Hydrogenation of Linolenate. IV. Kinetics of Catalytic and Homogeneous Chemical Reduction

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Kinetics for consecutive reactions of octadecatrienoate to octadecadienoate have been studied with the aid of radioactive tracers and gas chromatography. Evidence for a triene to monoene shunt has been obtained. Under "nonselective" conditions, kinetic measurements are discussed.

Baily summarized in 1949 the kinetic information available on catalytic reduction of triglyceride oils containing linolenic acid (1). First order equations for estimating the relative reaction rates of oleic, isononoleic, linoleic, and linolenic acids were adapted by him. Under "nonselective" conditions, the ratio of reaction rates of linolenate to linoleate of 1.7 was observed, whereas under "selective" conditions a ratio of 2.5 was found. Consideration of reaction rates led him to conclude that a large portion of linolenate was directly reduced to oleate not stopping at the linoleate stage. No further publications on the rates of hydrogenation of linolenate have appeared since Baily's summary.

In this work C\textsuperscript{14}-labeled fatty acid methyl esters were used to study the kinetics of catalytic reduction. Newly developed procedures for monitoring gas chromatography for labeled compounds (2) were exploited to estimate the specific activity of individual esters, to measure the rates of hydrogenation of linolenate and linoleate, and to study the steps of conversion of linoleate to octadecenoate, i.e., the "oleate shunt." These kinectics for heterogeneous catalysis were compared with those for the homogeneous chemical reduction of linolenate by hydrazine. This single-phase chemical reaction, in contrast to heterogeneous catalysis, is characterized by either minimal, or no shift, in position (3) or geometric configuration of double bonds (4). Also, in contrast to catalytic hydrogenation and its varying order of reaction, first order kinetics are observed for chemical reduction; no evidence is apparent for the oleate shunt in homogeneous phase reduction. The reaction rates for the chemical reduction of octadecatrienoate, octadecadienoate and octadeceanoate appear in approximately the same ratio as the number of double bonds present.

Experimental

An equimixture of methyl linolenate and methyl linoleate by weight was hydrogenated in all the experiments described. This procedure permitted relative reaction rates for the two esters to be determined under identical conditions in each experiment. It minimized variations caused from run to run by uncontrolled differences in conditions such as catalyst concentration or activity, pressure, stirring, and inhibitors.

Catalytic hydrogenations presented are of two types: a) those in which C\textsuperscript{14}-labeled linolenate is added to the equimixture and b) those in which C\textsuperscript{14} labeled linoleate is added.

Methyl linolenate and methyl linoleate were isolated in gas chromatographically pure state by the preparative countercurrent distribution technique (5). Linolenate randomly labeled with C\textsuperscript{14} was isolated by countercurrent distribution from soybeans grown in an atmosphere containing C\textsubscript{14}O\textsubscript{2} (6). Linoleate, carboxy labeled with C\textsuperscript{14}, was obtained from Nuclear-Chicago Corp.

Catalytic hydrogenation experiments were carried out on a 0.6-g. scale with approximately 3 microcuries of added labeled ester. A 50-ml. flask with slightly rounded bottom and a magnetic stirrer comprised the reactor. A temperature of 140°C., hydrogen gas at atmospheric pressure, and 0.5% of a commercial catalyst (electrolytically reduced nickel on kieselguhr) were used. The uptake of hydrogen was followed manometrically. Samples were removed through a rubber serum cap seal with a hypodermic needle and syringe at appropriate intervals of hydrogen absorption. At each sampling, approximately 50 mg. were removed, weighed in the syringe and made to 1 ml. in pentane-hexane solvent. After the catalyst settled out, 20 µl. of solution containing approximately 1 µl. of esters was injected into a 7-ft. gas chromatographic column packed with 20% (w/w) of polyethylene glycol succinate on 80- to 100-mesh Chromosorb. A conventional gas chromatograph with thermal conductivity detector was used. Eluent solutes were...
collected at the detector outlet into vials of scintillation solvent at 30- or 60-sec. intervals, and the radioactivity of the solutes was determined by a liquid scintillation spectrometer (2). The percentage composition of the separated fatty acid esters and their corresponding radioactivity plotted from scintillation spectrometer data were determined by measuring areas under Gaussian-type curves. "Relative specific activities" were then calculated as the ratio of the per cent of radioactivity to the weight per cent for the corresponding ester component.

Hydrazine reductions were carried out at 50°C in a flask, open to the air and provided with a magnetic stirrer. To 665 mg of linoleic and linolenic acid mixture, containing 3.3 microcuries of carboxy-labeled linoleic acid, were added 6.5 ml of ethanol and 1.6 ml of hydrazine hydrate. Samples were removed from the flask after 0.25-, 0.5-, 2-, 4-, and 8-hr. reaction times and were acidified with hydrochloric acid. Fatty acids were recovered from the mixtures by ether extraction and were converted to their methyl esters by diazomethane. Gas chromatographic analysis and radioactive assay of the individual esters were determined as described.

Kinetic data were handled as proposed by Bailey (1), by plotting the fatty acid composition data against the extent of reaction rather than against time. As he points out, for this analysis the first order equations are valid regardless of whether or not the reactions proceed in true first order fashion. They become invalid only if the relative reaction rates change. However, instead of using iodine value as Bailey proposed, an equivalent, the average number of double bonds remaining, was plotted.

Theoretical curves for the composition were calculated using the equations for first order consecutive reactions and assuming a value for K = kₐ/kₙ, the ratio of reaction rate of linolenate (triene) to that for linoleate (diene). Equations describing this simple system

\[ \begin{align*}
A & \xrightarrow{(k_a)} B \xrightarrow{(k_b)} D \\
\text{(Triene)} & \text{(Diene)} \text{(Monoene)}
\end{align*} \]

are to be found in textbooks of physical chemistry and are

\[ \begin{align*}
A_t &= A_0 e^{-k_at} \\
B_t &= B_0 e^{-k_bt} + \left(\frac{k_b}{k_a - k_b}\right) \left(e^{-k_at} - e^{-k_bt}\right) \\
D_t &= 1 - (A_t + B_t)
\end{align*} \]

Initial conditions, as pointed out, for these experiments are

\[ A_0 = B_0 = 0.5. \]

Theoretical curves for the analysis of radioactivity were calculated by these same equations. In experiments in which labeled linolenate is added \( A_0^* = 0.5 \) and \( B_0^* = 0 \) where the asterisk indicates that the substance is radioactive. When tagged linoleate is added \( A_0^* = 0 \) and \( B_0^* = 0.5 \).

Since nonconformity to this simple kinetic pattern became evident during the research, it was necessary to consider the formation of isolinoleate and the oleate shunt according to the scheme:

\[ \text{Linoleate} \rightarrow \text{Linolenate} \rightarrow \text{Oleate} \rightarrow \text{Isolinoleate} \]

Fig. 1. Catalytic hydrogenation of a linolenate-linoleate mixture with C₁₄-labeled linolenate calculated on the basis of a three-component system (Exp. 1).

Since no stearate was found in our reduced samples and since no saturates, oleate, or isolinoleate were in the original sample, \( k_d, D_o, \) and \( C_o \) are zero. Therefore, Bailey's equations describing this system can be simplified as follows:

Let

\[ \begin{align*}
A_0 &= \% \text{ linolenate in original mixture} \\
F_b &= \% \text{ fraction of } A \text{ going to linoleate} \\
F_c &= \% \text{ fraction of } A \text{ going to isolinoleates} \\
F_d &= \% \text{ fraction of } A \text{ going to oleates} \\
B_0 &= \% \text{ linoleate in original mixture}
\end{align*} \]

At any given time, \( t \),

\[ \begin{align*}
A_t &= \% \text{ linolenate in mixture} \\
B_t &= \% \text{ linoleate in mixture} \\
C_t &= \% \text{ isolinoleate in mixture} \\
D_t &= \% \text{ oleate in mixture}
\end{align*} \]

Let

\[ \begin{align*}
k_a &= \text{ relative reaction rate of linolenate} \\
k_b &= \text{ relative reaction rate of linoleate} \\
k_c &= \text{ relative reaction rate of isolinoleate}
\end{align*} \]

Then

\[ \begin{align*}
A_t &= A_0 e^{-k_at} \\
B_t &= B_0 e^{-k_bt} + A_0 F_b \left(\frac{k_b}{k_b - k_a}\right) \left(e^{-k_at} - e^{-k_bt}\right) \\
C_t &= A_0 F_c \left(\frac{k_a}{k_a - k_c}\right) \left(e^{-k_at} - 1\right) \\
D_t &= 100 - (A_t + B_t + C_t)
\end{align*} \]

In these experiments \( A_0 = B_0 = 50 \). In calculating the radioactive substances \( A_0 = 50, B_0 = 0 \) for tagged linolenate; \( A_0 = 0, B_0 = 50 \) for tagged linoleate.

Results

Induction periods and rates of hydrogenation varied greatly from run to run. For example, in the