Conjugation of Soybean Oil by Decomposition of Its Iron Tricarbonyl Complex with Carbon Monoxide[1]

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Abstract

Soybean and other vegetable oils are conjugated by decomposing their iron tricarbonyl complexes with carbon monoxide at elevated pressures. This procedure converts the iron tricarbonyl moiety of the complex into iron pentacarbonyl, which is recovered for reuse. When iron carbonyl-complexed soybean oil is heated at 180–200C at CO pressures of 1090–3750 psi, 90–97% of the complex is decomposed into $Fe(CO)_5$ and conjugated soybean oil. At 180C and 3600 psi CO, 84% of the $Fe(CO)_5$ is recovered, and 82% of the polyunsaturates in the oil is conjugated. At 200C and 1090 psi CO, 98% of the $Fe(CO)_5$ is recovered, but the oil is less conjugated (75%). The studies point the way to a possibly economical process for conjugating vegetable oils by consecutive reactions with $Fe(CO)_5$ and CO.

Introduction

STUDIES AT THE NORTHERN LABORATORY with iron carbonyl complexes of fatty esters have led to a procedure for conjugating vegetable oils. In this method, the polyunsaturated fatty esters were treated with iron pentacarbonyl to form iron tricarbonyl complexes which were then decomposed with ferric chloride (3). Although 90–97% of the polyunsaturates in the oils were conjugated by this procedure, the iron tricarbonyl moiety of the complex was completely decomposed and lost. New ways to decompose the iron tricarbonyl-complexed oils have been investigated in an attempt to regenerate free $Fe(CO)_5$ for reuse and to make this new method for the conjugation of fats more economical. An IR study of the reaction of iron tricarbonyl-complexed oils with CO revealed the appearance of two sharp bands at 4.94 and 5.00 μ attributable to $Fe(CO)_5$ (8) and the disappearance of the bands due to iron tricarbonyl complex at 4.88 and 5.07 μ (2,4). These observations suggested that the complexes could be decomposed with carbon monoxide under pressure and thus free $Fe(CO)_5$ could be regenerated and recovered.

Although many syntheses for metal carbonyls have been reported (6,7,9) no information is available to our knowledge on the decomposition of iron carbonyl-olefin complexes with CO. Our aim has been to determine the best conditions to react iron tricarbonyl complexes of vegetable oils with CO to recover conjugated oils and $Fe(CO)_5$.

Experimental

Materials and Methods

The vegetable oils used and methods of analysis (GLC, IR, UV) were the same as those already described (3,5).

Preparation of $Fe(CO)_3$ Complex

Since the complexes were prepared on a larger scale than before (3) a typical run is described in detail. This example includes also a procedure for conveniently and safely removing large amounts of unreacted $Fe(CO)_5$ from the reaction mixture by azeotropic distillation with benzene.

Soybean oil (238 g, containing 59.6% polyunsaturates) was charged into a 1-liter, magnetically stirred, high-pressure autoclave (Magna-Drive, Autoclave Engineers, Erie, Pa.) (10) equipped with sampling tube and cooling coil. To the oil maintained under a nitrogen atmosphere was added 225 ml (326 g) of freshly distilled $Fe(CO)_5$. The mixture was blanketed with nitrogen. The autoclave was then sealed and purged three times with nitrogen at 200 psi with stirring. After the pressure was released, the autoclave was charged again with nitrogen to approximately 30 psi. The reaction mixture was heated at 185C for 4.5 hr. During the reaction the pressure in the system increased to a maximum of about 300 psi after 1.5 hr and then fell to 200 psi. The contents in the autoclave were cooled to room temperature, the pressure carefully released and the reaction mixture was dissolved in benzene and transferred into a round-bottom flask. Unreacted $Fe(CO)_5$ and benzene were removed by azeotropic distillation at 81–88C at atmospheric pressure under a blanket of nitrogen. The last portions of benzene and $Fe(CO)_5$ were removed under vacuum at 60–80C and 2–3 mm Hg and collected in a dry ice trap. The complexed oil was washed with HCl and water as described earlier (3). The soybean oil-$Fe(CO)_3$ contained 58.8% complex (from IR) corresponding to 85.7% conversion[4] of total polyenes in the starting oil.

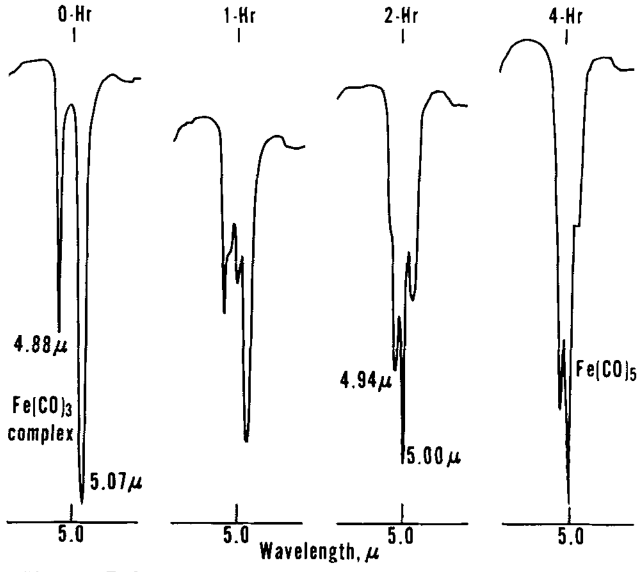

FIG. 1. Infrared spectra (in CCl_4) of soybean oil-$Fe(CO)_3$ decomposed at 180C and 3600 psi CO (run 5, Table I). Intensities are of relative magnitude only.

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[4] Calculation: weight of complex = 142 g polyenes × 434/294 = 209g; increase in weight = 209 g − 142 g = 67 g; conversion, calculated = 209/(238 + 67) × 100 = 68.6%; found = (58.8/68.6) × 100 = 85.7%.

TABLE I
Decomposition of Iron Tricarbonyl-Complexed Vegetable Oils with Carbon Monoxide

Run	Oils[a]	Temp, C	Time, hr	Pressure, psi CO	Decomposition[b] %	Conjugation[c] %	Yield $Fe(CO)_5$[d] %
1	Safflower	185	3.5	Atm.	3	......	......
2	Safflower	180	4	360	33	42.3	......
3	Linseed	185	5.5	1400	86	62.2	......
4	Soybean	185	4	500	12	......	......
5	Soybean	180	4	3600	88	82.4	83.8
6	Soybean	190	4	1500	97	80.8	84.5
7	Soybean	198	2	3750	95	83.1	71.0
8	Soybean	200	4	1090	90	75.6	98.0

[a] Initial concentration of $Fe(CO)_3$ complex: safflower, 64.6; linseed, 59.6; soybean, 58.8%.
[b] Based on decrease in complex.
[c] Based on total linoleate and linolenate in original oils and GLC analyses: safflower, 76.5; linseed, 62.6; soybean, 59.1%.
[d] See footnote 5.

Decomposition of Complex

All operations with CO were carried out in a barricaded, well-ventilated high-pressure stall equipped with a reliable CO alarm. Complexed soybean oil (72.1 g, containing 42.4 g complex, run 8, Table I) was charged into a one-liter magnetically stirred autoclave provided with a liner of about 150 ml in volume. The autoclave was then sealed, purged three times with CO at 200 psi and finally charged with 800 psi CO before heating. The reaction mixture was heated at 200C ± 2 for 4 hr. During this period the pressure reached a maximum of 1090 psi. The course of the reaction was followed by successive IR analyses. When the content of $Fe(CO)_3$ complex decreased (absorptivity at 4.88 and 5.07 μ) to a constant value, the decomposition was considered complete, and the autoclave was cooled to room temperature. The reaction mixture was transferred into a round-bottom flask, and the regenerated $Fe(CO)_5$ was distilled at 92C under a nitrogen blanket at atmospheric pressure. After the last portion of $Fe(CO)_5$ was removed by vacuum stripping at 100C, a conjugated soybean oil product (55.2 g, not including sample weights) was obtained that was free of $Fe(CO)_5$ as indicated by the absence of the characteristic IR bands at 4.94 and 5.00 μ. The stripped oil still contained 5.7% $Fe(CO)_3$ complex (by IR), equivalent to 90.2% decomposition of the original complex content. The $Fe(CO)_5$ recovered from the reaction product (16.9 g) corresponded to 98% of theory based on the weight of complex decomposed.[5]

Results

Iron tricarbonyl-complexed vegetable oils were treated with CO at various temperatures and pressures to optimize the method for preparation of conjugated oils and for regeneration of $Fe(CO)_5$. The course of the reaction was followed by periodic IR analyses. Figure 1 shows that when soybean oil-$Fe(CO)_3$ is subjected to CO pressure, the carbonyl bands of the complex (4.88 and 5.07 μ) disappear and those of the $Fe(CO)_5$ become stronger (4.94 and 5.00 μ). At the end of each run the $Fe(CO)_5$ was distilled from the reaction mixture. The distillate had the same IR spectrum (λ_{max} at 4.94 and 5.00 μ) as freshly distilled $Fe(CO)_5$. The results in Table I show that appreciable decomposition of the complex occurred only at temperatures exceeding 180C and CO pressures above 1000 psi. Decomposition of iron tricarbonyl complex reached 90–97% at 180–200C and CO pressures of 1090 to 3750 psi. At 180C and 3600 psi CO, the $Fe(CO)_5$ formed was 84% of theory and the conjugation corresponded to 82% of the polyunsaturates (run 5). Higher temperatures and lower CO pressure resulted in a lower level of conjugation (75%) but in a 98% yield of $Fe(CO)_5$ (run 8).

The effect of reaction time on decomposition of complex and on extent of conjugation is illustrated in Figures 2 and 3. At 200C the decomposition of complex reached a constant value of 90% after 2 hr, whereas at 180C this value was reached after 4 hr (Fig. 2). Maximum conjugation of 82.5% occurred after 1 hr at 200C; then conjugation decreased slowly to 75% after 4 hr (Fig. 3). At 180C the conjugation increased from 60 to 87% at a rate similar to the extent of complex decomposition depicted in Figure 2. These results indicate that at 200C a short residence time is essential for maximum conjugation. Prolonging the heating period lowers the conjugated polyunsaturates apparently as a result of polymerization. On the other hand, at 180C longer reaction times are necessary to decompose the complex and liberate the conjugated fatty esters.

Summarized in Table II are analyses of the conjugated soybean oils from decomposition of complex with CO. The degree of conjugation varies from 75

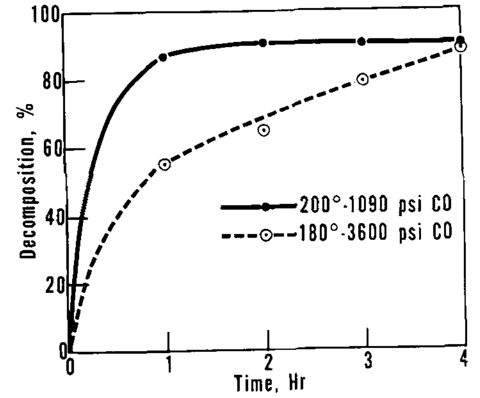

FIG. 2. Rate of decomposition of soybean oil-$Fe(CO)_3$ at 180C–3600 psi CO (run 5, Table I) and 200C–1090 psi CO (run 8).

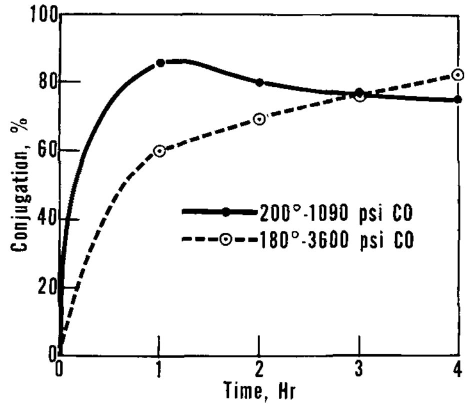

FIG. 3. Conjugation of soybean oil by decomposition of $Fe(CO)_3$ complex with CO (same runs as in Fig. 2).

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[5] Calculation: complex decomposed = 42.4 × 0.902 = 38.2 g; total $Fe(CO)_5$ expected = 38.2 g × 196/434 = 17.3 g; yield of $Fe(CO)_5$ = (16.9/17.3) × 100 = 98%.

TABLE II
Fatty Acid Composition of Conjugated Soybean Oils

Analyses	Runs[a]			
	5	6	7	8
Gas-liquid chromatography,[b] %				
Palmitate	12.5	11.5	11.5	11.8
Stearate	4.9	4.9	4.7	5.0
Monoene	26.5	26.1	26.1	27.2
Diene	7.4	12.3	8.5	11.5
Conjugated diene				
cis, trans[c]	5.7	12.5	7.5	10.3
trans, trans[d]	43.0	32.8	41.6	34.3
Conjugation[e]	82.4	80.8	83.0	75.4
Infrared, %				
Complex[f]	6.8	1.7	2.7	5.7
trans, trans-Conjugation[g]	38.8	29.9	37.5	25.0
Isolated *trans*[h]	30.5	36.4	36.2	36.8
Ultraviolet				
a_{231} mμ	42.6	42.5	39.4	33.1
a_{268} mμ	3.8	3.1	2.9	2.5

[a] Same runs as in Table I, analyzed after removing $Fe(CO)_5$ by distillation.

[b] Composition of original soybean oil: palmitate 10.1, stearate 4.5,

[c] Includes triene when not completely conjugated.

oleate 25.8 linoleate 51.9 and linolenate 7.2%.

[d] Includes conjugated diene-triene, i.e., triene with two conjugated double bonds and one isolated.

[e] Based on total linoleate and linolenate in original oil: 59.1%.

[f] Expressed as methyl octadecadienoate-$Fe(CO)_3$ (2).

[g] Using $a_{10.1}$ μ =1.25 (9,11-*trans, trans-methyl octadecadienoate*).

[h] Using $a_{10.4}$ $\mu = 0.473$ (methyl elaidate).

to 83% of the total polyunsaturated fatty esters. Analyses by GLC and IR show that the conjugated dienes and trienes are, as before (3), predominantly in the all-*trans* configuration. Although UV analyses show the presence of small amounts of conjugated triene (absorptivity at 268 mμ) this component was not detectable under the conditions used for GLC. As shown in Table II the conjugated oils contained more saturates and monoenes than the original oil. The higher values are attributable to residual $Fe(CO)_3$ complex and the presence of other nonvolatile products. If these products are polymers and if they are derived from the polyunsaturates, one may estimate their concentration from the ratio of saturates + monoene before and after conjugation. The calculated values for polymers range from 0.8% (run 5) to 3.2% (run 6). No evidence of carbonylation was indicated by IR and GLC of the products (alcohols, aldehydes or ketones).

Discussion

This CO procedure decomposes almost completely the $Fe(CO)_3$ complexes of vegetable oils, produces highly conjugated oils and regenerates $Fe(CO)_5$ in high yields for reuse. Although the yields of conjugated oils are 11 to 12% lower than by the previous $FeCl_3$ method (3), the conversion of the $Fe(CO)_3$ moiety into reusable $Fe(CO)_5$ makes the CO procedure more economical. The groundwork has now been laid for the development of an integrated process to conjugate oils by preparing and decomposing $Fe(CO)_3$ complexes of vegetable oils by consecutive reactions with $Fe(CO)_5$ and CO under pressure. Further pilot-plant studies are necessary to determine whether this new procedure is competitive with other methods used in industry to prepare artificially conjugated drying oils (1).

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