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Mechanism of Heterogeneous Catalytic *Cis–Trans* Isomerization and Double-Bond Migration of Octadecenoates

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Double-bond migration and *cis–trans* isomerization reactions occur in the catalytic hydrogenation of octadecenoates. With heterogeneous catalysts, the relative contribution of these processes is influenced by the occupation of the catalytic surface with hydrogen atoms.

Isomerization and double-bond migration of methyl oleate and methyl elaidate have been investigated under conditions of high hydrogen coverage (using $^3H_2$), on a silica-supported nickel catalyst. It is concluded that isomerization and double-bond migration occur at different sites of the catalytic surface of the NiH_2- and NiH-type, respectively.

INTRODUCTION

Double-bond migration and *cis–trans* isomerization are important in the catalytic heterogeneous hydrogenation of octadecenoates. Most studies concern the influence of reaction conditions (pressure, temperature, stirring) on the composition of the resulting oil and the selectivity of the hydrogenation (*1–3*). However, less attention has been paid to mechanistic implications, in particular in relation to findings in homogeneous catalysis. Dutton *et al.* (*4*) conclude from deuteration experiments with methyl oleate on Pt and Pd catalysts that double-bond migration and isomerization can be described by a Horiuti–Polanyi half-hydrogenated state (HHS) mechanism.

For experiments on an Ni catalyst, a systematic approach has been described by Den Boer and Wösten (*5*). It has been observed that the quotient of the rate constants for *cis–trans* isomerization and double-bond migration ($K_{ct}/K_m = g$) is influenced by the hydrogen coverage (Θ_H) of the catalytic surface. Conditions for which high values of Θ_H may be assumed (low temperature, high stirring intensity, active catalyst) favour the *cis–trans* isomerization process, while low values of Θ_H promote double-bond migration. At the same time, different reaction intermediates are assumed. Low values of Θ_H favour the formation of π-allyl complexes, resulting from hydrogen abstraction as the primary step, which do not allow direct *cis–trans* conversion ($g = 0$). Higher values of Θ_H will favour the HHS mechanism with hydrogen addition, as the primary step, in which the possibility for double-bond migration to both sides is equal to the possibility for the *cis–trans* isomerization ($g = 2$). However, at high hydrogen coverage, g values higher than 2 are experimentally obtained. In terms of the mechanism of the HHS, this means that abstraction of hydrogen from the hydrogenated position in the HHS is favoured over abstraction of hydrogen from the carbon atom adjacent to the double-bond. It is suggested (*5, 6*) that this may be due to the complete occupation of the catalytic surface with hydrogen atoms. Under these conditions hydrogen can only be transferred from an adsorbed intermediate to the catalyst in the same place where it was formerly released in the formation of the HHS, and double-bond migration is suppressed. In this picture, isomerization and double-bond migration are closely related and occur on the same sites of the catalytic surface via the HHS mechanism.

In this work, the validity of this concept is examined by investigating the incorporation of tritium ($^3H_2$) in isomerization and double-bond migration products during hydrogenation of methyl oleate and methyl elaidate with an Ni-catalyst for high values of Θ_H.

METHODS

Methyl oleate and methyl elaidate (>99%) were freed from traces of peroxides by passing a hexane solution over alumina. Labeled hydrogen gas was prepared by adding tritiated water to a solution of $LiAlH_4$ in diethylene glycol dimethyl ether (*7*). The specific activity of the hydrogen gas was 1–2 mCi/mmole. A silica-supported Ni catalyst containing 6.7% Ni was used. Hydrogenations were performed in a small hydrogenation apparatus with 1 ml methyl ester. After reduction of the catalyst, the hydrogen gas was pumped off and replaced by tritium-labeled gas. Hydrogenations were carried out at 30°C and took a few hours.

The composition of the reaction mixture was determined by GLC and by TLC on silver nitrate-impregnated silica (20% $AgNO_3$). After scanning, the plates were scraped off to separate *trans* monoene, *cis* monoene, and stearate, and the specific radioactivities were determined. From these data the composition of the reaction mixture was obtained. By reductive ozonolysis and determination of the aldehydic esters, the contribution of double-bond migration in the *cis* and the *trans* monoene fraction was found. The incorporation of ^3H into the various isomers was calculated from the specific radioactivities of the aldehydic esters, which were determined by radio GLC with a Nuclear Chicago High Temperature Proportional Counter (model 4998).

RESULTS

Hydrogenation of oleate and elaidate was continued until 14.4% and 13.3% stearate had been formed, respectively (see Table 1). The specific radioactivities (Table 1) agree with the incorporation of two labeled hydrogen atoms in the hydrogenation reaction and of one in isomerization and double-bond migration reactions. The activity of the *cis* and the *trans* monoene fraction is low due to the presence of unreacted oleate and elaidate resp. The amounts (M) aldehydic esters with 10, 9 and 8 C atoms, which reflect the distribution of the double bonds on 10–11, 9–10, and 8–9 positions in the *cis* and the *trans* monoene fractions, are given in Table 2.

TABLE 1
SPECIFIC RADIOACTIVITIES (α) AND COMPOSITION OF THE REACTION MIXTURE ON HYDROGENATION OF METHYL OLEATE AND ELAIDATE

	α (dpm/mmole $\times 10^{-8}$)		Amount (%)	
Compound	Oleate	Elaidate	Oleate	Elaidate
Stearate	30	37	14.4	13.3
Monoene (*trans*)	16	0.97	17.3	81.7
Monoene (*cis*)	0.53	19	68.3	5.0
Hydrogen (at start)	20–30	30–46		

Under the present conditions, double-bond migration to other positions is negligible. In terms of the model of Den Boer and Wösten (*5*) the *g* value K_{ct}/K_m is about 5. Included in Table 2 is the distribution of the activity (A) over the aldehydic esters.

DISCUSSION

Before conclusions can be drawn from the experimental results, it is important to know the amount of unreacted starting compounds. Since the same HHS will be obtained from oleate and elaidate, the formation of *cis*-Δ9 from elaidate will be representative of the formation of *cis*-Δ9 from oleate at the same stage of the reaction. In the two experiments the reactions were stopped at almost the same stage (at 14.4 and 13.3% stearate and 6.8 and 8.2% migrated products). This would mean that 3.5% *cis*-Δ9 is formed by reaction of oleate and 12.3% *trans*-Δ9 by reaction of elaidate. On the other hand, these figures compare well with those obtained by assuming that the isomerization patterns in the *cis*- and *trans*-fractions are the same. In the oleate case 0.72% *cis*-Δ8 and *cis*-Δ10 monoenes are

TABLE 2

RELATIVE ACTIVITIES (A) AND AMOUNTS (M) OF ALDEHYDIC ESTERS WITH CHAIN LENGTHS OF 10, 9 AND 8 C ATOMS AFTER OZONOLYSIS OF THE REACTION MIXTURE

	A		M (%)	
Aldehydic ester	Oleate	Elaidate	Oleate	Elaidate
C 8 *cis*	5.4	5.1	1.11[a]	0.75
trans	14.7	12.4	2.30	3.3
C 9 *cis*	53	175	66.9	3.5
trans	615	47	12.3	75
C 10 *cis*	37	42.3	0.72	0.75
trans	159	151	2.70	3.4

[a] Inaccurate due to presence of palmitoleate in the starting material; a value of 0.72 was taken for the double-bond migration to both sides.

formed and an average amount of 2.50% *trans*-Δ8 and *trans*-Δ10 monoenes. Furthermore, 12.3% *trans*-Δ9 is found (Table 2). This means that under the aforementioned assumption, 0.72/2.5 × 12.3 = 3.5% *cis*-Δ9 is formed from oleate. A similar calculation in the elaidate case leads to a value of 3.35/0.75 × 3.5 = 15.6% *trans*-Δ9 from elaidate.

In this way, it can be estimated that 63.4% oleate (66.9–3.5) and 62.7% elaidate (75.0–12.3) have not reacted at all. In combination with the data in Table 2, relative specific radioactivities (α = A/M), including values for the C_9 aldehydic esters from the reacted starting compounds, can now be obtained (Table 3).

In the Introduction an HHS mechanism with hindered double-bond migration was proposed. On using labeled hydrogen gas one would expect incorporation of ^3H from the HHS according to Fig. 1. Neglecting any possible isotope effects and taking the specific activity per atom of the hydrogen gas to be 100, one would expect the theoretical specific activities of the aldehydic esters given in Table 3.

Apparently the actual reaction scheme is more complicated: (1) C_8 aldehydic esters have a considerable activity; (2) the nonisomerized C_9 aldehydic esters have significant activities; and (3) the specific activities of C_{10} aldehydic esters are not twice as high as the specific activities of the C_9 aldehydic esters.

The presence of radioactivity in C_8 aldehydic esters indicates that readsorption and/or repeated reaction during the stay of the reacting molecule at the catalytic surface must have occurred (see Fig. 2). The secondary reactions are thought to be responsible for the observed extra incorpora-

TABLE 3

THEORETICAL AND EXPERIMENTAL RELATIVE SPECIFIC RADIOACTIVITIES (α = A/M) OF ALDEHYDIC ESTERS

	Oleate		Elaidate	
Aldehydic ester	Theoretical	Experimental	Theoretical	Experimental
C 8 *cis*	0 (7.6)	7.6	0 (6.8)	6.8
trans	0 (6.1)	6.1	0 (3.8)	3.8
C 9 *cis*	0 (11.4)	14.5	50 (50)	50
trans	50 (50)	50	0 (5.5)	3.8
C 10 *cis*	100 (108)	52	100 (107)	57
trans	100 (106)	59	100 (104)	45

The theoretical values, taking the secondary reactions into consideration, are given in parentheses.

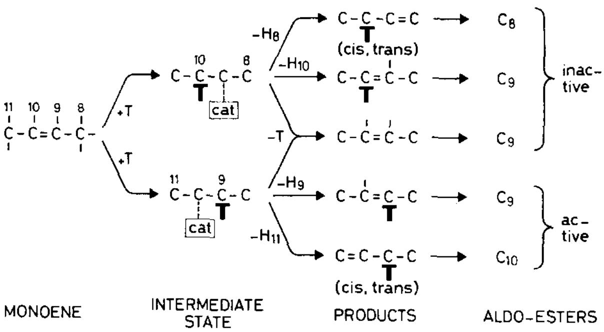

FIG. 1. Tritium incorporation based on HHS mechanism.

tion of tritium. By taking the C_8 aldehydic ester specific radioactivity (Table 3) as representative of the contribution of secondary isomerization, the theoretical specific radioactivities of C_9 and C_{10} aldehydic esters can be calculated taking secondary reactions into consideration (see Table 3, values in parentheses). From the agreement between the theoretical and experimental specific radioactivities of the aldehydic esters from non-isomerized monoenes, it follows that in the primary process no tritium is incorporated in the original isomer. Tritium is incorporated in isomerization and double-bond migration products. However, the remarkable difference of a factor of 2 between the experimental and the calculated specific activities of C_{10} aldehydic esters cannot be explained by the HHS model given in Figs. 1 and 2.

At this stage, contemplation of the findings in homogeneous catalysis seems useful. At present, a range of homogeneous hydrogenation catalysts is known (*8*) which shows the same type of reactivity towards monoenes and polyenes as the well-known heterogeneous catalysts. It is suggested that the dominating reaction type for a certain catalyst is primarily determined by the ability for hydrogen coordination.

Catalysts that cannot activate hydrogen by themselves (*8*) (e.g., $Fe(CO)_4$) can react with unsaturated molecules by hydrogen abstraction with the formation of π-allyl

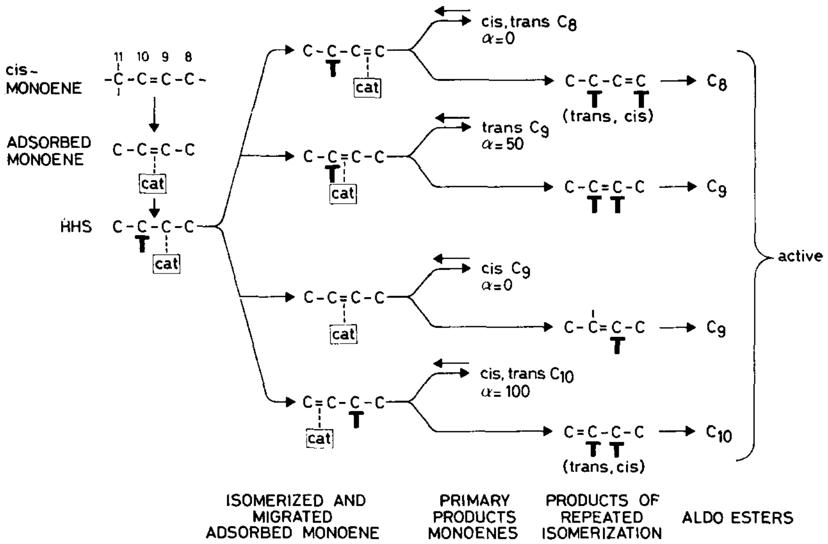

FIG. 2. Routes to the formation of secondary products (a few possible structures are given).

complexes. Mono- and dihydridic catalysts (e.g., $PtHSnCl_3(PPh_3)_2$ and $RhClH_2(PPh_3)_2$) will be able to form σ-alkyl complexes by hydrogen donation. For the monohydridic species (Me-H), double-bond migration reactions are observed, because a second hydrogen for further reaction is not immediately available. Also π-allyl complexes may be formed by hydrogen abstraction, while forming dihydridic metal complexes. Only for the dihydridic catalysts (MeH_2) do double-bond migration reactions become negligible, because in this case both hydrogens are transferred simultaneously (*9, 10*) or almost so (*11, 12*). The preference for a two-step mechanism with the formation of σ-alkyl complexes, also appears from the occurrence of *cis–trans* isomerization without double-bond migration with a modified dihydridic rhodium triphenylphosphine catalyst (*13*). This shows that, whereas double-bond migration reactions are quite common in the case of monohydridic catalysts and normally not in the case of dihydridic catalysts, *cis–trans* isomerization without double-bond migration can occur with dihydridic catalysts.

It is tempting to assume that a similar situation might exist in heterogeneous catalysis (*14*). The original concept that double-bond migration and isomerization should both be described by an HHS mechanism, with hindered migration due to the full occupation of the catalytic surface with hydrogen atoms, may not be correct. On the one hand, *cis–trans* isomerization can occur on a fully hydrogenated catalyst, which behaves like a dihydridic homogeneous catalyst. The same catalytic site that has supplied the hydrogen atom, forms a σ-alkyl bond and is used to abstract a hydrogen atom ($g = \infty$). Rotation around the Ni–C bond is considered to be slow, excluding double-bond migration. The similarity of the specific activity per hydrogen atom of the labeled hydrogen gas, of the isomerized monoene and of stearate shows that the hydrogen at the catalyst surface is in equilibrium with the gas phase. In this respect the present results differ from those of Dutton *et al.* (*4*).

On the other hand, in the double-bond migration reaction tritium is incorporated with half the specific activity per atom of the gas phase. This points to hydrogen abstraction prior to tritium addition to the double-bond, i.e., formation of π-allylic intermediates instead of half-hydrogenated states. It should further be assumed that on sites where double-bond migration is initiated, a 1:1 dilution of adsorbed tritium with abstracted hydrogen occurs, followed by tritium incorporation into migrated products with half the specific activity. The activity in the original isomers (*cis*-Δ9 from oleate and *trans*-Δ9 from elaidate) can be adequately explained by secondary *cis-trans* isomerization reactions. This means that no allyl exchange is observed and that the π-allyl mechanism leads to incorporation of ^{3}H only in the migrated products. In these reactions, the catalyst behaves like a monohydridic homogeneous catalyst.

We are therefore inclined to ascribe *cis-trans* isomerization and double-bond migration to separate processes, occurring on NiH_2- and NiH-sites, respectively. The mechanisms for the different reactions are formulated in Fig. 3.

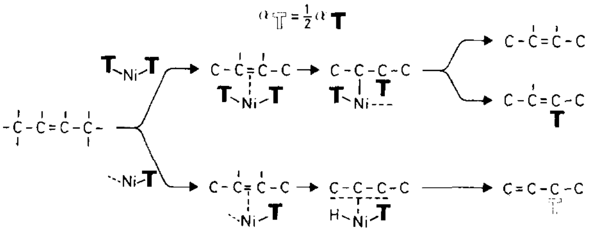

Fig. 3. Possible mechanism of *cis–trans* isomerization and double-bond migration reactions.

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