Homogeneous Catalytic Hydrogenation of Unsaturated Fats: Iron Pentacarbonyl[1]

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Abstract

Iron pentacarbonyl is an effective homogeneous catalyst for the reduction of polyunsaturated fats. Hydrogenation of soybean oil and its methyl esters has been achieved at 180C, hydrogen pressures of 100–1,000 psi, and 0.05–0.5 molar concentrations of catalyst. Analyses of partially reduced products show considerable isomerization of double bonds, reduction of linolenate and linoleate with little or no increase in stearate, and accumulation of cis,trans- and trans,trans-conjugated dienes, and isolated trans monoenes. The unreduced trienes include diene conjugated fatty esters. The nonconjugated dienes contain large amounts of trans and nonalkali conjugatable unsaturation. Considerable scattering of double bonds is evident in different fractions between the C_4 and C_{16} positions. Complex formation between iron carbonyl and unsaturated fats is also indicated.

The course of the homogeneous hydrogenation catalyzed by iron pentacarbonyl appears similar to the heterogeneous catalytic reaction. Metal carbonyls are well known for their isomerizing effects and their ability to form stable complexes with olefins. These homogeneous complexes provide suitable model systems to study the mechanism of catalytic hydrogenation of fats.

Introduction

STUDIES IN homogeneous catalytic hydrogenation with soluble ions or organic complexes of transition metals have generated considerable interest recently in elucidating the mechanism of heterogeneous catalysis (10,11,12,36). Greater selectivity also may be possible with certain homogeneous catalysts. For example, the selective reduction of sorbic acid (2,4-hexadienoic acid) was achieved by using pentacyanocobaltate (II) as catalyst under homogeneous conditions (8,19). With this catalyst the selective formation was obtained of 82% 2-hexenoic acid in aqueous solution and 93% in methanolic solution (21). Homogeneous catalytic hydrogenation, however, has been achieved in relatively few polyunsaturated compounds (13,19).

Metal carbonyls have received considerable attention recently because of their use in the hydroformylation (oxo) reaction and particularly their role in elucidating the chemistry of organometallic compounds. Several reviews have appeared on the structure of metal carbonyls and of olefin-metal carbonyl complexes (3,5,24). Homogeneous reactions catalyzed by metal carbonyls have been reviewed by Wender and Sternberg (36), but relatively little has been reported about these catalysts in homogeneous hydrogenation in the absence of carbon monoxide. This group of workers (32) recently found that cobalt and manganese carbonyls catalyze the hydrogenation of 1-octene at 80–150C and hydrogen pressures of 3,000–3,500 psi. With cobalt carbonyl, some nonyl alcohol was formed as a result of the hydroformylation reaction.

Waterman (34) reported the "homogeneous" hydrogenation of ethyl linoleate and linseed oil by means of nickel carbonyl at 50C and atmospheric pressure hydrogen. However, the catalyst was first decomposed at 120–145C in nitrogen to colloidal nickel. The slow accumulation of saturated fatty acids was taken as evidence of high selectivity. More recently, Hashimoto and Shiina (14) reported the hydrogenation of soybean oil with iron pentacarbonyl. At 180C and hydrogen pressure of 280 psi, the reaction was sluggish and the iodine value (I.V.) was not reduced below 100. However, when the catalyzed reaction mixture was first heated in nitrogen at 180–200C for 1 hr then cooled and the nitrogen replaced with hydrogen, subsequent hydrogenation at 180C and 280 psi proceeded smoothly and the I.V. was reduced to 40. The reduced product had measurable amounts of conjugation. Later, the same workers (15) obtained up to 30% conjugated dienes (cis,trans and trans, trans) and nonconjugated trans unsaturation by heating soybean oil and methyl linoleate with iron pentacarbonyl at 180–200C under nitrogen.

Research has been initiated at this Laboratory to survey potential fat-soluble organometallic complexes that may act as selective homogeneous hydrogenation catalysts for soybean oil. Metal carbonyls constitute a readily available source of fat-soluble transition metals that complex with various olefins, and catalyze reactions at the double bond. Because reactions catalyzed by metal surfaces are also catalyzed by metal carbonyls (33), our understanding of heterogeneous catalytic hydrogenation of fats may be improved by studies with these soluble catalysts.

In both studies of Waterman (34) and Hashimoto and Shiina (14) the extent of hydrogenation of oils was followed by I.V. determinations. This measure is in doubt since the decrease in I.V. may well be largely contributed by the conjugation and isomerization of the unsaturation in the oils. Therefore, the homogeneous hydrogenation of unsaturated fats with iron pentacarbonyl was investigated in detail; the products were analyzed by GLC, UV, and IR spectroscopy, countercurrent distribution, TLC, and oxidative cleavage. This paper deals with the reduction of soybean oil and its methyl esters. Reduction with manganese and cobalt carbonyls will be reported subsequently.

Experimental

Materials. The soybean oil was commercially refined and bleached, and laboratory deodorized. The methyl esters were obtained by transesterification of the oil with potassium methoxide and distilled from a Claisen flask under vacuum. The I.V. by hydrogen absorption (23) was 135.

Hydrogenation. Soybean oil and methyl esters were hydrogenated in either a 100-ml high-pressure rocking stainless steel autoclave, or in a 500-ml Magna-Dash autoclave. Low pressure hydrogenations were conducted in a heavy glass bottle of a Parr laboratory shaking apparatus. The hydrogenated products were

TABLE I

Hydrogenation of Soybean Oil[a] with Iron Pentacarbonyl (180C, 0.5 Mole Catalyst)

Run No.	Hydrogen pressure psi	Time hr	Bomb	I.V. (calc.[b])	Decrease		Increase	Conj. diene [a]233 mμ	Trans (as elaidate) %
					Triene %	Diene %	Monoene + saturates %		
1	50	3	Parr	130	0.7	1.0	0.3	0.9	0
2	100	2	Rocker	118	7.4	17.0	6.1	18.0	13.7
3	100	1 + 1[c]	Rocker	118	7.2	20.6	6.0	19.8	15.0
4	100	1(N₂) + 1[c]	Rocker	121	7.7	18.9	3.4	18.4	12.8
5	350	1 + 2[c]	Rocker	107	6.3	27.5	16.1	17.3	18.6
6	400 + 1000	1 + 2[c]	Rocker	90	9.2	33.2	28.4	11.6	32.7
7	120	2	Magna-Dash	91	9.2	36.5	33.5	13.6	34.8

[a] Composition (GLC), %: Palmitate 11.0, stearate 3.6, oleate 25.8, linoleate 50.5, linolenate 9.2; I.V.: 135.
[b] Calculated from GLC composition. Includes conjugated dienes.
[c] Interrupted runs. Example Run 3: react 1 hr, cool to room temp, release pressure, recharge with hydrogen, and react another hr.

dissolved in petroleum ether and washed 3–4 times successively, first with dilute HCl (2:1), then with dilute KOH (10%), and finally with distilled water until the washings were neutral. After drying over sodium sulfate and removal of solvent, the products were deep yellow. The reduced soybean oils were converted to methyl esters before analyzing by the transmethylation procedure of Luddy et al. (20). The reduced methyl esters were analyzed either directly after washing, or after vacuum distillation through a short Vigreaux column. Clear methyl esters were distilled at 120–140C/0.02 mm Hg in 90% yield, and a deep reddish-brown residue was left.

Analyses by GLC were carried out with a Hy-Fi flame ionization Aerograph and a 4 ft x ⅛ in. column packed with Chromosorb W, 60–80 mesh, coated with 15% diethylene glycol succinate. Optimum separations were obtained at 170–175C and nitrogen flow rate of 30–40 ml/min. Peak-area measurements were made by triangulation.

IR and UV spectrophotometric analyses of geometric and conjugated isomers were made by procedures described previously (29). The presence of iron carbonyl in the reduced products was detected by IR measurements in the 5 μ region (carbonyl stretching) with CCl₄ solutions. UV analyses of alkali-isomerized acids (45-min heating) were made by the procedure of Brice et al. (4).

Countercurrent distribution (CCD) between *n*-hexane and acetonitrile was used to fractionate fatty methyl esters according to degree of unsaturation (30). Individual fractions were monitored by GLC and TLC. Fractions were then combined into monoenes, dienes, and trienes for further analyses. TLC was carried out on glass plates coated with silica gel G and silver nitrate according to the procedure of Barrett et al. (2). The developing solvent used, however, was pure benzene and the spots were detected by charring with sulfuric acid.

Alkali-conjugated fatty methyl esters were prepared to serve as identification standards. Methyl linoleate was isomerized by the procedure of Kass and Burr (17) and linseed oil by a similar procedure except that the heating was done at 165C for only 30

min to minimize cyclization (26). The conjugated soaps were converted to methyl esters (methanol-sulfuric acid) and fractionated by CCD (hexane-acetonitrile). The diene fraction from alkali-conjugated linoleate had an absorptivity at 230 mμ of 105.2 and the triene fraction of alkali conjugated linseed oil, an absorptivity at 233 mμ of 66.4 and at 268 mμ of 59.2.

Permanganate-periodate oxidation was used to determine double bond position according to the procedure of Jones and Stolp (16), except that the cleavage acid products were transmethylated and analyzed by GLC with programmed temperature.

Results

Iron pentacarbonyl catalyzed the hydrogenation of soybean oil at 180C and hydrogen pressures of 100–1,000 psi. No reduction occurred at 50 psi or less (Table I). When some reactions were interrupted to remove any inhibiting carbon monoxide formed by decomposition of iron carbonyl, the extent of hydrogenation was not greater than equivalent continuous runs. Adequate agitation was necessary as evidenced by the greater reaction observed in the Magna-Dash bomb than in the rocking autoclave. Although the reaction occurs under homogeneous conditions, efficient diffusion of the hydrogen gas through the reaction mixture is necessary for effective hydrogenation.

Analyses of the hydrogenated products by GLC show relatively high reduction of triene and diene. The change in monoene and saturates is reported together in one column because of the poor separation of these components by GLC, but the observed increased appears almost entirely due to the monoene. The reduced products are characterized by high concentrations of conjugated dienes (*cis,trans* and *trans, trans*) and *trans* unsaturation.

Soybean oil methyl esters were hydrogenated at different concentrations of iron pentacarbonyl in the presence or absence of cyclohexane as solvent. Table II shows a small increase in hydrogenation at higher concentrations of catalyst. The hydrogenation was considerable in the presence of cyclohexane as solvent,

TABLE II

Hydrogenation of Soybean Oil Methyl Esters[a] with Iron Pentacarbonyl (180C)

Run No.	Catalyst mole	Hydrogen pressure psi	Time hr	Bomb	I.V. (calc.[b])	Decrease		Increase	Conj. diene [a]233 mμ	Trans (as elaidate) %
						Triene %	Diene %	Monoene + saturates %		
8	0.5	125	2	Rocker	116	7.3	20.5	6.2	18.2	14.5
9	0.1	125	1	Magna-Dash	116	4.8	21.2	9.6	12.6	17.6
10	0.05[c]	310[d]	1	Magna-Dash	109	9.5	16.4	10.5	5.9	15.8
11	0.1[c]	310[d]	1	Magna-Dash	103	9.5	19.2	18.4	7.7	16.6
12	0.2[c]	390[e]	1	Magna-Dash	94	9.5	28.5	27.8	9.2	23.1

[a] Composition (GLC), %: Palmitate 10.4, stearate 3.7, oleate 26.7, linoleate 50.4, linolenate 9.5; I.V.: 135.
[b] Calculated from GLC composition. Includes conjugated dienes.
[c] In solution in cyclohexane (40% w/w).
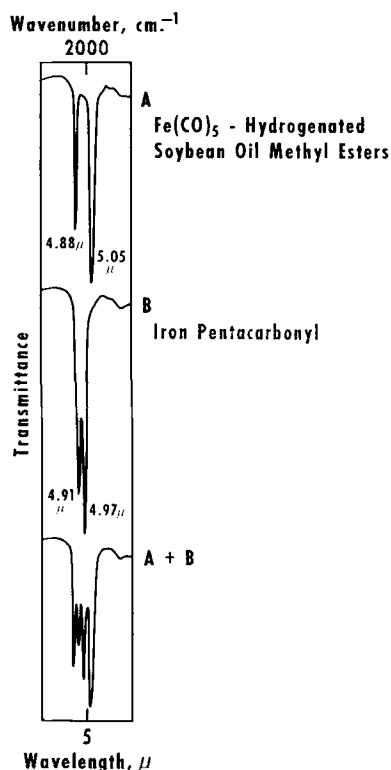[d] Initial pressure: 100 psi.
[e] Initial pressure: 125 psi.

FIG. 1. IR spectra of (A) iron carbonyl reduced soybean oil esters, (B) iron pentacarbonyl, and a mixture of A and B.

probably because of lower viscosity, better agitation, and diffusion of hydrogen gas through the reaction mixture. The hydrogenated soybean oil methyl esters are similar in gross composition to the hydrogenated soybean oils although the concentration of conjugated diene is somewhat lower. With both soybean oil and methyl esters the *trans* unsaturation is generally increased in proportion to the level of hydrogenation. The conjugated diene, on the other hand, appears to reach a maximum (absorptivity at 233 mμ, 18–20) and then decreases at lower I.V.

The relation between the increase in monoene and saturates and the decrease in trienes and dienes is not a simple one. Trienes and dienes are both conjugated and hydrogenated. Furthermore, the trienes may be hydrogenated successively to dienes and monoenes or
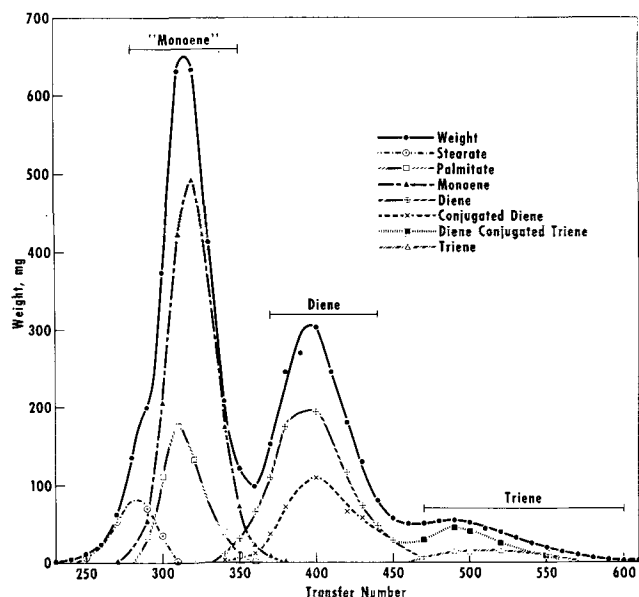

FIG. 2. CCD of iron carbonyl-reduced soybean oil methyl esters (*n*-hexane-acetonitrile), I.V. 116.
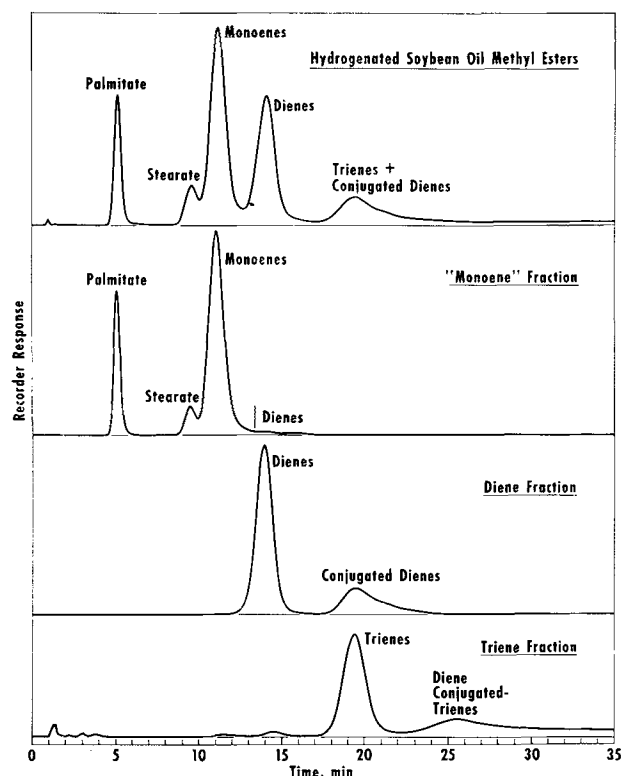

FIG. 3. GLC of iron carbonyl-reduced soybean oil methyl esters and corresponding CCD fractions.

directly to monoene. GLC analyses are also complicated by the formation of a complex between polyunsaturated fatty esters and iron pentacarbonyl as indicated later.

Hydrogenated products were deep yellow even after removal of the catalyst by washing with dilute acid and alkali. The yellow color was associated with two strong absorption bands in the IR at 4.88 and 5.05 μ in the carbonyl stretching region. These bands are not due to any free residual iron pentacarbonyl, which absorbs at 4.91 and 4.97 μ (31) as shown in Figure 1. The iron carbonyl material responsible for the absorption at 4.88 and 5.05 μ is soluble in organic solvents and nonvolatile. Efficient nitrogen stripping of the hydrogenated oils at 180C under vacuum did not decrease these carbonyl absorption bands. The iron carbonyl material also remains in the residue after vacuum distillation of the hydrogenated methyl esters. A distillation residue was chromatographed on an alumina column, and a deep yellow band was isolated by elution with *n*-hexane. The yellow material obtained in 75% yield gave the characteristic carbonyl absorption at 4.88 and 5.05 μ. Additional bands for CH (3.4–3.5 μ), ester carbonyl (5.7 μ), methyl-methylene (6.8–7.25 μ), ester (8.5 μ), and *trans* unsaturation (10.15 and 10.35 μ) indicate that an unsaturated fatty ester is associated with the iron carbonyl material. Since this material did not emerge from a GLC column, the presence of any noncomplexed fatty ester is ruled out. Therefore, a relatively stable molecular complex between iron carbonyl and unsaturated fatty esters is indicated.

Selected iron carbonyl-hydrogenated soybean oil and methyl esters were analyzed in more detail after countercurrent separation into monoene, diene, and triene fractions. Figure 2 shows the weight-composition curves for a nondistilled sample of reduced soybean oil methyl esters (run 9, Table II). Figure 3 gives the GLC separations of the original reduced esters and of the combined CCD fractions. Stearate
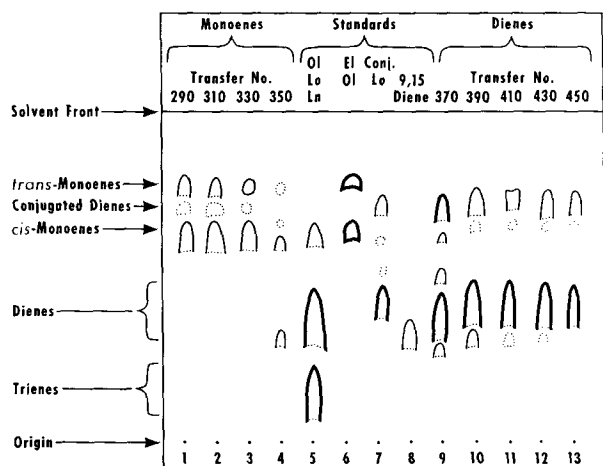
FIG. 4. TLC of CCD monoene and diene fractions of iron carbonyl-reduced soybean oil methyl esters (Ol: oleate, Lo: linoleate, Ln: linolenate, El: elaidate).

FIG. 5. TLC of CCD triene fractions of iron carbonyl-reduced methyl esters (Abbreviations: same as in Fig. 4).

and palmitate are distributed in the "monoene" peak and conjugated dienes in the diene and triene peaks. The UV-absorbing conjugated diene in the triene peak has the same GLC and TLC retention as the diene conjugated triunsaturated fatty acids obtained by CCD from alkali-conjugated linseed oil. This evidence, together with the IR absorption observed at 10.35 μ for an isolated trans configuration, indicates a triene consisting of a conjugated diene and a third isolated double bond. The triene CCD fraction was yellow and showed bands at 4.88 and 5.05 μ, which indicates the presence of the iron carbonyl-unsaturated fat complex. This complex can, therefore, be purified by CCD and this approach has been used to isolate it from iron carbonyl-hydrogenated methyl linoleate. Further characterization of the complex will be reported elsewhere.

Figures 4 and 5 present analyses of individual CCD fractions by TLC. The monoenes show three components, two of which correspond to methyl oleate and elaidate (sample 6). The dienes give spots corresponding to alkali-conjugated diene (sample 7), linoleate, and a slower moving component with retention similar to 9,15-diene [(sample 8): from hydrazine-reduced linolenate (28)]. The triene fractions in Figure 5 are most complex and include components corresponding to alkali-conjugated diene, eleostearate, linolenate, diene-conjugated triene (sample 7; alkali-conjugated linseed oil), several intermediate spots, and polar material at the origin.

Table III summarizes analyses of CCD fractions from three runs of hydrogenated soybean oil methyl esters and one run of hydrogenated oil after transmethylation. Fair agreement was obtained in the monoene concentrations as determined by CCD and GLC. The analyses of the diene and triene fractions by GLC are not reliable in the nondistilled samples. The diene fractions contain substantial amounts of conjugated dienes which on GLC are partly resolved into three components with considerable tailing (Fig. 3). Errors in the GLC analyses of the trienes arise from the poor separation between triene and conjugated dienes and the omission of conjugated trienes. The triene fraction from nondistilled samples shows by IR the presence of an iron carbonyl-fat complex (which is nonvolatile and does not analyze by GLC), accounting for the higher triene concentration obtained by CCD than by GLC. The presence of nonvolatile iron carbonyl-fat complex in these triene fractions is also indicated by the necessity of using about
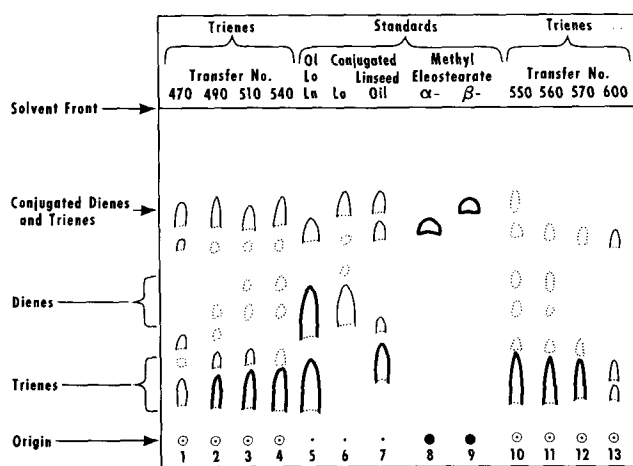
twice as much sample injection as the other fractions to obtain the same total peak area. These GLC chromatograms were further complicated by the appearance of volatile decomposition products near the injection point.

UV analyses for conjugation before and after alkali isomerization give the amount of conjugatable dienes and trienes, which is a measure of 1,4-diunsaturation. In the more highly hydrogenated samples (Table III) the unconjugated dienes are largely nonconjugatable by alkali and contain substantial isolated trans unsaturation. The double bonds are therefore separated by several methylene groups. A colloidal black filterable precipitate identified as iron was formed after alkali conjugation of the triene fractions from nondistilled samples. Apparently, the iron carbonyl-fat complex in these fractions is decomposed by the alkaliconjugation treatments. IR analyses show trans configuration in the monoenes; and for the dienes and trienes, nonconjugated trans unsaturation (10.35 μ), cis,trans (10.2 and 10.55 μ), and trans,trans conjugated unsaturation (10.15 μ). Trans,trans conjugation can be estimated from the ratios $a_{10.2\ \mu}/a_{10.6\ \mu}$, pure methyl 9-cis,11-trans octadecadienoate having a ratio of 1.198 (7).

Figures 6 and 7 show the dibasic acid analyses of CCD fractions from two soybean oil samples, one hydrogenated as the methyl esters and the other hydrogenated as the triglycerides. Considerable scattering of double bonds is evident in the monoene fractions between the C_6 and C_{16} positions. Most of the double bonds formed between the C_9 and C_{12} positions must have come from the original C_9 and C_{12} positions in linoleate and linolenate. The double bonds in the diene and triene fractions show less scattering. The picture is complicated, however, by the presence of internal dibasic acids derived from cleavage between two double bonds. If one assumes that the dibasic acids shorter than seven carbons are internal (27), the distribution of double bonds around the original C_9 position is skewed toward the C_{10} and C_{11} positions. These data pertain only to the double bond on the carboxyl end of the molecules. The double bond positions on the hydrocarbon end are reflected by the monobasic acid cleavage products which are not recovered quantitatively by the procedure used, especially the acids lower than C_6. Among the higher monobasic acids, those in the C_7 to C_9 range predominate in the monoenes, in agreement with the dibasic acid analyses. In the dienes and trienes, the C_6 to C_8 monobasic acids corresponding to the C_{12} to C_{10} double

TABLE III

Analysis of CCD Fractions—Iron Carbonyl-Reduced Soybean Oil and Methyl Esters

Analysis	Run 9 (undistilled, I.V. 116)			Run 11 (undistilled, I.V. 103)			Run 12 (distilled, I.V. 94)			Run 7 (distilled, I.V. 91)		
	Monoene	Diene	Triene[a]	Monoene	Diene	Triene[a]	Monoene	Diene	Triene	Monoene	Diene	Triene
Weight %												
CCD	56.5	34.8	8.7	59.1	32.6	8.3	75.0	23.5	1.5	85.3	13.7	1.0
GLC	52.5	(42.8)	(4.7)	61.7	(38.3)	0	74.1	(25.9)	0	80.2	(19.8)	0
GLC analysis												
Sat. (C16, C18, C20)	28.3	......	......	28.4	......	......	27.3	......	......	......	......	......
Monoene	68.6	......	(1.7)	70.4	......	(1.0)	70.7	......	......	26.4	0.6	......
Diene	3.2	68.1	(2.0)	1.2	86.2	(1.0)	1.0	74.5	......	69.9	34.8	......
Conjugated diene	......	(31.9)	(77.1)	......	(13.8)	(54.7)	1.0	(25.5)	(25.6)	2.7	(62.3)	......
Triene	......	......	(19.3)	......	......	(43.3)	......	......	(74.4)	0.9	2.3?	......
UV analysis												
$a_{233 m\mu}$	......	23.8	35.9	......	13.9	30.2	......	22.0	14.2	......	51.2	21.1
$a_{268 m\mu}$	......	......	11.0	......	......	6.5	......	......	10.7	......	......	7.3
After alkali isomerization												
$a_{233 m\mu}$	......	81.7	63.5	......	74.7	57.3	......	78.5	19.8	......	65.8	26.5
$a_{267 m\mu}$	......	......	15.5	......	......	9.0	......	......	17.7	......	......	7.9
IR analysis												
Trans as elaidate	23.1	12.2	8.9	22.9	10.6	5.3	30.4	14.0	8.8	44.8	25.7	12.63
$a_{10.2 \mu}/a_{10.6 \mu}$[b]	......	1.79	5.22	......	2.09	7.19	......	2.20	3.46	......	2.42	3.2

[a] Values in parentheses are estimated. Strong absorption at 4.9 μ and 5.05 μ.
[b] Pure 9-cis,11-trans methyl octadecadienoate has a ratio $a_{10.2 \mu}/a_{10.6 \mu}$ of 1.198 (7).

bond positions predominate. Double bonds in the C_{13} to C_{17} end of the molecule are not taken into account in these analyses.

Discussion

Reduction, isomerization, and migration of double bonds in soybean oil and methyl esters are effectively catalyzed by iron pentacarbonyl. Isomerization of linolenate and linoleate to conjugated dienes appears to be an important step in the reaction. The nonconjugated dienes include large amounts of trans unsaturation and double bonds separated by more than one methylene group. The trienes and dienes are predominantly reduced to monoenes as evidenced by the negligible increase in saturates and by the large accumulation of trans monoenes.

IR analyses of the hydrogenated products show evidence of complex formation between iron carbonyl and unsaturated fats. The absorption bands of iron pentacarbonyl in the carbonyl stretching region at 4.91 and 4.97 μ are shifted to 4.88 and 5.05 μ after hydrogenation. The latter IR bands are identical to those reported for 1,3-pentadiene-iron tricarbonyl and isoprene-iron tricarbonyl (18,22). These stable complexes are prepared by heating under nitrogen the dienes with triiron dodecacarbonyl or iron pentacarbonyl.

The active catalytic intermediates in the hydrogenation reaction may be iron carbonyl hydrides, which are known to isomerize and reduce olefinic double bonds (33,35,37). The mechanism of these reactions would be similar to that advanced for the hydroformylation reaction (33) involving the formation of an olefin-metal hydrocarbonyl complex catalyzing the transfer of hydrogen. This process may be analogous to the hydrogen transfer occurring on metal surfaces in heterogeneous catalysis (33). Further study of iron carbonyl-fat complexes would thus facilitate basic studies of fat hydrogenation.

The failure of unsaturated fats to hydrogenate with iron carbonyl at hydrogen pressures below 100 psi indicates that the formation of the active intermediate iron hydrocarbonyl may require higher hydrogen pressures. Alternatively, the carbon monoxide formed from the decomposition of iron carbonyl may compete with hydrogen at low pressures. Hydrogenation is
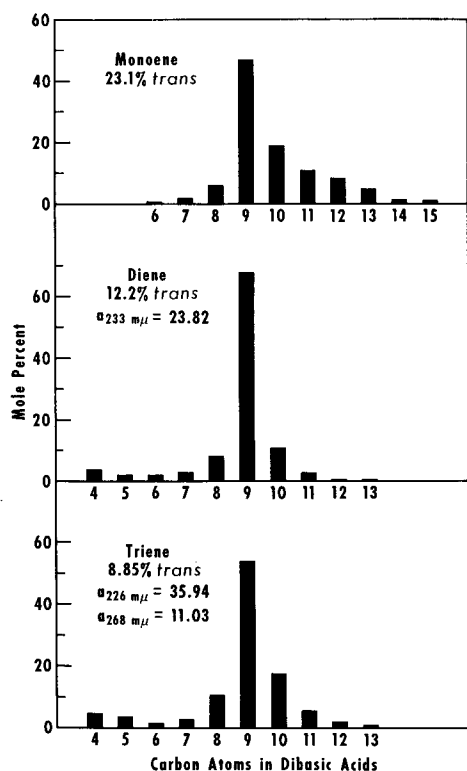

FIG. 6. Dibasic acids from CCD fractions of iron carbonyl-reduced soybean oil methyl esters (Run 9, Table II).
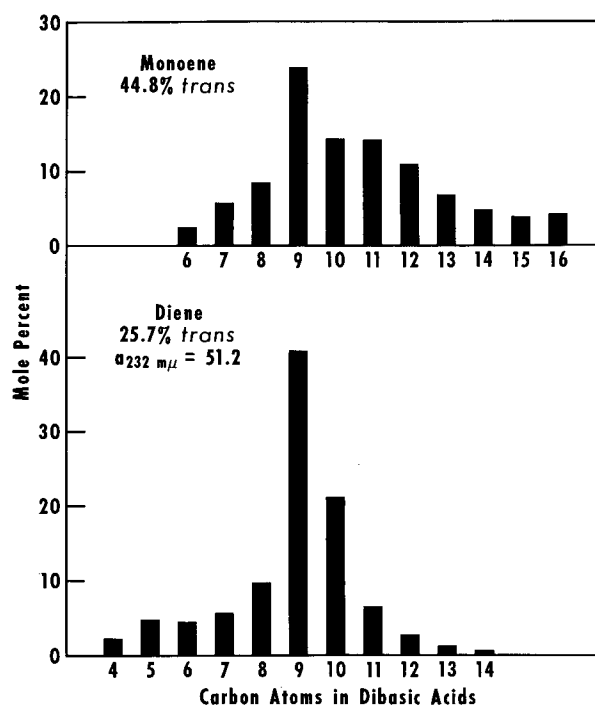

FIG. 7. Dibasic acids from CCD fractions of iron carbonyl-reduced soybean oil (Run 7, Table I).

not accelerated by interrupting the reaction to release any carbon monoxide formed. This result does not agree with those of Hashimoto and Shiina (14) and indicates that carbon monoxide does not inhibit the homogeneous hydrogenation catalyzed by iron carbonyl. By analogy, the failure of sulfur compounds to act as poisons has been used as evidence that the catalytic reactions of metal carbonyls (37) and platinum salts (25) are homogenous.

The reduced fat products from the homogeneous hydrogenation catalyzed by iron pentacarbonyl are similar to those of heterogeneous hydrogenation. Therefore, the course of these two catalytic reactions may be similar. Metal carbonyls are well known for their ability to form complexes with conjugated dienes (3) and unconjugated dienes in which the ligand becomes conjugated (18). The findings of Hashimoto and Shiina (15), that iron pentacarbonyl acts as an isomerization catalyst to conjugate unsaturated fats in inert atmosphere, has been confirmed in this laboratory. This evidence suggests that conjugation may be a requirement for the homogeneous catalytic hydrogenation reaction. There is much evidence to indicate that conjugated unsaturated systems are required for homogeneous hydrogenation (8,13,19,21). Therefore, a catalyst that isomerizes fats and also activates hydrogen should be one of the best ways to achieve homogeneous hydrogenation. Conjugation may also be an important process in heterogeneous catalytic hydrogenation of fats. The formation of conjugated intermediates during heterogeneous hydrogenation of fats has been demonstrated and suggested previously (1, 6,9,35). The greater susceptibility of these conjugated forms to hydrogenation and isomerization into unconjugated isomeric forms would account for their limited accumulation in hydrogenated fats.

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New Nonionic Detergents Derived from Epoxidized Oils[1]

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Abstract

A new class of nonionic detergents derived from epoxidized oils having an oxirane oxygen content of 6–10% is discussed. Their mol wt and micellar wt distributions, as studied in the ultracentrifuge, are presented and cited as partial explanations for their unique properties as compared to conventional nonionic detergents such as ethoxylated alkyl phenols. Critical micelle concentrations (CMC) determined by light scattering data are presented.

Discussion

THE MICELLAR structure and detersive ability for two families of derivatives are studied as a function of the weight percent of the polyoxyethylene hydrophil. The evaluation of these materials as emulsifiers, detergents, and lubricants is presented, with some theoretical reasons for their performance. Surface tension, foaming, and wetting characteristics are also given a comparative evaluation, and some second generation derivatives are briefly discussed.

The unique behavior of these materials as foaming agents, effects on surface tension, broad utility as emulsifiers, and unusual performance in scattering light, are explained by their broad distribution of molecular weight as verified by the ultracentrifuge. The broader distribution of mol wt is, however, not the whole story. The magnitude of the mol wt, being from 4–10 times as great as the materials currently available in this area, undoubtedly affects their properties. Perhaps these materials will do more efficient jobs in applications where the present nonionic detergents perform poorly.

During the past decade, the growth of the plastics industry and its attendant technology have resulted in the commercial production of a great many new materials. It is inevitable that the availability of such materials results in their application to other areas, e.g., the introduction of epoxidized unsaturated vegetable oils and their derivatives. These materials, designed primarily as combination plasticizer-stabilizers in plastic films and coatings, have made commercially available polyfunctional chemicals from which the organic chemist can fashion unique new molecules for a variety of applications.

Chemistry

The polyfunctionality of these materials and the wide spectrum of reactions that they may undergo