Hydrogenation of Triglycerides Containing Linolenic Acids. I. Calculation of Selectivity

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Abstract

A simple graphic method is presented for the determination of selectivity direct from the analytical data before and after hydrogenation of fatty oils. For the technically important hydrogenation of soybean oil, where trienoates are to be hydrogenated preferentially, a graph for the determination of the linolenate selectivity ratio was prepared.

It is shown by a generally valid mathematical derivation that it is possible in the hydrogenation of triglycerides containing linolenate to calculate the selectivity ratios in a relatively simple manner by eliminating the reaction time. As a result, one obtains a relationship between the initial and final concentrations of monoenoate, dienoate, and trienoate and the selectivity ratios. The exact calculation of such graphs as well as the exact determination of the selectivity ratios require no computer.

Introduction

According to investigations by Bailey (1), several reaction steps occur during the hydrogenation of triglycerides containing linolenic fatty acid, which are best illustrated by the reaction mechanism presented in the following scheme:

$$\begin{tikzcd}
 & \text{linoleic} & & \\
\text{linolenic} \arrow[ur] \arrow[dr] \arrow[rr] & & \text{oleic} \arrow[ul] \arrow[dl] \arrow[r] & \text{stearic} \\
 & \text{isolinoleic} & &
\end{tikzcd}$$

(Isolinoleic fatty acid = 9:10, 15:16, octadecadienoic acid.)

For the description of the hydrogenation kinetics according to this scheme, four different reaction-rate constants corresponding to the reacting components are necessary as well as three coefficients indicating the proportion of linolenic fatty acid which is converted to linoleic, isolinoleic, and oleic fatty acid. According to Bailey, all these reactions are irreversible and first-order. But even under these conditions, which are favorable for the calculation of kinetics, and under the assumption that the reactions take place without a change in volume, the amount of work involved in further calculations would be considerable. In addition, the determination of all components present in the reaction mixture requires extensive analytical operations.

Albright (2) therefore formulated a simpler reaction mechanism for the hydrogenation of unsaturated triglycerides:

linolenic → linoleic → oleic → stearic

This mechanism does not exactly correspond to the real run of reactions and ignores all isomeric fatty acids which might occur. Hence, in the hydrogenation of triglycerides containing linolenic fatty acid, it is better to speak of linolenic or trienoic acid, dienoic acid, monoenoic acid, and stearic acid. The reaction can then be described by the following scheme:

linolenic (trienoic) → dienoic →
monoenoic → stearic

The accuracy of this mechanism for the hydrogenation of fatty oils is sufficient in most cases. Many authors (3–6) have therefore based their investigations on this model, and it is also used for the calculations in this study.

The *cis-trans*-isomerism need not be considered in connection herewith because *cis-* and *trans*-compounds can be determined collectively and because there is no difference in the hydrogenation velocity of the two isomers (7).

Kinetic Calculations

The reactions taking place during hydrogenation can be expressed by the following equations ignoring *cis-trans*-isomerism:

$$A_3 + H_2 \xrightarrow{k_3} A_2$$
$$A_2 + H_2 \xrightarrow{k_2} A_1$$
$$A_1 + H_2 \xrightarrow{k_1} A_0$$

where

A_3 = trienoic fatty acid
A_2 = dienoic fatty acid
A_1 = monoenoic fatty acid
A_0 = stearic acid
k_i = reaction rate constants

The kinetic equations, according to this scheme for a batch irreversible first-order reaction, would be as follows:

$$[1] \quad \frac{dc_3}{dt} = -k_3c_3$$

$$[2] \quad \frac{dc_2}{dt} = -k_2c_2 + k_3c_3$$

$$[3] \quad \frac{dc_1}{dt} = -k_1c_1 + k_2c_2$$

$$[4] \quad \frac{dc_0}{dt} = k_1c_1$$

t = time
c_3 = concentration of the *trienoic* fatty acid at the time t
c_2 = concentration of the dienoic fatty acid at the time t
c_1 = concentration of the monoenoic fatty acid at the time t
c_0 = concentration of the stearic acid at the time t

The solutions of differential equations 1–4 are known:

$$[5] \quad c_3 = a_3 \cdot \exp(-k_3 \cdot t)$$

$$[6] \quad c_2 = \left(a_2 + a_3 \frac{k_3}{k_3-k_2}\right) \exp(-k_2 \cdot t) + a_3 \frac{k_3}{k_2-k_3} \exp(-k_3 \cdot t)$$

$$[7] \quad c_1 \quad \left[a_1 + a_2 \frac{k_2}{k_2-k_1} + a_3 \frac{k_2 \cdot k_3}{(k_2-k_1)(k_3-k_1)} \right] \exp(-k_1 \cdot t)$$

$$+\frac{k_2}{k_1-k_2}\left(a_2+a_3\frac{k_3}{k_3-k_2}\right)\exp(-k_2\cdot t)$$

$$+\,a_3\frac{k_2\cdot k_3}{(k_1-k_3)(k_2-k_3)}\exp(-k_3\cdot t)$$

$$[8]\quad c_0 = a_0+a_1+a_2+a_3-c_1-c_2-c_3$$

a_3 = concentration of the trienoic fatty acid at the time $t = o$
a_2 = concentration of the dienoic fatty acid at the time $t = o$
a_1 = concentration of the monoenoic fatty acid at the time $t = o$
a_0 = concentration of the stearic acid at the time $t = o$

Calculation of Selectivity

As mentioned already in other publications (1,7), the quantity t in Equations 5–7 merely has the meaning of a pseudo-time. It is therefore expedient to omit it from Equations 6 and 7 to obtain a relationship similar to Equation 8, which includes only initial concentration a_i, final concentration c_i, and reaction-rate constants k_i. This can be done by means of Equation 5, from which the time t can be calculated:

$$[9]\quad t = -\frac{1}{k_3}\cdot\ln\frac{c_3}{a_3}$$

When this term is put into Equations 6 and 7 and when s is substituted for the ratios of the reaction rate constants:

$$[10]\quad s_{32} = \frac{k_3}{k_2}$$

$$[11]\quad s_{31} = \frac{k_3}{k_1}$$

we obtain, after some transformations, the following equations:

$$[12]\quad \left(\frac{\dfrac{c_2}{c_3}+\dfrac{s_{32}}{s_{32}-1}}{\dfrac{a_2}{a_3}+\dfrac{s_{32}}{s_{32}-1}}\right)^{\frac{s_{32}}{s_{32}-1}} = \frac{a_3}{c_3}$$

$$[13]\quad \left[\frac{\dfrac{c_2}{c_3}+\dfrac{c_1}{c_3}\left(1-\dfrac{s_{32}}{s_{31}}\right)+\dfrac{s_{31}}{s_{31}-1}}{\dfrac{a_2}{a_3}+\dfrac{a_1}{a_3}\left(1-\dfrac{s_{32}}{s_{31}}\right)+\dfrac{s_{31}}{s_{31}-1}}\right]^{\frac{s_{31}}{s_{31}-1}} = \frac{a_3}{c_3}$$

In these equations the time t does not appear any longer, and selectivity ratios s_{32} and s_{31} can be calculated solely from the initial and final concentrations.

The third selectivity ratio

$$[14]\quad s_{21} = \frac{k_2}{k_1}$$

can be calculated easily from the two other selectivity ratios. From Equations 10 and 11 follows:

$$[15]\quad s_{21} = \frac{s_{31}}{s_{32}}$$

For the practical use of these formulae it is advisable to make the following additional transformations:

$$[16]\quad \frac{a_3}{c_3} = d$$

$$[17]\quad \frac{c_2}{c_3} = e$$

$$[18]\quad \frac{a_2}{a_3} = f$$

$$[19]\quad \frac{c_1}{c_3} = g$$

$$[20]\quad \frac{a_1}{a_3} = h$$

$$[21]\quad \frac{s_{32}}{s_{32}-1} = x$$

$$[22]\quad \frac{s_{31}}{s_{31}-1} = y$$

Thus, from Equations 12 and 13, result:

$$[23]\quad \left(\frac{e+x}{f+x}\right)^{x} = d$$

$$[24]\quad \left\{\frac{e+g\left[1-s_{32}\left(1-\dfrac{1}{y}\right)\right]+y}{f+h\left[1-s_{32}\left(1-\dfrac{1}{y}\right)\right]+y}\right\}^{y} = d$$

By approximation a numerical value for x which satisfies Equation 23 is quickly found. The selectivity ratio s_{32} is calculated from x by the reversion of Equation 21:

$$[25]\quad s_{32} = \frac{x}{x-1}$$

The numerical value is substituted for s_{32} in Equation 24, whereupon y can be determined therefrom. Then

$$[26]\quad s_{31} = \frac{y}{y-1}$$

It is thus possible to determine not only the ratio of the reaction-rate constants of trienoic fatty acid hydrogenation to dienoic fatty acid hydrogenation but also the ratio of reaction-rate constants of trienoic fatty acid hydrogenation to monoenoic fatty acid hydrogenation. The calculation can be carried out in a short time without the use of digital or analog computers, and the accuracy of the calculated values is unlimited. For the evaluation of a large number of test results it is, of course, better to employ a digital computer for solving Equations 12 and 13 respectively 23 and 24.

Estimation of Selectivity

When feed oils with a uniform concentration of unsaturated fatty acid are available, selectivity ratio s_{32} can be determined graphically. From Equation 12 the relationship between concentration c_2 and concentration c_3 at constant selectivity s_{32} can be derived. By transformation is obtained:

$$[27]\quad c_2 = c_3\left[\left(\frac{a_3}{c_3}\right)^{\frac{1}{x}}\cdot\left(\frac{a_2}{a_3}+x\right)-x\right]$$

where

$$[28]\quad x = \frac{s_{32}}{s_{32}-1}$$

In soybean oil the average concentration of trienoic fatty acid (linolenic acid) is about 8.0% and the concentration of dienoic fatty acid (linoleic acid), 52.0%. With these numerical values the curves in Fig. 1 were calculated by using selectivity ratio s_{32} as a parameter. For better graphic calculation of the selectivity from the analytical data the trienoic concentration is plotted logarithmically. Similar curves were already established on the basis of experiments (5).

With the aid of this chart the selectivity ratio of soybean oil hydrogenation can be estimated fairly well. For the evaluation of catalysts, which substantially influence the selectivity ratio, this graph has proved to be highly useful.

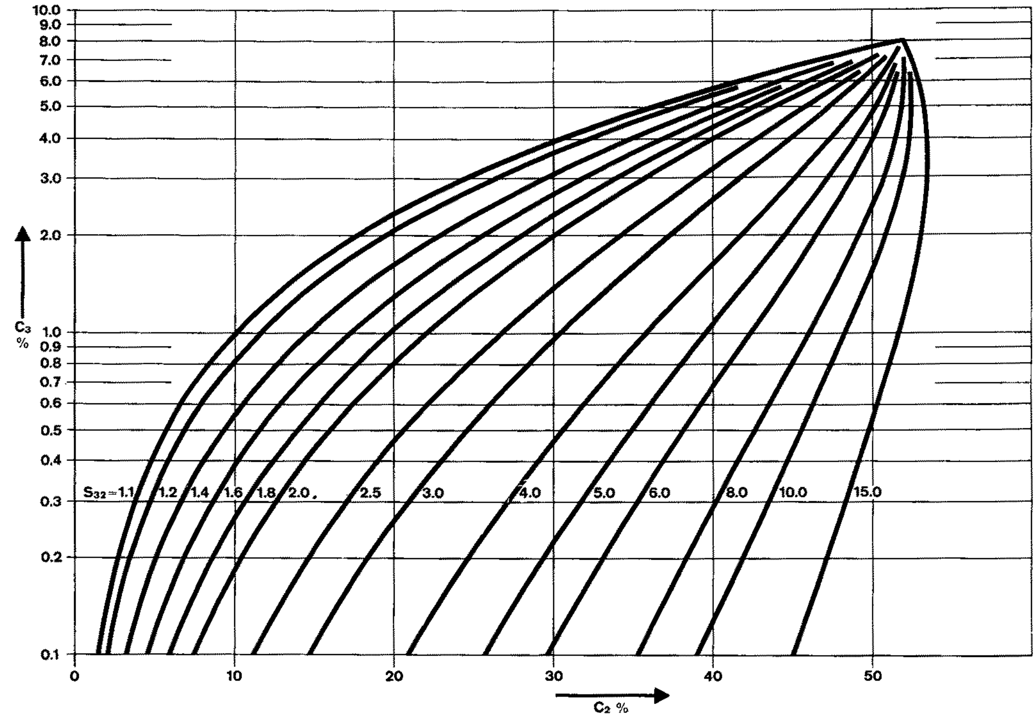

FIG. 1. Concentration of linolenic acid c_3 as a function of linoleic acid c_2 in hydrogenation of soybean oil by using selectivity ratio as s_{32} as a parameter. (Initial concentration: linolenic acid $a_3 = 8.0\%$, linoleic acid $a_2 = 52.0\%$.)

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