Deuteration of Methyl Linoleate with Nickel, Palladium, Platinum and Copper-Chromite Catalysts[1]

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ABSTRACT

Samples taken during deuteration of methyl linoleate with the title catalysts were separated into saturate, monoene and diene fractions. Monoenes were further separated into *cis* and *trans* fractions. A comparison of the double bond distribution in monoenes with those from hydrogenation of alkali-conjugated linoleate indicated that up to 59% of the linoleate was reduced through a conjugated intermediate with nickel catalyst. The respective percentages for palladium and platinum catalysts were 51 and 23. Copper catalysts have previously been shown to reduce linoleate solely through conjugated intermediates. Copper-chromite catalyst showed infinite selectivity for the reduction of linoleate, because stearate did not form. The decreasing order of various catalysts for the selective reduction was copper-chromite>>>Ni at 195 C>Pd>Ni at 100 C>Pt. Computer simulation of platinum reduction indicated that ca. 20% of the linoleate was directly reduced to stearate through a shunt. Geometrical isomers of linoleate were formed during reduction with all catalysts except copper-chromite. Nickel catalyst formed both *trans,trans*- and *cis,trans*-isomers, as well as nonconjugatable dienes. These isomers were favored at the higher temperature and deuterium was incorporated into them. Palladium and platinum did not isomerize linoleate to nonconjugatable dienes. Because conjugated dienes are more reactive than linoleate, they were not found in appreciable amounts during reduction. Conjugated dienes were the only isomers formed with copper-chromite catalyst. Deuterium was found in these conjugated dienes, which were also extensively isomerized. As a result of isomerization and exchange during reduction of linoleate—as well as further exchange between deuterium and monoenes—a wide distribution of isotopic isomers in monoenes was found with nickel, palladium and platinum catalysts. Since isomerization of monoenes with copper-chromite is negligible, the isotopic distribution of monoenes must be due to exchange of intermediate conjugated dienes followed by addition.

INTRODUCTION

Linoleic acid is the most important fatty acid reduced during commercial hydrogenation of vegetable oils. Under favorable conditions, this acid reacts ca. 50 times faster than oleic acid (1). This unusual selectivity for linoleic acid is due to the formation of even more reactive conjugated intermediates (2-5). The present study was undertaken to follow the reaction between deuterium and methyl linoleate in the presence of nickel, palladium, platinum and copper-chromite catalysts.

EXPERIMENTAL PROCEDURES

Methyl linoleate was either purchased from The Hormel Institute or isolated from safflower oil methyl esters (6). Deuterations were carried out in a 150 ml magnetically stirred Magna-Dash autoclave provided with cooling jacket and sampling valve. Heat was provided by an electrically heated furnace that surrounded the autoclave. A millivolt temperature recorder-controller with a high limit cut-off was employed to monitor and control the reaction temperature. About 30 g of the ester and the catalyst that was previously equilibrated with deuterium were heated under nitrogen to reaction temperature. Nitrogen was replaced by 99.7% deuterium. The extent of reaction was followed by the drop in pressure in an external tank, which constantly fed the gas to maintain the desired pressure in the reaction vessel. Four samples were obtained during the reaction, which was terminated when the final sample had an average of ca. 1.2 double bonds.

Catalysts came from the following sources: 65% nickel on Kieselghur (G-49A, Girdler catalyst, Chemetron Corp.), 5% palladium on carbon (Baker & Co.), 5% platinum on carbon (Englehard Industries) and copper-chromite (G-13, Girdler catalyst). Nickel was used at 100 C and 30 psi for nonselective reduction and at 195 C and 8 psi for selective reduction. Palladium and platinum catalysts were employed at 8 psi and at 25 C and 35 C, respectively. Copper-chromite reduction was carried out at 160 C and 30 psi.

Fatty acid compositions of partially deuterated products were determined with a Varian Aerograph GC instrument equipped with dual 5 ft x 1/8 in. stainless steel columns, packed with 15% EGSS-X on Gas Chrom P and with flame ionization detectors. Peak areas were determined with a disc integrator. Selectivity ratios (K_{Lo}/K_{Ol}) were determined with a digital computer based on a program written by Butterfield and Dutton (7) where Lo = linoleate, Ol = oleate and K = reaction rate. Conjugatable and nonconjugatable dienes were estimated by alkali isomerization (1 hr) method (8).

Deuterated products were separated into stearate, monoene and diene fractions by reverse-phase chromatography (9). Monoene fractions were further separated into *cis*- and *trans*-monoenes on a silver-exchanged resin column (10). Per cent *trans* in the monoene was calculated on the basis of weight recovery of *cis*- and *trans*-monoenes. Per cent *trans* in diene fractions was measured by IR spectroscopy with methyl elaidate as the standard.

Positional isomers of *cis*- and *trans*-monoene were estimated by reductive ozonolysis (11) followed by temperature-programed (50-190 C at 6 C/min) gas chromatography. The mole per cent of each isomer was calculated by triangulation of the aldehyde ester peaks.

Isotopic analyses of various fractions were obtained with a Nuclide mass spectrometer. Deuterium contents were calculated as atoms per molecule from parent peaks, after correcting for the natural abundance of carbon, hydrogen and oxygen isotopes.

RESULTS AND DISCUSSION

The composition of the products formed during deuteration of methyl linoleate with several catalysts is shown in Table I. Selectivity for the reduction of linoleate with nickel can be varied by judicious choice of deuteration conditions. Palladium showed moderate selectivity, while platinum had the poorest selectivity. Computer simulation

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[1] Presented at the AOCS Meeting, Ottawa, September 1972.

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TABLE I

Composition of Products Formed during Deuteration of Methyl Linoleate

Sample	Wt %			D		% *trans*		Selectivity
	St[a]	M	CD	Conjugatable	Nonconjugatable	Monoene[b] fraction	Diene[c] fraction	K_{Lo}/K_{Ol}
Ni-100C - 1	0.5	16.9	Tr	80.2	2.4	45.3	1.9	8
Ni-100C - 2	1.1	30.0	0.0	66.9	2.0	45.3	2.6	
Ni-100C - 3	3.2	50.0	0.0	44.6	2.2	41.3	5.6	
Ni-100C - 4	10.5	71.0	0.0	16.2	2.3	43.0	12.5	
Ni-195C - 1	Tr	10.1	1.4	87.9	0.6	51.7	2.8	114
Ni-195C - 2	Tr	26.4	0.6	71.0	2.1	55.7	5.2	
Ni-195C - 3	0.4	53.9	Tr	42.9	2.9	55.1	9.9	
Ni-195C - 4	1.1	78.0	Tr	16.3	4.6	59.9	22.0	
Pd-25C - 1	Tr	8.6	Tr	91.4	0.0	50.2	1.3	22
Pd-25C - 2	0.3	23.5	Tr	76.2	0.0	57.2	2.2	
Pd-25C - 3	0.6	39.2	0.0	60.2	0.0	57.6	4.3	
Pd-25C - 4	1.8	64.0	0.0	34.2	0.0	61.2	7.5	
Pt-35C - 1	3.4	11.1	Tr	85.5	0.0	27.6	1.3	2
Pt-35C - 2	7.5	23.5	Tr	69.0	0.0	33.4	1.7	
Pt-35C - 3	12.0	36.7	Tr	51.3	0.0	33.2	3.1	
Pt-35C - 4	23.6	49.9	Tr	26.5	0.0	30.1	3.4	
CuCr-160C - 1	00.0	15.3	3.8	80.9	—	67.5	Tr	∞
CuCr-160C - 2	00.0	30.0	3.3	66.7	—	68.6	Tr	
CuCr-160C - 3	00.0	54.3	0.8	44.9	—	69.8	Tr	
CuCr-160C - 4	Tr	83.7	Tr	16.1	0.2	76.8	Tr	

[a] St, stearate; M, monoene; D, diene; CD, conjugated diene; Tr, trace.

[b] By siliver resin chromatography.

[c] By IR with methyl elaidate as standard.

of the reduction with platinum indicated that 20% of the linoleate was reduced directly to stearate through a shunt, without the intermediate monoene ever desorbing from the catalyst surface.

After copper-chromite, palladium and nickel at 195 C gave the highest amount of *trans*-monoene isomers, while platinum formed the least amount. With nickel catalyst, increasing the temperature of deuteration increased the formation of *trans*-monoene isomers. During reduction of linoleate it appears that a constant amount of *trans*-monoene isomers is formed. However during the final stages of the reaction *trans*-isomers tended to increase in some cases due to increased isomerization of monoenes as linoleate is depleted and to reduction of geometrical isomers of linoleate.

Three types of linoleate isomers can be distinguished from the results: conjugated, geometrical and nonconjugatable positional isomers. Conjugated diene, the most important intermediate with all catalysts except platinum, does not accumulate in appreciable amounts because it is 10-18 times more reactive than linoleate (12). Furthermore, conjugated dienes are irreversibly adsorbed on palladium and platinum, but on nickel catalyst they are only slightly reversible (13). In contrast, the chemisorption of conjugated dienes on copper-chromite is freely reversible (14), which explains why more conjugated diene is found with copper-chromite than with other catalysts.

Geometrical isomers of linoleate were formed with all catalysts except copper-chromite, as indicated by *trans* absorption in IR. The percentage *trans* values for diene (Table I) are lower than true values because deuterium interferes with the *trans* absorption band (15). Platinum formed only a small amount of geometrical isomers. Evidently linoleate is adsorbed strongly on this catalyst. On the other hand, chemisorption of linoleate on nickel and palladium catalysts is freely reversible as evidenced by increased formation of *trans*-diene isomers as deuteration progressed. The formation of these isomers with nickel is greater at the higher reaction temperature. With copper-chromite catalyst, *cis*- to *trans*-isomerization of the double bonds in linoleate was absent and the only isomers observed were conjugated dienes. These facts are in line with the previous hypothesis (16) that linoleate is reduced through a conjugated intermediate.

During reduction with palladium, platinum and copper-chromite catalysts, all the remaining diene was alkali-conjugatable and thus positional isomerization to form nonconjugatable dienes was absent with these catalysts. On the other hand, nickel catalyst produced nonconjugatable dienes at both temperatures. During selective reduction with nickel at 195 C, nonconjugatable dienes increased continuously because they are only slightly more reactive than monoenes (1). However under nonselective conditions some of this isomer was reduced to monoene and as a result did not accumulate.

The composition of monoene isomers formed during progressive deuteration is given in Figures 1-5.

With nickel, palladium and platinum catalysts *cis*-monoenes with double bonds at 9 and 12 positions and *trans*-monoenes with double bonds at 10 and 11 positions were predominant products. Scheme 1 shows the two pathways by which these products could be formed. More Δ^{9} and Δ^{12} *cis*-monoenes were formed with nickel at 100 C than at 195 C (Figs. 1 and 2). Evidently a greater proportion of linoleate is reduced through conjugation at the higher temperature. With platinum catalyst (Fig. 4), Δ^{9} and Δ^{12} *cis*-monoenes were the major isomers, which indicates that conjugation is relatively unimportant.

The per cent linoleate hydrogenated through the conjugated intermediate can be estimated by comparing the proportions of Δ^{10} and Δ^{11} *trans*-monoenes formed from linoleate to those from alkali-conjugated linoleate (17), which was hydrogenated with these catalysts under similar conditions. For example, alkali-conjugated linoleate formed 64.3% of Δ^{10} and Δ^{11} *trans*-monoenes with nickel at 195 C (17). At the same temperature, linoleate gave 38.1% of these isomers in the second sample (Fig. 2), which was reduced approximately to the same extent as alkali-conjugated linoleate. Thus ca. 59% of the linoleate was reduced through conjugation with nickel at 195 C. The respective percentages for palladium and platinum were 51 and 23. The remainder was presumed to be reduced by 1,2-addition to the double bonds in linoleate.

Actually less than the calculated percentage of linoleate was conjugated with platinum, since a considerable proportion of the Δ^{10} and Δ^{11} *trans*-monoenes are formed by

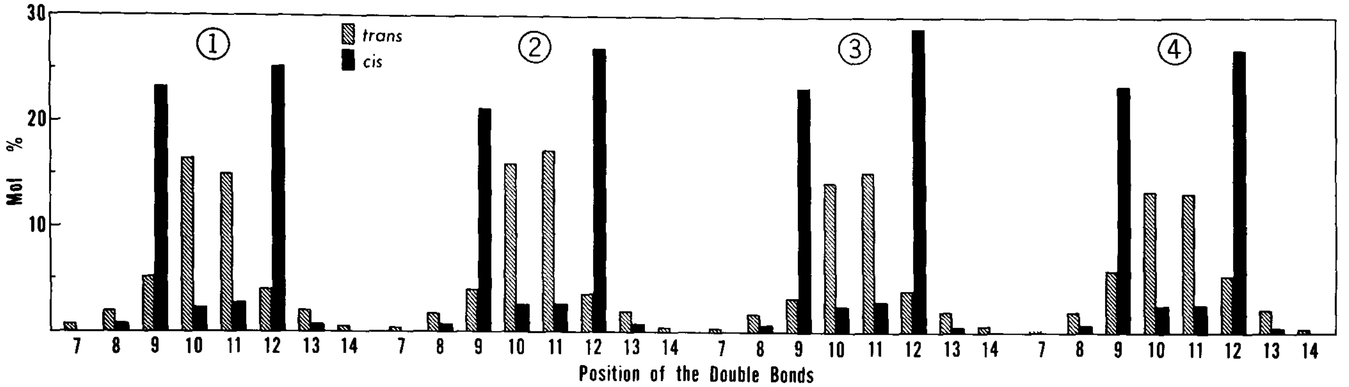


FIG. 1. Composition of monoene isomers formed during progressive deuteration of linoleate with nickel at 100 C and 30 psi.

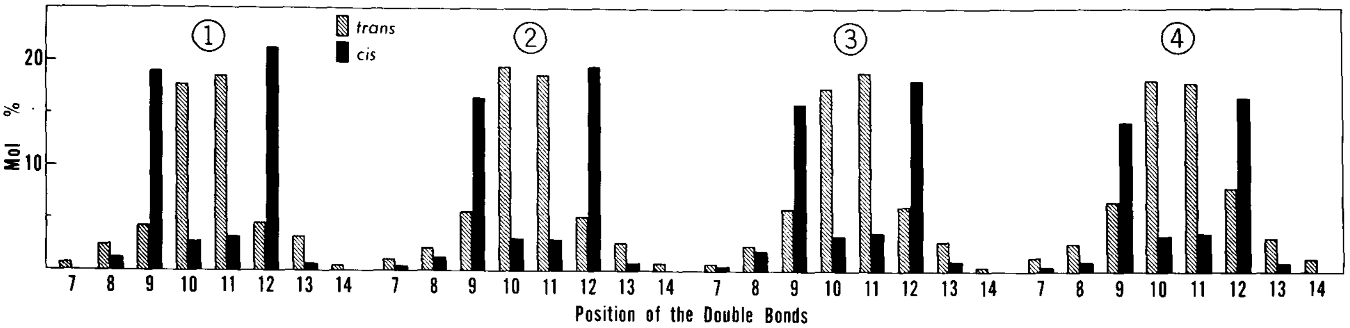


FIG. 2. Composition of monoene isomers formed during progressive deuteration of linoleate with nickel at 195 C and 8 psi.

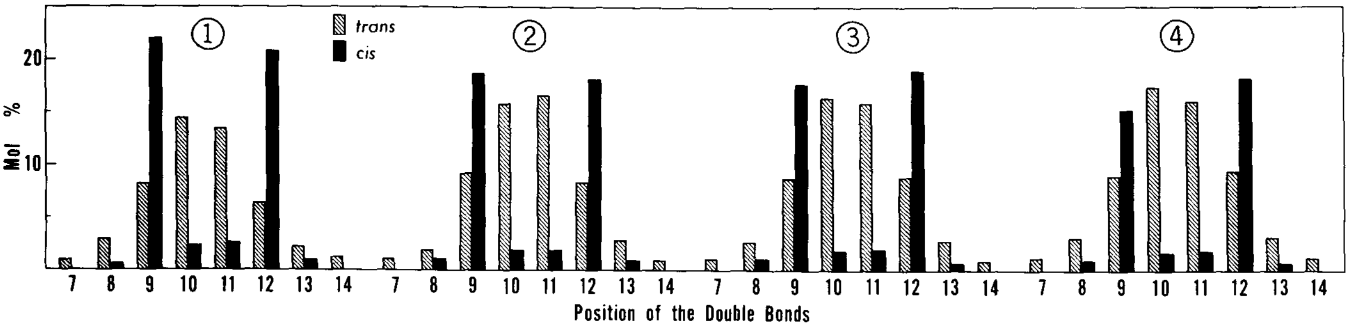


FIG. 3. Composition of monoene isomers formed during progressive deuteration of linoleate with palladium catalyst.

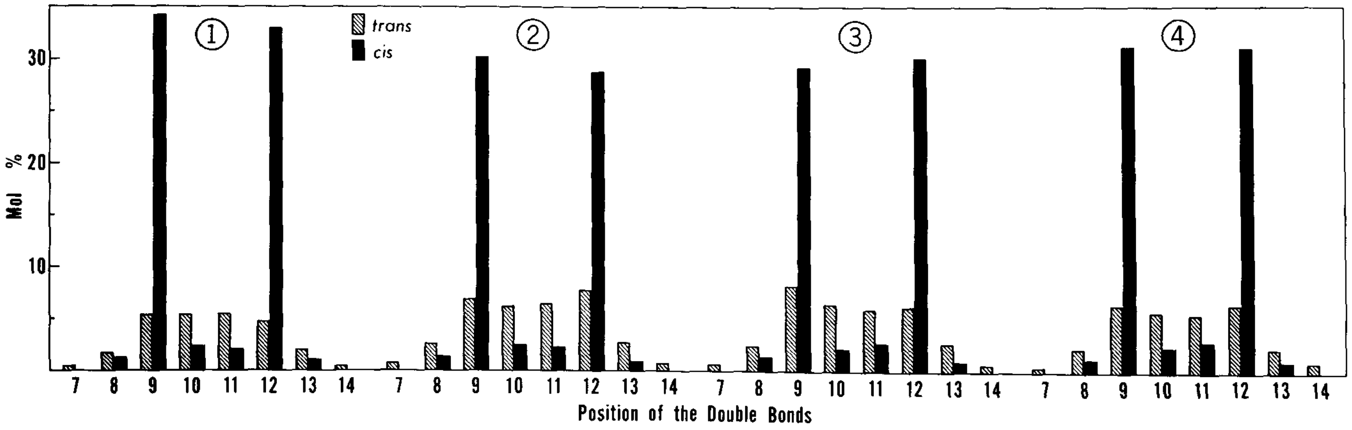


FIG. 4. Composition of monoene isomers formed during progressive deuteration of linoleate with platinum catalyst.

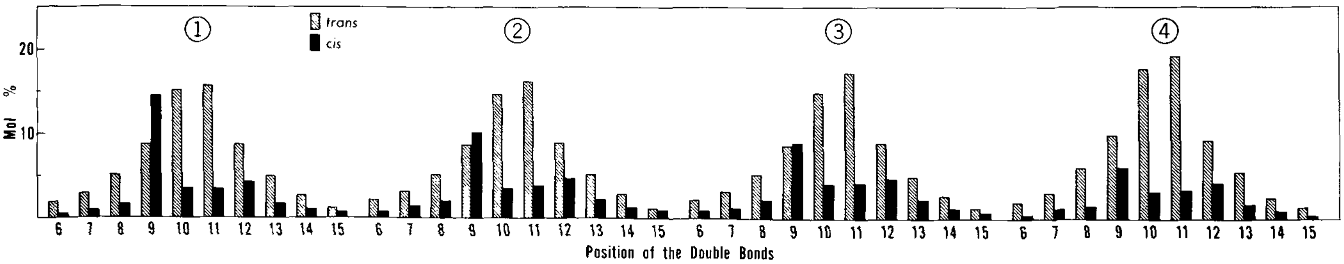


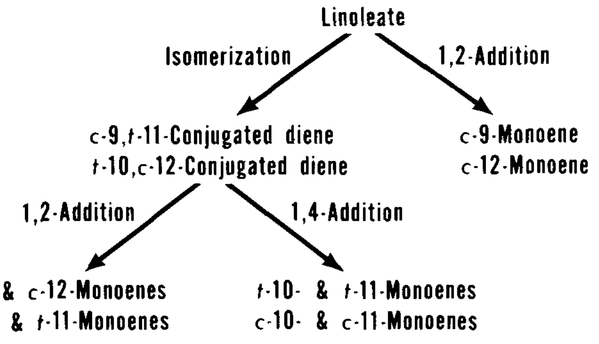
FIG. 5. Composition of monoene isomers formed during progressive deuteration of linoleate with copper-chromite catalyst.

isomerization of Δ^9 and Δ^{12} *cis*-monoenes as judged by the *trans-cis* ratios in Δ^{10} and Δ^{11} monoenes. As shown in Scheme 1, 1,4-addition to conjugated dienes results in a new bond, predominantly with *trans* configuration and only minor amounts with *cis* configuration (13). As a result the ratio of *trans-cis* in Δ^{10} and Δ^{11} monoenes would be expected to be very high. A ratio of 7 can be calculated for these isomers, which resulted from hydrogenation of alkali-conjugated linoleate with platinum catalyst (17). A high *trans-cis* ratio would also be expected during reduction of linoleate with platinum, if Δ^{10} and Δ^{11} monoenes were formed exclusively from conjugated dienes. Actually a value of 2-3, which nearly corresponds to equilibrium value, was calculated. Evidently Δ^9 and Δ^{12} *cis*-monoenes, which constitute the major products, isomerized during their reduction to stearate. Since double bonds migrate equally in both directions during reduction of monoene with platinum catalyst (15), the amounts of Δ^{10} and Δ^{11} *trans*-monoenes formed by isomerization of *cis*-monoenes are approximately equal to $\Delta 8$ and $\Delta 13$ *trans*-monoenes, respectively. If this correction is applied, the new Δ^{10} and Δ^{11} *trans*-monoene values indicate that only 13% of the linoleate was reduced through conjugation.

The calculated percentages of linoleate conjugating on the catalyst surfaces were only estimates. They do point out that conjugation plays an important role with nickel and palladium catalysts, which exhibited selectivity, whereas the same mechanism is relatively unimportant with nonselective platinum catalyst. Conjugation is an obligatory step (16) with copper-chromite catalyst, which showed infinite selectivity. Thus there is *prima facie* evidence relating selectivity to the conjugation of double bonds.

Copper-chromite catalyst initially formed an unexpectedly higher amount of Δ^9 *cis*-monoene than Δ^{12} *cis*-monoene (Fig. 5). One probable explanation of this peculiar phenomenon, which disappeared as deuteration progressed, is that the $\Delta^{10,12}$ conjugated diene isomerized more readily than the $\Delta^{9,11}$. The wide distribution of monoene isomers is in accordance with the previous hypothesis (16) that the obligatory conjugated diene intermediate isomerizes extensively during its reduction. The small amounts of conjugated dienes from fractions 1 and 2 (Table I) isolated by preparative gas liquid chromatography were found to consist of *cis,trans*- and *trans,trans*-isomers. Ozonolysis showed a wide distribution of positional isomers ranging from $\Delta^{5,7}$ to $\Delta^{14,16}$. Reduction at 30 psi resulted in monoenes with double bonds from 6 to 15 positions, whereas atmospheric pressure hydrogenation (18) gave all possible positional isomers. Positional isomerization of conjugated dienes is therefore suppressed, because conjugated dienes are reduced rapidly at the higher pressure.

With nickel, palladium and platinum catalysts, several monoene isomers other than the Δ^9 and Δ^{12} *cis*-monoenes and Δ^{10} and Δ^{11} *trans*-monoenes are formed (Figs. 1-4), either by isomerization of dienes followed by reduction or by isomerization of monoenes, or both. Because positional



SCHEME 1.

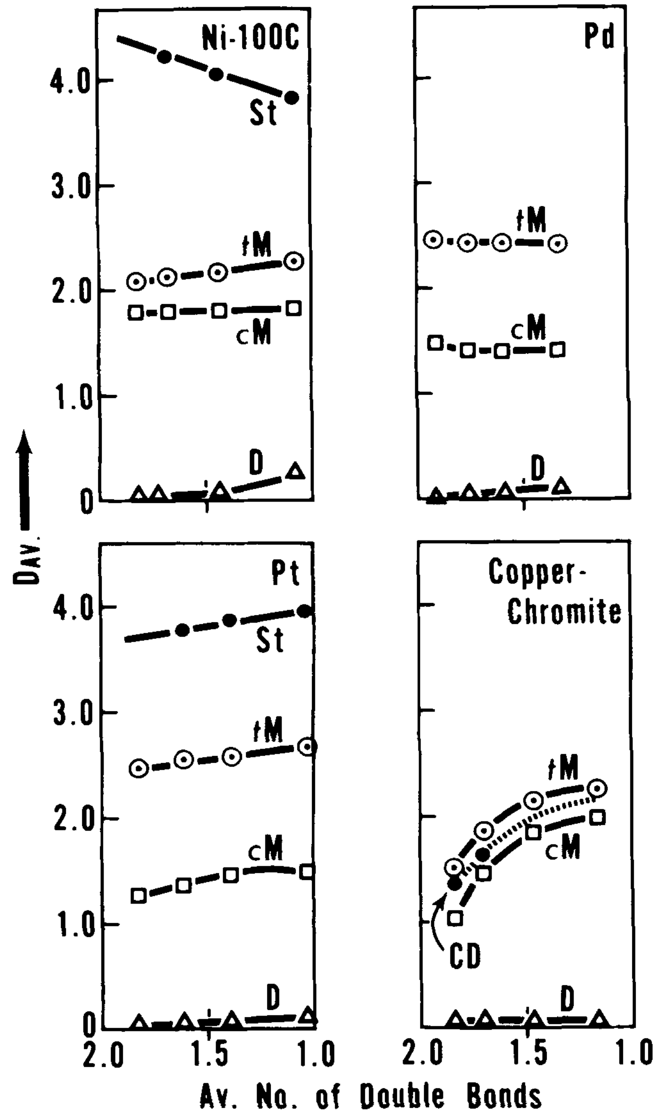
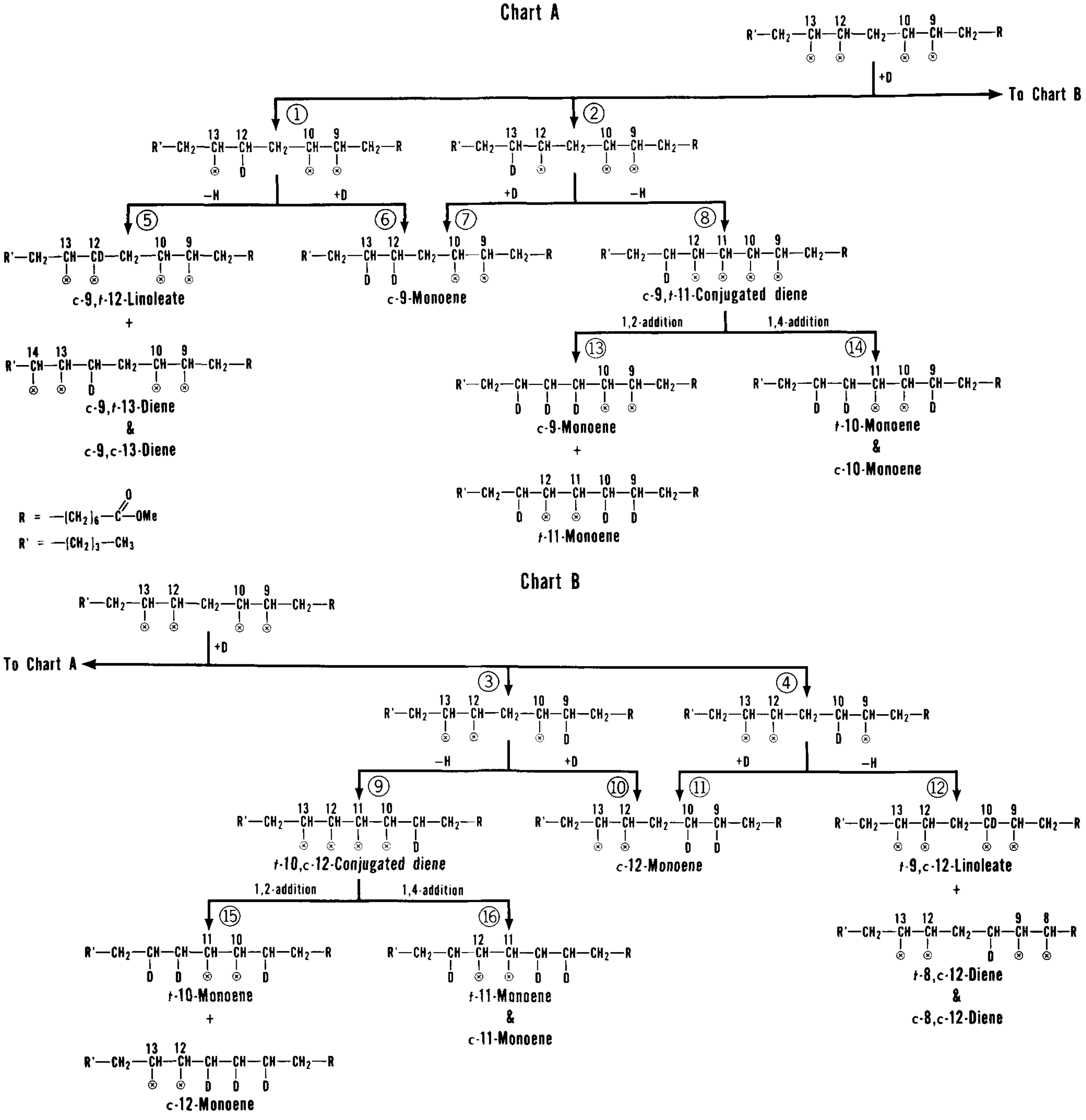


FIG. 6. Change in deuterium content of various products during reduction of linoleate with Ni at 100 C and 30 psi; palladium; platinum and copper-chromite catalysts. *t*M, *trans*-monoene; *c*M, *cis*-monoene; D, diene; St, stearate; CD, conjugate diene.



SCHEME 2.

and geometric isomerization of linoleate is negligible with palladium and platinum catalysts (Table I) and because conjugated dienes do not isomerize with these catalysts (13,17), these other isomers must have formed by isomerization of monoenes. In the case of nickel, these other isomers are formed to a limited extent by isomerization of dienes followed by reduction and to a large extent by isomerization of monoenes. With all three catalysts, measurable amounts of monoenes with double bonds at the 7 and 14 positions are formed. Since conjugated dienes (17) did not form these two isomers under similar conditions, they must result from isomerization of monoenes. It would thus appear that, whereas conjugated dienes (17) have a tendency to exclude monoenes from nickel, palladium and platinum catalyst surfaces, monoenes can effectively compete for the surface of these catalysts in the presence of linoleate. With copper-chromite catalyst, monoene isomerization is negligible (18) and the wide distribution of monoenes is due to extensive isomerization of conjugated dienes.

As shown in Scheme 1, Δ^9 and Δ^{12} *cis*-monoenes and Δ^{10} and Δ^{11} *trans*-monoenes are primary products resulting from reduction of linoleate. All other isomers in Figures 1-4 are formed by isomerization of monoenes. With nickel catalyst at 100 C, 11-12% of *cis*-monoene and 27-37% of *trans*-monoene were formed by isomerization. These values increased to 17-24% of *cis*- and 30-39% of *trans*-monoenes at 195 C. About 13-14% of *cis*- and 43-45% of *trans*-monoenes were calculated to be isomerized with palladium catalyst, whereas 9-11% of *cis*- and 62-63% of *trans*-monoenes were derived by isomerization with platinum catalyst. These values indicate that *trans*-monoenes are more extensively isomerized than *cis*-monoenes. The extensive isomerization in *trans*-monoenes formed with platinum catalyst is responsible for the low *trans* content in Δ^{10} and Δ^{11} monoenes. The percentages of monoenes *(trans + cis)* isomerized during linoleate reduction are 18-23% for nickel at 100 C and 23-33% at 195 C, 28-33% for palladium and 23-28% for platinum.

Typical distribution of deuterium in the products formed during reduction of linoleate with nickel catalyst at 195 C is given in Table II. Similar distributions obtained with other catalysts are graphically represented in Figure 6. *Trans*-monoenes contained more deuterium than the *cis* because of isomerization and consequent exchange of hydrogen for deuterium atoms. As seen from Scheme 2, *trans*- and *cis*-monoenes formed through the conjugated intermediate (steps 13-16) contain the same amount of deuterium. But the *cis*-isomers formed by 1,2-addition of linoleate (steps 6, 7, 10 and 11) contain one less deuterium. Isomerization of formed monoenes further increases the deuterium content by exchange (15); and since a greater percentage of *trans*- than *cis*-monoenes are formed through isomerization of monoenes, more deuterium is expected in the *trans*- than in the *cis*-monoene. The difference in the deuterium content between *cis*- and *trans*-monoenes is greatest with palladium and platinum catalysts, which also showed the highest isomerization in *trans*-monoenes. With copper-chromite catalyst, both *cis*- and *trans*-monoenes contained little deuterium initially and diene fraction showed only small amounts of deuterium. Preparative gas chromatography of the first two diene fractions indicated no deuterium in linoleate, whereas conjugated dienes are heavily deuterated. As reduction progressed, these deuterated conjugated dienes are reduced to give monoenes with increased deuterium content. These results indicate that the process of conjugated diene isomerization involves the presence of deuterium.

Palladium and platinum catalysts adsorb linoleate irreversibly, since very little deuterium was found in the diene. A considerable amount of deuterium was found in the diene with nickel catalyst, the higher temperature showing the greater amount of deuterium. To further identify the deuterium-containing species, the diene fraction of the final product from nickel reduction at 195 C was fractionated on a short silver-exchanged column into *trans,trans, cis,trans* and *cis,cis* fractions. Separation was incomplete as indicated by the presence of 18% *trans* in the *cis,cis* fraction. *trans,trans*-Diene (6%), which has necessarily undergone at least two alternations between chemisorption and half-hydrogenated state, contained on the average 0.93 deuterium atoms per molecule. *cis,trans*-Diene (30%), which has reacted with the catalyst at least once showed less deuterium (d_{av} = 0.65). Alkali isomerization indicated that 90% of this fraction is conjugatable. Ozonolysis showed that the double bonds are mostly at 9 and 12 positions. These results indicate that the *cis,trans*-diene fraction consists mostly of 9-*cis*,12-*trans* and 9-*trans*,12-*cis* octadecadienoates. The *cis,cis*-diene fraction (64%), which contained some deuterium (d_{av} = 0.25), was conjugated by alkali-isomerization and separated by preparative gas liquid chromatography into conjugated diene and nonconjugatable diene fractions. Nearly all the deuterium was found in the nonconjugatable diene (d_{av} = 0.69), which consisted of 27% of the *cis,cis* fraction. IR showed 70% *trans*, and ozonolysis indicated that they are composed of $\Delta^{9,13}$ and $\Delta^{8,12}$ isomers. Conjugated diene fraction, which consisted mostly of $\Delta^{9,11}$ and $\Delta^{10,12}$ *cis,trans*-isomers, was derived from linoleate and its deuterium content was low (d_{av} = 0.13). Analysis of the final diene fraction of nickel reduction at 100 C also showed similar isomers and similar deuterium contents, although their proportion and their deuterium content was smaller. These deuterium distributions indicate that linoleate is isomerized to geometrical and positional isomers and, in this process, incorporates deuterium.

The deuterium content of stearate progressively decreased as the deuterium content of monoenes increased

TABLE II

Distribution of Deuterium in Products Formed during Deuteration of Methyl Linoleate with Nickel Catalyst at 195 C

No. of deuterium atoms	Stearate				*cis*-Monoene				*trans*-Monoene				Diene			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
0	11.2	7.0	6.1	5.6	37.6	26.6	24.8	21.8	18.9	18.4	17.6	16.8	93.1	92.9	86.0	71.3
1	12.1	15.0	16.1	17.0	30.5	32.7	32.7	33.6	32.0	30.9	30.7	29.4	4.1	5.8	12.0	23.1
2	16.4	21.1	23.3	24.8	16.5	22.7	23.5	24.5	25.5	24.8	25.4	26.1	2.1	0.8	1.5	4.3
3	16.2	19.0	20.1	21.8	7.7	9.4	9.9	10.3	12.1	12.4	12.7	13.6	0.7	0.4	0.5	1.1
4	12.9	13.1	12.9	13.2	3.4	3.8	4.0	4.5	5.3	5.9	5.8	6.4				0.3
5	8.4	7.9	7.1	6.9	1.7	1.9	2.0	2.1	2.6	2.8	2.9	3.0				
6	5.0	4.6	4.1	3.5	0.9	1.0	1.0	1.1	1.4	1.5	1.6	1.7				
7	3.4	2.8	2.5	2.0	0.5	0.6	0.7	0.6	0.8	1.0	0.9	0.9				
8	2.5	1.9	1.5	1.3	0.4	0.4	0.4	0.4	0.4	0.7	0.7	0.6				
9	1.5	1.4	1.1	0.9	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4				
10	1.6	1.1	0.8	0.7	0.2	0.2	0.2	0.2	0.2	0.3	0.4	0.3				
11	1.1	0.9	0.8	0.5	0.3	0.1	0.1	0.1	0.2	0.3	0.2	0.2				
12	1.1	0.7	0.6	0.4	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2				
Others	6.6	3.5	3.0	2.4	—	0.2	0.3	0.4	0.2	0.3	0.3	0.4				
d_{av}[a]	4.40	3.70	3.47	3.12	1.30	1.54	1.60	1.68	1.83	1.95	1.97	2.01	0.10	0.09	0.17	0.36

[a] Average number of deuterium atoms per molecule.

during reduction with nickel catalyst. One possible explanation of this unusual behavior is that isomerization and addition reactions occur at different sites on the catalyst surface where the relative hydrogen and deuterium concentrations may be different.

With nickel catalyst at 195 C, up to four deuterium atoms were incorporated into diene by isomerization and exchange. Isotopic diene isomers above d_3 were not found with platinum, whereas palladium did not form dienes containing more than two deuterium atoms. Addition of deuterium to these isomers could result in monoenes containing up to six deuterium atoms. However small amounts of monoenes containing up to 20 deuterium atoms were formed. These perdeuterio monoenes must have resulted from isomerization and exchange of monoenes rather than from simple addition of 1 mol of deuterium.

From these experimental results, Scheme 2, which is an extension of the half-hydrogenated state mechanism first proposed by Horiuti and Polanyi (19) for the hydrogenation of ethylene, is developed to account for the isomerization reactions occurring during hydrogenation of linoleate. No experimental evidence exists for the proposed tetra-adsorbed species. However such a chemisorbed species is expected to be much more strongly adsorbed than monoenes. The formation of conjugated diene intermediates and their 1,4-addition can be explained with the proposed chemisorbed species.

Addition of a deuterium atom at any of the four different adsorption sites forms four different half-hydrogenated intermediates (steps 1-4). Addition of another deuterium atom to these four intermediates results in Δ^9 and Δ^{12} *cis*-monoenes (steps 6, 7, 10 and 11). This is the primary route for the reduction of linoleate with platinum catalyst. In accordance with the half-hydrogenated state pivot rule (20), removal of the added deuterium will result in original compound, whereas the loss of hydrogen from either adjacent carbon atom results in deuterated dienes which are geometrical and positional isomers of linoleate (steps 5 and 12). The addition of deuterium to carbons 9 and 13 of chemisorbed linoleate (steps 2 and 3) followed by abstraction of a hydrogen from the active methylene group results in the two conjugated dienes (steps 8 and 9), which undergo further addition to form Δ^9, Δ^{12} *cis*- and Δ^{10}, Δ^{11} *trans*-monoenes (steps 13-16). On the other hand, if the first deuterium adds to carbons 10 or 12 (steps 1 and 4), reversal by loss of hydrogen results in geometrical and positional isomers, which can further undergo addition and isomerization reactions. Palladium and platinum formed only small amounts of geometrical isomers and none of the positional isomers, probably because addition of another deuterium atom to form monoenes is faster, relative to loss of hydrogen.

ACKNOWLEDGMENTS

Technical assistance was provided by J. Snyder and W.L. Everhart.

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[Received December 11, 1972]