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Research paper

Mechanism and Kinetics Study in Homogenous Epoxidation of Vegetable Oil

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Abstract

Epoxide is an important chemical precursor for the production of alcohols, glycols and polymers like polyesters and epoxy resin. Commercial epoxides available in the market are mainly petroleum and animal based which are non-environmental friendly. The epoxidation of oleic acid was carried out by using *in situ* generated performic acid (HCOOOH) to produce epoxidized oleic acid. Performic acid was formed by mixing formic acid (as oxygen carrier) and hydrogen peroxide (as oxygen donor). The rate constant for epoxidation of oleic acid was found to be in the order of 4.203 x 10^{-5} mol^{-1} s^{-1} and activation energy is 7.58 $kcal.mol^{-1}$. In addition, thermodynamic parameters such as enthalpy, entropy and free energy of activation of 6.83 $kcal.mol^{-1}$, -57.36 $cal.mol^{-1}$ K^{-1} and 22.96 $kcal.mol^{-1}$ respectively.

Keywords: *Oleic acid, epoxidation, kinetics study, vegetables oil, peracids*

1. Introduction

Nowadays, utilizing renewable sources is one of the top priorities done by researcher around the world in order to maintain the synthesis of products based on chemicals [1]. Chemical production in the past were mainly focused on petroleum but it tends to depletes sooner or later [2]. Therefore, some of the renewable sources such as fats and oils is researched as a replacement of petroleum-based materials by treating them using available technology [1,3]. These sources can be obtained primarily from plant oils which are renewable and environmental friendly [4]. Vegetable oil is one of the renewable resources that can be chemically or enzymatically modified as a replacement of petrochemical based product in industries [1,3]. There are many types of vegetable oil produced around the world and palm oil is one of them. Palm oil consists of mainly unsaturated fatty acids such as oleic acid, linoleic acid and linolenic acid with one, two or three carbon-carbon bond present in it [5]. Malaysia is one of the major producers of palm oils in the world, that contribute approximately 4.2% of the nation's gross domestic in 2011 and it is expected that the value will increase up to 7.6% by year 2020 [1].

Among the chemical modifications of palm oil oleic acid (palm olein), epoxidation is an easy and effective method to produce a new type of reactive group that can be used in a variety of applications [1,3]. This oil is derived from epoxidation process in which the fatty acid carbon-carbon double bond is reacted with active oxygen to produce oxirane ring [6]. Eventhough there are many development of epoxidation procedures such as chlorohydrin process and halcon reaction [7], the usage of peroxy acids still considered to be used for a laboratory scaled research by reacting alkenes with oxygen in peroxy acid (RCO_3H) [2].

Chemical kinetics is concerned with the time of reaction and the mechanisms of the reaction. The rate constant is defined as the rate of concentration of substance involved in the reaction with a minus or plus sign attached, depending on whether the substance is a reactant or product. The rate depends on the active concentration of the reactants and is greatly influenced by temperature among other factors such as the nature and concentration of the reacting species [8]. Determination value of the rate constant is great importance since it helps to determine the value of any reaction applying its rate equation. In the industrial applications of kinetics, knowledge of chemical rate equation is essential in establishing the optimum condition of temperature, pressure, feed composition and space velocity [9].

In situ epoxidation using hydrogen peroxide with either acetic or formic acid as the oxygen carrier has achieved commercial importance [10]. Even though there are numerous studies regarding the potential benefits of epoxidized fatty acids, there is a lack of systematic studies focused on the kinetic of epoxidized fatty acids. In an *in situ* epoxidation process, the peracid forms within the same medium and the fatty acids are epoxidized simultaneously with the in-situ formed peracid [11]. This makes kinetic studies on the overall reaction rather complex and challenging. There are various ways in which the kinetic reactions of epoxidized fatty acids can be examined and they can be classified based on the epoxidation process, epoxidation reagent, catalyst and solvent. Therefore, this articles proposes a mathematical model for the reaction system at optimum conditions for maximum epoxide yield that have found previously[12].

2. Results and discussion

Epoxidized oleic acid with almost complete conversion of the unsaturated carbon and negligible ring opening can be synthesized by the *in situ* techniques described [12] . The chemistry of in situ epoxidation may be explained in terms of the following reaction process as shown below.

(a) Peracid formation

$$H_2O_{2(l)} + RCOOH_{(l)} \rightleftharpoons RCO_2OH_{(l)} + H_2O_{(l)} \quad (1)$$

(b) Epoxidation

$$R\text{-}CH{=}CH\text{-}R'_{(l)} + HCO_2OH_{(l)} \longrightarrow EpOA_{(l)} + HCOOH_{(l)} \quad (2)$$

In particular, this kinetic study has consided: (i) peracid formation is to be rate-determining step (ii) the concentration of this acid is assumed to be constant through the reaction. Thus, the rate of epoxidation will be given by expression as bellow.

$$\frac{d[EpOA]}{dt} = k\,\{[H_2O_2] - [EpOA]\}[RCOOH]_o \quad (3)$$

Here EpOA denotes the epoxide and the subscript o initial concentration. It follows that;

$$\ln\{[H_2O_2]_o - [EpOA]\} = k[RCOOH]_o t + \ln[H_2O_2] \quad (4)$$

Then, $\ln\{[H2O2]_o - [EpOA]\}$ vs. reaction time(t) based on (4) was plotted at different temperature as shown in Fig. 1. The deviations from linearity were considered to be due to epoxide degradation and the rates constant were obtained from the initial linear portions of the plots.

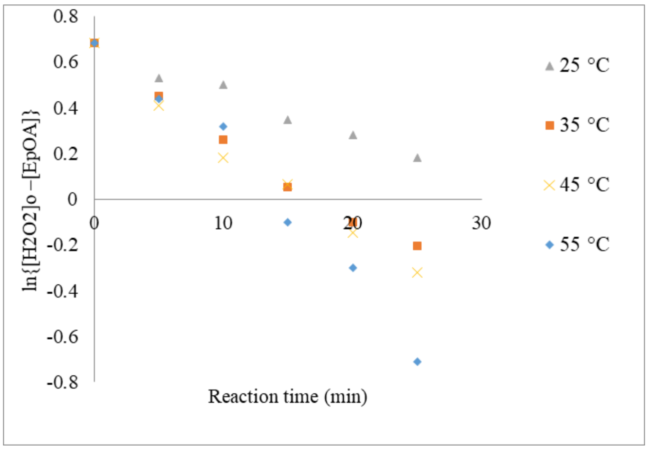

Fig. 1: Plot of $\ln\{[H2O2]_o - [EpOA]\}$ vs. reaction time (min) for epoxidation oleic acid

Table 1: Rate Constant of Epoxidation of Oleic Acid Determined at Various Reaction Temperatures

Temperature (°)	**Oxirane Oxygen Content (dimensionless unit)**	**Rate Constant *(k)* 10^{-5} ($mol^{-1}s^{-1}$)**
35	1.2119	3.448
45	1.3804	3.774
55	1.6518	4.203
65	1.3120	2.860

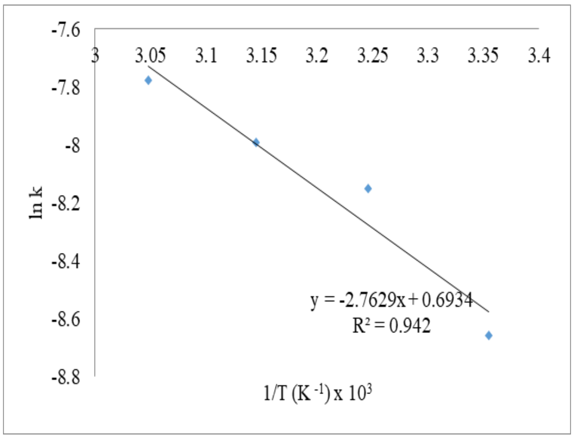

Fig. 2: Activation energy, *Ea* for epoxidation oleic acid by performic acid

The rate constants obtained for the in situ epoxidation of oleic acid palm kernel oil by performic acid (Table 1) are comparable with the values reported for soybean oil and rubber seed oil as in Table 2. According to [13], reaction rate can increases, decrease, remain constant, increases then decreases, decreases the increases or even discontinues with increases in temperature. The value of the rate constant showed the dependence on temperature and type of vegetable oil. Rate constants will be increases when increases the temperature until a certain point, the rate constant will be decreases again.

From the kinetic data, a good Arrhenius plot as depicted in Fig. 2 can be plot to determine the activation energy, *Ea* of epoxidation oleic acid. Activation energy can be hailed as the most important property in any kinetically controlled chemical reaction. The values was calculated to be 7.58 kcalmol^{-1}.

Table 2: Thermodynamic parameters for epoxidation of oils [13]

Oil	**Thermodynamic Parameters**			
	Ea **(kcal.mol^{-1})**	***ΔH*** **(kcal.mol^{-1})**	***ΔS*** **(cal.mol^{-1}.K^{-1})**	***ΔG*** **(kcal.mol^{-1})**
Soybean oil	10.72	10.06	-47.82	25.98
Sunflower oil	19.81	19.16	-17.75	24.98
Rapeseed oil	6.18	5.52	-52.58	22.78
Fatty acid methyl ester	7.60	6.93	-49.72	23.26
Oleic acid derived from PKO*	7.58	6.83	-57.36	22.96

*Determined based on experiments at optimum conditions in this study

2.1Thermodynamic of epoxidation OA

The enthalpy of activation, *ΔH*, was calculated using equation below

$$\Delta H = Ea - RT \quad (5)$$

where *Ea* is activation energy calculated from Arrhenius plot, T is absolute temperature at optimal condition and R is universal gas constant. The calculated value of enthalpy of activation at 55°C was 6.83 kcalmol^{-1}. The entropy of activation, *ΔS* and free energy of activation, *ΔF* were obtained using relationship below;

$$k = \frac{RT}{Nh} e^{\Delta S/R} e^{-E/RT} \quad (6)$$

$$\Delta F = \Delta H - T\Delta S \quad (7)$$

Hence *k*, rate constant; R, gas constant; T, absolute temperature; N, Avogadro constant; and h, Planck's constant.

The calculated value of *ΔS* and *ΔG* were -57.36 calmol^{-1}K^{-1} and 22.96 kcalmol^{-1} respectively. The results indicated that the present reaction was endothermic in nature since the enthalpy of activation was positive, hence an increases in the reaction temperature lead to an increases conversion to oxirane. Entropy also calculated to measure of disorder or randomness of the particles in a thermodynamic system. The negative value of entropy change indicated less disorder results due to the reaction is too fast and less reaction time to achieve maximum yield of epoxide. In addition, the free energy of activation was found to be positive, which indicates that the reaction is non-spontaneous under the present experimental conditions [14] and therefore external energy is needed to induce the reaction. With an increases temperature, the non-spontaneity of the reaction should increase since free energy activation to be positive. Hence any particular time instant, the yield of oxirane will increases. It is evident from the data presented in Table 2 that the apparent activation energy is different for different vegetable oils. This is thought to be attributed to several factors which include the variations in fatty acid composition in the oils, epoxidation reaction conditions as well as the chemical structure of the oils.

3. Experimental

3.1 Material

Crude oleic acid (75%) purity was obtained from Chung Chemical Sdn. Bhd, Malaysia. Formic acid, hydrogen peroxide (30% solution) and sulphuric acid were obtained from Merck Sdn. Bhd. All materials were used as received without further purification [12].

3.2 Method

The kinetic data obtained were represented by a kinetic model based on a modified reaction scheme whereby two assumptions were made: (i) peracid formation is to be rate-determining step (ii) the concentration of this acid is assumed to be constant throughout the reaction. The results from the kinetic model were further analyzed to calculate and investigate thermodynamic parameters of the epoxidation of oleic acid.

4. Conclusion

The kinetic of the *in situ* epoxidation process has been examined by treating the process as a homogeneous (single-phase) system. The reaction rate constant *k,* at various reaction temperatures have been determined. It was found that the kinetic parameters vary with temperature, which will be highly beneficial for scale-up production of epoxidized oleic acid using the *in situ* technique. Based on the rate constants obtained, the activation energy (Ea) and pre-exponential factor (A) were determined as 7.58 kcal.mol^{-1} and 2.0 respectively. Furthermore, thermodynamic analysis conducted on the epoxidation derived oleic acid indicated that the reaction was endothermic in nature and non-spontaneous.

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References

[1] D. Derawi, J. Salimon, and W. A. Ahmed, “Preparation of Epoxidize Palm Olein As Renewable Material By Using Peroxy Acids,” *Malaysian J. Anal. Sci.*, vol. 18, no. 3, pp. 584–591, 2014.

[2] M. J. Jalil, S. K. Jamaludin, and I. S. Azmi, “Characterisation of Epoxidation of Palm Kernel Oil based on Crude Oleic Acid,” no. 201606, 2017.

[3] D. Derawi and J. Salimon, “Optimization on Epoxidation of Palm Olein by Using Performic Acid,” *E-Journal Chem.*, vol. 7, no. 4, pp. 1440–1448, 2010.

[4] D. Darfizzi, “Experimental Design using Response Surface Methods for Palm Olein-Based Hydroxy-Ether Systhesis,” *sains Malaysiana*, vol. 45, no. 7, pp. 1149–1154, 2016.

[5] E. Milchert, K. Malarczyk, and M. Kłos, *Technological Aspects of Chemoenzymatic Epoxidation of Fatty Acids, Fatty Acid Esters and Vegetable Oils: A Review*, vol. 20, no. 12. 2015.

[6] S. Sen Gupta, A. Guchhait, and S. Sarkar, “Comparative Evaluation of the Physico-chemical Properties of Chemically and Enzymatically Epoxidised Soybean Oil,” vol. 1, no. 2, 2016.

[7] E. Milchert and a Smagowicz, “Epoxidation of the rapeseed oil with peracetic and performic acid,” *Czas. Tech.*, pp. 284–291, 2008.

[8] V. V Goud, A. V Patwardhan, S. Dinda, and N. C. Pradhan, “Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin,” vol. 62, pp. 4065–4076, 2007.

[9] E. Santacesaria, R. Tesser, M. Di Serio, R. Turco, V. Russo, and D. Verde, “A biphasic model describing soybean oil epoxidation with H 2 O 2 in a fed-batch reactor,” *Chem. Eng. J.*, vol. 173, no. 1, pp. 198–209, 2011.

[10] M. J. Jalil *et al.*, “An Overview of Epoxidation of Vegetable Oils with Peracid- Reaction Mechanism,” *Recent Innov. Chem. Eng.*, vol. 10, pp. 1–8, 2017.

[11] J. La Scala and R. P. Wool, “Effect of FA Composition on Epoxidation Kinetics of TAG,” vol. 79, no. 4, pp. 373–378, 2002.

[12] M. Jumain *et al.*, “Epoxidation of Palm Kernel Oil-based Crude Oleic Acid,” vol. 906, no. 1, pp. 125–130, 2014.

[13] C. Engineering, “Kinetics Of In Situ Epoxidation Of Hemp Oil Under Heterogenous Reaction Conditions : An Overview With Preliminary Results,” *eddBE2011 Proc. Kinet.*, pp. 106–111.

[14] K. Saremi, T. Tabarsa, A. Shakeri, and A. Babanalbandi, “Epoxidation of Soybean Oil,” vol. 3, no. 9, pp. 4254–4258, 2012.