# Competitive Hydrogenation Rates of Isomeric Methyl Octadecenoates[1]

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## ABSTRACT

Hydrogenation rates of isomeric methyl octadecenoates were compared by reducing mixtures containing a small weight of one radioactively labeled isomer and a much larger weight of another unlabeled isomer. As hydrogenation proceeded, samples were removed for analysis by a gas chromatograph, coupled with an ionization chamber so that mass peaks measured reduction of the unlabeled isomer and radioactive peaks of the labeled isomer. The ratio of hydrogenation rates best fitting these data was calculated with a digital computer. Reductions were made at atmospheric pressure generally with either nickel at 140 C or platinum at 50 C. A few were made with palladium at 50 C. Methyl oleate hydrogenated more rapidly than methyl elaidate and the *cis*-15-isomer more rapidly than oleate. Other variations among the positional *cis* isomers investigated were small.

## INTRODUCTION

Early studies on hydrogenation of fats revealed that isomeric fatty acids form as hydrogenation proceeds. Later research has demonstrated that *cis* and *trans* isomers, with double bonds moved to new positions along the chain, are present in partially hydrogenated fat products. The isomeric esters formed from methyl oleate and the effect of hydrogenation conditions on their composition have been described by Feuge and Cousins (1), and the esters formed during deuteration of methyl oleate have been examined at this Laboratory (2). A knowledge of the relative hydrogenation rates of such isomeric esters would be helpful in interpreting many hydrogenation studies. Many investigators (3-8) found that oleic and petroselinic acids and their esters are reduced more rapidly than their corresponding *trans* isomers. Information on positional isomers is less extensive but some differences in reduction rates have been reported (9,10).

At this Laboratory, Mounts et al. (11) investigated the relative hydrogenation rates of several methyl *cis* and *trans* octadecenoates with nickel catalyst by microvapor-phase hydrogenation. We are now reporting results of liquid-phase hydrogenation of methyl octadecenoate isomers in which the methods of analysis and calculation are much like those we used in the vapor-phase work.

## EXPERIMENTAL PROCEDURES

### Source of Materials

Petroselinic acid was prepared by low-temperature crystallization of parsley seed acids from acetone. Methyl *cis*-12-octadecenoate was prepared from partially hydrazine-reduced linoleic acid by low-temperature crystallization from acetone according to a procedure based on one described by Privett in a private communication. Methyl *cis*-15-octadecenoate was isolated by argentation chromatography of the monoene fraction from partially hydrazine-reduced linolenic acid (12). Methyl oleate was purchased from The Hormel Institute. *Trans* esters were prepared by treating the *cis* esters with nitrous acid as described by Litchfield et al. (13) and isolating the *trans* fraction with a silver resin column (14). The *cis*-5-, 7-, 8-, 10- and 11-, and the 17-octadecenoates were the same samples used in earlier work (11,15).

Oleic acid (-1-$^{14}$C) was purchased from Amersham-Searle Co. Methyl esters with the methoxyl group labeled with tritium were prepared according to Mounts and Dutton (16).

Catalysts were 5% platinum on carbon and 5% palladium on carbon purchased from Baker and Company and G-70 nickel in hardened cottonseed oil obtained from Girdler Company.

### Hydrogenation Procedure

The hydrogenation vessel was similar to one described by Low et al. (17) with a vibrating stirrer driven by an electric sander motor. During the reaction the vessel was immersed in a constant temperature oil bath. Hydrogen was dispensed from a gas syringe whose plunger was driven by a servo mechanism activated by a pressure sensor to keep the hydrogenation vessel at atmospheric pressure. The movement of the plunger as a measure of hydrogen uptake was recorded on a potentiometric strip chart recorder (18).

For a hydrogenation the catalyst was weighed into the hydrogenation vessel and the apparatus evacuated, flushed and filled with hydrogen. The methyl ester sample was introduced by a hypodermic syringe through a serum cap. The stirrer was started and hydrogen uptake was followed on the strip chart recorder. From 3 to 6 approximately 10 $\mu$l samples were withdrawn by syringe through the serum cap. These samples were diluted with petroleum ether and centrifuged to remove catalyst. Solvent was evaporated under nitrogen and the samples were saved for analysis.

In a typical run, 300 mg of methyl esters containing 150 $\mu$c of radioactivity was used. About 8 mg platinum or palladium on carbon or 85 mg G-70 nickel was added. Platinum and palladium hydrogenations were run at 50 C and nickel at 140 C.

Hydrogenation rates of two monoenes were compared by hydrogenating a mixture of one isomer with a very small weight of the second isomer containing a radioactive label. For radioactive oleate, carboxy-labeled $^{14}$C methyl oleate was used. Other isomers were labeled with tritium in the methoxy group.

### Analysis

The partially hydrogenated samples were analyzed for mass and radioactive composition by gas radiochromatography in a Cary-Loenco instrument (19). This apparatus provides for thermal conductivity detection and contains a 275 cc spherical ion chamber in the detector oven in tandem to monitor effluent for radioactivity.

Thus the composition of both inactive and radioactive esters was measured simultaneously after they were hydrogenated in the same mixture at the same time under the same conditions. Thermal conductivity measures the composition of the unlabeled esters. Radioactivity analysis measures the composition of the labeled component which is present in too small a mass to affect thermal conductivity.

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TABLE I

Competitive Hydrogenation
Rates of Methyl *Cis*-Octadecenoates

| Mixture | $k/k_{c\text{-}9}$[a] Pt | Pd | Ni | Least significant difference[b] |
|---|---|---|---|---|
| *Cis*-9,*cis*-9*[c] | 1.00[d] | — | 0.95[d] | --- |
| *Cis*-9,*cis*-5* | 1.39 | --- | 0.79 | 0.15 |
| *Cis*-9,*cis*-6* | 1.34 | 1.07 | 1.03 | 0.25 |
| *Cis*-9*,*cis*-6 | 1.22 | 1.04 | 0.96 | 0.25 |
| *Cis*-9,*cis*-7* | 1.55 | — | 1.29 | 0.15 |
| *Cis*-9,*cis*-8* | 0.85[d] | — | 1.05[d] | — |
| *Cis*-9,*cis*-10* | 1.12 | — | 1.07 | 0.15 |
| *Cis*-9,*cis*-11* | 1.09 | — | 1.17 | 0.15 |
| *Cis*-9,*cis*-12* | 1.15 | 0.73 | 1.30 | 0.25 |
| *Cis*-9*,*cis*-12 | 1.01 | 0.82 | 1.23 | 0.25 |
| *Cis*-9,*cis*-15* | 2.27 | 1.82 | 1.79 | 0.25 |
| *Cis*-9*,*cis*-15 | 1.70 | 1.28 | 1.43 | 0.25 |
| *Cis*-9,17* | >55 | --- | >92 | --- |

[a] Reaction rate of ester divided by that of methyl *cis*-9-octadecenoate.

[b] Smallest difference between two mean rate constant ratios that is significant at the 95% level.

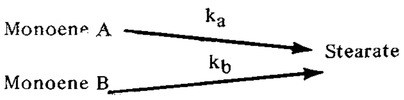
[c] Asterisk denotes radioactive ester.

[d] Single determination.

*Trans* unsaturation in the inactive ester was determined by comparing the absorbance of the ester peak at 8.55 μ and the *trans* peak at 10.36 μ (20).

## RESULTS AND DISCUSSION

The relative reaction rates were first calculated assuming the simple model



For explanation of the calculations we refer to Figure 1. Here the mass analysis of the inactive ester present in large amount is plotted against the remaining double bond content of the inactive esters. For monoenes these are equivalent so the points lie exactly on a line of slope one.

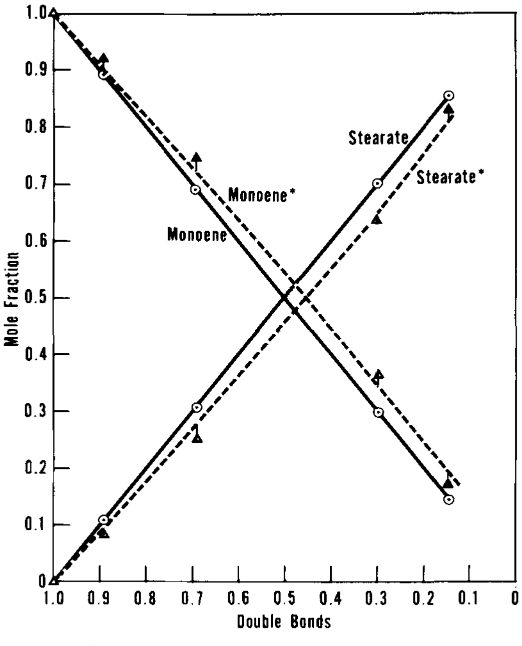


FIG. 1. Hydrogenation of a monoene mixture. Calculation of relative hydrogenation rates. Asterisk denotes radioactive esters. These are present in too small mass to affect thermal conductivity analysis.

TABLE II

Competitive Hydrogenation Rates
of *Trans* and *Cis* Methyl Octadecenoates

| Mixture | $k_t/k_c$ Pt | Ni | Least significant difference[b] |
|---|---|---|---|
| *Cis*-6,*trans*-6*[a] | 0.62 | 0.60 | 0.20 |
| *Cis*-9,*trans*-9* | 0.61 | 0.65 | 0.20 |
| *Cis*-12,*trans*-12* | 0.68 | 0.66 | 0.20 |
| *Cis*-15,*trans*-15* | 0.54 | 0.55 | 0.20 |

[a] Asterisk denotes radioactive ester.

[b] Smallest difference between two mean rate constant ratios that is significant at the 95% level.

The amounts of radioactive monoene and stearate in the samples are also plotted against the same abscissa used for the inactive plot. The ratio of rates, $k_a/k_b$, that gives the best fit is calculated by a digital computer. Specifically the value is such that the sum of the squares of distances from the radioactive points to the radioactive composition line is a minimum (21). These ratios are the values for *cis*-6, *cis*-12 and *cis*-15 esters in Table I where the rate for each position isomer is compared with that for methyl oleate. A similar calculation was used for the other values in Table I, except that for these synthetic esters corrections were made for other position isomers present as impurities. If the model is valid, it should be possible to exchange the role of the two isomers in the calculation. Similar results will be obtained approaching the same value as the goodness of fit of the data improves. Such similar results are obtained for the positional isomers in Table I except 15-octadecenoate.

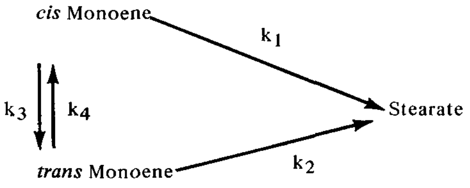
The model is oversimplified since *cis,trans* and position isomerization do take place during hydrogenation and some of the isomers formed will have different reduction rates. If the ratio of reaction rates is calculated step by step for each two adjacent points as the hydrogenation proceeds, a random scatter with no trend to higher or lower values occurs for most *cis* position isomers. This random scatter shows that the relative rates are not greatly affected by isomerization. For 15-octadecenoate the rate decreased as the reaction proceeded.

The model is not completely satisfactory for *cis*-15-octadecanoate. Values for $k_{c\text{-}15}/k_{c\text{-}9}$ are higher when the radioactive tag is on the 15- rather than the 9-isomer, and when the tag is on the 15-isomer, the relative rate drops as the reaction proceeds. Because these variations are caused by isomerization as hydrogenation proceeds, it seems likely that the higher value with radioactivity in the 15-isomer is more nearly correct.

The comparisons of radioactive and unlabeled methyl oleate in Table I were run as a check on experimental techniques and methods of calculation. The difference between the experimental values and the expected values for $k_{c\text{-}9}/k_{c\text{-}9}$ of 1.00 indicates the accuracy obtained in these reductions. The following statistical analysis of the relative rates in Table I shows greater variability in some other values in the Table.

All values are averages of two or more independent hydrogenations, except as noted in Table I. Statistical analysis indicates that the least significant difference at the 95% level between two values is 0.25 for the 6, 12 and 15 esters and 0.15 for the 5, 7, 10 and 11 esters. The least significance variation from 1.00—the value for oleate—depends upon the number of individual hydrogenation runs averaged. It is 0.11 for the 5, 7, 10 and 11 ester, 0.14 for Pt 9*,12, 9,15*, 9*,15, Ni 9,15* and 0.17 for the other 6, 12 and 15 values. (The asterisk denotes the radioactive ester.) Thus differences between the *cis* position isomers are mostly small except for *cis*-15-octadecenoate. The 15-double bond is known to be more reactive than those nearer the middle of the chain as illustrated by its more rapid reduction with hydrazine (22) and by the greater stability of its silver complex (12). Among the esters investigated here, with the exception of the 15-position, double bonds at positions greater than 9 tend to be hydrogenated at about the same rate as *cis*-9-octadecenoate, while those at positions less than 9 tend to be hydrogenated more rapidly. With nickel the opposite is true; double bonds at positions 11 and 12 are hydrogenated more rapidly while those at other positions are hydrogenated at about the same rate as *cis*-9-octadecenoate. 17-Octadecenoate was completely converted to stearate when the first samples were taken. Only minimum relative rates are given in Table I; the actual relative rates may be much higher.

When *trans* and *cis* esters are compared, a trend is observed with the ratio changing and approaching one as the two starting esters approach the same *cis,trans* equilibrium. Again, a smaller value of $k_{trans}/k_{cis}$ is obtained if the *trans* ester rather than the *cis* is constrained to lie on the straight line in Figure 1. Because of these deficiencies a model was chosen as follows to take into account geometrical isomerization.



$k_3 = 4k_4$

The ratio of $k_3$ and $k_4$ is chosen to give 80% *trans* in the monoene at equilibrium. This model is used for comparison of *trans* and *cis* isomers in Table II where the rate for the *cis* isomer is taken as one in each comparison.

Statistical analysis shows that the least significant difference at the 95% level for values in Table II is 0.20; there is no significant difference in $k_{trans}/k_{cis}$ between any of the position isomers or between the two catalysts. Nickel always produced more *trans* isomers than platinum. In agreement with other work, oleate is reduced faster than elaidate. With palladium isomerization proceeds so rapidly and the relative rate approaches one so early in the reduction that good values could not be obtained. Although for this reason we have done less work with palladium, still the $k_{trans}/k_{cis}$ ratio seems to be in the same range as for platinum and nickel. The value given by Plisov and Maleeva (5) for hydrogenation of methyl oleate and methyl elaidate with platinum-$BaSO_4$ in ethanol corresponds to $k_{trans}/k_{cis}$ of 0.88 and Jardine and McQuillin's (8) data for methyl oleate and elaidate in methanol with palladium on charcoal corresponds to 0.40.

Our results in this paper are comparable with those obtained at this Laboratory by microvapor-phase hydrogenation (11). Except for methyl *cis*-15-octadecenoate, the general increase in vapor-phase hydrogenation rate as double bonds move from the carbonyl is not found in the liquid phase results. In both systems oleate is hydrogenated faster than elaidate, but vapor-phase hydrogenation of other *trans* isomers compared to oleate was about the same as for the corresponding *cis* isomers. These differences are probably caused by differences in the hydrogenation procedures—liquid vs. vapor phase, difference in nickel catalysts, larger amount of catalyst used in vapor phase and temperature.

Most previous comparisons have been stated in qualitative terms and no recognition has been given to the effects of isomerization during hydrogenation. Our results have not fully taken into account positional and geometric isomerization. Accurate analysis for all the isomers in the many small samples would be difficult, and model and computer calculations would be complicated. We believe that we have taken isomerization into account to an extent to give useful and significant results close to the true values. These values will certainly vary somewhat with conditions of hydrogenation and catalyst characteristics.

In interpreting our results and comparing them with those in the literature it should be remembered that our experiments have been competetive hydrogenations in which two isomers are in the same reaction mixture competing for catalyst surface and hydrogen. Hussey et al. (23) and Jardine and McQuillin (8) presented examples of the effect of competition on relative hydrogenation rates. Results might be somewhat different for two isomeric esters hydrogenated in separate experiments. We have made no attempt to separate the steps of adsorption on the catalyst and hydrogen transfer. It seems likely that if competition for the catalyst surface plays a large part, we should get markedly different results when the mass and radioactive isomers are reversed, but any such differences are small.

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