JOURNAL OF CATALYSIS 21, 20–26 (1971)

Selectivity and Monoene Isomerization in the Catalytic Hydrogenation of Polyenoic Fatty Acid Methyl Esters

I. HEERTJE AND H. BOERMA

Unilever Research Laboratory, Vlaardingen, The Netherlands

Received March 5, 1970

In the selective catalytic hydrogenation of methyl esters of polyunsaturated fatty acids, the hydrogenation and isomerization of monoenoic esters is suppressed due to the preferential adsorption and reaction of polyenoate. The monoene isomerization of mixtures of methyl linoleate and methyl oleate had been investigated in a selective hydrogenation using [^{14}C]-labeled methyl oleate. Although the degree of isomerization of oleate is rather high under the conditions applied, the monoenoate coverage of the catalyst surface is only a few percent compared with the dienoate coverage at dienoate concentrations higher than 50%. The direct conversion of linoleate to stearate is to a great extent responsible for the formation of stearate in the first stage of the hydrogenation.

1. INTRODUCTION

In the selective catalytic hydrogenation of polyunsaturated fatty acids, hardly any monounsaturated fatty acid is hydrogenated at the beginning of the hydrogenation.

To explain this phenomenon it is assumed that polyunsaturated compounds are more strongly adsorbed on the catalyst surface than monounsaturated compounds (*1*). On the other hand, *trans*-isomers are rapidly formed by a side-reaction on the catalyst surface during the hydrogenation of *cis*-monoene.

The determination of the concentration of *trans*-isomers formed from *cis*-monoene is, as a result, a more sensitive method for calculating the degree of monoene adsorption on the catalyst surface than the determination of the concentration of saturated product. To study these reactions, a mixture of methyl linoleate and [^{14}C]-labeled methyl oleate has been hydrogenated under selective conditions. In this way, it is possible to distinguish between *trans*-monoenoate formed from oleate by isomerization and that formed from linoleate by hydrogenation. Likewise, the extent can be determined to which linoleate is converted directly into stearate—so without an intermediate being desorbed from the catalyst surface.

2. METHODS

Methyl linoleate (98%) and methyl oleate (99%) were used after passage over alumina in hexane. Labeled [1-^{14}C]-oleic acid (Amersham) (sp act, 36.9 mCi/mmole) was esterified with diazomethane and freed from an impurity of 1.7% *trans*-acid by thin-layer chromatography (TLC over $SiO_2/AgNO_3$). After addition of 150 μCi [1-^{14}C]-methyl oleate, a mixture (17 g) of methyl linoleate and methyl oleate (3:1; v/v) was hydrogenated, using a silica-supported nickel catalyst. The structural parameters of this catalyst (A 1) have been described previously (*2*). The catalyst was reduced at 450°C in the sidearm of a hydrogenation apparatus in a hydrogen flow of about 18 liters/hr. Then the reaction was started by adding the catalyst to the stirred oil. The hydrogenation was carried out at 100°C with an amount of catalyst containing 0.2% nickel, calculated on an oil charge of 20 ml. After certain time intervals, samples were drawn from the re-

TABLE 1
Composition of the Samples (GLC)

Sample	Time (min)	n_D^{65}	Unsaturation from GLC (L = 200 O = 100)	Content (%) of St	"O + E"	L
0	0	1.4411	170	ca. —	30	70
I	5	1.4400	164	ca. 0.16	35	65
II	10	1.4394	161	ca. 0.48	38	61.5
III	15	1.4387	155	ca. 0.78	43	56
IV	25	1.4370	144½	1.3	52.5	46
V	40	1.4365	127½	2.2	67.5	30
VI	70	1.4325	93	10.3	86	ca. 3.5
VII	100	1.4293	40	60	40	ca. 0
VIII	126	1.4258	0	100	—	—

action vessel. The rate of hydrogenation was followed by measuring the refractive index of these samples.

The amounts of linoleate, "elaidate + oleate"* and stearate in the samples were determined by gas–liquid chromatography (GLC) (5% PEGA on Diatoport S 80–100 mesh). TLC on silica impregnated with 20% $AgNO_3$ was used to separate linoleate, "oleate," "elaidate," and stearate (eluent: benzene–light petroleum 7:3). After elution and drying, the plates were scanned for radioactivity with a thin-layer scanner (Berthold). The specific radioactivities (activities/mg of product) were obtained by extraction of the separate components with refluxing ether, addition of known amounts of methyl palmitate as an internal standard, followed by determination of the amount and radioactivity of aliquots by GLC and liquid scintillation counting (Packard Tri-Carb, model 3375), respectively. In the following tables and figures, the degree of unsaturation has been calculated from GLC data (taking 200 for linoleate and 100 for oleate).

3. Results

The composition of the samples determined by GLC is given in Table 1. Table 2 gives the percentages of the radioactivity determined in the stearate, oleate and elaidate fractions by TLC scanning. The specific activities (α) of the separate components are also included. With the aid of these data, the distribution of the mononate fraction over *cis*- and *trans*-esters was calculated (Fig. 1). The proportion in which the "elaidate" fraction is formed from linoleate by hydrogenation (E_L) and from "oleate" by isomerization (E_O) is shown in Fig. 2. The quotient of the differential contribution of linoleate (ΔE_L) and oleate (ΔE_O) to the formation of elaidate (ΔE) in

TABLE 2
Radioactivity (TLC) and Specific Activity of the Samples

Sample	Percentage of radioactivity in St	O	E	Specific activity (α) of St	O	E
0	—	100		—	100	—
I	0.26	98.6	1.1	20.2[a]	96	7.5
II	0.50	97.1	2.4	20.7[a]	94	7.7
III	0.70	95.8	3.5	21.5[a]	89	8.2
IV	0.97	93.0	6.0	21.0[a]	81	8.7
V	1.95	88.7	9.3	18.0	70	9.5
VI	10.7	52.7	36.6	23.3	47.5	19.9
VII	57.6	9.1	33.3	27.3	30	27.0
VIII	100	—	—	29.8	—	—

[a] For calculations, an average value of 20.5 was taken.

---

* "Elaidate" and "oleate" refer to *trans*- and *cis*-monoenoic isomers, respectively, including elaidate and oleate.

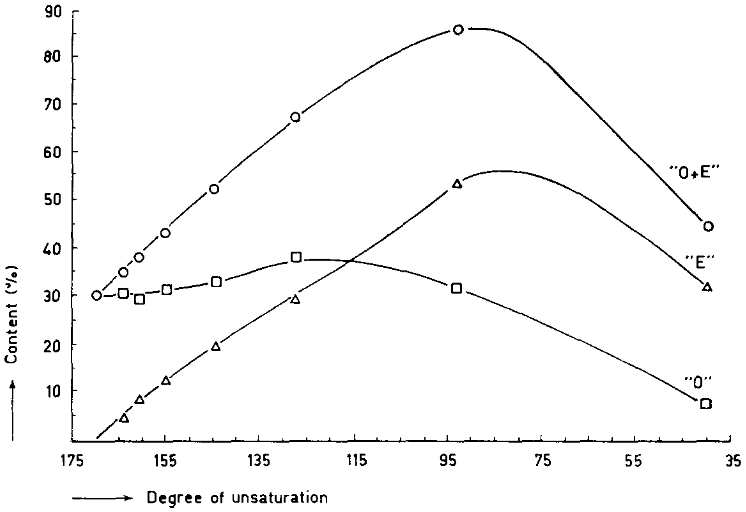


FIG. 1. Percentages of "oleate," "elaidate," and "oleate + elaidate" as a function of degree of unsaturation.

the course of the reaction (Fig. 3) can be calculated from the data in Fig. 2. Since the formation of "elaidate" from linoleate (E_L) and oleate (E_O) will be influenced by changes in the concentrations of linoleate and oleate in the bulk, we have corrected ΔE_L and ΔE_O accordingly. The results are shown in Fig. 4, where the quotient $(\Delta E_O/O)/(\Delta E_L/L)$ has been plotted against the degree of unsaturation.

4. DISCUSSION

It is known that the course of the concentrations in the bulk phase during the selective hydrogenations of fatty acid esters can be described by first-order consecutive reactions (*2–4*). Subsequently, the selective hydrogenation of linoleate can be described by the consecutive reaction $L \xrightarrow{k_1} M \xrightarrow{k_2} S$. In this work, the observed dependence be-

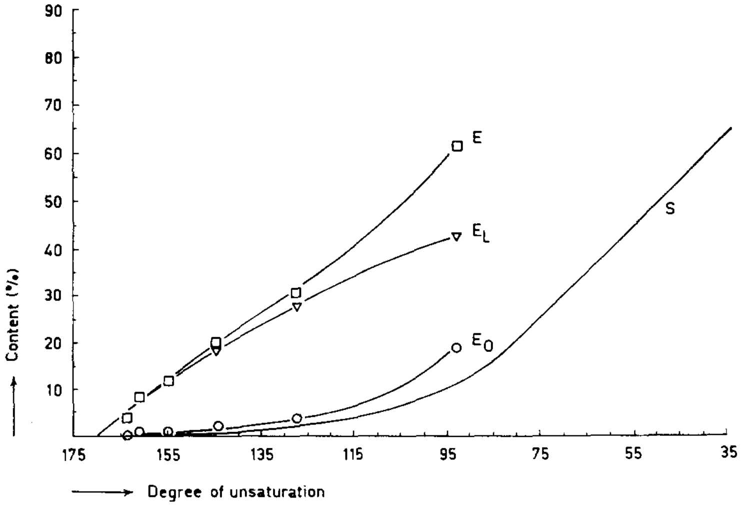


FIG. 2. Percentages of elaidate formed (E), elaidate formed from linoleate (E_L) and elaidate formed from oleate (E_O) as a function of degree of unsaturation. A correction has been made for the disappearance of elaidate by hydrogenation and isomerization.

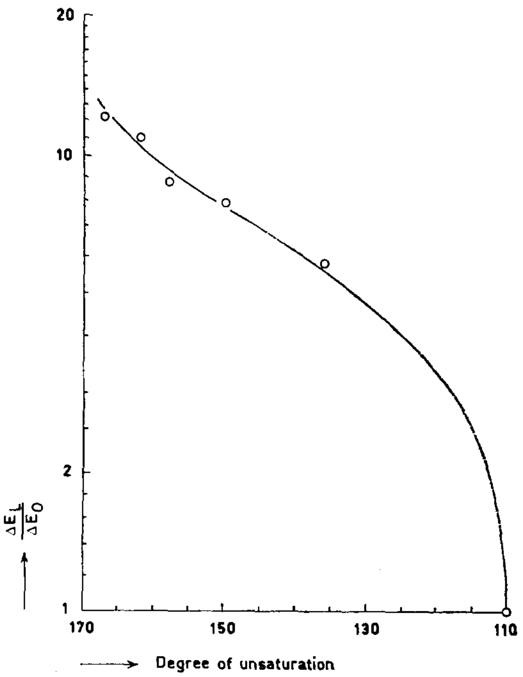
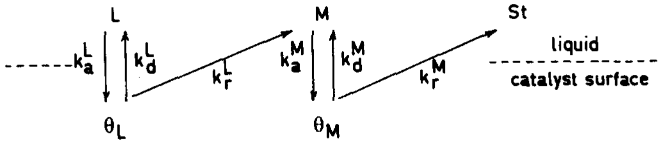


FIG. 3. Proportion in which elaidate is formed from linoleate and oleate.

tween composition and unsaturation can be explained by a ratio of the relative rate constants k_1 and k_2—a selectivity—of 21 (see Fig. 5).

The mechanism of this reaction might be represented as



SCHEME 1

in which k_a = adsorption constant; k_d = desorption constant; k_r = reaction constant; θ = degree of coverage of catalyst surface; L = linoleate, M = monoene.

On the basis of this scheme, the following relation can be derived between the ratios of the methyl ester coverage with respect to the ester concentrations in the bulk:

$$\frac{\theta_L/L}{\theta_O/O} = \frac{K_L}{K_O}$$

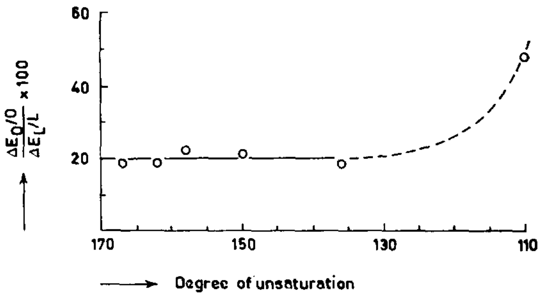


FIG. 4. Proportion in which elaidate is formed from linoleate and from oleate, corrected for the difference in concentration of linoleate and oleate in the bulk.

in which $K_L = k_a^L/(k_d^L + k_r^L)$ and $K_O = k_a^O/(k_d^O + k_r^O)$. This is in accordance with the observed dependence of the elaidate formation on the bulk concentrations L and O: the ratio of $\Delta E_O/O$ to $\Delta E_L/L$ is constant (Fig. 4).

However, it is evident from the low specific radioactivity of methyl stearate (Table 2) formed at the beginning of the hydrogenation that the reaction scheme given above is of limited applicability. If the reaction kinetics could indeed be described by means of a consecutive reaction without a significant contribution from a "straight-through" reaction, the stearate specific activity would have been equal to that of the bulk oleate from which it is mainly formed. The specific radioactivity of the methyl stearate formed at the beginning of the hydrogenation is, however, remarkably low. The conclusion that this must be due to a direct conversion of linoleate to stearate was confirmed in an experiment in which linoleate instead of oleate was labeled. A more realistic kinetic scheme describing the composition of the bulk phase introduces a shunt reaction (*4*):

$$\begin{tikzcd} L \arrow[r, "k_1"] \arrow[rr, bend right, "k_3"'] & M \arrow[r, "k_2"] & St \end{tikzcd}$$

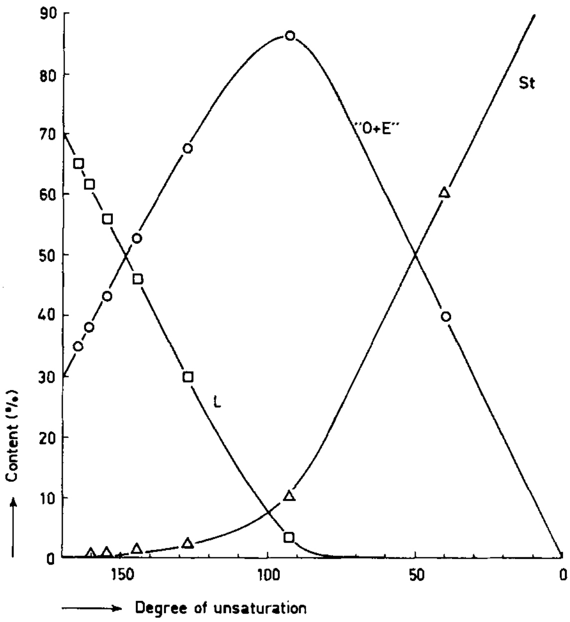


FIG. 5. Experimental data (points) and analog computer-drawn graph for $L \xrightarrow{k_1} M \xrightarrow{k_2} S$ with $k_1/k_2 = 21$.

The relative rate constants in this scheme can be calculated as follows: from the specific activity of the stearate and oleate it is possible to calculate the proportion in which stearate is formed from oleate (St_O) and from linoleate (St_L) with the following formula,

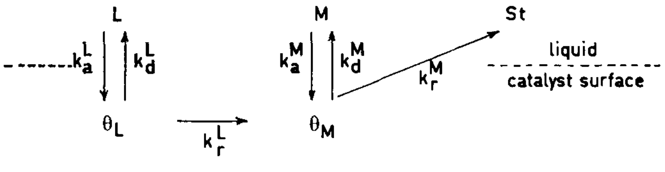
$$St_L/St_O = \alpha_O/\alpha_{St} - 1$$

For the first four samples, the formation of stearate from monoene is approximately equal to the stearate formation from oleate: $St_O = St_M$. In Table 3, for the first four linoleate conversion (ΔL) and the stearate samples, St_L and St_M are compared. Table 3 also includes the quotient of the formation from L (St_L). This quotient (~24) is approximately equal to k_1/k_3 in the afore-mentioned kinetic scheme. With the help of an analog computer, the best fit was obtained with relative values for k_1, k_2, and k_3 of 63, 1, and 2.7, respectively, giving $k_1/k_2 + k_3 = 17$. The latter value approximates the value of 21 for k_1/k_2 in the simple scheme.

TABLE 3
FORMATION OF St FROM M AND L

Sample	α_S	α_O	St	St_L	St_M	$\Delta L/St_L$
I	20.2	96	0.16	0.13	0.03	38
II	20.7	94	0.48	0.37	0.11	23
III	21.5	89	0.78	0.60	0.18	23
IV	21.0	81	1.3	1.00	0.30	24

The consecutive parallel reaction kinetic scheme is in accordance with the following mechanistic scheme, taking into account the role of the catalyst surface:



SCHEME 2a

According to this scheme, there is no complete exchange between monoene from the bulk (M) and adsorbed monoene (θ_M). The monoene has already reacted before it can be desorbed.

So the specific activity of the monoenoate adsorbed on the catalyst surface (α_{θ_M}) will not be equal to α_M but to α_S:

$$\alpha_{\theta_M} = \alpha_S$$

This specific activity is determined by the mass streams from L and M to the catalytic surface to yield θ_M.

The kinetic information given so far can be summarized in a mass stream scheme. For equal concentrations of L and M in the bulk, the following relative figures are obtained:

tion of elaidate from linoleate and oleate gives an approximation of the reactivities of linoleate and oleate.

Therefore, the above-mentioned data can be expressed as follows:

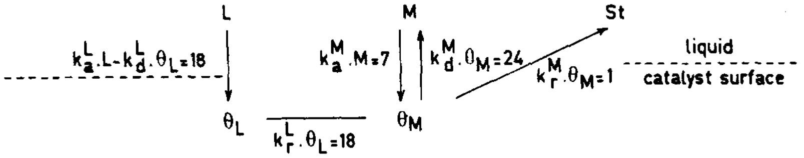
$$k_r^L \cdot \theta_L / k_r^O \cdot \theta_O = \tfrac{1}{8} \text{ in separate hydrogenations}$$

and

$$k_r^L \cdot \theta_L / k_r^O \cdot \theta_O = 5 \text{ for the combined experiments.}$$

Assuming k_r^L/k_r^O being equal in the two situations, the following relation is then found:

$$\left(\frac{\theta_L}{\theta_O}\right)_{\text{combined}} = 40 \times \left(\frac{\theta_L}{\theta_O}\right)_{\text{separate}}.$$



SCHEME 2b

The stream from L to θ_L is the net result of an adsorption and desorption process.

The selectivities in this scheme are determined by the contributions of the different reaction paths:

$$k_1/k_2 = \frac{k_r^L \cdot \theta_L \cdot k_d^M \cdot \theta_M}{k_a^M \cdot M \cdot k_r^M \cdot \theta_M} = 63,$$

$$k_1/(k_2 + k_3) = \frac{k_r^L \cdot \theta_L \cdot k_d^M \cdot \theta_M}{k_a^M \cdot M \cdot k_r^M \cdot \theta_M + k_r^L \cdot \theta_L \cdot k_r^M \cdot \theta_M} = 17.$$

The relative contribution of linoleate to the formation of elaidate (E_L) is, as we have seen, five times larger than that of oleate (E_O). In separate experiments with linoleate and oleate it was shown that, under similar conditions, the isomerization reaction from O to E is about 8 times as fast as the hydrogenation reaction from L to E. The contribution of oleate to the formation of elaidate is therefore decreased by a factor of 40 in the combined experiment. It is known that the relative formation of elaidate from linoleate and oleate gives an approximation of the reactivities of linoleate and oleate.

The decrease in the ratio θ_O/θ_L by a factor of 40 is responsible for the selectivity observed and for the low amount of E_O at the beginning of the reaction. This is in agreement with other investigations by Coenen and Boerma (*1*) in which it was qualitatively shown that in selective rapeseed oil hydrogenation, monene is hardly isomerized at the beginning of the hydrogenation. Similar conclusions were reached by Hilditch and Moore (*5*) and Van Vlodrop (*6*).

These quantitative conclusions only hold for the present experimental setup and conditions, such as reaction vessel, stirring intensity, hydrogen pressure, and type and amount of catalyst and methyl esters. The reason is that the reaction constants of the surface reactions—regarded as first-order rate constants—are in fact pseudo first-order, since the hydrogenation surface reaction rate may be expected to depend either linearly or quadratically on θ_H (the surface occupation with hydrogen atoms). This magnitude, however, will depend on experimental conditions (*7*). A decrease in stirring intensity or hydrogen pressure or an increase in catalyst concentration will lower θ_H and, therefore, also k_r^L and k_r^M, possibly without affecting the other rate constants, so that the ratio of the reaction constants will also be influenced.

A further complication arises from the fact that the reactions in the catalyst pore system (*2*) may be partly diffusion-controlled. This may lead to significant concentration gradients in the pores. These effects, if they contribute significantly, will tend to weaken the effect of adsorption monopolization. In this sense, the different ratios should be considered as minimum values, which may be significantly higher for a perfectly accessible (nonporous) catalyst.

The fact whether scheme 2 or scheme 1 and scheme 2 should be considered for the description of the catalytic hydrogenation cannot be decided on the basis of the present experimental results.

In selective hydrogenations other than of fatty acid esters, mainly the hydrogenation of conjugated hydrocarbons has been studied. Bond and Wells (*8*) give the following statement, which is mainly based on the hydrogenation of 1,3-butadiene: "in the first stage alkene and alkane are often produced together, the former generally being the major product."

This description is also valid in the present hydrogenation experiments with the nonconjugated methyl linoleate. However, according to the literature (*9*), conjugated intermediates play an important part in the mechanism of selectivity. Investigations in this direction are in progress.

ACKNOWLEDGMENT

We thank Professor J. W. E. Coenen, Dr. W. Wösten, and Dr. G. K. Koch for critical remarks and Messrs. G. van der Voet and K. P. Hissink for technical assistance.

REFERENCES

1. COENEN, J. W. E., AND BOERMA, H., *Fette, Seifen, Anstrichm.* **70,** 8 (1968).

2. COENEN, J. W. E., BOERMA, H., LINSEN, B. G., AND DE VRIES, B., *Proc. Intern. Congr. Catal., 3rd, 1964,* **2,** 1391 (1965).

3. BAILEY, A. E., *J. Amer. Oil Chem. Soc.* **26,** 644 (1949).

4. DE BOER, J. H., AND VAN DEN BORG, R. J. A. M., *Proc. Kon. Akad. Wetensch., Ser. B* **62,** 299, 308 (1959).

5. HILDITCH, F. P., AND MOORE, C. W., *J. Soc. Ind.* **42,** 151 (1923).

6. VAN VLODROP, C., thesis, Techn. Univ. Delft, 1938.

7. COENEN, J. W. E., *Actes Congr. Int. Catal., 2nd, 1960* **1961,** 2705.

8. BOND, G. C., AND WELLS, P. B., *J. Catal.* **4,** 211 (1964).

9. ALLEN, R. R., AND KIES, A. A., *J. Amer. Oil Chem. Soc.* **33,** 355 (1956).