



Kinetic aspects of stereoselectivity in hydrogenation of fatty acids

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ABSTRACT

Kinetic peculiarities of stereoselectivity in hydrogenation of fatty acids are discussed. The reaction mechanism should be able to account for independence of the reaction rate on hydrogen pressure and conversion, stereoselectivity on conversion as well as an increase in *cis/trans* ratio with pressure increase. Various mechanisms advanced in the literature for formation of *cis*- and *trans* mono-unsaturated acids and their derivatives are considered, showing behavior contradicting with experiments. A reaction mechanism is proposed, which is consistent with experimental observations.

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1. Introduction

Kinetic studies of heterogeneous catalytic reactions, based on understanding of underlying physico-chemical processes on the catalyst surfaces, are becoming more widespread.

One of the reactions, which attracted attention of researchers in academia and industry, is hydrogenation of various fatty acids and their derivatives [1–15]. It is an important process due to its wider application in the production of edible fats and margarine. Partial hydrogenation of di-unsaturated fatty acids and their esters improves stabilization towards oxygen. At the same time since the melting point should not be increased, a special case is usually taken on the ratio between *Z* (*cis*) and *E* (*trans*) isomers in mono-unsaturated acids.

The kinetic aspects of liquid-phase hydrogenation of fatty acids and fatty oils, including stereoselectivity, were addressed several times in the literature [2–4,6,8,11–13].

Migration of the double bond along with *cis–trans* isomerization of monoenes were included in the modeling. The most comprehensive study on kinetic peculiarities of *cis/trans* formation was done for hydrogenation of methyl linoleate over Pd/MgO, which was carried out in the conditions free from mass transfer [16]. In particular the effects of hydrogen pressure, temperature and conversion on *cis* and *trans* methyl oleate formation were reported and a mechanistic model was proposed to account for the kinetic regularities.

No kinetic equations were derived, however, from the advanced mechanism, thus even on the qualitative level the applicability of this mechanism requires further analysis.

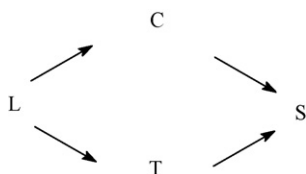
The aim of the present communication is to critically assess the mechanism, developed in ref. [16], derive kinetic equations from several mechanisms, proposed in the literature and compare kinetic regularities observed experimentally with predictions from the mechanistic models.

2. Kinetic regularities

It is worth to remind the kinetic regularities, established in ref. [16] for methyl linoleate hydrogenation over Pd/MgO:

- (i) *cis/trans* ratio of methyl oleate was not changed with conversion when methyl linoleate was present in the reaction mixture.
- (ii) This ratio, however, was decreasing after complete conversion of linoleate, showing that *cis–trans* isomerization in principle occurs when the surface is available for this reaction.
- (iii) The reaction followed the zero dependence in hydrogen pressure for methyl linoleate and even methyl oleate hydrogenations.
- (iv) The *cis/trans* ratio increased sharply in the range of hydrogen pressures 1–2 bar, while the increase was less pronounced in the pressure domain of 4.5–10 bar. This is in fact very interesting observation especially taking into account zero order in hydrogen.
- (v) The methyl linoleate hydrogenation was zero order in the substrate.

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Scheme 1. Parallel-consecutive mechanism of hydrogenation of di-unsaturated acids. L, C, T and S represent, respectively, linoleic, oleic, elaidic and stearic acid or their derivatives.

These regularities could be different for different substrates and catalysts. For instance, *cis/trans* isomerization could be more prominent over nickel catalysts, which in fact leads to dependence of *cis/trans* ratio on conversion [13]. This isomerization reaction was reported to be dependent on hydrogen concentration [17]. More recently Moulijn and co-workers [18] for hydrogenation of methyl esters fatty acids discussed a network of saturation consisting of consecutive steps, while the *cis-trans* isomerisation was considered as a parallel reaction of the unsaturated components. It was argued that for the hydrogenation hydrogen is needed leading generally to first order dependence, while according to ref. [17] in the isomerisation hydrogen is not consumed and the rate is only weakly dependent on the hydrogen pressure, although hydrogen must be present for the reaction to proceed.

3. Mechanistic models

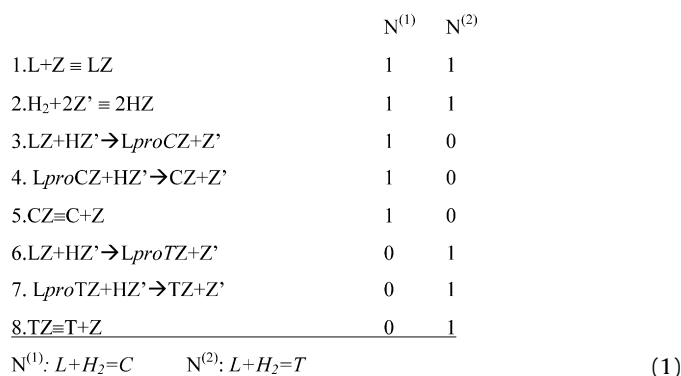
3.1. Quasi-equilibrium approximation

The majority of kinetic models invoke Langmuir–Hinshelwood approach, which essentially assumes quasi-equilibria in adsorption of organic substances and hydrogen. The latter was supposed in the literature to be adsorbed mostly in non-competitive fashion, which is reasonable taking into account the differences in sizes of hydrogen and other reacting species.

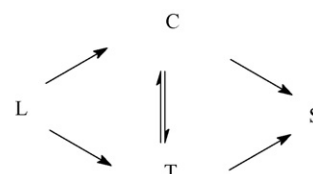
Let us consider first one of the models (Scheme 1), used in the literature to describe hydrogenation of linoleic acid over nickel catalysts [4].

For the sake of clarity the treatment below will be focused only on stereoselective formation of *cis* and *trans* mono-acids and their derivatives, therefore, hydrogenation of mono-unsaturated acids will be neglected, which is justified, since in ref. [16] formation of methyl stearate became visible only after almost complete consumption of methyl linoleate.

The following reaction scheme, which corresponds to parallel reactions, can be considered then



In the mechanism above, it is assumed, that hydrogen adsorbs (on site Z') with dissociation without competition with the bulky organic molecules (which adsorb on sites of Z type). It should be noted that adsorption is considered to be at quasi-equilibria for



Scheme 2. Parallel-consecutive mechanism of hydrogenation of di-unsaturated acids with *cis-trans* isomerization of mono-unsaturated acids. Notation is the same as in Scheme 1.

all reactants and products (denoted with the sign ≡). Addition of the first hydrogen atom (steps 3 and 6) leads to surface intermediates, which are, respectively, *proC* or *proT*, meaning that in the subsequent steps they produce either *cis* or *trans* mono-acids. In the steps 3, 4 and 5, 6 occurring along two parallel routes N(1) and N(2) the final products C and T are obtained.

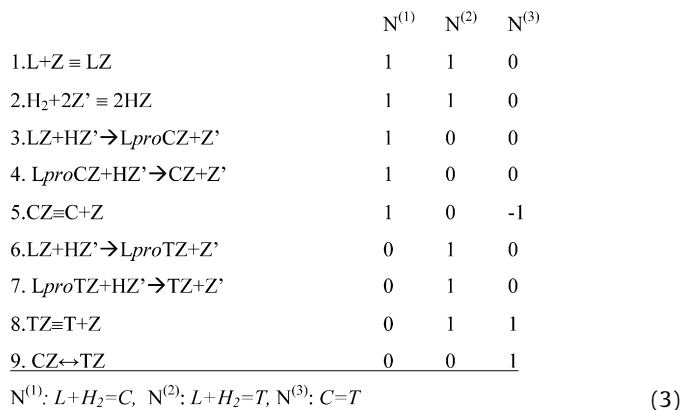
Derivation of the rate equations for mechanism (1) is rather straightforward. Without going into the details of derivation it should be noted that the ratio of product formation is given by

$$\frac{r_C}{r_T} = \frac{r_3}{r_6} = \frac{k_{+3}\theta_L\theta'_H}{k_{+6}\theta_L\theta'_H} = \frac{k_{+3}}{k_{+6}} \quad (2)$$

which means that this ratio is independent on conversion in agreement with experimental data [16], but at the same time it contradicts the dependence of stereoselectivity on hydrogen pressure.

A natural extension of the Scheme 1 would invoke *cis-trans* isomerization, also discussed in the literature [4], and is presented in Scheme 2.

In case of Scheme 2 an isomerization step should be added to the mechanism (1), meaning also that a third route appears, corresponding to *cis-trans* isomerization



The ratio of product formation is expressed in the following way

$$\frac{r_C}{r_T} = \frac{r_3 - r_9}{r_6 + r_9} = \frac{r_3 - r_{+9} + r_{-9}}{r_6 + r_{+9} - r_{-9}} = \frac{k_{+3}\theta_L\theta'_H - k_{+9}\theta_C + k_{-9}\theta_T}{k_{+6}\theta_L\theta'_H + k_{+9}\theta_C - k_{-9}\theta_T} \quad (4)$$

Assuming quasi-equilibrium adsorption of di-unsaturated acid or its derivative one can easily arrive at

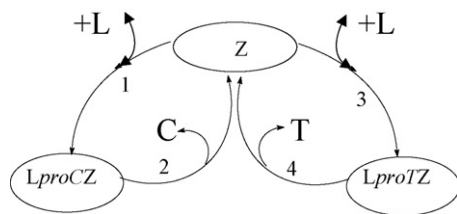
$$\theta_L = K_1 C_L \theta_V \quad (5)$$

where θ_L and θ_V are the coverage of the substrate and vacant sites, respectively. In an analogous fashion it can be demonstrated that

$$\theta_C = \frac{C_C}{K_5} \theta_V, \quad \theta_T = \frac{C_T}{K_8} \theta_V \quad (6)$$

Eq. (4) can be rewritten

$$\frac{r_C}{r_T} = \frac{k_{+3}K_1 C_L \theta'_H - k_{+9}C_C/K_5 + k_{-9}C_T/K_8}{k_{+6}K_1 C_L \theta'_H + k_{+9}C_C/K_5 - k_{-9}C_T/K_8} \quad (7)$$



Scheme 3. Catalytic cycles in hydrogenation of di-unsaturated fatty acids.

clearly showing the dependence of stereoselectivity on conversion, which contradicts with experimental data [16]. In addition the rate of linoleic acid (or its derivative) hydrogenation is expressed as follows

$$r = r_3 + r_6 = k_{+3}K_1C_L\theta_H' + k_{+6}K_1C_L\theta_H' \quad (8)$$

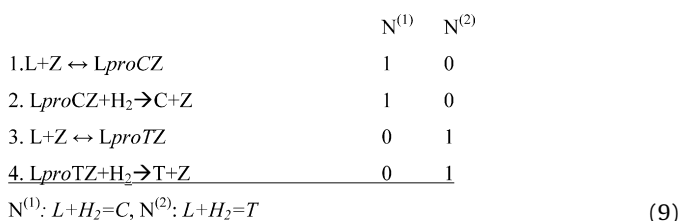
In case the hydrogenation rate is independent on hydrogen partial pressure [16], the coverage of hydrogen is close to unity (e.g. sites available for hydrogen are almost completely occupied), which in turn implies that the ratio of *cis/trans* products is independent on hydrogen pressure as well.

Some modifications of Scheme 2 could be done to account for hydrogen pressure dependence of stereoselectivity in case of zero order hydrogenation, for instance, by modifying the isomerization step 9 and including hydrogen in this step as an stoichiometric reactants, in the same spirit as discussed for double bond migration in di-unsaturated fatty acids [19,20]. Such modifications will still lead to dependence of stereoselectivity on conversion.

3.2. Steady-state approximation

In order to proceed further with mechanistic considerations in a search for a model, which is able to satisfy experimental observations, let us consider a mechanistic model, developed by Halpern [21,22] to account for hydrogen pressure dependence in enantioselective reactions (Scheme 3). This mechanism can be visualized using the catalytic cycle approach with the nodes and edges corresponding to the intermediates and steps, respectively.

In Scheme 3 there are two cycles which are coupled by the availability of the free form of the catalyst. Involvement of hydrogen is not described specifically, therefore in the mechanism (9) it can be initially proposed that hydrogen is taking part in the reaction from the fluid phase (e.g. dissolved in the liquid).



Steps 1 and 3 are considered to be reversible, while for the consistency with thermodynamics irreversibility of steps 2 and 4 can be assumed. From the steady-state approximation of steps 1 and 2, as well as 3 and 4, one arrives at the dependence of coverage of intermediates on the fraction of vacant sites

$$\theta_{LproC} = \frac{k_{+1}C_L}{k_{-1} + k_{+2}C_{H_2}}\theta_V, \quad \theta_{LproT} = \frac{k_{+3}C_L}{k_{-3} + k_{+4}C_{H_2}}\theta_V \quad (10)$$

Taking into account the balance equation ($1 = \theta_{LproC} + \theta_{LproT} + \theta_V$) the expression for the reaction rate is easily obtained

$$r = r_C + r_T = \frac{((k_{+1}k_{+2}C_{H_2}C_L)/(k_{-1} + k_{+2}C_{H_2})) + ((k_{+3}k_{+4}C_{H_2}C_L)/(k_{-3} + k_{+4}C_{H_2}))}{1 + ((k_{+1}C_L)/(k_{-1} + k_{+2}C_{H_2})) + ((k_{+3}C_L)/(k_{-3} + k_{+4}C_{H_2}))} \quad (11)$$

The ratio of rates for producing different stereoisomers is given by

$$\frac{r_C}{r_T} = \frac{k_{+1}k_{+2}C_{H_2}C_L}{k_{-1} + k_{+2}C_{H_2}} \frac{k_{-3} + k_{+4}C_{H_2}}{k_{+3}k_{+4}C_{H_2}C_L} = \frac{k_{+1}k_{+2}}{k_{+3}k_{+4}} \frac{k_{-3} + k_{+4}C_{H_2}}{k_{-1} + k_{+2}C_{H_2}} \quad (12)$$

It follows from Eq. (12) that stereoselectivity is independent on conversion. At sufficiently high pressures of hydrogen assuming $k_{-3} \ll k_{+4}C_{H_2}$ and $k_{-1} \ll k_{+2}C_{H_2}$ and neglecting two terms in the denominator other than unity instead of Eq. (11) we obtain

$$r = r_C + r_T = (k_{+1} + k_{+3})C_L \quad (13)$$

showing independence of the reaction rate on hydrogen pressure in agreement with experimental observations [16], at the same time the rate follows first order dependence on substrate concentration. Moreover, the selectivity depends on the ratio of the forward constants of the first steps, being independent on hydrogen pressure, which contradicts with experimental observations

$$\frac{r_C}{r_T} = \frac{k_{+1}k_{+2}k_{+4}}{k_{+3}k_{+2}k_{+4}} = \frac{k_{+1}}{k_{+3}} \quad (14)$$

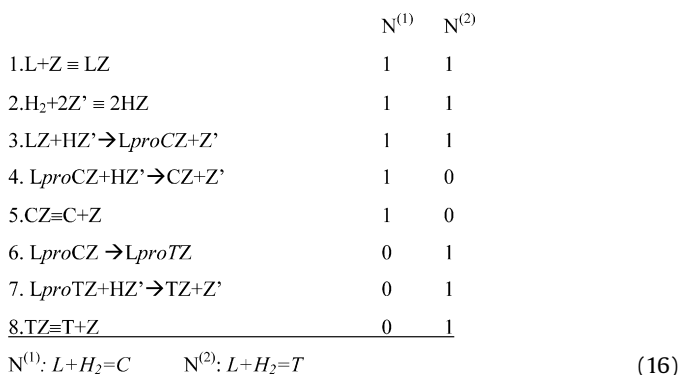
At low hydrogen pressures $k_{-3} \gg k_{+4}C_{H_2}$ and $k_{-1} \gg k_{+2}C_{H_2}$ leading to the first order dependence of the reaction rate on pressure, while at the same time the *cis-trans* ratio is pressure independent

$$\frac{r_C}{r_T} = \frac{k_{+1}k_{+2}k_{-3}}{k_{+3}k_{+4}k_{-1}} \quad (15)$$

The same conclusions, demonstrating contradicting behavior between experimentally observed data and predicted from the mechanism (9), are obtained if instead of hydrogen, dissolved in the fluid phase, involvement of either molecularly or atomically adsorbed hydrogen in non-competitive fashion is assumed. In particular in case of zero order in hydrogen for hydrogenation rate, modified steps 2 and 4 in mechanism (9), which include reactions with adsorbed hydrogen, would be fast anyway, therefore the *cis-trans* ratio is still given by Eq. (14).

3.3. Isomerization of half-hydrogenated intermediate

The preliminary conclusion that can be reached at this stage is that the models discussed above cannot account for experimental observations. In ref. [16] a reaction mechanism was proposed, which included besides hydrogenation of a half-hydrogenated intermediate ($\pi-\sigma$ complex) to *cis*-product also its isomerization to a *pro-trans* half-hydrogenated intermediate. Such a mechanism in a somewhat simplified fashion, taking into account, however, all the essential kinetic features can be written in a following way



Step 6 in this mechanism describes the isomerization of a half-hydrogenated intermediate in the adsorbed state. From the steady-state approximation for the coverage of this intermediate

$$r_3 = r_4 + r_6 \quad (17)$$

it holds

$$\theta_{LproC} = \frac{k_{+3}\theta'_H}{k_{+4}\theta'_H + k_{+6}} \theta_L = \frac{k_{+3}\theta'_H}{k_{+4}\theta'_H + k_{+6}} K_L C_L \theta_V \quad (18)$$

keeping in mind quasi-equilibrium for substrate adsorption (e.g. $\theta_L = K_L C_L \theta_V$).

From the steady-state conditions for *pro-trans* half-hydrogenated intermediate

$$r_6 = r_7 \quad (19)$$

and

$$\theta_{LproT} = \frac{k_{+5}\theta_{LproC}}{k_{+6}\theta'_H} = \frac{k_{+5}}{k_{+6}} \frac{k_{+3}}{k_{+4}\theta'_H + k_{+6}} K_L C_L \theta_V \quad (20)$$

Utilizing the balance equations ($1 = \theta_{LproC} + \theta_{LproT} + \theta_V + \theta_L + \theta_C + \theta_T$ and $1 = \theta' + \theta'_H$) and applying quasi-equilibria for steps 5 and 8 (e.g. $\theta_C = K_C C_C \theta_V$, $\theta_T = K_T C_T \theta_V$) the kinetic equation for hydrogenation rate is obtained

$$r = r_3 = k_{+3}\theta_L\theta'_H = \frac{k_{+3}K_L C_L \theta'_H}{1 + K_C C_C + K_T C_T + K_L C_L (1 + (k_{+3}\theta'_H)/(k_{+4}\theta'_H + k_{+6})(1 + (k_{+5})/(k_{+6}\theta'_H)))} \quad (21)$$

Introducing explicit expression for the coverage of hydrogen one finally arrives at

$$r = \frac{k_{+3}K_L C_L \sqrt{K_H C_{H_2}}}{\{1 + K_C C_C + K_T C_T + K_L C_L (1 + (k_{+3}\sqrt{K_H C_{H_2}})/(k_{+4}\sqrt{K_H C_{H_2}} + k_{+6}(1 + \sqrt{K_H C_{H_2}}/(\sqrt{K_H C_{H_2}}))))(1 + (k_{+5})/(k_{+6}(1 + \sqrt{K_H C_{H_2}}/(\sqrt{K_H C_{H_2}}))))\}}(1 + \sqrt{K_H C_{H_2}})} \quad (22)$$

The condition for the zero order in hydrogen pressure (concentration) requires that the surface coverage of hydrogen approaches unity, $\theta'_H \approx 1$, which in turn impose a certain restriction on the hydrogen pressure dependence of stereoselectivity, if mechanism (16) is valid. In particular it follows that the *cis/trans* ratio is independent on hydrogen pressure, which is not in agreement with experiments

$$\frac{r_C}{r_T} = \frac{k_{+4}\theta_{LproC}\theta'_H}{k_{+6}\theta_{LproC}} \approx \frac{k_{+4}}{k_{+6}} \quad (23)$$

3.4. Mechanism with a precursor for half-hydrogenated species

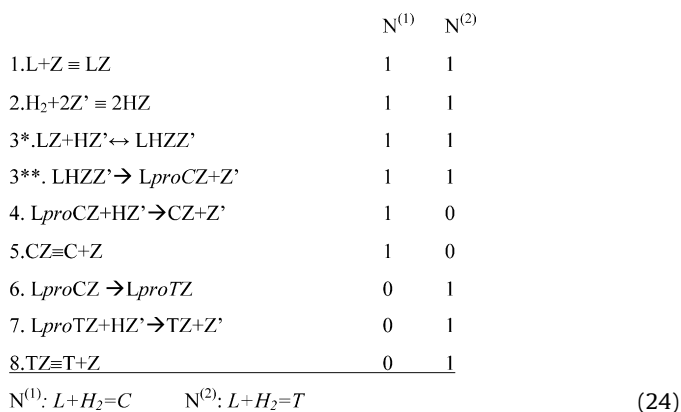
In order to account for experimentally observed kinetic regularities, more specifically zero order in hydrogen for hydrogenation

$$r = r_{+3**} = \frac{(k_{+3*}k_{+3**})/(k_{-3*} + k_{+3**})K_L C_L \theta'_H}{1 + K_C C_C + K_T C_T + K_L C_L (1 + (k_{+3*}\theta'_H)/(k_{-3*} + k_{+3**})(1 + (k_{+3**})/(k_{+4}\theta'_H + k_{+6})(1 + (k_{+5})/(k_{+6}\theta'_H)))} \quad (28)$$

of di-unsaturated acids and their derivatives when *cis/trans* ratio is pressure dependent, conceptually a rate limiting step in hydrogenation should be some sort of isomerization in the adsorbed state. Then the reaction rate will be proportional to the coverage of a certain intermediate. If this coverage is high enough the reaction rate ceases to depend on either hydrogen pressure or conversion.

Similar considerations were previously discussed in the literature in connection with the liquid-phase hydrogenation kinetics obeying zero order dependence in hydrogen and substrate [23–25].

Such isomerization step should precede in the reaction mechanism formation of a half-hydrogenated *pro-cis* intermediate. The mechanism (16) should be then modified



In essence step 3 in mechanism (16) is now split into two steps, one of them describes the formation of a precursor for a half-hydrogenated intermediate (*proC*) involving hydrogen atom addition, while the other accounts for isomerization of this precursor in the adsorbed state.

Surface concentration of the complex LH follows from the steady-state approximation

$$\theta_{LH} = \frac{k_{+3*}}{k_{-3*} + k_{+3**}} \theta_L \theta'_H = \frac{k_{+3*}}{k_{-3*} + k_{+3**}} K_L C_L \theta_V \theta'_H \quad (25)$$

Surface coverage for *pro-cis* and *pro-trans* intermediates is obtained in the same way as above

$$\theta_{LproC} = \frac{k_{+3**}\theta_{LH}}{k_{+4}\theta'_H + k_{+6}} = \frac{k_{+3**}}{k_{+4}\theta'_H + k_{+6}} \frac{k_{+3*}}{k_{-3*} + k_{+3**}} K_L C_L \theta_V \theta'_H \quad (26)$$

$$\theta_{LproT} = \frac{k_{+5}\theta_{LproC}}{k_{+6}\theta'_H} = \frac{k_{+5}}{k_{+6}} \frac{k_{+3**}}{k_{+4}\theta'_H + k_{+6}} \frac{k_{+3*}}{k_{-3*} + k_{+3**}} K_L C_L \theta_V \quad (27)$$

The rate expression for hydrogenation takes the form

When the term $K_L C_L k_{+3*}\theta'_H/(k_{-3*} + k_{+3**})$ is higher than the other terms in the denominator (e.g. the reactant is stronger adsorbed than the products of mono-hydrogenation and the steps 3* and 3** are slower than the ones which subsequently follow) the reaction rate is given by the expression

$$r = k_{+3**} \quad (29)$$

demonstrating zero order dependence in hydrogen pressure and substrate concentration in agreement with the experimental data [16].

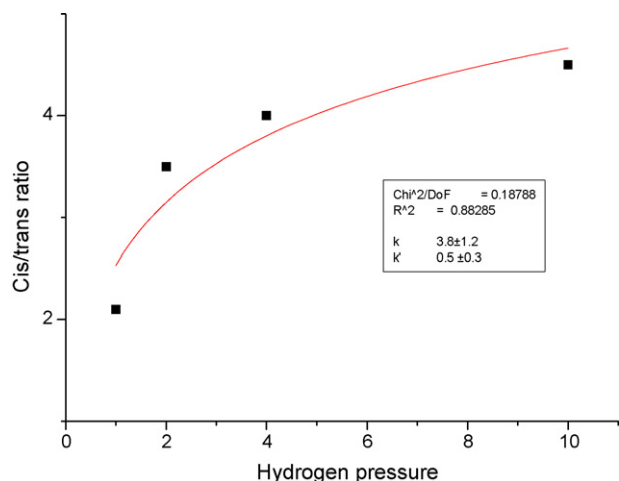


Fig. 1. Effect of hydrogen pressure (bar) on the *cis/trans* methyl oleate ratio. Comparison between experimental data [16] and calculations (Eq. (31)).

Let us now consider the stereoselectivity dependence. It is given by

$$\frac{r_C}{r_T} = \frac{k_{+4}\theta_{LproC}\theta'_H}{k_{+6}\theta_{LproC}} = \frac{k_{+4}\sqrt{K_H C_{H_2}}}{k_{+6}(1 + \sqrt{K_H C_{H_2}})} \quad (30)$$

for example displaying some sort of saturation type behavior with relation to hydrogen pressure/concentration and at the same time independence on conversion in accordance with observations [16]. At this point it is interesting to compare experimental data with calculated ones using Eq. (30). Rearranging (30) we get

$$\frac{C_C}{C_T} = \frac{k\sqrt{P_{H_2}}}{(1 + k'\sqrt{P_{H_2}})} \quad (31)$$

Comparison between experimental and calculated data is given in Fig. 1, showing rather good correspondence. When the *cis/trans* ratio approaches asymptote at high hydrogen pressures, it reflects the ratio between rate constants (e.g. k_{+4}/k_{+6}), and thus the ratio of rates along two routes N(1) and N(2) at complete hydrogen coverage.

Rearranging Eq. (30) we come to

$$\begin{aligned} \ln \frac{r_C}{r_T} &= \ln \frac{k_{+4}^0 \sqrt{K_H C_{H_2}}}{k_{+6}^0 (1 + \sqrt{K_H C_{H_2}})} e^{(\Delta E_6 - \Delta E_4)/RT} \\ &= \ln \frac{k_{+4}^0 \sqrt{K_H C_{H_2}}}{k_{+6}^0 (1 + \sqrt{K_H C_{H_2}})} + \frac{\Delta E_6 - \Delta E_4}{RT} \end{aligned} \quad (32)$$

Fig. 2, showing the effect of temperature on the *cis/trans* methyl oleate ratio for experimental data from ref. [16], demonstrates applicability of Eq. (32). The linear fit for the experimental data, using Eq. (32), gives a degree of explanation, close to 99% and the value of $\Delta E_6 - \Delta E_4$ equal to 11.7 ± 0.7 kJ/mole.

Interestingly enough if the line in Fig. 2 is extrapolated, it can be found that around $T = 373$ K the *cis/trans* ratio will become zero. This result would imply that under these conditions ($p = 4$ bar), at temperatures above 373 K only trans isomers are formed when methyl linoleate is hydrogenated, which is rather unrealistic. Therefore, it can be suggested that mechanism (24) at high temperatures could be more complicated.

In the present study we wanted to present mainly kinetic evidences and discuss models, which are generated from some mechanistic proposals, advanced in the literature. Careful analy-

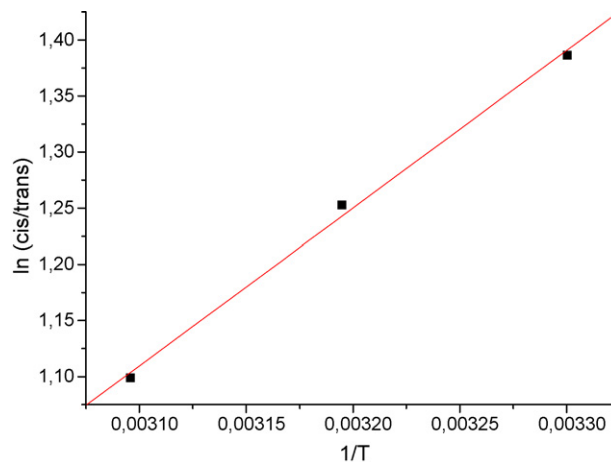


Fig. 2. Effect of temperature on the *cis/trans* ratio in methyl oleate hydrogenation. Data were taken from ref. [16].

sis of kinetic regularities called for an alternative explanation of stereoselectivity in hydrogenation of fatty acids. The key-feature in the proposed mechanism is a formation of a certain precursor for half hydrogenated species, which is isomerized in a rate limiting step. We are not aware about reports in the literature of a surface intermediate with a structure similar to the one considered in the mechanism (24), however, a transition state of such structure with a low activation barrier (only 15 kJ/mole) was reported in reaction of π -bonded ethylene with two hydrogen atoms as the first step in ethylene hydrogenation on Pt(111) surface [26]. Detailed discussion on the nature of the intermediate denoted as LHZZ' is outside of the scope of this paper, and will be a subject of a detailed theoretical study, which is currently in progress and utilizes advanced quantum chemical methods.

4. Conclusions

Analysis of kinetics and *cis/trans* stereoselectivity as a function of reaction parameters (pressure, temperature, conversion) was performed for hydrogenation of fatty acids and their derivatives. Essential kinetic features of this reaction are independence of the reaction rate on hydrogen pressure and conversion, independence of stereoselectivity on conversion as well as an increase in *cis/trans* ratio with pressure increase. Mechanisms proposed in the literature were analyzed and compared with experimental data, showing significant discrepancy. A reaction mechanism is proposed, which is consistent with experimental observations. Kinetic parameters are established for hydrogenation of *cis,cis,9,12* methyl linoleate over Pd/MgO.

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