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A Kinetic Study on the Esterification of Palmitic Acid in Methanol

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ABSTRAK

Tindak balas pengesteran ke atas asid palmitik dalam metanol berlebihan menggunakan mangkin tionil klorida telah dikaji. Didapati $SOCl_2$ mampu bertindak sebagai mangkin pengesteran yang baik. Hasil metil palmitat yang diperolehi telah dianalisis dengan menggunakan kaedah kromatografi gas - spektroskopi jisim. Kajian pengoptimuman juga telah dilakukan untuk menentukan peratus berat mangkin terhadap asid palmitik, suhu dan masa yang memberikan peratusan hasil yang tinggi. Keputusan yang didapati ialah: 0.3 % berat mangkin terhadap asid, suhu 80°C dan masa tindak balas 2 jam. Pemalar kadar dan seterusnya tenaga pengaktifan bagi tindak balas pengesteran yang dikaji telah dikira.

ABSTRACT

The esterification of palmitic acid in excess methanol using thionyl chloride as catalyst has been investigated. It was found that $SOCl_2$ behaved as a good esterification catalyst. The methyl palmitate product obtained has been analysed and characterized using gas chromatography and gas chromatography-mass spectrometry. Optimization studies to determine the weight percent of catalyst to acid, temperature and time to produce maximum yield of product have also been carried out. The optimum conditions were found to be 0.3% weight of catalyst to acid, 80°C and 2 hours. Subsequently, the rate constants at various temperatures and activation energy of the system were calculated.

Keywords: esterification, optimization, fatty acid, rate constant, order, activation energy

INTRODUCTION

In general, an esterification reaction is one that produces an ester and one example is the reaction between an acid and an alcohol (Equation 1) (Solomon 1976).

$$\begin{array}{lll} \text{RCOOH} + \text{R'OH} & \rightleftharpoons & \text{RCOOR'} + \text{H}_2\text{O} \\ \text{carboxylic acid} \quad \text{alcohol} & & \text{alkyl ester} \end{array} \qquad [1]$$

The above reaction is reversible and the rate of the reaction can be accelerated with the assistance of a catalyst. Common catalysts used are acids or bases. Although the acids are converted to esters, the use of the above mentioned catalysts has a number of disadvantages such as long reaction times, side reactions when an excess of catalyst is used which lead to unstable and discoloured products. Furthermore, when acids or bases are used as transesterification catalysts on triglycerides, the free fatty acids present are not converted to esters (Ayorinde *et al.* 1988).

The ability of $SOCl_2$ to catalyse an esterification reaction has been reported by a number of researchers. Filho and Goissis (1982) have successfully esterified sixteen amino acids in methanol at 100°C for an hour using 3M $SOCl_2$ as catalyst. High yields of the esters were obtained. In a separate study by Somitsu, he reported the esterification of acetic acid in Me_2CHOH at 55-60°C for 2 hours to obtain 81% of the ester, $MeCOOCHMe_2$. (Chemical Abstract 58509c). A number of tin-based compounds have been shown by Ariffin *et al.* (1986) to be effective esterification catalysts.

Many uses have been found for the fatty acid esters. Their non-corrosive nature makes them better raw material for the production of other oleochemicals compared to their acids (Ahmad and Kang 1997). The esters have been proven to be a potential fuel for the diesel engines and also as a drilling fluid (Ariffin *et al.* 1991). In addition, the esters are used in other industries concerned with the production of soaps, cosmetics, drugs and other synthetics.

The present research was carried out to determine the catalytic ability of $SOCl_2$ on the esterification of palmitic acid, primarily the optimum conditions for the esterification process, the rate constants at different reaction temperatures and subsequently the activation energy of the system using the data available.

MATERIALS AND METHODS

Chemicals and Instrumentation

Palmitic acid (% purity), purchased from Merck, Germany, and $SOCl_2$ (>99% purity) from Fluka, Germany, were used without purification. The solvent, methanol, was distilled over calcium hydride. The standard, methyl palmitate, was obtained from Aldrich, St. Louis United States.

Gas chromatographic analysis was performed on a Hewlett Packard, HP 5890 Series II spectrometer equipped with a 50% methylphenyl silicone capillary column (25 m × 0.25 μm); the temperature was programmed from 100 to 270 °C at 10°/min. The injection port was set at 350 °C and the amount of sample injected was 0.2 μl.

Esterification Reaction – Testing the Catalytic Activity of $SOCl_2$

Palmitic acid (3.00 g, 11.72 mmol) was placed in a reactor followed by dried methanol (70 ml) and 13% of $SOCl_2$ to fatty acid (w/w) (0.39 g, 3.28 mmol). The mixture was refluxed at 80°C for 3 hours, after which methanol was removed on the rotary evaporator. The product was analysed using GC and GC-MS.

Determination of Optimum Conditions for Esterification

Palmitic acid (3 g, 11.72 mmol) was placed in a reactor followed by dried methanol (70 ml) and 4% $SOCl_2$ (w/w) (0.12 g, 1.01 mmol) were added. The mixture was refluxed for 3 hours at 80°C followed by removal of methanol.

The above procedure was repeated using various weight percentages of $SOCl_2$ to fatty acid as below: 3, 2, 1, 0.7, 0.5 and 0.3%.

Kinetic Measurements and Analysis

Palmitic acid (3 g, 11.72 mmol) was placed in a reactor followed by dried methanol (70 ml). The catalyst, $SOCl_2$, 0.3% (w/w) was added to the reaction mixture. The mixture was stirred at 80°C and at different time intervals (20 – 180 min), 1 ml of the sample was withdrawn and analysed using GC to determine the percentage conversion into product. The above procedure was repeated at various temperatures: 70, 60, 50 and 40oC.

For the purpose of this study, the concentration of reactant, [A], is obtained from the chromatogram and is related to the percentage conversion into product. Therefore, the concentration of the reactant A at various times is equal to the concentration at t = 0 (*i.e.* 100%) less the concentration of product at different times. For example, for the reaction performed at 40°C, the concentration of A at t = 20 min would be equal to 81.73 (100 - 18.27). The calculation for the concentration of reactant this way is acceptable because the esterification proceeds cleanly to afford methyl palmitate and water only.

RESULTS AND DISCUSSION

Testing the Catalytic Activity of $SOCl_2$ on the Esterification of Palmitic Acid

The esterification of palmitic acid in methanol using 13% of $SOCl_2$ to fatty acid (w/w) proceeds cleanly to afford methyl palmitate and water (Equation 2).

$$CH_3(CH_2)_{14}COOH + CH_3OH \rightleftharpoons CH_3(CH_2)_{14}COOCH_3 \qquad [2]$$

The product was ascertained using GC by comparing peaks observed with that of standard methyl palmitate. *Fig. 1* shows that the peak at RT 8.73 min. in the chromatogram of the product is due to methyl palmitate while the acid peak at RT 9.51 min. has been reduced considerably. To verify that the product is actually methyl palmitate, the product was further analysed using GC-MS. The mass spectrum shown in *Fig. 2* reveals the presence of the molecular ion at m/z 270 corresponding to methyl palmitate.

Determination of Optimum Conditions for Esterification

To determine the optimum amount of catalyst for esterification to proceed, the esterification of palmitic acid was repeated using various weight percentages of catalyst to acid and the results obtained are summarized in Table 1. Using 0.3 - 4.0% by weight of $SOCl_2$ to acid, nearly complete conversion of the fatty acid

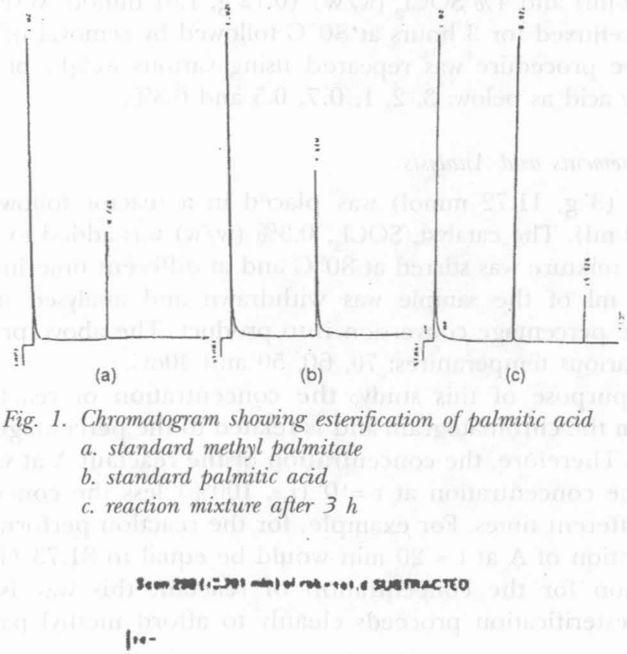
(a) (b) (c)

Fig. 1. Chromatogram showing esterification of palmitic acid
a. standard methyl palmitate
b. standard palmitic acid
c. reaction mixture after 3 h

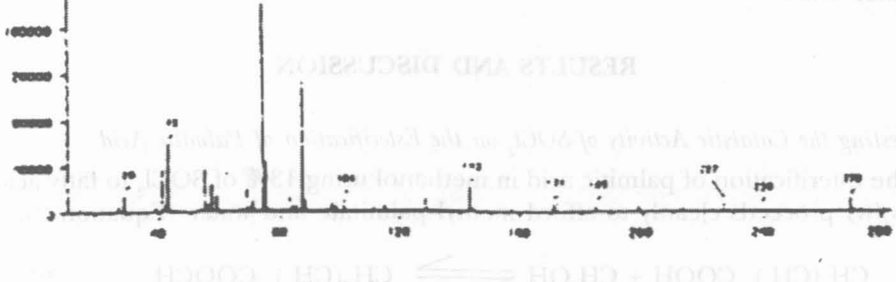

Fig. 2. Mass spectrum of product

TABLE 1
Effect of various weight % catalyst on the esterification of palmitic acid (Reaction time = 3 hr; reaction temperature = 80°C; Palmitic acid = 3.00 g; MeOH = 70 ml)

% $SOCl_2$ to acid (w/w)	% product
4.0	98.46
3.0	99.26
2.0	99.31
1.0	99.32
0.7	99.15
0.5	99.14
0.3	99.21

was obtained. Table 1 shows that the optimum condition for esterification occurred in the catalyst range 0.3 - 2%. Thus from an economic point of view, 0.3% catalyst was chosen as the optimum condition for the following kinetic study.

Kinetic Measurements and Analysis

The percentage conversion of reactant to product at various temperatures and times obtained from the chromatograms are shown in *Fig. 3*. It can be observed that in general, as the reaction times increase the percentage conversion of reactant to product also increases. In addition, increasing the reaction temperature also increases the percentage conversion of reactant to product. A 100% yield or complete conversion of the reactant to product was observed at 80°C after 2 hours.

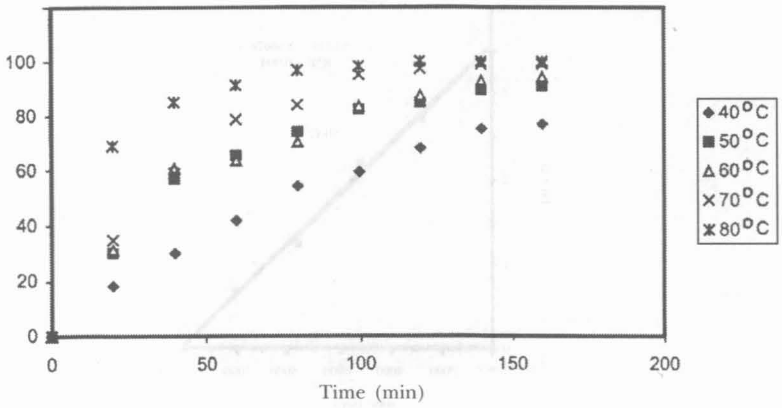

Fig. 3. Plot of percentage conversion of reactant to product versus time at various temperatures

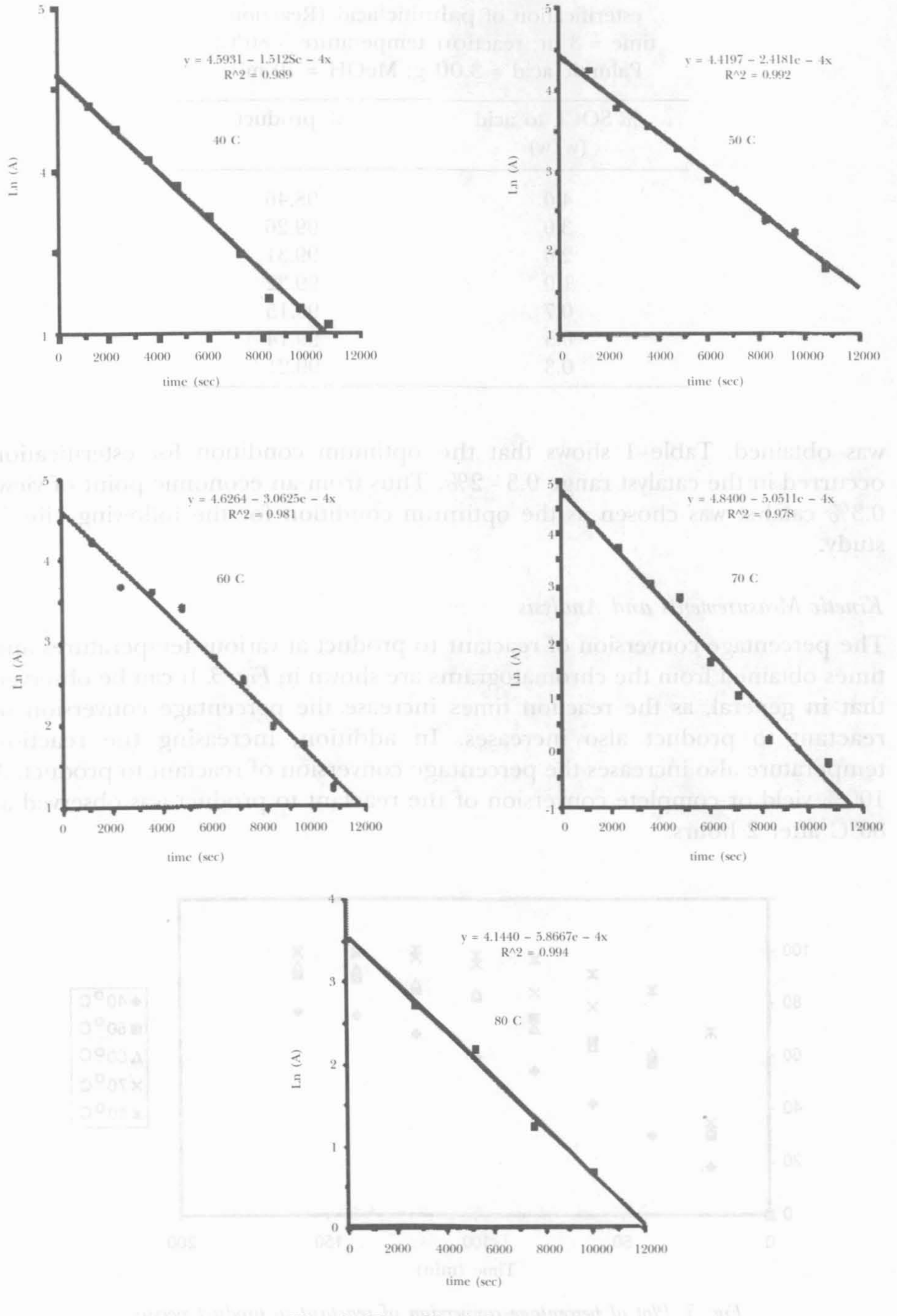

Fig. 4 Plot of ln [A] versus time

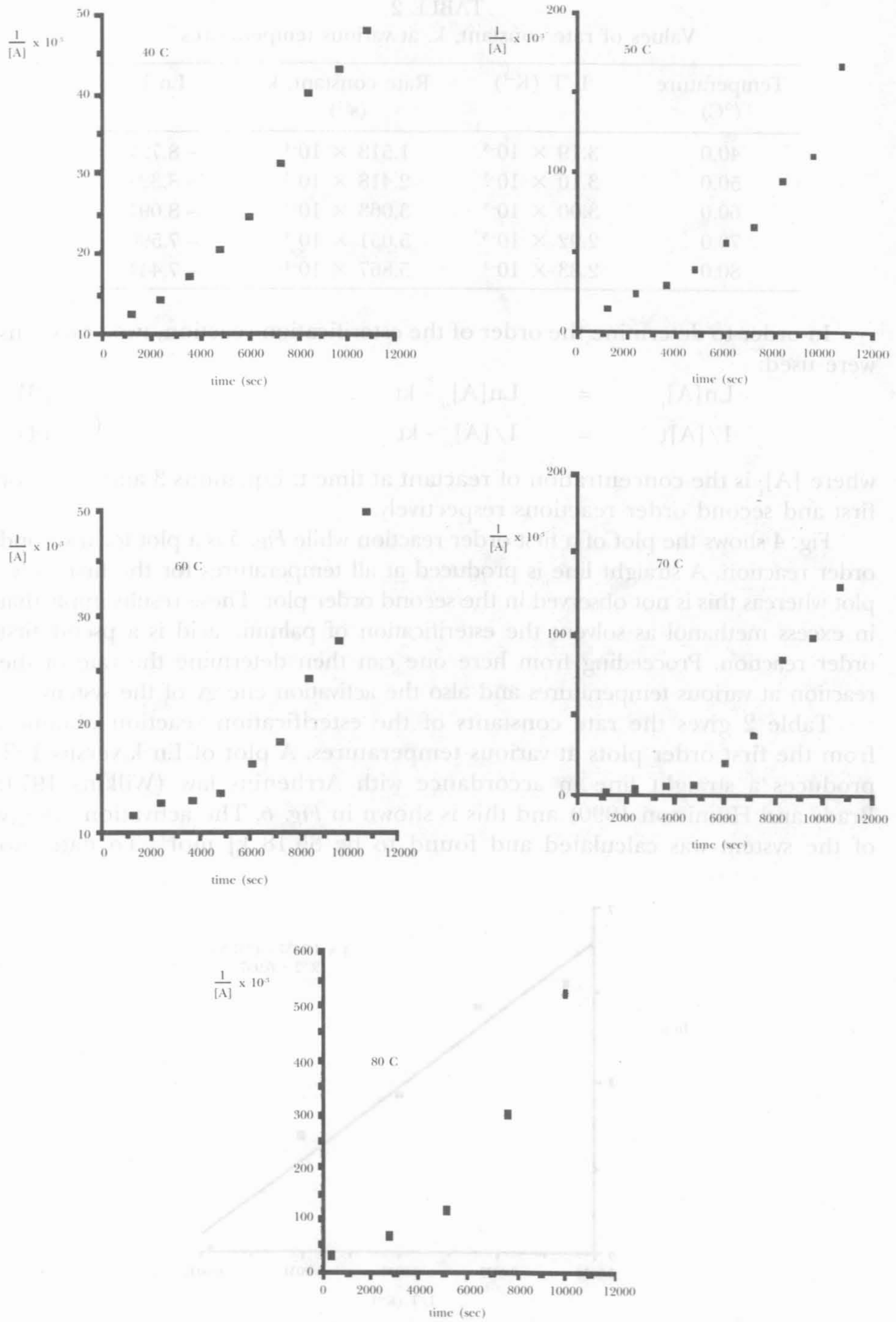

Fig. 5. Plot of 1/[A] versus time

TABLE 2
Values of rate constant, k, at various temperatures

Temperature (°C)	1/T (K^{-1})	Rate constant, k (s^{-1})	Ln k
40.0	3.19×10^{-3}	1.513×10^{-4}	- 8.797
50.0	3.10×10^{-3}	2.418×10^{-4}	- 8.327
60.0	3.00×10^{-3}	3.063×10^{-4}	- 8.091
70.0	2.92×10^{-3}	5.051×10^{-4}	- 7.590
80.0	2.83×10^{-3}	5.867×10^{-4}	- 7.441

In order to determine the order of the esterification reaction, two equations were used:

$$\mathrm{Ln}[A]_t = \mathrm{Ln}[A]_o - kt \qquad [3]$$

$$1/[A]t = 1/[A]_o - kt \qquad [4]$$

where $[A]_t$ is the concentration of reactant at time t. Equations 3 and 4 are for first and second order reactions respectively.

Fig. 4 shows the plot of a first order reaction while *Fig. 5* is a plot for a second order reaction. A straight line is produced at all temperatures for the first order plot whereas this is not observed in the second order plot. These results imply that in excess methanol as solvent the esterification of palmitic acid is a pseudofirst order reaction. Proceeding from here one can then determine the rate of the reaction at various temperatures and also the activation energy of the system.

Table 2 gives the rate constants of the esterification reaction obtained from the first order plots at various temperatures. A plot of Ln k versus 1/T produces a straight line in accordance with Arrhenius law (Wilkins 1974; Brady and Humiston 1990) and this is shown in *Fig. 6.* The activation energy of the system was calculated and found to be 35.18 kJ mol^{-1}. To date, no

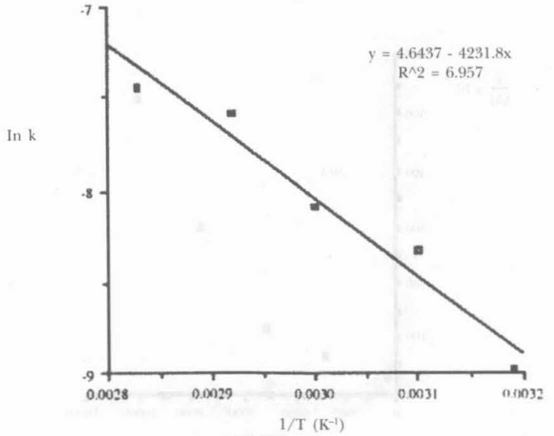

Fig. 6. Arrhenius plot for the esterification of palmitic acid in methanol

activation energy data on the esterification system has been reported except for the esterification of oleic acid in oleyl alcohol catalysed by $CoCl_2$ where the activation energy of the system is found to be 67.2 kJ mol^{-1} (Sanchez *et al.* 1985) .

CONCLUSION

The study shows that $SOCl_2$ has the potential to act as an esterification catalyst. The catalyst is able to convert most of the palmitic acid to methyl ester in a one-step reaction and the product could be directly analysed using gas chromatography. Optimum conditions obtained for the esterification of palmitic acid are 0.3% catalyst to acid by weight, 80°C and 2 hours reaction time.

A pseudofirst order reaction is observed for the esterification of palmitic acid in excess methanol. The activation energy of the system is 35.18 kJ mol^{-1}. Future work will concentrate on the use of $SOCl_2$ as a transesterification catalyst for palm oil.

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