Overall Mass Transfer Coefficient and Henry’s Law Constant for the Insitu Epoxidation of Tamanu Oil

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Overall Mass Transfer Coefficient and Henry’s Law Constant for the In-situ Epoxidation of Tamanu Oil

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Abstract

The stages of the double bond epoxidation process of tamanu oil include (1) the process of making peroxyacetic acid (PAA), (2) the mass transfer of several components, and (3) the epoxidation reaction, followed by further reactions within the organic phase. This study was dedicated to the determination and estimation of reaction and mass transfer parameters in the in-situ epoxidation of tamanu oil with PAA. The reaction constant values were observed to be directly proportional to the reaction temperature, except in the case of $k_3$. There is a slight deviation in $k_3$, where it decreases from $14.6178 \pm 0.0507 \text{ g.mol}^{-1}\text{.min}^{-1}$ at $40^\circ\text{C}$ to $13.6561 \pm 0.0081 \text{ g.mol}^{-1}\text{.min}^{-1}$ at $50^\circ\text{C}$. The mass transfer coefficient ($k_{ca}$) values increase with increasing temperature, where the $k_{ca}$ for PAA, H$_2$O, acetic acid (AA), and H$^+$ were $12.6654 \pm 0.0657$ to $23.0777 \pm 0.1384$, $12.3793 \pm 0.0549$ to $23.0790 \pm 0.1476$, $12.4912 \pm 0.0394$ to $23.0789 \pm 0.0978$, $12.4296 \pm 0.0821$ to $23.0790 \pm 0.1296$, respectively. Conversely, the Henry constant ($H$) values for each component vary. This constant is associated with the solubility of each component.

Keywords: Epoxidation, overall mass transfer coefficient, Henry’s constant

INTRODUCTION

Epoxidizing unsaturated acids using percarboxylic acids is highly favored due to its cost-effectiveness and reliance on natural and renewable sources like vegetable oils. Peroxyacetic acid (PAA) is used as a reagent for economic considerations. It’s crucial to pay close attention to the exothermic nature of the epoxidation process when working with vegetable oils and peracetate. Avoiding potential risks requires the use of the in-situ epoxidation method [1–3], in which a heterogeneous system is employed, namely the aqueous and the organic phases, where the PAA formation reaction and the actual epoxidation process,
respectively, take place. The step that governs the overall reaction rate is typically the slowest one; it often takes several hours of reaction time to get a high level of conversion [4].

Numerous prior investigations documented the epoxidation of various vegetable oils and fatty acids [1,5–10]. Notably, none of these studies, however, explored tamanu oil as a raw material for this process. Furthermore, despite existing literature on liquid-liquid phase epoxidation reaction kinetics [2,11,12], these studies predominantly relied on assumptions of homogeneity or pseudo-homogeneity within the reaction kinetics. A few studies ventured into the exploration of heterogeneous kinetics during in-situ epoxidation of vegetable oils [4,7,13–17]. However, these studies primarily considered mass transfer calculations under the assumption of equilibrium, represented by the aqueous phase-organic phase equilibrium constants. This assumption was based on the prevalence of vigorous stirring during the epoxidation process. Under real conditions, the organic phase and the aqueous phase remain immiscible with each other. Consequently, there exists a compelling need to investigate heterogeneous reaction kinetics in such scenarios. Thus, this study was dedicated to the determination and estimation of reaction and mass transfer parameters in the in-situ epoxidation of tamanu oil with PAA.

In this kinetic model, the mass transfer of various components, including PAA, AA, H$_2$O, and H$^+$, is quantified using the mass transfer coefficient ($k_{ca}$) and Henry’s constant ($H$), thus making it inherently non-phase balanced. The stages of the double bond epoxidation process of tamanu oil include (1) the process of making peroxyacetic acid, (2) the mass transfer of several components from the aqueous phase to the other one, and (3) the epoxidation reaction, which takes place irreversibly, followed by further reactions within the organic phase. The process scheme is shown in Figure 1.

![Figure 1. The process scheme of tamanu oil epoxidation](image-url)

**Peroxyacetic acid formation**
The formation of peroxyacetic acid (PAA) is a reversible reaction; the equilibrium can be expedited by introducing a strong acid catalyst into the mixture. Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) is a commonly employed catalyst for this purpose. Notably, this reaction takes place within the aqueous phase, and it can be represented by the following equation:

\[
\text{AA}_{aq} + \text{PA} \rightleftharpoons \text{PAA}_{aq} + \text{H}_2\text{O}_{aq}
\] (1)

**Mass transfer of some compounds**

Prior to the initiation of the epoxidation reaction, certain compounds in the reaction medium undergo mass transfer. These compounds encompass peroxyacetic acid (PAA), acetic acid (AA), H\textsubscript{2}O, and acid catalyst (H\textsuperscript{+}). However, it’s important to note that in this model, mass transfer is not depicted as a phase equilibrium process. Instead, the calculation of mass transfer rates is executed by involving the mass transfer coefficient (\(k_c\)) and Henry’s constant (\(H\)).

\[
\text{PAA}_{aq} \rightarrow \text{PAA}_{org}
\] (2)

\[
\text{H}_2\text{O}_{aq} \rightarrow \text{H}_2\text{O}_{org}
\] (3)

\[
\text{AA}_{aq} \rightarrow \text{AA}_{org}
\] (4)

\[
\text{H}^+_{aq} \rightarrow \text{H}^+_{org}
\] (5)

**Reversible Epoxidation Reaction**

An epoxidation reaction is a chemical process that opens a double bond by introducing an oxygen atom. In the context of tamanu oil, this reaction involves the double bond (DB) within the oil and peroxyacetic acid, resulting in the formation of a highly reactive epoxide compound (Ep). This reaction is unidirectional, meaning it proceeds irreversibly, and it takes place within the organic phase in situ, as illustrated below:

\[
\text{DB} + \text{PAA}_{or} \rightleftharpoons \text{AA}_{org} + \text{Ep}
\] (6)

**Further Reactions or Side Reactions**

Epoxy compounds possess highly reactive properties, which make them prone to further reactions. This sequence of reactions initiates with the protonation of the epoxy compound by H\textsuperscript{+\_org}. This reaction present in the organic phase, as depicted by equation (7).

\[
\text{Ep} + \text{H}^+_{org} \rightarrow \text{Ep}^*
\] (7)

After that, the protonated epoxy reacts with the remaining H\textsubscript{2}O and AA in the organic phase.

\[
\text{Ep}^* + \text{H}_2\text{O}_{org} \rightarrow \text{P1} + \text{H}^+_{org}
\] (8)
\[ \text{Eqn}^* \ + \ \text{AA}_{\text{org}} \rightarrow \text{P2} \ + \ \text{H}^+_{\text{org}} \] (9)

Where \( P_1 = \) side product 1 and \( P_2 = \) side product 2.

From the above reaction equations, the equation for the concentrations of several components in the aqueous phase can be written as follows:

\[ \frac{d[\text{PAA}_{\text{aq}}]}{dt} = k_1[\text{AA}]_{\text{aq}}[\text{PA}] - k_1[\text{PAA}]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}} - k_{c,\text{PAA}} \left( [\text{PAA}]_{\text{aq}} - H_{\text{PAA}}[\text{PAA}]_{\text{org}} \right) \] (10)

\[ \frac{d[\text{H}_2\text{O}_{\text{aq}}]}{dt} = k_1[\text{AA}]_{\text{aq}}[\text{PA}] - k_1[\text{PAA}]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}} - k_{c,H_2\text{O}} \left( [\text{H}_2\text{O}]_{\text{aq}} - H_{H_2\text{O}}[\text{H}_2\text{O}]_{\text{org}} \right) \] (11)

\[ \frac{d[H^+]_{\text{aq}}}{dt} = -k_{c,H^+} \left( [H^+]_{\text{aq}} - H_{H^+}[H^+]_{\text{org}} \right) \] (12)

\[ \frac{d[\text{AA}_{\text{aq}}]}{dt} = -k_1[\text{AA}]_{\text{aq}}[\text{PA}] + k_1[\text{PAA}]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}} - k_{c,\text{AA}} \left( [\text{AA}]_{\text{aq}} - H_{\text{AA}}[\text{AA}]_{\text{org}} \right) \] (13)

\[ \frac{d[\text{PAA}_{\text{aq}}]}{dt} = -k_1[\text{AA}]_{\text{aq}}[\text{PA}] + k_1[\text{PAA}]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}} \] (14)

Meanwhile, the equation for the concentration of several components in the organic phase can be written as follows:

\[ \frac{d[\text{PAA}_{\text{org}}]}{dt} = -k_{c,\text{PAA}} \left( [\text{PAA}]_{\text{aq}} - H_{\text{PAA}}[\text{PAA}]_{\text{org}} \right) - k_2[\text{PAA}]_{\text{org}}[\text{DB}]_{\text{org}} + k_2[\text{AA}]_{\text{org}}[\text{Ep}]_{\text{org}} \] (15)

\[ \frac{d[\text{H}_2\text{O}_{\text{org}}]}{dt} = k_{c,H_2\text{O}} \left( [\text{H}_2\text{O}]_{\text{aq}} - H_{H_2\text{O}}[\text{H}_2\text{O}]_{\text{org}} \right) - k_5[\text{H}_2\text{O}]_{\text{org}}[\text{Ep}^*]_{\text{org}} \] (16)

\[ \frac{d[H^+]_{\text{org}}}{dt} = k_{c,H^+} \left( [H^+]_{\text{aq}} - H_{H^+}[H^+]_{\text{org}} \right) - k_5[H^+]_{\text{org}}[\text{Ep}^*]_{\text{org}} + k_4[\text{AA}]_{\text{org}}[\text{Ep}^*]_{\text{org}} + k_5[\text{H}_2\text{O}]_{\text{org}}[\text{Ep}^*]_{\text{org}} \] (17)

\[ \frac{d[\text{AA}_{\text{org}}]}{dt} = k_{c,\text{AA}} \left( [\text{AA}]_{\text{aq}} - H_{\text{AA}}[\text{AA}]_{\text{org}} \right) + k_2[\text{PAA}]_{\text{org}}[\text{DB}]_{\text{org}} - k_4[\text{AA}]_{\text{org}}[\text{Ep}^*]_{\text{org}} \] (18)

\[ \frac{d[\text{Ep}^*]_{\text{org}}}{dt} = k_2[\text{PAA}]_{\text{org}}[\text{DB}]_{\text{org}} - k_2[\text{AA}]_{\text{org}}[\text{Ep}]_{\text{org}} - k_5[H^+]_{\text{org}}[\text{Ep}]_{\text{org}} \] (19)

\[ \frac{d[\text{DB}]_{\text{org}}}{dt} = -k_5[\text{PAA}]_{\text{org}}[\text{DB}]_{\text{org}} + k_2[\text{AA}]_{\text{org}}[\text{Ep}]_{\text{org}} \] (20)

\[ \frac{d[\text{Ep}^*]_{\text{org}}}{dt} = k_4[H^+]_{\text{org}}[\text{Ep}]_{\text{org}} - k_4[\text{AA}]_{\text{org}}[\text{Ep}^*]_{\text{org}} - k_5[H_2\text{O}]_{\text{org}}[\text{Ep}^*]_{\text{org}} \] (21)

\[ \frac{d[P1]_{\text{org}}}{dt} = k_4[\text{AA}]_{\text{org}}[\text{Ep}^*]_{\text{org}} \] (22)

\[ \frac{d[P2]_{\text{org}}}{dt} = k_5[H_2\text{O}]_{\text{org}}[\text{Ep}^*]_{\text{org}} \] (23)

Equation (10) to equation (23) are simultaneous ordinary differential equations with the initial conditions: \([\text{AA}]_{\text{aq}} = ([\text{AA}]_{\text{aq}})_0; [H^+]_{\text{aq}} = ([H^+]_{\text{aq}})_0; [H_2\text{O}]_{\text{aq}} = ([H_2\text{O}]_{\text{aq}})_0; [\text{PAA}]_{\text{aq}} = 0; [\text{PA}]_{\text{aq}} = ([\text{PA}]_{\text{aq}})_0; [\text{PAA}]_{\text{org}} = 0; [\text{AA}]_{\text{org}} = 0; [H_2\text{O}]_{\text{org}} = 0; [H^+]_{\text{org}} = 0; [\text{DB}]_{\text{org}} = ([\text{DB}]_{\text{org}})_0; [\text{Ep}]_{\text{org}} = 0; [\text{Ep}^*]_{\text{org}} = 0; [P1]_{\text{org}} = 0; \) and \([P2]_{\text{org}} = 0 \)
In this model, the reaction between the double bond (DB) and peroxyacetic acid (PAA) to produce epoxy (Ep) and acetic acid (AA) is considered reversible. Mass transfer is not assumed to be in phase equilibrium conditions, and the mass transfer rate of several components (PAA, AA, H₂O, and H⁺) incorporates the mass transfer coefficient (k_a) and Henry’s constant (H). Various reaction kinetics and mass transfer parameters, including $k_1$, $k_{-1}$, $k_{cPAA}$, $k_{cH₂O}$, $k_{cAA}$, $k_{cH⁺}$, $H_{PAA}$, $H_{H₂O}$, $H_{AA}$, $H_{H⁺}$, $k_2$, $k_{-2}$, $k_3$, $k_4$, and $k_5$, are estimated to calculate the concentration of each component in the reaction system. Solving this equation involves an objective function to minimize the resulting error. Equation (24) is utilized to compute this error, which represents the difference between experimental data and model calculation results for [Ep] and [DB]. Model completion follows the algorithm outlined in Figure 2.

$$SSE = \sum \left( \left( [DB]_{org}^{calc} - [DB]_{org}^{data} \right)^2 \right) + \sum \left( \left( [Ep]_{org}^{calc} - [Ep]_{org}^{data} \right)^2 \right)$$  \hspace{1cm} (24)$$

Figure 2. Algorithm for determining reaction kinetic and mass transfer parameters.

**Materials**

Tamanu oil was directly procured from local farmers. To prepare the raw material for this research, the oil underwent a degumming and purification process. Various chemicals, including AR Grade of glacial acetic acid, 98 wt% sulfuric acid, Wijs solution, 47 wt%
Epoxidation Process

A total of 70 grams of tamanu oil, sulfuric acid catalyst, and glacial acetic acid were added to the reactor. The mole ratio of oil: acetic acid was 2:1 [4]. The mixture was stirred at a constant speed of 600 rpm and heated to the desired reaction temperature (40°C, 50°C, 60°C, and 70°C). Then, hydrogen peroxide (H₂O₂) was added dropwise into the reactor. Reactions were run within 4 hours, with sampling carried out at 30-minute intervals. The samples are cooled and separated to obtain epoxidized tamanu oil, whose iodine and oxirane values will be analysed. The analysis was carried out using methods from previous research [1,3,18].

RESULTS AND DISCUSSION

Effect of Temperature on The Iodine Value and Oxirane Number

The effect of temperature on the epoxidation rate of tamanu oil was systematically investigated at temperatures of 40°C, 50°C, 60°C, and 70°C. As per the principles of chemical reaction kinetics, higher temperatures lead to an increase in reaction rates. The experimental findings regarding the influence of temperature on the epoxidation process are illustrated in Figure 3. At lower temperatures (40°C and 50°C), the oxirane number exhibited a gradual increase over the course of 240 minutes without subsequent decreases. In contrast, at higher temperatures (60°C and above), the oxirane number exhibited a rapid increase, reaching its maximum value at a specific point in time, followed by a subsequent decline. These results were consistent with prior research [2,10]. At 60°C, a noticeable drop in oxirane content was observed toward the end of the reaction, resulting in an oxirane number of approximately 2.40 g/eq. This decline was even more prominent at 70°C, where the oxirane number experienced a significant reduction from 120 minutes into the reaction. Ultimately, at the conclusion of the reaction, the oxirane number stood at approximately 1.60 g/eq.

This reduction could be attributed to the highly reactive nature of oxirane, which readily underwent further reactions with residual reactants. As the temperature increased, the rate of the epoxidation reaction accelerated, increasing the likelihood of hydroxylation reactions. The side product generated in this process was a hydroxyl compound (-OH). These observations suggested that the formation of hydroxyl groups (-OH) is contingent upon the presence of an oxirane ring, and their concentration increases when there is an abundance of hydrobromic acid in acetic acid, potassium iodide, 30 wt% aqueous hydrogen peroxide, potassium hydrogen phthalate, and crystal violet indicator, were employed in this study.
oxirane rings and heightened molecular kinetics in the reaction medium. This statement aligns with findings from previous research [2,3,19].

The iodine value (IV) is used to express the number of double bonds (C=C) present in fatty acids. Figure 3 also illustrates that IV consistently decreases over time for all temperature variations. This reduction occurs because, as the reaction time progresses, there is a greater frequency of contact and collisions between reactant particles. Consequently, an increasing number of double bonds in tamanu oil react, leading to a decrease in the iodine value. This finding is consistent with previous studies [19,20].

The values of the reaction kinetics and mass transfer parameters

Figure 4 illustrates the experimental and calculated [DB] and [Ep] values. In general, the model offers outstanding modeling results for [DB] and [Ep] at 40°C, 50°C, and 60°C. However, at 70°C, relatively high relative errors are observed, especially for [Ep]. In summary, this kinetics model effectively simulates both mass transfer and the kinetics of the reactions involved. Furthermore, it provides explicit parameter values for the mass transfer process ($k_c a$ and $H$ values).
Figure 4. Ep and DB concentrations from experimental and model results against reaction time at various temperatures.

The values of the mass transfer parameters and reaction kinetics resulting from the calculations are presented in Table 1. The data in the table are divided into two parts: reaction and mass transfer. The reaction constant values are observed to be directly proportional to the reaction temperature, except in the case of $k_3$. There is a slight deviation in $k_3$, where it decreases from $14.6178 \pm 0.0507$ g.mol$^{-1}$.min$^{-1}$ at 40°C to $13.6561 \pm 0.0081$ g.mol$^{-1}$.min$^{-1}$ at 50°C, although the decrease is relatively small (around 6.58%). At 60°C and 70°C, these constants exhibit significant increments. Notably, the constant $k_4$ is almost identical to $k_5$ across all reaction temperatures, suggesting that the reaction rates for forming side products P$_1$ and P$_2$ are nearly the same. These results are in accordance with those reported by previous research [4,13].

Meanwhile, the mass transfer coefficient ($k_c a$) value for components that change phases is almost the same. For example, at a temperature of 60°C, the values obtained for $k_{cPAAa}$, $k_{cH2Oa}$, $k_{cAAa}$, and $k_{cH+a}$ are $20.1499 \pm 0.0931$, $20.1411 \pm 0.0637$, $20.1467 \pm 0.0790$, and $20.1411 \pm 0.1079$ min$^{-1}$, respectively. This uniformity arises because temperature is the
primary factor influencing the mass transfer coefficient value. In this process, the same temperature is applied, leading to similar $k_c a$ values for the components. Moreover, the $k_c a$ value increases with rising temperature, as higher temperatures result in more active kinetics for the component particles or molecules, thereby accelerating the mass transfer process. Conversely, the Henry constant ($H$) values for each component vary. This constant is associated with the solubility of each component. The variation in $H$ values is expected since acetic acid, peroxyacetic acid, water, and acid catalysts possess different solubilities. The solubility of the material will affect its transfer rate [21,22].

Table 1. The values of the reaction kinetics and mass transfer parameters

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$40^\circ$C</th>
<th>$50^\circ$C</th>
<th>$60^\circ$C</th>
<th>$70^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>19.0687 ± 0.3121</td>
<td>30.2202 ± 0.2574</td>
<td>57.1146 ± 0.5708</td>
<td>59.0626 ± 0.8652</td>
</tr>
<tr>
<td>$k_{1,1}$</td>
<td>12.6904 ± 0.0923</td>
<td>14.7555 ± 0.1716</td>
<td>22.5876 ± 0.4901</td>
<td>24.9712 ± 0.7298</td>
</tr>
<tr>
<td>$k_2$</td>
<td>19.3061 ± 0.0891</td>
<td>22.9101 ± 0.0968</td>
<td>35.3358 ± 0.7346</td>
<td>38.0790 ± 0.9713</td>
</tr>
<tr>
<td>$k_{2,2}$</td>
<td>10.2852 ± 0.0423</td>
<td>13.2452 ± 0.0397</td>
<td>15.1516 ± 0.0932</td>
<td>16.7819 ± 0.0997</td>
</tr>
<tr>
<td>$k_3$</td>
<td>14.6178 ± 0.0507</td>
<td>13.6561 ± 0.0081</td>
<td>89.8351 ± 0.8129</td>
<td>95.0611 ± 0.9641</td>
</tr>
<tr>
<td>$k_4$</td>
<td>21.2667 ± 0.0658</td>
<td>50.0452 ± 0.1025</td>
<td>100.0284 ± 0.9043</td>
<td>105.0173 ± 1.2013</td>
</tr>
<tr>
<td>$k_5$</td>
<td>21.2660 ± 0.0661</td>
<td>50.0431 ± 0.1034</td>
<td>100.0246 ± 0.8979</td>
<td>105.0180 ± 1.2101</td>
</tr>
<tr>
<td>$k_{c,PAA}$</td>
<td>12.6654 ± 0.0657</td>
<td>15.1369 ± 0.0736</td>
<td>20.1499 ± 0.0931</td>
<td>23.0777 ± 0.1384</td>
</tr>
<tr>
<td>$k_{c,H_2O}$</td>
<td>12.3793 ± 0.0549</td>
<td>15.1501 ± 0.0701</td>
<td>20.1411 ± 0.0637</td>
<td>23.0790 ± 0.1476</td>
</tr>
<tr>
<td>$k_{c,AA}$</td>
<td>12.4912 ± 0.0394</td>
<td>15.1708 ± 0.0833</td>
<td>20.1467 ± 0.0790</td>
<td>23.0789 ± 0.0978</td>
</tr>
<tr>
<td>$k_{c,H^+}$</td>
<td>12.4296 ± 0.0821</td>
<td>15.1495 ± 0.1104</td>
<td>20.1411 ± 0.1079</td>
<td>23.0790 ± 0.1296</td>
</tr>
<tr>
<td>$H_{PAA}$</td>
<td>0.0663 ± 0.0012</td>
<td>1.0464 ± 0.0029</td>
<td>0.8622 ± 0.0045</td>
<td>0.7648 ± 0.0076</td>
</tr>
<tr>
<td>$H_{H_2O}$</td>
<td>30.7497 ± 0.1008</td>
<td>0.4928 ± 0.0017</td>
<td>3.9912 ± 0.0087</td>
<td>1.6532 ± 0.0099</td>
</tr>
<tr>
<td>$H_{AA}$</td>
<td>0.9238 ± 0.0024</td>
<td>9.2440 ± 0.0215</td>
<td>5.2042 ± 0.0761</td>
<td>6.8009 ± 0.0781</td>
</tr>
<tr>
<td>$H_{H^+}$</td>
<td>12.9531 ± 0.0518</td>
<td>9.3909 ± 0.0227</td>
<td>7.7322 ± 0.0802</td>
<td>2.5094 ± 0.0792</td>
</tr>
</tbody>
</table>

Unit of $k_i$ is g.mol$^{-1}$min$^{-1}$
Unit of $k_{c,i}$ is 1/min dan $H$ is dimensionless unit

The Concentration of Reactants and By-Products

The concentration of reactants and by-products as a function of time in the aqueous phase is shown in Figure 5. The concentration of AA at the beginning of the reaction decreased drastically to a minimum value followed by a gradual and very small increase in concentration. The time required to reach this minimum value varies with temperature, with higher temperatures requiring less time. In general, [AA] increases with rising temperature. At 60°C and 70°C, the concentration of AA remains nearly constant. This phenomenon is likely due to the substantial increase in side reactions for the formation of side products P1 and P2 at high temperatures (> 60°C).
Figure 5. Relationship between the concentrations of AA, PA, PAA, H$_2$O, P$_1$, and P$_2$ in the aqueous phase and modeling reaction time at various temperatures.

The concentration of peroxy acid (PA) decreases with increasing temperature and reaction time. PA is a reactant in the formation of peroxyacetic acid (PAA) in the aqueous phase. This reduction in concentration is relatively slow at low temperatures and accelerates at higher temperatures. On the other hand, at temperatures ranging from 40°C to 60°C, the concentration of H$_2$O increases with rising temperature and remains relatively constant with time. At 70°C, the concentration of H$_2$O increases slightly compared to 60°C but then decreases as reaction time progresses. This suggests that as the reaction time lengthens, solubility increases, and the side reaction for producing P$_1$ becomes relatively fast. Consequently, H$_2$O, which transfers to the organic phase, directly reacts with protonated epoxy compounds to produce P$_1$.

Figure 6 presents the concentrations of reactants and by-products as a function of time in the organic phase. The concentration of acetic acid (AA) at the beginning of the reaction experiences a drastic decrease to a minimum value, followed by a gradual and very small increase in concentration. The time required to reach this minimum value varies with temperature, with higher temperatures leading to shorter times. In this organic phase, the concentration of AA increases with increasing temperature. At 60°C and 70°C, the difference
in AA concentration is relatively small. It is possible that the formation of side products P\(_1\) and P\(_2\) increases drastically at high temperatures (> 60°C).

The concentration of H\(_2\)O decreases as the temperature increases and remains relatively constant over time. At 70°C, the H\(_2\)O concentration only experiences a slight decrease compared to 60°C. This phenomenon is likely due to H\(_2\)O reacting with protonated epoxy compounds, resulting in a relatively significant increase at high temperatures. In the temperature range of 40°C to 60°C, the concentration of the acid catalyst (H\(^+\)) shows an inverse correlation with temperature. However, at 70°C, the concentration of H\(^+\) increases drastically, even surpassing the concentration of H\(^+\) at 40°C. This phenomenon is closely related to the predominant formation of side products P\(_1\) and P\(_2\) at this temperature. According to the reaction

Figure 6. Relationship between the concentrations of AA, PA, PAA, H\(_2\)O, P\(_1\), and P\(_2\) in the organic phase and reaction time at various temperatures
mechanism, the formation of \( P_1 \) and \( P_2 \) generates \( H^+ \) as a side product, leading to a sharp increase in \( H^+ \) concentration at 70°C.

At 40°C and 50°C, the number of moles or concentrations of side products \( P_1 \) and \( P_2 \) during the reaction remains very small, almost coinciding with the \( x \)-axis. At these temperatures, any increase in their concentrations is minimal. However, at 60°C, the concentrations of \( P_1 \) and \( P_2 \) experience a significant increase. This increase becomes even more pronounced at 70°C. This behavior is a consequence of the sensitivity of the reaction constant values to temperature, particularly for the reactions that form these two side products, as discussed earlier. Additionally, at higher temperatures, the mass transfer of some components increases, contributing to the higher concentrations of \( P_1 \) and \( P_2 \) observed at 60°C and 70°C.

**The values of the collision factor (A) and activation energy (Ea)**

The Arrhenius equation is a commonly used equation for determining parameters related to reaction kinetics. To determine the collision factor (\( A \)) and activation energy (\( Ea \)) values, a linearization process is performed by plotting \( \ln k_i \) against \( 1/T \) at each constant temperature. The results of this linearization for the kinetics model are presented in Table 2.

<table>
<thead>
<tr>
<th>Constant</th>
<th>( A ) (g.mol(^{-1}).min(^{-1}))</th>
<th>( Ea ) (kcal/mol)</th>
<th>Mean of ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>(2.1918 ± 0.2753) x 10(^7)</td>
<td>36.1987 ± 0.0917</td>
<td>0.9254</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>(5.6933 ± 0.1964) x 10(^4)</td>
<td>21.9592 ± 0.0312</td>
<td>0.9431</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>(9.2867 ± 0.1821) x 10(^5)</td>
<td>22.1147 ± 0.0164</td>
<td>0.9374</td>
</tr>
<tr>
<td>( k_4 )</td>
<td>(2.6884 ± 0.3170) x 10(^3)</td>
<td>14.3988 ± 0.0921</td>
<td>0.9921</td>
</tr>
<tr>
<td>( k_5 )</td>
<td>(1.6506 ± 0.1026) x 10(^{12})</td>
<td>66.8907 ± 0.1238</td>
<td>0.7940</td>
</tr>
<tr>
<td>( k_6 )</td>
<td>(4.3137 ± 0.1002) x 10(^9)</td>
<td>49.4021 ± 0.6023</td>
<td>0.9114</td>
</tr>
<tr>
<td>( k_7 )</td>
<td>(4.3154 ± 0.1009) x 10(^9)</td>
<td>49.4032 ± 0.6058</td>
<td>0.9115</td>
</tr>
</tbody>
</table>

The quality of the linearization is indicated by the \( R^2 \) value, with higher values suggesting better linearization. The lowest average \( R^2 \) value, albeit still relatively high at around 0.7940, is obtained for \( k_3 \), which represents the kinetic constant for the reverse reaction of the PAA formation process. The \( Ea \) values at the three constants (i.e., \( k_1, k_2, \) and \( k_3 \)) are relatively small compared to the others, respectively 21.9592 ± 0.0312; 22.1147 ± 0.0164; and 14.3988 ± 0.0921 kcal/mol. Meanwhile, the \( Ea \) values for \( k_1 \) and \( k_3 \) were relatively large, namely 36.1987 ± 0.0917 and 66.8907 ± 0.1238 kcal/mol. The values of \( Ea \) and \( A \) for \( k_4 \) and \( k_5 \) are almost the same, indicating that the reaction rates for the formation of \( P_1 \) and \( P_1 \) are almost the same. The
A values for these constants vary, where the order is from $10^3$ to $10^{12}$. The lowest value occurs at $k_{-2}$, which is around $(2.6884 \pm 0.3170) \times 10^3$ g.mol$^{-1}$.min$^{-1}$. While the highest $A$ value occurs at $k_2$, which is around $(1.6506 \pm 0.1026) \times 10^{12}$ g.mol$^{-1}$.min$^{-1}$. This range is different compared to previous research, namely for tung oil its order was obtained from $10^4$ to $10^{25}$ [4].

CONCLUSIONS

Epoxidation of tamanu oil with peroxyacetic acid can be carried out successfully. The mass transfer coefficient ($k_c a$) value for components that change phases is almost the same. This uniformity arises because temperature is the primary factor influencing the mass transfer coefficient value. Moreover, the $k_c a$ value increases with rising temperature, as higher temperatures result in more active kinetics for the component particles or molecules, thereby accelerating the mass transfer process. Conversely, the Henry constant ($H$) values for each component vary, it is associated with the solubility of each component. The $E_a$ values at the three constants (i.e., $k_{-1}$, $k_2$, and $k_{-2}$) are relatively small compared to the others. Meanwhile, the $E_a$ values for $k_1$ and $k_3$ were relatively large, namely $36.1987 \pm 0.0917$ and $66.8907 \pm 0.1238$ kcal/mol. The values of $E_a$ and $A$ for $k_4$ and $k_5$ are almost the same, indicating that the reaction rates for the formation of P1 and P1 are almost the same. The $A$ values for these constants vary, where the order is from $10^3$ to $10^{12}$ g.mol$^{-1}$.min$^{-1}$.

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