

## Esterification of Fatty Acids and Short-Chain Carboxylic Acids with Stearyl Alcohol and Sterols

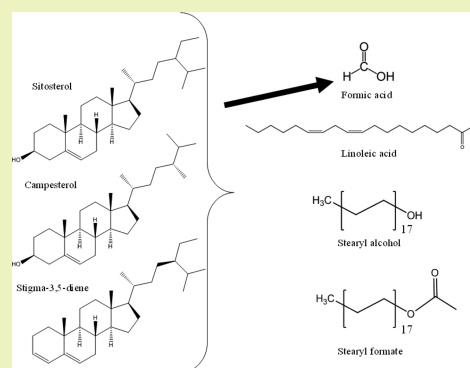
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## S Supporting Information

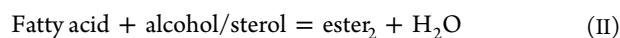
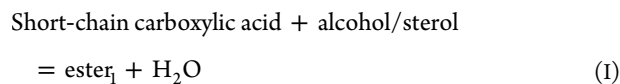
**ABSTRACT:** Esterification of tall oil fatty acids by neutral components, such as stearyl alcohol and sterols, is an undesired reaction; a potential solution is to eliminate the neutral components by a competing esterification with short-chain carboxylic acids. Esterification of fatty acids and short-chain carboxylic acids with stearyl alcohol and sterols was studied in a laboratory-scale glass reactor in the temperature range of 60–140 °C. Linoleic acid (LA) was used as a model component for fatty acid esterification with stearyl alcohol (StOH) and sitosterol (SitOH). Linoleic acid underwent esterification with stearyl alcohol and sitosterol. In the presence of short-chain carboxylic acids, such as formic and acetic acid, the esterification of linoleic acid by stearyl alcohol was efficiently suppressed because stearyl alcohol reacted with the short-chain carboxylic acid. Formic acid catalyzed the formation of dienes from sitosterol and campesterol. The esterification and dehydration processes were verified by gas chromatographic analysis and extensive kinetic studies. Mathematical models for esterification and dehydration were developed and successfully applied to a selected part of experimental data.

**KEYWORDS:** Esterification, Fatty acids, Formic acid, Linoleic acid, Stearyl alcohol, Sitosterol



## INTRODUCTION

Fatty acids are valuable byproducts from tall oils and birch oils, which are separated from oil mixtures via distillation. However, large amounts of fatty acids are lost due to their esterification with other components, such as alcohols and sterols, which are present in the oil mixtures.<sup>1–3</sup> Therefore, a method to suppress the esterification of fatty acids is highly desirable. It is known that esterification takes place at temperatures exceeding 55 °C, and thus, rapid cooling of the tall oils and birch oils is important. Another method to prevent the esterification of fatty acids is to esterify short-chain reactive carboxylic acids, such as formic acid, with the neutral compounds. The esterification rates of short-chain carboxylic acids are expected to be much higher than those of fatty acids, and thus, a protective esterification becomes possible. The reactions are summarized below



Reaction I is more rapid than reaction II and captures alcohols and sterols, thus preventing reaction II. The most important molecules are displayed in Scheme 1.

Esterification as is a very old process known since the 19th century. Numerous catalysts can be used to enhance the esterification rate, such as strong mineral acids, organic acids,

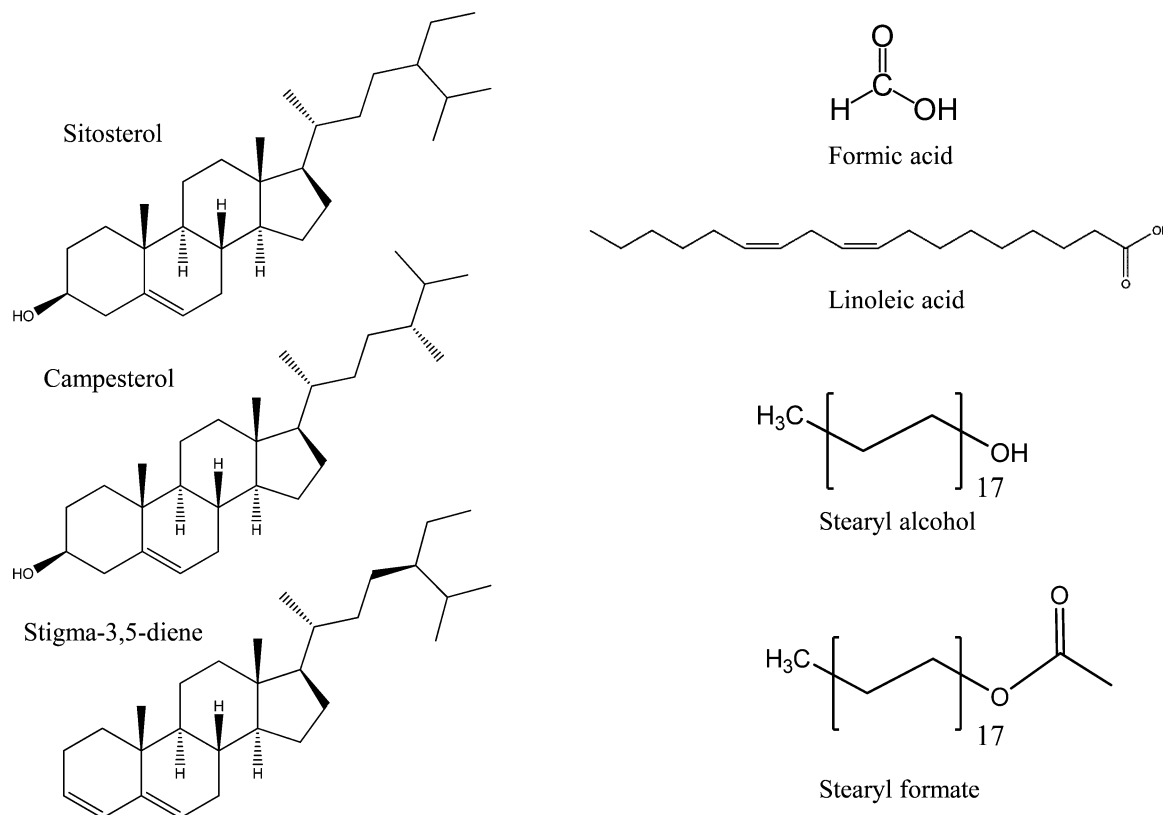
metal salts, fatty acid salts of metals, and ion-exchange resins, as well as enzymes.<sup>1</sup> Esterification of fatty acids has been studied extensively in the past because fatty acid esters are widely used in cosmetic and alimentary industries as emulsifiers and flavorants. The esterification reactions of fatty materials were reviewed in the pioneering article of Formo.<sup>2</sup> Thermal esterification kinetics of fatty acids is interesting because it is inevitable in the industrial tall oil process. In an extensive study by Wong,<sup>3</sup> degradation of crude tall oil was investigated at elevated temperatures. Kinetic data were provided, but no methods were proposed to avoid the undesired reactions. No studies on the esterification of sterols originating from tall oil with low molecular carboxylic acids have been reported. Preliminary studies have indicated that formic acid can be used to retard the esterification of tall oil fatty acids, and the method has been patented by our industrial partner.<sup>4</sup>

The work of Wong<sup>3</sup> is an extensive kinetic study of tall oil fatty acid esterification with stearyl alcohol and sterols (a sterol–stanol mixture). The component molar ratios that were used represented the ratios of crude tall oil (sterols appear in the range of 5–20% of fatty acids present in crude tall oil, and fatty alcohols appear in the range of 2–6% of fatty acids present). A binary mixture of 80 wt % of oleic acid and 20 wt % of mixed tall oil sterols or stearyl alcohol was thus used. The temperature was 90 °C, and the reaction was typically let to

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## Scheme 1. Most Important Molecules in This Work



proceed for at least 12 days without stirring. Esterification of stearyl alcohol and mixed tall oil sterols with oleic acid and decarboxylation of oleic acid were found to exhibit first-order kinetics. The rate constant for the esterification of oleic acid with stearyl alcohol was substantially larger than that for the esterification of oleic acid with tall oil sterols.

Sterols are also known to undergo dehydration in an acidic environment and at high temperature<sup>5–8</sup> and form dienes, e.g., stigmast-3,5-diene. This implies that dehydration reactions are expected to compete with esterification.

The aim of the current work is to screen the esterification kinetics of short-chain carboxylic acids with alcohols and sterols and thus suppress the esterification of fatty acids. Model compounds representing all crude oil were studied. Kinetic data for esterification of fatty acids and short-chain carboxylic acids with neutral components appearing in tall oil were obtained by using a laboratory-scale batch reactor. The main parameters were the reaction temperature and concentrations of short-chain carboxylic acids.

## EXPERIMENTAL EQUIPMENT AND PROCEDURES

**Reactants.** Linoleic acid (Fluka, technical grade, 65% linoleic acid, 15–20% oleic acid, LA) was used as a model compound to represent the fatty acids present in tall oil. Stearyl alcohol (StOH) and a mixture of sterols (90% sitosterol, 5% sitostanol, 1–3% campesterol and campestanol, SitOH or sterols) were used to represent the neutral components in tall oil. Formic acid (technical grade 85%, 15% water), acetic acid (100%, AcA), lactic acid (100%, LactA), oxalic acid (100%, OxA), and butyric acid (100%, ButA) were used to represent different short-chain carboxylic acids. A detailed list of the properties of all reactants and products is given in the Supporting Information.

**Laboratory Reactor.** A jacketed glass reactor (250 mL) under a nitrogen (AGA, 99.9999%) atmosphere was used in the kinetic experiments (Figure 1). The reactor was equipped with a mechanical

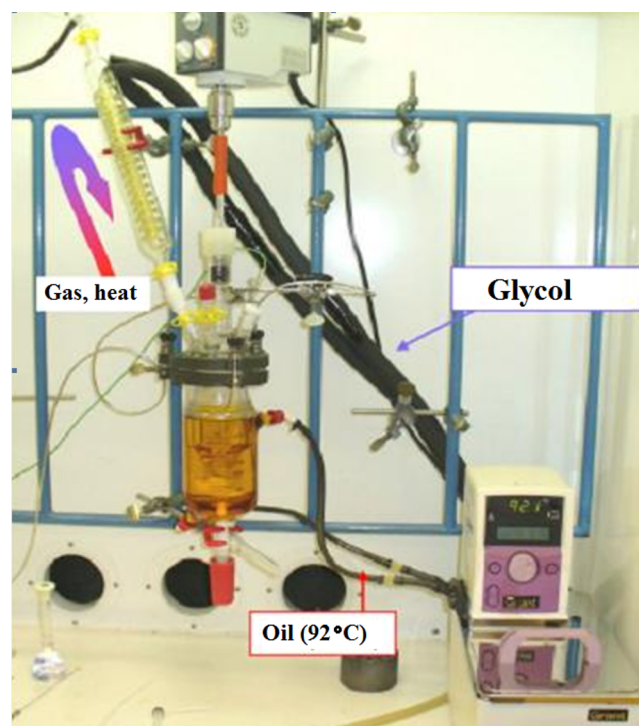


Figure 1. Reactor setup.

stirrer, gas condenser, and heated oil circulating for keeping a constant temperature. First, one of the components was poured into the reactor, and the reactor vessel was heated to the desired temperature, after which the other component(s) were added and an initial sample was withdrawn by suction and cooled rapidly to  $-4$  °C. Intensive stirring (500 rpm) was conducted to ensure good heat and mass transfer and

Table 1. Experiments with Stearyl Alcohol as an Alcohol Component<sup>a</sup>

entry	components/stoichiometry		T (°C)	Y <sub>240 min</sub> (%)	initial rate 10 <sup>-4</sup> mol min <sup>-1</sup> L <sup>-1</sup>
1	LA:StOH	1:1	75	2	2.35
2	LA:StOH	1:1	90	5	4.40
3	LA:StOH	1:1	120	18	17.2
4	LA:StOH	2:1	90	12	5.60
5	LA:StOH	2:1	90	100	n.a.
6	LA:StOH	4:1	75	3	1.93
7	LA:StOH	4:1	90	9	6.67
8	LA:StOH	1:4	75	1	1.22
9	LA:StOH	1:4	90	3	0.84
10	FA:StOH	1:1	60	90	<10000
11	FA:StOH	1:1	75	<99	<38000
12	FA:StOH	5:1	75	100	n.a.
13	FA:StOH	3:1	60	–	7500
14	LA:StOH:FA	1:2:1	75	1 LA/90 FA	n.a.
15	StOH:AcA	1:1	60	46	42

<sup>a</sup>Y is the yield of a formed ester (fatty acid stearyl ester or formate). The initial rate is the conversion rate of StOH to ester in the beginning of the experiment. LA = linoleic acid, StOH = stearyl alcohol, FA = formic acid, AcA = acetic acid, and SitOH = sterol mixture.

Table 2. Experiments with Sterols as Alcohol Components<sup>a</sup>

entry	components/stoichiometry		T (°C)	X <sub>240 min</sub> (%) (LA/form.)	Initial rate 10 <sup>-4</sup> mol min <sup>-1</sup> L <sup>-1</sup>
1	LA:SitOH	4:1	120	6	3.40
2	LA:SitOH	4:1	140	14	11.05
3a	LA:SitOH:FA	4:1:4	120–140	0/88	254
3b	LA:SitOH:FA	4:1:4	120–140	0/92	372
4	LA:SitOH:AcA	4:1:4	120–140	0/7	49

<sup>a</sup>X is the conversion of sterols to products.

Table 3. Experiments Carried Out in Ampules in an Oven<sup>a</sup>

entry	components/stoichiometry		T (°C)	X <sub>24h</sub> (%) (LA/form.)
1	SitOH:FA	1:1	90	
2	SitOH:FA	1:1	90	
3	SitOH:FA	2:1	90	
4	SitOH:FA	1:2	50	
5	SitOH:FA	1:2	22	
6	SitOH:FA	1:30	90	85
7	StOH:FA	1:10	25	82
8	SitOH:LA:LacA	1:1.85:1.85	90	2/23
9	SitOH:LA:FA	1:5:2	90	0/56
10	SitOH:LA:FA	1:8:0.8	60	
11	SitOH:LA:FA	1:4:4	60	
12	SitOH:LA:FA	1:0.8:0.8	60	
13	LA:OxA	1:1	60–150	not soluble
14	StOH:OxA	1:1	100	<50
15	StOH:ButA	1:1	60	41

<sup>a</sup>X<sub>24</sub> is the conversion of sterols or StOH to products after 24 h in the oven. LacA = lactic acid, OxA = oxalic acid, and ButA = butanoic acid.

to facilitate the measurement of intrinsic reaction kinetics. The temperature was monitored online by a computer. In some experiments where rapid reactions took place, a conductometer was installed into the reactor, and the reaction kinetics were calculated from the conductometric data.

**Experimental Procedures.** Different molar ratios of the reactants were studied at several temperatures (60–140 °C). The melting points and solubility properties of the reactants made it necessary to increase the reaction temperature or preheat the reactants in some experiments (e.g., sterols melt at significantly higher temperature, 140 °C, compared to stearyl alcohol, 60 °C). The duration of the experiments varied from 1 to 24 h, after which the samples were placed into an oven for several weeks to reach the equilibrium. The experiments performed can be classified into three different groups. Group one

consisted of experiments with linoleic acid, stearyl alcohol, formic acid (or other short-chain acid), and in some experiments sulfuric acid also was used as a catalyst (Table 1). Group 2 consisted of linoleic acid, sterols, and formic acid (or other short-chain acid) (Table 2). Group 3 consisted of experiments performed in ampules that were put into an oven for a certain period of time (Table 3). These experiments provided no kinetic information but gave important knowledge for future studies and reduced the reactant quantities needed.

In experiments with slow reaction kinetics, samples were usually withdrawn from the reactor at 0, 30, 60, 120, and 240 min, after which two samples were placed in the oven (same temperature as in the reactor) and taken from there after 1–2 weeks. In the case of fast reactions, the timeline for taking samples was usually as follows: 2 s, 30 s, 2 min, 5 min, 10 min, 20 min, and 60 min after which two samples

were put in an oven to attain the equilibrium stage. Samples were withdrawn quickly from the reactor and placed in a cold glycol bath (at  $-4\text{ }^{\circ}\text{C}$ ) to stop the reaction immediately.

To reveal how fast the esterification of formic acid with stearyl alcohol really is, few conductometric experiments were performed (Table 1, entry 13). In these experiments, an excess of water had to be inserted to get a sufficient reactant volume (the electrode must be immersed in the liquid phase). Diluted formic acid was heated to the reaction temperature. Stearyl alcohol was heated separately to liquidify it and, thereafter, was rapidly mixed with the formic acid in the reactor. The conductance was monitored online (Metrohm). The initial molar ratio of the reactants was 3 mol formic acid:1 mol StOH, and 200 mL excess water was added to increase the volume.

When adding formic acid to a sterol–fatty acid solution that had been preheated to  $140\text{ }^{\circ}\text{C}$ , the temperature dropped to  $120\text{ }^{\circ}\text{C}$  due to heavy condensation. Thus, the reaction mixture was kept at this temperature. Samples were withdrawn quickly and put into a glycol bath to get instant cooling.

**Chemical Analysis. Titration Methods.** Analysis of the samples was performed by titration, as well as with both gas chromatography (GC) and combined gas chromatography–mass spectrometry (GC-MS). Different kinds of titrations were used: the acid value and saponification value titrations. However, only the acid value titration was of interest because GC analysis was performed, and thus, the saponification value was not needed. For the acid value titration, typically an aliquot of 1 g of the sample was diluted with 30 mL of ethanol and 30 mL of diethyl ether, after which it was titrated with 0.2 M NaOH to the equivalence point. The acid value (AV) was calculated from

$$AV = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}} \times 40.0 \text{ g NaOH/mol}}{m_{\text{sample}}} \quad (1)$$

in which  $V_{\text{NaOH}}$  is the volume of NaOH consumed,  $N_{\text{NaOH}}$  is the molarity of NaOH, and  $m_{\text{sample}}$  is the mass of sample measured for titration. This acid value is based on the sodium hydroxide consumption. To convert this value to the potassium hydroxide consumption (which is more commonly used), the value must be multiplied by the factor of 1.40. To illustrate the kinetics more clearly, concentrations of the reactants and the products are reported instead of acid values, and thus, the acid values are converted to corresponding concentrations.

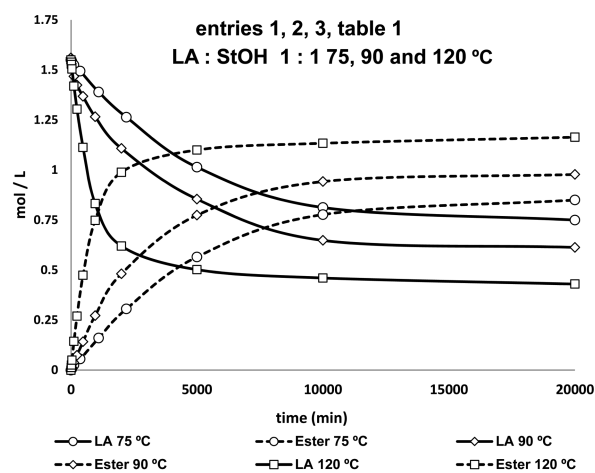
**Gas Chromatography.** The sample was diluted with acetone and dried under nitrogen flow. Thereafter, it was dissolved in a mixture of BSTFA-TMCS (N,O-bis-(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane proportion of 4:1) in pyridine and silylated at room temperature ( $22\text{ }^{\circ}\text{C}$ ) overnight. The silylated components were analyzed both with a short and long column. The short column was an HP-1 column (6 m, 0.53 mm, 0.15  $\mu\text{m}$  film thickness), which was used applying the following temperature program:  $100\text{ }^{\circ}\text{C}$  (1.5 min),  $12\text{ }^{\circ}\text{C}/\text{min}$ , and  $340\text{ }^{\circ}\text{C}$  (18 min). The injector and detector were SPI (septum-equipped programmable injector) of on-column type with the temperature program  $80\text{ }^{\circ}\text{C}$  (0.5 min),  $200\text{ }^{\circ}\text{C}/\text{min}$ , and  $340\text{ }^{\circ}\text{C}$  (18 min) and a FI detector working at  $340\text{ }^{\circ}\text{C}$ . The long column was an HP-1, (25 m, 0.20 mm, 0.11  $\mu\text{m}$  film thickness), and a FI detector at  $300\text{ }^{\circ}\text{C}$  was used. The split ratio was 1:20. As internal standards, heneicosanoic acid and bis(ethyl)hexylphthalate were used, respectively.

## KINETIC RESULTS AND DISCUSSION

### Esterification of Linoleic Acid with Stearyl Alcohol.

The yields and initial rates are summarized in Tables 1–3. Kinetic curves for selected experiments are given in Figures 2–4. Stearyl alcohol forms slowly esters with linoleic acid (LA) within the temperature range of  $60\text{--}120\text{ }^{\circ}\text{C}$ . To attain the equilibrium, several days if not weeks are necessary.

The ratio between the fatty acid and the alcohol changes the equilibrium toward the products if the proportion of fatty acid is increased. For instance, after 240 min at  $90\text{ }^{\circ}\text{C}$ , 9 mol % of fatty acid was converted to esters with the initial ratio of



$R^2 = 99.8\%$ ,  $E_{a1} = 52.1 \text{ kJ/mol}$ ,  $\Delta H = 38.1 \text{ kJ/mol}$   $k_{01} = 2.11 \cdot 10^{-4} \text{ L/(mol min)}$ ,  $K_{01} = 2.79$

**Figure 2.** Esterification of equimolar solutions of reactants (LA:StOH = 1:1) at 75, 90, and  $120\text{ }^{\circ}\text{C}$  (Table 1, entries 1, 2, and 3). Continuous lines represent model prediction.

LA:StOH = 4:1, but only 5 mol % conversion was achieved with the molar ratio of 1:1 and not more than 3 mol % with the molar ratio of 1:4 (Table 1, entries 2, 7, and 9, and Figure 3). The temperature dependence of the esterification process is shown in Figure 2. With equimolar solutions (LA:StOH = 1:1), the initial esterification rate was 1.87 times higher at  $90\text{ }^{\circ}\text{C}$  than at  $75\text{ }^{\circ}\text{C}$  and similarly 3.9 times higher at  $120\text{ }^{\circ}\text{C}$  than at  $90\text{ }^{\circ}\text{C}$  (Table 1, entries 1, 2, and 3, and Figure 2). Also the equilibrium constant ( $K$ ) changed within this temperature interval (Figure 2). The activation energy of the forward rate constant estimated from the initial rates is around 52 kJ/mol. The temperature behavior of the equilibrium constant was checked by plotting  $\ln K$  versus the absolute temperature. The plot was linear, as expected. The numerical values of the constants are shown in Figure 2.

Addition of the acid catalyst (sulfuric acid) dramatically enhanced the esterification rate as revealed by Figure 4. The esterification process reached equilibrium within 100 min in the presence of the acid catalyst, whereas typically 10,000 min was needed to reach the equilibrium in the absence of the catalyst. The rate is also strongly dependent on the acid concentration, as shown in Figure 4.

### Esterification of Linoleic Acid and Short-Chain Carboxylic Acids with Stearyl Alcohol.

In contrast to long-chain fatty acids, short-chain carboxylic acids form esters rapidly with stearyl alcohol. It can be stated in a simplified manner that typically the shorter is the carboxylic acid the more rapidly esters are formed. Thus, the fastest esterification was demonstrated to take place with formic acid, for which the reaction is almost instantaneous at  $75\text{ }^{\circ}\text{C}$ . Formic acid and stearyl alcohol reacted to esters even in solid form at room temperature (Table 3, entry 7).

It was demonstrated that stearyl alcohol can be rapidly esterified by formic acid, as shown in Figure 5 (Table 1, entry 11). Practically all stearyl alcohol reacted with formic acid. It is very probable that formic acid itself acts as a catalyst in this process.

The kinetics of formic acid esterification with specifically stearyl alcohol was observed to be so rapid that standard methods for off-line analysis were insufficient. Therefore, a method utilizing conductometry was implemented with a measurement cell that was placed in the reactor. Output data

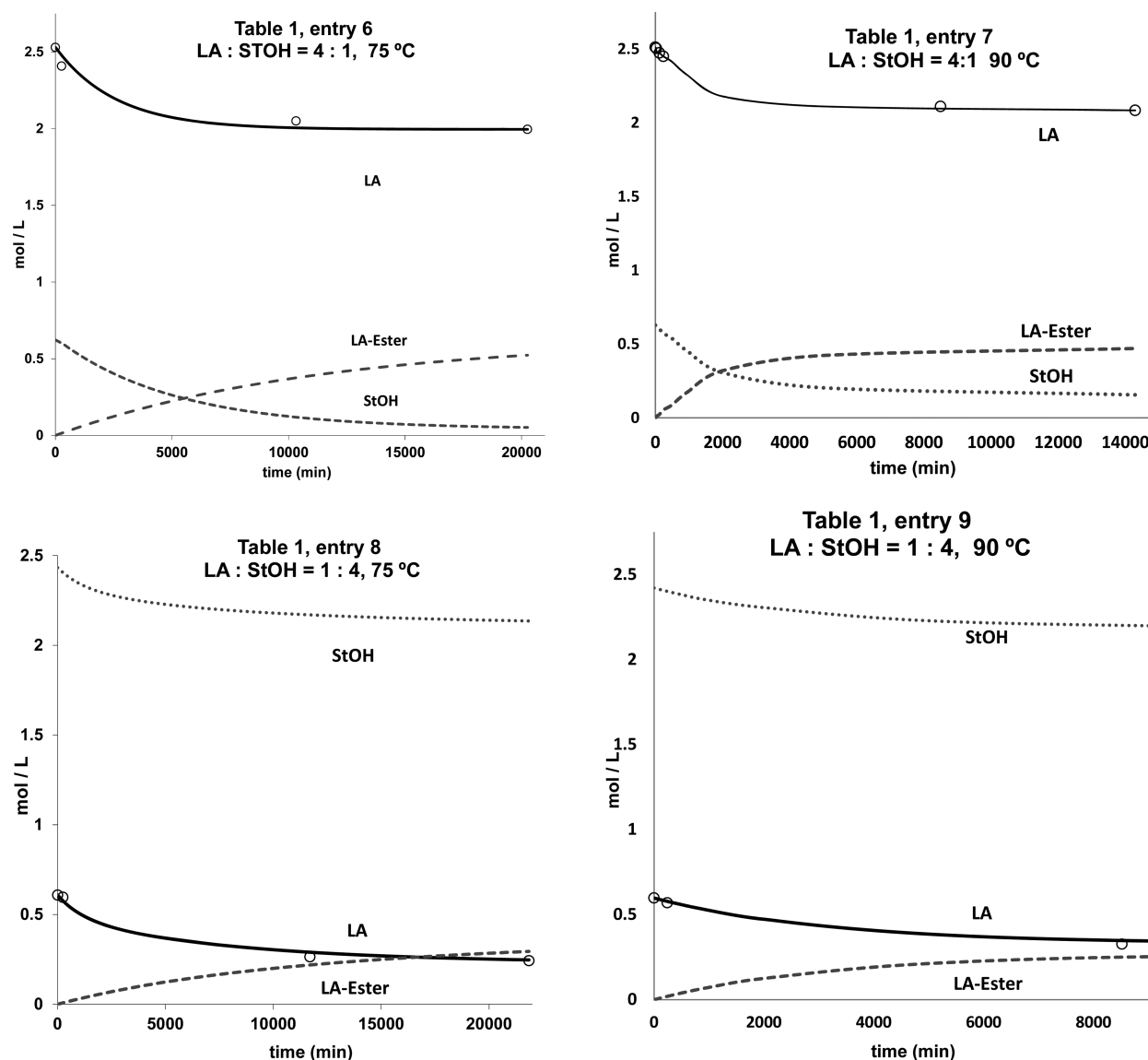


Figure 3. Esterification of nonequimolar solutions of reactants (LA:StOH = 1:4 and 4:1) at 75 and 90 °C (Table 1, entries 6–9).

(conductance) were then converted to concentrations. The fatty acid (LA) could not be included in these experiments because it forms an oily emulsion with the aqueous phase not suitable for conductometric measurements.

The conductance of a solution depends on the number and types of ions in the solution. Generally, small ions and highly charged ions conduct the current better than large ions and ions with a small charge. The size of the ions is important because it determines the speed with which the ions can travel through the solution. Small ions can move more rapidly than larger ones. The charge is significant because it determines the amount of electrostatic attraction between the electrode and the ions.<sup>9</sup> The degree of dissociation ( $\alpha$ ) is a fraction of the total number of moles of an acid or base or electrolyte that dissociates into ions in an aqueous solution when equilibrium is attained. For an acid with the dissociation process  $\text{HA} = \text{H}^+ + \text{A}^-$  and dissociation constant  $K$ , the degree of dissociation is obtained from

$$\alpha = \frac{2K}{\sqrt{K^2 + 4Kc} + K} \quad (2)$$

where  $c$  is the total concentration of the acid. For a strong acid,  $K$  is large and  $\alpha = 1$ , while for a weak acid,  $K \ll 1$ ,  $\alpha = (K/c)^{1/2}$  according to the above equation. By assuming that the reason for the conductance is the proton and the formate ion, the conductance in the beginning and after some time are given by equations

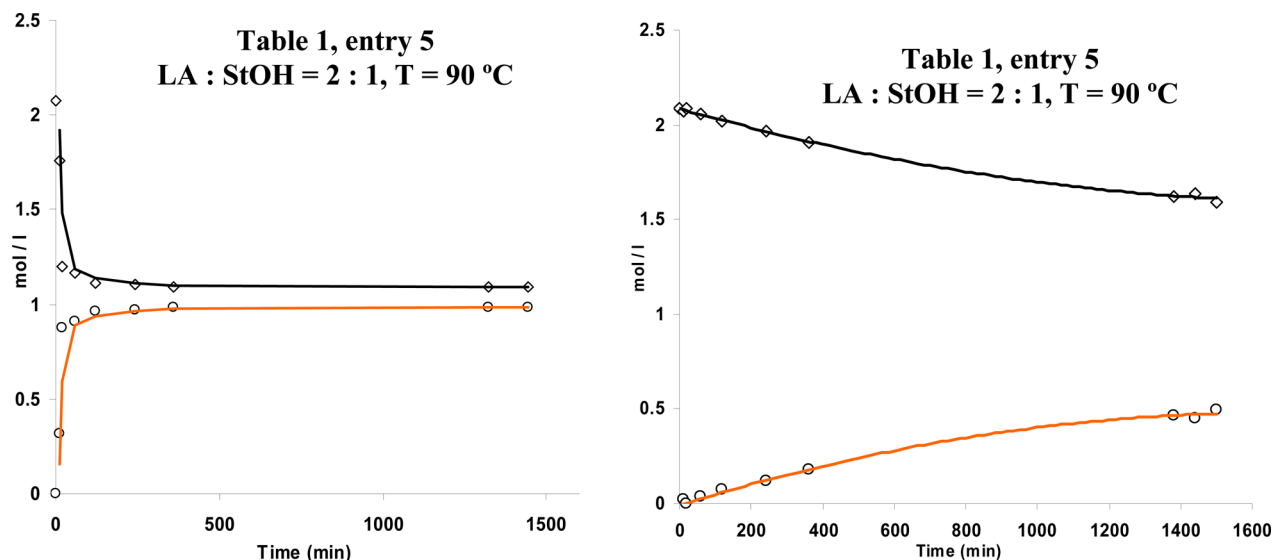
$$\gamma_0 = \gamma_{\text{H}}c_{\text{0H}} + \gamma_{\text{A}}c_{\text{0A}} = (\gamma_{\text{H}} + \gamma_{\text{A}})\alpha_0c_0 \quad (3)$$

$$\gamma = \gamma_{\text{H}}c_{\text{H}} + \gamma_{\text{A}}c_{\text{A}} = (\gamma_{\text{H}} + \gamma_{\text{A}})\alpha c \quad (4)$$

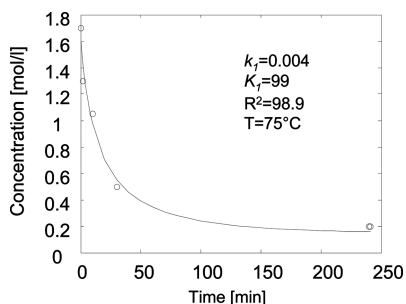
which implies that the concentration of free formate ions and protons are given by the following equations for strong ( $\alpha = \alpha_0 = 1$ ) and weak ( $\alpha_0 = (K/c_0)^{1/2}$ ,  $\alpha = (K/c)^{1/2}$ )

$$c = \frac{\gamma}{\gamma_0} \times c_0 \quad (5)$$

$$c = \left(\frac{\gamma}{\gamma_0}\right)^2 c_0 \quad (6)$$



**Figure 4.** Esterification of LA with StOH in the presence of sulfuric acid catalyst (Table 1, entries 4 and 5). Left: 1.0 wt % H<sub>2</sub>SO<sub>4</sub> as catalyst. Right: 0.0001 wt % H<sub>2</sub>SO<sub>4</sub> as catalyst.



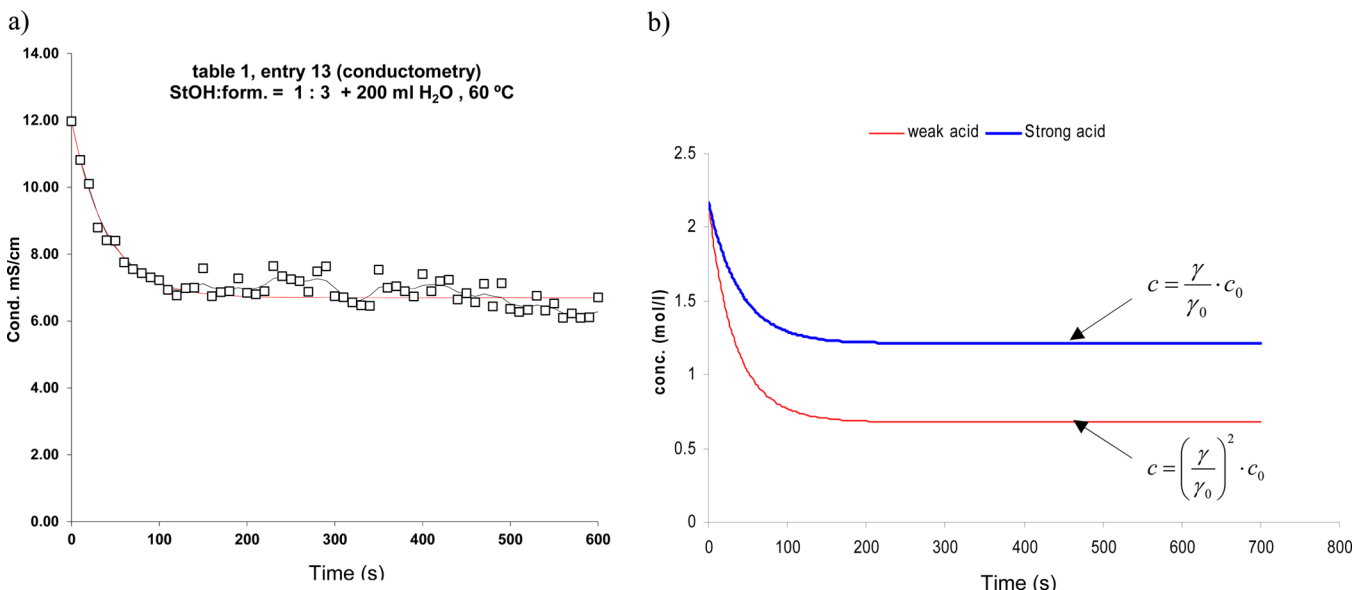
**Figure 5.** Esterification of formic acid with StOH (Table 1, entry 11) at 75 °C. Continuous lines represent model prediction.

The experiment revealed that even diluted formic acid reacts rapidly with stearyl alcohol, and the conductance dropped rapidly from 12 to 7 (mS/cm) in the experiment. Within a

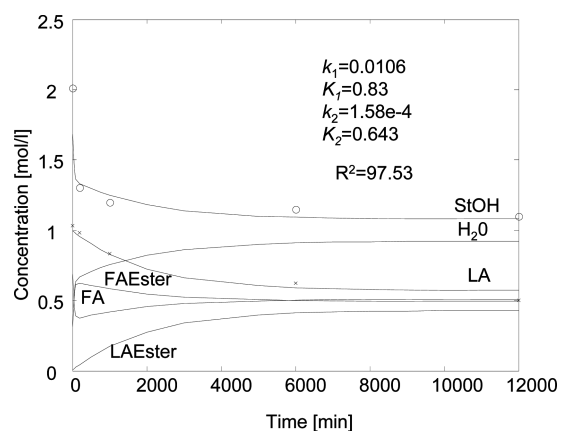
minute, all stearyl alcohol had converted to ester. Figure 6a shows the conductance, while Figure 6b demonstrates the corresponding concentration profile. Formic acid was noticed to act more as a strong acid than a weak acid in the actual reaction environment. The initial rate was calculated to be 7.50 mol/L min.

In the experiment with the molar ratio LA:StOH:formic acid = 1:2:1 (Table 1, entry 14), over 90 mol % of the initial formic acid forms ester with StOH within the first minutes, while the excess StOH only slowly esterifies with the fatty acid (Figure 7).

With a higher amount of formic acid, the esterification of fatty acids is even more efficiently prevented. The chain length of the carboxylic acid showed an importance in the esterification rate. If acetic acid was used instead of formic acid in addition to StOH, the initial rate dropped by a factor of 1000 (Table 1, entry 15). The experiments showed that lactic



**Figure 6.** Esterification of formic acid with StOH; conductometric analysis (Table 1, entry 13).



**Figure 7.** Esterification of formic acid (FA) and linoleic acid (LA) with StOH (Table 1, entry 14). Continuous lines represent the model prediction.

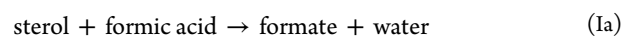
acid, butanoic acid, and oxalic acid were significantly slower to form esters with StOH.

**Esterification of Linoleic Acid and Short-Chain Carboxylic Acids with Sterols.** In preliminary experiments, small samples in ampoules were placed in an oven for a certain period of time (usually 24 h), after which they were analyzed with GC. The results gave valuable information for the subsequent experiments. In the experiments with sterols and formic acid present (Table 3, entry 1–6), it was found out that sterols did not dissolve in formic acid, but they seemed to stay in separate phases. GC analysis showed no product formation, which confirms this assumption. It was necessary to dissolve the solid sterols in the fatty acid before adding formic acid. As the sterols are solved in fatty acid, reactions can take place (Table 3, entries 9–13). At elevated temperatures (90 °C), diene formation was extensive (90% dienes, 10% formate esters), but it decreased as the temperature was decreased to 60 °C (60% dienes, 40% formate esters). Formic acid excess favors diene formation when comparing blue and black peaks in Figure 8. When preheated (red), the sterols form esters with the fatty acids, and addition of formic acid does not convert the esters back to sterols.

Sterols have significantly higher melting points than stearyl alcohol, which made it necessary to carry out experiments at elevated temperatures. The experimental results confirmed that the fatty acid had to be heated to 140 °C before the sterols were added, otherwise the sterols were not properly dissolved into the fatty acid. After the preheating period, the reaction temperature could be lowered in the current experiments to 90 or 120 °C. The sterols also formed esters with the fatty acid but significantly less than with stearyl alcohol, which is demonstrated in Figure 9.

When adding formic acid to this reaction system, some esters were formed, but most of the product consisted of dienes (stigmasta-5,3-diene and campesta-3,5-diene), as illustrated in Figure 10. In the experiment (Table 2, entries 3a,b), no fatty acid esters were found, and fatty acid concentrations remained unchanged. Sterols were mainly converted to dienes but not to esters.

The results are a consequence of dehydration due strong acid and high temperature. The esterification and dehydration reactions proceed in parallel as follows



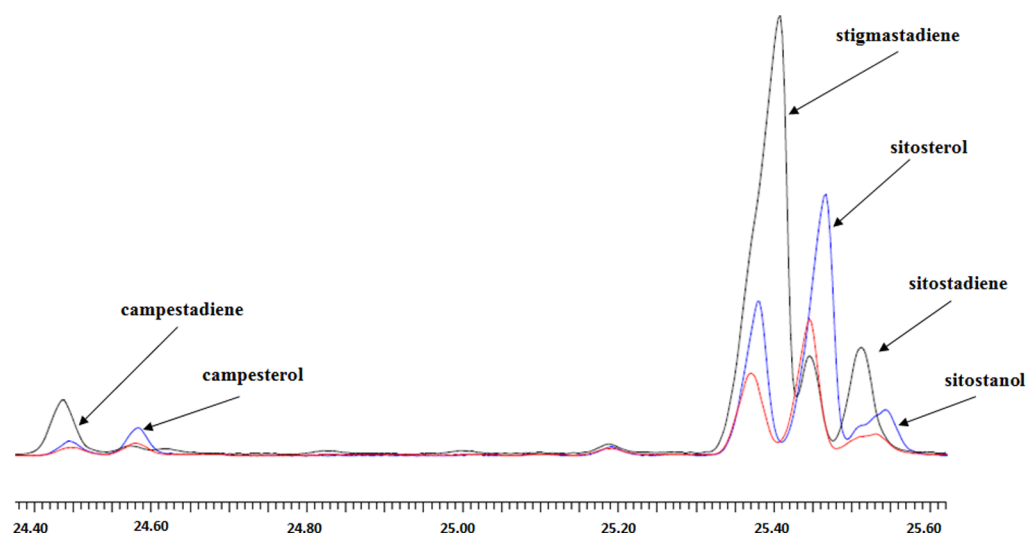
Reaction II is catalyzed by formic acid.

In the presence of acetic acid as an esterification reagent (Table 2, entry 4), no dienes were formed, only esters. However, the esterification reaction was much slower than with formic acid. At 120 °C, the conversion of sterols to esters became 90% in approximately 30 h, as shown in Figure 11.

## KINETIC MODELING

Selected experimental data were used for kinetic modeling (Figures 2,5,7, and 10). The aim was to quantify the effect of the protective esterification and to describe the kinetics of diene formation through dehydration.

**Balance Equations.** A fully agitated batch reactor was assumed in all cases. The change of liquid volume during the experiment was negligible. Consequently, the mass balances of the components are written as



**Figure 8.** Ampoule experiments: SitOH:FA:LA = 1:0.8:8 (black), SitOH:FA:LA = 1:4:4 (blue), and SitOH:FA:LA = 1:0.8:8 but preheated in 150 °C for 3 h (red). All samples were 24 h in the oven at 60 °C.

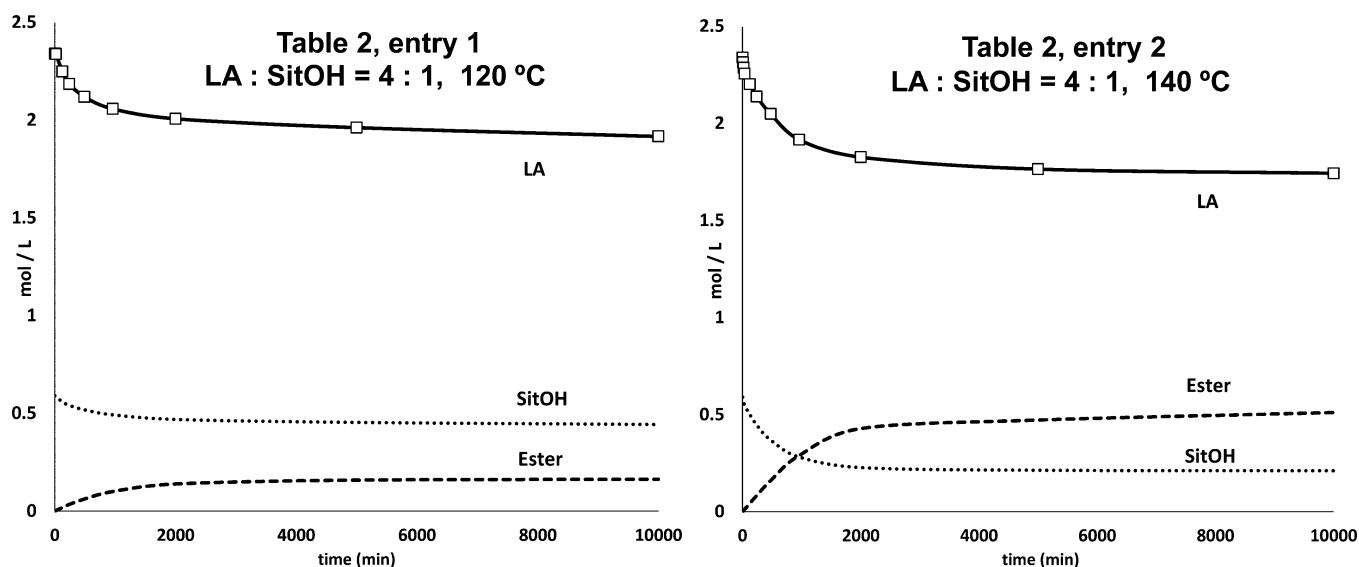


Figure 9. Esterification of LA with sterol (SitOH) at 120 and 140 °C (Table 2, entries 1–2).

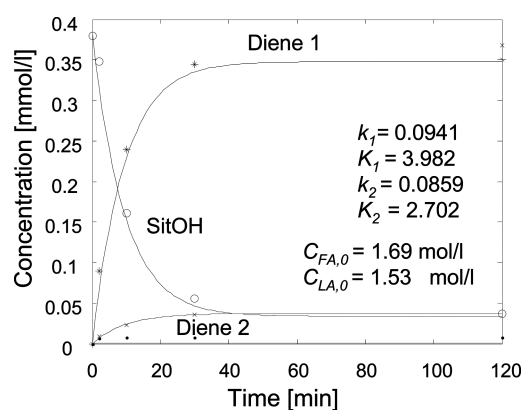


Figure 10. Formation of dienes from SitOH in the presence of formic acid and LA (Table 2, entries 3a,b). Continuous lines represent the model prediction.

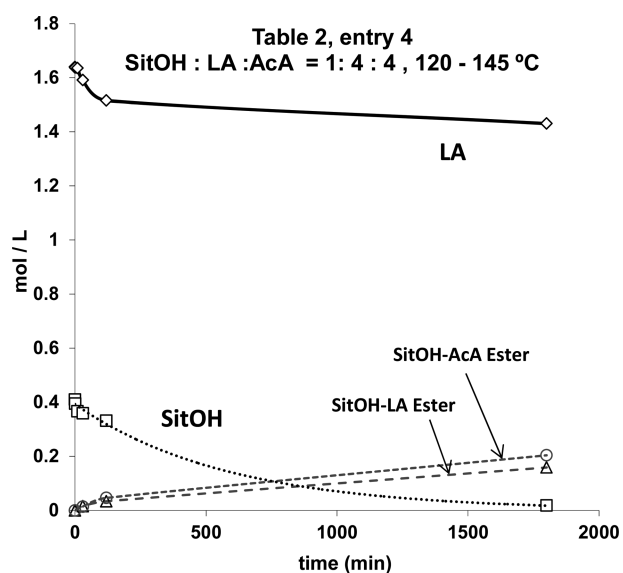


Figure 11. Esterification of LA and acetic acid with SitOH (Table 2, entry 4).

$$dc_i/dt = r_i \quad (7)$$

where the generation rate ( $r_i$ ) is obtained from the stoichiometry and the reaction rates ( $R_j$ )

$$r_i = \sum v_{ij}R_j \quad (8)$$

In eq 8,  $i$  and  $j$  refer to the component and reaction, respectively.

Two reaction systems were modeled mathematically: esterification and dehydration (diene formation). Both processes were assumed to be reversible. The diene formation was assumed to be catalyzed by formic acid.

**Esterification Stoichiometry and Kinetics.** The reaction scheme for esterification can be written as follows



where  $A_1$  = fatty acid,  $A_2$  = short-chain carboxylic acid (formic acid),  $B$  = stearyl alcohol,  $C_1$  and  $C_2$  = esters, and  $W$  = water.

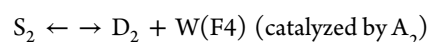
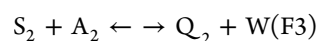
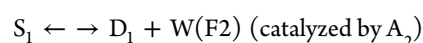
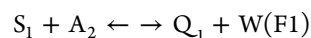
The reaction rates can now be expressed as

$$R_1 = k_1(c_{A1}c_B - c_{C1}c_W/K_1) \quad (9)$$

$$R_2 = k_2(c_{A2}c_B - c_{C2}c_W/K_2) \quad (10)$$

The adjustable parameters in the model are the rate ( $k_1$  and  $k_2$ ) and equilibrium constants ( $K_1$  and  $K_2$ ). The data displayed in Figures 2 (linoleic acid) and 5 (formic acid) were used in the modeling.

**Sterol Reaction Stoichiometry and Kinetics.** The reaction scheme for the sterol reactions with formic acid are



where  $S_1$  = sitosterol,  $S_2$  = campesterol,  $Q_1$  = sitosterol ester,  $D_1$  = diene 1 (stigma3,5-stadiene),  $Q_2$  = campesterol ester, and  $D_2$  = diene 2 (campestadiene).

The reaction rates are given by



$$R_1 = k_1(c_{S1}c_{A2} - c_{Q1}c_W/K_1) \quad (11)$$

$$R_2 = k_2c_{A2}(c_{S1} - c_{D1}c_W/K_2) \quad (12)$$

$$R_3 = k_3(c_{S2}c_{A2} - c_{Q2}c_W/K_3) \quad (13)$$

$$R_4 = k_4c_{A2}(c_{S2} - c_{D2}c_W/K_4) \quad (14)$$

The adjustable parameters in the model are the rate ( $k_1, k_2, k_3, k_4$ ), and equilibrium constants ( $K_1, K_2, K_3, K_4$ ). The experimental data in Figure 10 were used in the modeling.

**Parameter Estimation Methods and Results.** The temperature dependences of the rate and equilibrium constants were described by the laws of arrhenius and van't Hoff, respectively. The following formulation was used to suppress the mutual correlation between the pre-exponential factor and the activation energy ( $E_a$ )/reaction enthalpy ( $\Delta H$ )

$$k_i = k_0 \exp((-E_a/R)(1/T - 1/T_{ref})) \quad (15)$$

$$K_i = K_0 \exp(-\Delta H/R)(1/T - 1/T_{ref}) \quad (16)$$

where  $T$  and  $T_{ref}$  denote the temperature and the reference temperature, respectively. Parameters  $k_0$  and  $K_0$  represent the rate and equilibrium constants at the reference temperature, respectively; and  $R$  is the general gas constant ( $R = 8.3143 \text{ J/Kmol}$ ).

The model equations were solved numerically with backward difference method during parameter estimation that was carried out by nonlinear regression by minimizing the sum of square errors with Levenberg–Marquardt method. The software Modest<sup>10</sup> was used in all computations.

The parameter estimation results are shown in Figures 2, 5, 7, and 10, where the numerical values of the rate and equilibrium constants are also displayed. In general, the parameters were very well identified, and the errors were always less than 25%. The overall degree of explanation ( $R^2$ ) always exceeded 95%. The fit of the model to the experimental data was good, as revealed by Figures 2, 5, 7, and 10.

## CONCLUSIONS

The kinetics for selected esterification reactions were studied with varying molar ratios and temperatures in an isothermal laboratory-scale glass reactor and in static ampules. Stearyl alcohol reacted slowly with linoleic acid. Sterols formed esters with linoleic acid even slower than stearyl alcohol, and a higher temperature was necessary to obtain reasonable conversions. Formic acid was found to form esters extremely fast with stearyl alcohol, thus preventing them to react with fatty acids. By adding formic acid to a binary mixture with fatty acid and stearyl alcohol or sterols, the esterification of valuable fatty acids was efficiently hindered. Carboxylic acids with longer chain lengths, such as acetic acid, were shown to form esters with stearyl alcohol and sterols, but the rates were much slower than with formic acid. Dienes were formed from sterols due to an elimination reaction. Formic acid was discovered to catalyze the diene formation at high temperatures as sterols were used as reagents. Kinetic modeling was successfully applied to selected esterification and dehydration reactions.

## ASSOCIATED CONTENT

### Supporting Information

A detailed list of the properties of all reactants and products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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