

## Study of the Mechanism of Double-Bond Isomerization in Methyl 9-Octadecenoates

P. VAN DER PLANK AND H. J. VAN OOSTEN

*Unilever Research, Vlaardingen, The Netherlands*

Received December 9, 1973; revised October 21, 1974

Hydroisomerization experiments were performed with an unlabeled and a  $^{14}\text{C}$ -labeled mixture of 50% methyl oleate ( $\Delta_9^c$ ) and 50% methyl elaidate ( $\Delta_9^t$ ) at 100 and 130°C, using a nickel/silica catalyst. The results were compared with data obtained from the hydrogenation of pure  $\Delta_9^c$  and pure  $\Delta_9^t$  with the same catalyst.

It was found that the  $\Delta_9^t$  double bond migrates considerably faster than the  $\Delta_9^c$  double bond, even in the 50/50 mixture, in contrast with the hydrogenation rate which is independent of the configuration of the double bond. The initial  $\Delta_8^t/\Delta_8^c$  and  $\Delta_{10}^t/\Delta_{10}^c$  ratios appeared to be strongly dependent on the configuration of the double bond in the starting material; higher ratios were obtained from  $\Delta_9^c$ .

The results were explained on the basis of a half-hydrogenated intermediate or  $\sigma$ -complex for hydrogenations and for direct *cis-trans* rearrangements as well as on the basis of a  $\pi$ -allyl mechanism operating simultaneously for double-bond migration.

### INTRODUCTION

In a previous paper (1), some hydroisomerization experiments have been described concerning methyl oleate ( $\Delta_9^c$ ) and its geometrical isomer methyl elaidate ( $\Delta_9^t$ ). It was found that, at several temperatures, the initial migration rate of the  $\Delta_9^t$  double bond exceeds considerably the migration rate of the  $\Delta_9^c$  double bond. It also appeared that the initial *trans/cis* ratios of the  $\Delta_8$  and  $\Delta_{10}$  positional isomers formed were lower when  $\Delta_9^t$  was used as starting material. The migration rate of the  $\Delta_9^t$  double bond was also found to decrease strongly after a certain hydrogenation degree had been reached. The presence of positional *cis* isomers formed could be a possible reason for this phenomenon, because these isomers may suppress the reactivity of the *trans* isomers due to a preferential adsorption of *cis* molecules on the catalyst surface. To investigate this hypothesis, some experiments were performed with a mixture containing about 50%  $\Delta_9^t$  and 50%  $\Delta_9^c$ . The results of these

competitive hydroisomerization experiments are discussed in the light of current theories.

In this paper a positional isomer with the double bond in the  $(9 \pm i)$ th position is denoted as  $\Delta_{9 \pm i}$ .

### METHODS

Forty grams of a mixture of about 50%  $\Delta_9^t$  and 50%  $\Delta_9^c$  (for composition see Table 1) was hydrogenated with a nickel/silica catalyst using 0.07% of nickel based on the weight of methyl esters. The catalyst, containing 47.2% nickel (1) was reduced *in situ* at 450°C for 30 min. After reduction, the catalyst was poured into the mixture of esters previously heated to reaction temperature (100 or 130°C) under atmospheric hydrogen pressure and a stirring speed corresponding with a dispersed energy of about 70 W/kg ester. Samples were taken without interrupting the hydrogenation process. The percentage of methyl stearate in the reaction mixture was determined by glc. The total *trans*

TABLE I  
COMPOSITION OF THE MONOENE FRACTIONS  
OBTAINED AT 130°C (FIG. 1)

Double bond	Composition (%)						
	Start	1	2	3	4	5	6
<i>trans</i> -4			0.1	0.1	0.2	0.2	0.4
<i>cis</i> -4				0.04	0.08	0.1	0.2
<i>trans</i> -5		0.2	0.4	0.6	1.0	1.3	1.7
<i>cis</i> -5			0.1	0.1	0.2	0.3	0.5
<i>trans</i> -6		0.3	0.6	1.2	1.5	1.8	2.6
<i>cis</i> -6		0.1	0.3	0.4	0.5	0.7	1.0
<i>trans</i> -7	0.05	0.7	1.9	3.7	4.6	5.4	6.8
<i>cis</i> -7		0.3	0.7	1.0	1.3	1.5	1.9
<i>trans</i> -8	0.05	4.2	9.4	12.1	12.9	14.2	14.9
<i>cis</i> -8	0.05	0.9	2.5	3.3	4.1	4.3	3.8
<i>trans</i> -9	49.2	41.0	34.8	32.2	28.4	24.4	22.3
<i>cis</i> -9	48.6	42.6	29.6	19.2	14.0	10.5	6.3
<i>trans</i> -10	0.2	4.0	10.3	12.1	13.5	13.6	14.9
<i>cis</i> -10	0.1	0.9	2.1	3.1	3.5	4.2	3.3
<i>trans</i> -11	0.4	2.3	3.4	4.5	6.1	7.0	9.0
<i>cis</i> -11	1.2	1.0	1.0	1.2	1.3	1.8	1.5
<i>trans</i> -12	0.1	1.5	1.3	1.9	2.7	3.2	4.4
<i>cis</i> -12	0.1	0.1	0.2	0.4	0.4	0.7	0.6
<i>trans</i> -13			1.1	1.5	1.8	2.8	2.6
<i>cis</i> -13				0.4	0.2	0.3	0.5
<i>trans</i> -14			0.2	0.7	1.3	1.5	1.1
<i>cis</i> -14				0.2	0.2	0.1	0.2

content was calculated from ir measurements at 10.36  $\mu\text{m}$  (2). 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 (3). 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  $-80^\circ\text{C}$ . The ozonides were reduced at  $40^\circ\text{C}$  using a large excess of triphenylphosphine. Finally, the mixture of aldehydes and aldehydic esters was analyzed by glc (4).

Two hydrogenation experiments were performed with the same mixture to which about 100 mg  $\Delta_9^t$  were added with  $^{14}\text{C}$  incorporated in the carbonyl group. As the radioactive experiments had to be performed in other equipment with a far less stirring efficiency, the absolute values of the reaction rates obtained in both types of reactors cannot be compared. The radioactive  $\text{C}_8$ ,  $\text{C}_9$  and  $\text{C}_{10}$  aldehydic esters were isolated from the ozonized mixture by means of preparative glc. The amounts of

these isolated aldehydic esters were determined by glc using methyl palmitate as an internal standard. From the radioactivities determined by liquid scintillation counting, the specific radioactivities ( $\alpha_{\text{sp}}$ ), expressed in dpm/mmol, were calculated. The  $\alpha_{\text{sp}}$  of the saturated and of the overall *cis* and *trans* methyl ester fractions, obtained via tlc, were determined in the same way.

## RESULTS

Figure 1 shows the overall methyl ester composition obtained at  $130^\circ\text{C}$  as a function of time using the labeled mixture. The corresponding detailed composition of the monoene fractions has been listed in Table 1. Similar data were obtained from the other experiments using the same 50%  $\Delta_9^t$ /50%  $\Delta_9^c$  mixture (labeled and unlabeled). As described before (1,5), several types of initial rates can be derived from these data. In Table 2 some of these rates are given together with some results reported earlier (1,5). From these data it can be concluded that the hydrogenation rate is independent of the configuration of the double bond. It also appears that the hydrogenation rate is constant and indepen-

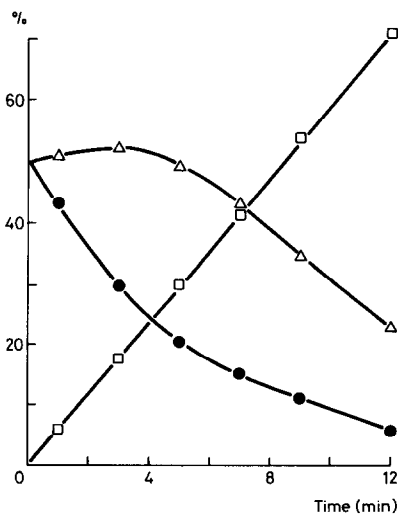


FIG. 1. Composition of samples obtained from the mixture of 50%  $\Delta_9^t$  and 50% labeled  $\Delta_9^c$  by partial hydrogenation at  $130^\circ\text{C}$ , vs time: ( $\Delta$ ) *trans*; ( $\bullet$ ) *cis*; ( $\square$ ) saturated.

TABLE 2  
 INITIAL REACTION RATES<sup>a</sup> FOR LABELED AND UNLABELED EXPERIMENTS

Starting material	Temp (°C)	$(dm'/dt)_{t \rightarrow 0}$	$(dm/dt)_{t \rightarrow 0}$	$(d \Delta_9/dt)_{t \rightarrow 0}$	$(d \Delta_9^c/dt)_{t \rightarrow 0}$	$(d \Delta_9^t/dt)_{t \rightarrow 0}$	$(d \text{ sat}/dt)_{t \rightarrow 0}$
$\Delta_9^{c,b}$	100	9	21	-17	-27	8	7.8
$\Delta_9^{t,b}$	100	30	67	-52	11	-62	7.7
$\Delta_9^t/\Delta_9^c (=1)$	100	34	83	-61	-21	-34	8.2
$\Delta_9^t/\Delta_9^c (=1)^c$	100	8	15	-12	-5	-7	3.3
$\Delta_9^{c,b}$	129	27	69	-52	-72	18	11.3
$\Delta_9^{t,b}$	130	116	245	-145	23	-168	12.0
$\Delta_9^t/\Delta_9^c (=1)^c$	130	11	24	-16	-6	-11	6.0

<sup>a</sup>  $(dm'/dt)_{t \rightarrow 0}$  rate of double-bond migration in the direction of the ester group ( $m' = \sum_{i=1}^7 \Delta_{9-i} i$ );  $(dm/dt)_{t \rightarrow 0}$  total rate of double-bond migration ( $m = \sum_{i=-7}^8 \Delta_{9+i} |i|$ ). The migration rates are given as the number of double-bond migrations per 100 molecules monoene/min. The other rates are expressed in mol%/min.

<sup>b</sup> Ref. (1).

<sup>c</sup> Labeled.

dent of the composition of the reaction mixture (Fig. 1). The same conclusion is also supported by the results of the competitive experiments with labeled  $\Delta_9^c$ . Figure 2 shows that the initial contribution of  $\Delta_9^t$  to the formation of methyl stearate equals that of  $\Delta_9^c$  because the value of  $\alpha_{sp}$  (stearate) is about 0.5 times the initial value of  $\alpha_{sp}$  of the labeled  $\Delta_9^c$ .

In contrast with the hydrogenation rates, Table 2 shows that the initial migration rate of the  $\Delta_9^t$  double bond exceeds considerably that of the  $\Delta_9^c$  double bond. This phenomenon was also observed at 75, 129 and 150°C (1). The large difference appears to be an initial isomerization effect. It was suggested that the *cis* double bonds

formed during isomerization would, to some extent, impede the migration of *trans* double bonds due to a possible preferred adsorption of *cis* double bonds. However, this assumption does not agree with the results of the experiment with the unlabeled 50%  $\Delta_9^t$ /50%  $\Delta_9^c$  mixture (Table 2) in which the initial migration rate of the  $\Delta_9^t$  double bond only dropped by about half the value obtained for pure  $\Delta_9^t$ . This suggests that double-bond migration can be described by a dilution effect in a first-order rate process. However, the migration rate of the  $\Delta_9^c$  double bond decreases far less in the presence of 50%  $\Delta_9^t$ . In spite of this it appears that the  $\Delta_9^t$  double bond still migrates faster than the  $\Delta_9^c$

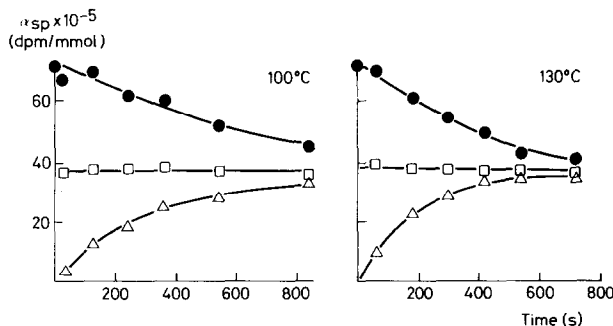


FIG. 2. Specific radioactivities of the methyl ester fractions vs reaction time at 100 and 130°C; ( $\Delta$ ) *trans*; ( $\bullet$ ) *cis*; ( $\square$ ) saturated.

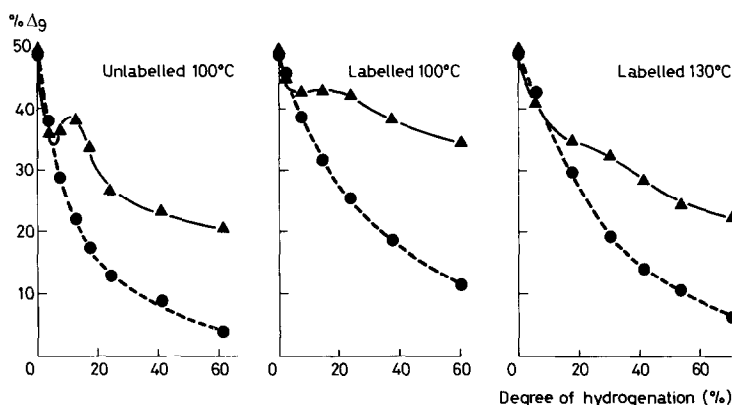


FIG. 3. Percentages  $\Delta_9$  isomers in the monoene fraction vs degree of hydrogenation; (●) *cis*; (▲) *trans*.

double bond at the beginning of the reaction. Similar results were obtained from experiments with the mixture containing labeled  $\Delta_9^c$  (Fig. 3). Initially, the  $\Delta_9^t$  percentage strongly decreases due to the migration process. However, this decrease is compensated by a direct *cis-trans* rearrangement of  $\Delta_9^c$  resulting in the formation of  $\Delta_9^t$ . This reaction can even lead to a maximum in the  $\Delta_9^t$  percentage (see Fig. 3).

We tried to determine the  $\alpha_{sp}$  values of the  $\Delta_8$  and  $\Delta_{10}$  isomers directly from the isolated  $C_8$ - and  $C_{10}$ -aldehydic esters. However, at low conversions, the amounts of these esters obtained were too small for an accurate determination of the  $\alpha_{sp}$  values. For this reason, we calculated the values indirectly via a mass and radioactivity balance.

Figure 4 shows that, initially, both the

*cis* and *trans* isomers of  $\Delta_8$  and  $\Delta_{10}$  are mainly formed from  $\Delta_9^t$ , which agrees with the data in Table 2 and Fig. 3. The same holds for a temperature of 100°C.

#### Calculation of $\alpha_{sp}$ of $\Delta_8$ and $\Delta_{10}$ Isomers (example)

The first sample obtained at 130°C contained 51.0% *trans* isomers with a  $\alpha_{sp} = 9.8 \times 10^5$  dpm/mmol. Thus, the contribution to the total activity of a 100 mmol sample due to the presence of 51.0% *trans* isomers is  $51.0 \times 9.8 \times 10^5 = 500 \times 10^5$  dpm. On the basis of the detailed monoene composition and the percentage methyl stearate in the sample we derive that this sample contains 38.7%  $\Delta_9^t$  with a  $\alpha_{sp} = 6.5 \times 10^5$  dpm/mmol (measured via  $C_9$  aldehydic ester). This implies that  $38.7 \times 6.5 \times 10^5 = 252 \times 10^5$  dpm in a 100 mmol sample must be attributed to  $\Delta_9^t$  and  $(500 - 252) \times$

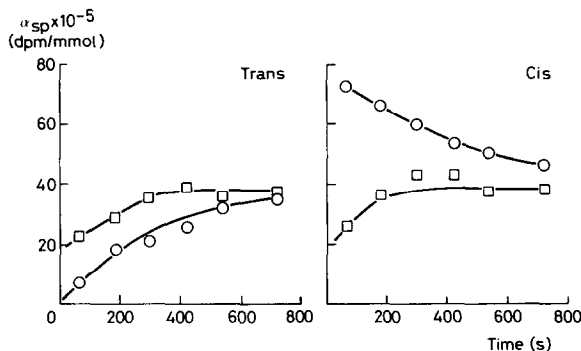


FIG. 4. Specific radioactivities of some isomeric methyl octadecenoates obtained at 130°C; (□)  $\Delta_8$ ; (○)  $\Delta_9$ .

$10^5 = 248 \times 10^5$  dpm must be ascribed to the positional *trans* isomers formed by double-bond migration. The sample contains  $51.0 - 38.7 = 12.3\%$  of these *trans* isomers. As a matter of fact, not all of these isomers originate from  $\Delta_9^t$  or  $\Delta_9^c$  because some were already present (Table 1) in the original mixture and others might have been arisen from the original *cis* isomers (other than  $\Delta_9^c$ ) due to *cis-trans* rearrangement.

From the composition of the starting mixture we estimate that about 11.3% positional *trans* isomers present in the analyzed sample have been formed from  $\Delta_9^c$  and  $\Delta_9^t$ . We now assume that all these isomers have the same  $\alpha_{sp}$ . From this it follows that  $\alpha_{sp}$  of  $\Delta_8^t$  and  $\Delta_{10}^t$  is  $248 \times 10^5 / 11.3 = 22 \times 10^5$  dpm/mmol.

## DISCUSSION

Numerous papers deal with double-bond migration catalyzed in heterogeneous or homogeneous media by basic, acidic or neutral metallic catalysts [for reviews see Refs. (6-8)]. It is still a subject of debate whether double-bond migration proceeds via the Horiuti-Polanyi (addition-abstraction) mechanism with a  $\sigma$ -alkyl complex as a half-hydrogenated intermediate or via an abstraction-addition mechanism with a  $\pi$ -allyl complex as intermediate. Many investigators have provided a vast corpus of evidence in support of the existence of this intermediate. Hightower and Hall (9-12), who studied the isomerization of *n*-butene over alumina and alumina-silica using tracer techniques with  $^{14}\text{C}$  and deuterium, concluded that the *cis-trans* rearrangement and double-bond migration, at least on silica-alumina, proceeds via a half-hydrogenated intermediate in the form of a carbocation. Probably, more than one mechanism operates on alumina (9,12). Another group of authors (13) claims that, in contrast with this polyfunctional catalysis by alumina, only the half-hydrogenated intermediate is responsible

for the geometrical as well as positional isomerization on this type of catalyst. However, the same authors (14) report that no direct *cis-trans* rearrangement of the double bond in 3,4-dimethyl-3-hexenes could be detected, neither on alumina nor on palladium-alumina. This may be attributed to a steric effect preventing a direct stereomutation, although it has been established that this reaction occurs in a homogeneous medium with phosphoric acid in dioxan at 50°C (15).

Bond and Wells (16) assume that the half-hydrogenated  $\sigma$ -alkyl complex is the relevant intermediate in the reaction path for the process of double-bond migration on transition metal catalysts. It is suggested (17) that on alumina-supported ruthenium at 0-70°C and on osmium, at 60-140°C, the rate-determining steps are: (a) abstraction of hydrogen from the half-hydrogenated intermediate for the stereomutation process and (b) addition of adsorbed hydrogen to adsorbed 1-butene, resulting in the formation of the half-hydrogenated intermediate for the process of double-bond migration. Bond and Winterbottom (18) explain their results obtained for alumina-supported palladium on the basis of an associative mechanism although other rate-determining steps are assumed. These ideas were supplemented by Mellor and Wells (19,20) who could not provide any evidence for a dissociative  $\pi$ -allyl mechanism for butene isomerization over iridium-alumina. Moreover, Wells and Wilson (21) found a considerable activity for double-bond migration on alumina-supported metal catalysts in the absence of hydrogen at 100°C, whereas little or no activity was found when the same catalysts were used without support. They assumed that the hydrogen necessary for the formation of the half-hydrogenated intermediate originated from the support by migration of adsorbed hydrogen atoms from this support to the metals. Also Holbrook and Wise (22) ex-

plained their results obtained for butene isomerization over supported and unsupported palladium catalysts on the basis of the half-hydrogenated intermediate.

Although a common intermediate for several reaction paths facilitates the mathematical treatment of results, it is impossible to generalize the addition-abstraction mechanism because a vast amount of experimental facts cannot be explained by this universal mechanism. With regard to our hydroisomerization experiments with methyl 9-octadecenoates (I), it is hard to understand on the basis of an associative mechanism (involving mono-adsorbed  $\sigma$ -alkyl intermediates) why  $\Delta_9^t$  gives initially lower *trans/cis* ratios between the geometrical isomers of  $\Delta_8$  and  $\Delta_{10}$  than does  $\Delta_9^c$ . Assuming a  $\pi$ -allyl mechanism for double-bond migration, it is not difficult to give a qualitative explanation for this phenomenon. The stability of the allylic intermediates arising from a *cis* (I and II) or a *trans* (III and IV) double bond will not be equal (Fig. 5). If, on the basis of steric effects, we assume that the stability can be written in the following order:

$$S_{IV} > S_{III} = S_{II} > S_I,$$

we can forecast the relative magnitude of the initial *trans/cis* ratios between the geometrical isomers. Correlating the activa-

tion energy for double-bond migration with the stability of the complexes (lower activation energy for relatively stabler intermediates) so assuming that hydrogen abstraction is the rate-determining step in the migration process, we can, starting from  $\Delta_9^t$ , expect that the reaction path via intermediate IV is preferred to that of intermediate III. The first gives a *trans* isomer on double-bond migration while the second results in a *cis* isomer, implying that initial *trans/cis* ratios  $> 1.0$  are obtained. The same argument can be used for  $\Delta_9^c$ . In this case, the main reaction route is via intermediate II, which also leads to *trans/cis* ratios  $> 1.0$ . However, the formation of intermediate I will be strongly obstructed by steric effects. This means that the formation of *cis* positional isomers from *cis* isomers via I is very difficult, whereas these isomers can easily arise from *trans* *n*-alkenes via III. In agreement with theory, we initially obtained higher percentages of  $\Delta_8^c$  from  $\Delta_9^t$  than from  $\Delta_9^c$  (Fig. 6), resulting in lower ratios between  $\Delta_8^t$  and  $\Delta_8^c$  when the former reactant was used.

A similar reasoning can be used for the rates of double-bond migration. On the basis of the steric hindrances in the configurations given in Fig. 5 we arrive at the conclusion that the main reaction route for

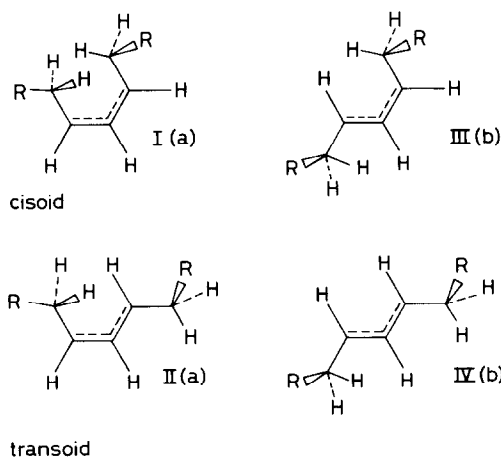


FIG. 5. Configurations of  $\pi$ -allyl complexes formed from *cis* (a) and *trans* (b) monoenes.

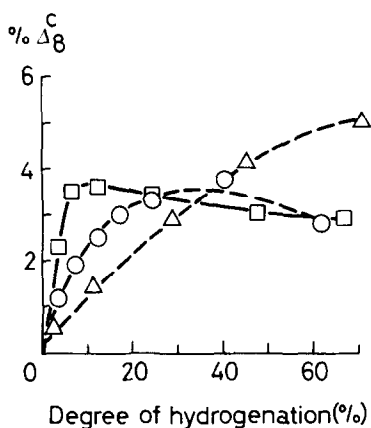


FIG. 6. Percentage  $\Delta_8^c$  obtained from  $\Delta_9^c$ ,  $\Delta_9^c$  or from a mixture of these isomers at 100°C: (□)  $\Delta_9^c$ ; ( $\Delta$ )  $\Delta_9^c$ ; (○) 50%/50% mixture (unlabeled).

double-bond migration from a *cis* position runs via intermediate II. However, a *trans* double bond has not only an equivalent reaction route via intermediate III, but also a still better one via intermediate IV because this intermediate is sterically the most favored. The same arguments are used by Cerceau *et al.* (23) for the interpretation of their results obtained from an isomerization study of alkenes. They found that *cis*-2-heptene gave considerably higher *trans*-3-heptene/*cis*-3-heptene ratios than *trans*-2-heptene on double-bond migration under the influence of strong basic catalysts such as potassium *tert*-butoxide in a homogeneous medium.

Guisnet *et al.* (24) assume that at 250°C on palladium-alumina, isomerization of alkenes proceeds via an associative and a dissociative mechanism operating simulta-

neously. We arrived at a similar conclusion because a pure  $\pi$ -allyl mechanism only allows a geometrical isomerization via positional isomers. This would for example result in a minimum at the 9-position in the initial double-bond distribution in the *trans* fraction, when  $\Delta_9^c$  is used as starting product. We did not find such a minimum except at rather high temperatures or at a low hydrogen supply (Fig. 7).

We have already shown that double-bond migration proceeds via a stepwise mechanism (1). This implies that the adsorption and desorption of unsaturated molecules is very fast under the reaction conditions applied. It has also been found that the hydrogenation rate is independent of the configuration of the double bond. From these data it can be concluded that the addition of hydrogen to a half-hydrogenated intermediate is the rate-determining step for the hydrogenation reaction.

Further evidence for the two reaction mechanisms operating simultaneously during the hydrogenation of methyl 9-octadecenoates was obtained by Heertje *et al.* (25). Using tritiated hydrogen, they concluded that direct stereomutation proceeds via the half-hydrogenated intermediate and double-bond migration via a  $\pi$ -allyl complex.

We observed a strong increase with temperature in the ratio between the initial rate of double-bond migration and that of the *cis*-*trans* rearrangement (Table 2).

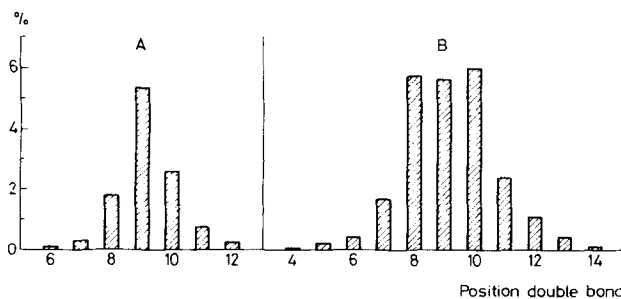


FIG. 7. Percentages of positional *trans* isomers in the monoene fraction using  $\Delta_9^c$  as starting product; (A) at 3% conversion after hydrogenation at 100°C; (B) at 4.5% conversion after hydrogenation at 175°C.

This suggests that, under identical reaction conditions, the *cis-trans* rearrangement will dominate at low temperatures, whereas at high temperatures, the double-bond migration is the favored reaction process. Probably, this must partly be attributed to the concentration of adsorbed hydrogen, which will be lower at high temperatures. It is very plausible that low hydrogen concentrations induce the dissociative  $\pi$ -allyl mechanism.

To sum up, the experimental facts suggest that: (a) the direct *cis-trans* rearrangement proceeds via a  $\sigma$ -alkyl complex as half-hydrogenated intermediate; (b) the hydrogenation of  $\Delta_9^c$  and  $\Delta_9^t$  can be described by the Horiuti-Polanyi mechanism, the rate-determining step being the H-addition to the half-hydrogenated intermediate; (c) a  $\pi$ -allyl mechanism operates for double-bond migration with formation of the  $\pi$ -allyl complex as the rate-determining step.

#### ACKNOWLEDGMENT

Thanks are due to Mr. C. W. van Oosten for preparing the methyl esters of oleic and elaidic acid.

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