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Hydrogenation of Unsaturated Fatty Esters With Copper-Chromite Catalyst: Kinetics, Mechanism and Isomerization[1]

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Abstract

Hydrogenation of linolenate with copper chromite produced a large amount of conjugated diene and minor amounts of nonconjugatable dienes. The double bonds in conjugated dienes and monoenes were scrambled all along the chain. This product distribution can be explained if it is assumed that conjugation of the double bonds is followed by hydrogenation. In competitive hydrogenation, fatty esters with conjugated double bonds were reduced preferentially over fatty esters with methylene-interrupted double bonds. Isomerization of conjugated double bonds (geometric and positional) occurred more rapidly than reduction. Reduction of conjugated double bonds in the presence of deuterium resulted in a majority of the products containing no deuterium. Most of the added deuterium was incorporated into the unreacted material. Mechanisms are proposed to account for the products formed during the hydrogenation of linolenate, linoleate and their isomers.

Introduction

Adkins described the preparation of active copper-chromite catalysts for the hydrogenation of organic

TABLE I
Analyses of Products Formed During Hydrogenation of Methyl Linolenate and Its Isomers

Catalyst	Position of double bonds in trienes	Composition, %						UV abs.	Ref.
		S[a]	M	D	T	CD	CDT		
Copper chromite	9,12,15	....	29.8	8.9	22.9	33.8	4.6	31.6	17
Nickel	9,12,15	0.9	37.2	40.8	21.1	......	....	0.5	20
Copper chromite	5,9,12	0.8	27.3	39.4	30.2	0.9	1.4	......	18
Copper chromite	3,9,12	1.2	22.3	69.4	6.7	......	....	......	18

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

compounds (1-3). Some early work on the selective partial hydrogenation of triglycerides was carried out in Japan (4). The remarkable selectivity characteristics of copper-containing catalysts toward the preferential hydrogenation of linolenate in soybean oil is well documented in the literature (5-12). More active and selective copper catalysts have been prepared at the Northern Laboratory (13,14).

There is a dearth of information concerning the mechanism of hydrogenation with copper catalysts. A conjugation mechanism has been proposed, based on kinetic studies, to explain the unusual selectivity of copper catalysts toward linolenate (15,16). A series of reports from this laboratory (17-19) deal extensively with such mechanistic studies. In this review,
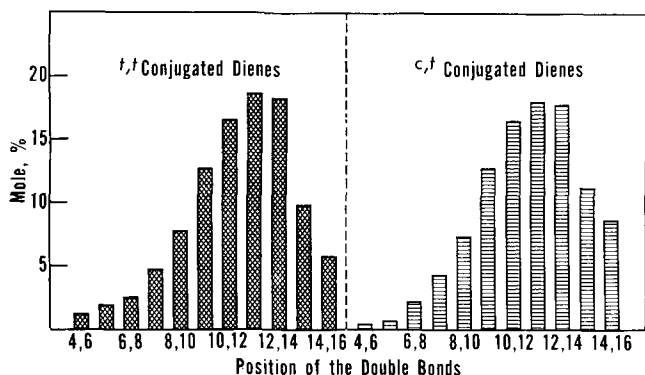

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FIG. 1. Composition of isomeric conjugated dienes formed during hydrogenation of linolenate with copper chromite (17).

some of our work will be described and reactions of unsaturated fatty esters with copper chromite based on conjugation of double bonds before hydrogenation will be explained.
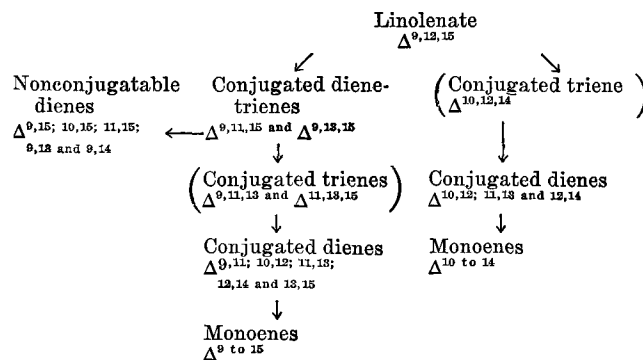
Hydrogenation of Linolenate and Its Isomers

The first indication that conjugation of double bonds plays a vital role in hydrogenating with copper catalysts came from the analysis of products formed during partial reduction of linolenate (Table I). Conjugated dienes are the major products with copper chromite. Only minor amounts of nonconjugated dienes which are not conjugated by alkali are formed. Nickel catalyst produces only nonconjugated dienes, some of which are alkali conjugatable (20). Conjugated dienes and monoenes formed with copper catalyst consist of a vast array of isomers (Fig. 1 and 2). Scheme 1 is proposed to account for the products formed.

Linolenate is first conjugated on the catalyst surface. Since conjugated trienes are much more reactive than linolenate (see further discussion), they do not accumulate appreciably in the products. They preferentially hydrogenate to conjugated dienes before they desorb. The conjugated double bonds in conjugated diene-trienes are (a) reduced to form the nonconjugatable dienes and (b) isomerized (18) to form conjugated trienes and then reduced to conjugated dienes. Conjugated dienes are further reduced to monoenes. Conjugated trienes are reduced by 1,2 and 1,6 addition of hydrogen, whereas conjugated dienes are reduced by both 1,2 and 1,4 addition (19). Only the primary products are shown in Scheme 1. Actually, a vast array of isomeric monoenes and dienes forms (Fig. 1 and 2). These other isomers arise by the rather extensive isomerization of the conjugated double bond systems during hydrogenation (19). Indeed, the initial rate of isomerization of conjugated double bond systems is much greater than hydrogenation (Koritala and Selke, unpublished data). The ability to isomerize conjugated double bonds during hydrogenation is unique for

copper catalysts since nickel, platinum and palladium catalysts do not possess this property (21,22 and unpublished data from this laboratory). Substantial amounts (12%) of monoene with a terminal double bond are formed (Fig. 2). This unusual isomer has not been detected with other catalysts.

The nature of the products formed during hydrogenation of other linolenate isomers ($\Delta^{5,9,12}$ and $\Delta^{3,9,12}$) also strongly suggests conjugation of the

Linolenate
$\Delta^{9,12,15}$

Nonconjugatable dienes
$\Delta^{9,15}$; 10,15; 11,15; 9,13 and 9,14

Conjugated diene-trienes
$\Delta^{9,11,15}$ and $\Delta^{9,13,15}$

(Conjugated triene)
$\Delta^{10,12,14}$

(Conjugated trienes)
$\Delta^{9,11,13}$ and $\Delta^{11,13,15}$

Conjugated dienes
$\Delta^{10,12}$; 11,13 and 12,14

Conjugated dienes
$\Delta^{9,11}$; 10,12; 11,13; 12,14 and 13,15

Monoenes
Δ^{10} to 14

Monoenes
Δ^{9} to 15

Scheme 1

double bonds before hydrogenation (Table I). Scheme 2 helps to explain the products.

Both triene isomers produce monoenes during hydrogenation. If conjugation had not taken place, then nonconjugatable dienes would be formed exclusively since neither monoenes nor isolated double bonds are reduced by copper chromite. Conjugation of the pentadiene group, followed by isomerization, forms conjugated triene, which is first reduced to conjugated diene and then to monoene. The conjugated diene system formed from $\Delta^{3,9,12}$ triene isomer is farther removed from the isolated double bond than it is in the $\Delta^{5,9,12}$ isomer. Therefore, the conjugated double bonds formed from $\Delta^{3,9,12}$ triene isomer have a greater chance of being reduced to nonconjugatable dienes than the conjugated double bonds formed from the $\Delta^{5,9,12}$ triene isomer. Consequently, less monoene is formed from $\Delta^{3,9,12}$ isomer than from $\Delta^{5,9,12}$ isomer (Table I). Isomers other than those in Scheme 2 are formed (Fig. 3) because conjugated double bonds are isomerized before hydrogenation.

Conjugated double bond systems are more reactive than methylene-interrupted double bonds in competitive hydrogenation (Table II). Eleostearate is reduced more than 200 times faster than linolenate. Eleostearate is competitively adsorbed on the catalyst surface and as long as eleostearate is present, linolenate is excluded from the catalyst surface. This unusually high reactivity of eleostearate helps to explain why conjugated trienes do not accumulate during hydrogenation of linolenate (Scheme 1). Linolenate, which contains three methylene-interrupted double bonds, is several orders more reactive than linoleate with only two. $\Delta^{5,9,12}$ Triene isomer containing one isolated
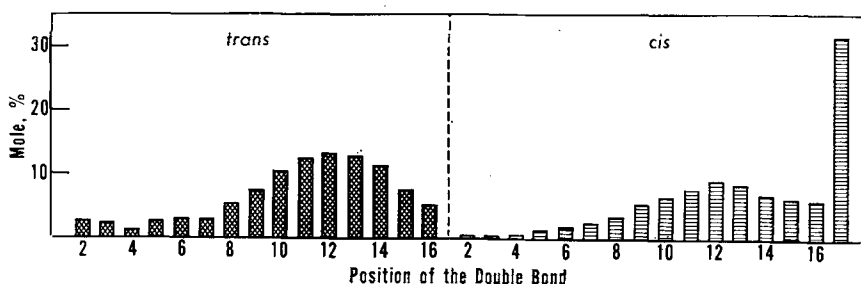

FIG. 2. Double bond distribution in *cis* and *trans* monoenes formed during hydrogenation of linolenate with copper chromite (17).
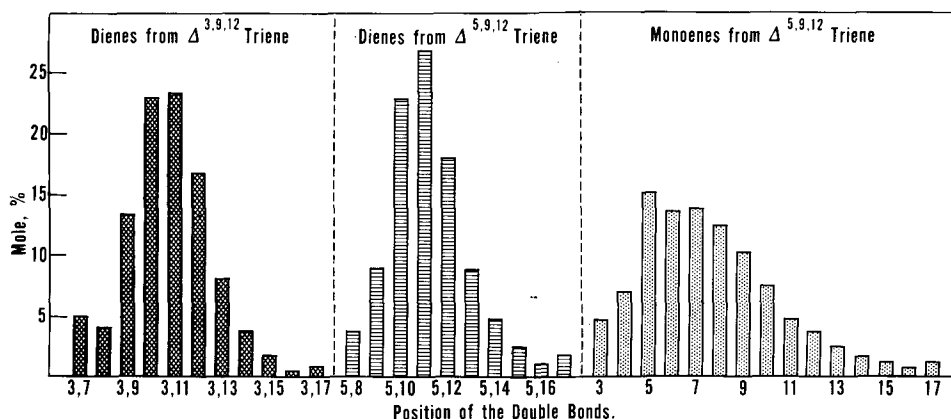
FIG. 3. Composition of isomeric monoenes and dienes formed during hydrogenation of $\Delta^{5,9,12}$- and $\Delta^{3,9,12}$-octadecatrienoates with copper chromite (19).

double bond behaves much like linoleate in competitive hydrogenation. Linolenate is much more reactive than this isomer. The unique selective characteristic of copper catalysts is attributable to their ability to conjugate the double bonds in linolenate more readily than the double bonds in linoleate and to their ability to adsorb preferentially and reduce conjugated trienes.

Hydrogenation of Linoleate and Its Isomers

Reduction of conjugated isomers of linoleate in the presence of copper chromite occurs by both 1,2 and 1,4 addition of hydrogen. Extensive isomerization of the conjugated double bonds during hydrogenation is indicated (19). Scheme 3 shows the pathway for the hydrogenation of linoleate.

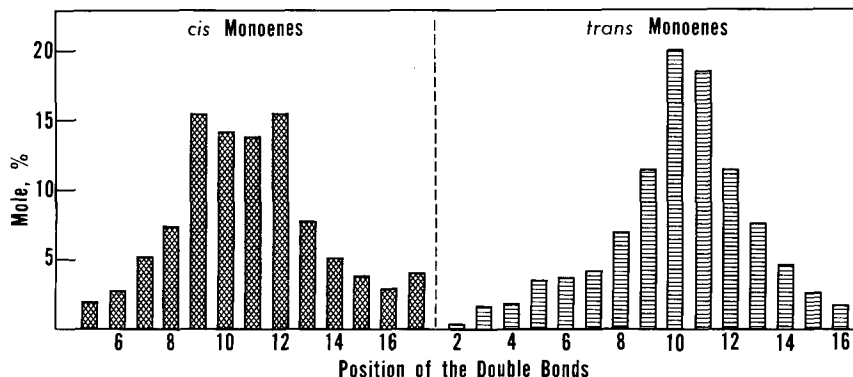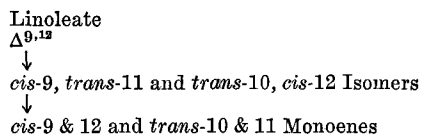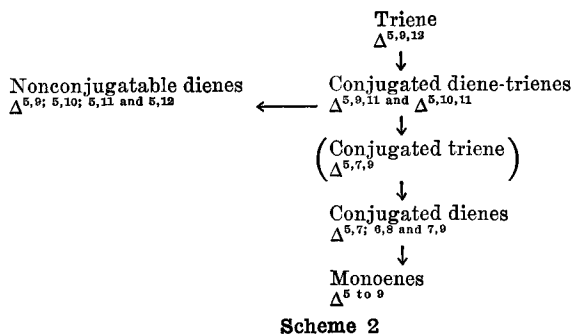Some conjugated diene is found during hydrogenation

Triene
$\Delta^{5,9,12}$
$\downarrow$

Nonconjugatable dienes   Conjugated diene-trienes
$\Delta^{5,9;\ 5,10;\ 5,11\ \text{and}\ 5,12}$ $\longleftarrow$ $\Delta^{5,9,11\ \text{and}\ \Delta^{5,10,11}}$
$\downarrow$

$\left(\begin{array}{c}\text{Conjugated triene}\\ \Delta^{5,7,9}\end{array}\right)$
$\downarrow$

Conjugated dienes
$\Delta^{5,7;\ 6,8\ \text{and}\ 7,9}$
$\downarrow$

Monoenes
$\Delta^{5\ \text{to}\ 9}$

Scheme 2

Linoleate
$\Delta^{9,12}$
$\downarrow$
cis-9, trans-11 and trans-10, cis-12 Isomers
$\downarrow$
cis-9 & 12 and trans-10 & 11 Monoenes

Scheme 3

of linoleate (19). While unreacted linoleate is largely unaffected, conjugated diene that formed during reduction is extensively isomerized. Because of this isomerization, the product distribution (Fig. 4) becomes more complex than is indicated in Scheme 3. The identical product distribution obtained during hydrogenation of linoleate and alkali-isomerized linoleate (19) strongly suggests a conjugation mechanism.

A conjugation mechanism has been proposed for the hydrogenation of linoleate with nickel catalyst (23–25). However, it is not the sole mechanism by which linoleate is reduced. Conjugation is an essential step during hydrogenation of linoleate with copper chromite because isolated double bonds are not reduced.

Deuterium Tracer Studies

A major portion of the initial products formed during hydrogenation of conjugated triene and diene with copper chromite in the presence of deuterium contained no deuterium (Table III). A large amount of the incorporated deuterium was found in the unreacted material. The addition reaction is much slower than isomerization and exchange reactions. Isomerization and exchange are suppressed with a sintered catalyst (Koritala and Selke, unpublished data), and a majority of the products are formed by direct 1,2 and 1,4 addition of two deuterium atoms to conjugated diene. Scheme 4 offers a mechanism to account for the reactions. Since no reaction occurs in the absence of hydrogen or deuterium, Step I involves the addition of one deuterium atom to carbon 9 to form monoadsorbed species (Horiuti-Polyani mechanism). Reversal of this step results in diadsorbed species. Since the ninth carbon atom of the monoadsorbed species is free to rotate, the reversal step (II) can occur by the loss of either hydrogen


FIG. 4. Double bond distribution in cis and trans monoenes formed during hydrogenation of linoleate with copper chromite (19).

TABLE II

Competitive Hydrogenation of 50:50 Binary Mixtures of Fatty Esters With Copper Chromite (18)

Ester mixture	Composition, %						Rate ratio
	M	D	T	CD	CDT	CT	
Eleostearate + linolenate	1.6	0.5	46.4	45.7	3.0	2.8	>200
Linolenate + linoleate	11.6	45.2	8.9	30.5	3.8	....	8
Linoleate + $\Delta^{5,9,12}$ triene	28.1	29.9 +9.1[a]	28.5	4.4	....	....	1
Linolenate + $\Delta^{5,9,12}$ triene	10.6	4.0	57.3[b]	23.0	5.1	....	14

[a] Diene formed from $\Delta^{5,9,12}$ triene.
[b] 13.0% Linolenate and 44.3% $\Delta^{5,9,12}$ triene.

TABLE III

Distribution of Deuterium in the Products Formed from Reduction (150 C and Atmospheric Pressure) of β-Eleostearate and Trans,trans 9,11-Octadecadienoate[a]

No. of deuterium atoms	Conjugated dienes from β-eleostearate at 5% reduction		Monoenes from trans,trans 9,11-octadecadienoate at 7.9% reduction	
	Trans, trans Conjugated diene, %	Cis, trans Conjugated diene, %	Trans monoene, %	Cis monoene, %
0	69.1	74.8	69.1	65.1
1	17.1	15.9	22.5	23.9
2	5.9	4.1	5.6	6.7
3	2.8	1.8	1.8	2.2
4	1.7	1.2	0.7	1.0
Other	Trace	Trace	Trace	Trace
D_{av}	0.63	0.49	0.43	0.55

[a] Koritala and Selke, unpublished data.

or deuterium. Loss of hydrogen produces a *cis,trans* isomer containing a deuterium atom. Since monoenes or isolated double bonds are not reduced by copper chromite, direct addition across a double bond is not plausible. The neighboring double bond must in some way be involved. The π

Trans-9,*trans*-11-conjugated diene
(Diadsorbed)
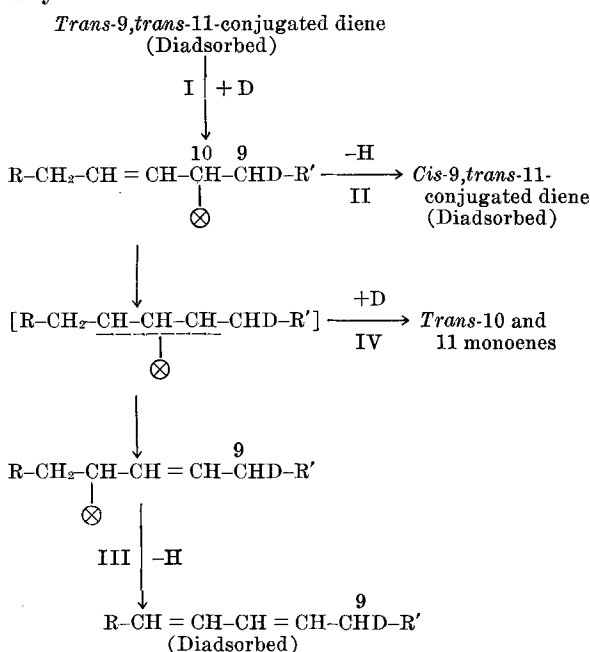
Scheme 4

electrons of the 11,12 carbon double bond could be delocalized along 10,11,12 carbon atoms to form π allyl-adsorbed species (26). Addition of another deuterium at the 10 or 12 carbon atom will result in Δ^{10} or Δ^{11} monoene. Positional isomerization occurs through Step III by the loss of a hydrogen atom on carbon 13. If deuterium is added on to the 10th carbon instead of the 9th at Step I, then no π allyl-adsorbed species could be formed. However, reversal to diadsorbed species through loss of hydrogen on carbon 10 would result in *cis,trans* isomerization. A similar

mechanism could be developed by first adding deuterium to the 11,12 double bond. Conjugated diene must not be strongly adsorbed on the catalyst surface. If it were, then it would not be desorbed unless it is hydrogenated and one would not see isomerized conjugated dienes in the products. Steps I and III, which result in isomerization and exchange, occur at a rate faster than Step IV, which is the addition reaction. Since Steps I and III increase concentration of hydrogen atoms on the catalyst surface, other conjugated diene molecules adsorbed on the catalyst surface will add hydrogen to obtain monoenes containing no deuterium.

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