A Second-Order Model for Catalytic-Transfer Hydrogenation of Edible Oils

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ABSTRACT: A second-order kinetic model for hydrogenation of fatty acids in series has been developed and analyzed. The model is applied to the data obtained for sodium formate-catalyzed hydrogenation of soybean, peanut, corn, and olive oils. There is good agreement between the experimental data and predicted values obtained from the model as evidenced by the analysis of r^2 and F-test values. The effect of individual fatty acid composition of various edible oils on the rate of hydrogenation has been explained in view of the mathematical model developed. The individual rate constants seem to obey the Arrhenius rate law. The second-order kinetic analysis discussed is found to be suitable for mathematically describing hydrogenation of vegetable oils by hydrogen donors as compared to the traditional first-order kinetic analysis.

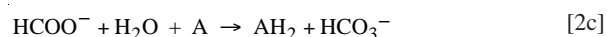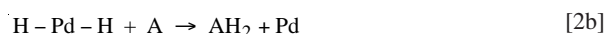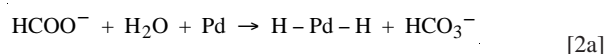Paper no. J9262 in *JAOCS* 77, 1–8 (January 2000)

Edible oils mainly consist of saturated and unsaturated octadecanoic fatty acids. In order to improve the stability of oil as well as to change its physical properties, oils are generally hydrogenated. During the hydrogenation reactions, the double bonds of the polyunsaturated acids are saturated. In the past (1), the process of hydrogenation of edible oils has been represented as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \qquad [1]$$
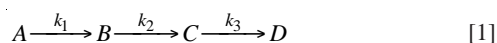
where A, B, C, and D are linolenic acid, linoleic acid, oleic acid, and stearic acid, respectively. In a series of recent papers, authors have presented data on the use of a hydrogen donor transfer agent (formate ions) for the hydrogenation of oils (2–5). The advantages of this approach involving hydrogen transfer agent are that high-pressure and high-temperature operations are not required. The other major advantage is that the rate of *trans* fatty acid formation reaction, which is favored at high temperatures, is minimized. The reaction is carried out at atmospheric pressure and at a temperature of 80°C. The reaction mixture contains 2.8 M formate with an

oil/water ratio of 1:2, by weight. The mechanism of the rate of reaction can be explained by the following hypothetical reactions:

$$HCOO^- + H_2O + Pd \rightarrow H-Pd-H + HCO_3^- \qquad [2a]$$

$$H-Pd-H + A \rightarrow AH_2 + Pd \qquad [2b]$$

$$HCOO^- + H_2O + A \rightarrow AH_2 + HCO_3^- \qquad [2c]$$

Thus, this reaction cannot be treated as a first-order reaction. However, for the sake of simplicity, Smidnovik *et al.* (3–5) used the simplified first-order irreversible reaction mechanism.

Blandermer *et al.* (6) discussed the kinetics of the second-order reaction

$$A + Q \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_3} C \qquad [3]$$
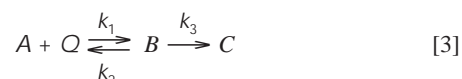
Summers *et al.* (7) provided a more detailed mathematical treatment of the kinetics of such a second-order reaction. The authors showed that the transient concentrations of components A and Q could be found by numerically solving two coupled first-order differential equations. The differential equations resulted from the four rate equations for concentration plus two conservation laws. Klemm and Klemm (8) considered a more complex reaction mechanism:

$$A + Q \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C \qquad [4a]$$

$$A + B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} D + C \qquad [4b]$$

$$D + Q \underset{k_6}{\overset{k_5}{\rightleftharpoons}} 2B \qquad [4c]$$

In arriving at their solution, the authors (8) assumed that only A and Q had initial concentrations and that the reverse reactions were extremely slow as compared to the forward reaction.

In this publication, we have considered a relatively more complex reaction mechanism constructed out of three second-

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order irreversible reactions, in which all components have different initial concentrations. Such a set of reactions is common in the catalytic transfer hydrogenation of edible oils and especially among the ones described by Naglic *et al.* (5).

Model second-order reactions. The reaction mechanism used in this publication considers the following irreversible reactions in series:

$$A + P + W \xrightarrow{k_1} B + Q \qquad [5a]$$

$$B + P + W \xrightarrow{k_2} C + Q \qquad [5b]$$

$$C + P + W \xrightarrow{k_3} D + Q \qquad [5c]$$
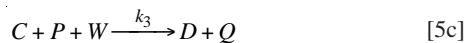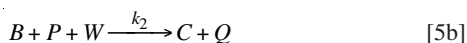
The forward rate of reaction of Equations 5a–5b can be given by pseudo second-order reactions as described Equations 6–8 if the concentration of water (W) is assumed to be large in comparison to the concentrations of the reactants, A, B, C, D, and the catalytic hydrogen transfer agent P.

$$\frac{dA}{dt} = -(k_1 A)P \qquad [6]$$

$$\frac{dB}{dt} = (k_1 A - k_2 B)P \qquad [7]$$

$$\frac{dC}{dt} = (k_2 B - k_3 C)P \qquad [8]$$

$$\frac{dD}{dt} = k_3 C P \qquad [9]$$

$$\frac{dP}{dt} = -\frac{dQ}{dt} = -(k_1 A + k_2 B + k_3 C)P \qquad [10]$$

The overall mass balance on reactants A, B, C, and D (i.e., the sum of the Eqs. 6–9) clearly satisfies the following conservation law:

$$A + B + C + D = C_t = A_o + B_o + C_o + D_o \qquad [11]$$

where A_o, B_o, C_o, and D_o are the initial values of the respective components.

The use of Equation 11 eliminates the need for one out of the four differential equations (Eqs. 6–9). The solution to the differential equations listed above involves expressing the concentrations of various reactants in terms of the concentration of one species (for instance, A) and then solving the resultant differential equation. In other words, the differential equations are reduced to the form representing the relative reaction rates with respect to the reaction rate of any one component. The resulting differential equations obtained by dividing Equations 7 and 8 by Equation 6 are given as follows:

$$\frac{dB}{dA} - \alpha \frac{B}{A} = -1 \qquad [12]$$

where $\alpha = k_2/k_1$ and

$$\frac{dC}{dA} - \beta \frac{C}{A} = -\alpha \frac{B}{A} \qquad [13]$$

where $\beta = k_3/k_1$.

The solution to the linear, first-order differential equation (Eq. 10) is given by:

$$B = -\left(\frac{1}{1-\alpha}\right)A + C_1 A^\alpha \qquad \alpha \neq 1 \qquad [14a]$$

$$= -A \ln A + C_1 A \qquad \alpha = 1 \qquad [14b]$$

where the constant of integration, C_1, is found by the initial condition, $A = A_o$, $B = B_o$:

$$C_1 = \left(B_o + \frac{A_o}{1-\alpha}\right)A_o^{-\alpha} \qquad \alpha \neq 1 \qquad [15a]$$

$$= \frac{B_o}{A_o} + \ln A_o \qquad \alpha = 1 \qquad [15c]$$

The solution to Equation 13 is given by:

$$C = -\alpha A^\beta \int \left(\frac{B}{A}\right)A^{-\beta} dA + C_2 A^\beta \qquad [16]$$

where C_2 is the constant of integration.

Substitution of B from Equations 15a and 15b results in the quantification of the concentration of C in terms of the concentration of A. The following five distinct cases are treated and the results obtained are reported in Tables 1 through 5:

(i) $\alpha \neq \beta$, $\beta \neq 1$, $\alpha \neq \beta$

(ii) $\alpha \neq 1$, $\beta \neq 1$, $\alpha = \beta$

(iii) $\alpha \neq 1$, $\beta = 1$

(iv) $\alpha = 1$, $\beta \neq 1$

(v) $\alpha = \beta = 1$

Concentration of species P is determined by the linear combination of Equations 6–9 as shown below:

$$\frac{dP}{dt} = 3\left(\frac{dA}{dt}\right) + 2\left(\frac{dB}{dt}\right) + \left(\frac{dC}{dt}\right) \qquad [17]$$

Integration of the above equation between the limits $P = P_o$, $P = P$; $A = A_o$, $A = A$; $B = B_o$, $B = B$; and $C = C_o$, $C = C$ gives us:

$$P = 3A + 2B + C + (P_o - 3A_o - 2B_o - C_o) \qquad [18]$$

The at concentration of P in terms of A is given in Tables 1–5. Finally, using the expression for P in terms of A, the concentration of A as a function of time is determined by inte-

TABLE 1
Fatty Acid and Formate Ion Profiles as a Function of Linolenic Acid Concentration for Case I[a]

Case I $\alpha \neq 1$, $\beta \neq 1$, $\alpha \neq \beta$

$$B = -\frac{1}{(1-\alpha)}A + C_1 A^\alpha \tag{i}$$

$$\text{where } C_1 = \left(B_o + \frac{A_o}{1-\alpha}\right)A_o^{-\alpha} \tag{ii}$$

$$C = \frac{\alpha A}{(1-\alpha)(1-\beta)} - \frac{\alpha C_1 A^\alpha}{(\alpha-\beta)} + C_2 A^\beta \tag{iii}$$

$$\text{where } C_2 = C_o A_o^{-\beta} - \frac{\alpha A_o^{1-\beta}}{(1-\alpha)(1-\beta)} + \frac{\alpha C_1 A_o^{\alpha-\beta}}{\alpha-\beta} \tag{iv}$$

$$P = P_o + a(A - A_o) + C_1\left(1 - \frac{\beta}{\alpha-\beta}\right)\left(A^\alpha - A_o^\alpha\right) + C_2\left(A^\beta - A_o^\beta\right) \tag{v}$$

$$\text{where } a = 1 - \frac{\alpha}{1-\alpha} + \frac{\alpha\beta}{(1-\alpha)(1-\beta)} \tag{vi}$$

[a]$\alpha = k_2/k_1$; $\beta = k_3/k_1$; A, B, C, and D stand for linolenic, linoleic, oleic, and stearic acids, respectively, which participate in the hydrogenation reaction *via* the following equation:

$$A + P \xrightarrow{k_1} B + P \xrightarrow{k_2} C + P \xrightarrow{k_3} D$$
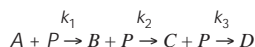
where P represents the hydrogen donor.

grating Equation 6:

$$\int_{A_o}^{A} \frac{dA}{A \cdot P} = -k_1 t \tag{19}$$

Equation 19 can be solved numerically rather readily by using appropriate mathematical software available commercially.

RESULTS AND DISCUSSION

The above model for a series second-order reaction was applied to the hydrogenation of olive, peanut, corn, and soybean

TABLE 2
Fatty Acid and Formate Ion Profiles as a Function of Linolenic Acid Concentration for Case II[a]

Case II $\alpha \neq 1$, $\beta \neq 1$, $\alpha = \beta$

$$B = -\left(\frac{1}{1-\alpha}\right)A + C_1 A^\alpha \tag{i}$$

$$\text{where } C_1 = \left(B_o + \frac{A_o}{1-\alpha}\right)A_o^{-\alpha} \tag{ii}$$

$$C = \frac{\alpha A}{(1-\alpha)^2} - \alpha C_1 A^\alpha \ln A + C_2 A^\alpha \tag{iii}$$

$$\text{where } C_2 = C_o A^{-\alpha} + \alpha C_1 \ln A_o - \frac{\alpha A_o^{1-\alpha}}{(1-\alpha)^2} \tag{iv}$$

$$P = P_o + a(A - A_o) + (2C_1 + C_2)\left(A^\alpha - A_o^\alpha\right) - \alpha C_1\left(A^\alpha \ln A - A_o^\alpha \ln A_o\right) \tag{v}$$

$$\text{where } a = 1 - \frac{\alpha}{1-\alpha} + \left(\frac{\alpha}{1-\alpha}\right)^2 \tag{vi}$$

[a]See Table 1 for definitions.

TABLE 3
Fatty Acid and Formate Ion Profiles as a Function of Linolenic Acid Concentration for Case III[a]

Case III $\alpha \neq 1$, $\beta = 1$

$$B = -\left(\frac{1}{1-\alpha}\right)A + C_1 A^\alpha \tag{i}$$

$$\text{where } C_1 = \left(B_o + \frac{A_o}{1-\alpha}\right)A_o^{-\alpha} \tag{ii}$$

$$C = \frac{\alpha}{1-\alpha}A \ln A - \frac{\alpha C_1 A^\alpha}{1-\alpha} + C_2 A \tag{iii}$$

$$\text{where } C_2 = \frac{C_o}{A_o} + \frac{\alpha}{1-\alpha}\left[C_1 A_o^{\alpha-1} - \ln A_o\right] \tag{iv}$$

$$P = P_o + \left(1 - \frac{\alpha}{1-\alpha} + C_2\right)(A - A_o)$$
$$+ \frac{\alpha}{1-\alpha}\left(A \ln A - A - A_o \ln A_o + A_o\right)$$
$$+ C_1\left(1 - \frac{1}{1-\alpha}\right)\left(A^\alpha - A_o^\alpha\right) \tag{v}$$

[a]See Table 1 for definitions.

oils. The edible oils contain triglycerols of the saturated fatty acids, palmitic and stearic acids, and unsaturated fatty acids, oleic, linoleic, and linolenic acids. During hydrogenation, unsaturated fatty acids are slowly converted to the saturated state. The various oils used in this study have varying fatty acid compositions. For example, of all the oils selected in this

TABLE 4
Fatty Acid and Formate Ion Profiles as a Function of Linolenic Acid Concentration for Case IV[a]

Case IV $\alpha = 1$, $\beta \neq 1$

$$B = -A \ln A + AC_1 \tag{i}$$

$$\text{where } C_1 = \frac{B_o}{A_o} + \ln A_o \tag{ii}$$

$$C = \frac{A}{(1-\beta)^2}\left[(1-\beta)(\ln A - C_1) - 1\right] + C_2 A^\beta \tag{iii}$$
where
$$C_2 = C_o A_o^{1-\beta} - \frac{A_o^{1-\beta}}{(1-\beta)^2}\left[(1-\beta)(\ln A_o - C_1) - 1\right] \tag{iv}$$

$$P = P_o + a(A - A_o) - b(A \ln A - A - A_o \ln A_o + A_o)$$
$$+ C_2\left(A^\beta - A_o^\beta\right) \tag{v}$$
where
$$a = 1 + C_1 - \frac{\beta}{(1-\beta^2)}\left[1 + (1-\beta)C_1\right] \tag{vi}$$
and
$$b = 1 - \frac{\beta}{1-\beta} \tag{vii}$$

[a]See Table 1 for definitions.

TABLE 5
Fatty Acid and Formate Ion Profiles as a Function of Linolenic Acid
Concentration for Case V[a]

Case V $\alpha = \beta = 1$

$$B = -A \ln A + A C_1 \qquad (i)$$

$$\text{where } C_1 = \frac{B_o}{A_o} + \ln A_o \qquad (ii)$$

$$C = A\left[\frac{1}{2}(\ln A)^2 - C_1 \ln A + C_2\right] \qquad (iii)$$

$$\text{where } C_2 = \frac{C_o}{A_o} + (\ln A_o)\left[C_1 - \frac{1}{2}\ln A_o\right] \qquad (iv)$$

$$P = P_o + (3 + 2C_1 + C_2)(A - A_o) - C_1(A \ln A - A_o \ln A_o)$$
$$+ \frac{1}{2}\left[A(\ln A)^2 - A_o(\ln A_o)^2\right] \qquad (v)$$

[a]See Table 1 for definitions.

study, soybean oil has the largest initial amount of linolenic acid followed by peanut oil. Corn oil has negligible amounts of linoleic acid while olive oil contains none. The diene (linoleic acid) concentration was found to be inversely proportional to the triene (linolenic acid) concentration for the edible oils considered in this study. It is known that conjugated dienes have a higher reactivity. Hydrogenation of trienes could result in the formation of conjugated double bonds. In addition, during the initial stages of hydrogenation, migration of double bonds occurs resulting in the formation of conjugated dienes. Thus, the initial amount of trienes and dienes and their positional isomers affect the overall rate con-

stants of the classes of fatty acids. This has been observed in the experimental results.

As discussed earlier, Bailey's simplified model as used by Smidnovik *et al.* (3–5) appears to fit the experimental data reasonably. In the model presented here, the assumption of first-order kinetics has been replaced by second-order kinetics. As seen from Figures 1–4, the model predictions fit well with the experimental values obtained from the work done by Naglic *et al.* (5). The prediction of the fatty oil composition of peanut oil and soybean oil is best explained by case I of our model (Table 1), while case IV (Table 4) can be used to explain the data for corn oil. It must be noted that in the case of corn oil, the numerical value of α is equal to 1, i.e., the rate constants for linolenic acid and linoleic acid hydrogenation at 80°C are equal to one another. The r^2 values along with the rate constants and their respective *F*-values are provided in Table 6. The high r^2 values indicate that the predictions made using the model presented in the paper are in good agreement with the experimental data. However, a good correlation between experimental and model-predicted values does not necessarily represent the goodness of the fit. For this purpose, an *F*-test was conducted for each fatty acid. The *F*-test (Table 6) yielded extremely favorable results, indicating that the model predicts the kinetics of the reaction reasonably well. Although only two of the five cases have been illustrated through the example provided, the other three cases could apply to other data obtained under different temperatures and catalysts. For such cases, analysis of the data to evaluate the kinetics should be done according to the respective tables provided in this paper.

The data in Table 6 show that for all edible oils, the rate constant for linolenic acid hydrogenation is the highest while
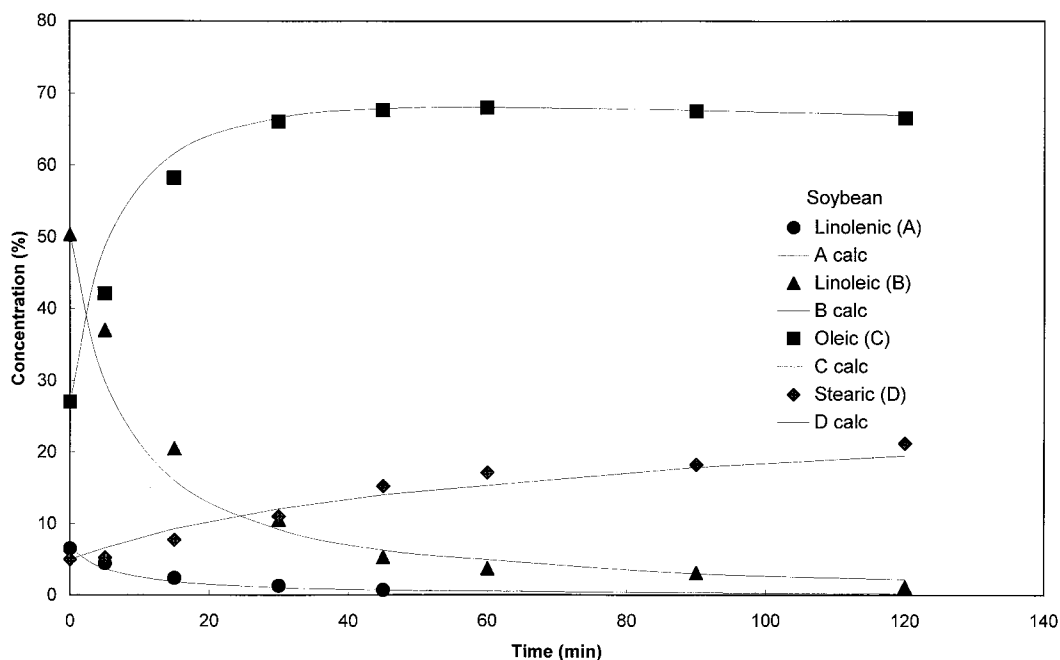

FIG. 1. Fatty acid profile vs. time for soybean oil. Experimental data from Nalgic *et al.* (5).
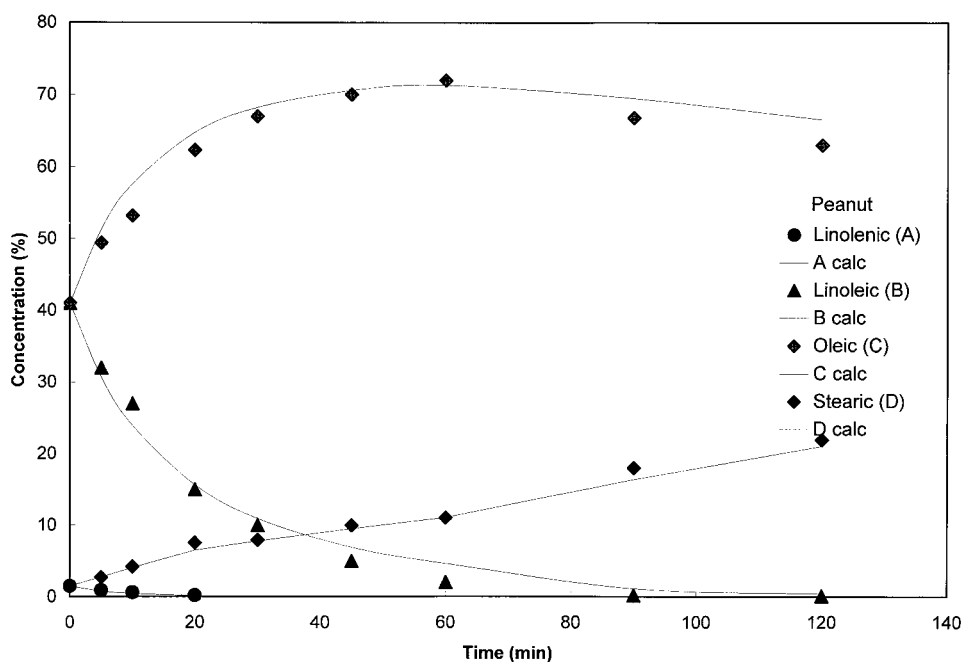
FIG. 2. Fatty acid profile vs. time for peanut oil. Experimental data from Nalgic *et al.* (5).

the rate constant for oleic acid is the lowest. This is in agreement with published data and also with the notion that a higher degree of unsaturation in the fatty acids results in more reactive species. In the case of corn oil, the rate constants for linolenic and linoleic acids are almost equal to one another according to the model predictions. It is also observed in Table 6 that the rate constants for linolenic, linoleic, and oleic fatty acid hydrogenation are of the same order of magnitude

for all the edible oils considered in this study. However, they are obviously not equal to one another because of the complex nature of the oils as well the fact that the reaction mixtures are heterogeneous.

The observations during the experimentation were well collaborated by the results in the model predictions as explained below. The change in iodine value was found to be directly proportional to the change in formate ion concentra-
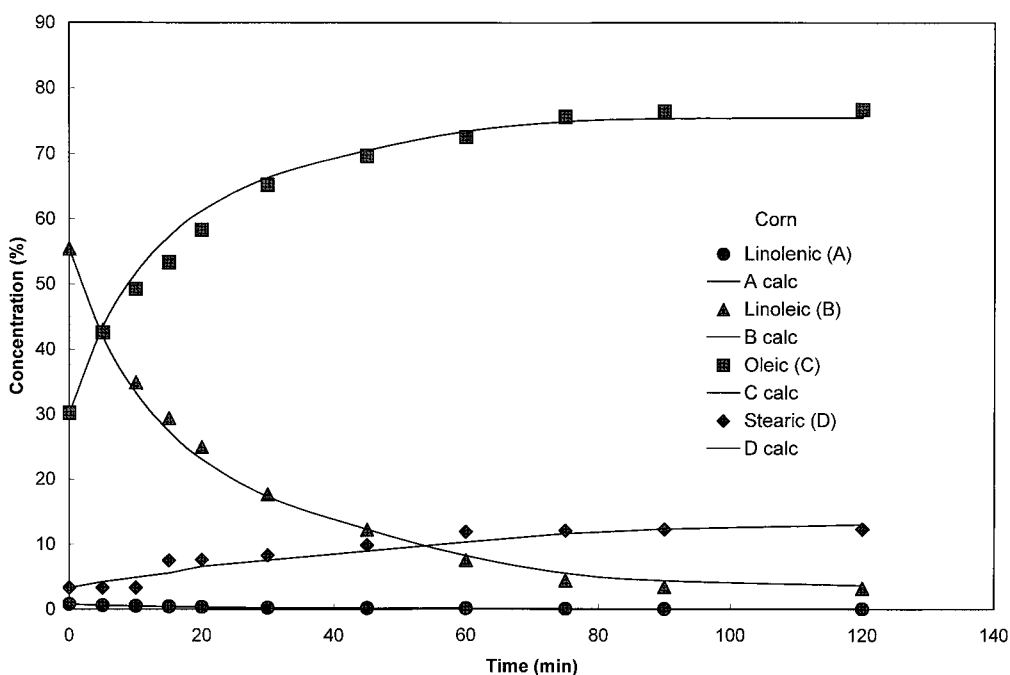

FIG. 3. Fatty acid profile vs. time for corn oil. Experimental data from Nalgic *et al.* (5).
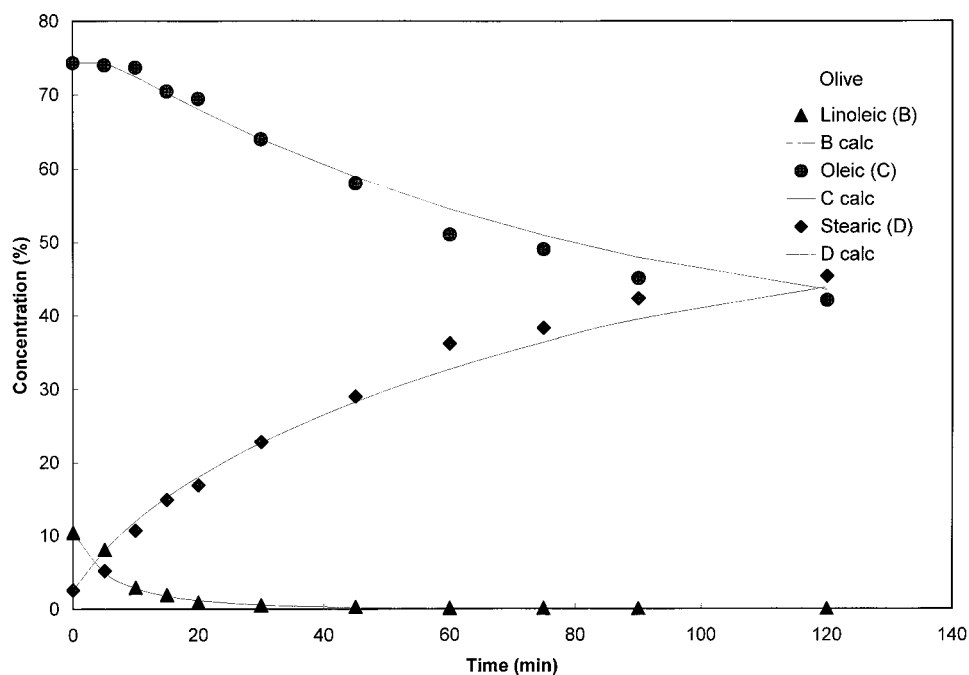
FIG. 4. Fatty acid profile vs. time for olive oil. Experimental data from Nalgic *et al.* (5).

tion as calculated from Equation 18. This illustrates the fact that the set of reactions in hydrogenation of soybean oil follows second-order kinetics. Figure 5 illustrates the predicted rate of change of formate ion concentration as a function of time (the formate ion concentration). This figure gives us a clear indication of the rate of hydrogenation as a function of time. As stated previously, the rate of change of formate ion concentration is a measurement of the rate of hydrogenation. From the figure it is seen that the initial rate of hydrogenation is highest in the case of soybean oil followed by peanut and corn oils. Olive oil has the lowest initial rate of hydrogena-

tion, while corn oil has the second-lowest overall hydrogenation rate. This observation agrees well with the belief that the presence and amount of linolenic acid affect the rate of hydrogenation (4). Generally, the rate of hydrogenation (i.e., rate of depletion of formate ion concentration) decreases with time (i.e., decrease in formate ion concentration). However, in the case of olive oil, the rate of hydrogenation increases initially and then decreases. As seen from Figure 4, the initial rate of hydrogenation of linoleic acid is faster than oleic acid hydrogenation. And, as the total hydrogenation rate is the sum of linoleic and oleic acid hydrogenation, the rate of hydro-

TABLE 6
Estimated Rate Constants for Various Oils and the Goodness of Fit Indicators

Oil	Correlation coefficient[a]	α^b	β	k_1	k_2	k_3	Stearic	Oleic	Linoleic	Linolenic
					$(mol\%)^{-1}\ min^{-1}$					
Olive	—	0.097	—	$9.82 \cdot 10^{-4}$	$9.55 \cdot 10^{-5}$					
	r^2						0.994	0.993	0.936	—
	(Prob)						0.050	0.040	0.150	—
Corn		1.000	0.052	$8.22 \cdot 10^{-4}$	$8.22 \cdot 10^{-4}$	$4.29 \cdot 10^{-5}$				
	r^2						0.922	0.987	0.995	0.977
	(Prob)						0.200	0.050	0.030	0.060
Peanut		0.470	0.025	$1.68 \cdot 10^{-3}$	$7.91 \cdot 10^{-4}$	$4.23 \cdot 10^{-5}$				
	r^2						0.961	0.972	0.992	0.984
	(Prob)						0.010	0.030	0.050	0.020
Soybean		0.337	0.002	$3.44 \cdot 10^{-4}$	$1.16 \cdot 10^{-4}$	$6.54 \cdot 10^{-7}$				
	r^2						0.964	0.934	0.993	0.984
	(Prob)						0.030	0.025	0.030	0.010

[a]r^2 indicates the fit between predicted values and experimental data. Prob provides the probability that the two data sets, experimental and predicted, do not belong to the same population.
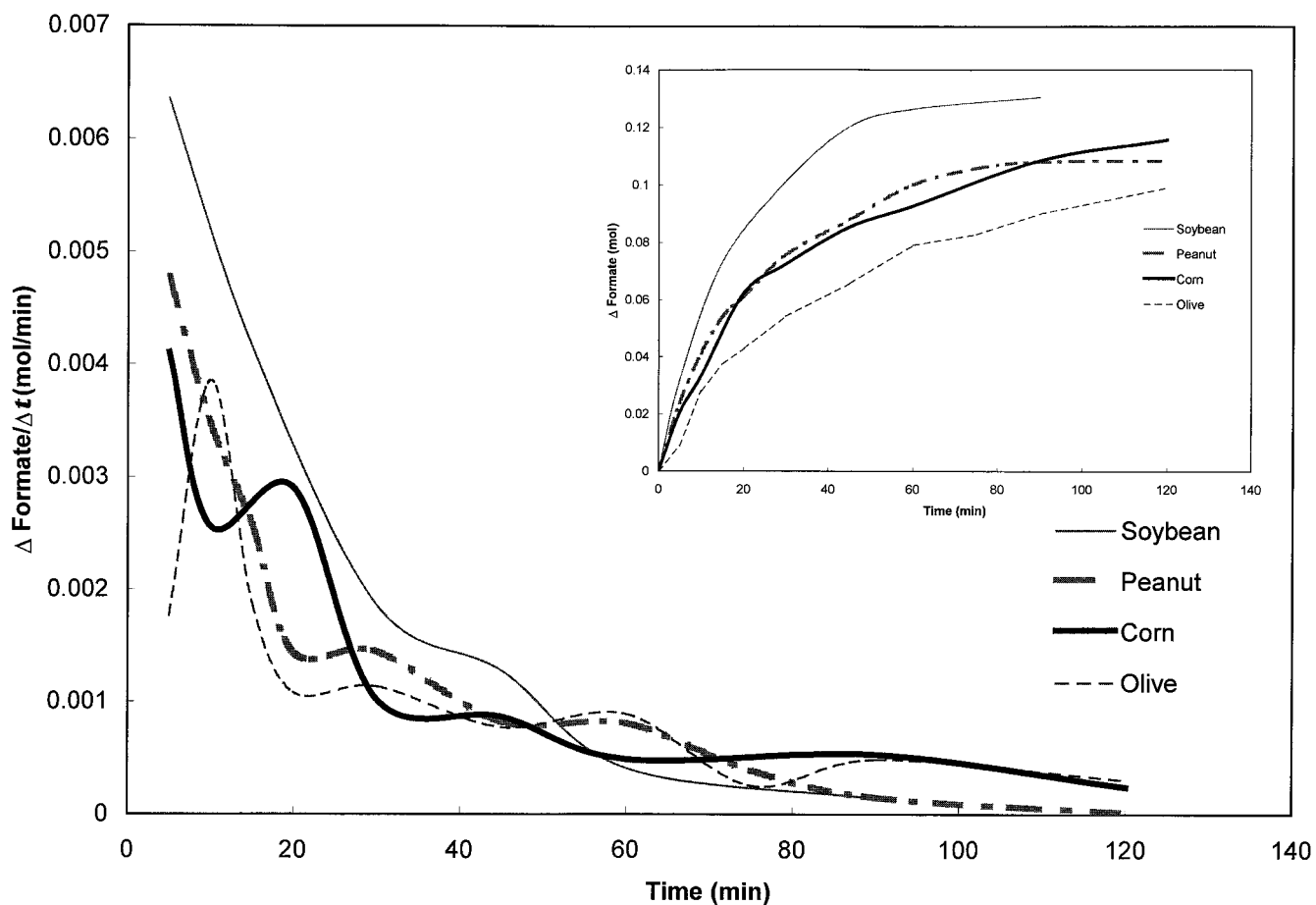[b]α and β as per Table 1.

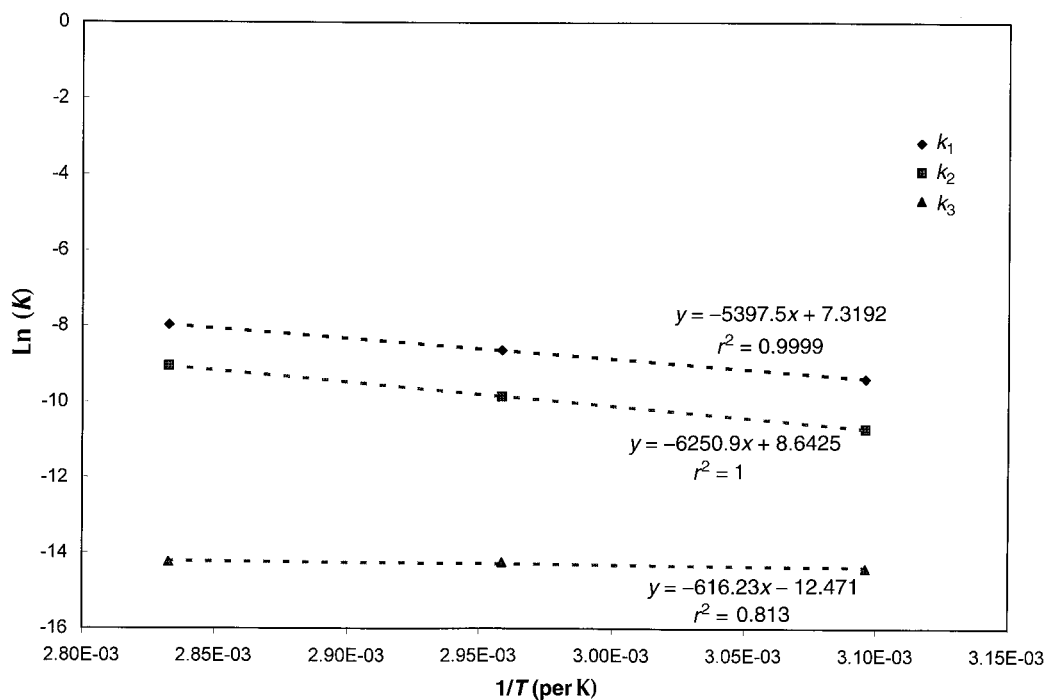**FIG. 5**. Rate of formate ion consumption vs. time.

FIG. 6. Rate constant vs. temperature for soybean oil. Fitted line is $y = ax + b$ for each rate constant, where $a = E/R$ and $b = \ln (K_0)$ (Eq. 20).

genation is observed to increase initially. Subsequently, the rate of hydrogenation of linoleic acid decreases, and hence the overall rate of hydrogenation decreases. However, if the individual rate of hydrogenation of linoleic acid becomes greater than that of oleic acid, then the overall hydrogenation rate also increases. This gives rise to a local minimum, as shown in Figure 5. However, any subsequent decrease in individual rates of fatty acid hydrogenation will result in a local maximum. This, in part, explains the oscillatory nature of hydrogenation rate vs. time plot. In the case of soybean oil, this oscillatory nature is not apparent due to the high amounts of linolenic acid, which dampen the oscillatory nature until late in the reaction.

The good agreement between the experimental data and the predicted values justifies the use of the model for further inferences about the reactions. The rate constants exhibit an Arrhenius relationship to the temperature according to the equation

$$\ln k = \ln k_0 - \frac{E}{RT} \qquad [20]$$

The temperature dependence of the rate constants was evaluated for soybean oil at 50, 65, and 80°C. The plot of ln k vs. 1/T, as shown in Figure 6, yielded a straight line for all three rate constants. Based on the regression line for each of these rate constants, the activation energy E was 44.88, 51.97, and 5.12 kJ/mol for linolenic, linoleic, and oleic acids, respectively. The frequency factor k_o was calculated as

1509.00, 5567.48, and $3.84 \cdot 10^{-6}$ mol%$^{-1}$ min^{-1} for linolenic, linoleic, and oleic acids, respectively.

ACKNOWLEDGMENTS

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