

HYDROGENATION OF FATTY ACID ESTERS. II. KINETICS OF HYDROGENATION OF METHYL (*Z*)- AND (*E*)-9-OCTADECENOATE CATALYZED BY A ZIEGLER NICKEL CATALYST

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

Kinetics of the title reactions has been studied, using nickel(II) 2,4-pentanedionate/triethylaluminium system as a model catalyst. Initial rate measurements showed that in both cases the hydrogenation is first order in hydrogen, zero order in the octadecenoate and a fractional order (close to one) in the catalyst. Both hydrogenations have similar activation energies ($30.2 \pm 2.3 \text{ kJ mol}^{-1}$ and $28.9 \pm 2.6 \text{ kJ mol}^{-1}$ for the (*Z*)- and (*E*)-9-octadecenoate, respectively). Based on these data and the results of competition experiments, two models have been proposed to describe isomerization of the octadecenoates (either direct or via an intermediate).

In the preceding work¹ we reported on the activating effect of sodium dihydridobis-(2-methoxyethoxy)aluminate in formation of nickel catalysts for hydrogenation of fatty acid esters. Comparison of several Ziegler systems based on different nickel salts and activating agents confirmed similar features of the course of the reaction, including mild reactions condition, low degree of trans-isomerization and relatively high selectivity to monoene formation. In this respect Ziegler systems differ from heterogeneous nickel catalysts. The indicated absence of C=C double bond conjugation was further finding which differentiated homogeneous from heterogeneous fatty acids hydrogenation. However, in contrast to heterogeneous processes there are scarce data in literature concerning the role of Ziegler type catalysts²⁻⁵. Kinetics of the reaction has received only partial attention⁶, being focused on supported Ziegler catalysts. To obtain further data which would contribute to the knowledge of mechanism of this reaction we decided to perform a more systematic study, combining kinetic and product analysis. In the present communication we report on hydrogenation of C₁₈ monoenic acid esters. Kinetics of hydrogenation of polyunsaturated C₁₈ acids will be the subject of a subsequent work.

EXPERIMENTAL

Chemicals

Nickel(II) 2,4-pentanedionate (95%, Aldrich) was recrystallized twice from methanol and the blue-green crystals obtained were dried at 100 °C. Their recrystallization from toluene with azeotropic removal of traces of water gave after vacuum drying (60 °C, 0.6 Pa) the sample with Ni content 22.87% (calculated 22.89%).

Triethylaluminium (purris.) and triisobutylaluminium (purris.), both Fluka A.G., were used as obtained. The other compounds used are characterized in the text when first mentioned.

Methyl (Z)-9-Octadecenoate (Methyl Oleate)

The ester was prepared by esterification of oleic acid (obtained by hydrolysis of olive oil and purified to 98% purity by selective recrystallization from 50% acetone solution at -30 °C) with methanol using *p*-toluenesulfonic acid as the catalyst. After salting out the solution, extraction with three portions of petroleum ether, washing the extract with water and drying over sodium sulfate, vacuum distillation under argon yielded methyl (Z)-9-octadecenoate of 97% purity (b.p. 153 – 160 °C/133 Pa, acidity number 0.118).

Ethyl (Z)-9-Octadecenoate (Ethyl Oleate)

The ester was obtained by reesterification of the above mentioned methyl oleate with ethanol in the presence of *p*-toluenesulfonic acid as the catalyst. The conversion was followed by gas chromatography. Vacuum distillation under argon gave ethyl (Z)-9-octadecenoate of 97% purity (b.p. 164 – 168 °C/133 Pa, acidity number 0.120).

Methyl (E)-9-Octadecenoate (Methyl Elaidate)

The ester was obtained by esterification of (E)-9-octadecenoic acid⁷ with methanol, using the procedure described for synthesis of methyl oleate. The product was of 98% purity, being contaminated by 1.5% of methyl oleate (m.p. 10 °C, acidity number 0.300).

Ethyl (E)-9-Octadecenoate (Ethyl Elaidate)

The ester was obtained by reaction of elaidic acid with ethanol in the presence of *p*-toluenesulfonic acid as the catalyst, using chloroform for azeotropic removal of the water formed. Vacuum distillation under argon yielded ethyl elaidate (170 – 174 °C/135 Pa, acidity number 0.300) of 98% purity (with admixture of 1.5% of methyl oleate).

Catalyst Preparation

A 50 ml Schlenk flask was charged with a weighed amount (ca 0.25 g) of nickel(II) 2,4-pentanedionate (Ni(acac)₂), evacuated and flushed with argon. Then cyclohexane (dried over sodium and distilled) was added under a constant stream of argon so that the resulting Ni concentration in solution was $8.5 \cdot 10^{-5}$ mol Ni/ml. The flask was fitted with condenser topped with argon adapter, and the mixture was stirred and heated to 50 °C for 10 min. Then 10% (v/v) cyclohexane solution of triethylaluminium was added to the Al : Ni molar ratio 3 : 1. The reaction mixture which immediately turned black was stirred and heated for another 15 min and then slowly cooled to room temperature with continuous stirring. As preliminary experiments showed the catalyst underwent changes on longer standing. The catalyst solution was prepared

only for 1 day measurements and the constant catalytic behaviour was checked by repeating the first experiment after completion of each series of kinetic measurements.

Kinetic Measurements

Hydrogenation apparatus. Kinetic measurements were made with the use of an apparatus working at a constant hydrogen pressure and enabling automatic recording of hydrogen consumption with sufficient accuracy in both slow and high hydrogenation rates (half times around half minute). The same apparatus has been used in the preceding work¹ and was described in detail elsewhere⁸, including the reaction vessel.

Procedure. The vessel equipped with a side arm topped with a septum (serving for feeding) was connected to the hydrogenation apparatus and the whole system was evacuated three times with intermittent filling with hydrogen (which was passed through palladium membrane to remove oxygen traces). Then the hydrogen pressure was set to the required value, cyclohexane was introduced through a silicone septum via syringe, followed by a substrate injection to the stirred solution. Then the reaction mixture was allowed to warm up to the reaction temperature (the reactor was placed in a thermostated bath). Both the solvent and fatty acid esters were stored under argon and were fed by syringes purged several times with argon. The reaction was started by injection of the catalyst solution. The course of the reaction was followed by hydrogen consumption and in some cases also by removing the samples during the reaction and analyzing the content of individual components by gas chromatography.

Product analysis. Gas chromatograph Chrom 5 (Laboratorní přístroje Praha) equipped with a flame-ionization detector and a glass column packed with 12% Silicone elastomer OV 275 on Chromosorb PAW DMCS (6 m long and 3 mm i.d.) at 206 °C (injection port temperature 255 °C, nitrogen as a carrier gas, pressure 130 kPa) was used for general analysis. The isomers were determined with the aid of standards, using a capillary column 30 m long with 0.25 mm i.d., filled with DB-WAX (hydrogen as a carrier gas, pressure 90 kPa, injection port temperature 240 °C, column temperature 180 °C). The product analysis was made by the method of internal standard with appropriate calibration. The standard was methyl hexadecanoate (methyl palmitate, C 16 : 0). Molar concentrations of the products formed were calculated from the expression:

$$\text{mole \% A} = (\text{mole \% S}) (\% \text{ A}) / k (\% \text{ S}),$$

where (mole % S) is known molar concentration of the standard in the reaction mixture, (% A) and (% S) are integrated peak areas for compound A and S, respectively, and k is the calibration factor of compound A.

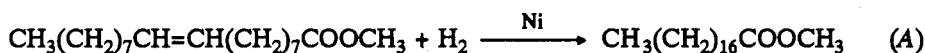
Treatment of kinetic data. With respect to the specific properties of the catalytic system studied and experimental technique used, kinetic data on hydrogenation of single compounds were obtained by the method of initial reaction rates. By this way, the rate dependencies on catalyst and substrate concentrations and on hydrogen pressure and temperature were determined (linear relationship between time and hydrogen consumption up to 20 – 30 % substrate conversion was used). The reaction orders in the individual components were obtained from experimental data by regression analysis. Findings made on single compounds were then used in treatment of the more complex systems. In this case, the solution of a set of differential equations derived for proposed models was made numerically. The values of rate constants were optimized such that the set of experimental data was described as best as possible by function of the variables (i.e. by the kinetic equation). The method chosen had optimized rate constants on the basis of minimalization of the objective function given by the sum of weighed squared deviations of experimental points from the calculated ones. A programme for parametric nonlinear optimization of the objective function reported and verified elsewhere⁹ was applied for this purpose. It is based on the algorithm proposed by Marquardt combined with Newton–Raphson method and also a simultaneous solution of differential equations set using Runge–Kutta method was incorporated.

RESULTS AND DISCUSSION

As shown in the preceding work¹, hydrogenation of polyunsaturated fatty acid esters when catalyzed by Ziegler type systems, can be divided into two stages. The first one including hydrogenation of trienic and dienic C₁₈ acid esters to the monoenic ones takes place with relatively high selectivity and is accompanied by only low trans-isomerization. The final stage of the reaction involves hydrogenation of isomeric monoenic acid (C 18 : 1) esters to the saturated product (octadecanoate, C 18 : 0).

Although several approaches can be thought of to analyze this system, we considered it useful to base it on kinetics of the reactions of single components and combination of the so obtained data with the results of competition experiments of different esters and product distribution analysis. To simplify further the situation, instead of natural triglycerides we made use of methyl esters, as usual in such studies. The fact that from the standpoint of product changes the course of the reaction does not depend significantly on the type of nickel salt and of the activating organoaluminium compound used in formation of Ziegler Ni catalysts (cf. ref.¹) made the choice of the catalyst easier. To make comparison with other studies possible, the Ni(acac)₂-(C₂H₅)₃Al system was chosen and the catalyst was prepared at optimum Ni : Al molar ratio (1 : 3, see Experimental). It was found that kinetic data were reproducible within 10 rel.%, and the activity of individual catalyst samples within ± 5 rel. %.

The approach mentioned above led us to investigate first the final stage of the reaction, i.e. hydrogenation of C 18 : 1 acid esters, Eq. (A). Preliminary experiments showed that hydrogenation of both isomeric (*Z*) and (*E*) methyl esters proceeds fast under very mild conditions and with practically quantitative conversion, after very short induction period.



The method of initial reaction rates yielded the following dependencies of the rate on catalyst concentration c_K and hydrogen pressure $p(\text{H}_2)$ for methyl oleate (MeO):

$$\ln r = 0.84 \ln c_K - 3.06; \quad (25^\circ \text{C}, p(\text{H}_2) = 131 \text{ kPa}, c_{(\text{MeO})} = 0.25 \text{ mol l}^{-1})$$

$$\ln r = 1.26 \ln p(\text{H}_2) - 12.58; \quad (25^\circ \text{C}, c_{(\text{MeO})} = 0.25 \text{ mol l}^{-1}, c_K = 6.4 \cdot 10^{-3} \text{ mol l}^{-1})$$

$\ln c_K$ has changed from -6.50 to -4.50 (mol l⁻¹), $\ln p(\text{H}_2)$ has been between 4.00 and 5.00 (kPa).

The dependence on substrate concentration ($c_{(\text{MeO})}$) is documented by data in Fig. 1 which show that the reaction is zero order in the substrate for the region of low methyl oleate concentrations. Negative effect of the higher than about 0.4 mol l⁻¹ substrate concentrations is at present difficult to explain since, as found by further experiments,

it does not relate to the substrate to catalyst ratio (the breakdown of the zero order dependence has been observed at the above substrate concentration for the MeO/Ni ratios ranging from 87 to 35).

The rate constants of initial stage of reaction obeyed well the Arrhenius plot ($\ln k = -3.635/T - 10.95$), giving the activation energy of methyl oleate hydrogenation $E_0 = 30.2 \pm 2.3 \text{ kJ mol}^{-1}$.

Changes in product distribution in the course of hydrogenation of methyl oleate are illustrated in Fig. 2. Worth mentioning in this connection is the (*E*)-isomer, the rate of formation of which as well as its maximum content increases with increasing temperature (Figs 2a, 2b) and decreasing hydrogen pressure (Figs 2c, 2d), analogously to the heterogeneous nickel catalyzed hydrogenation (cf. ref.¹⁰). The observed lack of isomerization activity of Ni(acac)₂-Et₃Al system in the absence of hydrogen under otherwise identical reaction conditions with those used in the hydrogenation as well as the above mentioned rate dependence of isomerization on hydrogen pressure provides evidence for the hydride route of the above trans-isomerization.

As found by initial rate measurements, hydrogenation of the (*E*)-isomer, methyl elai-date (MeE), can be described by the following relations:

$$\ln r = 1.18 \ln c_K - 0.939; \quad (25 \text{ }^\circ\text{C}, p(\text{H}_2) = 134 \text{ kPa}, c_{(\text{MeE})} = 0.25 \text{ mol l}^{-1})$$

$$\ln r = 1.004 \ln p(\text{H}_2) - 11.7; \quad (25 \text{ }^\circ\text{C}, c_{(\text{MeE})} = 0.25 \text{ mol l}^{-1}, c_K = 6.4 \cdot 10^{-3} \text{ mol l}^{-1})$$

$\ln c_K$ has changed from -6.50 to -4.50 (mol l^{-1}) and $\ln p(\text{H}_2)$ from 3.50 to 5.50 (kPa).

Similarly to methyl oleate, the hydrogenation was zero order in the substrate (Fig. 3). It is worth mentioning that in this case the zero order reaction was observed also for the substrate concentrations at which the steep rate decrease was observed for methyl oleate. The activation energy of the process E_E obtained from the Arrhenius plot ($\ln k =$

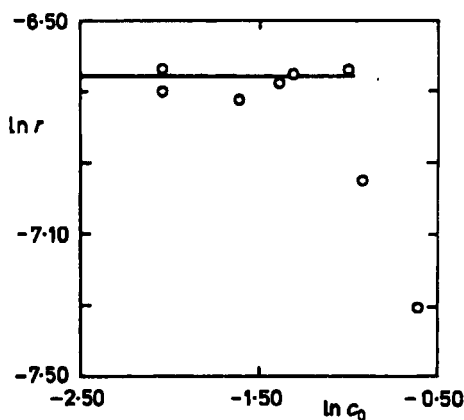


FIG. 1

Determination of the reaction order in methyl oleate (Ni(acac)₂-Et₃Al, 1 : 3, temperature 25 °C, $p(\text{H}_2) = 133 \text{ kPa}$, $c_K = 7.7 \cdot 10^{-3} \text{ mol l}^{-1}$)

$-3.44/T - 11.98$) equals to $28.9 \pm 2.6 \text{ kJ mol}^{-1}$ and is very close to that found for methyl oleate ($30.2 \pm 2.3 \text{ kJ mol}^{-1}$).

Product distribution changes during hydrogenation of methyl elaidate are shown in Fig. 4. *trans*-Isomerization and similar activation parameters for both processes rule out the possibility that the small amount of the (*Z*)-isomer observed is caused by the markedly higher reactivity of methyl oleate and thus its preferential hydrogenation once this product is formed.

Further information has been obtained by competitive hydrogenation of the pairs of isomeric esters differing by alkyl group (methyl oleate + ethyl elaidate vs ethyl oleate + methyl elaidate). It was confirmed that the reactivity of methyl and ethyl esters was

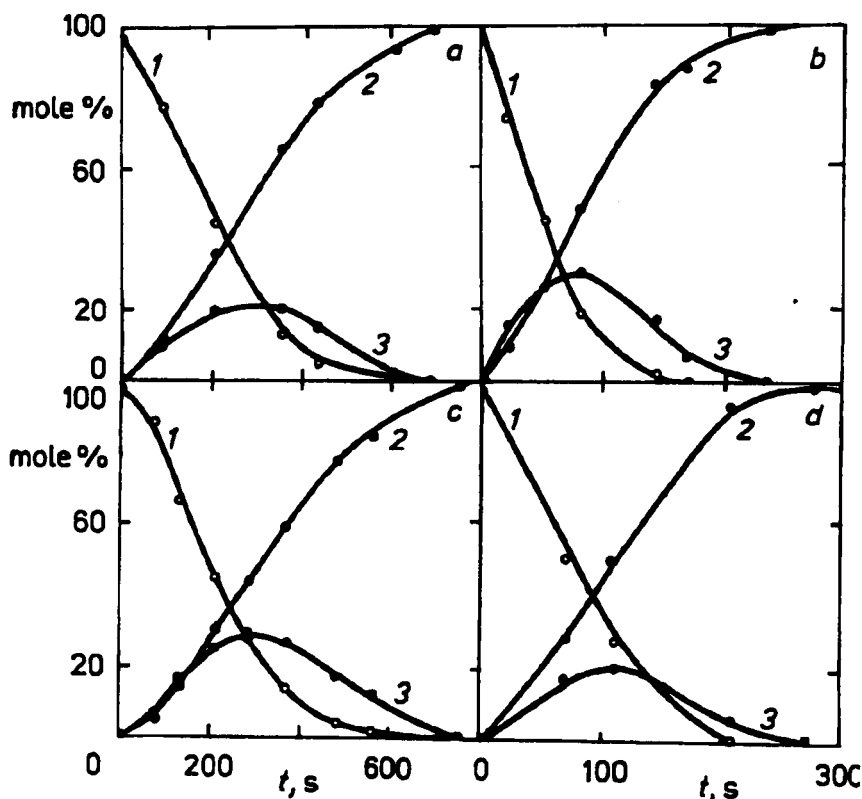


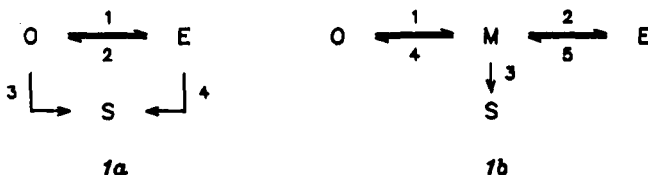
FIG. 2

Product distribution during hydrogenation of methyl oleate catalyzed by $\text{Ni}(\text{acac})_2\text{-Et}_3\text{Al}$ (1 : 3) catalyst; 1 methyl oleate, 2 methyl stearate, 3 methyl elaidate; a temperature 7°C , $p(\text{H}_2) = 128 \text{ kPa}$, $c_{(\text{MeO})} = 0.25 \text{ mol l}^{-1}$, $c_K = 7.1 \cdot 10^{-3} \text{ mol l}^{-1}$; b temperature 45.5°C , other conditions see a; c $p(\text{H}_2) = 52.2 \text{ kPa}$, $c_{(\text{MeO})} = 0.25 \text{ mol l}^{-1}$, $c_K = 7 \cdot 10^{-3} \text{ mol l}^{-1}$, temperature 25°C ; d $p(\text{H}_2) = 159 \text{ kPa}$, other conditions see a

the same within limits of experimental accuracy. The course of this hydrogenation in which strictly identical conditions were ensured for both isomers is graphically represented in Fig. 5. The figure confirms the already mentioned features of the reaction: hydrogenation of oleate is accompanied by isomerization of the ester to elaidate, while elaidate is converted into saturated product without significant isomerization of the (*Z*)-isomer (ca 2% amount of the ethyl oleate in the figure comes from the starting sample). Similar reactivity of both esters is further documented by parallel and nearly identical increase of both saturated products (MeS and EtS) in the course of the reaction.

The comparable reactivities of both isomers are further responsible for the fact that time dependence of hydrogen consumption at constant hydrogen pressure shows zero order in the substrate, although methyl oleate consumption significantly deviates from the zero order dependence (Fig. 5).

With the aim to describe the above discussed course of the hydrogenation of methyl oleate and elaidate we have analyzed two reaction models (Scheme 1).



SCHEME 1

The model 1a is frequently used to describe heterogeneously catalyzed hydrogenation of oleic acid esters (cf. refs¹¹⁻¹³ and references cited therein). The model 1b then involves formation of a common intermediate M for hydrogenation and isome-

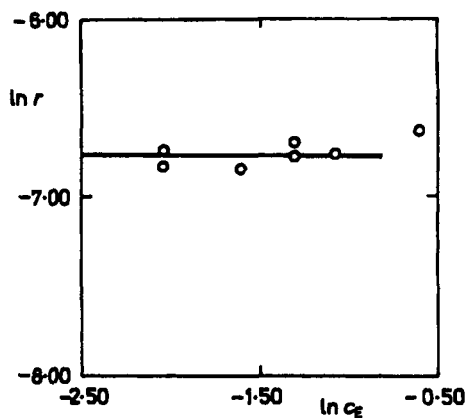
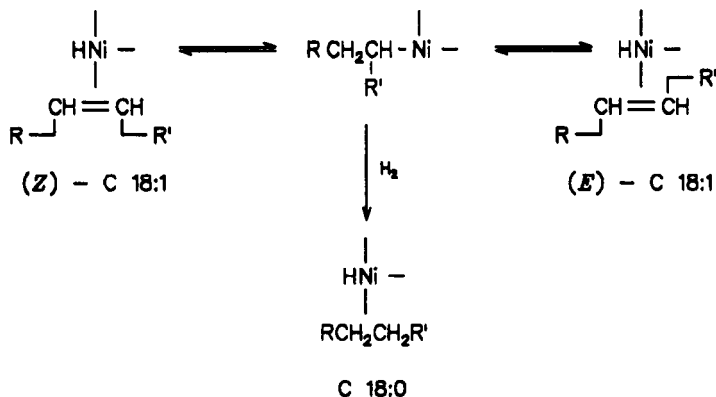


FIG. 3
Determination of the reaction order in methyl elaidate (conditions as in Fig. 1)

rization, and it relates to the widely accepted hydrogenation via metal hydride formation⁴ (Scheme 2).



SCHEME 2

For these models two sets of differential equations were derived and solved then numerically. The orders found of hydrogenation reaction in the single components were taken from experimental initial rate data and the parameters subjected to optimization

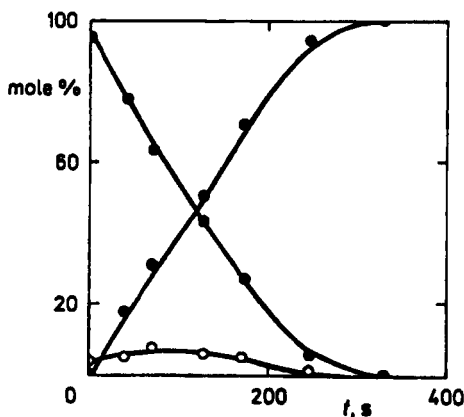


FIG. 4

Composition of the reaction mixture during hydrogenation of methyl elaidate catalyzed by $\text{Ni}(\text{acac})_2\text{-Et}_3\text{Al}$ (1 : 3) catalyst (temperature 25 °C, $p(\text{H}_2) = 131$ kPa, $c_{(\text{MeE})} = 0.25$ mol l⁻¹, $c_{\text{K}} = 5.4 \cdot 10^{-3}$ mol l⁻¹). ○ Methyl oleate, ⊕ methyl elaidate, ● methyl stearate

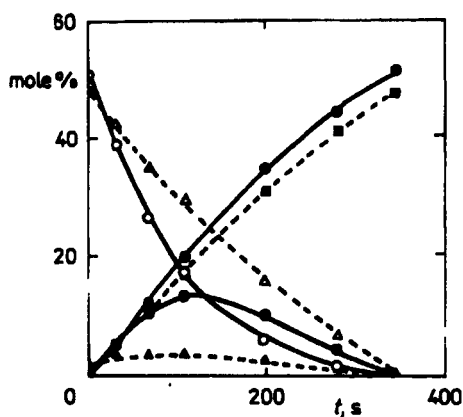


FIG. 5

Product distribution changes during competitive hydrogenation of methyl oleate (MeO) and ethyl elaidate (EtE); (temperature 25 °C, $p(\text{H}_2) = 131$ kPa, $c_{(\text{MeO})} = 0.124$ mol l⁻¹, $c_{(\text{EtE})} = 0.118$ mol l⁻¹, $c_{\text{K}} = 6.8 \cdot 10^{-3}$ mol l⁻¹). ○ Methyl oleate, ⊕ methyl elaidate, ● methyl stearate, ■ ethyl elaidate, Δ ethyl oleate, ▲ ethyl stearate

were rate constants. Other preconditions were applied: isomerization reactions are reciprocal ones and first order in substrates, catalyst and hydrogen. Model 1a (Scheme 1) is described by the following set of differential equations:

$$\begin{aligned} dc_O/dt &= k_1 c_E^1 p_H^1 c_K^1 - k_2 c_O^1 p_H^1 c_K^1 - k_3 c_O^1 p_H^1 c_K^1 \\ dc_E/dt &= k_2 c_O^1 p_H^1 c_K^1 - k_1 c_E^1 p_H^1 c_K^1 - k_4 c_E^0 p_H^1 c_K^1 \\ dc_S/dt &= k_3 c_O^1 p_H^1 c_K^1 + k_4 c_E^0 p_H^1 c_K^1. \end{aligned}$$

Model 1b contains common intermediate for hydrogenation and isomerization reactions which concentration is ruled by Bodenstein principle:

$$\begin{aligned} dc_O/dt &= k_4 c_M^1 p_H^1 c_K^1 - k_1 c_O^1 p_H^1 c_K^1 \\ dc_E/dt &= k_5 c_M^1 p_H^1 c_K^1 - k_2 c_E^0 p_H^1 c_K^1 \\ dc_S/dt &= k_3 c_M^1 p_H^1 c_K^1 \\ dc_M/dt &= k_1 c_O^1 p_H^1 c_K^1 + k_2 c_E^0 p_H^1 c_K^1 - k_4 c_M^1 p_H^1 c_K^1 - \\ &\quad - k_5 c_M^1 p_H^1 c_K^1 - k_3 c_M^1 p_H^1 c_K^1 \\ c_M &= (k_1 c_O + k_2) / (k_4 + k_5 + k_3). \end{aligned}$$

The solution of both sets for the conditions given in Fig. 5 yields the following rate constants (in $l \text{ mol}^{-1} \text{ MPa}^{-1} \text{ s}^{-1}$):

$$k_1 = 0.89, k_2 = 9.48, k_3 = 1.53, k_4 = 0.37 \text{ (MPa}^{-1} \text{ s}^{-1}\text{)}.$$

$$\text{Model 1b, } k_1 = 11.2, k_2 = 2.47 \text{ (MPa}^{-1} \text{ s}^{-1}\text{)}, k_3 = 17.7, k_4 = 0.90, k_5 = 99.7.$$

The similar values of standard error deviations in one point fitting for both models ($\sum = 4.87 \cdot 10^{-3} \text{ mol l}^{-1}$ and $6.00 \cdot 10^{-3} \text{ mol l}^{-1}$ for models 1a and 1b, respectively) do not allow their differentiation. However, the inspection of data relating to the trans-isomerization in model 1a (i.e. the ratio $k_2/k_1 = 9.48/0.89 = 10.6$) makes the model less realistic because of the predicted high isomerization constant. This conclusion is based on the finding that even under more drastic conditions of heterogeneously catalyzed hydrogenation (temperatures 150 – 200 °C) the equilibrium isomerization constant does not exceed the value of 3 – 4 (refs^{14–16}). An indirect support for the above assumption is provided also by the low oleate to elaidate molar ratio at maximum of elaidate formation, observed during hydrogenations of methyl oleate under different conditions (see Fig. 2).

SYMBOLS

| | |
|-----------------|--|
| c_K | catalyst concentration related to nickel compound, mol l^{-1} |
| c_O | concentration of methyl oleate, mol l^{-1} |
| c_E | concentration of methyl elaidate, mol l^{-1} |
| E_O | activation energy of hydrogenation of methyl oleate, kJ mol^{-1} |
| E_E | activation energy of hydrogenation of methyl elaidate kJ mol^{-1} |
| $p(\text{H}_2)$ | partial hydrogen pressure, kPa |

| | |
|-----------------------|---|
| k_n ($n = 1 - 5$) | rate constants for hydrogenation models in Scheme 1, $l \text{ mol}^{-1} \text{ MPa}^{-1} \text{ s}^{-1}$, $\text{MPa}^{-1} \text{ s}^{-1}$, respectively |
| MeO | methyl oleate |
| MeE | methyl elaidate |
| MeS | methyl stearate |
| M | intermediate for isomerization and hydrogenation reactions |

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