Isomerization Phenomena During Hydrogenation of Methyl Oleate and Methyl Elaidate Over Nickel-Silica Catalysts[1]

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ABSTRACT

Methyl oleate was hydrogenated at temperatures varying from 50-175 C over three nickel-silica catalysts of different pore-size distribution. Methyl elaidate was reduced over one of these catalysts at temperatures between 75-150 C. From the detailed double bond distributions information was obtained on transport phenomena in the pores of the catalyst. It was established that the migration of the double bond in methyl oleate proceeds with a stepwise mechanism, and evidence was obtained that the double bond in methyl elaidate migrates significantly faster than that in methyl oleate, while the rate of hydrogenation of these esters was equal. The *trans-cis* ratio of the geometrical isomers which are formed by double bond migration varies strongly during hydrogenation.

INTRODUCTION

Many studies have been made on the isomerization reactions occurring during the hydrogenation of unsaturated fatty acid esters. The conclusions from these studies are mostly limited to pronouncements about the equilibrium ratio between the various geometrical isomers which arise, and about whether the double bond migration proceeds randomly or not. For example Allen and Kiess (1) found evidence for equal rates of migration in both directions for the double bond in methyl oleate, the geometrical isomers being formed in a *trans-cis* equilibrium ratio of 2. These results were (amongst others) confirmed by Albright and Wisniak (2). Cousins and Feuge (3) agree with these findings, but find indications that the *trans-cis* ratio depends on the experimental conditions, such as the type of catalyst. Subbaram and Youngs (4) supported the idea of a random migration process of the double bond, but found strongly divergent values for the *trans-cis* ratios. Dutton et al. (5) made a more sophisticated study of the migration and the *cis-trans* rearrangement of the double bond in methyl oleate by substituting deuterium for hydrogen. On the basis of a simple reaction scheme they calculated a product distribution which agreed fairly well with the experimental value they derived from mass spectral data. The experiments were, however, performed at rather low temperature, which resulted in relatively low rates of isomerization. Moreover in their reaction scheme they assume the removal of an H-atom from a C-atom adjacent to the C-atom that is attached to the metal surface in the partially hydrogenated intermediate, and describe this removal as a completely random process. For the interpretation of a detailed double bond distribution it is necessary to abandon these assumptions—they would lead to a *trans-cis* ratio of 1, which is in contrast to the phenomena observed—and to take into account the influence of diffusion limitation on the isomerization reactions. Unfortunately the system of parameters obtained in this way is too complicated for mathematical calculations and even for a quantitative computer evaluation.

In this paper we shall briefly describe how information on mass transport phenomena occurring in catalyst particles can be obtained from double bond distributions. For full details we refer to (6). Attention will further be focused on the *trans-cis* ratios of the various geometrical isomers which arise during reduction of methyl oleate and methyl elaidate.

EXPERIMENTAL PROCEDURES

Some essential data on the catalysts and the compositions of the model compounds methyl oleate and methyl elaidate are given in Tables I and II. The experiments were performed batchwise under atmospheric hydrogen pressure and at a stirring speed of 3000 rpm, corresponding with 70

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[1] The following symbols are used in this paper:

$m = \sum_{i=-7}^{8} \left(\Delta_{9+i}^{c} + \Delta_{9+i}^{t}\right)|i|$ = difference between forward and backward double bond migrations in 100 unsaturated molecules. The isomers are expressed in percentages of the unsaturated fraction;

$m' = \sum_{i=1}^{7} \left(\Delta_{9-i}^{c} + \Delta_{9-i}^{t}\right)i$ = as m, but only the double bond migrations in the direction of the ester group are taken into account;

r $= -2\left(\frac{dm'}{dt}\right)_{t\to 0} \Big/ \left(\frac{d\Delta_9}{dt}\right)_{t\to 0}$;

S_{BET} = BET-surface (m^2/g Ni);

S_{Ni} = metallic nickel surface (m^2/g Ni);

$\left(\frac{dm}{dt}\right)_{t\to 0}$ = number of effective migration steps per time unit at the beginning of the reaction per 100 unsaturated molecules $\left(\frac{\text{migr.}}{100\ \text{mol.min}}\right)$;

$\left(\frac{dm'}{dt}\right)_{t\to 0}$ = as above for double bond migration in the direction of the ester group $\left(\frac{\text{migr.}}{100\ \text{mol.min}};\right)$

$\left(\frac{d\Delta_9}{dt}\right)_{t\to 0}$ = rate of disappearance of Δ_9-isomers owing to double bond migration, at the beginning of the reaction (mole %/min);

$\left(\frac{d\Delta_9^{c}}{dt}\right)_{t\to 0}$ = rate of formation of methyl oleate owing to double bond migration and *cis-trans* rearrangement at the beginning of the reaction (mole %/min);

$\left(\frac{d\Delta_9^{t}}{dt}\right)_{t\to 0}$ = as above, but now for methyl elaidate (mole%/min);

$\left(\frac{d\,\text{sat.}}{dt}\right)_{t\to 0}$ = rate of hydrogenation (mole%/min);

$\Delta_i^{c}, \Delta_i^{t}$ = positional isomer with the double bond in the i^{th}-position in the *cis* and *trans* configuration, respectively.

TABLE I

Characteristic Values of the Nickel-Silica Catalysts

Catalyst	A	B	C
Ni in unreduced state, %	47.2	43.6	45.6
Degree of reduction, %	97.9	89.2	79.4
Mean size of Ni crystallite, Å	60	52	29
Mean pore diameter, Å[a]	12(6) 73(94)	129	17(50) 106(50)
S_{BET} (m^2/g total Ni)	259	311	522
S_{Ni} (m^2/g reduced Ni)	72	89	151

[a] The pore volumes of catalysts A and C, expressed between brackets in volume percentages, can be divided into two parts, each part corresponding to a mean pore diameter.

w/kg oil. The catalyst was reduced in situ at 450 C and poured into the oil under reaction conditions. The samples were analyzed by separation of the *cis, trans* and saturated fractions by thin layer chromatography on silica impregnated with silver nitrate, ozonolysis of the unsaturated fractions and reduction of the ozonides with triphenylphosphine, and gas chromatographic analysis of the aldehydes and aldehydic esters. The evaluation of the gas chromatograms was based on both aldehydes and aldehydic esters. A special method, based on a certain ratio between these degradation products, was developed to correct overlapped peak areas. This method will be published in due course. The total amounts of *cis, trans* and saturated products were derived direct from a gas chromatographic analysis of the sample, combined with IR absorption measurement.

RESULTS AND DISCUSSION

Essential information can be obtained from the ratio of the rate of double bond migration and the rate of disappearance of molecules with the double bond in the original position. The rate of migration can be derived from the composition in the monoene fraction as derived from IR and gas liquid chromatography analysis and the double bond distributions. The effective number of double bond migrations, being the difference between the number of forward and backward double bond migrations, can be calculated from these data.

When the double bond displacement in a methyl oleate molecule is given by 9 → 10 → 11 → 12 → 11, and that in another molecule by 9 → 10 → 11, the contribution to the total effective number of double bond displacements is two in both cases, though in the first molecule four real double bond migrations have occurred. Thus the effective number m of double bond migrations which have taken place in 100 unsaturated molecules can be calculated from:

$$m = \sum_{i=-7}^{8} \Delta_{9+i} |i| \qquad [1]$$

where Δ_{9+i} represents the sum of geometrical octadecenoic isomers with the double bond in the (9+i)-position, the sum being expressed in percentages of the monoene fraction. In a similar way m' is defined as the effective number of double bond migrations in the direction of the ester group:

$$m' = \sum_{i=1}^{7} \Delta_{9-i} |i| \qquad [2]$$

TABLE II

Original Composition (%) of Methyl Oleate and Methyl Elaidate

Position of double bond	4	5	6	7	8	9	10	11	12
Methyl oleate			0.05	0.03	0.03	96.0	0.3	3.1	0.6
Methyl elaidate	0.2	0.08	0.13	1.8	0.27	97.9	0.23	0.14	0.26

TABLE III

Reaction Rates for Methyl Oleate and Methyl Elaidate Under Variable Reaction Conditions[a]

Starting product	Catalyst	Temperature, C	$\left(\frac{dm'}{dt}\right)_{t\to 0}$	$\left(\frac{dm}{dt}\right)_{t\to 0}$	$\left(\frac{d\Delta_9}{dt}\right)_{t\to 0}$	$\left(\frac{d\Delta_9^c}{dt}\right)_{t\to 0}$	$\left(\frac{d\Delta_9^t}{dt}\right)_{t\to 0}$	$\left(\frac{d\,\text{sat}}{dt}\right)_{t\to 0}$	r
Δ_9^c	A	50	0.20	0.47	-0.35	-0.90	0.42	1.2	1.1
		75	1.8	4.4	-3.7	-5.3	2.2	3.6	1.0
		100	9	21	-17	-27	8	7.8	1.0
		129	27	69	-52	-72	18	11.3	1.0
		150	47	101	-64	-90	21	15	1.5
		175	61	134	-80	-128	18	19	1.5
Δ_9^c	B	129	23	45	-45	-61	19	7.5	1.0
		150	52	107	-84	-113	31	11.5	1.2
Δ_9^c	C	100	4.5	11	-5.8	-7.2	1.4	2.6	1.5
		129	12	25	-14	-18	3.6	5.0	1.7
Δ_9^t	A	75	8.2	17.5	-18	2.8	-23	4.8	1.0[b]
		100	30	67	-52	10.6	-62	7.7	1.2[b]
		130	116	245	-145	23	-168	12.0	1.3[b]
		150	158	374	-240	13	-240	16.3	1.4[b]

[a] Reaction rates expressed in mole %/min or in the number of double bond migrations per 100 molecules of monoene and per min. For explanation of symbols see Footnote 1.

[b] These values were derived from a m' vs. Δ_9 plot as given in Figure 1B.

The rate of double bond migration at time $t \to 0$ can now be derived from the slope of the tangent at $t = 0$ to the curve obtained by plotting m and m' vs. time. The initial rate of double bond migration in both directions and in the direction of the ester group is equal to $(dm/dt)_{t \to 0}$ and $(dm'/dt)_{t \to 0}$, respectively.

In a similar way the initial rate of disappearance of Δ_9-isomers can be derived from the plot representing the sum of the percentages of geometrical Δ_9-isomers in the monoene fraction vs. time. The slope of the tangent to this curve through $t = 0$ gives the initial rate expressed in the number of Δ_9-molecules that has disappeared because of the process of double bond migration, per unit of time and

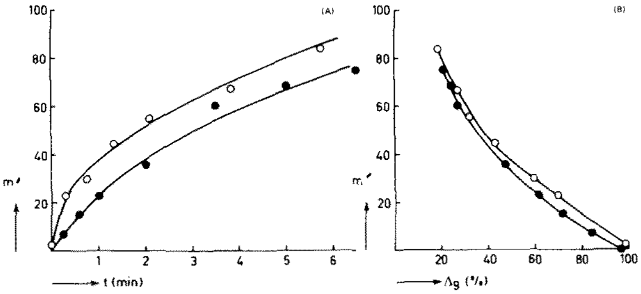

FIG. 1. m' vs. time (A) and vs. Δ_9-content in monoene fraction (B) for experiments performed on catalyst A; o methyl oleate at 129 C, x methyl elaidate at 130 C.

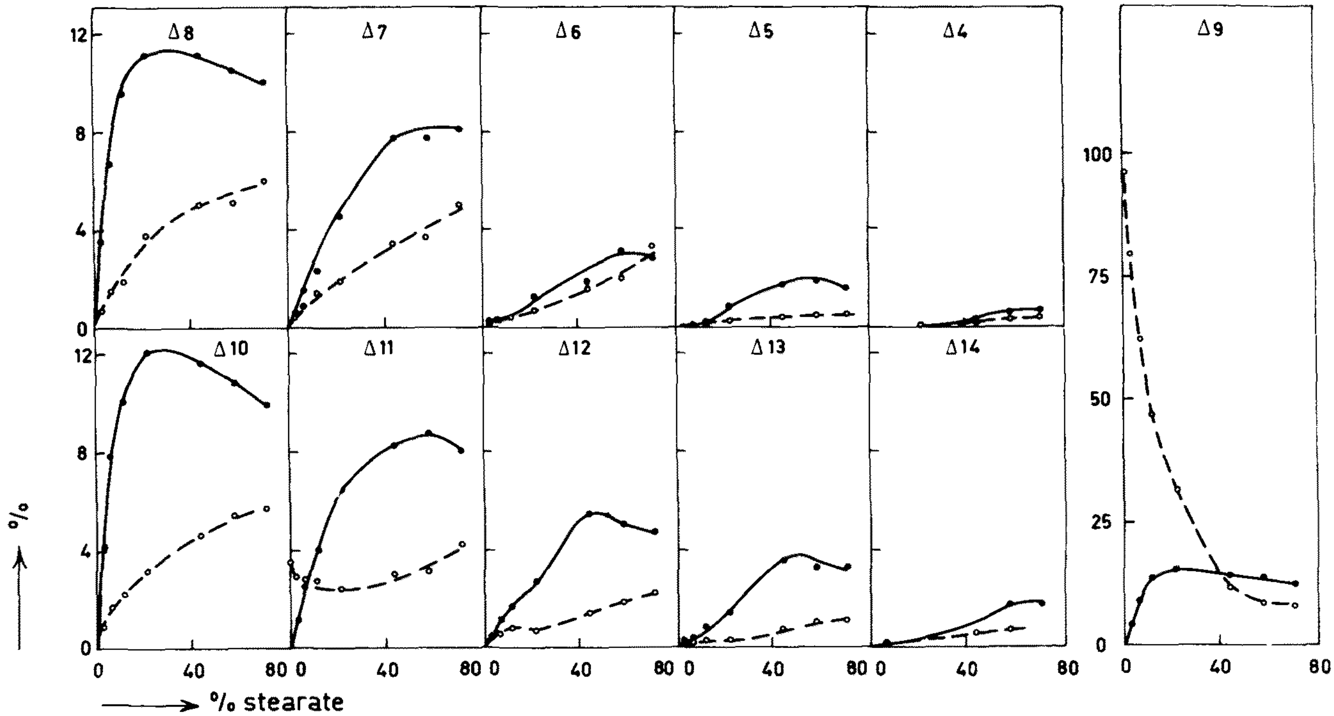

FIG. 2. Percentage of various positional and geometrical isomers in the monoene fraction as a function of methyl stearate formed at 129 C over catalyst A, starting with methyl oleate; ○ = *cis*, ● = *trans*.

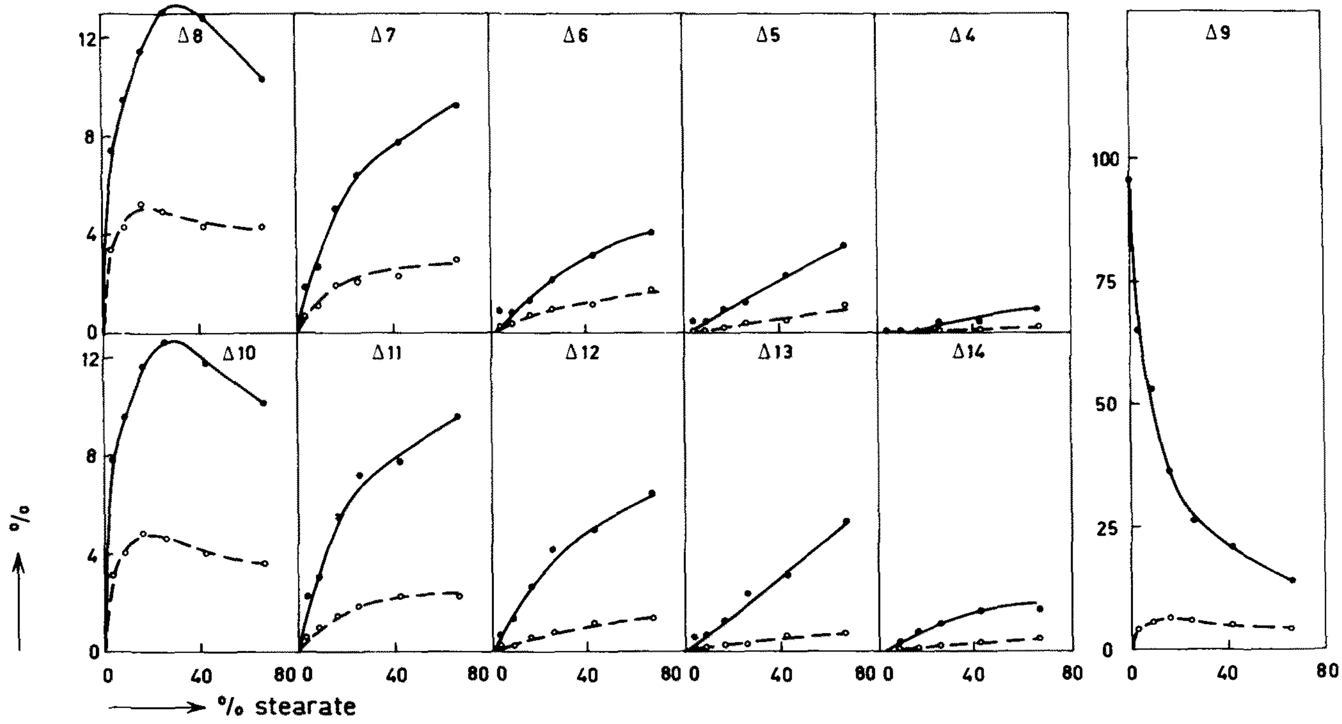

FIG. 3. Percentage of various positional and geometrical isomers in the monoene fraction as a function of methyl stearate formed at 130 C over catalyst A, starting with methyl elaidate; ○ = *cis*, ● = *trans*.

TABLE IV

Maximum Values of *trans-cis* Ratios Obtained From Methyl Oleate Over Different Catalysts at Different Temperatures

Position of double bond	*trans-cis* Ratios						
	Catalyst A			Catalyst B		Catalyst C	
	100 C	129 C	150 C	129 C	150 C	100 C	129 C
4		1.8	3.3	5.5	2.8	4.6	2.4
5		4.1	3.1	7.0	4.2	2.8	2.8
6	2.5	2.0	1.7	3.5	2.2	2.8	2.1
7	2.7	2.7	2.4	4.5	2.6	2.6	2.1
8	4.7	4.9	3.6	6.5	5.2	4.3	4.0
9	>1.4[a]	1.7	1.2	>2.5[a]	2.4	>0.35[a]	1.0
10	4.8	5.1	4.0	8.0	5.3	5.0	4.4
11	2.3	3.0	2.6	6.0	2.8	2.5	2.4
12	3.5	4.2	3.5	8.5	3.6	3.9	3.3
13		5.1	4.0	7.5	4.2	4.5	3.6
14					4.0	2.8	2.4

[a] No maximum value obtained.

per 100 unsaturated molecules. It will be clear that the ratio between the initial rate of double bond migration and the corresponding rate of disappearance of Δ_9-isomers expresses the number of double bond displacements that has occurred on an average in a molecule subjected to the process of double bond migration, during the residence time in a catalyst particle at the beginning of the reaction. To exclude the influence of the Δ^{c}_{11} isomer, about 3.5 % of which is always present in purified methyl oleate, twice the rate of double bond migration in the direction of the ester group has been taken as the total rate of migration. The ratio between the rates is now defined as:

$$r = -2(dm'/dt)_{t \to 0} \,/\, (d\Delta_9/dt)_{t \to 0} \qquad [3]$$

The experimental values for the initial reaction rates, expressed in mole%/min or in the number of double bond migrations per 100 molecules of monoene and per minute, together with the r-values, have been listed in Table III.

From the definition of r it follows that $r \geqslant 1$. It will be clear that $r = 1.0$ if from every Δ_9-molecule in which the double bond migrates only Δ_8- and Δ_{10}-isomers can arise as primary products and moreover if these molecules are removed from the catalyst particles before they also get an opportunity for double bond migration. Should these secondary reactions occur during the residence time in the catalyst particle, then r will be greater than 1.0. However an intrinsic catalytic activity resulting in more double bond migrations during one sojourn on the catalyst surface will also lead to $r > 1$. It is possible to discriminate between the latter two possibilities by comparing catalysts which greatly differ in pore-width distribution. This has been done (6) and it could be concluded that $r > 1$ must be ascribed to transport hindrances of ester molecules, resulting in readsorption of unsaturated molecules during the residence time in the catalyst particles. Thus the double bond migration from the 9 position proceeds via a stepwise mechanism, which implies that the rate of desorption is very high with respect to the rate of double bond migration under the circumstances used. An apparent multiple mechanism ($r > 1$) is found in cases where the residence time of a molecule in a catalyst particle is so long that two or more double bond migrations can occur before it leaves this particle. On the basis of this reasoning strong transport hindrances are introduced for methyl oleate in catalyst A at temperatures above 129 C. However these hindrances are reduced when catalyst B with wider pores is used. The influence of mass transport can be enhanced by using a catalyst with very narrow pores such as catalyst C. In this case high r values will be found even at relatively low temperatures, as is shown in Table III. Another interesting aspect emerging from this table is that under identical circumstances the reduction of methyl oleate proceeds as fast as that of methyl elaidate in contrast to the rate of double bond

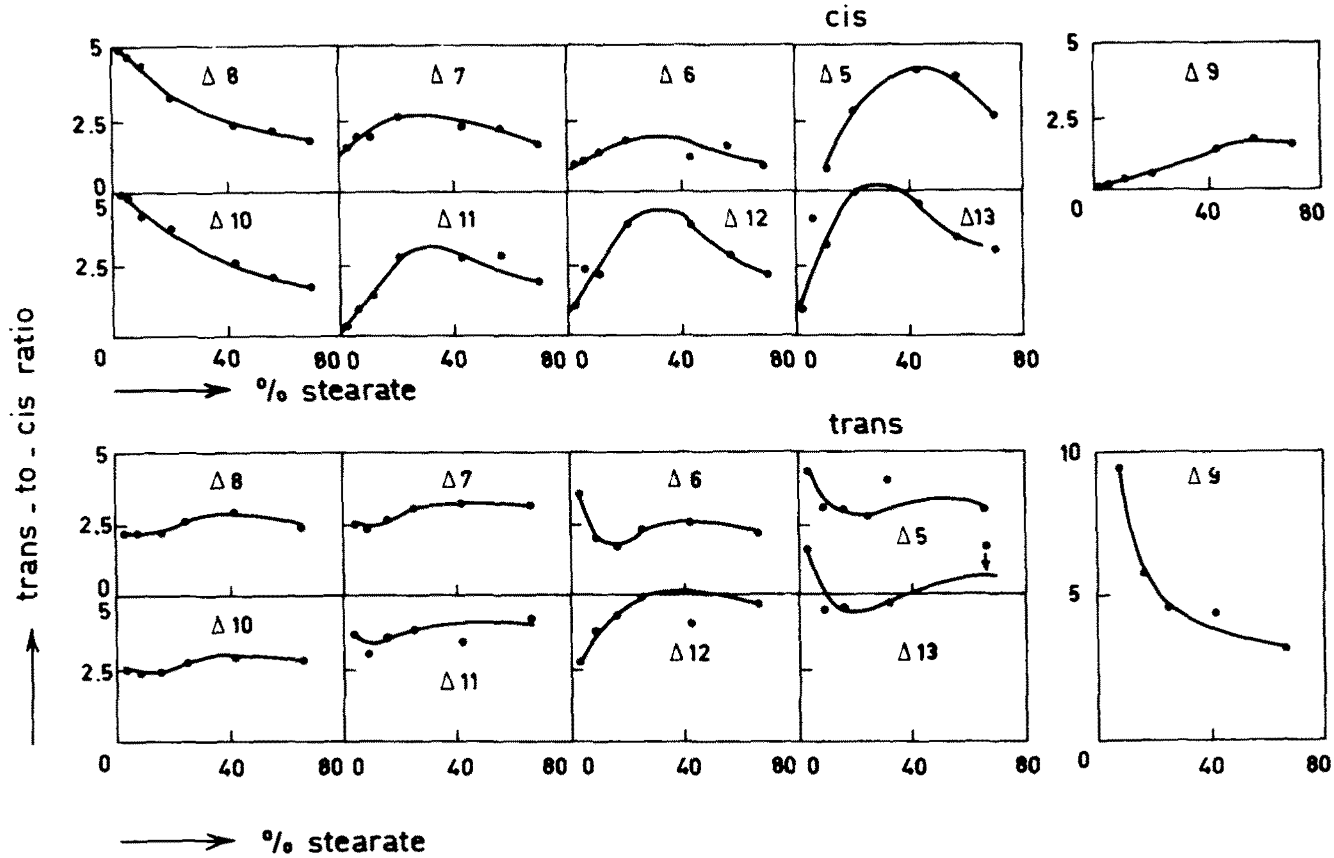

FIG. 4. *Trans-cis* ratios of the positional isomers from methyl oleate (above) and methyl elaidate (below), as derived from Figures 2 and 3.

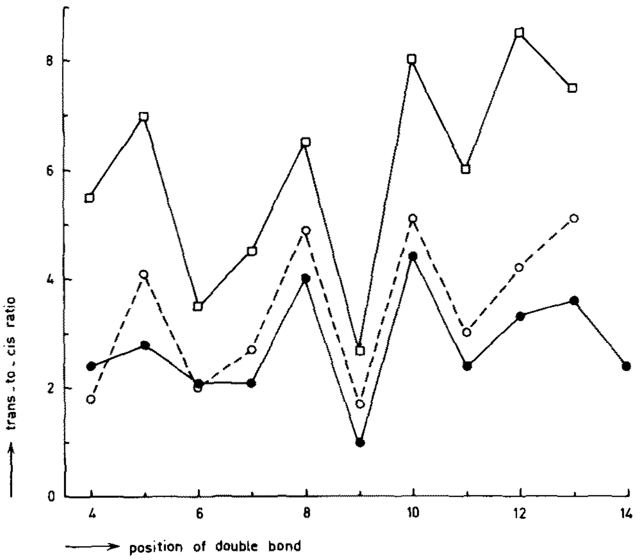

FIG. 5. Maximum *trans-cis* ratios of the positional isomers from methyl oleate as a function of the double bond position, at 129 C over catalysts A (○), B (□) and C (●).

migration, which is three to four times higher for the latter compound. This is also illustrated by Figure 1, where *m* has been plotted vs. time (A) and vs. the Δ_9-content in the monoene fraction (B) for experiments performed at about 129 C. In the latter case the influence of time has been eliminated, resulting in fluent curves, which demonstrates the accuracy of the analyses. Exactly the same phenomena were observed at the other experimental temperatures, which shows that indeed the initial rate of double bond migration in methyl elaidate exceeds that of methyl oleate considerably. This is of course only an initial effect because in both cases the product distribution has a tendency to converge to the same composition at a high degree of hydrogenation. For this reason both curves in Figure 1A are almost parallel after a certain reaction time.

The isomers formed from methyl oleate over catalyst A at 129 C are plotted as a function of the saturation degree in Figure 2. Similar pictures were obtained with catalyst A at the other temperatures mentioned in Table III and with catalysts B and C at 100, 129 and 150 C. Figure 3 shows the isomer pattern obtained from hydrogenating methyl elaidate at 130 C on catalyst A. This figure is also representative of the other experiments performed with this ester (Table III).

Again the difference between the chemical behavior of methyl elaidate and that of methyl oleate is shown by the steeper slopes of the curves of the Δ_8- and Δ_{10}-isomers which are formed from the former ester at a low degree of hydrogenation. Moreover maxima arise in the Δ_8^c- and Δ_{10}^c-curves, which are not found with methyl oleate as a reactant.

The maxima in the *trans* curves of positional isomers obtained from methyl oleate form another striking fact, resulting in maxima in *trans-cis* ratios. These ratios, derived from Figures 2 and 3, have been plotted in Figure 4. It can be concluded that it is out of the question that the geometrical isomers are formed in a *trans-cis* equilibrium, as was earlier supposed by many authors (1,2).

The maximum values of *trans-cis* ratios derived from pictures like Figure 4 have been given in Table IV. For some experiments these values have been plotted vs. the double bond position in Figure 5. The peculiar alternating behavior as observed from this figure was also found by Subbaram and Youngs (4) for the isomers formed from methyl oleate and methyl erucate during hydrogenation over a nickel catalyst, and by Raju et al. (7) for the isomerization reactions occurring during the reduction of potassium oleate over Rufert nickel. Reitz et al. (8) observed a similar behavior for the acyl transferase activity of *cis*-octadecenoic acids. The latter authors tried to correlate their data with the melting points of the acids which show the same alternating effects (9). Their correlation is based on the idea that a certain preferential orientation with respect to the active center may play a significant role in the enzymatic reaction. It is imaginable that the melting point, and thus the stability of the crystals, forms a yardstick for the ease with which the molecules concerned can be pressed to a stereo-specific shape.

FIG. 6. *Trans-cis* ratios at 150 C as a function of the double bond position; ○ = maximum values over catalyst B, with methyl oleate as a reactant; ● = values at 70% conversion over catalyst B, with methyl oleate as a reactant; □ = values at 65% conversion over catalyst A, with methyl elaidate as a reactant.

It is possible that the same reasoning holds for the intrinsic activity of metal catalysts in relation to the stability of the complexes formed at the catalyst surface. Morris et al. (10) and Gunstone et al. (11) for example, observed that the stability of a silver ion complex with a double bond depends upon the position and configuration of that bond. In this connection the work of Scholfield et al. (12) should be mentioned; they concluded from competitive hydrogenation experiments that methyl oleate is hydrogenated faster than methyl elaidate, the rate of hydrogenation of methyl oleate being exceeded by the rate at which the *cis*-isomers with bonds in the 12 and 15 positions are reduced on a nickel catalyst at 140 C. Similar phenomena were observed by Mounts et al. (13) in gas-phase reactions with the methyl esters concerned. It is quite possible that these effects can be ascribed to pure intrinsic catalytic properties, and one is inclined to assume that the same is valid for the *trans-cis* ratios found by us (Table IV). However the ratio concerned appears also to be dependent on the rate of supply and removal of the molecules in question, as can be concluded from Figure 4.

The higher *trans-cis* ratios are obtained on catalysts with wider pores; thus more *trans*-isomers are formed. Apparently they are either formed preferentially, or the *cis*-isomers are removed specifically accompanied with *cis-trans* isomerization. The latter process may be fast as compared with the other chemical reactions, which would imply that the *trans-cis* ratios are strongly influenced by the residence time of an unsaturated molecule in a catalyst particle. The faster the molecule can leave this particle, the greater the chance of its having the *trans*-configuration.

During the hydrogenation process these ratios change considerably, as can be seen from Figure 6. They all decrease with increasing degrees of conversion and the ratios obtained with the double bond in the 8, 9 and 10 position even undergo an "umbrella" change. For comparison, data are given which originate from the hydrogenation of methyl elaidate over catalyst A.

Achaya and Raju (14) assume an equilibrium *trans-cis* ratio of about 4, which they almost reached in their experiments. They were, however, confronted with a strong decrease in this ratio at a high degree of saturation of unsaturated fatty acid esters, just as we were in our experiments. Achaya and Raju ascribed this phenomenon to a preferential reduction of *trans*-isomers at the end of the hydrogenation process. As it is hard to believe that only the intrinsic catalytic activity is responsible for this change in preferential hydrogenation, the following possibilities should be considered: (a) The equilibrium ratio at the reaction temperature is lower than 4. At the end of the hydrogenation equilibrium is reached, resulting in the *trans-cis* ratios found experimentally; and (b) The reaction orders of the isomerization and hydrogenation reactions change drastically at a high degree of saturation. This implies a modified behavior of the reaction system with respect to mass transport effects.

The objections to low equilibrium *trans-cis* ratios stem from the literature. Gunstone and Ismail (9) established equilibrium values varying from 3.0-4.0 at 200 C, dependent on the position of the double bond. Egger (15), studying the iodine-catalyzed isomerization of heptenes, found an equilibrium value of about 4 for the *trans-cis* ratios of the isomers with the double bond in the 3 position at 150 C. At 200 C this value had decreased to 3.5. Both values were measured in the gas phase. A theoretical equilibrium value of 2.3 at 150 C can be calculated from thermodynamical data (16). However more confidence should be given to the values found experimentally, implying that indeed a preferential removal of *trans*-isomers is involved, owing to mass transport effects.

It is clear that further investigations are necessary to find a more quantitative basis to prove this statement.

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