JOURNAL OF CATALYSIS 26, 42–50 (1972)

A Criterion for Detecting Mass Transport Effects on Double Bond Migration During the Hydrogenation of Methyl Oleate Using Nickel-on-Silica Catalysts

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Received July 2, 1971

To investigate the influence of mass transport on double bond migration, methyl oleate was hydrogenated at different temperatures using Ni/SiO_2 catalysts with relatively narrow, medium and wide pores. From the product distribution obtained—expressed as a function of time—a dimensionless number r was derived, being the ratio between the rate of double bond migration and the rate of disappearance of methyl 9-octadeceoate irrespective of the configuration of the double bond.

The r value varied between 1.0 and 1.7 from which it was concluded that the double bond migration proceeds here via a stepwise mechanism and that r values larger than 1.0 must be ascribed to mass transport hindrances in the catalyst particles.

INTRODUCTION

Dutton *et al.* (*1*) investigated the migration kinetics and the *cis–trans* rearrangement of the double bond in methyl oleate during its hydrogenation on carbon supported platinum and palladium catalysts. Their publication also gives some data on deuterium exchange. Starting from the Horiuti–Polanyi mechanism (*2*), Dutton *et al.* calculated the composition of the reaction products, which agreed fairly well with the one observed. However, the influence of mass transport effects and chemical behavior—depending on position and geometry of the double bond—was not included in their model. Taking into account these influences results in a reaction scheme hardly suitable for mathematical treatment or for simulation or calculation on a computer because too many parameters are involved.

In this investigation we have studied the mass transport effects and the effect of the position and geometry of the double bond on the isomerization kinetics taking place during the hydrogenation of unsaturated fatty acid esters. Attention is also drawn to mass transport effects occurring during the hydrogenation of methyl oleate. A quantitative method is derived for establishing mass transport hindrances concerning double bond migration.

EXPERIMENTAL

The experiments were carried out in batch. An amount of 30 g methyl oleate (for composition, see Table 1) was introduced into a stirred reactor while hydrogen was introduced (1 atm) above the ester level and thoroughly dispersed in the liquid with rapid stirring (3000 rpm, cor-

TABLE 1
COMPOSITION OF METHYL OLEATE

Location double bond	Percentage
6	0.05
7	0.38
8	0.26
9	96
10	0.3
11	3.5
12	0.7

responding with a dispersed energy of 70 W/kg oil). The experiments were made at temperatures varying between 50 and 175°C. Next, 50 mg catalyst—reduced *in situ*—was added. The hydrogen required for the hydrogenation process and the reduction of the catalyst had been purified by passing it through a column filled with a copper catalyst (*ex* BASF) and subsequently through a column with zeolite for removing traces of oxygen and water. Any catalyst poisons, present in the unsaturated esters, were removed by chromatography over an alumina column using light petroleum as a solvent. After the reaction time had elapsed, the reaction mixture was cooled and the catalyst removed by filtration. The catalysts were prepared by precipitating nickel with soda or sodium hydroxide from nickel sulfate solution on guhr as a carrier. The precipitation conditions for catalyst C were adapted, resulting in a catalyst with very narrow pores and giving a pore volume of 60% against a pore volume of catalysts A and B of 80%. The pores of the catalyst particles were generally slit-shaped. For further data see Table 2.

TABLE 2

SOME CHARACTERISTIC VALUES OF THE Ni/SiO_2 CATALYSTS USED; PARTICLE DIAMETER 2–3 μm

Catalyst	A	B	C
% of 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)	129	17 (50)
	73 (94)		106 (50)
S_{BET}(m^2/g total Ni)	259	311	522
S_{Ni} (m^2/g reduced Ni)	72	84	151

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

The percentage of methyl stearate in the reaction mixture was determined by glc while the total *trans* content was calculated from ir measurements at 10.36 μm (*3*). About 50 mg of the reaction mixture was separated into a saturated, a *cis* and a *trans* fraction by tlc on silica impregnated with silver nitrate, as described by de Vries and Jurriens (*4*). The fractions were extracted with peroxide free diethyl ether. After removal of the ether, the *cis* and *trans* fractions were separately ozonized in carbon disulfide at −80°C. The ozonides were reduced at 40°C using a large excess of triphenylphosphine. Finally, the mixture of aldehydes and aldehydic esters was analyzed by glc. The method of evaluating the gas chromatogram from which the double bond distribution (DBD) was finally calculated will be published elsewhere (*5*).

RESULTS

Table 3 shows the influence of catalyst texture on the overall composition of par-

TABLE 3

INFLUENCE OF CATALYST TEXTURE ON OVERALL COMPOSITION ACCORDING TO IR AND GLC OF SOME SAMPLES OF METHYL OLEATE HYDROGENATED AT 129°C

Catalyst A			Catalyst B			Catalyst C		
Time (min)	*trans* (%)	Sat. (%)	Time (min)	*trans* (%)	Sat. (%)	Time (min)	*trans* (%)	Sat. (%)
0.25	14	2.5	0.5	21	2.4	1	13.4	4.5
0.58	28	6	0.9	34	4.6	2	23.4	10
1.0	38	11.5	1.5	50	9.3	4	37.5	21.5
2.0	44	21	3.0	57	23.2	6	38.9	34.5
3.5	38	43.5	5.5	43	43.6	11	28.7	53
5.0	29	57	7.7	28	62.7	14	24.9	56
6.5	19	70						

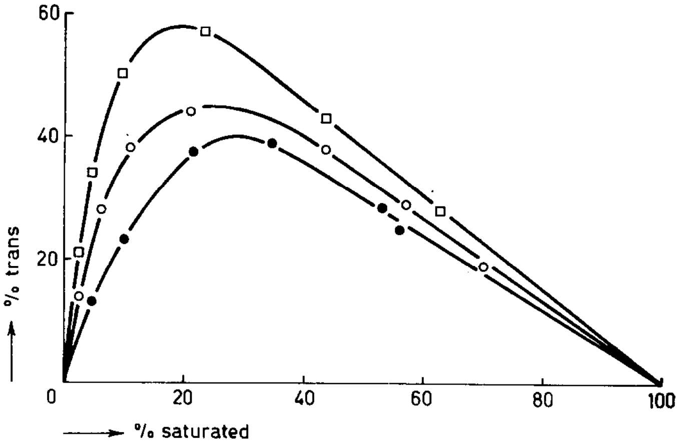

FIG. 1. Total *trans* content as a function of the percentage of methyl stearate formed at 129°C on catalyst A (○), catalyst B (□), and catalyst C (●).

tially hydrogenated methyl oleate as a function of time. The catalyst with the narrowest pores forms fewer *trans* isomers than the other catalysts (see Fig. 1). In Fig. 2, the percentage of *trans* products has been plotted against the percentage of methyl stearate formed at different temperatures, with catalyst A and methyl oleate ($\Delta_9{}^c$) as starting material. In Fig. 3 the amounts—expressed in percentages of unsaturated fraction—of some monoenes formed during hydrogenation have been plotted as a function of the percentage of methyl stearate formed at 129°C on catalyst A. The *trans/cis* ratios, which are also given in Fig. 3, clearly show that the reaction products are not formed in a *trans/cis* equilibrium, as is sometimes assumed (*8*). Especially the *trans* isomers with the double bond in the 8- or 10-position accumulate at the beginning, an effect which increases with the accessibility of the catalyst particles. Higher *trans* concentrations, which greatly surpass the equilibrium value, can be obtained when the catalyst possesses wider pore diameters. From the present data it cannot be concluded whether, on double bond migration, *cis* isomers are formed preferentially and accumulation of *trans* isomers occurs because the *cis* isomers are removed preferentially, for instance by hydrogenation, or whether the accumulation of *trans* isomers must be explained on the simple basis that these isomers are

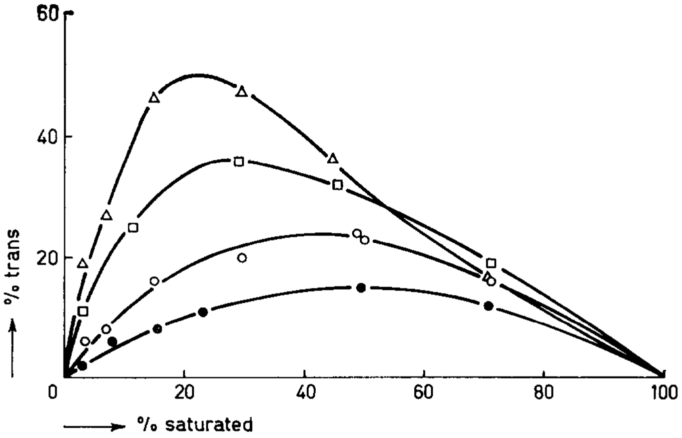

FIG. 2. Total *trans* content as a function of the percentage of methyl stearate formed at 50 (●), 75 (○), 100 (□) and 150°C (△) on catalyst A, using methyl oleate, $\Delta_9{}^c$, as starting material.

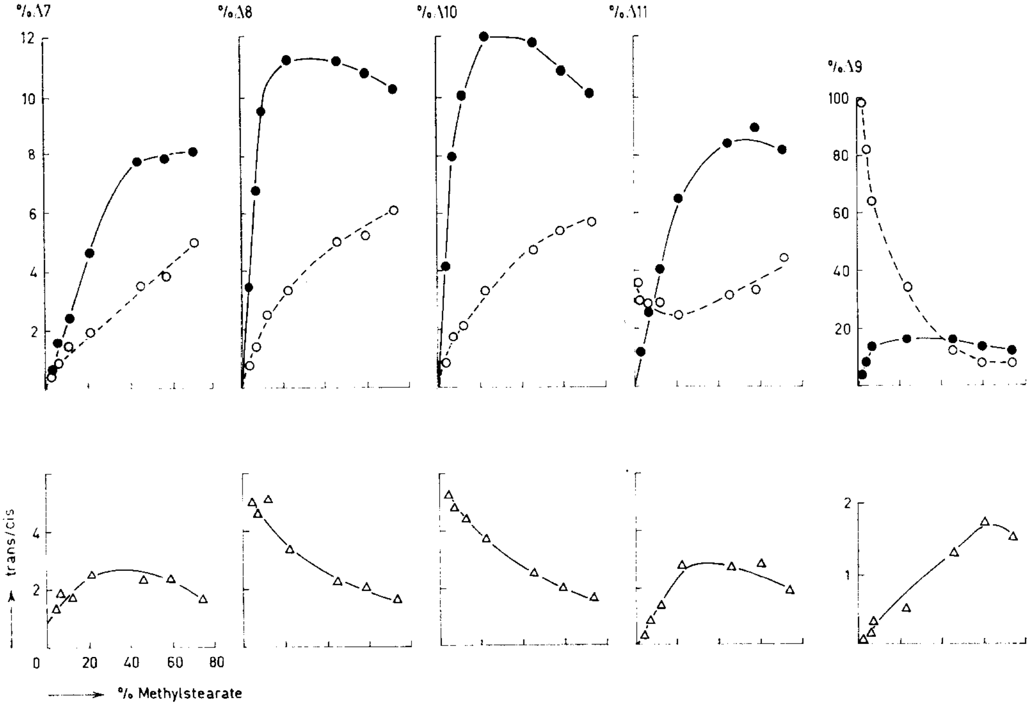

FIG. 3. Percentages of some positional and geometrical isomers together with corresponding *trans/cis* ratios as a function of methyl stearate formed at 129°C on catalyst A: ● *trans* isomer (in percentages of monoene fraction); ○ *cis* isomer (in percentages of monoene fraction); △ *trans/cis* ratio.

formed in excess. It is also difficult to understand why after a certain degree of hydrogenation the *trans/cis* ratio decreases below the equilibrium value. Similar phenomena were also found with other catalysts and other reaction temperatures, except with the experiment performed at 50°C. At this temperature the isomerization process proceeded so slowly compared with the hydrogenation process, that no maxima were found in the *trans* curves. More data about these anomalous effects will be published elsewhere.

DERIVATION OF MIGRATION RATE

The migration rate of the double bond is derived for the total migration in both directions as well as for the migration in the direction of the ester group. These rates cannot be determined from the rate of formation of Δ_8 and Δ_{10} isomers, because these isomers are also susceptible to the migration process. However, the rate of migration of the original double bond can be approached by taking into account the double bond migrations of all the positional isomers formed during the reaction time. At the beginning of the reaction the catalyst surface is covered only with the original isomer, say $\Delta_9{}^c$, the coverage of which correlates with a certain migration rate of the double bond. However, as soon as other isomers are formed, the net number of double bond migrations from the 9-position per unit of time decreases for two reasons; either the reaction products compete with $\Delta_9{}^c$ for active sites, or they react to form Δ_9 isomers. In either case, it is better to consider the total number of net double bond migrations than the net number of migration reactions of the double bond from the 9-position. The total number of net double bond migrations, being the difference between forward and backward double bond migrations, can easily be calculated from the composition. The contribution of a molecule with, for instance, the double bond in the 7- (or 11-) position to the total number of net double bond migrations is two, independent of the formation of this molecule via, for example, 9 → 8 → 7 or 9 → 8 → 7 → 6 → 7. In the latter case, four double bond migrations have occurred, but the actual contribution to the net number is still two. On the basis of this reasoning the total net number of double bond migrations in 100 molecules of monoene is given by

$$m = \sum_{1=7}^{8} \Delta_{9+i}|i|, \tag{1}$$

where Δ_{9+i} is the sum of the geometrical isomers with the double bond in the $(9 + i)$-position expressed in percentages of the monoene fraction. The effect of competition is, as it were, introduced by weight number i, because a Δ_{9+i} molecule has used the catalytic surface at least i times to migrate its double bond from the 9- to the $(9 + i)$-position. Undoubtedly, also *cis–trans* rearrangements take place. These reactions have not been taken into account in Eq. (1). By plotting m vs time and taking the slope through the origin, a fairly good approximation is obtained for the rate of displacement of the double bond along the carbon chain. This method also allows the calculation of the reaction rates of the *cis–trans* rearrangement, the rate of disappearance of $\Delta_9{}^c$ and $\Delta_9{}^{c*}$ and the rate of the hydrogenation process itself. The asterisk denotes that the concentration of the product is based on the total reaction mixture, whereas in the other case the unsaturated products are expressed in percentages of the unsaturated fraction. The rate of double bond migration in the direction of the ester group is derived from

$$m' = \sum_{i=1}^{7} \Delta_{9-i} \cdot i. \tag{2}$$

The results are given in Table 4. The correctness of the data can be checked by means of the mass balance. It will be clear that in the monoene fraction, the rate of disappearance of Δ_9 isomers—caused by migration of the double bond—added to the rate of formation of $\Delta_9{}^t$, must be equal to the rate of disappearance of $\Delta_9{}^c$ found experimentally.

A corresponding relation can be derived for $\Delta_9{}^{c*}$ in the total reaction mixture. As a matter of fact, the rates of disappearance or formation in the total reaction mixture should be used. However, a fairly good approximation can be obtained by combining the values for the monoene fraction and the rate of hydrogenation. The sum of these rates must be equal to the rate of disappearance of $\Delta_9{}^{c*}$ in the total reaction mixture. The results of these calculations are given in Table 5. The data obtained are consistent, as can be concluded from the mass balance given in this table, except for the experiments performed at 175°C on catalyst A. In this case, the

TABLE 4

Reaction Rates for Double Bond Migration, *cis–trans* Rearrangement and Hydrogenation at Different Temperatures and on Different Catalysts. The Migration Rates are Given as Number of Double Bond Migrations per 100 Molecules Monoene per min. The Other Rates are Expressed in mol %/min.

Catalyst	T (°C)	$(dm'/dt)_{t\to0}$	$(dm/dt)_{t\to0}$	$(d\Delta_9/dt)_{t\to0}$	$(d\Delta_9{}^c/dt)_{t\to0}$	$(d\Delta_9{}^t/dt)_{t\to0}$	$(d\Delta_9{}^{c*}/dt)_{t\to0}$	$(d\,\mathrm{sat}^*/dt)_{t\to0}$
A	50	0.20	0.47	−0.35	−0.90	0.42	−2.0	1.2
	75	1.8	4.4	−3.7	−5.3	2.2	−8.7	3.6
	100	9	21	−17	−27	8	−37	7.8
	129	27	69	−52	−72	18	−80	11.3
	150	47	101	−64	−90	21	−98	15
	175	61	134	−80	−128	18	−165	19
B	129	23	45	−45	−61	19	−67	7.5
	150	52	107	−84	−113	31	−120	11.5
C	100	4.5	11	−5.8	−7.2	1.4	−9.8	2.6
	129	12	25	−14	−18	3.6	−22.5	5.0

TABLE 5

VALUES CALCULATED FROM THE MASS BALANCE TOGETHER WITH VALUES FOR THE CHARACTERISTIC RATIO r

Catalyst	T (°C)	$-(d\Delta_9{}^c/dt)_{t\to0}$	a[a]	$-(d\Delta_9{}^{c*}/dt)_{t\to0}$	b[b]	r[c]
A	50	0.90	0.77	2.0	2.0	1.1
	75	5.3	5.9	8.7	9.5	1.0
	100	27	25	37	33	1.0
	129	72	70	80	81	1.0
	150	90	85	98	100	1.5
	175	128	98	165	117	1.5
B	129	61	64	67	72	1.0
	150	113	115	120	127	1.2
C	100	7.2	7.2	9.8	9.8	1.5
	129	18	18	23	23	1.7

[a] $a = -(d\Delta_9/dt)_{t\to0} + (d\Delta_9{}^t/dt)_{t\to0} \equiv -(d\Delta_9{}^c/dt)_{t\to0}$.

[b] $b = a + (d\,\text{sat.}/dt)_{t\to0} \equiv -(d\Delta_9{}^{c*}/dt)_{t\to0}$.

[c] $r = -2(dm'/dt)_{t\to0}/(d_{\Delta 9}/dt)_{t\to0}$.

isomerization rate was so high that too few data could be obtained at the beginning of the reaction, leading to less reliable results. Table 5 also gives the ratio between two different reaction rates indicated by r.

DISCUSSION

If we assume that the migration of the double bond from the 9-position proceeds randomly, the value for $(dm'/dt)_{t\to0}$ should be half that established for $(dm/dt)_{t\to0}$. Table 4 shows that this is not true. It is evident that the presence of 3.5% of $\Delta_{11}{}^c$ in the original product affects the value of m, so that even at equal rates of double bond migration in both directions

$$(dm/dt)_{t\to0} > 2(dm'/dt)_{t\to0}.$$

For this reason, twice the migration rate in the direction of the methyl group will be taken as the total rate of the double bond migration.

If an unsaturated molecule could be followed on its way through a catalyst particle, the following might be observed:

(1) The molecule enters and leaves the particle without touching the catalyst surface;

(2) Elastic collisions take place without entailing any chemical change of the molecule;

(3) The unsaturated molecule adsorbs and desorbs while retaining its original structure;

(4) After adsorption, the molecule reacts, resulting in a chemical change.

The occurrence of any of these processes depends not only on the activity of the catalyst but also on the rate of mass supply to and mass removal from the catalyst surface. From the point of view of catalytic activity and selectivity, mass transport plays a significant role. Thiele, Sherwood, Satterfield and others [see (*6*)] derived rules for simple systems to predict whether hydrogen concentration gradients occur in the pores of the catalyst. However, these rules are inadequate to indicate when transport phenomena influence the isomerization of reactants like methyl oleate.

The hydrogenation of fatty acid ester molecules proceeds via a zero order reaction in unsaturated molecules, as can be derived from Table 3. The net rate at which the double bond moves from the original position to the 8- and 10-positions depends on the concentrations of the isomeric products formed from the original Δ_9-isomer, because the Δ_8- and Δ_{10}-isomers give rise to the formation of Δ_9-isomers on account of the reversible character of these reactions. We are interested in the net amount of double bond displacements per unit of time and it will be clear that for isomerization reactions the net rate in the pores of the catalyst is more sensitive to concentration gradients in fatty acid ester molecules than the rate of hydrogenation because the latter process is of zero order in unsaturated molecules. This implies that the rate of isomerization depends more strongly on the rate of mass transport of monoenes in the catalyst particles than the rate of hydrogenation does.

The ratio

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

given in Table 5, can be used as a source of information on the occurrence of transport hindrances influencing the process of double bond migration. In processes resulting in double bond migration, a molecule may be subject to the following reactions:

(1) During the residence time in the catalyst particle, the double bond migrates over only one carbon–carbon distance;

(2) Because of readsorption, more than one double bond displacement per molecule can occur during the residence time in the particle;

(3) The double bond migrates over more than one carbon–carbon distance during one sojourn to the internal surface of the catalyst particle; as sub (1), mass transport is so fast that only one such adsorption process can take place per visit to the particle.

A combination of the three reaction processes may occur. To some extent, the reactions that are possible have been idealized (see Fig. 4), because in (1) and (2) it is assumed that the desorption rate of the unsaturated molecules is infinitely fast with respect to the rate of double bond migration on the surface.

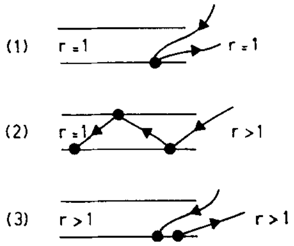

FIG. 4. Scheme of the behavior of an unsaturated molecule in the pores of a catalytic particle. (1) One reaction, (2) several reactions by readsorption and (3) several reactions on catalyst surface.

Ratio r indicates the average number of double bond migrations occurring at time $t \to 0$ in a molecule submitted to the process of double bond migration. Because of extrapolation to time $t \to 0$, the chance of a molecule reentering the catalyst particle can be neglected; r thus reflects the double bond migrations occurring in molecules during time interval dt lying between $t = 0$ and $t = dt$. If we assume that a molecule which has penetrated a catalyst particle does not have a second opportunity of reentering another or the same catalyst particle, r can be related directly to the above-mentioned processes (1) to (3), to which the original Δ_9 molecules are subject. In principle we can determine r by counting, during interval dt, both the number of double bond migrations and the number of original unsaturated molecules that has disappeared because of double bond displacements. The ratio between these numbers is then equal to r. From this it follows that

$$r \geq 1.$$

Ratio $r = 1.0$ indicates a situation in which every Δ_9 molecule submitted to double bond migration gives isomers with the double bond in the 8- or 10-position during the first residence time in the catalyst particle, or in other words: a Δ_9 molecule can only be converted into a Δ_8 or a Δ_{10} isomer during time interval dt lying between $t = 0$ and $t = dt$. In this case the double bond migration must be characterized as a stepwise process.[1]

Only one migration step occurs during one visit to the catalyst surface and, moreover, mass transport in the catalyst particle is so fast that a molecule does not undergo a second migration reaction during its residence time in the catalyst particle. Thus, a clear pronouncement can be made if r is 1.0, corresponding with reaction process (1). However, the r value becomes

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[1] A similar method as described here is applied by Dwyer *et al.* (7) for mass transport hindrances occurring in porous catalysts during deuterium exchange in neopentane.

ambiguous when it is found that $r > 1.0$, because reactions (2) and (3) and a combination of these reactions result in r values deviating from 1.0. Only in the pores of the catalyst do differences in r arise; this depends on what happens inside the catalyst—the progress of the double bond migration may be influenced by mass transport leading to readsorption or by catalytic intrinsic activity resulting in several double bond displacements during one visit of the molecule to the catalyst surface. In the former case, the r value within the pores is equal to 1.0, whereas in the latter case a higher value will be found. Unfortunately, samples cannot be drawn from the interior of the catalyst particles so that it is impossible to conclude on the basis of an r value measured outside these particles whether, for example, Δ_7 isomers are primary migration products (due to the intrinsic activity of the catalyst) or must be regarded as secondary products formed as a result of readsorption during the residence time of the molecule in the catalyst particle at the beginning of the reaction. However, when it is assumed that the intrinsic activity of the catalyst is independent of its texture, such as pore diameter distribution and size of the metal crystallites, then severe transport hindrances must be reduced considerably by using catalysts with wider pores, resulting in decreasing r values.

From Table 5 it can be concluded that between 50 and 129°C, the double bond at $\Delta_9{}^c$ migrates step by step when catalysts are used with pores equal to or wider than those of catalyst A. When catalysts with smaller pores (catalyst C) are used, severe transport hindrances occur, resulting in high r values and a low selectivity for isomerization (Fig. 2) as far as the amount of *trans* isomers formed are representative of the amount of positional isomers formed from $\Delta_9{}^c$. At temperatures above 129°C, r strongly increases when catalyst A is used. However, the effect of temperature on r can be reduced considerably by using catalyst B with wider pores. This means that the reaction rates for double bond migration found with catalyst A above 129°C are limited by mass transport effects.

Similar trends are observed when $\Delta_9{}^t$ is used as a starting product. However, the rate of double bond migration strongly depends on the configuration. It has been found that the *trans* double bond migrates 3–4 times faster than the *cis* double bond does. For this reason, mass transport starts playing a role at lower temperatures when $\Delta_9{}^t$ instead of $\Delta_9{}^c$ is used (established by experiment).

Summarizing, the following conclusions can be drawn:

1. In methyl oleate the double bond migration proceeds via a stepwise mechanism from the 9-position.
2. The intrinsic catalytic activity resulting in a stepwise double bond migration can be used as an important tool to establish when mass transport of fatty acid esters starts playing a role in the process of double bond migration. Thus, the apparent multiple mechanism ($r > 1$) for double bond migration found at high temperatures and with catalysts with narrow pores must be ascribed to readsorption of unsaturated molecules during their residence time in a catalyst particle.
3. The geometrical isomers are not formed in a *trans/cis* equilibrium. The *trans/cis* ratio changes drastically during the hydrogenation. Maxima for *trans* isomers are observed, which is in contrast to what was found, for example, during the isomerization of 1-butene where, generally, maxima for *cis*-2-butene are obtained (*9–11*).

ACKNOWLEDGMENT

Thanks are due to Mrs. I. A. M. Spruijt-van Kessel for her assistance in carrying out the analyses.

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