Kinetics of Catalytic Transfer Hydrogenation of Soybean Oil

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The catalytic transfer hydrogenation of soybean oil was studied by using various concentrations of sodium formate solutions, an emulsifier and paladium on a carbon catalyst. Sodium formate concentration and addition of the emulsifier significantly affect the reaction rate because of their influence on the liquid/liquid interface. Under conditions in which diffusion effects are eliminated, all reactions carried out in diluted sodium formate solution obey first-order kinetics with respect to fatty acids. This allows control over the hydrogenation process of soybean oil, needed to obtain partially hydrogenated oil containing about 1% linolenic acid and a relatively high level of linoleic acid with no increase in the stearic acid concentration.

KEY WORDS: Catalytic transfer hydrogenation, kinetics, soybean oil.

The hydrogenation of edible oils, containing high contents of polyunsaturated fatty acids (FAs), is carried out to produce more oxidatively stable products, namely partially hydrogenated oils, semi-solid or solid fats. The present paper is concerned with a novel, alternative hydrogenation process called catalytic transfer hydrogenation (CTH). The generalized equation (1,2):

$$DH_x + nA \xrightarrow[\text{solvent}]{\text{catalyst}} D + nAH_x \qquad [1]$$

in which A is the acceptor and D is the hydrogen donor, represents this process. CTH uses the molecules of hydrogen donors as a source of hydrogen instead of molecular hydrogen. Hydrogenation with molecular hydrogen is carried out at a high hydrogen gas pressure, up to 10 Atm, and at a high temperature, typically 150–225°C, in the presence of an Ni catalyst (3). The CTH process works at a relatively low temperature, typically 50–80°C, and atmospheric pressure, in the presence of palladium on carbon catalyst (4,5). Therefore, the pressure vessel, gas containment and work precautionary measures can be eliminated and replaced with a simple vessel with appropriate stirring. CTH of oil takes place in organic solvents or in aqueous medium that contains a dissolved hydrogen donor. In industrial applications, it is preferable to work in water solutions of donors because the unreacted donors and the resulting salt after work-up remain in the aqueous phase. In addition, special purification processes are needed when an organic solvent is used, where the solvent and the donor have to be removed from the product by special chemical and separation processes.

Bailey (6) was the first to demonstrate a chemical model that could be used to measure the relative reaction rate constants for each hydrogenation step of conventional (gaseous) hydrogenation. That model does not indicate either positional or geometrical isomers that are always formed during hydrogenation. The model that represents all possible reactions is highly complicated. Later, Albright and Wisniak (7), who used a more complicated reaction scheme, found that the reactivities of geometrical isomers are comparable at hydrogenation conditions similar to those used commercially. However, several reasonable approximations can be made, and a simplified Bailey's set of reactions, based on the assumption of first-order and irreversible reactions, is in satisfactory agreement with experimental data at various operating conditions. This was verified by Albright (8) and Okkerse *et al.* (9). As we demonstrated earlier (5), this set of reactions is also ideal for describing CTH and for the calculation of CTH selectivity:

$$\mathrm{Le} \xrightarrow{k_{Le}} \mathrm{L} \xrightarrow{k_L} \mathrm{Ol} \xrightarrow{k_{Ol}} \mathrm{S} \qquad [2]$$

where k_{Le}, k_L and k_{Ol} are rate constants of linolenic, linoleic and oleic acid, respectively, and S is stearic acid. It is believed that the sodium formate concentration determines the activity of both the formate and the water. Water also participates stoichiometrically in the reaction (10):

$$HCOO^- + H_2O + A \xrightarrow{\text{catalyst}} HCO_3^- + H_2A \qquad [3]$$

In our previous work (5), in which the basic kinetics of oil hydrogenation was studied, the effect of donor concentration was eliminated because the reaction was carried out with a 6.4 M sodium formate solution at an oil-to-water ratio of 1:2. At this concentration, the amount of donor was 15-fold in excess, based on the amount of desired product, which is an oil with less than 1% Le acid. By a careful selection of the emulsion stabilizer and by intensive stirring, the mass transfer resistance was eliminated. At such conditions, all considered hydrogenation reactions obey first-order kinetics. Thus, the pre-exponetial factors and activation energies were easily derived from the experimental data.

In the present paper, the kinetics of CTH of soybean oil in a diluted aqueous sodium formate solution in the presence of an emulsifier are considered.

EXPERIMENTAL PROCEDURES

Materials. The commercially refined soybean oil, supplied by Helios-Domzale (Domzale, Slovenia), was used for hydrogenation. The hydrogen donor (sodium formate) was purchased from Merck (Darmstadt, Germany), the catalyst, 10% Pd-on carbon was from Fluka (Buchs, Switzerland), and the emulsifier Mayodan BS from Grindsted Products (Denmark). All chemicals were of the highest purity available.

Hydrogenation procedures. All reactions were conducted in a 250-mL round-bottom test flask, equipped with a mechanical stirrer with a 3-cm round-shaped Teflon blade. The flask was immersed in a thermostated water bath. The range of operating conditions is shown in Table 1. The hydrogenation progress was monitored by analyzing the FA composition periodically by gas chromatography (GC).

Methods of chemical analysis. The FA were analyzed as fatty acid methyl esters (FAME) prepared by the International Union of Pure and Applied Chemists method II.D.19 (11), by GC (Varian 3400; Varian Associates, Palo Alto, CA), equipped with an all-glass splitter system and a flame-ionization detector, on a SP-2300 fused-silica

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TABLE 1

Fatty Acid Composition of Soybean Oil and Operating Conditions

Fatty acid composition (%)	
C16:0	11.5
C18:0	4.0
C18:1	24.0
C18:2	53.2
C18:3	7.4
Soybean oil (g)	30
Water (g)	30
Donor (HCOONa) (g)	5.7-17
Catalyst (10% Pd/C) (mg)	300-600
Emulsifier (Mayodan BS) (mg)[a]	120
Temperature (°C)	50-80
Agitation (rpm)	650

[a]Mayodan BS from Grindsted Products (Denmark).

capillary column, 30 m × 0.25 mm i.d., 0.20 μm film thickness. The GC was operated at 170–210°C, with a heating rate of 4°C/min and a helium carrier gas flow rate of 1.2 mL/min.

Determination of the liquid/liquid interface. The kinetic results largely depend on the liquid/liquid interface as an important parameter. The surface of the dispersed phase droplets was calculated by multiplying the average number of droplets per unit volume of the dispersion with the average surface of a droplet. The average surface of a droplet was calculated by using the average diameter of emulsion droplets. The average diameter was determined with a microscope (Laboral:Carl Zeiss, Jena, Germany) in appropriate small volumes of emulsion, by dividing the sum of diameters of all droplets present by their number. The average number of dispersed-phase droplets was calculated from a known volume of dispersed phase on the basis of the average volume of one droplet, which was calculated from the average diameter.

RESULTS AND DISCUSSION

To optimize the CTH procedure, the effect of several chemical and physical parameters on the reaction rate was examined. CTH with a donor in aqueous medium proceeds in a complex three-phase system (oil-water-solid catalyst). Several authors (10,12,13) suggested that the reaction proceeded *via* competitive adsorption of water and formate to identical active sites on the catalyst surface. An excess of either of the donors would result in blocking the access of the other. They concluded this fact to be rate-controlling for the overall reaction. They determined the 10 M solution of potassium formate to be the most efficient concentration for the hydrogenation of FAME. At this concentration, the solution contains 3 mol H_2O/mol KOOCH. We had previously carried out the reaction in 6.4 M sodium formate (5). This was an almost saturated solution (the water/formate ratio was 6.7), but it is not close to the optimum ratio suggested by Arkad *et al.* (10) for FAME for potassium formate solution. Two concentrations were used, 17 g/30 mL H_2O and, for practical reasons, a more dilute sodium formate solution (5.7 g/30 mL H_2O), to determine the effect of donor concentration on the reaction rate. It was also noticed that the addition of a stabilizing agent, Mayodan M-612, significantly increased the reaction rate in comparison with the experiments where no stabilizer was used. This prompted an additional study on the effect of emulsifier on the reaction rate at different concentrations of the sodium formate solution.

Effect of the emulsifier. The emulsifier Mayodan BS was used to study the effect on the reaction rate of CTH in an aqueous medium. The addition of 120 mg Mayodan BS to the reaction mixtures, where all other conditions are the same, significantly increases the reaction rate constant for the overall reaction, $d(IV)/dt = -k_{IV}\,(IV)$, from 0.86×10^{-3} to 1.98×10^{-3} min^{-1} where IV is iodine value. The effect is shown in Figure 1. Surfactants, particularly emulsifiers, markedly lower the interfacial tension between the two phases. This has an influence on droplets of both liquids; they become smaller and, therefore, their numbers and their surface areas significantly increase. As indicated previously, hydrogenation takes place only after effective contact of three reactants—donors (sodium formate and water) and fats (unsaturated fatty acid chain) with the active portion of catalyst—is established. The catalyst floats exclusively in the bulk of the oil phase, which is also the acceptor. The catalyst is effective only on the surface of the oil phase (in the case of water-in-oil emulsion, on the surface of the oil droplets), where it can get in contact with the water and sodium formate. The increase of the liquid/liquid interface also increases the amount of the catalyst available for such contact. It is already known that the hydrogenation rate increases proportionally to the amount of catalyst. Consequently, the addition of an emulsifier directly influences the reaction rate by increasing the interfacial surface and the concentration of the catalyst exposed.

Effect of the sodium formate concentration (in the absence of an emulsifier). The effect of the donor on CTH in a water medium without an emulsifier was studied at two different sodium formate concentrations, 5.7 g/30 mL H_2O and 17 g/30 mL H_2O. A decrease in the donor concentration from 17 g/30 mL H_2O to 5.7 g/30 mL H_2O

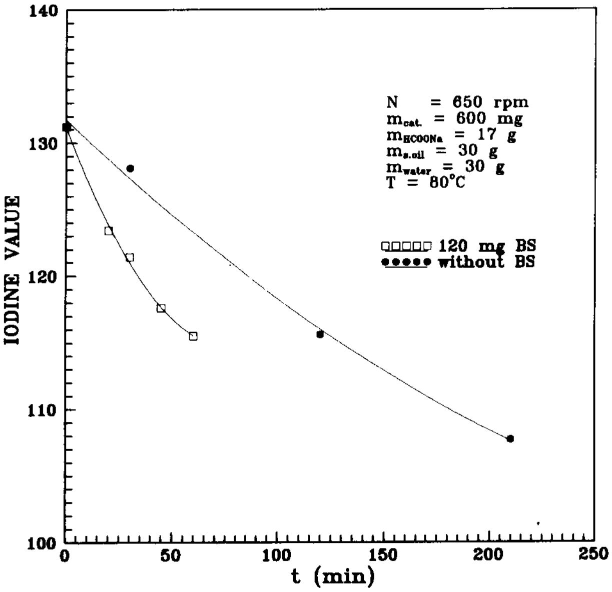

FIG. 1. Effect of emulsifier Mayodan BS (Grindsted Products, Denmark) on the hydrogenation of soybean oil. Abbreivations: Cat., catalyst; s. oil, soybean oil; N, stirrer speed (min^{-1}); m, mass (g); T, temperature; t, time.

caused a substantial slow down of the reaction rate, as shown in Figure 2, with a resulting decrease of the rate constant from 0.86×10^{-3} min^{-1} to 0.20×10^{-3} min^{-1}. We noticed a great difference in the liquid/liquid surface between these two experiments. It seems that in the presence of a catalyst, the donor acts as an electrolyte in the manner of lowering the interfacial tension, as indicated by the increase of the reaction rate.

Effect of the donor concentration in the presence of an emulsifier. In all experiments, 120 mg of the emulsifier Mayodan BS was used to study the effect of donor concentration on the reaction rate in the presence of an emulsifier. A decrease in the concentration of donor from 17 g/30 mL H_2O to 11.3 g/30 mL H_2O and 5.7 g/30 mL H_2O resulted in a rate constant increase from 1.98×10^{-3} to 2.9×10^{-3} and 5×10^{-3} min^{-1}, respectively. The explanation for this result must be the solubility of the emulsifier. The water-soluble emulsifier BS is poorly soluble in an almost saturated donor solution and therefore not very effective, but in a dilute donor solution it is almost completely soluble and therefore very effective in producing a more stable emulsion. That means an increase in liquid/liquid surface area and, consequently, an expected increase in the reaction rate. As shown in Figure 3, these experiments exhibt a linear relationship between the droplet surface area and the rate constant.

Kinetics of CTH in a diluted (5.7 g/30 mL H_2O) aqueous sodium formate solution. Soybean oil contains triacylglycerols of saturated FAs, palmitic and stearic and unsaturated FAs, Ol, L and Le. During hydrogenation, unsaturated FAs are gradually converted to the saturated state.

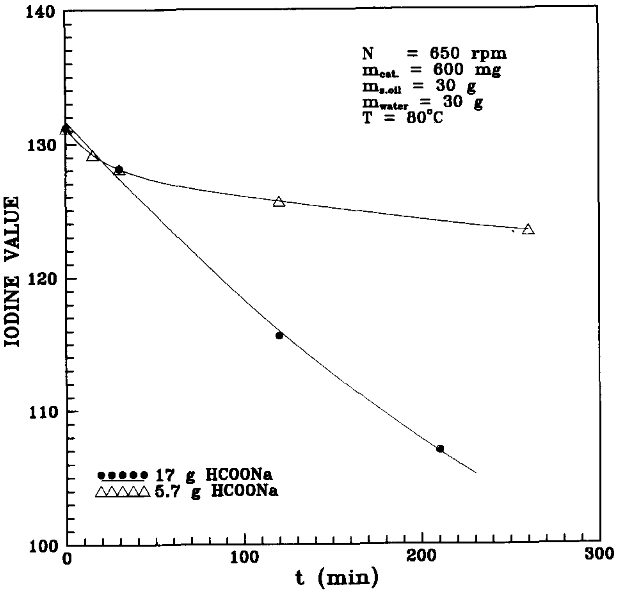

FIG. 2. Effect of donor concentration in the absence of emulsifier on the hydrogenation rate of soybean oil. See Figure 1 for abbreviations.

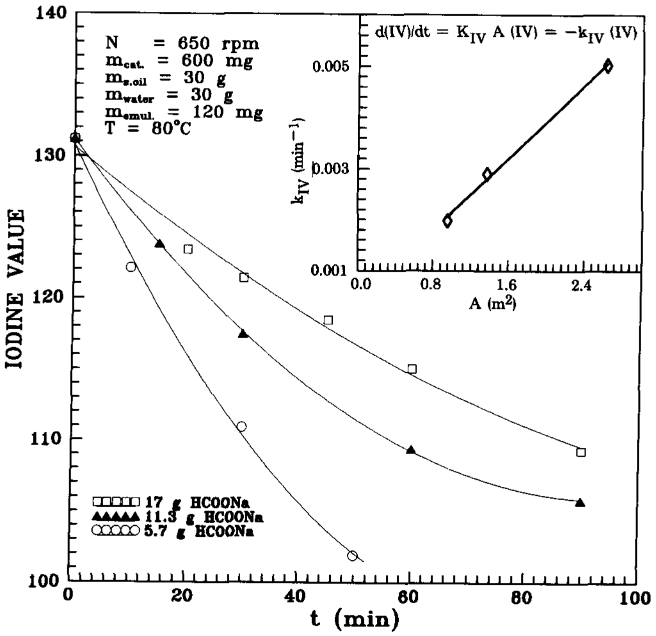

FIG. 3. Effect of donor concentration in the presence of emulsifier (emul) on the hydrogenation rate of soybean oil. A, droplet surface, area (m^2); k_{IV}; iodine value rate constant (min^{-1}). See Figure 1 for other abbreviations.

As discussed earlier (5), Bailey's simplified model represents the experimental data reasonably well for the batch CTH of soybean oil in an almost saturated alkali formate solution. The same behavior was found for CTH in a diluted alkali formate solution (5.7 g/30 mL H_2O), in which the donor is still in great excess (about 3-fold) in relation to the desired product. In this model it is assumed that the consecutive reactions are irreversible and follow first-order kinetics. Any isomers of Le and L formed during the hydrogenation were assumed to be as reactive as the original L or Le. Adequate kinetic equations for the above model are:

$$\frac{dC_{Le}}{dt} = -k_{Le}C_{Le} \qquad [4]$$

$$\frac{dC_L}{dt} = -k_LC_L + k_{Le}C_{Le} \qquad [5]$$

$$\frac{dC_{Ol}}{dt} = -k_{Ol}C_{Ol} + k_LC_L \qquad [6]$$

$$C_{Le} = C_{Leo}e^{-k_{Le}t} \qquad [7]$$

$$C_L = C_{Lo}\left(\frac{k_{Le}}{k_L - k_{Le}}\right) \cdot (e^{-k_{Le}t} - e^{-k_Lt}) + C_{Lo}e^{-k_Lt} \qquad [8]$$

$$\begin{aligned} C_{Ol} = {} & C_{Leo}\left(\frac{k_{Le}}{k_L - k_{Le}}\right) \cdot \left(\frac{k_L}{k_{Ol} - k_{Le}}\right) \cdot \left(e^{-k_{Le}t}\, e^{-k_{Ol}t}\right) - \\ & -C_{Leo}\left(\frac{k_{Le}}{k_L - k_{Le}}\right) \cdot \left(\frac{k_L}{k_{Ol} - k_L}\right) \cdot (e^{-k_Lt} - e^{-k_{Ol}t}) + \\ & +C_{Lo}\left(\frac{k_L}{k_{Ol} - k_L}\right) \cdot (e^{-k_Lt} - e^{-k_{Ol}t}) + C_{Ol}e^{-k_{Ol}t} \end{aligned} \qquad [9]$$

where C_{Le}, C_L and C_{Ol} are the concentration of Le, L and Ol, C_{Leo}, C_{Lo} and C_{Olo} are the initial concentrations, and k_{Le}, k_L and k_{Ol} are the rate constants for the appropriate fatty acids.

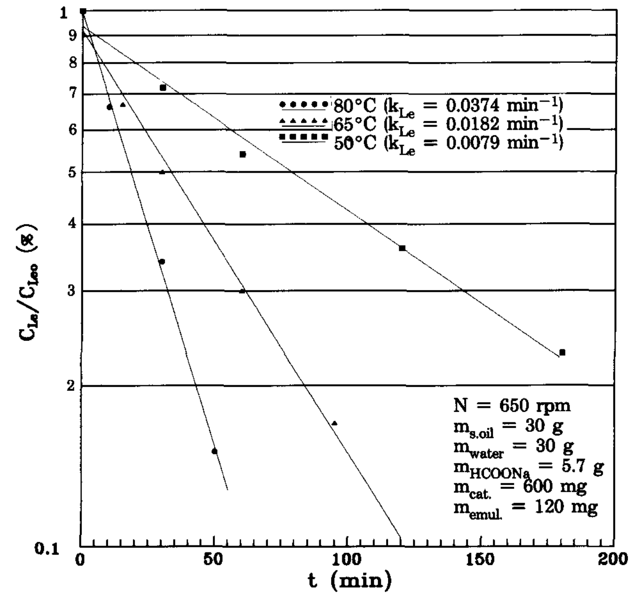

FIG. 4. Hydrogenation of linolenic (Le) acid. Comparison of the experimental data with predictions from the first-order kinetics model (Equation 7). C_{Le}, concentration of linolenic acid; C_{Leo}, initial concentration of linolenic acid; k_{Le}, rate constant of linolenic acid. See Figures 1 and 3 for other abbreviations.

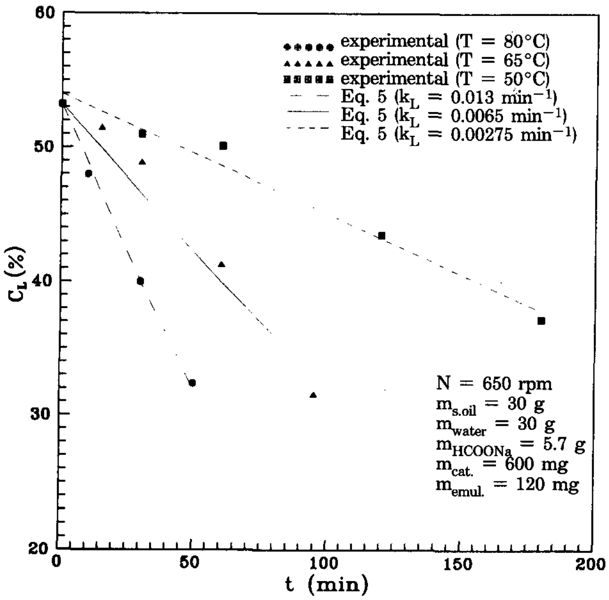

FIG. 5. Time course of the linoleic acid concentration. Comparison of the experimental data with prediction according to Equation 8. L, linoleic; C_L, concentration of linoleic acid; k_L, rate constant of linoleic acid. See Figures 1 and 3 for other abbreviations.

The good agreement between the experimental data and Equations 7, 8 and 9 at moderate temperatures (50–80°C) justifies the use of this set of equations for further calculations of the rate constants for appropriate FAs at given operating conditions (Figs. 4–6). Considerable disagreement between the predicted and observed time course of the oleic concentration at 65 and at 80°C can be attributed to the scattering of the experimental data that formed the basis for the kinetic analysis by the bisection method.

The rate constants exhibit an Arrhenius relationship to temperature according to the equation $\ln k = \ln k_o - E/RT$, which was used to obtain the value of appropriate constants, the pre-exponential factor k_o and the activation energy E (Figs. 7–9).

The apparent reaction rate constants are much higher for the reaction carried out in a diluted sodium formate solution with the emulsifier Mayodan BS in comparison to the reactions where an almost saturated solution was used. However, the activation energies for appropriate FAs are almost equal, indicating that the exposed catalyst is very important for the reaction rate.

CONCLUSIONS

The CTH of soybean oil follows pseudo first-order kinetics with respect to the oil compounds in a diluted sodium formate solution. The same behavior was established earlier (5) for an almost saturated sodium formate solution. Therefore, at the conditions in which diffusional effects were eliminated by intensive stirring and/or by adding emulsifier, satisfactory agreement was achieved between experimental data at various operating conditions and the data calculated by pseudo first-order kinetic equations of a simplified Bailey's model.

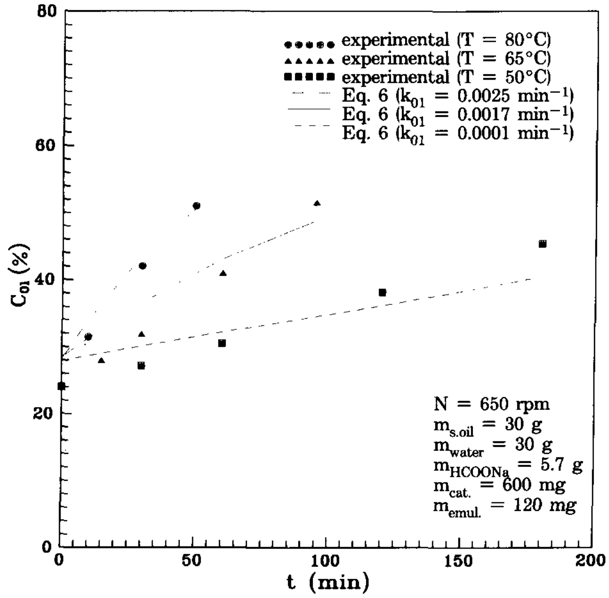

FIG. 6. Time course of the oleic acid concentration. Comparison of the experimental data with prediction according to Equation 9. Ol, oleic; k_{Ol}, rate constant of oleic acid; C_{Ol}, concentration of oleic acid. See Figures 1 and 3 for other abbreviations.

The effect of donor concentration on the reaction rate was examined at conditions where no emulsifier was used. A drastic reduction of the reaction rate was observed as the concentration of donor was decreased from 17 g/30 mL to 5.7 g/30 mL H_2O.

The effect of donor concentration was also examined in the presence of the emulsifier Mayodan BS by lowering the concentration of donor over the range from 17 g/30 mL to 5.7 g/30 mL H_2O. A systematic increase of the

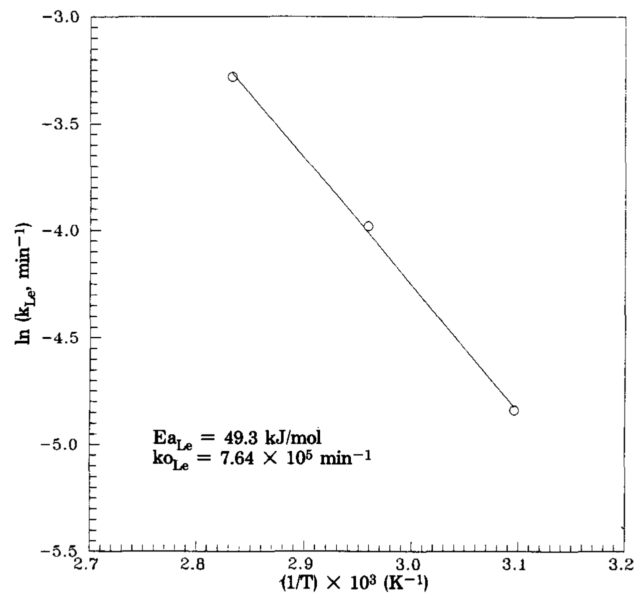

FIG. 7. Temperature dependence of the reaction rate constant for the hydrogenation of linolenic (Le) acid. Other abbreviations: ko_{Le}, pre-exponential factor of linolenic acid; k_{Le}, rate constant of linolenic acid; k_{Le}, rate constant of linolenic acid; Ea_{Le}, activation energy of linolenic acid.

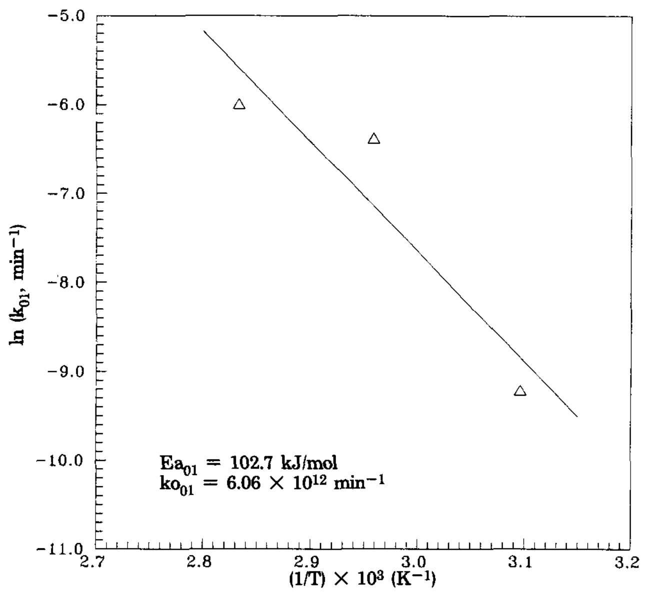

FIG. 9. Temperature dependence of the reaction rate constant for the hydrogenation of (OL) oleic acid. Other abbreviations: k_{OL}, rate constant of oleic acid; Ea_{Ol}, activation energy of oleic acid; ko_{Ol}, pre-exponential factor of oleic acid.

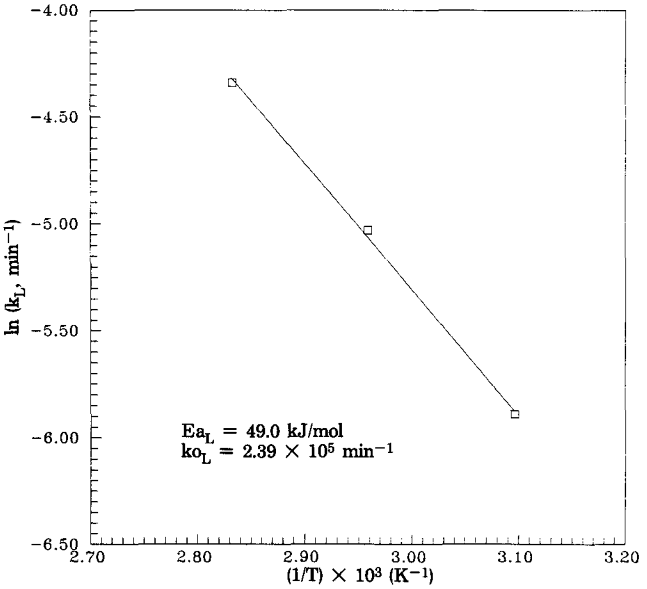

FIG. 8. Temperature dependence of the reaction rate constant for the hydrogenation of linoleic (L) acid. Other abbreviations: k_L, rate constant of linoleic acid; Ea_L, activation energy of linoleic acid; Ko_L, prelinoleic acid.

reaction rate was observed. The explanation of such behavior was found in the increased solubility of the emulsifier in the water phase, leading to an increase of the liquid/liquid interface at which the hydrogenation takes place. A linear relationship between the measured surface and the apparent reaction rate constants was observed. The calculated activation energies suggest that the liquid/liquid surface is one of the major rate-controlling factors for the overall reaction.

Kinetic studies and Arrhenius plot parameters can be a source of valuable information about the course of the reaction. With an appropriate choice of experimental conditions (hydrogenation temperature, agitation rate, oil/water ratio, concentration of sodium formate solution, amount of catalyst and amount of emulsifier), an appropriate selectivity for the desired oil modification can be achieved. These kinetic studies allow the preparation of various hydrogenated oils with low concentrations of linolenic acid (about 1%) at an acceptable level of L acid and with no increase in the S acid concentration.

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