Kinetics of Hydrogenation of Conjugated Triene and Diene with Nickel, Palladium, Platinum and Copper-Chromite Catalysts

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ABSTRACT

A mixture of methyl linoleate and alkali-conjugated methyl linoleate was reduced with nickel, palladium, platinum and copper-chromite catalysts. The course of hydrogenation was followed by gas liquid chromatography of samples withdrawn at intervals. Relative rate constants of reactants and inermediates were calculated by a computer. Conjugated linoleate was 10-18 times more reactive than methyl linoleate with all catalysts except platinum, which showed no selectivity at 60 C. At 150 C conjugated diene reacted four times faster than methyl linoleate with platinum catalyst. A conjugated diene-to-stearate shunt was observed with palladium and platinum catalysts. When β-eleostearate was hydrogenated with the same catalysts, 50-97% of the triene was reduced directly to monoene with all catalysts except copper chromite, which selectively reduced conjugated triene to conjugated diene. On the basis of present kinetic data and previous knowledge about the mode of hydrogen addition to conjugated systems, a scheme has been proposed to account for the products formed during hydrogenation of methyl linolenate.

The selective hydrogenation of polyunsaturated over monounsaturated fatty acids has been attributed to the formation of highly reactive conjugated intermediates (1-4). Products formed from conjugated fatty acids have already been characterized (5-7). This report concerns the kinetics of hydrogenation of fatty esters containing conjugated double bonds.

EXPERIMENTAL PROCEDURES

The preparation of alkali-conjugated linoleate and β-eleostearate was described previously (8,9). Methyl linoleate was purchased from The Hormel Institute. Hydrogenations were carried out at atmospheric pressure in a modification of the apparatus described by Rohwedder (10). The fatty acid composition of samples withdrawn at intervals was determined by gas liquid chromatography. From these

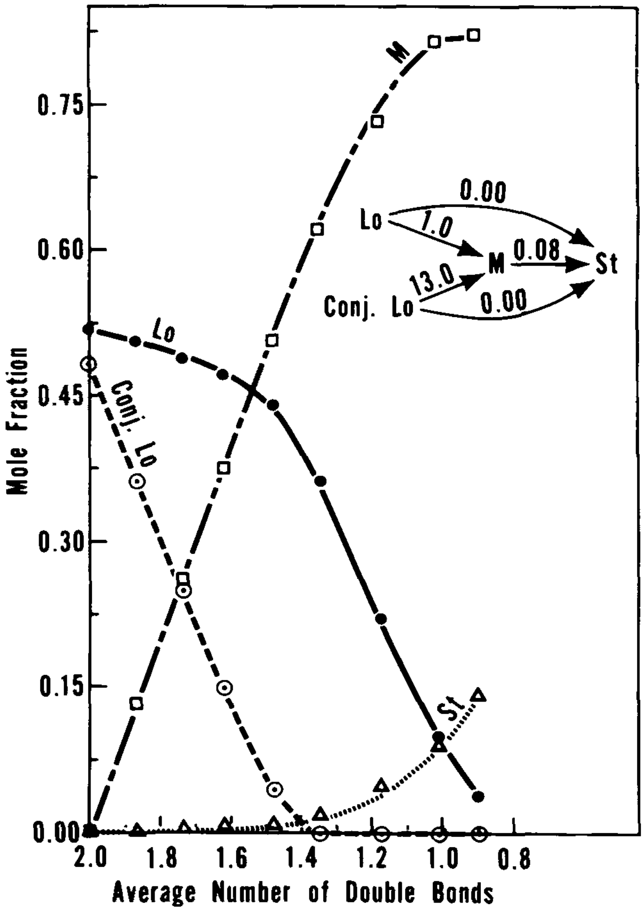

FIG. 1. Course of hydrogenation of a methyl linoleate-conjugated linleate mixture with nickel catalyst at 100 C, as plotted by a computer to best fit experimental values according to reaction scheme shown in inset. Lo, linoleate; conj. Lo, conjugated linoleate; M, monoene; St, stearate.

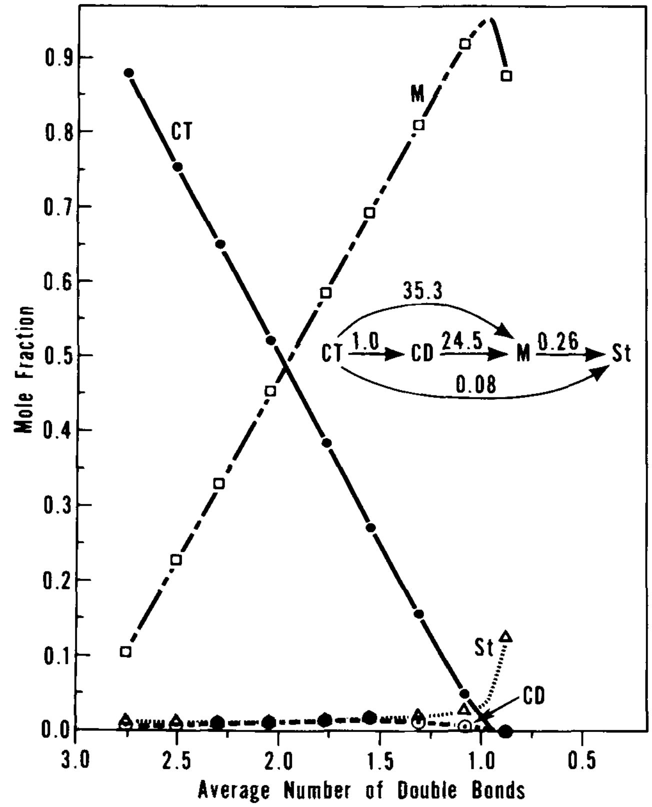

FIG. 2. Change in fatty acid composition during hydrogenation of β-eleostearate with palladium catalyst at 25 C. Curves drawn by computer when experimental values best fit computer simulation according to reaction scheme shown in inset. CT, conjugated triene; CD, conjugated diene; M, monoene; St, stearate.

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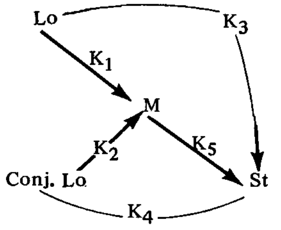
TABLE I

Relative Rate Constants for a Methyl Linoleate-Conjugated Linoleate Hydrogenation[a]



Catalyst	Hydrogenation temperature, C	Relative rate constants				
		K_1	K_2	K_3	K_4	K_5
Nickel	100	1.0	13.0	0.00	0.00	0.08
Nickel	160	1.0	16.3	0.00	0.00	0.03
Palladium	25	1.0	12.7	0.00	0.16	0.03
Palladium	150	1.0	17.6	0.00	0.00	0.04
Platinum	60	1.0	1.3	0.00	0.27	0.03
Platinum	150	1.0	4.2	0.00	0.00	0.07
Copper chromite	160	1.0	9.8	0.00	0.00	0.00

[a] Lo, linoleate; conj. Lo, conjugated linoleate; M, monoene; St, stearate.

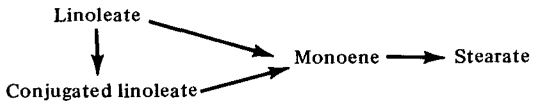
experimental values, relative rate constants were calculated by a computer (11).

RESULTS AND DISCUSSION

Figure 1 shows a computer plot of experimental data on the progress of hydrogenation of a methyl linoleate-conjugated linoleate mixture with nickel catalyst at 100 C. These computer-drawn curves represent the "best fit" for the experimental values. The corresponding relative rate constants appear in the inset in Figure 1. Similar data obtained with other catalysts are found in Table I. Conjugated linoleate is reduced 13-18 times faster than linoleate with nickel and palladium catalysts, whereas conjugated linoleate reacted only 10 times faster than linoleate with copper chromite. During hydrogenation of linoleate a maximum of 10% of the unreacted diene (5% of the reaction product) was conjugated with copper chromite (9,12), whereas only minor amounts were with nickel and palladium catalysts (3,12). This difference is apparently due to irreversible adsorption of conjugated dienes on nickel and palladium catalysts (7), whereas some conjugated diene desorbs from the surface of copper catalysts (13).

Platinum at 60 C showed no selectivity, and both linoleate and conjugated linoleate disappeared at nearly equal rates. However at the higher temperature the same catalyst exhibited some selectivity for the reduction of conjugated linoleate. Part of the conjugated diene was reduced directly to stearate with palladium at 25 C and with platinum at 60 C. This conjugated diene-to-stearate shunt disappeared at the higher temperature of hydrogenation.

When reduction was simulated according to the following scheme, the relative rate constant for linoleate to conjugated linleate was nearly zero with all the catalysts.

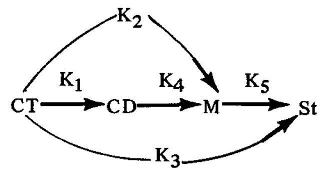


A similar result was previously reported (8) with copper-chromite catalyst. These results do not rule out the conjugation mechanism. In fact, they reinforce the hypothesis that almost all the conjugated intermediate is not desorbed from the catalyst surface until after reduction to monoene occurs.

In Figure 2 is shown the course of hydrogenation of β-eleostearate with palladium catalyst at 25 C, as drawn by

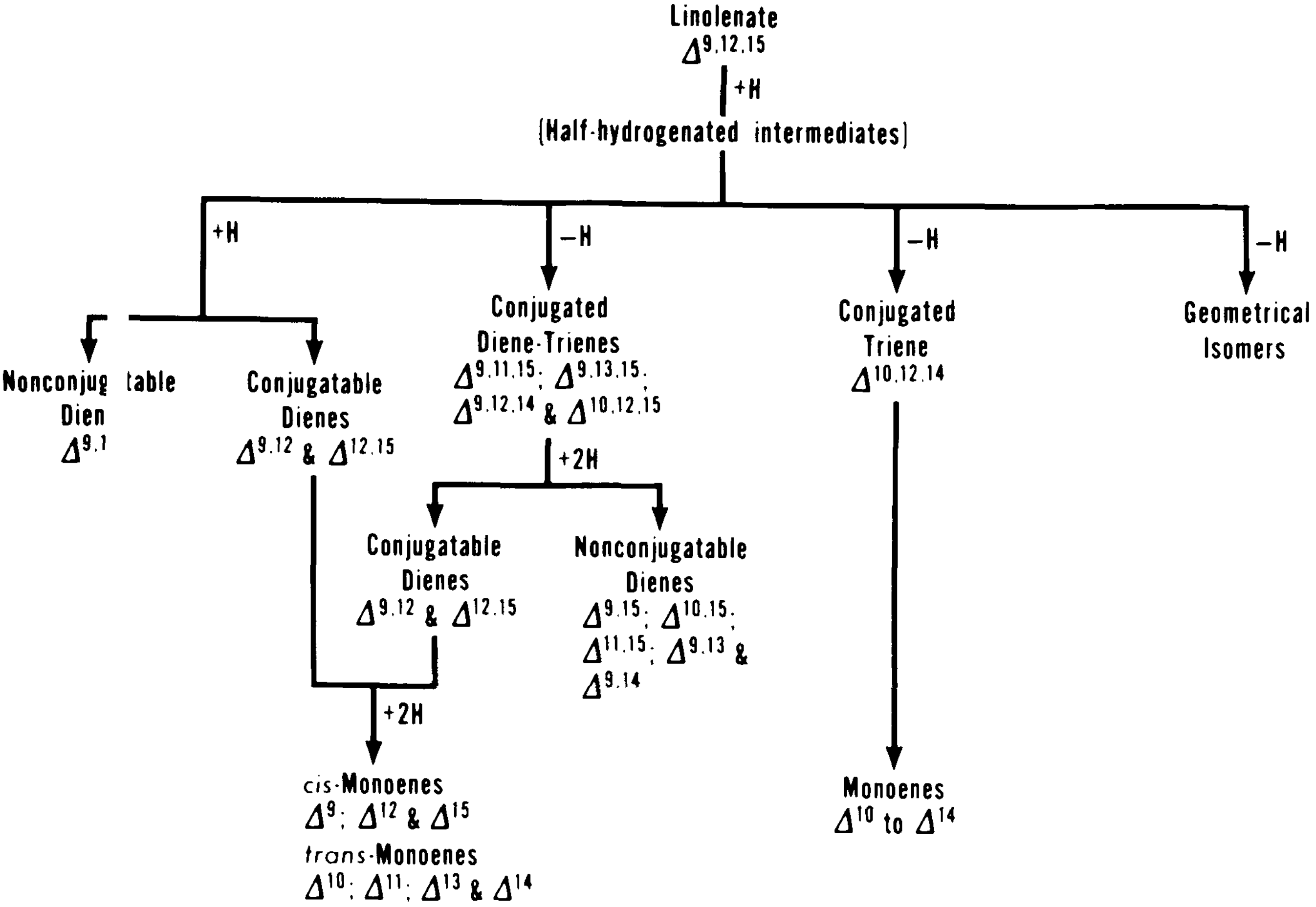
TABLE II

Relative Rate Constants for Conjugated Triene Hydrogenation[a]



Catalyst	Hydrogenation temperature, C	Relative rate constants				
		K_1	K_2	K_3	K_4	K_5
Nickel	100	1.0	1.0	0.00	1.0	0.01
Nickel	160	1.0	1.2	0.00	1.0	0.01
Palladium	25	1.0	35.3	0.08	24.5	0.26
Palladium	150	1.0	1.5	0.03	1.3	0.02
Platinum	60	1.0	16.8	2.0	8.4	1.2
Platinum	150	1.0	2.8	0.05	2.6	0.05
Copper chromite	160	1.0	0.0	0.00	0.01	0.00

[a] CT, conjugated triene; CD, conjugated diene; M, monoene; St, stearate.



SCHEME 1.

the computer from the experimental data. The relative rate constants shown in the inset were obtained when the experimental data best fit the computer simulation of the reaction. Similar data for other catalysts are given in Table II. It is evident from Figure 2 that nearly all the conjugated triene is hydrogenated directly to monoene. Only trace amounts of intermediate conjugated diene desorb from the catalyst surface. Almost all the conjugated triene was also reduced through a shunt with platinum at 60 C (Table II). Increasing the temperature of hydrogenation decreased this shunt for both palladium and platinum. Even at the higher temperature, 60 and 74% of the conjugated triene was directly reduced to monoene with palladium and platinum, respectively. With nickel catalyst, 50% of the conjugated triene was reduced to monoene directly at both temperatures. From the kinetic data, it appears that ca. 10% of the conjugated triene ($K_3 \times 100/[K_1 + K_2 + K_3]$) is reduced directly to stearate with platinum and that this shunt largely disappears at the higher temperature. This triene-to-stearate shunt either is too small to measure or is absent with other catalysts. Apparently both conjugated triene and diene are irreversibly adsorbed on nickel, palladium and platinum surfaces (7), and desorb only after monoene forms.

Copper chromite is distinguished from other catalysts due to the simplicity of the kinetic pathway for the reduction of conjugated triene. No shunts were observed and the triene is selectively reduced first to conjugated diene (maximum concentration, 95%), which is then reduced to monoene. The selectivity ratio for conjugated triene over conjugated diene ($[K_1 + K_2 + K_3]/K_4$) is ca. 100, which is much higher than with the other catalysts.

From present kinetic data and from previous information on the mode of hydrogen addition to conjugated double bonds (7), Scheme 1 is proposed to account for the products formed during hydrogenation of linolenate with nickel (14), platinum (15) and copper-chromite (16) catalysts.

Addition of a hydrogen atom to chemisorbed olefin forms half-hydrogenated intermediates (17). Six half-hydrogenated intermediates are possible from the three double bonds in linoleate. Three different types of isomers could result by loss of a hydrogen atom from these half-hydrogenated intermediates. If a hydrogen is removed from the same carbon atom that initially added hydrogen, then geometrical isomers of linolenate result. However a hydrogen from the neighboring active methylene group is more likely to be abstracted, to form conjugated diene-trienes. Conjugated triene could result only by repetition of the addition-abstraction process to conjugated diene-trienes. A fourth, but unlikely, possibility of positional isomerization, e.g., $\Delta^{8,12,15}$ and $\Delta^{9,12,16}$, could occur if hydrogen were abstracted from a methylene group situated away from the neighboring double bond. However such isomers have not been detected (14-16).

Hydrogenated products are formed from these isomers and also from the half-hydrogenated intermediates by the addition of another hydrogen atom. Some or all of these processes occur simultaneously with various catalysts. The final product composition is reflected by the relative importance of these four pathways.

Hydrogenation with copper chromite occurs through conjugated triene and conjugated diene-triene (18), which further isomerizes to conjugated triene. The accumulation of large amounts of conjugated dienes during hydrogenation of linolenate (16) is consistent with the present kinetic data and the previously proposed conjugation mechanism (18).

Hydrogenation of linolenate with nickel catalyst through conjugated triene intermediate should be, at the most, minimal, since the first conjugated diene-triene intermediate that forms will be expected to be reactive for hydrogenation and, consequently, to resist further isomerization. Also conjugated triene should give conjugated diene, whereas hydrogenation of linolenate produced mostly nonconjugated diene (14). Hydrogenation through conjugated diene-triene results predominantly in nonconjugatable dienes which, being nonreactive, will accumulate during hydrogenation. Addition to the double bonds in linolenate forms conjugatable dienes ($\Delta^{9,12}$ and $\Delta^{12,15}$), which further hydrogenate to form Δ^{9}, Δ^{12} and Δ^{15} *cis*-monoenes. Δ^{10}, Δ^{11}, Δ^{13} and Δ^{14} *trans*-monoenes form through conjugation of the dienes (12). Geometrical isomers of linolenate will participate in all the reactions described above, although they are not expected to be as reactive as all-*cis*-linolenate (19,20).

Conjugation plays a relatively minor role with platinum catalyst (12). Successive addition of the two hydrogen atoms to the double bonds in linolenate should be the major pathway. Because platinum is a nonselective catalyst, monoenes formed during hydrogenation isomerize further. Consequently, Δ^{9}, Δ^{12}, and Δ^{15} *cis*-monoenes isomerize to *trans* configuration. In contrast to nickel catalyst, platinum (15) forms *trans*- as well as *cis*-monoenes with double bonds at the 9, 12 and 15 positions as the predominant isomers.

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