Homogeneous Catalytic Hydrogenation of Unsaturated Fats: Group VIB Metal Carbonyl Complexes[1]

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Abstract

Carbonyl complexes of Cr, Mo and W have been studied as soluble catalysts for the hydrogenation of methyl sorbate and of methyl esters from soybean oil. With methyl sorbate, relative catalytic activity decreased in the approximate order: mesitylene-$Mo(CO)_3$, cycloheptatriene-$Mo(CO)_3$, cycloheptatriene-$Cr(CO)_3$, bicyclo (2,2,1)hepta-2,5-diene-$Mo(CO)_4$, chlorobenzene-$Cr(CO)_3$, methyl benzoate-$Cr(CO)_3$, mesitylene-$W(CO)_3$, benzene-$Cr(CO)_3$, toluene-$Cr(CO)_3$, mesitylene-$Cr(CO)_3$, and hexamethylbenzene-$Cr(CO)_3$. Order of catalytic activity was related to thermal stability of the complexes during hydrogenation. With mesitylene-$M(CO)_3$ complexes, selectivity varied in the order $Cr > Mo > W$. Under certain conditions the mesitylene complexes of W, Cr and Mo reduced methyl sorbate respectively to methyl 2-, 3-, and 4-hexenoates as main products.

The more active and thermally stable $Cr(CO)_3$ complexes catalyzed effectively the hydrogenation of linoleate and linolenate in soybean oil esters with little or no stearate formation. The hydrogenated products formed with the benzoate complex at 165–175 C contained 50–67% monoene, 18–30% diene, 2–7% conjugated diene, and only 3–7% *trans* unsaturation. Linolenate-linoleate selectivity values varied from 3 to 5 and linoleate-oleate selectivity from 7 to 80. Monoene fractions had 40–50% of the double bond in the C-9 position; the rest of the unsaturation was distributed mainly between the C-10 and C-12 positions. Conjugation is apparently an intermediate step in the hydrogenation of linoleate and linolenate. The $Cr(CO)_3$ complexes are unique in catalyzing the hydrogenation of polyunsaturated fatty esters to monounsaturated fatty esters of low *trans* content.

Introduction

In previous papers of this series, we showed that polyunsaturated fats and esters were effectively hydrogenated with fat-soluble organometallic and coordination compounds, including $Fe(CO)_5$ (7,9,13); diene- and triene-$Fe(CO)_3$ complexes (7,9,12); $Co_2(CO)_8$ (10); $Mn_2(CO)_{10}$ (5); and metal acetylacetonates (4). Related studies with the water-soluble catalyst pentacyanocobaltate (II) demonstrated a high selectivity toward the reduction of the Δ4 double bond of sorbic acid (2,4-hexadienoic acid) (3,22). Further work at the University of Illinois revealed that polyunsaturated fatty esters were selectively reduced to monoenes with various soluble triphenylphosphine derivatives of platinum, palladium and nickel in the presence of tin(II) chloride (1,17). A high selectivity for the hydrogenation of pure methyl linolenate to dienes has been observed when $Fe(CO)_5$ (7) and Pt-Sn complexes (8) were used as catalysts. This linolenate selectivity has been explained by the formation of unreactive dienes with double bonds separated by several methylene groups. All these soluble catalysts have been generally selective in hydrogenating polyunsaturates to monounsaturates. However, they have been similar to conventional heterogeneous catalysts in accelerating other reactions, such as *cis,trans* isomerization and double bond migration.

We recently discovered that the chromium tricarbonyl complexes of aromatic compounds catalyze the selective hydrogenation of methyl sorbate to methyl 3-hexenoate (6). Also, in dehydrated methyl ricinoleate and tung oil only the conjugated fatty esters were selectively reduced. The mechanism of homogeneous hydrogenation of methyl sorbate catalyzed by the chromium tricarbonyl complex of methyl benzoate was elucidated by deuterium tracer studies (15). Now we have found that under certain conditions some of the more active chromium tricarbonyl complexes can catalyze the hydrogenation of unconjugated fatty esters into monoenes of low *trans* unsaturation. Other carbonyl complexes of molybdenum and tungsten have been examined and their catalytic activity compared.

Experimental Procedures

Materials

Methyl sorbate was prepared by methylation of sorbic acid (Eastman; recrystallized from water and then diethyl ether) with methanol and HCl. The distilled product (70–75 C/2 mm) showed one peak by gas liquid chromatography (GLC) on a diethylene glycol succinate (DEGS) column. Methyl esters of commercially refined and bleached soybean oil were made by transesterification with methanol and sodium methoxide and then were distilled (140–150 C/0.015 mm).

Methyl benzoate-$Cr(CO)_3$ and cycloheptatriene-$Cr(CO)_3$ were prepared according to procedures described by King (19); toluene-$Cr(CO)_3$ and hexamethylbenzene-$Cr(CO)_3$ according to Nichols and Whitting (23). Other complexes were purchased: benzene-$Cr(CO)_3$, mesitylene-$Cr(CO)_3$, mesitylene-$W(CO)_3$, cycloheptatriene-$Mo(CO)_3$ (Strem Chemicals, Danvers, Mass.), bicyclo(2,2,1)hepta-2,5-diene-$Mo(CO)_4$, mesitylene-$Mo(CO)_3$, and cyclopentadiene-$Mo(CO)_3$ dimer (Alfa Inorganics, Beverly, Mass.).

Hydrogenations

Hydrogenations were carried out in a Magne-Dash 150 ml, stainless-steel autoclave, in a solution of cyclohexane (50 ml). Solvent was removed from the final product under vacuum on a rotating evaporator. Residual catalyst was decomposed with $FeCl_3$. The hydrogenated product was dissolved in 95% ethanol and N_2 bubbled into the solution with magnetic stirring. Freshly ground $FeCl_3$ was then added (ca. 1 g) in three portions during 30 min with constant N_2 bubbling. The solution was then diluted with water and the product extracted with petroleum ether and dried (Na_2SO_4). The products were usually analyzed either directly or after distillation and fractionation.

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Analyses

Products of the hydrogenation of methyl sorbate were analyzed by GLC. The instrument used was equipped with a hydrogen flame detector and a 5 ft × 1/8 in. column of 25% DEGS on Chromosorb W 60/80, and the temperature was programmed between 55 and 95 C. Hydrogenated soybean esters were analyzed by GLC, by IR and UV spectroscopy, and by alkali conjugation as described previously (13). Products were separated into monoene and diene fractions by rubber column chromatography (16). Position of double bonds was determined in the monoene fractions by an adaptation of the reductive ozonolysis-GLC procedure of Stein and Nicolaides (24). Averaged analyses of both aldehyde and aldehyde ester fragments were made by GLC on a 25% DEGS column programmed between 50 and 215 C. Determination of metal carbonyl complexes during hydrogenation was made by IR analyses. The metal carbonyl stretching bands in the region 1900–2000 cm^{-1} were determined in CCl_4 solution and compared to those of the pure metal carbonyl complexes.

Results

Hydrogenation of Methyl Sorbate

Methyl sorbate is a convenient model compound for hydrogenation studies because all the products can be readily determined by GLC (22). Furthermore, the product distribution provides information on selectivity (6) and mechanism of catalytic activity (15). Hydrogenation data from various chromium, molybdenum and tungsten carbonyl complexes are recorded in Table I. Methyl 3-hexenoate was the major product from $Cr(CO)_3$ complexes. Methyl 2-hexenoate and methyl hexanoate were only minor products. Because catalytic activity of these carbonyl complexes varied widely, it was evaluated by comparing the temperature and times at which rapid hydrogenation was observed. Among the chromium complexes examined, those of cycloheptatriene, chlorobenzene and methyl benzoate were the most active. Catalytic activity decreased with the number of methyl substituents on the benzene ring. Mesitylene-$Cr(CO)_3$ was the least active of the complexes tested at 175 C. Hexamethylbenzene-$Cr(CO)_3$ had no activity until the hydrogenation temperature was raised to 200 C.

The molybdenum carbonyl complexes were more active at lower temperatures than were the chromium carbonyl complexes. Catalytic activity and selectivity may be related to the metal in mesitylene complexes. The relative order of activity with these complexes was Mo>W>Cr. The carbonyl complexes of Mo and W were not so selective for the formation of methyl 3-hexenoate as was the carbonyl complex of Cr. At 150 C, mesitylene-$Mo(CO)_3$ yielded methyl 4-hexenoate as the major product; at 165 C, the major product with the W complex was methyl 2-hexenoate.

Further insight into the catalytic activity and selectivity of the mesitylene carbonyl complexes of Cr, Mo and W can be derived from the kinetic curves in Figure 1. These complexes could not be compared under the same reaction conditions because of wide differences in their activity. Hydrogenation conditions were chosen to obtain changes in concentration within a reasonable time. The hydrogenation catalyzed by the $Cr(CO)_3$ complex was characterized by an induction period. After this period the rate of disappearance of sorbate and appearance of methyl 3-hexenoate followed a reciprocal relation. The fate of the catalyst complex during hydrogenation was determined by IR analysis of metal carbonyl stretching bands at 1972–1981 cm^{-1}. Essentially no decomposition of mesitylene-$Cr(CO)_3$ complex occurred during hydrogenation of methyl sorbate. The formation of small amounts of free mesitylene (up to 2%) during hydrogenation was detected by GLC. The formation of free mesitylene would be expected to be accompanied by a corresponding decrease in concentration of $Cr(CO)_3$ complex. However, the GLC determination of mesitylene was more sensitive (ca. ± 1%) than the IR determination of the complex (ca. ± 10%). The other $Cr(CO)_3$ complexes listed in Table I exhibited the same thermal stability as the mesitylene Cr complex, except for cycloheptatriene-$Cr(CO)_3$ which decomposed rapidly during hydrogenation. Cycloheptatriene-$Cr(CO)_3$ was also the most active of the Cr complexes for the reduction of methyl sorbate and did not exhibit an induction period.

The absence of an induction period in the reactions catalyzed by the mesitylene carbonyl complexes of Mo and W (Fig. 1B and 1C) may account for their activity being greater than that of the Cr complex (Table I, compare runs 7, 14 and 20). Also, the concentration of Mo and W complexes decreased during hydrogenation, and a larger amount of free

TABLE I

Hydrogenation of Methyl Sorbate With Group VIB Metal Carbonyl Complexes

Run No.	Catalysts	Reaction conditions[a]			Product composition, %				
		Cat. conc., mole %	Time, hr	Temp, C	Methyl sorbate	Methyl hexenoates			Methyl hexanoate
						2-	3-	4-	
1	Cycloheptatriene-$Cr(CO)_3$	5	1	120	0	1	98	0	1
2	Chlorobenzene-$Cr(CO)_3$[b]	5	2	150	0	0	96	0	4
3	Methyl benzoate-$Cr(CO)_3$	5	4	160	0	4	95	0	1
4	Benzene-$Cr(CO)_3$	5	4	175	0	4	94	0	2
5	Toluene-$Cr(CO)_3$	5	4	175	0	5	95	0	0
6	Mesitylene-$Cr(CO)_3$	5	6	175	20	3	76	0	1
7	Mesitylene-$Cr(CO)_3$	5	6	165	99	0	1	0	0
8	Mesitylene-$Cr(CO)_3$	10	6	165	37	2	60	0	1
9	Mesitylene-$Cr(CO)_3$	20	4.5	165	0	3	96	0	1
10	Hexamethylbenzene-$Cr(CO)_3$	5	6	200	8	5	84	1	2
11	Cycloheptatriene-$Mo(CO)_3$	5	6	100	0	10	90	0	0
12	Cycloheptatriene-$Mo(CO)_3$	5	1.5	120	0	12	88	0	0
13	Mesitylene-$Mo(CO)_3$	5	2	100	0	11	86	2	1
14	Mesitylene-$Mo(CO)_3$	5	1	120	0	10	68	19	3
15	Mesitylene-$Mo(CO)_3$	5	0.5	150	0	8	28	55	9
16	Bicyclo(2,2,1)hepta-2,5-diene-$Mo(CO)_4$	5	6	120	0	10	90	0	0
17	[Cyclopentadiene-$Mo(CO)_3]_2$	5	4	150	95	1	1	1	2
18	[Cyclopentadiene-$Mo(CO)_3]_2$	5	6	180	69	8	6	4	13
19	Mesitylene-$W(CO)_3$	5	4	150	84	11	3	1	10
20	Mesitylene-$W(CO)_3$	5	6	165	71	17	6	3	3
21	Mesitylene-$W(CO)_3$	10	6	165	23	43	13	9	12

[a] Methyl sorbate (9.5 mM), 440 psi H_2 in cyclohexane solution (50 ml).

[b] Data from reference 6.

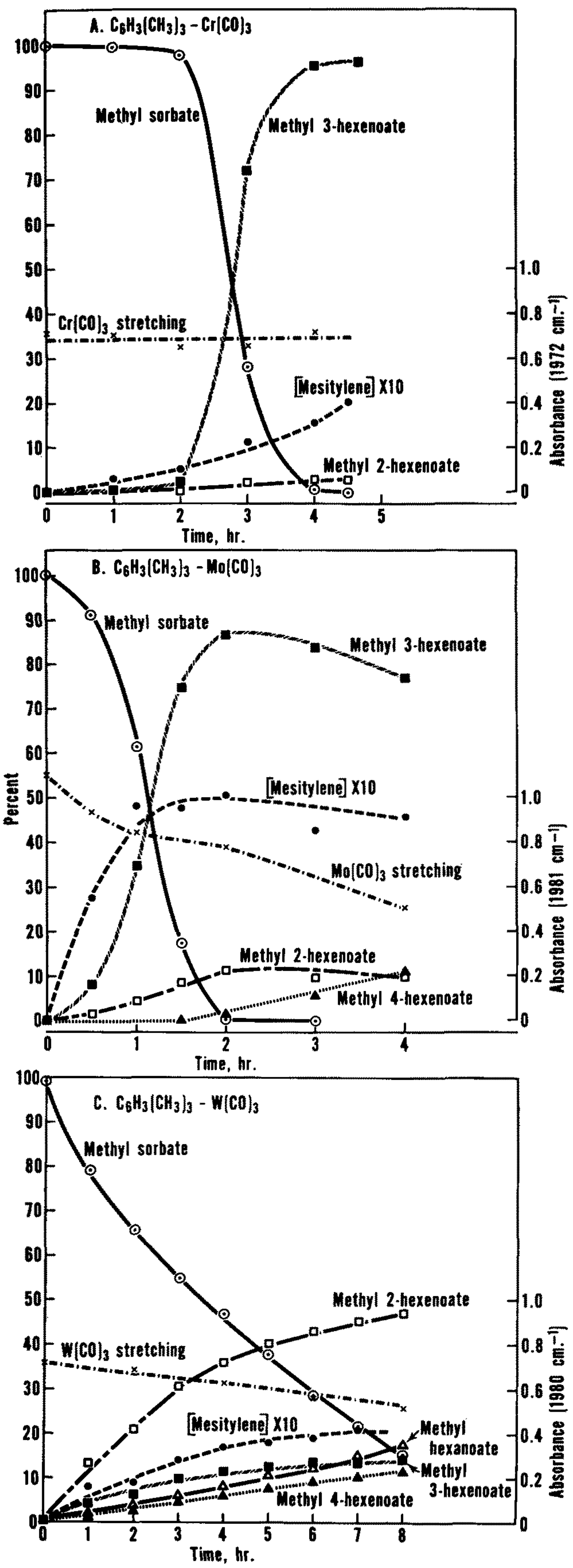


FIG. 1. Rate of hydrogenation of methyl sorbate with (A) mesitylene-$Cr(CO)_3$, run 9, Table I; (B) mesitylene-$Mo(CO)_3$, run 13, Table I; and (C) mesitylene-$W(CO)_3$, run 21, Table I.

mesitylene was formed with the Mo complex than with either W or Cr complex. The Mo carbonyl complexes listed in Table I were the most thermally labile and showed a decrease in concentration during hydrogenation, except for the cyclopentadienyl-$Mo(CO)_3$ dimer which was very stable. The catalytic activity is related to the thermal stability of these complexes. For example, the mesitylene-$Cr(CO)_3$ complex was thermally very stable and relatively inactive as a catalyst. In contrast, the corresponding $Mo(CO)_3$ complex was more labile and served as a very effective catalyst. The dimer of cyclopentadiene-$Mo(CO)_3$, on the other hand, was very stable and ineffective as a hydrogenation catalyst (Table I).

Mesitylene-$Mo(CO)_3$ and the Mo complexes of bicycloheptadiene and cycloheptatriene showed a new band in their IR spectra at 1995 cm^{-1} during hydrogenation. The intensity of this band increased during hydrogenation and leveled off after 2 hr (Table I, run 13). Although this new band at 1995 cm^{-1} was not exhibited by the original Mo complexes, it corresponds to the band observed with $Mo(CO)_6$. Whether free $Mo(CO)_6$ is formed as an intermediate during hydrogenation remains to be established. The selectivity of mesitylene-$Mo(CO)_3$ was similar to that of mesitylene-$Cr(CO)_3$ in yielding methyl 3-hexenoate as the major product. However, after methyl sorbate was completely converted with the $Mo(CO)_3$ complex into methyl 3-hexenoate, this product was apparently isomerized to methyl 4-hexenoate (Fig. 1B). This isomerization increased at higher temperatures and methyl 4-hexenoate became the major product (Table I, run 15).

The mode of action and the selectivity of mesitylene-$W(CO)_3$ were completely different from those of the corresponding Mo and Cr complexes. With mesitylene-$W(CO)_3$ methyl 2-hexenoate was the most important product throughout the hydrogenation period, followed by methyl 3- and 4-hexenoates (Fig. 1C). Also, methyl hexanoate was a significant product with the $W(CO)_3$ complex even during initial stages of hydrogenation. Mesitylene-$W(CO)_3$ was the least selective in this class.

Hydrogenation of Soybean Methyl Esters

Because $Cr(CO)_3$ complexes were the most selective, they were further evaluated for the hydrogenation of unsaturated fatty esters. Also, the thermal stability of these chromium complexes permitted temperatures sufficiently high to hydrogenate unconjugated fatty esters. The relative catalytic activities of different $Cr(CO)_3$ complexes were compared for the hydrogenation of methyl esters from soybean oil (Table II). Methyl benzoate-$Cr(CO)_3$ was the most active catalyst for the hydrogenation of linolenate and linoleate on soybean methyl esters. Cycloheptatriene- and mesitylene-$Cr(CO)_3$ were the least active.

Again, relative catalytic activity can be related to the thermal stability of these complexes. Cycloheptatriene-$Cr(CO)_3$ was too labile and decomposed completely after 1 hr of hydrogenation at 175 C. At lower temperatures (110–120 C) cycloheptatriene-$Cr(CO)_3$ was more stable but did not catalyze hydrogenation of the unconjugated esters of soybean oil. However, it did catalyze hydrogenation of conjugated dienes and trienes (14). Therefore, to hydrogenate the unconjugated diene and triene fatty esters of soybean oil, it is necessary to use sufficiently high temperatures without completely decomposing the catalytic complexes. Mesitylene-$Cr(CO)_3$ was too stable and did not cause hydrogenation at 175 C. On

TABLE II

Hydrogenation of Soybean Oil Methyl Esters with $Cr(CO)_3$ Complexes[a]

Run No.	$Cr(CO)_3$ complexes	Product composition, %					IV[c]	CD, $a_{232\,m\mu}$	*trans*,[d]
		Pal	St	M	D	T[b]			%
Control	....	10.3	4.5	26.6	50.2	8.4	131.0	....	...
22	Methyl benzoate	10.3	4.7	67.0	18.0	0.0	88.4	2.0	7.3
23	Benzene	10.3	4.5	54.0	29.6	1.6	101.4	0.4	15.4
24	Toluene	10.3	4.5	33.7	45.3	6.2	123.0	0.8	5.1
25	Cycloheptatriene	10.3	4.5	31.8	48.5	4.9	123.6	1.8	9.9
26	Mesitylene	10.3	4.7	26.9	50.0	8.1	130.3	0.0	0.0

[a] Conditions: 10 M% catalyst, 175 C, 440 psi H_2, 6 hr; Abbreviations: Pal, palmitate; St, stearate; M, monoene; D, diene; T, triene; IV, iodine value; CD, conjugated diene.

[b] T and CD peaks overlapped by GLC and T was estimated by subtracting CD ($a_{232\,m\mu} = 100$) from triene determined by GLC.

[c] Calculated on the basis of GLC analysis.

[d] As methyl elaidate.

TABLE III

Hydrogenation of Soybean Methyl Esters with Methyl Benzoate-$Cr(CO)_3$[a]

Run No.	Catalyst, mole %	Temp, C	Product composition, %					IV	CD, $a_{232\,m\mu}$	*trans*,	Selectivity[b]	
			Pal	St	M	D	T			%	T/D	D/M
Control	....	......	10.3	4.5	26.6	50.2	8.4	131.0	....	....	....	......
27	5	165	10.4	4.8	30.8	48.8	5.2	123.9	2.2	3.5	5.1	6.8
28	10	165	10.6	4.8	38.1	42.8	3.5	115.4	3.2	5.5	3.4	10.1
29	5	175	10.3	4.7	50.2	34.0	0.8	103.7	7.4	5.8	4.3	76.7
22[c]	10	175	10.3	4.7	67.0	18.0	0.0	88.4	2.0	7.3	....	......

[a] See footnotes a, b, c, d, Table II.

[b] Calculated with digital computer assuming that hydrogenation follows the sequence: T → D → M → St. Selectivity values could not be calculated for run 22 because % T was 0.

[c] See Table II.

the other hand, methyl benzoate-$Cr(CO)_3$ was more labile and catalyzed effectively the hydrogenation of linoleate and linolenate in soybean oil. IR measurements of residual methyl benzoate-$Cr(CO)_3$ (absorbance at 1931 cm^{-1}) after hydrogenation of soybean methyl esters at 175 C showed 40% decomposition of the complex (Table II, run 22). Hydrogenation at 165 C decomposed 32% of the methyl benzoate-$Cr(CO)_3$. These results are in contrast to those obtained with methyl sorbate as substrate where no decomposition of methyl benzoate-$Cr(CO)_3$ complexes was observed.

Hydrogenation of linoleate and linolenate is apparently preceded by conjugation (14). Such a step is suggested by the small amount of diene conjugation observed in the hydrogenated product (Table II). The high temperature required for conjugation (above 150 C) causes decomposition of the catalytic complexes. Table II shows that the $Cr(CO)_3$ complexes are selective for the hydrogenation of linolenate and linoleate and that they produce little or no stearate. The relatively low *trans* content of the hydrogenated products is also remarkable.

Table III contains hydrogenation data obtained with methyl benzoate-$Cr(CO)_3$, which proved to be the most effective catalyst for the hydrogenation of soybean methyl esters at 165–175 C. Polyunsaturates were hydrogenated to monounsaturates with only a little increase in stearate. The products had about 2–7% conjugated diene and only 3.5–7.3% *trans* unsaturation. Selectivity values were calculated with a digital computer programmed by Butterfield and Dutton (2). Selectivity for linolenate vs. linoleate varied from 3.4 to 5.1 and for linoleate vs. oleate from 6.8 to 76.7.

TABLE IV

Analysis of Rubber Chromatography Fractions—Soybean Methyl Esters Hydrogenated with Methyl Benzoate-$Cr(CO)_3$

Analyses	Run 29[a] (IV: 103.7)		Run 22[a] (IV: 88.4)	
	Monoene	Diene	Monoene	Diene
GLC, %				
Palmitate	18.2	......	15.3	......
Monoene	81.8	0.9	84.7	1.1
Diene	......	94.1	......	97.2
Conj. diene	......	5.0	......	1.7
IR				
trans,[b] %	4.6(5.6)[c]	6.2	9.1(10.8)[c]	7.9
UV, alkali conjugatable,[d] %	......	73.5	......	62.2

[a] See Table III.

[b] As methyl elaidate.

[c] Calculated to account for per cent palmitate in monoene fractions.

[d] ($a_{232\,m\mu}$ after alkali conjugation/$a_{232\,m\mu}$ of methyl linoleate after alkali conjugation) × 100.

Hydrogenated soybean esters were separated by rubber column chromatography into monoene and diene fractions (Table IV). The monoenes at two levels of hydrogenation had only 6–11% *trans* unsaturation. The dienes were slightly conjugated (ca. 2–5%). The respective amounts of diene conjugatable with alkali were 73.5% and 62.2% in the fractions

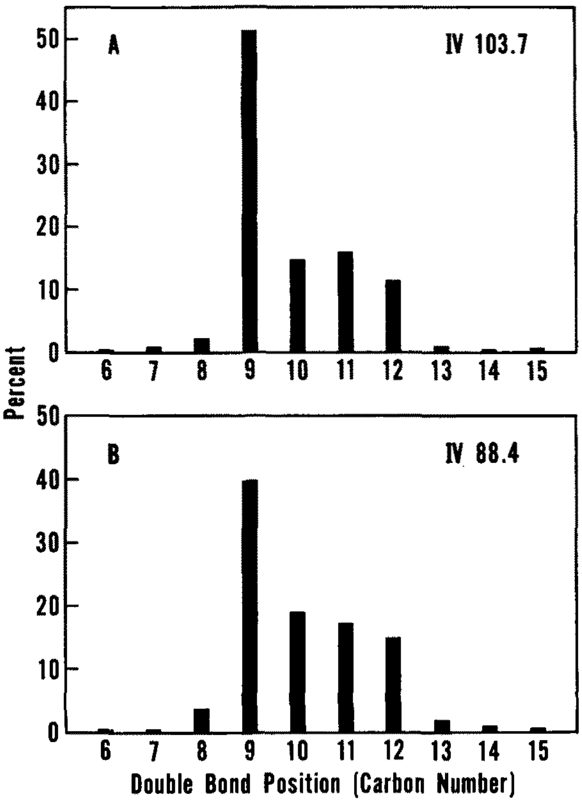


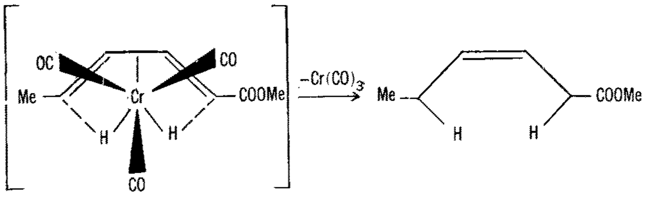
FIG. 2. Double bond distribution in monoene fractions from hydrogenated soybean methyl esters: (A) Run 29, Table IV; (B) Run 22, Table IV.

from esters hydrogenated to an IV of 103.7 and 88.4. Unconjugatable dienes have double bonds separated by more than one methylene group. The more highly hydrogenated esters (IV 88.4) had no triene (Table III, run 22). Therefore, the unconjugatable diene in these samples reflect the amount of linolenate hydrogenation. Reductive ozonolysis-GLC (Fig. 2) shows that 40–50% of the double bond in the monoene fractions remained in the original C-9 position. The rest of the unsaturation was distributed mostly between the C-10 and C-12 positions. Our results can be interpreted by assuming that these monoenes were derived mainly from linoleate hydrogenated after conjugation into a mixture consisting of 9,11- and 10,12-dienes. Further support for this interpretation has been afforded from studies of the hydrogenation of pure linoleate and its conjugated diene isomers (14).

Discussion

The selectivity of various soluble catalysts in the hydrogenation of methyl sorbate varies considerably. The homogeneous catalyst $Co^{II}(CN)_5$ when used with sorbic acid yields 2-hexenoic acid as the main product (3,22). On the other hand, $Fe(CO)_5$ and Fe carbonyl olefin complexes reduce methyl sorbate into a mixture of 2-, 3- and 4-hexenoates, as well as hexanoate (11). In contrast with these catalysts, $Cr(CO)_3$- and usually $Mo(CO)_3$-complexes produce mainly methyl 3-hexenoate. The low specificity of mesitylene-$W(CO)_3$ in yielding all four products from methyl sorbate is similar to that of $Fe(CO)_5$ and olefin-Fe carbonyl complexes.

By using deuterium as a tracer we now have direct proof that reduction catalyzed by methyl benzoate-$Cr(CO)_3$ proceeds by 1,4 addition of hydrogen (15). An intermediate cisoid methyl sorbate-$Cr(CO)_3$ dihydride (I) would account for the product methyl *cis*-3-hexenoate obtained selectively.



I

Methyl *cis* 3-hexenoate

The multitude of products obtained with $Fe(CO)_5$, olefin-Fe carbonyl complexes, and mesitylene-$W(CO)_3$ can be explained by invoking 1,2 and 1,4 addition of hydrogen, as well as direct reduction of diene to saturates and positional isomerization. Furthermore, these catalytic complexes probably involve monohydride intermediates as has been demonstrated with $Co^{II}(CN)_5$, which can undergo either 1,2 or 1,4 addition according to the Co/CN ratio used (21).

The selectivity of mesitylene carbonyl complexes was markedly modified by only changing the metal within group VIB in the Periodic Table; at 165 C the Cr complex produced methyl 3-hexenoate from methyl sorbate and the W complex, mainly methyl 2-hexenoate; at 150 C the Mo complex produced mainly methyl 4-hexenoate. Changes in the nature of the ligands in $Cr(CO)_3$ complexes did not modify their selectivity. Only the order of catalytic activity was affected. With substituted benzene complexes, the activity varied with the substituents in the order $Cl > COOCH_3 > H > CH_3 > (CH_3)_3 > (CH_3)_6$. Electron-withdrawing substituents increased catalytic activity, whereas electron-repelling substituents decreased it. The inductive effect of electron-donating substituents is known to strengthen the π-bond between arene and $Cr(CO)_3$ as shown by an increase in dipole moment (25). Therefore, electron-donating substituents would be expected to decrease the ease of dissociation of $Cr(CO)_3$ complexes, whereas electron-withdrawing substituents would facilitate dissociation. The order of catalytic activity can thus be related to the ease of dissociation of these complexes. This dissociation was postulated as the first and most probable rate-determining step in the homogeneous hydrogenation (15). The occurrence of this dissociation is supported by our observation that the free ligand of the complex is formed during hydrogenation (Fig. 1). A better understanding of the mechanism of action of these model catalysts may eventually lead to tailor-made catalysts of known activity and selectivity.

Although it was previously observed that only conjugated fatty esters in a mixture were hydrogenated with the chromium complexes (6), we have now found that under sufficiently high temperatures the more active and thermally stable complexes can also catalyze the hydrogenation of unconjugated fatty esters. Kinetic studies showed that although conjugated and unconjugated dienes are readily hydrogenated individually, in a mixture competition occurs and the conjugated dienes are selectively reduced (14). In the hydrogenation of unconjugated fatty esters, conjugation is indicated as an intermediate step. With soybean esters the linolenate-linoleate selectivity of methyl benzoate-$Cr(CO)_3$ ranged between 3 and 5. Although this selectivity was higher than that reported for conventional heterogeneous catalysts (1.33 to 2.71) (18), it is not so high as that for copper-chromium catalysts (6–13) (20). Of more importance, however, was the relatively low *trans* content of the hydrogenated products. The mechanism of 1,4 addition of hydrogen via a cisoid intermediate of type I would account for the formation of *cis* monoene from linoleate after conjugation. Any other homogeneous or heterogeneous catalysts that have been examined so far in our laboratory have produced much higher levels of *trans* unsaturation at corresponding degrees of hydrogenation than these $Cr(CO)_3$ complexes. Evidently, we are dealing with a new class of selective homogeneous catalysts unique in their ability to reduce diene and triene fatty esters into mostly *cis* monoene fatty esters.

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