Characterization of a Methyl Linoleate-Iron Carbonyl Complex

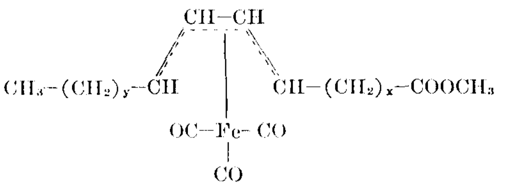
AN IRON CARBONYL complex is formed with unsaturated fats during homogeneous hydrogenation catalyzed by iron pentacarbonyl (3). Current interest in the role of *pi*-bonded organometallic intermediates in catalysis (11) led us to isolate and characterize the complex formed from methyl linoleate and iron pentacarbonyl. Two methods were used: a) hydrogenating at 180C with half a mole $Fe(CO)_5$ at 400 psi hydrogen for 2 hr, and b) heating at 180C with 1 mole $Fe(CO)_5$ under nitrogen for 4 hr.

The methyl octadecadienoate-iron carbonyl complex formed by Method "a" was isolated as a deep yellow liquid in 23% yield by countercurrent distribution between hexane and acetonitrile (12). The complex was separated from the monoenoic and dienoic fatty esters. Its peak assumed a position intermediate between dienoic and trienoic fatty esters (Transfer 500). (Found: C, 61.6; H, 8.0; Fe, 12.5%; methyl octadecadienoate-iron tricarbonyl, $C_{22}H_{34}O_5Fe$, requires: C, 60.8; H, 7.8; Fe, 12.9%). The IR spectrum of the complex shows intense absorption bands at 4.88 μ (ϵ 1970) and 5.05 μ (ϵ 3450), characteristic of iron carbonyl complexes (9). The UV spectrum shows strong end absorption at 215 mμ (ϵ 23100) corresponding to that reported for (1,3-butadiene)-iron tricarbonyl (8). When methyl linoleate was heated with iron pentacarbonyl (Method "b"), appreciable conjugated dienes were formed (a_{230} mμ : 38.3). Alumina chromatography yielded on elution with *n*-hexane ca. 10% of a yellow material with the same IR characteristics as the iron carbonyl complex isolated from hydrogenated linoleate. (Found: C, 61.8; H, 8.0; Fe, 12%, ϵ 4.88 μ 2250, ϵ 5.05 μ 3700).

NMR spectra (obtained in carbon tetrachloride solution with a Varian A60 spectrometer using tetramethyl silane as reference) of the two complexes isolated are identical. The olefinic protons are split into two pairs. One pair gives a signal at low field in the normal region for olefins at 5.0 τ (methyl linoleate gives a signal at 4.6 τ equivalent to 4 olefinic protons). The second pair is shifted upfield in the normal aliphatic region. Such a shift characterizes conjugated olefins bound to metals (13). Also, NMR spectra show elimination of the signal at 7.2 τ due to methylenic protons adjacent to two double bonds, a characteristic of conjugated dienes. The signal at 7.9 τ due to protons of methylene alpha to olefinic double bonds is also absent and is apparently shifted in the normal aliphatic region.

The methyl octadecadienoate-iron tricarbonyl complex (Method "a") was oxidatively cleaved with $KMnO_4-KIO_4$ (6) to determine the position of double bonds in the dienoic ligand. Analysis of cleavage monobasic and dibasic acids showed that the principal dienes included, in per cent: 9,11- (33.7), 10,12- (31.5), 8,10- (13.3), 11,13- (11.8), 7,9- (3.8), 12,14- (3.0), 5,7- (1.9), and 6,8- (1.0) methyloctadecadienoates. The complex was decomposed by heating with alkali under conditions used for isomerization (2) (6.6% KOH in ethylene glycol, 180C, 45 min) or with excess triphenyl phosphine (7) (150C, evacuated tube, 12 hr). The alkali treatment yielded a finely divided black precipitate identified as iron. The resulting conjugated diene had an absorptivity at 230 mμ of 71.2 compared to 85.6 for methyl linoleate alkali-conjugated under the same conditions. The product obtained from triphenyl phosphine decomposition absorbed strongly at 10.10 μ, a characteristic of *trans, trans* conjugated methyl octadecadienoate (5). These results confirm the NMR spectra and the degradation study in showing that the iron carbonyl is attached to a conjugated dienoic fatty ester.

The structure proposed below is similar to that given for the well-known stable complexes of metal carbonyls and conjugated dienes (1,10), involving overlapping of atomic orbitals of iron and *pi*-orbitals of the diene as in ferrocene.



x,y: 7,5; 8,4; 6,6; 9,3; 5,7; 10,2; 3,9; 4,8.

Isolation of a *pi*-bonded iron carbonyl complex of methyl linoleate during hydrogenation supports the existence of similar *pi*-bonded species on metallic surfaces during heterogeneous catalysis as suggested by Rooney et al. (4,11). The importance of intermediate conjugated dienoic systems, which enter in the formation of such *pi*-bonded complexes during hydrogenation of fats, is also indicated by our observations. Further study of fat-iron carbonyl complexes may thus elucidate the mechanism of heterogeneous catalytic fat hydrogenation.

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