Chapter 4

Reaction engineering of synthesis of coconut fatty acid-sucrose esters and epoxidised oleate

4.1 Background and objectives of kinetic and thermodynamic modeling of synthesis of coconut fatty acid-sucrose esters and epoxidised oleic acid/ methyl oleate

The empirical investigations on synthesis of coconut fatty acid-sucrose esters and epoxidised oleates were conducted with an objective of tuning of diverse process variables for optimisation of base catalysed transesterification (Chapter 2) and homogenous peracid epoxidation (Chapter 3), respectively. In tune with these process developments, at least some indication of the performance of the reactor is needed through use of principles of Chemical Reaction Engineering (CRE) before any commercial feasibility assessment of the process as a whole can be made. For example, applications of principles of chemical kinetics permit prediction and regulation of the rate at which sucrose/ oleic acid react, in response to various reaction variables, so as to produce sucrose ester/ epoxidised oleate with desirable chemical characteristics and purity in a controllable manner [e.g. sucrose ester- control of specific degree of substitution, epoxidised oleic acid- control of ring opening]. On the basis of knowledge of various kinetic and thermodynamic parameters such as rate constants, catalyst activity, energy of activation, equilibrium compositions and enthalpy of reaction, CRE permits calculations of holding time/ space velocity, energy requirement, and dimensions of reactor. The various design options for the homogeneously catalysed synthesis of sucrose ester and epoxidised oleate in terms of mode of operation (batch or continuous), flow pattern for continuous reactors (mixed vs. plug flow), arrangement of multiple reactors (cascading/ parallel), reactor size (volume of reactors and/ or amount of catalyst) and mode of heat transfer and instrumental control for the given design of reactor system can thus be worked out.

Although numerous references exist in the technical literature concerning the utilisation of sucrose ester and methods of epoxidation of different olefinic substrates, very few are concerned with systematic kinetic studies. For example, the literature on synthesis of sucrose ester, in general, and kinetics of its synthesis, in particular, is scarce. The abundant patent literature (Ref. 1-37 in Chapter 2) on sucrose ester doesn’t include even a single reference on investigations on kinetic modeling. Kinetics and thermodynamics of epoxidation of vegetable oils is a well searched topic (section 1.3.3, Chapter 1). But one
doesn’t find specific research references on oleic acid. Moreover no attempt has been made so far in the development of combined kinetic and thermodynamic modeling of epoxidation and ring opening reactions. The limited investigations and literature on reaction engineering of synthesis of the sucrose esters and epoxidation of oleic acid is introducing the great difficulty in the design of different available reactor options (batch/semi batch, PFR/CFSTR, slurry/packed bed reactor) and call for additional R & D input.

In present work, a kinetic model for the K₂CO₃ catalysed synthesis of the coconut fatty acid- sucrose esters in presence of DMF solvent (i.e. homogeneous liquid phase) was developed. The dependence of the kinetics of transesterification on number and nature of available hydroxyl groups in the reacting polyol molecule (i.e. sucrose or residual hydroxy groups in mono/di/poly ester) and thus the corresponding development and evaluation of irreversible and reversible selective and nonselective kinetic models were investigated. The aim of this modeling study was to predict the variation in rate constant as function of experimental conditions, improve the selectivity of the targeted product and facilitates the reactor scale-up studies.

The second objective of the present work was to study the kinetic and thermodynamic modeling of catalytic/non-catalytic peracid epoxidation of oleic acid as a model compound in a batch reactor system. The results of the batch in situ and ex situ per acid epoxidation of oleic acid (Chapter 3) were used to determine the rate constants, the activation energies and other thermodynamic parameters of the epoxidation reactions. The oxirane formation, during peracid epoxidation, accompanies the degradation reactions such as ring opening and glycol formation. Thus the modeling and simulation studies included the kinetic and thermodynamic analysis of sequential degradation reactions through development of a series-parallel kinetic model for the reaction system and the estimation of the unknown kinetic and thermodynamic parameters of the proposed model.

The modeling studies in present chapter, therefore, aims at in-depth evaluation of reaction engineering of base catalysed transesterification and homogenous peracid epoxidation in reference to process variables such as reaction temperature, molar ratios and concentration of the reactants and amount of the catalysts.

4.2 Methods of interpretation of batch transesterification/epoxidation data

In present investigations on chemical kinetics of synthesis of sucrose ester and epoxidised oleate, the progress of transesterification and epoxidation reactions were monitored through measurement of concentration of one of the reactants- sucrose hydroxyls or double bonds oleic acid (ex situ mode of measurements) and/ or other
properties (FTIR and \(^1\)H NMR spectrometry, RI) dependent on concentration of reactants/products \((in\ situ\ mode)\). The setup involves six station reaction flasks, modelled as batch reactor, maintained under identical conditions (temperature, reactant molar ratio, catalyst concentration etc.). For the purpose of end product analysis, the reaction mixture was quenched at different time intervals so that no reaction occurs during the \(ex\ situ\) and \(in\ situ\) analysis. Volumetric estimation techniques such as AV (acid value, measure of -COOH groups in oleic acid), HV (hydroxyl value, disappearance of hydroxy groups during sucrose transesterification with coconut FAME, formation of -OH groups through ring opening of epoxidised oleate), IV (Iodine value, disappearance of double bonds in oleic acid during epoxidation), SV (saponification value, measure of molecular weight of sucrose mono/polyesters), EEW (epoxy equivalent weight, extent of epoxidation/measure of molecular weight of pure epoxy compounds) and spectroscopic tools such as FTIR and \(^1\)H NMR (functional group analysis and quantitative formation of monoester/diester/polyester and epoxy/hydroxy acetate/glycol) were used to provide the basis for calculations of extent of reactions. Table 2.3 \((Chapter\ 2)\) and Table 3.4 \((Chapter\ 3)\) present results on synthesis of coconut fatty acid sucrose ester and batch peracid epoxidation of oleic acid respectively.

The general kinetic form of component ‘i’ participating in the reaction for constant density system is written as: \(\frac{dC_i}{dt} = r_i = k x C_a^m x C_i^p x \cdots\) where \(C_i\) is the concentration of component i (gmol/lit), \(r_i\) the reaction rate (gmol/(lit.min)) and \(V\) the volume of reactor (lit) and \(m, - - p, - -\) denote reaction order with reference to the participating component \(a, - - i, - -\), respectively. The derivatives and calculations which were carried out to obtain the kinetic constants \((k)\) may be of two kinds, depending on whether the rate equation is to be used in its original (differential) form, or in its integrated form.

4.2.1 Integral method of analysis and second order bimolecular kinetics of synthesis of sucrose ester and \(ex\ situ\) epoxidation of oleic acid

Integral method was used to evaluate the bimolecular second order transesterification/\(ex\ situ\) epoxidation kinetic models on the basis of integrated expressions in terms of disappearance of hydroxyl groups (sucrose ester) and double bonds (epoxidation) and provide the predicted extent of transesterification/\(ex\ situ\) epoxidation as a function of time (t). The magnitude of the second order rate constant \((k_2)\) is found by fitting the experimental data. In order to provide the basis for irreversible transesterification and \(in\ situ\) epoxidation kinetics, this method takes under the
calculations of \( k_2 \) based on the conversion of the limiting reactant over short reaction period (e.g. 30 min). The evaluation of energy of activation requires the determination of bimolecular rate constant at 2/3 different temperatures (T). The simulation method consists of comparing the observed and the predicted reactant concentrations as a function of time.

### 4.2.2 Differential method of analysis and kinetic modeling of sequential epoxidation and degradation/reversible transesterification reactions

The concentrations of hydroxy acetate, glycols etc. and by product (water) of ring degradation reactions were obtained by solving the material balance equations of batch reactor for the given epoxidation reaction. Since the differential form was to be used for the kinetic modeling of the sequential epoxidation and degradation reactions/reversible transesterifications, the method requires the differentiation of the experimental concentration \( (C_i) \) data as a function of time \( (t) \) to obtain a rate form which was solved to obtain the magnitude of rate constants for intermediate reaction stages. Competitive epoxidation and degradation reactions are combinations of parallel and series reactions. Hence it is necessary to identify the relative importance of yield, selectivity, and production rate of a desired product (epoxidised oleate) in association with the type, size, mode of operation, and configuration of reactor. It is more difficult to develop general guidelines regarding the selection and design of a reactor for a series-parallel reaction network than for a parallel-reaction or a series-reaction network separately. A number of statistics and spreadsheet software packages like excel spreadsheet and polymath are available for linear regression, and also for nonlinear regression of algebraic expressions. However, few software packages are designed for parameter estimations involving numerical integrations of the differential equations containing the rate form.

### 4.3 Kinetic modeling of synthesis of coconut fatty acid-sucrose ester

In a typical homogeneous (presence of solvent and high stirring) potassium carbonate catalysed transesterification of sucrose with coconut FAME, a complex product mixture consisting of mono-, di-, tri- and polyesters is formed (Fig. 4.1). Kinetic modeling of synthesis of coconut fatty acid sucrose ester was undertaken on the basis of following hypothesis:

i. The bimolecular, second order transesterification reaction mechanism of base catalyzed synthesis of sucrose esters presenting generation of tetrahedral intermediate through nucleophilic attack is already illustrated in Fig. 1.4 under Chapter 1. As per this mechanism, the reaction partial orders are equal to 1. Although the reaction is reversible in
nature, in absence of enough product (i.e. during initial period), irreversibility of transesterification can be safely assumed and the forward rate constant can be easily determined. Overall kinetic evaluations however require application of mathematical model based on reversible kinetics.

![Diagram of sucrose ester synthesis](image)

**Fig. 4.1 Product composition and equilibrium in the synthesis of sucrose esters by transesterification with FAME**

**ii.** Reaction mixture is perfectly stirred and follows homogeneous kinetics for constant density batch system. The synthesis implies the reaction of dispersed sucrose powder with liquid FAME (RCOOCH₃) in the presence of solid K₂CO₃ catalyst, reaction medium being provided by nitrogenous solvent DMF. The reaction leading to sucrose monoester (SE) formation is a solid/ liquid transesterification reaction between sucrose powder dissolved/ dispersed in DMF (highly polar) and FAME/ oil (hydrophobic) whereas the formation of disubstituted sucrose esters is a liquid/ liquid reaction between SE and additional FAME, which is favoured by hydrophobic effects. Thus, this later reaction is favoured with respect to the reaction leading to the monoesters formation. Polysubstituted reaction kinetics is similar to that of diesters, because they are both liquid/ liquid reactions.
iii. The extent of saponification of mono and higher esters by K₂CO₃, which is used as catalyst, is negligible because K₂CO₃ is nonsaponifying base.

iv. The selective and nonelective response of sucrose hydroxyl groups towards transesterification is entirely governed by availability (stoichiometrically deficient or excess) of coconut FAME.

Case I: Kinetic modeling on the basis of equal transesterification opportunity for all 8 hydroxyl groups of sucrose [nonselective kinetics]

The sucrose is a polyol carrying 8 hydroxyl groups and with use of FAME at stochiometric ratio or in excess, all eight hydroxyl present in sucrose avail fair and equal opportunity for participation in formation of tetrahedral intermediate with FAME molecules. Thus the bimolecular second order kinetic model, depicting the irreversible (case 1A) and reversible (case 1B) reaction between fatty ester and hydroxyl functional compound (sucrose polyol, sucrose mono/ di/ tri/ tetra/ penta/ hexa/ hepta ester) based on equivalence of all 8 hydroxyl positions in sucrose, were proposed as given below and the kinetics of alcoholysis was examined by application of integral method of analysis for constant volume batch reactor system¹.

Case I A Irreversible nonselective transesterification kinetic model

\[ -\text{OH} + \text{RCOOC}_2\text{H}_3 \xrightarrow{k_2} \text{OCOR} + \text{CH}_3\text{OH} \]

Eq. 4.1

where, \( A = \text{-OH} = \text{any hydroxyl group of sucrose/ hydroxyl group present in partial esters.} \)
\( B = \text{FAME, } C = \text{Sucrose ester, } D = \text{Methanol} \)

Irreversible second order bimolecular nonselective kinetic model is given by Eq. 4.2.

\[
\begin{align*}
-\left\{ N\ln\left[ \frac{(1-X_A)}{(1-NX_A)} \right] \right\} &= C_{A_0} (1-N)k_2t \quad \text{for } N<1 \\
\frac{X_A}{1-X_A} &= k_2C_{A_0}t \quad \text{for } N = 1 \\
\ln\left[ \frac{(N-X_A)}{N(1-X_A)} \right] &= C_{A_0} (N-1)k_2t \quad \text{for } N>1
\end{align*}
\]

Eq. 4.2

where, \( N = \frac{N_{\text{B}_0}}{8\times N_{A_0}} = \frac{M}{8} \)

\( = \text{ester functionality per unit hydroxyl functionalities} \)

\( M = \frac{N_{\text{B}_0}}{N_{A_0}} = \text{initial molar ratio of FAME to sucrose} \)
Fractional transesterification conversion for given run \((X_A)\),

\[
X_A = \frac{(\text{Initial HV}) - (\text{final HV})}{(\text{Initial HV})}
\]

Eq. 4.3

\(k_2\) = second order bimolecular nonselective transesterification rate constant \(\text{lit/}(\text{gmol}.\text{min})\)

\(C_{A_0}\) = initial hydroxyl concentration, gmol/lit.

The results obtained by using data of Table 2.3 of Chapter 2 and subsequently solving Eq. 4.2 are reported in Table 4.1.

**Case I B Reversible transesterification nonselective kinetic model**

Irreversible kinetics is valid only for initial holding period < 30min. Since the reaction was observed to retard after 1 hr and transesterification mechanism has indicated reversibility of the synthesis (Fig. 1.4, Chapter 1), the modeling of synthesis of sucrose ester is undertaken on the basis of reversible kinetics.

\[
A + B \xrightleftharpoons[k_{2b}]{k_{2f}} C + D
\]

Eq. 4.4

The rate equation is:

\[
-r_A = -\frac{dC_A}{dt} = k_{2f} C_A C_B - k_{2b} C_C C_D
\]

Eq. 4.5

Here, \(k_{2f}\) and \(k_{2b}\) represent second order nonselective transesterification forward rate and backward rate constants, respectively.

\[
C_A = C_{A_0} (1-X_A) \Rightarrow -\frac{dC_A}{dt} = C_{A_0} \frac{dX_A}{dt}
\]

Eq. 4.6

Material balance equations:

\[
C_B = C_{B_0} - C_{A_0} X_A = C_{A_0} (N - X_A)
\]

Eq. 4.7

\[
C_{A_0} X_A = C_C = C_D
\]

Eq. 4.8

Using Eqs. 4.6, 4.7 and 4.8. Eq. 4.5 was modified as,

\[
\frac{dx_A}{dt} = C_{A_0} \left[ k_{2f} (1-x_A) (N-x_A) - k_{2b} x_A^2 \right]
\]

Eq. 4.9

The quadratic equation in rectangular bracket was solved followed by integration by partial fractions. Thus the reversible second order bimolecular nonselective transesterification kinetic model was as given by Eq. 4.10:
The results obtained by using data of Table 2.3 of Chapter 2 and subsequently solving Eq. 4.10 are reported in Table 4.1.

Case II: Kinetic modeling on the basis of selective transesterification opportunity for 6- OH of glucose unit

In reference to the results and discussion presented under section 2.5.1-Synthesis of coconut fatty acid-sucrose esters (Chapter 2), it is clear that when \( M \leq 1 \), the transesterification is selective. The fructose moiety of sucrose appears to be less reactive and the reaction was rather selective on the glucose moiety and the reactivity order is 6 \( \text{OH} > 6' \text{OH} >> 1' \text{OH} \). Thus when one initiates synthesis by providing \( M= \text{fatty ester/sucrose molar ratio} \leq 1 \), the mono-substitution in sucrose takes place preferentially at C-6 in the glucose unit. Hence in present work, the second order bimolecular transesterification kinetic model based on the selective reaction between the FAME and 6- \( \text{OH} \) of the glucose unit, as given below, was proposed and evaluated.

Case II A Irreversible selective transesterification kinetic model

\[
\text{Sucrose-6OH+RCOOCH}_3 \xrightarrow{k_i} \text{Sucrose-6OCOR+CH}_3\text{OH}
\]  

Eq. 4.11

\[A + B \xrightarrow{k_i} C + D\]

where Sucrose -6OH represents 6-\( \text{OH} \) of glucose unit of sucrose.

Eq. 4.12 presents irreversible second order bimolecular selective transesterification kinetic model.

\[
\begin{align*}
M \ln \left[ \frac{(1-X_A)}{(1-MX_A)} \right] & = C_{A_i} (1-M)k_2t \quad \text{for} \quad M<1 \\
\frac{X_A}{1-X_A} & = k_2C_{A_i}t \quad \text{for} \quad M=1 \\
\ln \left[ \frac{(M-X_A)}{M(1-X_A)} \right] & = C_{A_i} (M-1)k_2t \quad \text{for} \quad M>1
\end{align*}
\]

Eq. 4.12

\[
M= \text{initial molar ratio}= \frac{N_{B_i}}{N_{A_i}}
\]
where $k_2^r$ represents selective irreversible rate constant and $C_{A_0}$ = initial sucrose concentration, gmol/lit (it needs to be noted that, in nonselective model, $C_{A_0}$ represents initial hydroxyl group concentration). The results obtained by using data of Table 2.3 of Chapter 2 and subsequently solving Eq. 4.12 are reported in Table 4.1.

**Case II B Reversible selective transesterification kinetic model**

Combining the logic of selective modeling of case II-A with reversible selective reaction between sucrose -6-OH and FAME, the bimolecular reversible second order selective kinetic model takes the form proposed under Eq. 4.13

$$
A + B \xrightarrow{k_{2}^r} C + D
$$

\[
\ln \left( \frac{2Mk_{2}^r + x_A \left( k_{2}^r + Mk_{2}^r \right) + x_A \left( \sqrt{\left( k_{2}^r - Mk_{2}^r \right)^2 + 4Mk_{2}^r k_{2}^b} \right)}{2Mk_{2}^r + x_A \left( k_{2}^r + Mk_{2}^r \right) - x_A \left( \sqrt{\left( k_{2}^r - Mk_{2}^r \right)^2 + 4Mk_{2}^r k_{2}^b} \right)} \right) = C_{A_0} \left( \sqrt{\left( k_{2}^r - Mk_{2}^r \right)^2 + 4Mk_{2}^r k_{2}^b} \right) t
\]

Eq. 4.13

Here, $k_{2}^r$ and $k_{2}^b$ represent second order selective transesterification forward rate and backward rate constants respectively. The results obtained by using data of Table 2.3 of Chapter 2 and subsequently solving Eq. 4.13 are reported in Table 4.1.

**4.4 Results and discussion on kinetic modeling of synthesis of coconut fatty acid-sucrose ester on the basis of irreversible and reversible transesterification-nonselective and selective kinetic modeling**

The development of mathematical models for transesterification of sucrose with coconut FAME for nonselective reactions of all hydroxyl groups (Model-I) and selective reaction of 6-OH of glucose (Model-II) in sucrose or partial esters have been illustrated in previous section. While assumption of irreversible kinetics is valid only for initial period, it simplifies the calculations and permits determination of forward rate constants by integral method of analysis (i.e. by using Eq. 4.2 and 4.12). With availability of elaborate concentration- time data and good software backup for differential method of analysis, forward and backward transesterification rate constants can be determined by using Eq. 4.10 and 4.13. Thus the chemists involved in the design calculations could avail flexibility.
of choosing either simplified determination methods with same sacrifice in accuracy or complex methods with highly involved calculations of higher degree of accuracy.

The bimolecular second order nonselective \( k_2 \) and selective rate constants \( k'_2 \), calculated on the basis of irreversible conditions using equations 4.2, and 4.12, respectively, are reported in Table 4.1. Batch SE1 carried lowest catalyst dosing (1.1%). Hence it was associated with lowest nonselective \( 1.15 \times 10^{-4} \) and selective \( 8.49 \times 10^{-3} \) specific reaction rates. In remaining batches (excluding those corresponding to coconut oil), around 2.0% catalyst loading and 50% solvent were utilized. Transesterification of coconut oil was extremely slow under these conditions. Hence the batches- SE8 and SE9 were conducted at higher catalyst loading (3% and 4% respectively) and reduced solvent usage (i.e. higher reactant concentration). Even with use of high catalyst and reactant concentration, the coconut oil transesterification rate constant, as shown in Table 4.1, was \( 1.15 \times 10^{-4} \) versus \( 9.04 \times 10^{-5} \) or \( 1.24 \times 10^{-4} \) comparable or slightly better in reference to that of batch SE1 (a batch conducted at lowest catalyst loading). Selective specific reaction rates of coconut oil however are of lower magnitude even at 4%. Since the magnitudes of transesterification rate constant for coconut oil are low, the time required to attain equilibrium would have been longer. Calculations based on differential method of analysis (Eq. 4.10 and 4.13) have indicated that the ratio of forward to backward rate constants \( k_f / k_b \) is greater than 8. Thus even after conducting reaction for 2 hrs, the product concentrations are expected to display insignificant effect on kinetics. Hence calculations for coconut oil based on assumption of irreversible kinetics have fair accuracy and are reported in Table 4.1.

**Nonselective kinetics versus selective kinetics**

For same source of fatty monoester (Batches- SE2, SE3, SE4, SE5), identical catalyst loading (2%) and reaction temperature (120°C), the magnitude of nonselective rate constant \( k_2 \) increases from \( 1.15 \times 10^{-4} \) to \( 8.31 \times 10^{-3} \) \text{lit/(g.mol.min)} \) with rise in M from 0.73 to 6.0 (or N from 0.0455 to 0.750). The rate constant \( k_2 \) represents average specific transesterification rate per hydroxyl group for all eight hydroxyls in sucrose and hydroxyl groups in partial esters. The increase in M from 0.73 to 6.0 represents more availability of fatty esters for reaction with -OH groups which results in increase in average activity per hydroxyl group and leads to the enhancement in magnitude of \( k_2 \) with rise in M/N. On the other hand, when M < 1, the reaction would be rather selective or oriented specifically towards primary hydroxyl of the glucose moiety due to its abundant
Table 4.1 Kinetic modeling of synthesis of coconut fatty acid-sucrose ester

<table>
<thead>
<tr>
<th>Batch code</th>
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<th>Reaction Parameters</th>
<th>Transesterification Rate Constant, lit/(gmol.min)</th>
<th>Reversible Rate Constant, lit/(gmol.min)</th>
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<td></td>
<td></td>
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<td>$k'_2$ (Model IIA)</td>
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<td></td>
<td></td>
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<td>$t$, min</td>
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<td>9.27 E-03</td>
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<td>3.07 E-02</td>
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<td>120</td>
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A. Synthesis of sucrose ester from FAME and sucrose
### B. Synthesis of sucrose ester from methyl laurate and sucrose

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### C. Synthesis of sucrose ester from methyl myristate and sucrose

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### D. Synthesis of sucrose ester from coconut oil and sucrose

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<td>4.30E-03</td>
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<td>1.25E-03</td>
<td>1.53E-03</td>
<td>2.68E-03</td>
</tr>
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</table>

Cat % (by wt on A & B) and % DMF: SE1#: 1.1 & 62.1; SE5*, 3.0 & 32.0; SE8#: 4.0 & 38.4; in rest of the batches: 2.0 & 50.0, respectively.

Note: Model I A: Eq. 4.2; Model I B: Eq. 4.10; Model II A: Eq. 4.12; Model II B: Eq. 4.13
availability in relation to the ester functionality. Hence for M < 1 the selective rate constant k'2 (specific reaction rate of 6-OH group) increases with M and attained highest magnitude of 2.89 X 10^-2 at M=0.73 / N=0.0913. When M exceeds 1, esters happen to be available for reactions with other hydroxyls besides 6-OH groups. Thus with increase in M, the transesterification became more nonselective. Correspondingly one observes decline in selective specific reaction rate from 1.93 X 10^-2 (M=1.5) to 1.23 X 10^-2 (M=6.0).

Table 4.1 also presents magnitudes of forward (k2f and k'2f) and backward rate constants (k2b and k'2b) calculated using Eq. 4.10 and 4.13. The ascending order of nonselective forward rate constants (k2f) (for t=120min) from 9.7 X 10^-4 (M=0.364/ N=0.0455) to 2.08 X 10^-3 (M=6.0/ N=0.75) is in tune with the rising trend exhibited by transesterification nonselective rate constant (irreversible kinetics). The selective forward rate constants (k'2f) exhibited initially the rising mode (from 4.03 X10^-3 to 4.16 X 10^-3) for M < 1 and declined thereafter and attained lowest value of 2.82 X 10^-3 at M=6.0/ N=0.75.

**Influence of molecular weight/ chain length on kinetics of transesterification**

The objective in choosing different raw materials of medium molecular weight fatty acids- mixed FAME derived from coconut oil (batch SE3, chain length: C6-C18), methyl laurate (SE6, C12), methyl myristate (SE7, C14) and coconut oil (SE9, triester) was to understand the influence of molecular weight and chain length on kinetics of transesterification, other parameters being maintained constant.

As shown previously, coconut oil, a triester with MW 672, exhibited lowest rate constant in spite of use of 3-4% catalyst. Let us now compare the forward specification reaction rate of the three monoesters (SE3, SE6 and SE7), keeping all other reaction parameters constant: temperature (120°C), time (60 min), % catalyst (2%), % DMF (50%) and M (1.5). The magnitude of nonselective and selective rate constants were found to follow the descending order in relation to the ascending order of molecular weight: mixed FAME (3.07 X 10^-3, 6.47 X 10^-3) ≥ methyl laurate (3.02 X 10^-3, 6.24 X 10^-3) > methyl myristiate (2.93 X 10^-3, 5.87 X 10^-3). Thus the presence of low molecular weight fatty acids- C6, C8 and C10 in mixed FAME contributed to 5-10% rise in the magnitude of rate constant over that of myristate.
Series-parallel transesterifications and their influence on average rate constants

The specific reaction rates must be constant for a single reaction at a given temperature. However, they were observed to decrease as a function of reaction period. For example, the nonselective forward rate constants \( k_{f1} \) for methyl laurate and methyl myristate, calculated for progressive conversions at different time intervals over the reaction period of 150 min, decrease as follows: 3.02 X 10^{-3}, 2.07 X 10^{-3}, 1.57 X 10^{-3}, 1.25 X 10^{-3} and 2.93 X 10^{-3}, 2.04 X 10^{-3}, 1.55 X 10^{-3}, 1.25 X 10^{-3} respectively. Selective forward transesterification rate constants \( k'_{f1} \) also displayed similar decline with time. On the other hand, nonselective and selective backward rate constants (\( k_{b1} \) and \( k'_{b1} \)) exhibited the rising trend. Thus there appears to be conflict between the results and the rate rule.

These contradictions could be easily interpreted on the basis of the fact that the sucrose transesterification is not a single reaction but it deals with series-parallel combinations of mono/ di/ poly transesterifications. For example, in reference to sucrose, the mono/ di/ poly transesterifications follow series mode while in reference to FAME, the reactions pursue parallel mode. As all the hydroxyls other than 6-OH on glucose portion being less active and their participation will increase with retention time, the specific speed of reaction, under nonselective conditions, will drop with participation of these hydroxyls for transesterification with additional methyl esters. Besides this, the rate of mono-transesterification is higher than that of di-transesterification which in turn will be higher than that of tri-transesterification and so on. With increase in holding time, the opportunities for polytransesterifications will be augmented. Hence one observes drop in the magnitude of overall forward rate constants. On the other hand, backward rate constants will follow opposite trend.

Influence of Temperature

Although rise in reaction temperature from 120 to 140\(^0\)C (SE1, SE2, SE4) caused increase in magnitude of second order rate constants, % enhancement was marginal. The reaction was conducted in batch reactor (i.e. no removal of by product methanol) for the purpose of kinetic modeling. In case, one works out the combination of elevated temperature with rapid removal of byproduct methanol (semi batch system), the rise in temperature would enhance equilibrium conversion through shift of reaction equilibrium.
The selective and nonselective reversible and irreversible kinetic modeling of synthesis of sucrose-coconut fatty acid esters were thus proved to be a facile and quantitative means to follow the specific substitutions occurring at the various OH positions within the sucrose as a function of degree of conversion and reactant molar ratio. It should be noted that the selective and nonselective kinetic models are not exclusive, rather they complement each other. While model 1A and B presents average transesterification rate/overall kinetic activity of all eight hydroxyl in sucrose, Model 2A and B explains the transesterification activity of 6-OH group in sucrose. One needs knowledge of both $k_{2,i}$ and $k'_{2,i}$ in the evaluation of overall kinetics of transesterification as well as in the facilitation of preferential synthesis of particular sucrose- mono/ di/ polyesters.

4.5 Kinetic and thermodynamic modeling of peracid ex situ and in situ batch epoxidation of oleic acid

The various reactions that occur during peracid epoxidation of oleic acid are shown in Fig. 4.2. The mechanism\(^3\) for the *in situ* peracid homogeneous epoxidation in the presence/absence of a catalyst is generally described as follows: (i) formation of peroxyacetic (PAA)/ performic acid (PFA) in the aqueous phase in the presence of a catalyst or $\text{H}^+$ in reversible mode: reaction 4.14; (ii) transfer of peracid from the aqueous phase to the oil phase (oleic acid + solvent); (iii) the desired oxygen-transfer reaction of peracid in the oil phase to produce epoxidised oleate (EOA) and release acetic/formic acid (AA/ FoA): reaction 4.15; (iv) degradation of the epoxide ring in the oil phase, as well as at the oil–aqueous interface: reactions 4.16 and 4.17; (v) transfer of AA/ FoA from the oil phase back to the aqueous phase where it reacts again with the hydrogen peroxide to reform a peracid.

The mechanism implies two transport steps in addition to three kinetic steps. It has been already reported under Chapter 3 (section 3.5.1.3) that the reaction mixture was agitated at high rpm to eliminate mass transfer resistance. Thus, these transport steps were not included in kinetic and thermodynamic modeling of epoxidation. The deleterious consecutive reactions 4.16 and 4.17 would become significant with even a trace availability of $\text{H}^+$ ions and water, which might be there owing to the fact that PAA/ PFA is formed from AA/ FoA and $\text{H}_2\text{O}_2$. Other degradation possibilities are: (i) oleic acid (OA) + hydroxyacetate (ROP) leading to the corresponding ester; (ii) OA + dihydroxy (terminal-glycol) oleic acid leading to monohydroxy ester; and (iii) dimerization of OA, and
possibly trimerization. Since these degradation reaction are feasible only at high temperature (> 100°C) and epoxidation was conducted at temperature < 80°C, these additional degradation reactions were not included in the development of kinetic model for epoxidation.

\[
\begin{align*}
R'O\text{-}O\text{-}OH & + H_2O_2 \xrightarrow{H^+} R'O\text{-}O\text{-}OH + H_2O & \text{Eq. 4.14} \\
H_2C\text{-}(CH_2)_7\text{O}_2\text{OR} & + \text{PAA/PFA} \xrightarrow{k_1} R'\text{COOH} & \text{Eq. 4.15} \\
EOA & + R'\text{COOH} \xrightarrow{k_2} H_2C\text{-}(CH_2)_7\text{O}_2\text{OR} & \text{Eq. 4.16} \\
\text{ROP (ring opened product)} & + H_2O \xrightarrow{k_3} H_2C\text{-}(CH_2)_7\text{O}_2\text{OR} + R'\text{COOH} & \text{Eq. 4.17}
\end{align*}
\]

Fig. 4.2 Epoxidation of oleic acid and the ring degradation reactions
[Where AA/ FoA-acetic/ formic acid, PAA/ PFA-peracetic/ formic acid, EOA-epoxidised oleic acid, R/ R'=H/ CH_3, k_1, k_2, and k_3 are the epoxidation, ring opening and hydroxylation reaction rate constants, respectively].

The general form of the rate equation for the conversion of ethylenic unsaturation in oleic acid by PAA/ PFA may be written as:

\[
-r_{OA} = -\frac{dC_{OA}}{dt} = k_1C_{OA}C_{PAA}
\]

Eq. 4.18

where \(r_{OA}\) is the rate of disappearance of carbon-carbon double bonds, \(C_{OA}\) is the concentration of double bonds in oleic acid, \(C_{PAA}\) is the concentration of peracid, and \(k_1\) is the second-order rate constant. The expression for PFA epoxidation would be obtained by replacing \(C_{PAA}\) by \(C_{PFA}\).

A. Second order kinetic model for ex situ epoxidation (kinetic modeling based on absence of degradation reactions)

Results presented under Chapter 3- Table 3.4 have already indicated that ex situ epoxidation of oleic acid was highly selective and the degradation reactions were more or
less completely insignificant. Hence the kinetic equations corresponding to the
degradation reactions were not included in the formulation of kinetic model for *ex situ*
epoxidation of oleic acid. Since peracid is preformed, the transport steps are eliminated.
Thus the mechanism involves only one step- the desired oxygen-transfer reaction of
peracid causing epoxidation of oleic acid. Thus the second order disappearance of oleic
acid through *ex situ* epoxidation, upon integration of Eq. 4.18, is expressed as

\[
\ln \left( \frac{C_{OA}C_{PAA}}{C_{PAA}C_{OA}} \right) = \ln \left( \frac{M-X_{OA}}{M(1-X_{OA})} \right) = C_{OA_0} \left( M-1 \right) k_1 t
\]

\[
= (C_{PAA_0}-C_{OA_0}) k_1 t
\]

where \(X_{OA}\) = the fractional double bond conversion during epoxidation of oleic acid, \(M = \)
the initial molar ratio=\(C_{PAA_0}/C_{OA_0}\) at \(t = 0\).

The initial PAA/ PFA concentration (\(C_{PAA_0}/C_{PFA_0}\)), which is essential for the
determination of \(M\), was calculated through the knowledge of chemical equilibrium
constant (\(K_w^{eq}\)) for the formation of PAA/ PFA from AA/ FoA (0.7 and 0.76 for the
formation of PAA and PFA, respectively \(^{4,5}\)) in the water phase (W) using following
equation:

\[
K_w^{eq} = \frac{k_w}{k_w^w} = \frac{C_{PAA}^{w}C_{H_2O}^{w}}{C_{AA}^{w}C_{H_2O_2}^{w}}
\]

The *ex situ* kinetic data obtained by using data of Table 3.4 of Chapter 3 and
subsequently solving above equation are reported in Table 4.2.

**B. Kinetic modeling of *in situ* epoxidation of oleic acid and ring opening reactions**

The derivation of Eq. 4.19 for *ex situ* epoxidation assumes the absence of ring
opening reactions. However the results reported for *in situ* peracetic acid epoxidation of
oleic acid (Chapter 3- Table 3.4) have implied significant existence of ring degradation
reactions. It is apparent from Fig. 4.2 that the degradation reactions 4.16 and 4.17 are
consecutive reactions of the products of reactions- 4.15 and 4.14 respectively (acid
catalysis and hydrolysis, respectively). When ring opening occurs in series with
epoxidation, then the differential form of rate equation Eq. 4.18 applies. Because the rate
of formation of peracid is much faster than the rate epoxidation, and the peracid
concentration is essentially constant throughout the reaction, the epoxidation reaction can
be assumed to be pseudo-zero order in peracid concentration. If the pseudo-first-order rate
constant is defined as \( k'_1 = k_1 C_{PAA} \), the rate equation, pseudo-first order in concentration of ethylenic unsaturations, can be written as:

\[
\frac{dC_{OA}}{dt} = k'_1 C_{OA} \tag{Eq. 4.21}
\]

The rate data for the epoxidation with peracetic acid are fitted in the above equation. The same equation form is used for fitting kinetics data for epoxidation with performic acid (PFA), except that the rate constant in this case would be defined as \( k'_1 = k_1 C_{PFA} \). After integration, the Eq. 4.21 becomes:

\[
\ln \frac{C_{OA_0}}{C_{OA}} = k'_1 t \quad \text{or} \quad -\ln X_{IN} = k'_1 t \tag{Eq. 4.22}
\]

where \( C_{OA_0} \) is the initial concentration of oleic acid in terms of carbon-carbon double bonds and \( X_{IN} \) represents the fraction of total double bonds in oleic acid undergoing the epoxidation. If \( \ln \frac{C_{OA_0}}{C_{OA}} \) or \( -\ln X_{IN} \) is plotted vs. time, a linear plot should result, with a slope equal to \( k'_1 \).

In addition to the epoxidation reaction, the ring opening reactions are represented by following differential expressions:

\[
\frac{dC_{EOA}}{dt} = k'_1 C_{OA} - k_2 C_{EOA} C_{AA} \tag{Eq. 4.23}
\]

\[
\frac{dC_{ROP}}{dt} = k_2 C_{EOA} C_{AA} - k_3 C_{ROP} C_W \tag{Eq. 4.24}
\]

\[
\frac{dC_G}{dt} = k_3 C_{ROP} C_W \tag{Eq. 4.25}
\]

where \( k'_1, k_2, k_3 \) are the rate constants for the formation of epoxide, hydroxyacetate, and 1,2-glycol, respectively.

Rate equations 4.23 and 4.24 include AA/ FoA concentrations (\( C_{AA}/ C_{FOA} \)) which were assumed to remain constant throughout the reaction and approximated to \( C_{AA0}/ C_{FOA0} \) for the following reasons: (i) the equilibrium constant (\( K_{eq} \)) for the peracetic acid formation\(^4\) (\( \sim 0.7 – 5 \)) is much larger than the dissociation constant of the AA\(^6\) \( K_{AA} \) (\( \sim 1.75 \times 10^{-5} \)); (ii) AA is regenerated in the epoxidation and glycol formation process. Gan\(^7\) have reported similar type of explanation for the epoxidation of rubber latex by formic acid. Thus the two differential equations Eq. 4.23 and 4.24 were simplified by substituting
k'₂ - the pseudo first order rate constant in place of k₂C_{AA}. The magnitudes of k'₁, k'₂ and k₃ were obtained by solving above three differential equations 4.23, 4.24 and 4.25 as per the procedure presented under section 4.2.2. Following mass balance was used to obtain unknown concentrations, where suffix ‘0’ indicates concentrations at t=0 and suffix ‘t’ indicates concentrations at given time (t).

**i) Double bond balance**
\[ \text{IN}_0 = \text{IN}_t + \text{EN}_t + \text{ROP}_t + \text{GN}_t \] or in terms of concentrations
\[ C_{OA_0} = C_{OA_t} + C_{EOA_t} + C_{ROP_t} + C_{G_t} \] Eq. 4.26

**ii) Hydroxy group balance**
\[ \text{HN}_t = \text{ROP}_t + 2\text{GN}_t \] Eq. 4.27

**iii) Acetic acid balance**
\[ C_{AA_0} = C_{AA_t} + C_{ROP_t} \] Eq. 4.28

**iv) Water balance**
\[ C_{H_2O_0} = C_{H_2O_t} + \left( C_{H_2O_0} - C_{H_2O_t} \right) C_{G_t} \] Eq. 4.29

The terms IN/ HN/ ROPN/ GN in material balance equations have been defined under Chapter 3 (section 3.5.1.2) where they were utilized in the calculations of epoxidation conversion, yield and selectivity. In present case, Eq. 4.27-4.29 were solved simultaneously to obtain concentrations of hydroxyacetate (ROP), glycol and water\([C_{ROP}, C_{G}, C_{H_2O}]\) which were essential for differential analysis of rate equations 4.23 to 4.25 and subsequent determination of rate constants k'₂ and k₃. The concentration and kinetic data obtained by using data of Table 3.4 of Chapter 3 and subsequently solving above equations are reported in Table 4.2.

C. Thermodynamic modeling of peracid batch epoxidation

The activation energy, Eₐ of epoxidation, was calculated from the Arrhenius relationship:
\[ k = Ae^{-\frac{E_a}{RT}} \] Eq. 4.30

The enthalpy of activation, ΔH, was calculated by using Eq. 4.31
\[ \Delta H = E_a - RT \] Eq. 4.31

The average entropy of activation ΔS and free energy of activation ΔG were obtained by using Eq. 4.32 and Eq. 4.33, respectively.

\[ \Delta S \] 9,10
\[ \Delta G \] 11
\[
\frac{R}{Nh} e^{\frac{AS}{R}} e^{-\frac{E}{RT}}
\]
\(\text{Eq. 4.32}\)

Free energy of activation: \(\Delta G = \Delta H - T\Delta S\) \(\text{Eq. 4.33}\)

where \(k\) is the rate constant, \(A\) the frequency factor, \(R\) the universal gas constant, \(N\) the Avogadro constant \(= 6.023 \times 10^{23}\) mol\(^{-1}\), \(T\) the absolute temperature and \(h\) Planck’s constant \(= 6.626 \times 10^{-34}\) Js.

The results obtained by using data of Table 3.4 of Chapter 3 and subsequently solving Eqs. 4.30-4.33, are reported in Table 4.3.

4.6 Results and discussion on kinetic and thermodynamic modeling of peracid batch epoxidation of oleic acid

The mathematical modeling of \textit{ex situ} PAA and PFA epoxidation (Eq. 4.19), due to the freedom from ring opening reactions, was simplified and is illustrated in section 4.5 A. Kinetics of \textit{in situ} PAA and PFA epoxidation, which also included the kinetics of ring degradation reactions, has been presented under section 4.5 B. Eqs. 4.21-4.25, based on the development of said series-parallel models, were used for the calculations of epoxidation and degradation rate constants. The results of the calculations of reactant, intermediate and product concentrations based on material balance Eqs. 4.26-4.29 and the calculated magnitudes of rate constants under diverse batch epoxidation conditions have been reported in Table 4.2. Various thermodynamic parameters (\(E_a, \Delta H, \Delta S, \Delta G\)) of PAA batch \textit{in situ} epoxidation of oleic acid, calculated in accordance to Eqs. 4.30-4.33 (section 4.5 C), are reported in Table 4.3.

Reaction engineering of desirable epoxidation and undesirable degradation reactions

The pseudo first order rate constant for uncatalysed \textit{in situ} PAA epoxidation at 50\(^{\circ}\)C were found to be in the range of 0.0110-0.0138 min\(^{-1}\). The apparent activation energy for the epoxidation reaction, determined on the basis of the estimated kinetic constants, was found to be in the range of 4.98-5.85 kcal/gmol. In comparison to the reported results for vegetable oils (Table 1.3 of Chapter 1), rate constant \(k_1^*\) and \(E_a^*\) of oleic acid epoxidation were found to be of higher and lower magnitude, respectively. Thus the epoxidation of oleic acid takes place at higher speed and lower temperature in comparison to vegetable oils. The magnitude of the uncatalysed degradation reaction rate constants- \(k_2\) and \(k_3\) and the corresponding activation energies- \(E_{a2}\) and \(E_{a3}\), were found to be 0.0075-0.0084 min\(^{-1}\) and 0.0057-0.0065 lit gmol\(^{-1}\)min\(^{-1}\) and 1.44-1.69 kcal/gmol and 1.49-2.46 kcal/gmol, respectively (Table 4.2 and 4.3). Thus the desirable specific epoxidation
Table 4.2 Kinetic modeling of *in situ* and *ex situ* peracid batch epoxidation of oleic acid (OA) and methyl oleate (mOA)

Solvent used: toluene, Org. acid-acetic/ formic acid

<table>
<thead>
<tr>
<th>Batch Code</th>
<th>$T_0$, °C</th>
<th>Initial concentrations, gmoles/lit</th>
<th>$t$, min</th>
<th>Concentrations at time $t$, gmoles/lit</th>
<th>Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{OA0}$</td>
<td>$C_{H2O20}$</td>
<td>$C_{org. Acid0}$</td>
<td>$C_{H2O0}$</td>
<td>$C_{OA1}$</td>
</tr>
<tr>
<td><strong>In situ peracetic acid epoxidation, no catalyst</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>50</td>
<td>0.9525867</td>
<td>4.30527</td>
<td>4.30527</td>
<td>8.37862</td>
</tr>
<tr>
<td>E2</td>
<td>50</td>
<td>0.54032</td>
<td>0.20</td>
<td>0.2788</td>
<td>0.0667</td>
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<tr>
<td>E3</td>
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<td>0.385</td>
<td>0.4</td>
<td>0.2346</td>
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<td>50</td>
<td>0.4850</td>
<td>4.3836</td>
<td>2.1825</td>
<td>8.3859</td>
</tr>
<tr>
<td>E5</td>
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<td>0.4889</td>
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<td>2.2084</td>
<td>8.4541</td>
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<tr>
<td>E6</td>
<td>80</td>
<td>0.9525867</td>
<td>4.30527</td>
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<td>80</td>
<td>0.64334</td>
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<td>2.9076</td>
<td>11.1247</td>
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<td><strong>In situ peracetic acid epoxidation, 1% H$_2$SO$_4$ catalyst on wt. of OA</strong></td>
<td></td>
<td></td>
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<tr>
<td>E8</td>
<td>50</td>
<td>0.814</td>
<td>4.6825</td>
<td>4.6825</td>
<td>9.16716</td>
</tr>
<tr>
<td><strong>In situ Peracetic acid epoxidation of methyl oleate, 1% H$_2$SO$_4$ catalyst on wt. of mOA</strong></td>
<td></td>
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</tr>
<tr>
<td>E12</td>
<td>50</td>
<td>0.814</td>
<td>4.685254</td>
<td>4.6759</td>
<td>9.164356</td>
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<tr>
<td><strong>In situ performic acid epoxidation, no catalyst</strong></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>E10</td>
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<td>5.730</td>
<td>4.07989</td>
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In situ Performic acid epoxidation of methyl oleate, 1% H2SO4 catalyst on wt. of mOA

<table>
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<tr>
<td>E13</td>
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<td>0.8663</td>
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<td>4.97626</td>
<td>11.66678</td>
<td>60</td>
<td>0.2468</td>
<td>0.32651</td>
<td>0.357708</td>
<td>0.1970639</td>
<td>0.0209</td>
<td>0.0162</td>
<td>0.0126</td>
<td></td>
</tr>
</tbody>
</table>

Ex situ peracetic acid epoxidation

| E9  | 50  | 0.814 | 4.6825 | 4.6825 | 9.16716 | 60  | 0.1623 | 0.6520 | 0     | 0.1850 |

Ex situ performic acid epoxidation

| E11 | 50  | 0.8663 | 5.08169 | 5.08169 | 11.89116 | 60  | 0.0654 | 0.801 | 0     | 0.5530 |

Note: 1. Refer section 3.3.1.1-A and B for process details

Table 4.3 Thermodynamic modeling of peracetic batch in situ epoxidation of oleic acid

<table>
<thead>
<tr>
<th>Temp., K</th>
<th>Ea1, kcal/gmol</th>
<th>ΔH1, kcal/gmol</th>
<th>ΔS1, cal/(gmol.K)</th>
<th>ΔG1, kcal/gmol</th>
<th>Ea2, kcal/gmol</th>
<th>ΔH2, kcal/gmol</th>
<th>ΔS2, cal/(gmol.K)</th>
<th>ΔG2, kcal/gmol</th>
<th>Ea3, kcal/gmol</th>
<th>ΔH3, kcal/gmol</th>
<th>ΔS3, cal/(gmol.K)</th>
<th>ΔG3, kcal/gmol</th>
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<tr>
<td>For batch E3 and E6</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>323</td>
<td>5.85</td>
<td>5.21</td>
<td>-60.1</td>
<td>24.6</td>
<td>1.44</td>
<td>0.80</td>
<td>-74.4</td>
<td>24.83</td>
<td>2.46</td>
<td>1.82</td>
<td>-71.9</td>
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<tr>
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<td>5.15</td>
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<td></td>
<td>1.76</td>
<td>-72.0</td>
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<tr>
<td>For batch E4 and E7</td>
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<td>4.34</td>
<td>-63.0</td>
<td>24.66</td>
<td>1.69</td>
<td>1.052</td>
<td>-74.0</td>
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<td>4.28</td>
<td>-63.1</td>
<td>26.55</td>
<td>0.992</td>
<td>-74.0</td>
<td>27.1</td>
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<td>0.8</td>
<td>-75.1</td>
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reaction rates were found to be approximately 1.5-1.6 and 1.9-2.1 times higher over undesirable specific hydroxy acetylation and glycol formation reaction rates, respectively (this ratio also defines the selectivity). However, in order to ensure complete oxirane ring stability, the selectivity ratios as defined by the ratio of kinetic constants, are required to carry still higher magnitudes. In competing series-parallel combination reactions, the Ea-temperature relationships is governed by following rule\(^1\): reactions with higher Ea are more heat sensitive. Hence the rate of reaction with higher Ea was more influenced by rise in reaction temperature than those competing reactions with lower Ea values. The Ea of desirable epoxidation reaction was 3.5 times higher over those of degradation reactions. Thus when the uncatalysed in situ PAA epoxidation was conducted at 80\(^0\)C, the selectivity ratios as defined by the ratio of kinetic constants, were found to be enhanced approximately to 2.26-2.43 and 2.92-3.0. Thus the kinetic and thermodynamic modeling of series-parallel epoxidation reaction was verified on the basis of chemical reaction engineering (CRE) principles. Nevertheless this rise in selectivity ratio was still too low to ensure stability of oxirane ring. The influence of temperature on epoxidation as well as degradation reactions was, therefore, found to be the major parameter and has been discussed from different perspectives under section 3.5.1.3 of Chapter 3.

**PAA and PFA as epoxidation reagents**

The rate constant for uncatalysed in situ batch PAA epoxidation at 50\(^0\)C (0.0110-0.0138 \text{ min}^{-1}) was found to be lower than that for uncatalysed in situ batch PFA epoxidation (0.0155 \text{ min}^{-1}). One observes multiplication of this difference in epoxidation activity of the two peracids for ex situ epoxidation process: 0.185 for PAA versus 0.553 for PFA. The rate constants for degradation reactions were also compared for both peracids: 0.0075 - 0.0084 and 0.0057-0.0065 for PAA in situ epoxidation and 0.0059 and 0.0052 for PFA in situ epoxidation. While the activity of PFA in promoting the desirable epoxidation reaction was greater, its activity in suppressing the undesirable reaction was also found to be better. Thus on both accounts, PFA was established as more selective peracid.

The concentration of PAA generated in situ cannot be built up due to the epoxidation reaction. Therefore, the PAA concentration is always lower than that of the preformed PAA method. Hence ex situ PAA reaction rates were 13-17 times higher over that of in situ PAA epoxidations (0.185 for ex situ versus 0.0110-0.0138 for in situ). Same observations were found to hold true for PFA epoxidations (0.0155 for in situ versus 0.553
for *ex situ*). The 35 times rise in *ex situ* rates over *in situ* rates indicated that PFA was more adaptable to *ex situ* epoxidation process.

**Catalytic activity of H\textsubscript{2}SO\textsubscript{4}**

Use of H\textsubscript{2}SO\textsubscript{4} catalyst caused *in situ* epoxidation reaction of oleic acid at 50\(^{\circ}\)C to proceed at an appreciable rate (0.0493 for catalytic versus 0.0110-0.0138 for uncatalysed route) but at the same time, it caused rise in degradation rates (0.0364 and 0.0126 for catalytic versus 0.0075-0.0084 and 0.0057-0.0065 for uncatalysed route). Thus H\textsubscript{2}SO\textsubscript{4} was found to be non-selective epoxidation catalyst.

**Oleic acid versus methyl oleate as feedstock for epoxidation**

The epoxidation rate constant at 50\(^{\circ}\)C for catalysed *in situ* PAA batch epoxidation of oleic acid was found to be more than twice of that for methyl oleate (0.0493 for oleic acid versus 0.0218 for methyl oleate). But similar relationships were also observed for degradation reactions. Methyl oleate displayed more selectivity in epoxidation reaction in reference to the competing hydroxy acetylation reaction (ratio of kinetic constants: 1.5 for methyl oleate versus 1.35 for oleic acid) while oleic acid exhibited more selectivity in epoxidation reaction in reference to the competing glycol formation reaction (ratio of kinetic constants: 2.3 for methyl oleate versus 3.4 for oleic acid). Thus oleic acid was viewed as better feedstock for epoxidation reactions.

**Thermodynamic parameters for *in situ* PAA batch epoxidation**

The enthalpy of activation (\(\Delta H\), kcal gmol\(^{-1}\)) for *in situ* PAA epoxidation, hydroxy acetylation and glycol formation were found to be 4.28-5.21, 0.741-1.052, and 0.8-1.82 respectively (*Table 4.3*). These thermodynamic values (i.e. positive enthalpies of activation), therefore, proved that, the epoxidation and the ring degradation reactions are endothermic in nature. Since the enthalpy of epoxidation was found to be greater than those of ring degradation reactions, an increase in the reaction temperature eventually would lead to more increase in the conversion to oxirane oxygen than that for conversions for ring opening reactions.

For endothermic process, the entropy (\(\Delta S\)) of the surrounding is always negative. The entropy of *in situ* PAA epoxidation reaction [-60 cal/ (gmol. K) at 50\(^{\circ}\)C] was also found to be negative. On the other hand, the free energy of activation of epoxidation (\(\Delta G\), kcal gmol\(^{-1}\)) was found to be positive. Thus the epoxidation reaction is non-spontaneous under the present setup of experimental conditions. With an increase of temperature from 50 to 80\(^{\circ}\)C, the entropy of epoxidation (\(\Delta S\)) was found to decrease from -60 to -63,
respectively while ΔG was found to increase from 24.6 to 26.5, respectively. Thus the
non-spontaneity of the epoxidation reaction should increase with increase in reaction
temperature and hence, at any particular instant, the yield of oxirane would increase with
rise in reaction temperature. However, similar outcome in terms of ΔS and ΔG were
observed for the ring opening reactions. Thus the use of temperature alone as reaction
parameter would provide catastrophic results in terms of oxirane stability. Hence in order
to maximize the net conversion to oxirane, optimization of different reaction parameters
(moderate temperature, appropriate reaction period as governed by reactant molar ratio
and concentrations, use of hydrocarbons as reaction solvent, selection of PFA as peracid,
ex situ process or semibatch mode of additions of hydrogen peroxide and/or organic acid
etc.) were really essential as presented under sections 3.5.1.3 and 3.5.1.4 of Chapter 3.

References

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