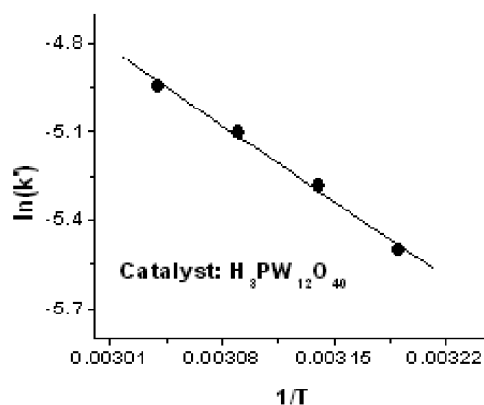


Fig. 5. Arrhenius plot of esterification of lauric acid with methanol catalysed by $H_3PW_{12}O_{40}$.

The data points satisfactorily maintained linearity with negative slope. The apparent activation energies (E_a) were determined from the slopes (E_a/R) and listed in Table 2.

The activities of the four Bronsted acids ($H_3PW_{12}O_{40}$, H_2SO_4 , HCl, and HNO_3) in the esterification of lauric acid

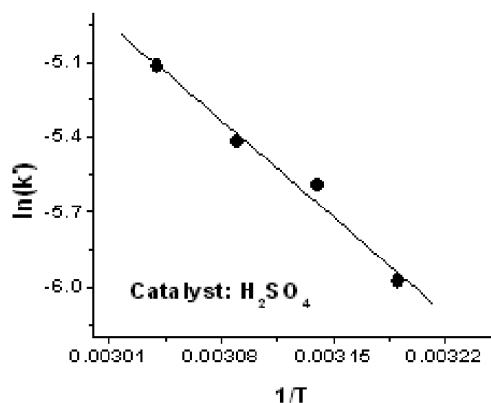


Fig. 6. Arrhenius plot of esterification of lauric acid with methanol catalysed by H_2SO_4 .

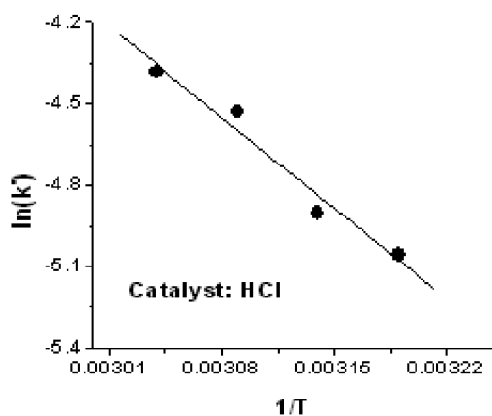


Fig. 7. Arrhenius plot of esterification of lauric acid with methanol catalysed by HCl.

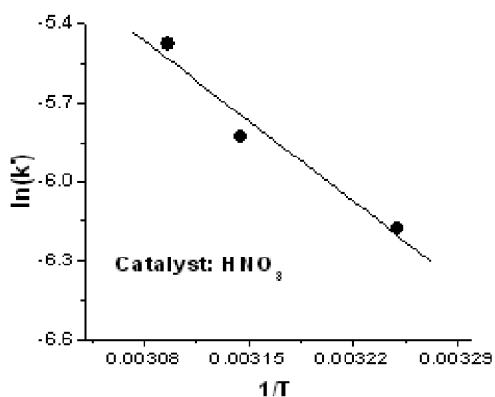


Fig. 8. Arrhenius plot of esterification of lauric acid with methanol catalysed by HNO_3 .

Table 2. Apparent activation energy of esterification of lauric acid with methanol catalysed by Bronsted acids

Catalyst	Activation energy, E_a (kJ mol^{-1})
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	30.63
H_2SO_4	45.88
HCl	40.00
HNO_3	36.42

with methanol are compared at a glance in Table 1. The results clearly show that the rate of the reaction catalysed by HCl is much higher than that catalysed by the other three Bronsted acids. Activity of HCl is more than double to that of H_2SO_4 , which is used frequently. $\text{H}_3\text{PW}_{12}\text{O}_{40}$, also exhibited excellent activity. In spite of great specific activity, HCl is not a preferred catalyst in concentrated form due to its volatile and corrosive nature. However, when sufficiently diluted, as in this study (0.002 mol L^{-1} , $\text{pH} \sim 2.7$), HCl can be used safely. Human lower stomach experiences HCl concentration of this level or higher^{13,14}. $\text{H}_3\text{PW}_{12}\text{O}_{40}$, being non-hazardous, is also a potential candidate^{3,10-12}. It also exhibited lowest activation energy among the four Bronsted acids applied in this study.

Conclusions

Kinetic investigations of esterification of lauric acid catalysed by four Bronsted acids ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, H_2SO_4 , HCl, and HNO_3) were carried out. In terms of specific reaction rate, the catalysts can be graded as: $\text{HCl} > \text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_2\text{SO}_4 > \text{HNO}_3$. Being highly active, HCl deserves attention; it can be successfully applied in sufficiently diluted form. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ also exhibited excellent activity. Being environmentally friendly and possessing excellent activity, it can be a potential candidate.

Acknowledgements

Ajit Das gratefully thanks Council of Scientific and Industrial Research (CSIR), New Delhi for a Senior Research Fellowship.

References

1. A. Zaidi, J. L. Gainer, G. Carta, A. Mrani, T. Kadiri, Y. Belarbi and A. Mir, *J. Biotechnol.*, 2002, **93**, 209.
2. A. Q. Yaakob and S. Bhatia, *IJUM Eng. J.*, 2004, **5**, 35.

Mahato *et al.*: Kinetics of methyl esterification of lauric acid catalysed by Bronsted acids

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. D. G. Cantrell, L. J. Gillie, A. F. Lee and K. Wilson, *Appl. Catal. A: Gen.*, 2005, **287**, 183.
6. M. G. Kulkarni, R. Gopinath, L. C. Meher and A. K. Dalai, *Green Chem.*, 2006, **8**, 1056.
7. 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.
8. A. A. Kiss, A. C. Dimian and G. Rothenberg, *Adv. Synth. Catal.*, 2006, **348**, 75.
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. Alsalmeh, E. F. Kozhevnikova and I. V. Kozhevnikov, *Appl. Catal. A: Gen.*, 2008, **349**, 170.
13. E. M. M. Quigley and L. A. Turnberg, *Gastroenterology*, 1987, **92**, 1876.
14. G. McLauchlan, G. M. Fullarton, G. P. Crean and K. E. L. McColl, *Gut*, 1989, **30**, 53.