Kinetics of the Hydrogenation of Fatty Oils

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ABSTRACT

Hydrogenation results for fatty oils were analyzed by using a nonlinear least squares method. The rate of the hydrogenation for diunsaturated fatty groups to monounsaturated groups and the rate of the geometrical isomerizations between monounsaturated groups were found to be half order with respect to hydrogen concentration, whereas the hydrogenation rate of monounsaturated groups was the first order. A detailed reaction mechanism is presented to explain the kinetic behavior.

INTRODUCTION

Partial hydrogenation processes of fatty oils are important in the production of oleomargarine stock, shortening, soap stock and industrial greases and oils. Fatty oils are mixtures of triglycerides consisting of mono- and polyunsaturated fatty acids as well as saturated ones. One of the purposes of the partial hydrogenation of fatty oils is to obtain selectively monounsaturated fatty acid groups.

The reaction mechanism of the hydrogenation of triglyceride oils has been recognized to be highly complicated because of the occurrence of several side reactions. The most important side reactions from a practical point of view are *cis-trans* geometrical isomerization and positional isomerization which comprises the migration of the double bonds along the fatty acid chain.

Hydrogenation processes of fatty oils belong to typical heterogeneous gas-liquid reactions catalyzed by solids in which several mass transfer steps are involved. These steps affect both the rate and selectivity of hydrogenation. Therefore, in order to get reliable information on the kinetics, we have to select the data in which the mass transfer effects are essentially eliminated.

The purpose of this paper is to present a kinetic model and a reaction mechanism for the hydrogenation of triglyceride oils using the data which have been published by Eldib and Albright (7) and by Wisniak and Albright (13). A reaction scheme and the rate constants are determined by a nonlinear least squares method which was found to be efficient in identification problems (6,8).

The effect of mass transfer on the selectivity in the hydrogenation is discussed in another paper (9).

PREVIOUS WORK

Experimental Results

Eldib and Albright (7) used a semi-batch reactor for the hydrogenation of cottonseed oil at relatively low pressures (20 to 140 psig), and examined the effects of operating variables of temperature, pressure, nickel catalyst concentration and agitation in the course of the reaction. Wisniak and Albright (3, 13) extended the range of conditions investigated to high pressures (300 to 1500 psig) in order to clarify the reaction mechanism. In these investigations, mass transfer resistances seem to be negligible in most of the runs at high rate of agitation. Therefore, it may be reasonable to use their experimental data to establish the reaction mechanism.

In the dissertation of Wisniak (12), the experimental data were tabulated and included the relationship between the compositions of liquid components and reaction time. The results of Eldib and Albright (7) for the low pressures were shown only in the forms of logarithm of iodine values against time and concentration of linoleic acid groups and *trans*-oleic acid groups versus iodine value. These data were converted to the form of mole fraction vs. time by standard procedures (1).

Induction Period

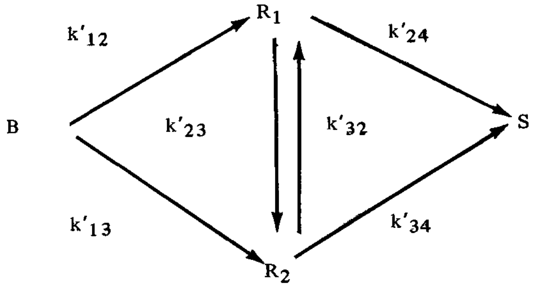
The reaction was followed by plotting the logarithm of the iodine values against reaction time. These plots showed essentially straight lines after a certain period of time. The induction period, t_{ind}, is defined at the time at which the extrapolated straight line coincide with the initial iodine value.

Solubility of Hydrogen in Oil

Hydrogen solubilities in cottonseed oil expressed as ml of hydrogen at STP/g of oil were measured in the range from 125 to 283 F and 150 to 1500 psig (13). We converted these data to the concentration of hydrogen in the oil phase taking 0.91 g/ml as densities of the two fatty oils.

A KINETIC MODEL FOR HYDROGENATION OF FATTY OILS

Several attempts have been made to treat the catalytic hydrogenation of triglyceride oils kinetically. The following kinetic model was found to be applicable for the hydrogenation of cottonseed oils, using first-order rate equations with respect to the compositions of the various liquid components in the liquid phase.



[1]

B, R_1, R_2 and S represent diunsaturated, *cis*-monounsaturated, *trans*-monounsaturated and saturated fatty acid groups, respectively. The (k′)'s are the respective pseudo-first-order reaction rate constants in which the effect of hydrogen pressure are included. In the above model, all positional isomerizations and geometrical isomerization steps are not taken into account because of their complexities.

The following kinetic equations are derived:

$$
\begin{aligned}
\frac{df_B}{d\theta} &= -(k'_{12} + k'_{13})f_B \\
\frac{df_{R_1}}{d\theta} &= k'_{12}f_B - k'_{23}f_{R_1} + k'_{32}f_{R_2} - k'_{24}f_{R_1} \\
\frac{df_{R_2}}{d\theta} &= k'_{13}f_B + k'_{23}f_{R_1} - k'_{32}f_{R_2} - k'_{34}f_{R_2} \\
\frac{df_S}{d\theta} &= k'_{24}f_{R_1} + k'_{34}f_{R_2}
\end{aligned}
\qquad [2]
$$

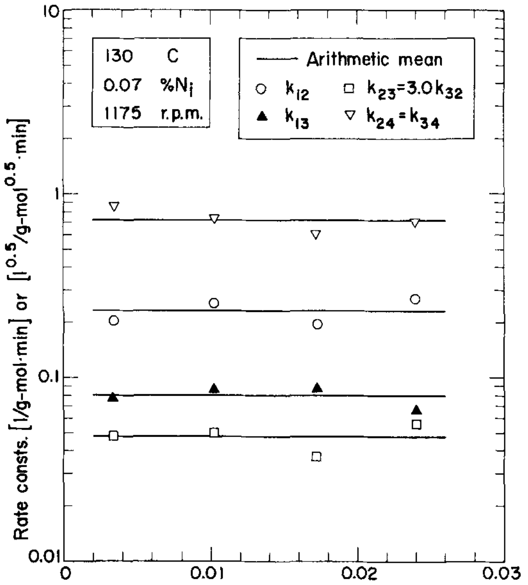


FIG. 1. Check of independence of hydrogen concentration on rate constants for low pressure data (7).

As the total number of moles of liquid components is held constant, the above equations were expressed in terms of mole fractions instead of concentrations. In $\theta=(t-t_{ind})$, the pseudo reaction time, t is the real time of reaction and t_{ind} is the induction period, which has already been defined.

Limitations Among Rate Constants

The number of parameters to be determined is six. Preliminary nonlinear estimations indicated that the correlations among the parameters were high and some parameters converged to negative values. Hence, reasonable limitations among the parameters seem to be necessary.

Various investigators reported that the equilibrium ratio of the *trans/cis* of monounsaturated fatty acid groups varies from 2 to 4 (2). The ratio of the two rate constants for the reversible isomerization, k'_{23}/k'_{32} then also varies from 2 to 4. The choice of the ratio of the rate constants within the above mentioned range was found to give negligible effects upon the estimation; thus the ratio 3, which is based on the recent results of Litchfield et al. (10), was selected. As hydrogenation progresses, the *trans/cis* ratio approaches the thermodynamic ratio and in some cases the ratio is maintained for the last portion of the reaction (3). This fact suggests that the rates of hydrogenation for the *cis-* and *trans*-monounsaturated fatty acid groups are almost equal. This relationship was also approximately confirmed by the preliminary nonlinear estimation. Consequently, the following two simplifications for the rate constants are assumed in the subsequent analysis:

$$k'_{32} = k'_{23}/3.0 \qquad [3]$$
$$k'_{24} = k'_{34}$$

Thus the number of parameters to be evaluated is decreased from 6 to 4.

Evaluation of Rate Constants by Nonlinear Least Squares Method

There are two effective methods of estimating parameters when the experimental data are represented by a set of ordinary linear differential equations such as Equation 2. The first method consists of analytical integration of them and subsequent application of iterative nonlinear least squares regression techniques. The second method comprises the numerical integration using postulated parameters, followed by iterative nonlinear least squares method. Since the analytical integration of Equation 2 is tedious and the resulting equations are expected to become complicated, the second method was adopted in the present case.

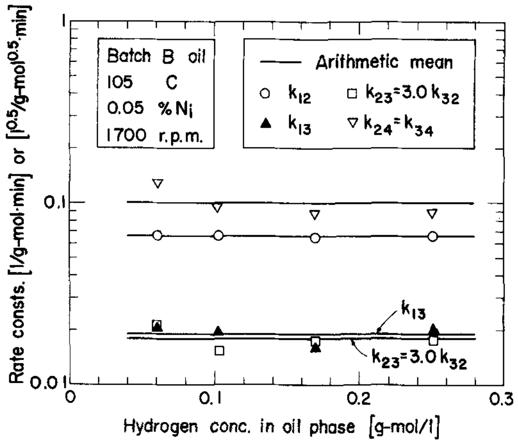


FIG. 2. Check of independence of hydrogen concentration on rate constants for high pressure data (12,13).

The computer program used is essentially the same as that in the previous paper (8). It consists of the following two major parts: the numerical integration using the Runge-Kutta-Gill method and the nonlinear least squares method developed by Marquardt (11) to minimize the sum of squares of residuals Φ, which is defined as

$$\Phi = \sum_{i=1}^{N} \left\{(\overset{o}{f}_{Bi} - f_{Bi})^2 + (\overset{o}{f}_{R1i} - f_{R1i})^2 + (\overset{o}{f}_{R2i} - f_{R2i})^2 + (\overset{o}{f}_{Si} - f_{Si})^2\right\} \qquad [4]$$

where the $\overset{o}{f}_i$'s are the respective mole franctions measured at the pseudo reaction time θ_i, the f_i's are the computed values corresponding to the $\overset{o}{f}_i$'s.

RESULTS OF ANALYSIS

Dependence of Hydrogen Concentration on Reaction Rates

The low pressure data shown in Figure 7 of the reference (7) were first analyzed and then the high pressure experimental results corresponding to Figure 5 and 6 of the paper (13) were examined. The estimated pseudo-first order rate constants for each pressure level were plotted against the concentration of dissolved hydrogen in the oil phase to find the influence of pressure on the reaction rates. The following dependences were found:

$$k'_{12} = k_{12}\sqrt{[H_2]}$$
$$k'_{13} = k_{13}\sqrt{[H_2]}$$
$$k'_{23} = k_{23}\sqrt{[H_2]}$$
$$k'_{32} = (k_{23}/3.0)\sqrt{[H_2]} \qquad [5]$$
$$k'_{24} = k_{24}\,[H_2]$$
$$k'_{34} = k_{24}\,[H_2]$$

where $[H_2]$ represents the concentration of hydrogen in the oil phase which is essentially equal to that at catalyst surface when the steps of chemical reactions are assumed to

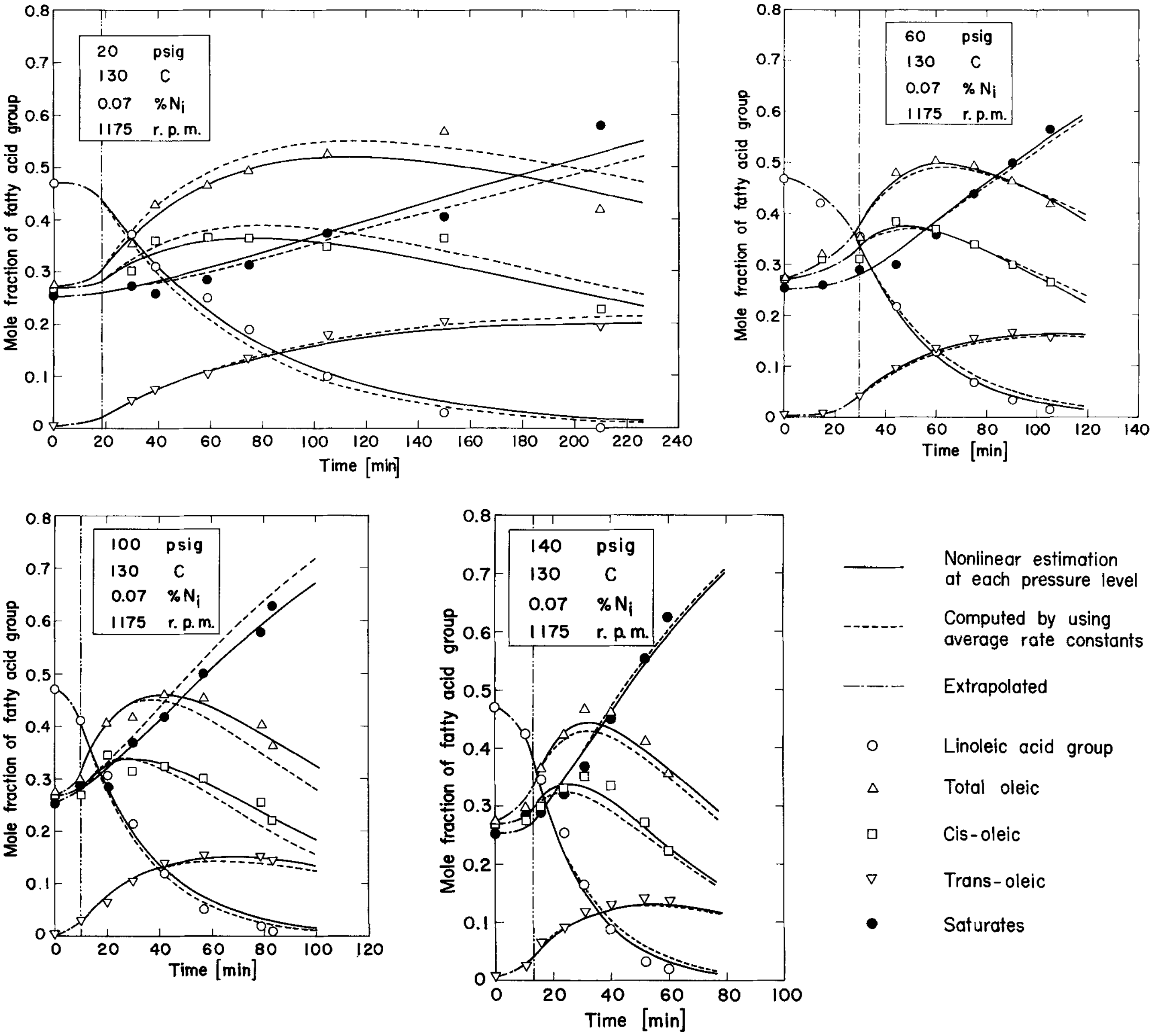


FIG. 3 a,b,c,d and e. Comparison of computed curves with low pressure experimental data (7).

be rate controlling.

Substituting Equation 5 into 2 and again applying the nonlinear least squares method, we obtained more precise values of the rate constants, k_{ij} instead of k'_{ij}. These values are plotted in Figure 1 for low pressure and in Figure 2 for high pressure experiments as a function of hydrogen concentration $[H_2]$. The rate constants are found to be substantially independent of hydrogen concentration. Therefore dependences of hydrogen concentration on the pseudo-rate constants were found to be well described by Equation 5. Comparison of Figures 1 and 2 shows that the magnitude of corresponding rate constant for low pressure experiments is generally higher than that for high pressure. These differences may be due to the fact that both of the reaction temperature and catalyst concentration for low pressure experiments were higher than those for high pressure experiments.

Comparison of Calculated With Experimental Results

The experimental data points and calculated curves are shown in Figures 3 and 4. The solid curves denote the computed results with the rate constants obtained at each pressure level using the nonlinear least squares method, while the dotted curves are calculated by use of the arithmetic mean values of the rate constants estimated at various pressure levels. The agreement of the experimental data points with the solid curves is relatively good for both series of experiments.

REACTION MECHANISM

A more detailed reaction mechanism is developed for hydrogenation and isomerization to explain the above kinetic behavior. The appearance of the hydrogen concentration as a square root probably indicates that hydrogen atoms formed by the dissociation of hydrogen molecules on the catalyst surface play an important part in the reaction. Allen and Kiess (4,5) have presented an interesting mechanism for both geometrical and positional isomerizations during hydrogenation of triglyceride oils. Their basic concept is that a single activated hydrogen atom attacks the double bond to yield an unstable partially unsaturated complex. If the concentration of hydrogen atom is high on the catalyst surface, the complex will probably react with another hydrogen atom to complete the saturation of the

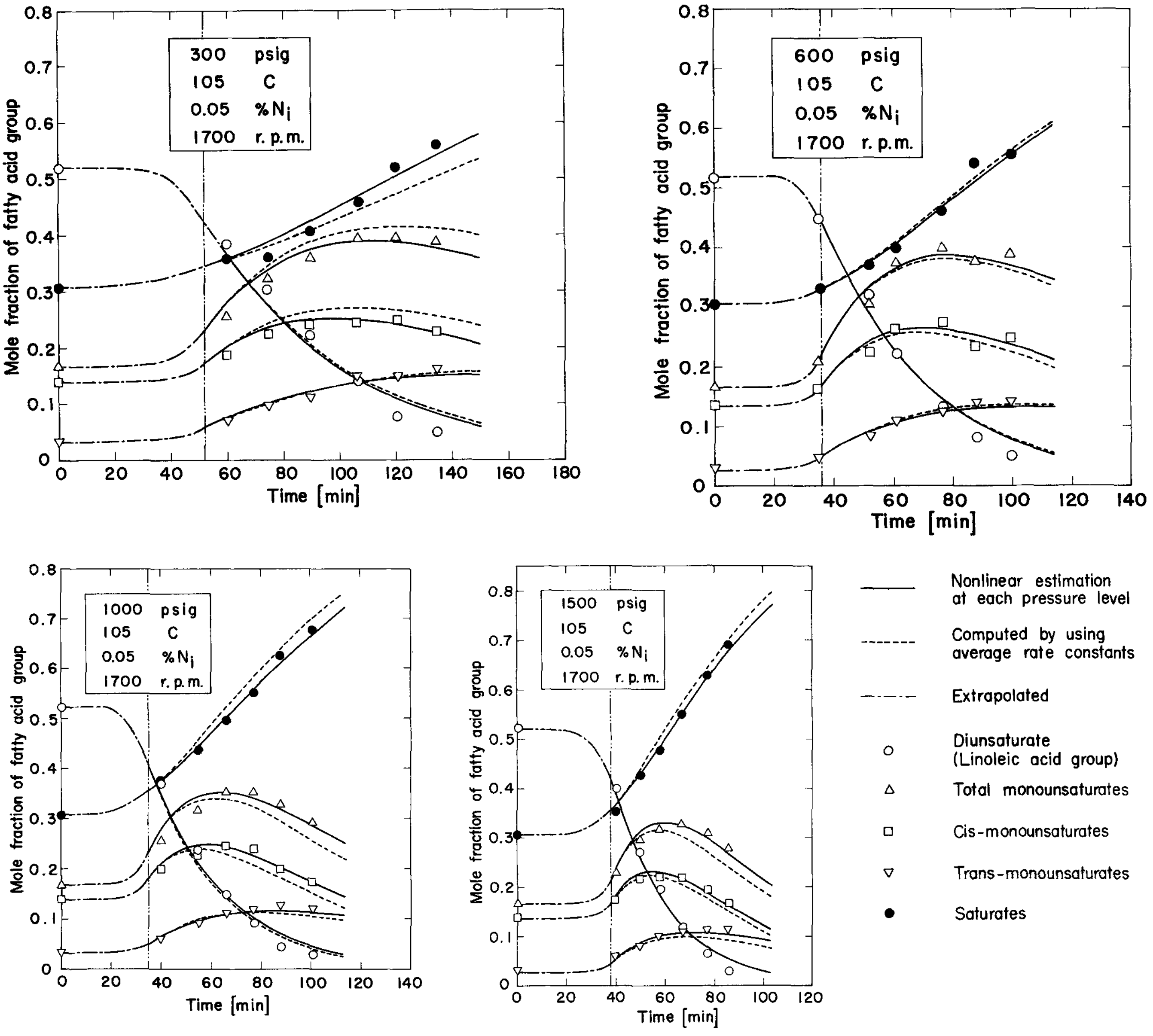


FIG. 4 a,b,c,d and e. Comparison of computed curves with high pressure experimental data (12,13).

double bond and thus the hydrogenation occurs. On the other hand, in the case of low concentration of a hydrogen atom, the complex will decompose to reform a double bond. However this double bond may be in the original position or in the adjacent position because either of the hydrogen atoms adjacent to the free radical center may be removed. Since the complex may obtain free rotation, the subsequent removal of a hydrogen atom results in the production of the double bond in either the *cis* or the *trans* forms. In this way both the positional and geometrical isomerizations occur simultaneously.

The following reaction mechanism is proposed on the basis of the original concept of Allen and Kiess:

$$H_2+2\sigma \underset{k_{-A}}{\overset{k_A}{\Leftrightarrow}} 2H\sigma$$

$$B+\sigma \underset{k_{-B}}{\overset{k_B}{\Leftrightarrow}} B\sigma$$

$$B\sigma+H\sigma \underset{k_{-0}}{\overset{k_0}{\Leftrightarrow}} BH\sigma+\sigma \qquad [6]$$

$$BH\sigma+H\sigma \xrightarrow{k_1} R_1\sigma+\sigma \underset{k_{R_1}}{\overset{k_{-R_1}}{\Leftrightarrow}} R_1+2\sigma$$

$$BH\sigma+H\sigma \xrightarrow{k_2} R_2\sigma+\sigma \underset{k_{R_2}}{\overset{k_{-R_2}}{\Leftrightarrow}} R_2+2\sigma$$

$$R_1\sigma+H\sigma \underset{k_{-3}}{\overset{k_3}{\Leftrightarrow}} RH\sigma+\sigma$$

$$R_2\sigma+H\sigma \underset{k_{-4}}{\overset{k_4}{\Leftrightarrow}} RH\sigma+\sigma$$

$$RH\sigma+H\sigma \xrightarrow{k_5} S\sigma+\sigma \underset{k_S}{\overset{k_{-S}}{\Leftrightarrow}} S+2\sigma$$

where σ represents an unoccupied active center on the catalyst surface, $H\sigma$, $B\sigma$, $R_1\sigma$, $R_2\sigma$ and $S\sigma$ refer to the adsorbed forms of hydrogen, diunsaturated, *cis*-monounsaturated, *trans*-monounsaturated and saturated acid groups respectively. $BH\sigma$ is an adsorbed complex that is formed by attack of a hydrogen atom to one of the two double bonds of diunsaturated fatty acid groups B, and $RH\sigma$ is an adsorbed complex formed from monounsaturated acid groups containing both of the *cis* and *trans* configurations.

To derive the rate equations, the following assumptions were made: all rates of adsorption and desorption processes are very rapid compared with those of surface reaction steps, and these steps easily reach to equilibrium; the catalyst surface is sparsely covered by adsorbed components, hence the concentration of unoccupied adsorption sites is practically independent of the concentration of components in the liquid phase during the reaction; the following restrictions among the rate constants are held:

$$\begin{gathered} k_{-0} << (k_1+k_2)\sqrt{K_A}\sqrt{[H_2]} \\ k_{-3}+k_{-4} >> k_5\sqrt{K_A}\sqrt{[H_2]} \end{gathered} \qquad [7]$$

Under the assumptions mentioned above, application of the steady state approximation gives the following rate expressions:

$$\begin{aligned} \frac{d[B]}{dt} &= -k_{12}[B]\sqrt{[H_2]} - k_{13}[B]\sqrt{[H_2]} \\ \frac{d[R1]}{dt} &= k_{12}[B]\sqrt{[H_2]} - k_{23}[R_1]\sqrt{[H_2]} + k_{32}[R_2]\sqrt{[H_2]} \\ &\quad -k_{24}[R_1][H_2] \\ \frac{d[R_2]}{dt} &= k_{13}[B]\sqrt{[H_2]} + k_{23}[R_1]\sqrt{[H_2]} - k_{32}[R_2]\sqrt{[H_2]} \\ &\quad -k_{34}[R_2][H_2] \\ \frac{d[S]}{dt} &= k_{24}[R_1][H_2] + k_{34}[R_2][H_2] \end{aligned} \qquad [8]$$

where

$$\begin{aligned} k_{12} &= k_1 k_0 [\sigma_o]^2 K_B \sqrt{K_A}/(k_1+k_2) \\ k_{13} &= k_2 k_0 [\sigma_0]^2 K_B \sqrt{K_A}/(k_1+k_2) \\ k_{23} &= k_3 k_{-4} [\sigma_0]^2 K_{R_1} \sqrt{K_A}/(k_{-3}+k_{-4}) \\ k_{32} &= k_4 k_{-3} [\sigma_0]^2 K_{R_2} \sqrt{K_A}/(k_{-3}+k_{-4}) \\ k_{24} &= k_5 k_3 [\sigma_0]^2 K_{R_1} K_A/(k_{-3}+k_{-4}) \\ k_{34} &= k_5 k_4 [\sigma_0]^2 K_{R_2} K_A/(k_{-3}+k_{-4}) \end{aligned}$$

$$K_A = k_A/k_{-A}, \quad K_B = k_B/k_{-B}, \; K_{R_1} = k_{R_1}/k_{-R_1}$$

$$K_{R_2} = k_{R_2}/k_{-R_2}, \; K_S = k_S/k_{-S}$$

where the K's represent the adsorption equilibrium constants, k_i the rate constant for respective elementary reaction, k_{ij} the rate constant for the stoichiometric reaction, and $[\sigma_o]$ is the concentration of active sites on the catalyst surface.

It is evident that a derived set of rate equations is identically equal to that obtained using the nonlinear least squares method, indicating that the proposed reaction mechanism for both hydrogenation and isomerization of triglycerides can explain the experimental results.

Special abbreviations: A = hydrogen; B = diunsaturated fatty acid groups; f = mole fraction based on mixture of liquid components; K = adsorption equilibrium constant; $k_A, k_B, \cdots$ = rate constants for adsorption of componnets A, B, etc. (see Equation 6); k_{-A}, k_{-B}, $\cdots$ = rate constants for desorption of components A, B, etc. (see Equation 6); k_0, k_1, $\cdots$ = forward-reaction rate constants (see Equation 6); k_{-0}, k_{-3}, $\cdots$ = reverse-reaction rate constants. (see Equation 6); k_{12}, k_{13}, $\cdots$ = reaction rate constants (see Equation 8); k'_{12}, k'_{13}, $\cdots$ = pseudo first order rate constants (see Equation 3); N = number of experimental points; R_1 = *cis*-monounsaturated fatty acid groups; R_2 = *trans*-monounsaturated fatty acid groups; S = saturated fatty acid groups; t = reaction time (min); t_{ind} = induction period (min); θ = pseudo reaction time = $t - t_{ind}$ (min); Φ = sum of squares of residuals; σ = unoccupied active center on catalyst surface. Subscripts B, R_1, R_2, S = components; i = ith data point; 0 = initial value. Superscript o = measured value. Symbol [ ] = concentration [g mol/liter], [B] = concentration of diunsaturated fatty acid groups.

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