Kinetic Investigation for in-situ Epoxidation of Unsaturated Fatty Acid Based on the Pseudo-steady-state-hypothesis (PSSH)

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Abstract: Oleic acid is a mono-unsaturated fatty acid that can be found abundantly in various vegetable oils and potentially attractive to be used as raw material for epoxide chemical. In-situ epoxidation of oleic acid was conducted in batch reactor using peroxy-formic at 30-60 °C. Pseudo-steady-state-hypothesis (PSSH) was applied to develop the kinetic model. Heterogeneous liquid-liquid system was chosen and four models which emphasized on the ring opening agent (ROA) and reversibility of the epoxidation reaction were proposed. It has been suggested that reversible model is well suited to represent the experimental data. Activation energy obtained from Arrhenius equation is in the range of 40-195 kJ/mol.

Key words: oleic acid, kinetic investigation, in-situ epoxidation

1 Introduction

Epoxidation of unsaturated fatty compounds is one of the main routes to synthesize valuable fatty chemicals for wide range applications, e.g. plasticizer, lubricant, and starting material for various bio-based polymeric materials¹⁻⁵. Unsaturated fatty compounds vary in the form of triglycerides, fatty esters, or fatty acids. Epoxidation reaction with unsaturated vegetable oil triglycerides as starting material is the most common subject in epoxidation that has been intensively explored because it does not require the additional process such as hydrolysis or esterification. Fatty esters or fatty acid are usually employed for epoxidation in order to simplify the kinetic evaluation and to enhance the oleochemical product diversification. Meanwhile, amongst the various unsaturated fatty acids, oleic acid is the most frequently used for epoxidation²⁻¹⁶.

It is commonly known that oleic acid is the most unsaturated fatty acid recurrently used in the wide range of research topics, from agricultural to medical, biochemical, chemistry, and other related fields. The reason behind this fact is based on the nature of oleic acid; it can be found effortlessly in most of vegetable oils and animal fats. The first major source of oleic acid is originated from olive oil which comprise 55-83% from the total fatty acid content⁶. Palm and soybean oils as the most popular cooking oils contain oleic acid in notable quantity. Typical oleic acid content in palm oil and soybean oil are 23.3% and 39.2%, respectively⁷. When the issue of food stability is rising, oleic acid still can be found in non-edible vegetable oil such as: rubber seed oil, jatropha oil, neem oil, karanja oil, etc. Thus, the use of oleic acid as raw material for epoxidation reaction is potentially attractive.

Several methods of oleic acid epoxidation have been identified, however, in-situ method was chosen in this study. In-situ method with peroxy-carboxylic acid as the oxygen source was adopted by many researchers, due to the raw material availability, relatively low cost, and prominent reactivity¹¹. Peroxy-carboxylic acid is generated in-situ from the reaction between hydrogen peroxide and short chain carboxylic acid. This reaction step is frequently called as the carboxylic acid perhydrolysis reaction. The next step is the main reaction itself i.e. epoxidation of oleic acid, which takes place in the same reaction system where double bond in oleic acid reacts with peroxy-carboxylic acid to produce epoxidized oleic acid and carboxylic acid. The overall reaction mechanism has been widely known as...
Prileszhaev or Prileshajew epoxidation method. Formic acid and acetic acid are typically employed in this method. Formic acid reacts with hydrogen peroxide to produce peroxy-formic acid. Analogously, peroxy-acetic acid is produced from the reaction between acetic acid and hydrogen peroxide. Peroxy-formic acid is more reactive than peroxy-acetic acid, however, peroxy-acetic acid is observed to be more resistant to degradation. In this study, formic acid was used instead of acetic acid and lower reaction temperature (30-60°C) was chosen to overcome its instability.

Kinetic of epoxidation of oleic acid using in-situ method was first investigated by Chou and Chang. They suggested that acetic acid was considered to become an oxygen transfer agent which brought oxygen atom from hydrogen peroxide in the aqueous phase to oleic acid in oil phase by transforming into peroxy-acetic acid. Leveneur et al. used oleic acid as the representative of fatty acid in the development of liquid-liquid kinetic model for in-situ epoxidation reaction with peroxy-formic acid. The reactor used was a semi-batch mode. The kinetic equations involved the rate of formic acid perhydrolysis, peroxy-formic acid decomposition, epoxidation, and ring opening reaction but the kinetic data for the first two reaction were obtained from another literature. In-situ epoxidation of oleic acid which emphasized on kinetic model was also conducted by Aguiera et al. Two-phase kinetic model was applied for in-situ epoxidation of oleic acid with peroxy-acetic acid without catalyst in order to quantitatively compare the effect of microwave irradiation and conventional heating. It was concluded that microwave irradiation enhanced all the rate of reaction, which meant that the rate of ring opening was also enhanced. Another work on the epoxidation of oleic acid was conducted using ion exchange resin as catalyst in the perhydrolysis reaction step.

In-situ epoxidation of oleic acid and other vegetable oil-based raw materials is a complex reaction system with combined series-parallel reaction. Some reactions are considered to be reversible reaction model with intermediate product. Several authors assumed that the reaction producing an intermediate is in equilibrium so that the forward and reverse reaction are generally at the same rate. In this study, a different approach is used to give a new insight into the kinetic model of in-situ epoxidation. This approach is called pseudo-steady-state-hypothesis (PSSH). PSSH deals with the active intermediates in the reaction system, which are formed and reacted with other components very quickly so that the accumulation of these intermediates is negligible. PSSH was applied in fluid-solid reaction, adsorption process, and enzymatic reaction. In this study, the possible active intermediates are generated in the perhydrolysis and ring opening reaction.

Epoxidation of oleic acid using in-situ method with peroxy-formic acid was performed in this study. The kinetic study of oleic acid epoxidation was done by several groups as can be found in the cited literature review. Most of them utilized equilibrium assumption in order to obtain the concentration of intermediate product. This study focuses on the application of PSSH as a new approach in the kinetic model development for in-situ epoxidation of oleic acid. The reversibility of the epoxidation reaction and the combination of ring-opening agents were taken into account in the proposed model. The heterogeneous two-phase liquid-liquid approach is implemented and mass balance equation based on the individual phase is conducted to obtain the kinetic parameter. Based on the minimum average of relative error between experimental and calculated data, the best suited kinetic model is selected.

2 Experimental Procedures
2.1 Materials
Technical grade oleic acid with iodine number of 90 grams I/gram was obtained from Sigma-Aldrich. H₂O₂ (30%), HCOOH (98%), and all reagents for analysis were purchased from Merck and were used without purification.

2.2 Epoxidation reaction
The epoxidation reaction was carried out in a 500 mL three neck flask equipped with magnetic stirrer and reflux circulation. Calculated amount of oleic acid (100 g) and formic acid (8 g) were fed all at once to the reactor and heated to the desired temperature. Hydrogen peroxide (39.3 g) was added slowly to the reactor for 20 minutes. The stirring speed for all experiments was maintained at 650 rpm. Reaction progress was monitored by collecting samples at the specified time interval. The samples were then quenched with cold water to immediately stop the reaction and washed with water until free from remaining acid afterwards. The trace of water was removed with centrifugation prior to analysis.

2.3 Analytical methods
Double bond concentration in oleic acid and epoxide concentration in epoxidized oleic acid were obtained from iodine number and oxirane number, respectively. Oxirane number was analyzed using direct titration with HBr, while iodine number determination was conducted according to Wij method.

3 Results and Discussion
3.1 Effect of reaction temperature
In order to study the reaction kinetic, effect of reaction temperature on the oxirane number and iodine number was monitored in the range of 30-60°C. The molar ratio used was oleic acid (OA): formic acid (FA): hydrogen
peroxide (HP) = 1:0.5:1.1 without any added catalyst. The effect of temperature on the double bond and epoxide concentration for \textit{in-situ} epoxidation of oleic acid with peroxy-formic can be seen in Fig. 1. Figure 1 shows that the observed concentration of double bond in oleic acid (DB) consistently decreases. From the initial slope of each temperature, the rate of reaction is faster as the reaction temperature increases. Therefore, based on the raw material point of view, the reaction progress has a good tendency.

Also, from Fig. 1, the observed epoxide concentration (EP) generally increases as the reaction time (t) and temperature are increasing. However, there is an anomaly at the highest temperature where the epoxide concentration starts to decrease after about 150 minutes of reaction time. It has been suggested that the anomaly may be caused by the ring opening reaction of epoxide. The occurrence of ring opening reaction in the \textit{in-situ} epoxidation has been experienced by almost all previous studies in epoxidation. The epoxide itself is known for its high reactivity. This can be advantageous but when it comes too early in the reaction system, the effect is deleterious. All components in the reaction system can contribute as the ring opening agent, but the most contribution comes from acids\textsuperscript{30}.

It can be concluded that double bond concentration is always in decreasing trend, but epoxide concentration is not always so. This means that the rate of consumption of double bond is independent of the epoxide formation rate especially at the temperature of 60°C. The different tendency of epoxide and double bond concentration at the maximum temperature studied in this work can be explained with detailed evaluation on the reaction performance. According to the stoichiometry of the epoxidation reaction, if one mole of double bond is consumed, then one mole of epoxide is produced. When the mole of epoxide produced is lower than the mole of double bond consumed, the side reaction may interfere with the epoxidation reaction. Therefore, conversion (X) only is not sufficient to represent the reaction performance. Selectivity (S) is also a critical parameter to be involved in the overall evaluation. Double bond conversion (X) and epoxide selectivity from double bond (S) can be written as follows\textsuperscript{26}:

\[ X = \frac{I_0 - I_t}{I_0} \times 100\% \quad (1) \]
\[ S = \frac{O_t}{(I_0 - I_t)/253.8} \times 100\% \quad (2) \]

Where, \( I_0 \) and \( I_t \) are the initial iodine number and the iodine number at a certain reaction time, respectively and \( O_t \) is the oxirane number a certain reaction time.

The plot of selectivity against conversion can be seen in Fig. 2. From Fig. 2, it can be seen that all selectivity data are less than 100\%. It means that the epoxide produced is lower than double bond consumed. This might be caused by the series reaction that convert epoxides into other species (ring opening reaction). Therefore, ring opening reaction occurs at all temperature range studied. Although the selectivity data are fluctuating and do not follow specific trend with temperature, there is a tendency that the maximum selectivity is attained at the conversion range of 30-45\%. It can also be seen that at higher conversion, the selectivity value is more likely to decrease. At low temperature, the rate of epoxidation is faster than the rate of ring opening reaction so that the epoxide concentration is increasing with reaction time. However, at higher temperature, the rate of ring opening reaction is faster than the epoxidation reaction. In this case, epoxide concentration is increasing in the early reaction time until reaching a
certain value and it subsequently starts to decrease.

3.2 Kinetic model

The pseudo-homogeneous kinetic model was applied to in-situ epoxidation of oleic acid with peroxy-acetic acid and the results indicated that the significant deviations were observed at 60 and 70°C. Therefore, in this study, the more detailed kinetic model is developed under heterogeneous liquid-liquid consideration. Based on previous investigations, in-situ epoxidation of oleic acid consisted of three main reaction steps: perhydrolysis, epoxidation, and ring opening. The overall reaction steps can be summarized as follows:

Step 1: Perhydrolysis

\[
\text{HCO}_2\text{H}_{\text{aq}} + \text{H}^+ \rightleftharpoons \text{HCO}_2\text{H}_{2\text{aq}} + \text{H}_2\text{O}
\] (3)

\[
\text{HCO}_2\text{H}_{2\text{aq}} + \text{H}_2\text{O}_\text{aq} \rightleftharpoons \text{HCO}_2\text{H}_{\text{aq}} + \text{H}_2\text{O} + \text{H}^+_{\text{aq}}
\] (4)

Step 2: Epoxidation

\[
\text{HCO}_2\text{H}_{\text{org}} + \text{DB}_{\text{org}} \rightleftharpoons \text{E}_{\text{org}} + \text{HCO}_2\text{H}_{\text{org}}
\] (5)

Step 3: Ring opening

\[
\text{E}_{\text{org}} + \text{H}^+_{\text{org}} \rightleftharpoons \text{E}^*_{\text{org}}
\] (6)

\[
\text{E}^*_{\text{org}} + \text{ROA}_1_{\text{org}} \rightleftharpoons \text{SP}_1_{\text{org}} + \text{H}^+_{\text{org}}
\] (7)

\[
\text{E}^*_{\text{org}} + \text{ROA}_2_{\text{org}} \rightleftharpoons \text{SP}_2_{\text{org}} + \text{H}^+_{\text{org}}
\] (8)

Phase equilibrium

\[
\text{HCO}_2\text{H}_{\text{org}} \rightleftharpoons \text{HCO}_2\text{H}_{\text{org}}
\] (9)

\[
\text{H}^+_{\text{aq}} \rightleftharpoons \text{H}^+_{\text{org}}
\] (10)

\[
\text{HCO}_2\text{H}_{\text{aq}} \rightleftharpoons \text{HCO}_2\text{H}_{\text{org}}
\] (11)

\[
\text{H}_2\text{O}_{\text{aq}} \rightleftharpoons \text{H}_2\text{O}_{\text{org}}
\] (12)

In the perhydrolysis step, formic acid reacted with H\(^+\) and produced an active intermediate product (HCOH\(^+\)). The next reaction is between an active intermediate and hydrogen peroxide to produce peroxy-carboxylic acid, water, and regenerated H\(^+\). The first reaction is assumed to be reversible with the forward and reverse reaction rate constants are \(k_1\) and \(k_{-1}\) respectively. The second reaction is irreversible with \(k_2\) as the reaction rate constant.

Peroxy-formic acid of reaction 4 migrates from aqueous phase to organic phase and reacts with double bond of oleic acid (DB) to produce epoxidized oleic acid (EP). Many studies assumed that this reaction is irreversible. However, Chou and Chang proposed two reaction steps involving the intermediate product and considered it as complex. The first step is reversible reaction between oleic acid and peroxy-acetic acid, producing complex that further undergo irreversible reaction to produce epoxidized oleic acid and acetic acid. This mechanism is rarely discussed in the literature. In this study, the reversibility of this reaction step will be taken into account in the kinetic model. When the epoxidation reaction is assumed to be irreversible, there is only one reaction rate constant (\(k_3\)). Correspondingly, there are two reaction rate constants when the reaction is assumed to be reversible (\(k_3\) and \(k_{-3}\)).

The last step in the in-situ epoxidation of oleic acid is the ring opening reaction. This step is a series reaction taking place in the organic phase and catalyzed by acid or only attributed to certain component based on reactivity consideration. In this study, these reactions are assumed to be irreversible with two ring opening agents which have the most contribution on the reaction system. In order to accommodate the existence of heterogeneous liquid-liquid phase, the component that exist in both phases are assumed to be in equilibrium. Therefore, interphase distribution coefficient (\(K_i\)) is used to correlate the concentration of the related component in aqueous (\(C_{iaq}\)) and organic phase (\(C_{iong}\)) and can be written as follows:

\[
K_i = \frac{C_{iaq}}{C_{iong}}
\] (13)

From the aforementioned reaction mechanism, there are two intermediate products that can be treated as active intermediate (HCOH\(^+\) and E\(^*_\)). With pseudo-steady-state-
hypothesis (PSSH), the rate of each active intermediate is equal to zero:

\[
\frac{dC_{HCO_2H_2}^{aq}}{dt} = 0
\]  
(14)

\[
\frac{dC_{EP}^{org}}{dt} = 0
\]  
(15)

Equations 14 and 15 can be solved and yield the following equation, respectively:

\[
C_{HCO_2H_2}^{2ad} = \frac{k_1 C_{HCO_2H_2}^{aq} C_{H^+}^{aq}}{k_1 + k_2 C_{H_2D_2}^{aq}}
\]  
(16)

\[
C_{EP}^{org} = \frac{k_4 C_{EP}^{org} C_{H^+}^{aq}}{k_4 C_{ROA_1}^{org} + k_6 C_{ROA_2}^{org}}
\]  
(17)

Components that act as ring opening agents are the components in the aqueous phase, therefore the concentration of ROA 1 and ROA 2 can be expressed based on the individual concentration of each component in aqueous phase, instead of organic phase by incorporating the inter-phase distribution coefficient. The concentration of H+ in organic phase can also be treated analogously, so that equation 17 can be written as follows:

\[
C_{EP}^{org} = \frac{k_4 C_{EP}^{org} C_{H^+}^{aq}}{k_4 C_{ROA_1}^{org} + k_6 C_{ROA_2}^{org}}
\]  
(18)

Where k4’, k5’, k6’ are the combined constant between reaction rate constant and distribution coefficient for corresponding component.

Reaction kinetic for in-situ epoxidation of oleic acid in this study is then divided into four selected model with 7-8 reaction parameters to be estimated. The difference between each model is mainly based on the two points of view: ring opening agent and reversibility of epoxidation reaction. The selected components for ROA 1 are water or peroxy-formic acid, while formic acid is chosen for all models as ROA 2. The combination of water and acetic acid as ring opening agent was proposed by Sinadinovic-Fišer et al. because it gave the best fit between experimental data and predicted values.30 The consideration to choose peroxy-formic acid and formic acid as the next combination of ring opening agent is based on the fact that they are involved in the main reaction so that the concentration of these two acids in the organic phase is higher than that of other components (water and hydrogen peroxide). This combination was also chosen by Campanella et al.31 The proposed model can be seen in Table 1. Model 1 assumed that epoxidation reaction step is irreversible with water and formic acid as ring opening agents. Therefore, there are seven kinetic parameters to be estimated. Model 2 used the same combination of ring opening agents with model 1 but assumed that the epoxidation reaction is reversible. For model 2, since there is one additional number of reaction parameter i.e. reverse reaction rate constant, the number of kinetic parameters become eight parameters. Model 3 and model 4 used the same approach as model 1 and model 2 except for the combination of ring opening agent. The ring opening agents for both models are peroxy-formic acid and formic acid.

Since there are four models proposed, consequently, there are four different sets of mass balance equation. However, only detailed mass balance equation for model 1 is used as the representative. Rate of all reactions are assumed to follow the elementary rate law and concentration of each component is expressed as mol/gram. The overall mass balance for model 1 is summarized as follows:

\[
\frac{dC_{HCO_2H_2}^{aq}}{dt} = -k_1 C_{HCO_2H_2}^{aq} + k_2 C_{H_2D_2}^{aq} - k_3 C_{EP}^{org} C_{H^+}^{aq}
\]  
(19)

\[
\frac{dC_{EP}^{org}}{dt} = -k_4 C_{EP}^{org} C_{H_2D_2}^{aq} + k_6 C_{ROA_2}^{org} - k_5 C_{EP}^{org} C_{H^+}^{aq}
\]  
(20)

\[
\frac{dC_{HCO_2H_2}^{2ad}}{dt} = -k_2 C_{HCO_2H_2}^{2ad} + k_1 C_{HCO_2H_2}^{aq} + k_3 C_{EP}^{org} C_{H_2D_2}^{aq}
\]  
(21)

\[
\frac{dC_{ROA_2}^{org}}{dt} = -k_6 C_{ROA_2}^{org} + k_5 C_{EP}^{org} C_{HCO_2H_2}^{aq}
\]  
(22)

\[
\frac{dC_{HCO_2H_2}^{aq}}{dt} = -k_2 C_{HCO_2H_2}^{aq} + k_1 C_{HCO_2H_2}^{2ad} - k_3 C_{EP}^{org} C_{H_2D_2}^{aq}
\]  
(23)

\[
\frac{dC_{ROA_1}^{org}}{dt} = -k_4 C_{ROA_1}^{org} + k_6 C_{ROA_2}^{org}
\]  
(24)

\[
\frac{dC_{EP}^{org}}{dt} = -k_5 C_{EP}^{org} C_{H^+}^{aq} + k_4 C_{EP}^{org} C_{HCO_2H_2}^{aq}
\]  
(25)

\[
\frac{dC_{HCO_2H_2}^{org}}{dt} = -k_6 C_{HCO_2H_2}^{org} - k_4 C_{EP}^{org} C_{H^+}^{aq}
\]  
(26)

\[\text{Table 1} \quad \text{Proposed kinetic model for in-situ epoxidation of oleic acid with peroxy-formic acid.}\]

| Model no. | ROA 1     | ROA 2     | Reversibility | Reaction parameters |
|----------|-----------|-----------|---------------|---------------------|
| 1        | Water     | Formic acid | Irreversible  | k1, k2, k3, k4, k5, k6 |
| 2        | Water     | Formic acid | Reversible    | k1, k2, k3, k4, k5, k6 |
| 3        | Peroxy-formic acid | Formic acid | Irreversible  | k1, k2, k3, k4, k5, k6 |
| 4        | Peroxy-formic acid | Formic acid | Reversible    | k1, k2, k3, k4, k5, k6 |

a) reversibility of epoxidation reaction (reaction 5)
The quantitative comparison for each model is used to choose the best kinetic model that well represents the experimental data. This comparison is based on the average percentage of relative error and the coefficient of determination ($R^2$) as can be seen in Table 2.

From Table 2, the proposed kinetic model can be divided into two combinations which the average percentage of relative error are in the same order of magnitude. The first combination is model 1 and model 3, with average of relative error >10% and the second combination is model 2 and model 4 with average relative error <10%. Model 2 and model 4 also give a better value of $R^2$ than model 1 and model 3. This means that model 2 and model 4 are then become the selected model and the assumption that epoxidation reaction follows the reversible reaction is well fitted to experimental data. From the combination of ring opening agent point of view, model 2 and model 4 give the comparable result. Cai et al. studied the effect of ring opening agents on the epoxidation of cottonseed oil and found that peroxy-carboxylic and carboxylic acid gave the great effect on the ring opening of epoxide when compared to water and hydrogen peroxide. The relatively small difference between the two model can be concluded that water, formic and peroxy-formic acid have the contribution in the ring opening reaction. However, model 4 shows better performance than model 2. Therefore, only the detailed value of each reaction parameter obtained from model 4 is reported and can be shown in Table 3.

The kinetic model proposed in this study involves reaction parameters that have different form. For the first two reaction, the reaction parameter is intrinsic rate of reaction constant, but for other reactions, the kinetic parameters are a combination between reaction rate constant and dissociation constant, but for other reactions, the kinetic parameters are a combination between reaction rate constant and dissociation constant. The quantitative comparison for each model is used to choose the best kinetic model that well represents the experimental data. This comparison is based on the average percentage of relative error and the coefficient of determination ($R^2$) as can be seen in Table 2.

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### Table 2 Relative error and coefficient of determination.

| Model No. | Relative error, % | Average | $R^2$ |
|-----------|------------------|---------|------|
| 1         | 9.50             | 18.57   | 14.04 | 0.907 |
| 2         | 3.89             | 4.10    | 4.00  | 0.988 |
| 3         | 7.46             | 15.05   | 11.26 | 0.939 |
| 4         | 3.83             | 4.11    | 3.97  | 0.990 |

### Table 3 Reaction parameters for in-situ epoxidation of oleic acid with peroxy-formic acid (model 4).

| Rate constant$^a$ | Temperature, °C | Activation Energy, kJ/mol |
|-------------------|-----------------|---------------------------|
|                   | 30              | 40                        | 50                        | 60                        |
| $k_0$             | 12.97 ± 0.14    | 48.61 ± 0.26              | 265.55 ± 0.30             | 538.89 ± 0.50             |
| $k_1$             | 12.16 ± 0.09    | 25.37 ± 0.33              | 147.24 ± 0.41             | 395.42 ± 0.46             |
| $k_2$             | 10.36 ± 0.08    | 16.86 ± 0.15              | 17.47 ± 0.44              | 51.17 ± 0.34              |
| $k_3$             | 12.45 ± 0.51    | 39.50 ± 0.23              | 74.81 ± 0.99              | 242.77 ± 0.32             |
| $k_4$             | 16.00 ± 0.14    | 42.66 ± 0.35              | 353.37 ± 0.88             | 879.27 ± 0.87             |
| $k_5$             | 27.82 ± 0.42    | 50.24 ± 0.18              | 193.96 ± 0.32             | 314.97 ± 0.27             |
| $k_6$             | 9.50 ± 0.28$^b$ | 64.96 ± 0.39              | 709.48 ± 1.63             | 1169.18 ± 2.91            |

$^a$ unit in gr·mol⁻¹·min⁻¹  
$^b$ mean ± deviation
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It is difficult to directly compare the value of these parameters with other studies found in literature. However, the relative comparison between each parameter in this study can possibly be made. From Table 3, for the first reaction in perhydrolysis step, it can be seen that for all temperature, the forward reaction rates ($k_1$) are greater than reverse reaction rates ($k_{-1}$). The difference between them is relatively large, this means that the formation of intermediate product is fast. The rate of the second reaction in perhydrolysis step ($k_2$) is quite slower than the first reaction, but still in the same order. For the next step (epoxidation reaction), since the

![Fig. 3](image-url) Concentration profile of: (a) water, (b) hydrogen peroxide, (c) hydrogen ion, (d) formic acid, (e) peroxo-formic acid, (f) side product 1, and (g) side product 2, in the kinetic investigation for in-situ epoxidation of oleic acid with peroxo-formic acid (model 4).
selected model is the reversible reaction, it can be seen that although the forward reaction rate (k') is greater than the reverse reaction rate (k'–1), the difference between them is relatively small. The rate constants for the last step (ring opening reaction) consist of three reaction rate constants (k'4, k'5, k'6). It can be seen that the smallest value is k'4(protonation), followed by k'5(ring opening by peroxo-formic acid) and k'6(ring opening by formic acid). Although it has the smallest value among the other two constants, it cannot be concluded that the protonation reaction is the slowest reaction in the ring opening step because of the incorporation of distribution coefficient in the rate constant. From the activation energy point of view, the lowest value is Ea. In the other hand, activation energy in the perhydrolysis step (Ea, E1, and E2) are ones that have the highest value. The overall order of activation energy for in-situ epoxidation of oleic acid with peroxo-formic acid in increasing order are: epoxidation, ring opening, followed by perhydrolysis.

The time-dependent changes in the concentration of double bond and epoxide concentration can also be seen in Fig. 1. The good fit between the observed (obs) and calculated (calcd) value of these compounds is observed in all range of temperature studied. Meanwhile, the time-dependent changes in the concentration of other compounds (water, hydrogen peroxide, hydrogen ion, formic acid, peroxo-formic acid, side product 1, and side product 2) can be seen in Fig. 3.

Figure 3 shows the calculated concentration profile for each compound in the reaction system as a function of reaction time and temperature. The concentration of water, peroxo-formic acid, SP1, and SP2 generally increase with temperature and reaction time, while the others decrease. The decreasing/increasing rate of all compounds is proportional to the increase of reaction temperature. The significant increase is observed for SP1 with increasing temperature. The reaction rate for ring opening reaction at 30 °C is very low and then increase dramatically at higher temperature. At 60 °C, the concentration of SP1 achieves the highest value. Since SP1 is the reaction product from protonated epoxide and peroxo-formic acid, the concentration profile of peroxo-formic acid at 60 °C is different with other temperature (Fig. 3(e)). This can also be used to explain the decrease in epoxide concentration at the same temperature as can be seen in Fig. 1. In this case, the rate of formation of peroxo-formic acid is slower than the rate of its consumption for epoxidation and ring opening reaction.

4 Conclusions

Kinetic model for in-situ epoxidation of oleic acid with peroxo-formic acid based on pseudo steady state hypothesis (PSSH) was studied. Heterogeneous liquid-liquid kinetic model with the use of interphase distribution coefficient was applied. Four kinetic models considering the reversibility of the reaction and the combination of ring opening agent was proposed. The best model was chosen based on the average percentage of relative error and the R². A good agreement between experimental data and calculated concentration was achieved. From the reversibility point of view, the tendency that the epoxidation reaction is reversible was shown. Water, peroxo-formic and formic acid were shown to have a significant contribution as the ring opening agent.

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