Selective Hydrogenation With Copper Catalysts: II. Kinetics[1]

SAMBASIVARAO KORITALA, R. O. BUTTERFIELD and H. J. DUTTON,
Northern Regional Research Laboratory,[2] Peoria, Illinois 61604

Abstract

To explain the unusually high selectivity of copper catalysts toward linolenate, model compounds were hydrogenated (150 C and atmospheric pressure) and the reaction products analyzed. Products varied depending upon location of the double bonds. Monoenes were not reduced by copper chromite except when the double bond was next to a carboxyl group. Dienes with isolated double bonds also were not reduced. Binary mixtures of model compounds were hydrogenated with copper chromite. From the composition of the initial and final products, a competitive rate ratio of the two compounds was determined. Esters with conjugated double bonds reacted faster than esters containing methylene interrupted double bonds. Kinetic data on the hydrogenation of linolenate indicated conjugation of the double bonds. Simulation of the kinetic data gave competitive reaction rates for the different isomers formed.

Introduction

Copper catalysts are more selective than nickel, platinum or palladium for the reduction of linolenate in soybean oil (1–3). This superior selectivity may be due to a difference in the mechanism, which is not known for the copper catalysts. Conjugated dienes are the principle products of hydrogenation of linolenate with copper chromite (4), whereas only traces of conjugation are produced by nickel and platinum catalysts (5). This paper reports some kinetic studies on the hydrogenation of specific unsaturated fatty acid esters with copper chromite.

Experimental Procedures

Materials

Methyl linolenate was prepared from methyl esters of linseed oil by countercurrent distribution (CCD) between acetonitrile and hexane (6). Analysis by gas liquid chromatography (GLC) indicated better than 99% purity. UV and IR analyses showed the absence of conjugation and isolated *trans* bonds. Eleostearic acid was prepared from tung oil according to the procedure of Hoffmann et al. (7). Methyl eleostearate was prepared from eleostearic acid with BF_3-methanol reagent (8). GLC analysis showed 63% α- and 37% β-eleostearate. Linoleate was purchased from The Hormel Institute. $\Delta^{5,9,12}$-Octadecatrienoate was prepared from methyl esters of *Thalictrum polycarpum* seed oil (9) by CCD. The diene fraction, which consisted of a mixture of linoleate and $\Delta^{5,9}$-octadecadienoate, was the source of the $\Delta^{5,9}$ isomer. $\Delta^{3,9,12}$-Octadecatrienoate was isolated from *Stenachaenium macrocephalum* seed oil methyl esters by reverse phase chromatography on a rubber column (10). Alkali-isomerized linoleate was prepared by heating 50 g of methyl linoleate under nitrogen with 100 g of 25% KOH in ethylene glycol at 180 C for ½ hr. The soaps were decomposed with hydrochloric acid, and the isomerized acids were converted into methyl esters with sulfuric acid catalyst. $\Delta^{5,9,12}$-Octadecatrienoate was similarly treated to obtain a mixture of $\Delta^{5,9,11}$ and $\Delta^{5,10,12}$-octadecatrienoates. $\Delta^{9,11,15}$ and $\Delta^{9,13,15}$-octadecatrienoate mixture (conjugated diene-triene) was prepared by refluxing 5 g methyl linolenate with 30 ml of 5% potassium in tertiary butanol for 4 hr (11). The isomerized acids were methylated and separated into conjugated trienes and conjugated diene-trienes on a silver-saturated resin column described by Emken et al. (12). $\Delta^{9,15}$-Octadecadienoate was prepared as described previously (13). Δ^{2}-*Trans*-octadecenoate was prepared according to the procedure of Myers (14).

Hydrogenations

Hydrogenations were carried out in a glass manometric apparatus as reported earlier (15) at 150 C and atmospheric hydrogen pressure. Copper chromite (0.1 g) heated to 350 C in air for 2 hr was placed in the hydrogenation flask. The system was flushed with hydrogen gas and heated to the temperature. Ester or ester mixture (1 ml) was added with a syringe through the serum cap. The magnetic stirrer was started and the uptake of hydrogen was measured with the aid of a manometer. When the appropriate amount of gas was consumed, the reaction was stopped by turning off the heat and the stirrer and by flushing the system with nitrogen. The hydrogenated product was separated from the catalyst by filtration. In some experiments hydrogenation was stopped at intervals by stopping the stirrer and withdrawing samples through the serum cap.

Analytical Methods

Methyl esters were analyzed with a Pye argon gas chromatograph, equipped with a 4 ft × ¼ in. glass column packed with 10% EGSS-X on 100–120 mesh Gas-Chrom P (organosilicon polyester packing obtained from Applied Science Laboratories, Inc., State College, Pa.) and with a radium D ionization detector. The column was held at 170 C with a gas flow of 45 ml/min. Areas under peaks were determined from an electronically integrated curve. Alkali isomerization and UV analyses were made according to AOCS Official Methods (16).

TABLE I

Hydrogenation of Linolenate and Its Isomers With Copper Chromite

Position of double bonds in trienes	Composition,[a] %						GLC IV
	S	M	D	CD	T	CDT	
9,12,15	....	19.1	6.7	47.4	19.8	6.9	179
	1.5	82.7	15.8	......	......	....	98
5,9,12	0.8	27.3	39.4	0.9	30.2	1.4	175
3,9,12	1.2	22.3	69.4	......	6.7	....	156
9,11,13	....	4.9	0.8	88.1	6.2	....	174
	1.9	98.1	......	......	....	....	84
+							
5,9,11	0.6	18.4	44.5	5.3	....	31.2	183
5,10,12	1.9	35.9	58.3	....	....	3.9	141
+							
9,11,15	....	15.3	16.7	46.6	....	21.4	178
9,13,15	1.5	69.3	28.6	0.6	....	....	110

[a] S, stearate; M, monoene; D, diene; CD, conjugated diene; T, triene; CDT, conjugated diene-triene.

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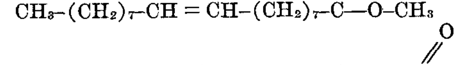
[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

Results and Discussion

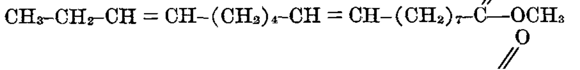
Fatty acid composition of partially hydrogenated linolenate and its isomers is shown in Table I. Methyl linolenate, which contains methylene-interrupted double bonds, produced mostly conjugated dienes and little unconjugated diene whereas nickel and platinum catalysts produced only traces of conjugation (5). Part of the unreduced triene was isomerized to conjugated diene-triene. The end products of hydrogenation were monoene and nonconjugated diene with traces of stearate. This diene, as well as the diene formed from other isomers indicated in Table I, was not alkali conjugatable and was not further reduced.

Some model compounds tested that did not hydrogenate with copper chromite were

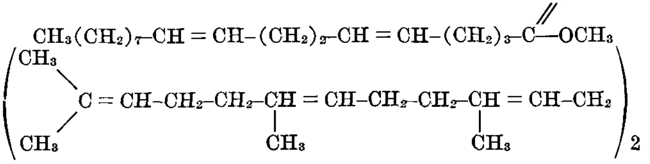
$CH_3{-}(CH_2)_7{-}CH = CH{-}(CH_2)_7{-}\overset{\overset{O}{/\!/}}{C}{-}O{-}CH_3$



$CH_3{-}CH_2{-}CH = CH{-}(CH_2)_4{-}CH = CH{-}(CH_2)_7{-}\overset{\overset{O}{/\!/}}{C}{-}OCH_3$



$CH_3(CH_2)_7{-}CH = CH{-}(CH_2)_2{-}CH = CH{-}(CH_2)_3{-}\overset{\overset{O}{/\!/}}{C}{-}OCH_3$



Because methylene-interrupted double bonds in linolenate produced conjugated dienes and because isolated double bonds in unconjugatable dienes did not hydrogenate, apparently conjugation precedes hydrogenation. The validity of this hypothesis is also borne out from hydrogenation of $\Delta^{5,9,12}$ and $\Delta^{3,9,12}$ isomers (Table I). In these two isomers since only two of the double bonds can conjugate, hydrogenation should form unconjugatable diene. Indeed, this type of diene was the major product. The formation of monoene from the two triene isomers can be explained by isomerization of the pentadiene group after conjugation (17). If the conjugated system of double bonds moves toward the isolated double bond, then hydrogenation should result first in conjugated diene and second in monoene. The isolated double bond in $\Delta^{3,9,12}$ isomer is farther removed than in $\Delta^{5,9,12}$ isomer (by two more carbon atoms) and, hence, the pentadiene group in $\Delta^{3,9,12}$ isomer has a greater chance of being reduced to form unconjugatable diene. Because less monene was formed from $\Delta^{3,9,12}$ triene than from $\Delta^{5,9,12}$ isomer, this difference supports the hypothesis that conjugation precedes hydrogenation. Alkali-isomerized $\Delta^{5,9,12}$ triene gave similar results.

Eleostearate was selectively reduced to conjugated dienes and little monoene was formed. Evidently conjugated trienes completely dominate the surface of the catalyst and exclude conjugated dienes from being further reduced. With conjugated diene-triene ($\Delta^{9,11,15}$ and $\Delta^{9,13,15}$ mixture), conjugated diene was the major product even though one double bond was insulated by two methylene groups. The conjugated double bond system must move rapidly along the chain and conjugate with the isolated double bond before hydrogenation. Some hydrogenation of the conjugated double bonds does occur before the isolated bond is conjugated as seen from the formation of unconjugatable diene.

TABLE II

Hydrogenation of 50:50 Binary Mixtures

Methyl esters	Composition,[a] %						Rate Ratio
	M	D	T	CD	CDT	CT	
Linolenate + linoleate	11.6	45.2	8.9	30.5	3.8	....	8
Linolenate + $\Delta^{5,9,12}$	10.6	4.0	57.3[b]	23.0	5.1	....	14
Linoleate + $\Delta^{5,9,12}$	28.1	29.9 +9.1[c]	28.5	4.4	....	....	1
Eleostearate + linolenate	1.6	0.5	46.4	45.7	3.0	2.8	>200
CDT + linolenate	4.9	11.0	35.2	20.8	28.1	....	2
Eleostearate + conjugated diene	5.3	1.4	......	89.9	....	3.5	40
Linoleate + conjugated linoleate	30.6	43.0	......	26.4	....	....	9

[a] M, monoene; D, diene; T, triene; CD, conjugated diene; CDT, conjugated diene-triene; CT, conjugated triene.

[b] 13.0% Linolenate and 44.3% $\Delta^{5,9,12}$ isomer.

[c] Diene formed from $\Delta^{5,9,12}$ isomer.

All the triene isomers in Table I produced traces of stearate, but oleate is not reduced under the conditions used for hydrogenation. However, Δ^2-octadecenoate was readily reduced to stearate. Δ^2-Octadecenoate has a UV absorption spectrum that is typical for conjugated diene (14). Δ^2 Monoenes were indeed found in the products formed during hydrogenation of linolenate (4) and would explain the small amount of stearate formation.

The results of hydrogenation of binary mixtures of fatty esters are given in Table II. From the fatty acid composition of the initial mixture and the final product, competitive reaction rate ratios were calculated with a digital computer assuming consecutive reactions; i.e., triene→diene→monoene (18). Linolenate was reduced eight times faster than linoleate. However $\Delta^{5,9,12}$ isomer was reduced at a rate equal to linoleate. Also from a mixture of linolenate and $\Delta^{5,9,12}$-octadecatrienoate, the fatty ester with methylene-interrupted double bonds was 14 times more reactive than the triene isomer with an isolated double bond. These results indicate that a triene with an isolated double bond kinetically behaves much like a diene. Conjugated diene-triene ($\Delta^{9,11,15}$ and $\Delta^{9,13,15}$ mixture) was slightly more reactive than linolenate. Eleostearate was much more reactive than linolenate

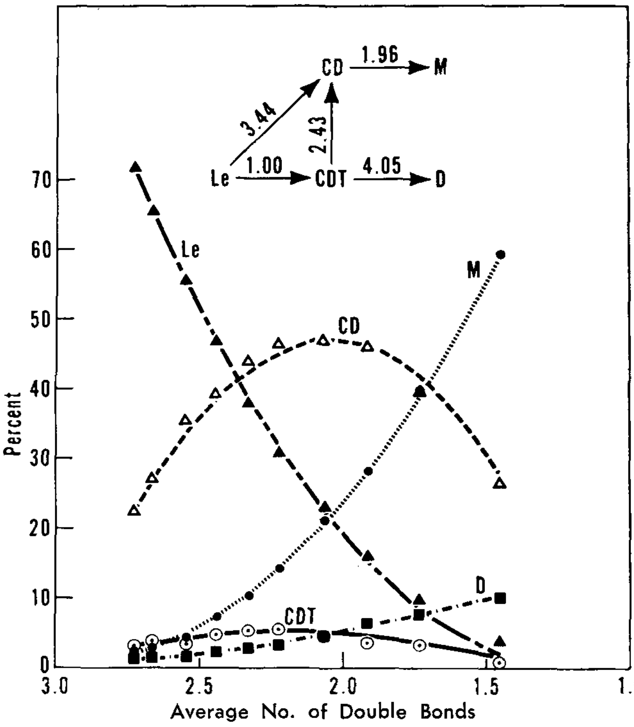


FIG. 1. Hydrogenation of linolenate and conjugated linoleate. Le, linolenate; CDT, conjugated diene-triene; CD, conjugated diene; D, nonconjugated diene; M, monene.

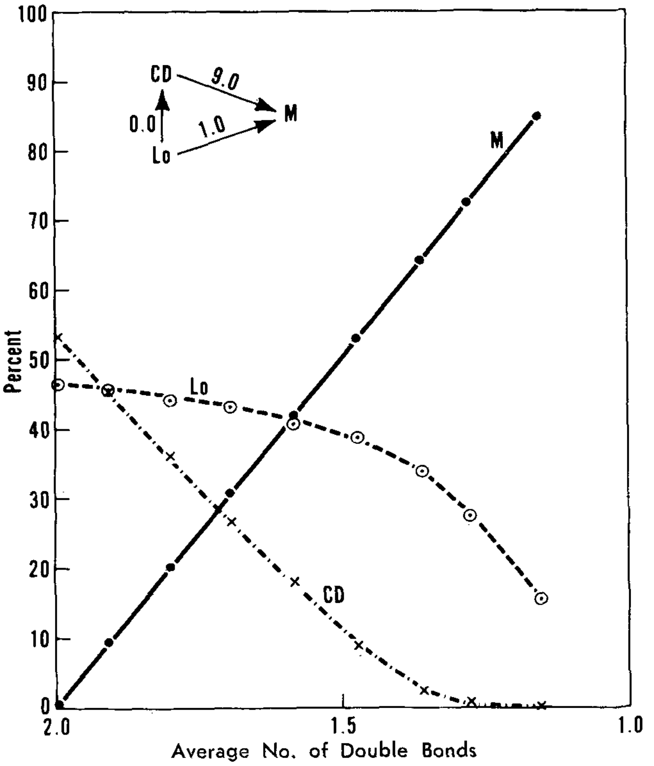


FIG. 2. Hydrogenation of linoleate and conjugated linoleate. Lo, linoleate; Conj. Lo, conjugated linoleate; M, monene.

(rate ratio greater than 200) and as long as eleostearate was present in the reaction mixture, little, if any, of the linolenate was reduced by the catalyst. Eleostearate was also reduced 40 times faster than conjugated diene. Alkali-isomerized linoleate reacted nine times faster than linoleate. All pure isomers were individually reduced at nearly equal hydrogenation rates. Thus, the competitive ratios reported are more a ratio of absorption equilibrium constants between isomer and catalyst than the ratio of hydrogenation rates. Evidently conjugated double bonds have greater affinity for the catalyst surface than methylene-interrupted double bonds. Linolenate would conjugate faster than linoleate because of the presence of two pentadiene structures. The resulting conjugated trienes, because of their greater affinity for the catalyst surface, will be hydrogenated in preference to other compounds.

Since conjugated dienes are the major products of hydrogenation of linolenate with copper chromite, a mixture of linolenate and conjugated linoleate was reduced and the reaction was followed by analysis of samples taken periodically (Fig. 1). As linolenate is reduced, conjugated diene concentration reached a maximum and then decreased. Conjugated diene-triene, which resulted from the conjugation of two double bonds in linolenate, also reached a maximum and diminished. The concentration of conjugated diene-triene is small because it is slightly more reactive than linolenate. Both monoene and nonconjugated diene continuously increased since they are the end products. This reaction was simulated on a digital computer (18) according to the scheme on Figure 1. When the theoretical computer curves best fitted the experimental data, the relative reaction rates shown in Figure 1 were obtained. Linolenate is first isomerized to conjugated diene-triene or conjugated triene. Since conjugated triene is preferentially adsorbed on the catalyst surface, it is first hydrogenated to conjugated diene before it is desorbed from the catalyst surface and, thus, is not seen in appreciable quantities. UV spectrophotometric analyses during the early stages of hydrogenation indicated 0.06% to 0.08% conjugated triene. Conjugated diene-triene was either hydrogenated to form nonconjugatable diene or was further isomerized and hydrogenated to form conjugated diene. Conjugated diene was then reduced to monoene. The competitive reaction rates obtained showed that most of the linolenate was reduced through the formation of conjugated triene.

Similar kinetic data for linoleate and conjugated linoleate are plotted in Figure 2. In the mixture, conjugated linoleate was reduced nine times faster than linoleate. Also the rates obtained from the digital computer indicated that little, if any, of the linoleate went through a conjugated diene, which desorbs from the catalyst surface. However, this result does not imply that linoleate is not conjugated on the catalyst surface. Some conjugated diene is formed when linoleate alone is reduced with copper chromite. An alternative scheme involving a common intermediate between chemisorbed linoleate and chemisorbed conjugated linoleate has been proposed to explain similar results with homogeneous catalysts (Frankel and Butterfield, submitted for publication). It would appear that hydrogenation of linoleate is more complex than indicated in the scheme. Further work with deuterium might explain the mechanism of hydrogenation of linoleate.

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