Isomerization of Unsaturated Fatty Esters by Iron Pentacarbonyl. Preparation of Iron Tricarbonyl Complexes of Polyunsaturated Fats

E. N. FRANKEL, E. A. EMKEN and V. L. DAVISON,
Northern Regional Research Laboratory, Peoria, Illinois

Abstract
Iron pentacarbonyl is a powerful isomerization agent of unsaturated fatty esters. Highly conjugated fats are obtained when polyunsaturated fatty esters are treated with an excess Fe(CO)\textsubscript{5} to form complexes followed by decomposition of the complexes with FeCl\textsubscript{3}. Iron tricarbonyl complexes were prepared in 80 to 95\% yields from methyl linoleate, linolenate and polyunsaturated fatty esters of soybean, linseed and safflower oils by heating at 180-185\°C with 2 moles Fe(CO)\textsubscript{5} per mole ester under nitrogen pressure. Decomposition of these complexes with FeCl\textsubscript{3} resulted in 90 to 97\% conjugation of the polyunsaturated fatty esters mainly in the all \textit{trans} configuration. Isolated \textit{trans} unsaturation reached levels of 18 to 30\%. Methyl oleate yielded 74\% \textit{trans} unsaturation but no complex of iron carbonyl was obtained.

Introduction
Artificially conjugated drying oils can be prepared by many different procedures, all aimed at accelerating conjugation of the polyunsaturated fatty acids with a minimum of polymerization. Various aspects of the preparation and properties of artificially conjugated drying oils have been reviewed by Cowan (3) and Bush (1). Studies in this Laboratory with homogeneous catalysts for the hydrogenation of unsaturated fats showed that iron pentacarbonyl is a powerful isomerization agent (11), and that it forms stable iron carbonyl complexes with polyunsaturated fatty esters (10). Diene complexes from methyl linoleate were characterized as mixtures of isomeric, conjugated methyl octadecadienoate-iron tricarbonyl (8). Triene complexes from linolenate proved to be mixtures of isomers containing a conjugated diene-Fe(CO)\textsubscript{3} unit and a noncomplexed cis or trans olefinic bond either \(\alpha,\beta\) to the \(\pi\)-complexed system or separated by several methylene groups (7). Hashimoto and Shima (14) reported the formation of up to 30\% conjugated dienes from soybean oil by heating with Fe(CO)\textsubscript{5} at 180 and 200\°C under nitrogen. However they did not consider the formation of iron carbonyl complexes. From methyl linoleate conjugated with Fe(CO)\textsubscript{5} they obtained a mixture of \textit{trans,trans} 9,11- and 10,12-methyl octadecadienoate (15). More recently, Misono et al. (21) and Ogata and Misono (22) reported the formation of iron tricarbonyl complexes from cottonseed oil and dehydrated castor oil methyl esters by hydrogenation or reaction with Fe(CO)\textsubscript{5}, under nitrogen pressure. This work is in good agreement with ours (8,10) and was published the same year.

Practically, our present studies are aimed at converting soybean, linseed and other vegetable oils into conjugated drying oils, and into new organometallic derivatives by treatment with Fe(CO)\textsubscript{5}. Theoretically, we are interested in the mechanism of isomerization and conjugation catalyzed by soluble organometallic complex such as Fe(CO)\textsubscript{5}. A procedure was developed leading to nearly complete conjugation of polyunsaturated fatty esters or oils by the formation of stable iron tricarbonyl complexes. These complexes can be easily and completely decomposed with ferric chloride to give high yields of conjugated oils. Decomposition with FeCl\textsubscript{3} (24) is formulated below as an oxidation-reduction. The diene-Fe(CO)\textsubscript{3} complexes [1] investigated in this work yield \textit{trans,trans} conjugated dienes as follows:

\[
\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 2 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

The respective triene-Fe(CO)\textsubscript{3} complexes [2] and [3] give conjugated diene-trienes (trienes with a conjugated diene system and an isolated double bond) and conjugated trienes as follows:

\[
\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 3 \text{CO} + 3 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 2 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 3 \text{CO} + 3 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

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\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 2 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

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\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 3 \text{CO} + 3 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

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\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 2 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

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\begin{align*}
\text{R-CH} & \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{R'} + 3 \text{CO} + 3 \text{FeCl}_3 \\
\text{Fe} & \text{(CO)}_3 \\
\end{align*}
\]

Experimental

Materials
The soybean, linseed and safflower oils used were commercially refined. Their methyl esters were obtained by transesterification with potassium methoxide and distillation under vacuum. Methyl oleate and linoleate were obtained from the Hormel Insti-
tute and analyzed 100% by gas-liquid chromatography (GLC). Methyl linolenate was prepared from linseed esters by counter double current distribution (2), and showed by GLC 98.8% triene and 1.2% diene.

Fractionations and Analyses

Fractionations by countercurrent distribution (CCD), between hexane and acetoneitrile, and argentation chromatography on AgNO3-treated cation exchange column were the same as described previously (8,9). The methodology relating to GLC, IR and UV was also the same (9,11). Conjugated dienes (cis, trans and trans,trans) used as standards for GLC were prepared from alkali-conjugated methyl linoleate. Conjugated diene-trienes and conjugated trienes were prepared from alkali-conjugated linseed oil (11). The iron tricarbonyl complex was determined by IR in the carbonyl stretching region (4-6 μ) in CCl4 solutions. Pure methyl octadecadienoate-Fe(CO)3 derived from methyl linoleate (8) was used as standard. Its respective absorptivity at 4.88 and 5.05 μ was 4.64 and 7.55, and followed Beer-Lambert's Law in the range of 10 to 100% complex. Double bond location in fractionated fatty esters was determined by the KMnO4-KIO4 cleavage technique of Jones and Davison (17).

Preparation of Fe(CO)3 Complex

All complex preparations were made in a 150-ml or 300-ml magnetically stirred Magne-Dash, high-pressure autoclave adapted with sampling tube and cooling coil. All operations with Fe(CO)3 were carried out in a well-ventilated hood and without exposure to direct light. In a typical run (run 4, Table I) 30.22 g of soybean oil methyl esters (0.1 mole) was charged into a 150-ml autoclave together with 28 ml (39.2 g, 0.2 moles) of Fe(CO)5. The mixture was degassed by gentle nitrogen bubbling and 60 g FeCl3 was added in small portions. Stirring was continued 2 hr under nitrogen for 1 hr. The mixture was then diluted with water and extracted three times with petroleum ether. The washed extract was dried (Na2SO4), and the solvent removed to give 7.90 g conjugated esters.

Complexed soybean oil esters (10.05 g, run 4, Table I) were dissolved in 95% EtOH in an Erlenmeyer flask, and the mixture was stirred magnetically with nitrogen bubbling. Small portions of FeCl3 · 6H2O were added to the solution until no more CO was evolved (30 g FeCl3 used). Stirring was continued under nitrogen for 1 hr. The mixture was then diluted with water and extracted three times with petroleum ether. The washed extract was dried (Na2SO4), and the solvent removed to give 7.90 g conjugated esters.

Decomposition of Complex

Complexed soybean oil esters (10.05 g, run 4, Table I) were dissolved in 95% EtOH in an Erlenmeyer flask, and the mixture was stirred magnetically with nitrogen bubbling. Small portions of FeCl3 · 6H2O were added to the solution until no more CO was evolved (30 g FeCl3 used). Stirring was continued under nitrogen for 1 hr. The mixture was then diluted with water and extracted three times with petroleum ether. The washed extract was dried (Na2SO4), and the solvent removed to give 7.90 g conjugated esters.

Complexed triglycerides were decomposed by a similar procedure as the methyl esters except that they were dissolved in a mixture of benzene and 95% EtOH and that more FeCl3 was used. In a typical example (run 18, Table I) 12.02 g of complexed linseed oil was dissolved in a mixture of 200 ml benzene and 350 ml 95% EtOH. The solution was stirred with nitrogen bubbling and 60 g FeCl3 was added in small portions. Stirring was continued 2 hr under nitrogen. The conjugated oil (9.40 g) was isolated as above.

Results

The effect of reaction conditions on yields of iron tricarbonyl complex was studied. The results in Table I show that the yield of complex increased with initial concentration of Fe(CO)3 at 180°C. Moreover, the reaction proceeded much more smoothly at 180°C and 185°C than at 175°C, giving 90 to 92% yields of complex. Temperatures higher than 185°C would be expected to result in polymerization of the conjugated esters (21). With methyl oleate no stable complex was formed by reaction with Fe(CO)3, but extensive positional and geometric isomerization of the double bond occurred. With methyl linoleate it was necessary to use 2 moles Fe(CO)3 per mole ester to obtain 90% conversion to complex at 180°C. With methyl linolenate a yield of 78% complex was obtained by heating 2 hr with 2 moles Fe(CO)3, cooling to room temperature, releasing the CO formed and reheating for another 2 hr. With triglycerides the yield of complex obtained ranged from 85 to 95%.