Isomerization During Hydrogenation. V. Methyl *cis* 6-, *cis* 9-, *cis* 12-Octadecenoates[1]

R. R. ALLEN, Anderson, Clayton and Company, Foods Division, Sherman, Texas

Abstract

The partial hydrogenation of mixtures of methyl *cis* 6-, *cis* 9- and *cis* 12-octadecenoates followed by the determination of the unreacted monoenes indicated the double bonds in these positions are hydrogenated at the same rates. However, study of a hydrogenation under high isomerization conditions indicated the double bonds very near the carboxyl hydrogenate faster than those near the terminal methyl.

Introduction

THE RELATIONSHIP between the position occupied by a double bond in a hydrocarbon chain of a fatty acid and its ease of hydrogenation has received some attention (3,4,7). However, as stated in a recent review (5), "There is growing acceptance of the belief that ease of hydrogenation in a series of alkenoic acid increases as the double bond is removed further from the carboxyl group. This belief is based upon relatively little experimental evidence." Also, this belief has been quoted (2,4) as argument the double bonds do not migrate equally in either direction when methyl oleate is hydrogenated as has been shown in several studies (1,6). The study reported here is intended to shed some light on this question by the use of new techniques for analysis.

The past studies on relative rates of hydrogenation have been accomplished by measurement of the rate of hydrogen uptake of pure material under a controlled set of conditions. This rate then was compared to the rate of hydrogenation of another pure material under the same conditions. Although this technique yielded good information, it is open to serious question. The materials used in this type of study, although highly purified either from natural or synthetic sources, may contain traces of materials that could be catalyst poisons or promotors. Thus the effect of the catalyst would be uncontrollable in each of the different runs and could lead to erroneous conclusions. The technique used in this study was to cancel the effect of any catalyst promotors or poison in the materials by hydrogenation of mixtures of the materials to be compared, followed by analysis of partially hydrogenated samples for the amounts of the original constituents of the mixtures that had not reacted. In this way the rate of reaction of one double bond could be directly compared to another under exactly the same conditions.

Preparation

A mixture of *cis* 9- and *cis* 12-methyl octadecenoate was obtained by the partial hydrogenation of safflower oil acids using hydrazine as described by Scholfield (8). The partially hydrogenated acids were esterified with methanol, fractionated by distillation and the 18 carbon methyl esters subjected to low temp crystallization in acetone to separate the methyl octadecenoates. The *cis* 12-ester was found to be concn during the crystallization presumably because of its higher mp.

Methyl oleate and methyl petroselinate were prepared from olive oil and parsley seed oil respectively, by the usual method of methanolysis followed by distillation and low temp crystallization from acetone solution.

The determination of double bond position was made by ozonolysis of the methyl esters in acetic acid solution and reductive hydrolysis with zinc and water followed by a determination of the aldehydes and aldehyde esters by gas chromatography.

To determine the positions of the double bonds, ca. 50 mg of sample was dissolved in 0.5 ml acetic acid in a small test tube. The solution was cooled to ca. 10C and an excess of ozone in oxygen passed through the sample. Ca. 50 mg 10-mesh zinc and 1 drop water were added, the tube dipped into an oil bath at 120C until the reaction started. After ca. 1 min of reflux the tube was cooled, 0.5 ml ether and ca. 2 ml saturated aqueous sodium chloride added. The tube was shaken with vigor several times, the ether layer separated and transferred to a clean tube. The acetic acid extracted by the ether was neutralized to phenolphthalein end point with 1N NaOH. Solid NaCl was added, the tube agitated and a few μl of the ether layer that separated was injected into the gas chromatograph. A 10 ft, ¼ in. column of 20% XE nitrile silicone was used for the separation of the aldehydes. Temp was linear programmed from 130–240 at 11°/min and then held at 240C with a He flow of 60 ml/min. As shown in Figure 1, the aldehydes were well separated, with each aldehyde ester preceding the aldehyde that was six carbon atoms longer. The aldehyde esters with less than six carbons are completely decomposed during the reductive hydrolysis and part of the six carbon aldehyde ester is lost. The aldehyde esters longer than six carbons are recovered quantitatively. However, the thermal conductivity response of the aldehyde esters is lower than the aldehydes, so must be corrected. The areas of each peak divided by the mol wt of the compound gives the mole equivalent. The sum of the mole equivalents divided into each then gives mole fraction of aldehydes and thus mole fraction of octadecenoate with the double bond at the position represented by the aldehyde. The detector response seems to be the same for aldehydes and fatty acid esters.

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[1] Presented at the AOCS Meeting in Atlanta, 1963.

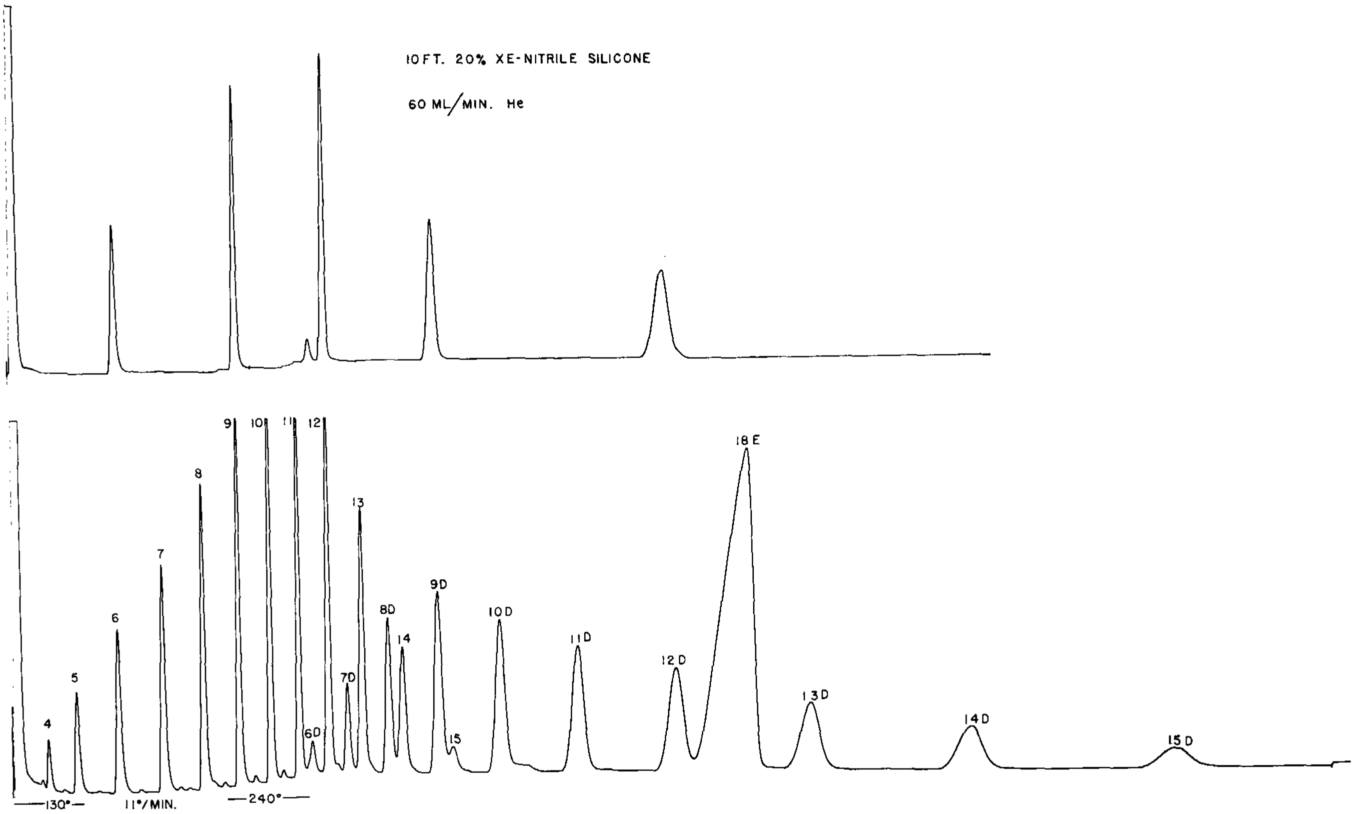

FIG. 1. Gas chromatography of aldehydes and aldehyde esters from ozonization of methyl octadecenoates. Upper Curve—Mixture of methyl *cis* 6-, *cis* 9-, *cis* 12-octadecenoate. Lower curve—Mixture after partial hydrogenation. Numbers are carbon chain length. D = aldehyde esters, E = methyl ester.

The method seems to give good quantitative results as shown in Table I. The total mole percentage of aldehydes and methyl stearate produced by ozonolysis of partially hydrogenated mixtures of octadecenoates are compared to the percentage methyl stearate determined by iodine value (I.V.) measurement. As can be seen, the results agree quite well, which indicates quite quantitative formation of aldehydes from the ozonide with little loss during the subsequent procedure.

The triphenyl phosphine reduction of ozonides as described by Nicolaides (9) was attempted and found to be quite good. The short chain aldehyde esters were formed and obtained quantitatively. However, due to the large amount of methyl stearate in some samples, the ozonization temp could not be kept low enough to prevent some ester formation in the methylene chloride solvent used. Also, the excess triphenyl phosphine came out of the chromatograph at the same position as the longer chain aldehyde esters. It was necessary to measure these long chain aldehyde esters because they indicated the double bonds toward the terminal methyl group. The aldehydes formed from the double bonds at the 14,15,16 and 17 position would be obscured by the solvent peaks. For these reasons, the zinc-acetic acid method was used in this study.

TABLE I
Analysis of Hydrogenated Methyl Octadecenoates by Ozonization and by I.V.

Mole %		
Aldehydes	Stearate	
		From I.V.
97.5	2.0	2.6
89.4	10.6	11.1
79.1	20.9	20.7
62.7	37.3	37.0
41.7	58.3	58.8
19.5	80.5	80.0

Procedure

The hydrogenations were carried out in a 1-liter size Paar medium pressure apparatus that was adapted to small samples. The stirrer blades and sampling tube were removed from the apparatus and replaced by a 1-in. diam, three-blade stirrer and a ⅛-in. O.D. stainless steel sampling tube. The stirrer shaft support was pushed to the top of the shaft. A small glass cup, 4.5 cm x 8 cm, was clamped over the small agitator blade and the ⅛-in. diam sample tube and gas inlet using the thermocouple well for a support.

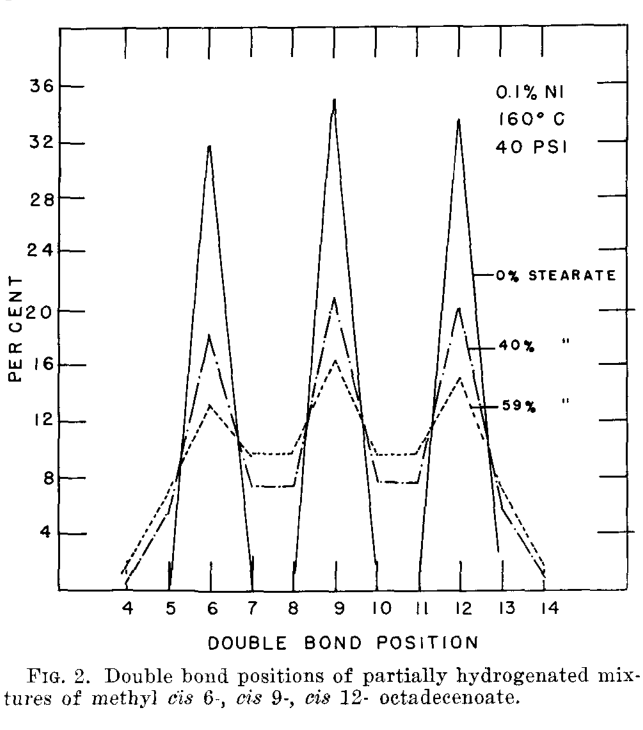

FIG. 2. Double bond positions of partially hydrogenated mixtures of methyl *cis* 6-, *cis* 9-, *cis* 12- octadecenoate.

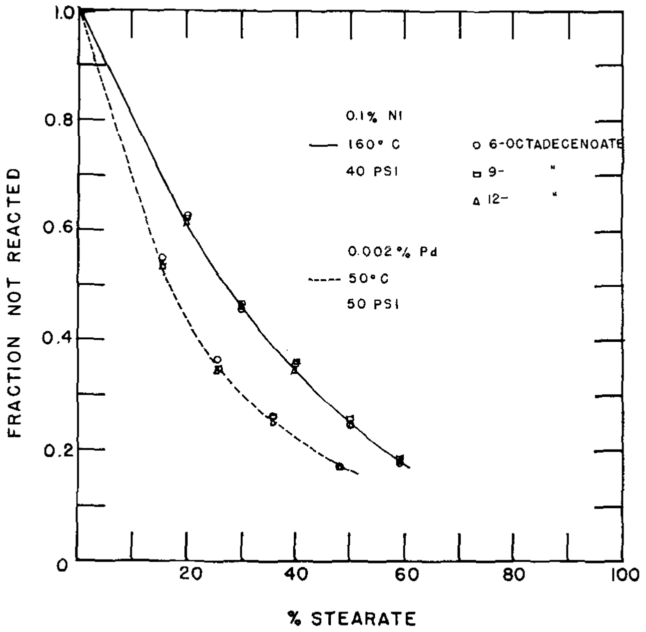

FIG. 3. Comparative reactivity of methyl *cis* 6-, *cis* 9-, *cis* 12-octadecenoate.

The catalyst and material to be hydrogenated were weighed into the glass cup before it was clamped in position. Oil in the outer bomb served as a heating medium for the cup contents. The bomb head and bomb were bolted together and operated as usual. The bomb was flushed four times with hydrogen and then evacuated. The oil was heated to the operating temp, hydrogen admitted and the stirrer started. Samples were taken periodically and the hydrogenation followed by refractive index change. Representative samples were then analyzed for *trans*, stearate and double bond positions.

Results and Discussion

Figure 2 shows the results of the determination of the double bond distribution during the hydrogenation of a mixture of *cis* 6-, *cis* 9- and *cis* 12-octadecenoate. Not only are the monoenes reduced to stearate but the double bonds migrate away from their original position. Figure 3 shows the comparative rates of hydrogenation and isomerization of the three positional isomers during hydrogenation under two different conditions and catalysts. The results shown were obtained by analyzing for the per cent of the various positional isomers in the total mixture. This, divided by the per cent of each of the three isomers present before hydrogenation, gives the fraction of each isomer that has not reacted by hydrogenation or isomerization. As is apparent from the two curves, the 6-, 9- and 12-isomers react at the same rates even under very different hydrogenation conditions using two different catalysts. The curve showing the results obtained, using a palladium catalyst, has a steeper slope initially than the curve obtained using nickel catalyst because of the extensive isomerization caused by the palladium catalyst. From these data it can be concluded that monoenes with double bonds in the 6-, 9- and 12-positions hydrogenate or isomerize with equal ease under the conditions described.

To gain some insight as to what may be the relative rates of hydrogenation of bonds very near the carboxyl and those near the terminal methyl, a mixture of the *cis* 6-, *cis* 9- and *cis* 12-octadecenoates were reacted under conditions of very high isomerization compared to hydrogenation. As shown in Figure 4, there is an accumulation of bonds away from the carboxyl as hydrogenation and isomerization proceeds. This may be explained by examination of the curves. During the early stages of reaction, the distribution curve is almost symmetrical about the 9-position because of the migration of the original 6-, 9- and 12-bonds in both directions thus causing an accumulation about the 9-position. However, as bonds migrate further in each direction more double bonds accumulate away from the carboxyl. This is believed to be due to the double bonds that migrate into the 2-position are hydrogenated rapidly and may not shift back to the 3-position, as will be shown in a subsequent publication. Thus very little 3-isomer is present. Also, it appears the double bond in the 3-position is hydrogenated faster than the 2-position. However, those double bonds migrating toward the terminal methyl group get to the 16-position and then may be isomerized back to the 15- and lower positions. Thus the number of double bonds in these near terminal positions tend to increase while the double bonds going toward the carboxyl show a decrease. One very interesting observation was the absence of any double bonds between the 17- and 18-carbons of the chain. Either the method of analysis was unable to detect this isomer, although the procedure produced the expected aldehyde ester from the ozonization of methyl 10-undecylenate, or the terminal methyl group of the hydrocarbon chain did not participate in the reaction on the catalyst. An investigation of the hydrogenation and isomerization of the terminal and near terminal bonds is being carried out and will be reported in the future.

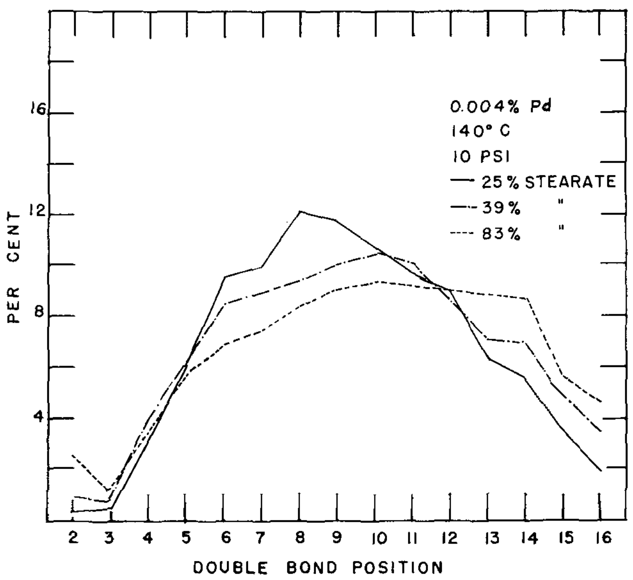

FIG. 4. Double bond distribution of partially hydrogenated mixture of methyl *cis* 6-, *cis* 9-, *cis* 12-octadecenoate.

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[Received August 21, 1963—Accepted February 7, 1964]