Micro Vapor-Phase Hydrogenation Monitored with Tandem Chromatography-Radioactivity. II. Evaluation of Catalyst Selectivity for Linolenate[1]

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Abstract

Micro vapor-phase hydrogenation is a rapid and effective method of studying the kinetic characteristics of hydrogenation catalysts. Eight catalysts were investigated, and reaction rates and selectivity ratios determined by an analog computer. Fatty esters labeled with C^{14} were utilized to clarify reactions and to assist in achieving a unique simulation of the data for a particular catalyst.

Introduction

TECHNIQUES have already been reported for micro vapor-phase hydrogenation of fatty esters with subsequent analysis of the products by gas-liquid chromatography (GLC) (6) or by tandem GLC-radioactivity analysis (GLCR) (4). Relative rates of hydrogenation of methyl linoleate and oleate were determined (4) for the reactions occurring over nickel, platinum and palladium catalysts. The differing rates and kinetic patterns observed suggested that this vapor-phase hydrogenation procedure might be used for the practical evaluation of catalysts. Results of investigations of several hydrogenation catalysts are reported here. Kinetic patterns and catalyst characteristics are compared and selectivities are determined for methyl linolenate in a mixture with methyl linoleate.

Experimental

Apparatus

Only minor changes have been made in the design of the microreactor, illustrated previously (4). To obtain a more efficient temperature control, the catalyst tube is enclosed in a brass block supplied with cartridge heaters. The carrier gas is diverted from the normal chromatograph gas flow system by a valve and enters the microreactor through an exterior fitting. This design eliminates the prior requirement for a machined end on the catalyst tube to force the gas to the head of the reactor. Simple construction of several interchangeable catalyst tubes is thus facilitated. In the present reactor, the column of packed hydrogenation catalyst has dimensions of 50 × 3 mm.

To facilitate the injection of samples at specified column depths, a guide track is designed to fit the face of the microreactor. A repeating dispenser, commercially available, is modified to set in the guide track. Spacer bars, which have dimensions calculated from first-order kinetics to give equal increments of reaction, are used in conjunction with a 50-μl syringe having a 4-in. needle, to vary reproducibly the depth of injection of sample. The microreactor, guide track, spacer bars and syringe are pictured in Fig. 1.

Chromatograph-Radioactivity System

The microreactor is screwed to the injection port of a Cary-Loenco chromatography-radioactivity analyzer (8). This instrument has the capability of thermal conductivity or hydrogen flame detection of mass peaks and contains a 275-cc spherical ion chamber in the detector oven to monitor the effluent for radioactivity. Aluminum columns (6 ft × ¼ in.) packed with 17% DEGS on 60–80 mesh Chromosorb W are used in the dual column chromatograph.

Electronic integrators determine the area under both the mass curve and the ion current curve.

Analog Computer

The use of an analog computer for simulation of kinetic data has been described previously (2). The procedures used here were similar; however, the computer used was the more sophisticated EAI-TR-48.

Materials

Catalysts

The eight catalysts evaluated were prepared by diluting and mixing commercially available catalysts with Chromosorb W, except for the platinum and palladium catalysts which were prepared as described earlier (6). The percentage of catalyst noted is based on the ratio of the weight of metal to the weight of support. The eight catalysts investigated were: 0.81% nickel, 0.16% platinum, 0.12% palladium, 1.2% cobalt, 0.65% rhodium, 0.24% copper chromite, 1.2% copper barium chromite and 1.7% copper magnesium chromite.

Samples

Unlabeled methyl linolenate and methyl linoleate were obtained from The Hormel Institute. These

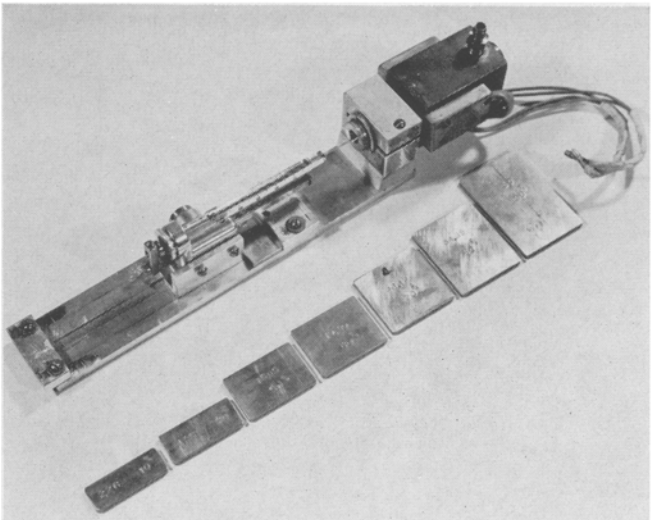

FIG. 1. Micro vapor-phase hydrogenation accessory with guide track, syringe, repeating dispenser and spacer bars.

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[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

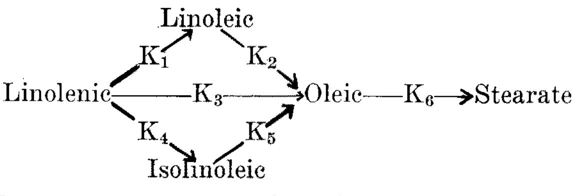
were checked by GLC and found to be >99% pure. To the equimixture of these esters were added radioactive esters in amounts such that ca. 1 μc of radioactivity was present per milligram of ester mixture. GLCR analysis indicated that methyl linoleate-1-C^{14} (Tracerlab, Inc.) was both chemically and radioactively pure. The specific activity was 9.3 mc/mM. Methyl linolenate-U-C^{14} (uniformly labeled) was prepared biosynthetically by exposure of a nearly mature perilla plant to high specific activity $C^{14}O_2$ and by subsequent extraction of the oil, transesterification with methanol and isolation of the radioactive methyl linolenate (7).

Procedure

After each catalyst mixture was packed by tamping into one of the interchangeable tubes, the microreactor was set up for conditioning. The reactor was heated to 200C and hydrogen was passed through the catalyst for 1 hr. The microreactor was then fitted to the injection port of the gas chromatograph and the microsyringe, in the repeating dispenser, was mounted on the guide track. A spacer bar for the desired depth of injection was placed on the track; the needle was pushed through the septum; the dispenser was moved along the track until stopped by the spacer; and then the plunger was pushed injecting 1 μl of sample. For each catalyst, 10 separate injections are made corresponding to the 10 calibrated spacers. The partially hydrogenated esters pass from the microreactor to the chromatographic column and elute successively through the thermal conductivity detector and through the radioactivity detector. The thermal conductivity signal was fed to one pen of a double pen recorder. Simultaneously, the electrometer signal for radioactivity was recorded by the second pen. Quantitative analysis of the curves was accomplished by electronic integrators. The percentage composition in terms of both labeled and unlabeled esters was calculated and plotted against the averaged double bonds remaining. Data were then simulated by the analog computer by varying rate constants to fit the data points. The potentiometers, which are analogs of the relative reaction rates, are read off when the "best" fit is attained.

Results and Discussion

Bailey (1) suggested that the reactions occurring in the hydrogenation of linolenic acid could be represented by the following schematic:



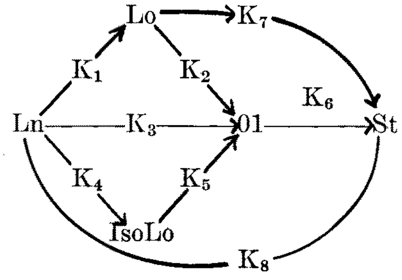
Subsequent research by Scholfield, Nowakowska and Dutton (9) confirmed the existence of the oleate shunt (K_3) and isolinoleate (K_4 and K_5) pathways for liquid-phase heterogeneous hydrogenations; however, no shunt was observed during the reduction of linolenate with hydrazine. Bailey's simple scheme was the first considered when attempting to fit the analog computer curves to the experimental data points.

With each catalyst investigated, it was apparent that the reaction scheme shown above was inadequate to represent the reactions involved and that modifications were required. The minimum number of paths were proposed and programmed that would achieve the most accurate fit of the experimental data. The reaction scheme shown below was the most complex required.

TABLE I
Relative Reaction Rates and Ratios for Catalysts

Rate	0.81% Nickel		0.65% Rhodium		0.24% Copper chromite	
	Relative reaction rate	Ratio[a]	Relative reaction rate	Ratio[a]	Relative reaction rate	Ratio[a]
K_1	0.265	0.83	0.584	1.50	......	......
K_2	0.318	1.00	0.390	1.00	0.390	1.00
K_3	0.146	0.46	......	......	0.726	1.86
K_4	......	......	......	......	0.412	1.06
K_5	......	......	......	......	......	......
K_6	0.243	0.76	0.121	0.31	......	......
K_7	0.145	0.46	......	......	......	......
K_8	0.292	0.92	......	......	......	......

[a] K_n/K_2.



For each catalyst the ratio of each of the relative reaction rates to that of the reduction of linoleate to oleate (K_2) was calculated. Several of the catalysts exhibited similar kinetic patterns. Reaction schemes for platinum, palladium, and cobalt catalysts were similar to that for the nickel catalyst which produced the relative reaction rates given in Table I. The three catalysts containing copper chromite yielded data which were simulated by the same relative reaction rate coefficients. Data for three catalysts having widely differing characteristics are given.

Kinetic curves (Fig. 2–5) were matched to the data points for mass and radioactivity analyses simultaneously by using identical rate coefficients for the given pathway. To simulate the data for the nickel catalyst, stearate shunts (K_7 and K_8) are required in addition to the oleate shunt (K_3). The operation of the stearate shunts shifts the monoene maximum and the resulting kinetic curves are shaped quite differently from those reported previously (1,

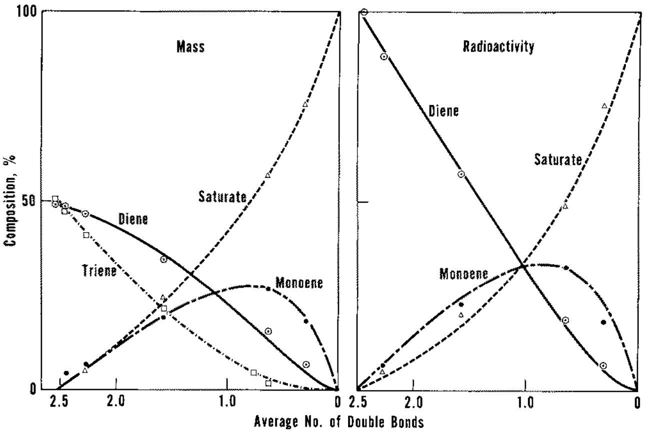


FIG. 2. Kinetic curves simulated by an analog computer from data for hydrogenation with a 0.81% nickel catalyst (methyl linolenate + methyl linoleate-1-C^{14}).

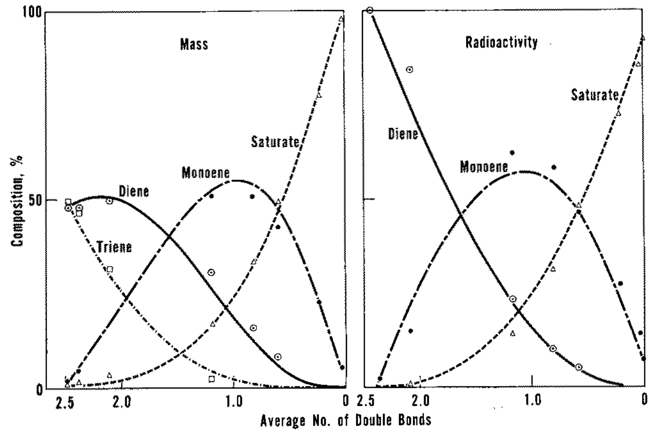


FIG. 3. Kinetic curves simulated by an analog computer from data for hydrogenation with a 0.65% rhodium catalyst (methyl linolenate + methyl linoleate-1-C^{14}).

4,9). Qualitatively, the operation of the stearate shunt is indicated by the early appearance of stearate and by the shifted and skewed monoene peak. Visual observation of the kinetic curves (Fig. 2) indicates that the skewing of the monoene peak is greater with the curves for mass than with the curves for radioactivity. This difference results since the linolenate-to-stearate and the linoleate-to-stearate shunts are operative in the mass data but only the linoleate-to-stearate shunt is involved in the radioactive data. The difference is accentuated further because the shunt with the linolenate has a reaction rate twice that of the shunt with linoleate.

For rhodium (Fig. 3) the computer simulation required invoking only the simple scheme $\text{Ln} \xrightarrow{K_1} \text{Lo} \xrightarrow{K_2} 01 \xrightarrow{K_6} \text{St}$. The straightforward reduction yields a simple kinetic curve with data from both the unlabeled and labeled analyses not unlike the curves for the homogeneous hydrogenations with hydrazine. As with the hydrazine, there is no evidence for either the oleate or the stearate shunt with the rhodium catalyst.

Initial simulations for the copper-chromite catalyst (Fig. 4) indicated that it was markedly different from the other catalysts. Whereas the labeled linoleate was completely reduced, the unlabeled diene content remained comparatively high.

To clarify the exact nature of the reactions occurring during hydrogenation, the experiment was repeated on a second equimixture containing labeled linolenate (Fig. 5). The diene produced from labeled linolenate increases slowly to a constant level while the monoene increases more rapidly to a higher value and also becomes constant. Rate constants determined for the tagged linolenate experiments were used without change to simulate the tagged linoleate experiments. The analog simulation of data for copper chromite indicates that the reactions involved can be represented by the following scheme:

$$\begin{tikzcd}
\text{Lo} \arrow[dr, "K_2"] & \\
\text{Ln} \arrow[r, "K_3"] \arrow[dr, "K_4"'] & 01 \\
& \text{IsoLo}
\end{tikzcd}$$

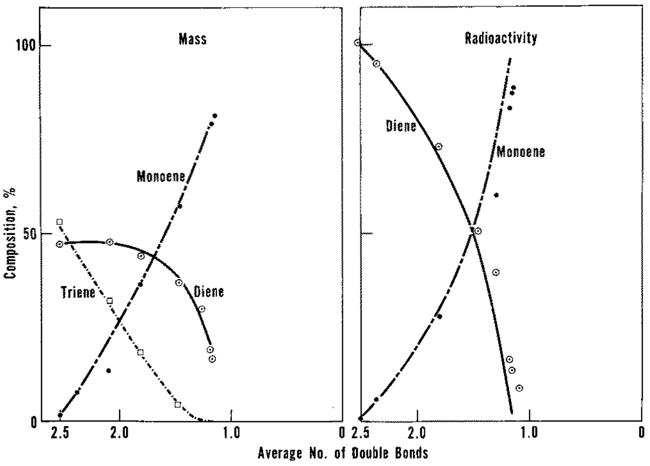


FIG. 4. Kinetic curves simulated by an analog computer from data for hydrogenation with a 0.24% copper-chromite catalyst (methyl linolenate + methyl linoleate-1-C^{14}). Radioactive data indicates that 9,12-diene is completely reduced to monoene.

Previous investigations showed that the 9,15-isolinoleate with its octadiene structure was quite unreactive compared to the pentadiene structure of methyl linoleate (4). In fact, due to the isolation of the double bonds in the 9,15 compound, these bonds hydrogenate no more rapidly than does the double bond in methyl oleate. Since monoene is not reduced with the catalysts containing copper chromite, both monoene and isolinoleate constituents build up in the mixture. This effect can be observed easily by use of the radiotracer. The implication from the kinetic data is that these catalysts convert linolenate to nonconjugatable dienes almost exclusively. This implies that the middle double bond is selectively attacked.

The selectivity of the catalyst for linolenate is determined by the ratio of the sum of all the relative rates of the reactions leading to the disappearance of linolenate to the sum of those leading to the disappearance of linoleate. Let K_a = relative reaction rate of linolenate and K_b = relative reaction rate of linoleate.

$$\text{Then} \quad K_a = K_1 + K_3 + K_4 + K_8$$

$$\text{and} \quad K_b = K_2 + K_7$$

The selectivity is then equal to

$$K_a/K_b \text{ or } \frac{K_1 + K_3 + K_4 + K_8}{K_2 + K_7}$$

This calculation is made for each catalyst and the results are presented in Table II.

It is readily apparent from Table II that the catalysts containing copper chromite exhibit the most selective hydrogenation of linolenate. Recent research into flavor stability of soybean oil by Takumi (10), DeJonge et al. (3) and Koritala and Dutton (5)

TABLE II
Catalyst Selectivities

Catalyst	K_a/K_b
0.81% Nickel	1.53
0.16% Platinum	1.28
0.12% Paladium	1.70
1.2% Cobalt	1.71
0.65% Rhodium	1.50
0.24% Copper-chromite	2.92
1.2% Copper barium chromite	2.92
1.7% Copper magnesium chromite	2.92

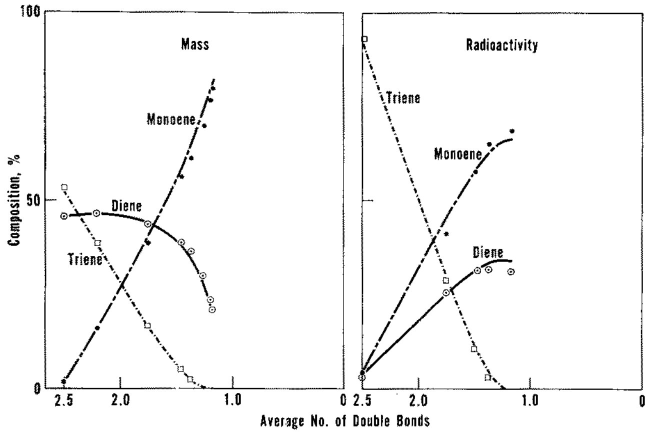


FIG. 5. Kinetic curves simulated by an analog computer from data for hydrogenation with a 0.24% copper-chromite catalyst (methyl linolenate-U-C^{14} + methyl linoleate). Radioactive data indicate that triene is reduced to monoene and isomeric diene.

with liquid-phase hydrogenations has also indicated that copper chromite catalysts are very selective for linolenate.

It had been observed that short beds of concentrated catalyst accomplished complete hydrogenation of the esters. Since we desired to observe the kinetic pattern of the hydrogenation reaction, the particular concentrations of catalyst used in each experiment were chosen so that complete hydrogenation of the sample would occur only when the full depth of catalyst bed was involved. With the nickel, platinum, palladium, cobalt and rhodium catalysts, the percentage concentration of the metal is roughly indicative of the activity of the catalyst; that is, the catalyst having the lowest percentage of the particular metal is the most active. The catalysts containing copper chromite do not completely saturate the sample even when utilizing the full depth of catalyst bed; therefore, the activities cannot be compared with those of other catalysts. However, a comparison among these catalysts indicates that barium and magnesium metals, which are added as stabilizers, tend to reduce the activity of the catalyst.

The experimental design employing the equimixture of methyl linolenate and methyl linoleate permits relative reaction rates for the two esters to be determined under identical conditions (9). Further, the use of the tagged ester allows the experimenter to observe the fate of the particular ester individually though a component of a complex mixture. The data for the radioactivity analysis are obtained at the same time as that for the mass analysis. When simulating the kinetic curves and determining the relative reaction rate coefficients, these two sets of data must be satisfied simultaneously. This doubling of independent experimental observations insures the uniqueness of the solution.

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