

### HYDROGENATION OF FATTY ACID ESTERS. III. HYDROGENATION OF METHYL (9Z,12Z)-OCTADECADIENOATE AND METHYL (9Z,12Z,15Z)-OCTADECATRIENOATE

Jana KRUPÍČKOVÁ, Jaroslav VČELÁK and Jiří HETFLJEŠ

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát*

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*Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.*

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The title hydrogenation catalyzed by nickel(II) 2,4-pentanedionate-triethylaluminium system has been studied with the use of combination of initial rate measurements with time changes of product distribution. It was found that the hydrogenation of methyl (9Z,12Z)-octadecadienoate is first order in the octadecadienoate. Similar results were obtained also for (9Z,12Z,15Z)-octadecatrienoate. The course of both reactions has been described by models involving set of parallel and consecutive hydrogenation steps and reversible isomerizations. Computed rate constants for hydrogenation of methyl (9Z,12Z)-octadecadienoate support qualitative conclusions deduced from the product analysis.

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Hydrogenation of polyunsaturated C<sub>18</sub> fatty acid glycerides represents the widely industrially applied process of soybean and rape seed oil valorization<sup>1</sup>. Recent advances in this field has been reviewed<sup>2</sup>, including both heterogeneous and homogeneous catalysts. The course of the hydrogenation catalyzed by arene-chromium<sup>3,4</sup>, ruthenium-phosphine<sup>5</sup>, rhodium-phosphine<sup>5-7</sup>, platinum- and palladium-phosphine complexes<sup>8,9</sup> has been examined in more detail, using in some cases<sup>5-8</sup> methyl (9Z,12Z)-octadecadienoate (methyl linoleate) and (9Z,12Z,15Z)octadecatrienoate (methyl linolenate) as model compounds. A similar study of the hydrogenation of both esters catalyzed by nickel(II) stearate-triethylaluminium catalyst has been reported recently<sup>10</sup>, providing data on distribution of isomers during the reaction. To our best knowledge, no attempt has been so far made to describe the reaction course quantitatively. As a continuation of our previous works<sup>11-13</sup> on hydrogenation of fatty acid esters catalyzed by Ziegler nickel catalysts we now report the results of study of hydrogenation of methyl (9Z,12Z)-octadecadienoate and methyl (9Z,12Z,15Z)-octadecatrienoate.

## EXPERIMENTAL

## Materials Used

Cyclohexane used as the solvent for catalyst preparation and hydrogenation (analytical purity grade, Lachema Brno) was dried by sodium and stored under argon. Nickel(II) 2,4-pentanedionate and triethylaluminium were the same as in the previous work<sup>13</sup>.

Methyl oleate was prepared in the previous work<sup>13</sup> (97% purity, acidity number 0.118).

## Methyl (9Z,12Z)-Octadecadienoate (Methyl Linoleate)

The ester was prepared by reported procedure<sup>14</sup> based on reesterification of sunflower oil with sodium methoxide. Separation of methyl linoleate from the mixture of sunflower oil methyl esters so obtained was made by fractional crystallization of urea complexes<sup>14</sup>. The final distillation yielded methyl linoleate (b.p. 165 – 170 °C) of 97.2% purity (acidity number 0.116). The sample contained 2.6% methyl oleate and 0.2% methyl linolenate as admixtures.

## Propyl (9Z,12Z)-Octadecadienoate (Propyl Linoleate)

The ester was prepared by reesterification of methyl linoleate (20 g) with propanol (100 ml) in the presence of *p*-toluenesulfonic acid (0.5 g). The course of the reaction carried out under reflux was followed by GLC analysis. After its completion the methanol was distilled off. Vacuum distillation of the residue gave propyl linoleate (b.p. 169 – 172 °C /132 kPa, acidity number 0.120) of 97.0% purity. The sample contained 2.6% propyl oleate and 0.4% propyl linolenate.

## Methyl (9Z,12Z,15Z)-Octadecatrienoate (Methyl Linolenate)

Methyl esters of linseed oil (50 – 60% of linolenic acid) were prepared similarly as those from sunflower oil. However, the ester purification by means of urea complexes was in this case unsuccessful. Methyl linolenate of high purity was obtained from the mixture by HPLC method in reverse phase (mobile phase methanol–water 9 : 1, stationary phase C<sub>18</sub> hydrocarbon, temperature 25 °C). The product (b.p. 162 – 166 °C/133.5 kPa, acidity number 0.210) contained the following admixtures: 2.0% methyl linoleate, 1.5% methyl oleate, and 0.5% unidentified compounds.

## Hexyl (9Z,12Z,15Z)-Octadecatrienoate (Hexyl Linolenate)

The ester was obtained by reesterification of methyl linolenate with hexanol, using the procedure described above for propyl linoleate. Vacuum distillation yielded hexyl linolenate (b.p. 190 – 196 °C/135 kPa, acidity number 0.21) of 95% purity. The sample contained 1.6% hexyl linoleate, 3% hexyl oleate and 0.4% of unidentified admixtures.

## Analytical Methods

The purity of starting esters and analysis of reaction mixtures were made by gas chromatography (Chrom 5, Laboratorní Přístroje Praha, 600 cm × 3 mm column packed with 12% silicone elastomer OV-27 on Chromosorb PAW DMCS, flame ionization detector, column temperature 206 °C, injection port temperature 255 °C, nitrogen as carrier gas, pressure 130 kPa). The products formed were determined with the use of standards using a capillary column (30 m × 0.25 mm) filled with DB-WAX (hydrogen as carrier gas, pressure 90 kPa, column temperature 180 °C, injection port temperature 240 °C).

The presence of (*E*)-isomers was followed by IR spectrometry (for details see ref.<sup>11</sup>) and the isomers with conjugated C=C bonds were detected spectrophotometrically, using UV-VIS Varian DMS 300 instrument equipped with IBM PC/AT data base.

The acidity of the samples was reduced prior to their final purification by distillation. The free acids were removed by passing 10% toluene solution of an ester through a 250 × 20 mm column filled with  $\gamma$ -alumina.

### Kinetic Measurements

Hydrogenation experiments were made on a apparatus with an automatic record of hydrogen consumption at constant hydrogen pressure. The shape of the reactor and the intense magnetic stirring ensured that the experiments took place in kinetic region. The catalyst was prepared from nickel(II) 2,4-pentanedionate-triethylaluminium at 1 : 3 molar ratio in cyclohexane which was chosen also as the reaction medium. In addition to initial rate measurements, time changes in product distribution during the reaction were followed by GLC, using the method of internal standard (methyl hexadecanoate). Initial rate data obtained were used to determine the orders of the reaction to individual components, using regression analysis. The changes in product distribution during hydrogenation were described by a set of differential equations derived for proposed kinetic models which were solved numerically. Details on all the items mentioned in this paragraph are given in our preceding work<sup>13</sup>.

## RESULTS AND DISCUSSION

### Hydrogenation of Methyl Linoleate

A typical course of the hydrogenation of methyl linoleate catalyzed by a Ziegler Ni catalyst is shown in Fig. 1. Data demonstrate that the reaction proceeds under mild

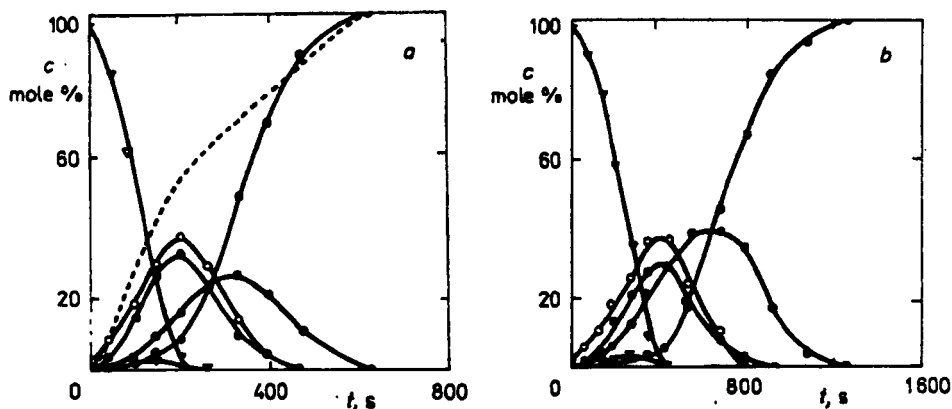


FIG. 1

Effect of hydrogen partial pressure on product distribution in hydrogenation of methyl linoleate catalyzed by  $\text{Ni}(\text{acac})_2\text{-Al}(\text{C}_2\text{H}_5)_3$  (1 : 3 mol/mol) system. Designation of points:  $\nabla$  methyl linoleate,  $\blacktriangledown$  methyl esters of isomeric C 18 : 2 acids,  $\bullet$  methyl 12-octadecenoate,  $\circ$  methyl oleate,  $\bullet$  methyl elaidate,  $\bullet$  methyl stearate, - - - course of hydrogen consumption during hydrogenation. Reaction conditions: 25 °C,  $c_L = 0.24 \text{ mol l}^{-1}$ ,  $c_K = 6.8 \cdot 10^{-3} \text{ mol l}^{-1}$ ; a  $p(\text{H}_2) = 159.6 \text{ kPa}$ , b  $p(\text{H}_2) = 52.2 \text{ kPa}$

conditions at a reasonable rate to practically 100% conversion, which allows to analyze also later stages of the process. Of interest in this connection is the shape of the curve of hydrogen consumption which indicates change of hydrogenation rate at about 50% conversion (Fig. 1a). At this point practically all the linoleate has reacted and the relative amounts of both possible products of its one C=C bond hydrogenation i.e. methyl oleate and methyl ester of C 12 : 0 attain maximum. The reaction course can be thus reasonably divided into two stages, as suggested by us earlier<sup>11,12</sup>. The difference observed justifies also our decision to analyze these stages separately. The suppressing effect of methyl linoleate on hydrogenation of the C 18 : 1 monoene esters has been observed recently<sup>10</sup> for nickel(II) stearate-triethylaluminium catalyst. In that case isomerization of the esters (both positional and geometrical) has been efficiently inhibited. The relatively high content of the (*E*)-isomer (methyl elaidate) in our case (around 20 mole %) indicates the lower selectivity of the Ziegler system used in the present study in this respect. In a study of hydrogenation of methyl oleate and methyl elaidate we concluded<sup>13</sup> that the extent of trans-isomerization increases with increasing temperature and decreasing hydrogen partial pressure. The shape of the curves for methyl elaidate formation illustrating the effect of hydrogen pressure (compare Figs 1a and 1b) and temperature (see Figs 2a and 2b) supports this assumption.

From the kinetic point of view, initial rate measurements showed that the reaction is second order in the catalyst (the relation found by regression analysis was  $\ln r = 1.9 c_K - 2.89$  for Ni(acac)<sub>2</sub>-Et<sub>3</sub>Al (3 : 1) system, 25 °C,  $p(\text{H}_2) = 131.7$  kPa,  $c_{(\text{Me})} = 0.24$  mol l<sup>-1</sup>,  $\ln c_K$  range was -5.80 to -5.00 mol l<sup>-1</sup>), first order in hydrogen ( $\ln r = 0.92 \ln p(\text{H}_2) - 12.50$  for the same conditions, except  $p(\text{H}_2)$ ,  $c_K = 6.8 \cdot 10^{-3}$

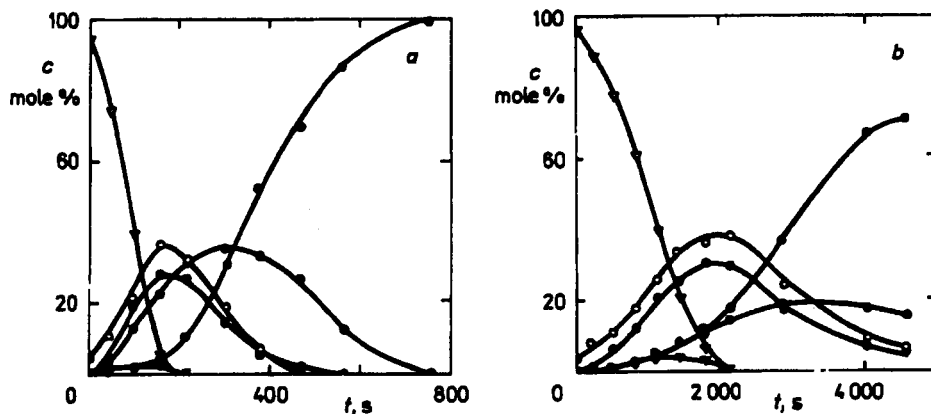


FIG. 2

Effect of temperature on product distribution in hydrogenation of methyl linoleate catalyzed by Ni(acac)<sub>2</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (1 : 3 mol/mol) system. For designation of points see Fig. 1. Reaction conditions:  $p(\text{H}_2) = 121$  kPa,  $c_L = 0.22$  mol l<sup>-1</sup>,  $c_K = 6.2 \cdot 10^{-3}$  mol l<sup>-1</sup>; a 47 °C, b 7.5 °C

mol l<sup>-1</sup>, ln  $p(\text{H}_2)$  range was 5.50 to 7.50 kPa) and zero order in the linoleate (Fig. 3). Similarly to methyl oleate<sup>13</sup> the validity of the zero order dependence is also here restricted (it holds only for narrow low concentration region), the reason of which is not yet clear. As far as temperature dependence is concerned, the shape of the curves of hydrogen consumption at different temperatures indicates that the second part (formation of methyl stearate) is more dependent, so that the activation energy of the hydrogenation of methyl linoleate to methyl C 18 : 1 esters would be lower than that determined for the hydrogenation of methyl oleate and elaidate to the stearate ( $30.2 \pm 0.2$  and  $28.9 \pm 2.6$  kJ mol<sup>-1</sup>, respectively, ref.<sup>13</sup>).

Comparison of product distribution changes in Figs 1 and 2 shows that in contradiction to C 18 : 1 esters, methyl linoleate suffers only minor isomerization (ca 2%). As to the structure of the C 18 : 2 isomer formed, the spectroscopic analysis showed that it does not contain conjugated C=C bonds and (*E*)-isomers. Thus, the two isomers which would meet this findings are (8*Z*,12*Z*)- and (9*Z*,13*Z*)-octadecadienoates. According to the very detailed analysis of the structure of isomers formed by hydrogenation of C 18 : 3 and C 18 : 2 acid esters, the occurrence of the (8*Z*,12*Z*)-isomer is less probable, being detected in only trace amounts<sup>15</sup>.

The inspection of product distribution curves in Figs 1 and 2 further show that both C=C bonds in the linoleate (both in the position 9 and in 12) are hydrogenated with the same probability since the molar ratio between the two corresponding isomers formed varies within narrow range (1.0 to 1.3). The structure of the isomers formed confirms that hydrogenation proceeds without preceding isomerization and as 1,2-addition. This mode of the far prevailing addition differentiates Ziegler type systems from some other transition metal catalysts, such as e.g. cobalt or arene-chromium compounds (for more detailed discussion of these aspects see e.g. ref.<sup>16</sup>), where conjugation of C=C bonds is prerequisite.

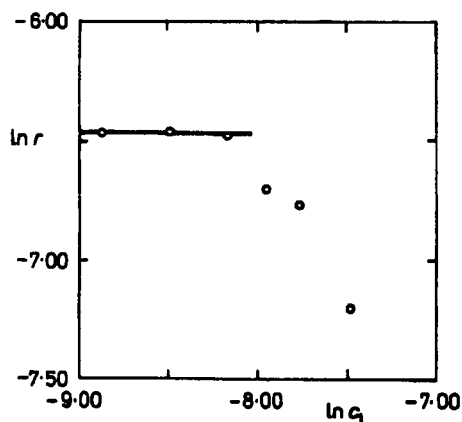
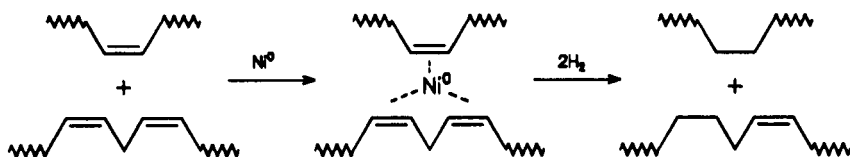


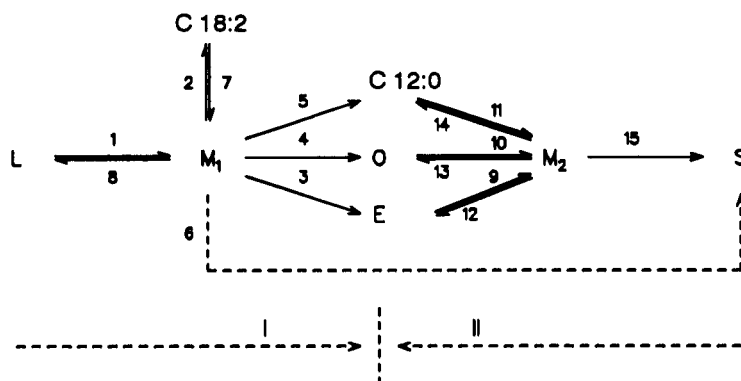
FIG. 3  
Reaction order in the substrate of hydrogenation of methyl linoleate.  $(\text{Ni}(\text{acac})_2\text{-Al}(\text{C}_2\text{H}_5)_3$  (1 : 3 mol/mol),  $c_K = 6.8 \cdot 10^{-3}$  mol l<sup>-1</sup>,  $p(\text{H}_2) = 131.7$  kPa, temperature 25 °C

Apparent formation of the stearate in the initial stage of the reaction deserves comment. Its presence was already observed in hydrogenations of soybean oil and methyl linoleate catalyzed by Ziegler nickel catalyst prepared from nickel carboxylate and triethylaluminium<sup>16</sup>. In the latter case it was explained<sup>16</sup> by assumption about simultaneous coordination of one molecule of C 18 : 2 diene and one molecule of C 18 : 1 monoene to the catalytically active metal centre (Scheme 1). The authors pointed out that according to this concept, there is one third probability of formation of the stearate molecule per addition of hydrogen. However, the analysis of our data does not corroborate fully this suggestion.



SCHEME 1

The above facts have been incorporated into the model of the course of the discussed hydrogenation proposed in Scheme 2. The presence of two intermediates M1 and M2 is not purely formal but is justified both by the different orders of the hydrogenation in the catalyst (second order for C 18 : 2 and first order for all C 18 : 1) and by the already mentioned preferential hydrogenation of methyl linoleate. As usual, hydrogenations were taken as irreversible and isomerizations as reversible reactions. Furthermore, with respect to the observed break in product distribution and with the aim to make numerical solution easier, Scheme 2 was divided into two parts and these were treated separately. The reaction orders in individual components were taken from initial rate measurements.



SCHEME 2

Part I of the scheme was described by the following set of differential equations:

$$dc_L/dt = k_8 c_{M1} P_H c_K - k_1 c_L^0 P_H c_K^2$$

$$dc_{C18:2}/dt = k_2 c_{M1} P_H c_K - k_7 c_{C18:2} P_H c_K$$

$$dc_{C12:0}/dt = k_5 c_{M1} P_H c_K$$

$$dc_O/dt = k_4 c_{M1} P_H c_K$$

$$dc_E/dt = k_3 c_{M1} P_H c_K$$

$$dc_S/dt = k_6 c_{M1} P_H c_K$$

$$dc_{M1}/dt = (k_1 c_L + k_7 c_{C18:2} - (k_3 + k_4 + k_5 + k_6 + k_2 + k_8) c_{M1}) P_H c_K.$$

Their numerical solution gives the rate constants (in  $l \text{ mol}^{-1} \text{ MPa}^{-1} \text{ s}^{-1}$ ):

$$k_1 = 150, k_2 = 77, k_3 = 63, k_4 = 180, k_5 = 170, k_6 = 30, k_7 = 36, k_8 < 0.001.$$

To solve part II, the following differential kinetic equations have been written:

$$dc_E/dt = k_{12} c_{M2} P_H c_K - k_9 c_E^0 P_H c_K$$

$$dc_O/dt = k_{13} c_{M2} P_H c_K - k_{10} c_O P_H c_K$$

$$dc_{C12:0}/dt = k_{14} c_{M2} P_H c_K - k_{11} c_{C12:0} P_H c_K$$

$$dc_S/dt = k_{15} c_{M2} P_H c_K$$

Computed rate constants had the following values (in  $l \text{ mol}^{-1} \text{ MPa}^{-1} \text{ s}^{-1}$ ):

$$k_9 = 1.2 \text{ MPa}^{-1} \text{ s}^{-1}, k_{10} = 10, k_{11} = 11, k_{12} = 150, k_{13} < 0.001, k_{14} < 0.001, k_{15} = 84.$$

Medium standard deviation of the determination of single point was  $0.00603 \text{ mol l}^{-1}$ .

Good agreement of the model with experimental data is demonstrated in Fig. 4. The sharp transition on product distribution curves is due to the division of the calculation to two parts, as already mentioned.

The results obtained thus seem to suggest or support the following conclusions:

1) Concentration of both intermediates M1 and M2 is  $2 \cdot 10^{-3}$  to  $5 \cdot 10^{-3} \text{ mol l}^{-1}$  and steady. 2) Except M1-C 18 : 2 ( $k_2, k_7$ ) and M2-E ( $k_9, k_{12}$ ) steps all the other isomerizations (i.e. M1-L, C12 : O-M2, O-M2) are practically "one-way" route. 3) Comparable rate constants  $k_4$  and  $k_5$  indicate comparable reactivity of the C=C bonds in

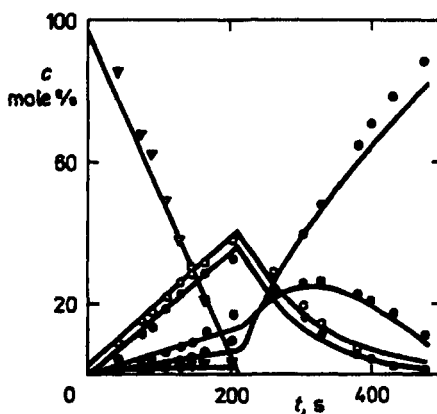


FIG. 4

Comparison of experimental data with those computed according to the proposed model (Scheme 2). Experimental data taken from Fig. 1a, curves are computed

position 9 and 12 of the linoleate, in accordance with recently reported data<sup>10</sup>. 4) Similar values of the pairs  $k_{10}$ ,  $k_{13}$  and  $k_{11}$ ,  $k_{14}$  speak for the similar reactivity of both C 18 : 1 isomers.

In connection with the last conclusion also trans-isomerization of both octadecenoates can be expected to proceed to a similar extent. Because of imperfection of our separation technique this prediction could not be verified and in the model just discussed, the amount of E-C 18 : 1 isomers was expressed as that of the elaidate (E).

### Hydrogenation of Methyl Linolenate

With the aim to obtain further data relating to possible extension of the model proposed, product distribution changes were examined also for the hydrogenation of methyl linolenate. A typical course of the reaction with respect to the formation of individual groups of the esters (for clarity individual isomers are not depicted) is represented graphically in Fig. 5. The qualitative analysis of the dependencies obtained under different reaction conditions led us to the following conclusions: 1) Isomerization of methyl linolenate is largely temperature and concentration insensitive and proceeds under all the conditions used to a similar and small extent (around 4 mole %). 2) Similarly to the hydrogenation of methyl linoleate, also here formation of the stearate takes place already from the beginning of the reaction, indicating that the polyunsaturated esters can be directly transformed into the saturated (i.e. via one step hydrogenation). This process is however of minor importance. 3) In the first stage of the reaction, methyl linolenate is preferentially hydrogenated, giving a mixture of C 18 : 2 and C 18 : 1 isomers. In this respect, hydrogenation of methyl linolenate is thus less selective compared to methyl linoleate. The diene fraction (C 18 : 2) formed in this case contains greater number of isomers. As found by combined GLC-MS analysis, the main C 18 : 2 isomer formed in our case was methyl 9,15-octadienoate, the amount of which varied around 50 mole %.

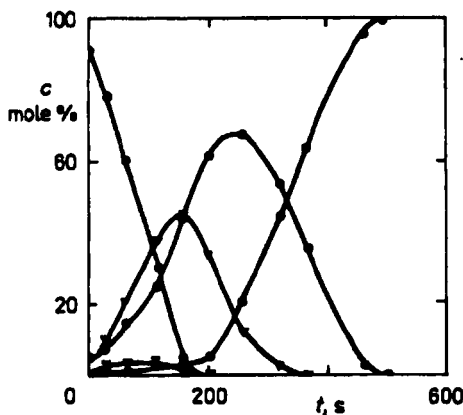


FIG. 5  
Product distribution changes during hydrogenation of methyl linolenate ( $\text{Ni}(\text{acac})_2\text{-Al}(\text{C}_2\text{H}_5)_3$  (1 : 3 mol/mol),  $p(\text{H}_2) = 121 \text{ kPa}$ ,  $c_{\text{MeLn}} = 0.24 \text{ mol l}^{-1}$ ,  $c_{\text{K}} = 6.9 \cdot 10^{-3} \text{ mol l}^{-1}$ ). Designation of points:  $\ominus$  methyl linolenate,  $\nabla$  methyl esters of C 18 : 3 acids,  $\blacktriangledown$  methyl esters of C 18 : 2 acids,  $\boxplus$  methyl esters of C 18 : 1 acids,  $\bullet$  methyl stearate



About 15% content of the fraction was formed by 9,12- and 12,15-isomers. This fact confirms the 1,2-addition. 4) Similarly to hydrogenation of methyl linoleate, the main components of C 18 : 1 fraction are methyl oleate and methyl 12-octadecenoate. 5) The lower selectivity is also demonstrated by formation of the stearate in greater amounts already after reduction of C 18 : 2 isomers below 30%, which could be ascribed to the lower reactivity of some C 18 : 2 isomers formed during hydrogenation of methyl linolenate.

### *Competitive Hydrogenation of Methyl Oleate, Propyl Linoleate and Hexyl Linolenate*

The results described above provided useful information about course of the linolenate hydrogenation but still left some questions unanswered. These relate to the routes by which some products are formed. Particularly it was of interest to find another support for the assumption about the direct route from linolenate to stearate or similarly from linolenate to monoenes as well as whether elaidate is formed directly from linolenate or rather by rapid isomerization of the oleate formed. For that reason we decided to make experiments with a mixture of C 18 : 3, C 18 : 2 and C 18 : 1 esters which were differentiated from each other by the alkyl groups (hexyl for C 18 : 3, propyl for C 18 : 2 and methyl for C 18 : 1). This method was already used with success for structural

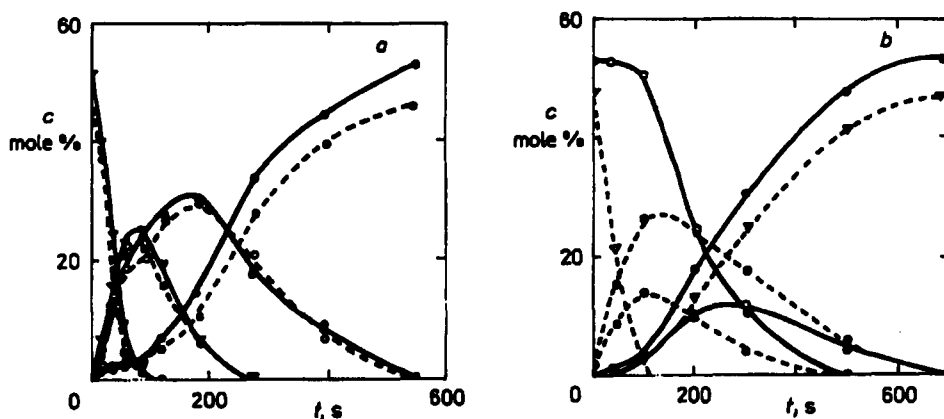


FIG. 6

Competitive hydrogenations of the pairs of fatty acid esters. Conditions:  $\text{Ni}(\text{acac})_2\text{-Al}(\text{C}_2\text{H}_5)_3$  (1 : 3 mol/mol,  $c_K = 7 \cdot 10^{-3} \text{ mol l}^{-1}$ ,  $p(\text{H}_2) = 121.5 \text{ kPa}$ ,  $c_{\text{ester}} = 0.108 \text{ mol l}^{-1}$  for all the esters. *a* Methyl linolenate and hexyl linolenate; designation of points:  $\nabla$  methyl linolenate,  $\Delta$  isomeric methyl C 18 : 2 esters,  $\otimes$  isomeric methyl C 18 : 1 esters,  $\bullet$  methyl stearate,  $\ominus$  hexyl linolenate,  $\oplus$  isomeric hexyl C 18 : 2 esters,  $\circ$  isomeric hexyl C 18 : 1 esters,  $\omin�$  hexyl stearate; *b* propyl linolenate and methyl oleate; designation of points:  $\nabla$  propyl linolenate,  $\ominus$  propyl 12-octadecenoate,  $\otimes$  mixture of propyl oleate and propyl elaidate,  $\blacktriangledown$  propyl stearate,  $\circ$  methyl oleate,  $\bullet$  methyl elaidate,  $\bullet$  methyl stearate

analysis of C 18 : 2 and C 18 : 1 isomers<sup>16</sup>. Its application is based on the condition that there is no reesterification during the hydrogenation, and in our case in which we attempted to describe the hydrogenation quantitatively also on the presumption of the same reactivity of the one type esters containing different alkyl groups. As shown in Fig. 6a on example of methyl linolenate and hexyl linolenate the last mentioned presumption is fulfilled in our case, as well as the first condition (see Fig. 6b) about the absence of reesterification during the hydrogenation. The results of competitive experiments which were obtained for series of measurements under different reaction conditions are illustrated by one typical example in Fig. 7.

Figures 6b and 7 provide the following information: a) the Ziegler system used is selective to formation of monoenes. Methyl esters of C 18 : 1 acids which are formed by hydrogenation of the higher unsaturated C 18 : 2 and C 18 : 3 esters accumulate during the reaction and begin to be hydrogenated only after practically complete disappearance of the C 18 : 3 esters and after substantial decrease of C 18 : 2 esters concentration. In the case of hydrogenation of methyl oleate and propyl linoleate (Fig. 6b) the C 18 : 1 esters becomes hydrogenated only after complete hydrogenation of the C 18 : 2 ester. b) In the competitive hydrogenation of all three esters (Fig. 7), hexyl linolenate reacts at fastest rate compared of other starting esters but at the same time also hydrogenation of propyl linoleate is taking place. Similarly, the rate of formation of propyl esters of the C 18 : 1 acids is comparable to the rate of formation of hexyl esters of the C 18 : 2 acids. c) The fact that C 18 : 3 and C 18 : 2 esters react simultaneously could in terms of the nickel zero-valent species as catalytic centre (Scheme 2) indicate that already two coordinated C=C bonds "saturate" this centre. We believe that some support for this idea is given by the already mentioned composition of the diene fraction with almost 50% content of the esters of 9,15-octadecadienoic acid. This speaks for the coordination of linolenic acid to nickel by the pair of the closest C=C bond in positions 9,12 or 12,15. d) Formation of hexyl esters of C 18 : 1 acids cannot

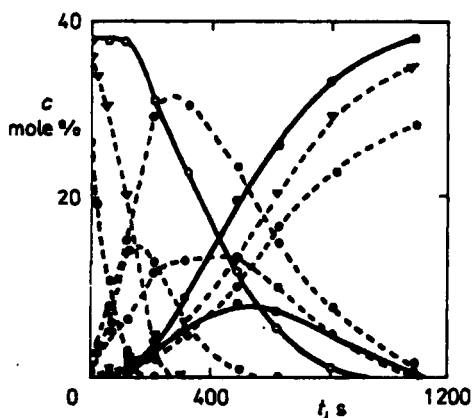
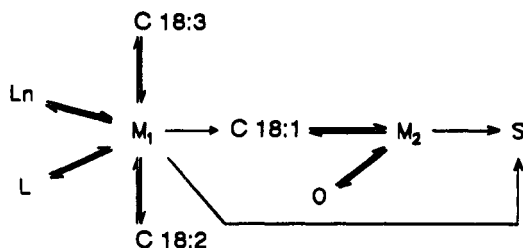


FIG. 7

Product distribution in hydrogenation of methyl oleate ( $0.118 \text{ mol l}^{-1}$ ), propyl linoleate ( $0.110 \text{ mol l}^{-1}$ ) and hexyl linolenate ( $0.048 \text{ mol l}^{-1}$ ) catalyzed by  $\text{Ni}(\text{acac})_2\text{-Al}(\text{C}_2\text{H}_5)_3$  system ( $25^\circ\text{C}$ ,  $p(\text{H}_2) = 120.7 \text{ kPa}$ ,  $c_{\text{K}} = 6.8 \cdot 10^{-3} \text{ mol l}^{-1}$ ). Designation of points:  $\circ$  methyl oleate,  $\bullet$  methyl elaidate,  $\bullet$  methyl stearate,  $\nabla$  propyl linoleate,  $\bullet$  propyl esters of C 18 : 1 acids,  $\nabla$  propyl stearate,  $\otimes$  hexyl linolenate,  $\oplus$  isomeric hexyl C 18 : 2 esters,  $\ominus$  isomeric hexyl C 18 : 1 esters,  $\ominus$  hexyl stearate

be interpreted unambiguously. They can either arise from direct hydrogenation of C 18 : 3 to C 18 : 1, or be the product of the consecutive C 18 : 3 to C 18 : 2 to C 18 : 1 hydrogenation. The presence of greater amount of the C 18 : 1 esters could indicate that both routes play a role in the hydrogenation process.

The above mentioned results led us to suggest the following model of the hydrogenation (Scheme 3). It stresses the possibility of simultaneous coordination of lino-



SCHEME 3

lenic and linoleic acid to the catalytic centre without marked preference of the C 18 : 3 acid. The preferential coordination of polyunsaturated acids compared to monoenes is analogously to Scheme 2 expressed by the intermediate M<sub>2</sub>. The reason for which introduction of second intermediate is not purely formal was already discussed. However, further accumulation of relevant kinetic and product distribution data is needed before the model can be subjected to numerical solution.

## SYMBOLS

$c_K$	Ni(acac) <sub>2</sub> -Et <sub>3</sub> Al (3 : 1) catalyst concentration (based on Ni, mol l <sup>-1</sup> )
$c_O$	methyl oleate concentration, mol l <sup>-1</sup>
$c_E$	methyl elaidate concentration, mol l <sup>-1</sup>
$c_L$	methyl linoleate, mol l <sup>-1</sup>
$p(H_2)$	hydrogen partial pressure, kPa
C 18 : 1	monoenic C <sub>18</sub> fatty acids
C 18 : 2	dienic C <sub>18</sub> fatty acids
C 18 : 3	trienic C <sub>18</sub> fatty acids
E	elaidic acid
L	linoleic acid
Ln	linolenic acid
O	oleic acid
C12:O	12-octadecenoic acid
S	stearic acid

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