Vapor-Phase Hydrogenation of Methyl Oleate in the Presence of a Supported Nickel Catalyst

J.-O. LIDEFELT, J. MAGNUSSON and N.-H. SCHÖÖN, Department of Chemical Reaction Engineering, Chalmers University of Technology, S-412 96 Göteberg, Sweden

ABSTRACT

The reaction order with respect to hydrogen was found to be higher than unity and increased with increasing temperature in the vapor-phase hydrogenation of methyl oleate in the presence of a supported nickel catalyst. These findings may be of certain interest in understanding the role that hydrogen plays in fat hydrogenation selectivity. Two reaction mechanisms were discussed to explain the high reaction order. The two reaction models were shown to give the same rate equation.

INTRODUCTION

It is well known that the study of the intrinsic activity and selectivity of a solid catalyst in liquid-phase hydrogenation is rather complicated. This is particularly the case in the fat hydrogenation process. The reaction system will be simplified if the triglycerides are replaced by the corresponding methyl esters. A decisive improvement may be obtained when, as described recently (1,2), the study is performed as a vapor-phase hydrogenation of these methyl esters.

The present study of vapor-phase hydrogenation of methyl oleate is a part of a series of papers dealing with the influence of various factors on the selectivity of fat hydrogenation.

PREVIOUS KINETIC WORK

No work concerning kinetic studies of vapor-phase hydrogenation of methyl oleate has hitherto been reported in the literature. Previous kinetic work referred to here deals with liquid-phase hydrogenation of oleic acid in triglycerides or as a methyl ester.

Wisniak and Albright (3) studied the hydrogenation of cottonseed oil and found that a probable mechanism included a reaction between adsorbed hydrogen on the catalyst and an unsaturated fatty acid in the liquid phase, i.e., an example of the so-called "dive bomb" reaction mechanism. The rate of reaction was found to be proportional to the hydrogen pressure raised to the power 0.6.

Mørk (4) objected to Wisniak's and Albright's mechanism and was of the opinion that both unsaturated fatty acid and hydrogen are adsorbed on the surface of the catalyst and also compete for the same active sites. Despite the fact that Mørk assumed an adsorption of the two reactants, he supposed that the chemical reaction proceeds between adsorbed unsaturated fatty acid and hydrogen molecules in the liquid phase. This reaction mechanism, together with the assumption of Langmuir adsorption, resulted in a rate equation which was first order with respect to hydrogen at low hydrogen pressure and half order at high hydrogen pressure. The half order may explain the value 0.6 found by Wisniak and Albright at high pressure and the first order agrees with the observations made by the same authors at low pressure.

The hydrogenation of methyl oleate in the liquid phase in the presence of a palladium-on-carbon catalyst was shown by Cordova and Harriott (5) to be a half-order reaction with respect to hydrogen.

Hashimoto et al. (6) evaluated data from hydrogenations of cottonseed oil performed by Eldib and Albright (7) and by Wisniak and Albright (3), and found the reaction to be half order with respect to hydrogen in the hydrogenation of linoleic acid and first order in the hydrogenation of oleic acid. Hashimoto presumed that the two reactants are adsorbed on the surface and that the reaction in the first step gives a half-hydrogenated adsorbed complex, which subsequently reacts with adsorbed hydrogen. Under certain simplified assumptions, Hashimoto mentioned that it was possible to derive a rate equation on the basis of this mechanism which may explain the experimental results with respect to the influence of the hydrogen pressure.

Similar results have also been reported by Pihl and Schöön (8), who found that the reaction order with respect to hydrogen increased with increasing temperature. At 190 C, the reaction order was found to be 1.32 in the hydrogenation of oleic acid in cottonseed oil.

EXPERIMENTAL

Hydrogenations

Hydrogenations were carried out with the same equipment and under the same reaction conditions with regard to the mass transfer steps as described previously (2). The same applies to the method of calculating the rate of reaction.

Catalyst

The carrier (alpha-alumina) and the procedure of catalyst preparation were the same as those used in a recent study of the hydrogenation of methyl linoleate in the presence of a supported copper catalyst (2). The catalyst was also conditioned in the same way prior to hydrogenation. The nickel content was 0.1% and the H_2 uptake in the adsorption study was 0.86×10^{-3} mol H/kg catalyst.

Chemicals and Analyes

Methyl oleate and hydrogen were of an analytical grade quality, better than 99.9% purity. An on-line gas chromatograph was used for the analysis in the kinetic experiments.

RESULTS AND DISCUSSION

In all, 68 hydrogenations were performed at three different temperatures (148, 180, and 214 C) and at hydrogen pressures between 3.6 and 56 mbar and at oleate pressures between 0.15 and 1.1 mbar. Nitrogen was in excess and the total pressure was 1 bar (=0.987 atm). The absence of a pore transport limitation was checked by a method developed by Roberts (9).

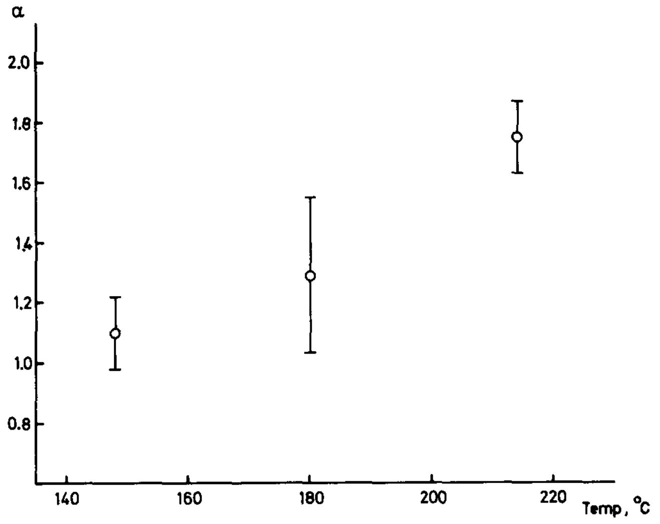

FIG. 1. Reaction order with respect to hydrogen pressure. I corresponds to 95 % confidence limits.

One Example of a Typical Run

In ordinary kinetic studies of fat hydrogenation performed batchwise, it is possible to follow the continuous change of the composition of the fat vs time of reaction. The rate of reaction is calculated indirectly from the slope of the iodine-value curve vs time. It is often possible to determine the rate of reaction for about ten different fat mixtures in one and the same run. The result of the hydrogenation is also easily reported by giving the content of the various fatty acids as a function of time in a diagram. The present vapor-phase hydrogenation study is performed in a perfectly mixed reactor with continuous inflow and outflow. The reactor is, moreover, working at stationary conditions, which means that the composition of the gas in the reactor does not change with time. One important advantage of this technique is the possibility to calculate the rate of reaction directly from a material balance and not via the slope of a curve. Another advantage is the fact that mass and heat transport can be easily eliminated as rate-determining steps of the process. The disadvantage of this technique, is that the rate of reaction is obtained for only one composition of the reactant mixture in every run. It is therefore not easy to summarize the result of the hydrogenation in a diagram. A complete report of the results in tables is not possible either, from a publishing point of view. A typical run will instead be presented.

The conditions of the inflow to the reactor in this run were: partial pressure of hydrogen: 18.52 mbar; partial pressure of methyl oleate: 1.252 mbar; total pressure: 1.003 bar; nitrogen was the only gas component besides hydrogen and methyl oleate; temperature: 179.0 C; and total inlet molar flow rate: 33.87 μ mol/s.

The conditions of the outflow from the reactor were: partial pressure of hydrogen: 18.43 mbar; partial pressure of methyl oleate: 1.154 mbar; partial pressure of methyl stearate: 0.0983 mbar; total pressure: 1.003 bar; degree of methyl oleate conversion: 0.0983/1.252 = 0.0784; and temperature: 179.6 C.

Since the mass of catalyst in the reactor was 2.3160 g, the rate of reaction may be calculated as

$$\text{rate} = \frac{33.87 \times 1.252}{1003} \times 0.0784/2.3160 \times 10^{-3} =$$

$$1.43\ \mu\ \text{mol/s kg cat}$$

Reaction Order with Respect to Hydrogen

The first step in the analysis of kinetic data is often a test of the influence of various factors on the reaction rate (10). A simple power rate equation was fitted to the experimental data in the introductory analysis. This calculation gave a reaction order (α) with respect to hydrogen which was definitely higher than unity (Fig. 1) and increased with increasing temperature. There is a certain risk that this high value of the reaction order was merely a computational artifact; this assumption is based on the phenomena that measurement errors randomly influencing the values of observed rates may be structured and highly correlated by the calculation procedure. In order to prove that the high value of the reaction order was indeed chemically based, some series of experiments were designed, in which all factors except hydrogen pressure was kept constant. Since the inflow composition was controlled, it was not easy to find experiments with reactor and outflow conditions fulfilling these requirements. Therefore, it was necessary to include some series with a low content of methyl linoleate (from another study) in order to obtain sufficient data (Table I). The small content of methyl linoleate may not influence

TABLE I

Influence of Hydrogen Pressure on the Rate of Formation of Methyl Stearate

Temperature (C)	Oleate (mbar)	Linoleate (mbar)	Hydrogen (mbar)	r_S (μ mol/s kg cat)	α
148	0.26	0.07	5.56	0.85	1.26
148	0.26	0.09	3.57	0.43	
180	1.16	0	18.4	1.34	1.31
180	1.17	0	11.5	0.71	
180	0.20	0.04	22.7	0.63	1.26
180	0.20	0.05	11.5	0.30	
214	0.83	0.16	55.1	1.11	1.78
214	0.84	0.17	38.1	0.57	
214	1.07	0	55.1	1.26	1.98
214	1.07	0	26.7	0.30	

the value of the reaction order.

In these particular experiments, where only the hydrogen pressure was varied, the rate of methyl stearate formation may be written as

$$r_S = k\, p_{H_2}^{\alpha} \qquad [1]$$

where k = constant dependent on temperature and on partial pressures of methyl oleate and methyl linoleate, r_S = rate of formation of methyl stearate, p_{H_2} = partial pressure of hydrogen; and α = exponent to be calculated.

Table I confirms the result given in Figure 1 because the reaction order (α) with respect to hydrogen is higher than unity and increases with increasing temperature.

Proposal of a Reaction Mechanism

In previous papers on hydrogenation of methyl fatty esters, the reaction order with respect to hydrogen was found to be unity or less. It was realtively easy to propose a reaction mechanism which accounts for this reaction order. It appears more difficult, however, to find a reaction mechanism where the reaction order is higher than unity and increases with increased temperature. There are two possible mechanisms which can reasonably explain the high reaction order found in this study. In the first one the coverage of the catalyst surface with methyl oleate is assumed to be enhanced in the presence of hydrogen. In the second mechanism, the rate-determining step is assumed to be the hydrogenation of a half-hydrogenated radical of methyl oleate, which is supposed to be formed as an intermediate of the hydrogenation of methyl oleate (11).

I. Enhanced adsorption of methyl oleate in the presence of hydrogen. It is a well known experimental fact (10) for certain systems that, contrary to the Langmuir's theory of adsorption, two different compounds do not compete for the active sites but cooperate instead to give an enhanced adsorption. This adsorption may be explained by the formation of a complex between the two compounds and one or more active sites on the surface. The complex formation may proceed in two steps. One of the compounds is adsorbed in the first step on an active site on the surface. This surface compound then may be regarded as a new active site onto which the second compound is bound in the second adsorption step. If this model of adsorption is applied for the hydrogenation of methyl oleate, we assume that hydrogen is first dissociatively adsorbed on nickel sites. Methyl oleate is then adsorbed on adsorbed hydrogen giving an adsorbed complex compound. The adsorbed hydrogen will thus act as a so-called effective site (12) or hydrogen site. The subsequent hydrogenation is assumed to proceed between this adsorbed complex compound and adsorbed hydrogen atoms. It is also assumed that the reaction between methyl oleate adsorbed on an ordinary nickel site and adsorbed hydrogen atoms proceeds much more slowly. The first step of this mechanism is the formation of hydrogen sites, H·s, which may be written:

$$2s + H_2 \rightleftharpoons 2H{\cdot}s, \quad K_{H_2} \qquad [2]$$

where s is an active site of the nickel surface.

Adsorption of methyl oleate (01) on this hydrogen site gives the adsorbed complex on a nickel site according to:

$$01 + H{\cdot}s \rightleftharpoons 01{\cdot}H{\cdot}s, \quad K_{01}^{H} \qquad [3]$$

Methyl oleate is also adsorbed on a nickel site according to

$$01 + s \rightleftharpoons 01{\cdot}s, \quad K_{01} \qquad [4]$$

The surface reaction may thus be written:

$$01{\cdot}H{\cdot}s + 2H{\cdot}s \rightarrow St + H{\cdot}s + 2s, \quad k_s \qquad [5]$$

Methyl stearate (St) was found not to adsorb at all on the surface.

If the reaction step 5 is assumed to be rate-determining of the hydrogenation, the rate of hydrogenation of methyl oleate is easily derived on the basis of the assumed mechanism above to be

$$r = \frac{k' p_{01}\, p_{H_2}^{3/2}}{(1 + K_{01}^{H} p_{01})(1 + \sqrt{K_{H_2} p_{H_2}})^3} \qquad [6]$$

where

$$k' = k_s K_{01}^{H} K_{H_2}^{3/2}$$

p_{01}, p_{H_2} = pressures of methyl oleate and hydrogen, respectively, and r = rate of hydrogenation.

As may be seen from Equation 6, the limiting reaction order with respect to hydrogen will be 1.5 at high temperature, since K_{H_2} in the denominator decreases with increasing temperature. At low temperature, the limiting reaction order will be zero. It should also be noted that adsorption of methyl oleate and hydrogen on nickel sites were assumed not to compete. This assumption seems to be most probable since methyl oleate is a much larger molecule than hydrogen (13). If methyl oleate and hydrogen compete for the active sites, the term K_{01} p_{01} has to be added to the second parenthesis in the denominator of the rate Equation [6]. It is obviously very difficult to discriminate between these two models. Such a discrimination will be given in a forthcoming paper (14) and will be shown to favor the non-competition model.

It should be observed that the rate-determining step 5 has to include two atoms of hydrogen instead of one, in order to give the desired reaction order 1.5 with respect to hydrogen. If this reaction step, on the other hand, includes one hydrogen molecule instead of two adsorbed hydrogen atoms, the reaction order will still be 1.5 with respect to hydrogen, but the rate equation will be changed in other respects. The exponent 3 in the denominator is changed to the value one. It was easily shown by regression analysis of the kinetic data, that the mechanism including one hydrogen molecule was less probable in comparison to that one given by Equation 5. This alternative mechanism, moreover, resulted in a change of the meaning of k' to $k' = k_s K_{01}^{H}\, K_{H_2}^{1/2}$. The temperature dependency of k_s calculated from this equation was found to be negative, which also decreases the probability of this second mechanism.

II. Hydrogenation of a half-hydrogenated methyl oleate radical as a rate-determining step. Bond et al. (15), who studied the kinetics of the hydrogenation of acetylenic

TABLE II

Kinetic Parameters in the Rate Equation for Methyl Oleate Hydrogenation in the Vapor Phase

Number of experiments	Temperature (C)	k′ mol (kg cat s)$^{-1}$ bar$^{-5/2}$	$K_{01}^{H} \times 10^{-3}$ (bar^{-1})	K_{H_2} (bar^{-1})	$k_s \times 10^6$ (kg cat s)$^{-1}$
26	148	818 ± 403	25.1 ± 15.6	284 ± 120	6.81 ± 6.36
24	180	37.7 ± 13.0	4.1 ± 2.1	85.5 ± 30	11.63 ± 8.54
18	214	2.97 ± 1.40	2.3 ± 1.7	16.8 ± 6.7	18.75 ± 19.90

The K_{H_2} values are from separate adsorption measurements to be published (16). All confidence limits are calculated at the 95% level.

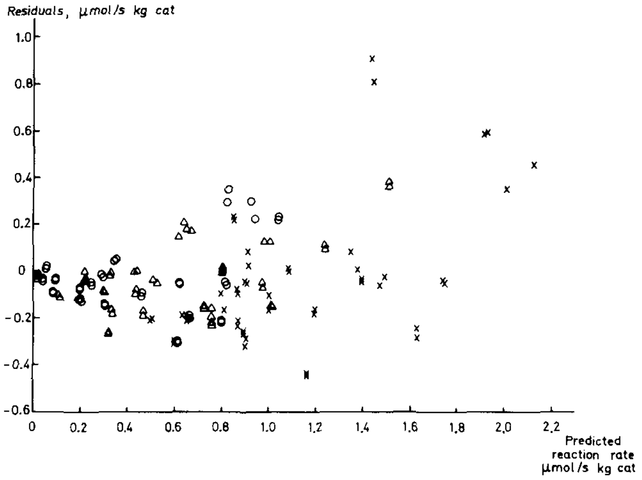

FIG. 2. Residuals of reaction rate vs predicted reaction rate: △ runs at 148 C, X runs at 180 C, ○ runs at 214 C.

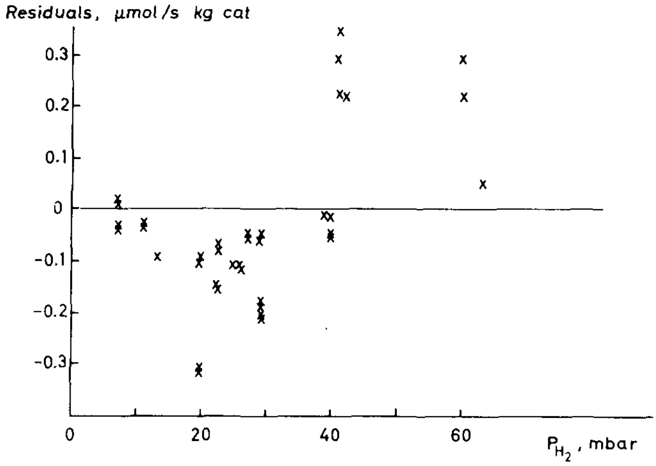

FIG. 3. Residuals of reaction rate vs hydrogen pressure at 214 C.

compounds, found that the reaction order with respect to hydrogen was 1.5 when the reaction was performed in the presence of a platinum catalyst. They found that the high reaction order could be explained by the assumption that the hydrogenation of a half-hydrogenated radical was the rate-determining step. It should be noted that Allen and Kiess (11) proposed as early as 1956 that a half-hydrogenated radical could be formed as an intermediate in fat hydrogenation. Hashimoto et al. (6) also derived a rate equation on the basis of Allen and Kiess' mechanism, as mentioned above, giving half-order and first-order dependencies with respect to hydrogen.

In the present study, the formation of the half-hydrogenated methyl oleate radical is given by Equation 3. This equation is the net equation of the adsorption process of methyl oleate as given by Equation 4 and the reaction

$$01{\cdot}s + H{\cdot}s \rightarrow 01{\cdot}H{\cdot}s + s \qquad [7]$$

Moreover, Equation 5 shows the reaction between this radical and two adsorbed hydrogen atoms. If this reaction is assumed to be the rate-determining step, the rate of the process will be described by Equation 6. The two reaction mechanisms proposed here will thus result in the same rate equation and it is thus impossible to discriminate between them by kinetic experiments. From a chemical point of view, it may be easier to accept the formation of a half-hydrogenated radical than the existence of a hydrogen site which is active in the adsorption of methyl oleate on the surface. Therefore, the hydrogenation of methyl oleate will henceforth be discussed in terms of the radical mechanism.

It should be noted that Bond (15) proposed the rate-determining step to be a reaction between the half-hydrogenated radical and one hydrogen molecule. The disadvantages of this alternative mechanism were discussed under section I and this mechanism was found to be less possible in comparison to the mechanism including two adsorbed hydrogen atoms of the rate-determining step 5.

Estimation of Kinetic Parameters

There are two parameters, k′ and K_{01}^{H}, to be estimated from the kinetic experiments. The equilibrium constant K_{H_2} was separately estimated from adsorption measurements reported elsewhere (16). Since the rate of reaction may be calculated directly from the difference of inflow and outflow conditions of the reactor (see above), the constants k′ and K_{01}^{H} were easily calculated by regression analysis. The calculation was performed separately for each temperature. The results are given in Table II.

A residual analysis in Figure 2, where the difference between the experimental and predicted reaction rates is plotted vs predicted values, shows that the rate equation 6 may be accepted for statistical reasons. There is some doubt concerning the residuals at high reaction rates, however, so the goodness of fit should be checked at high pressure and high temperature. Since the hydrogen pressure is a key variable in the proposed mechanism, the residuals of the reac-

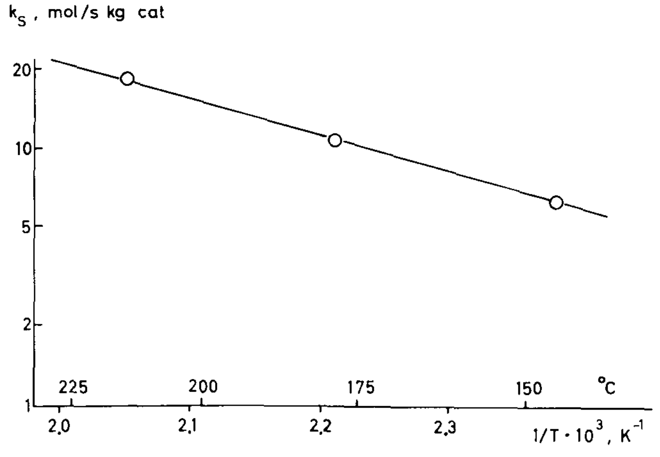

FIG. 4. The rate constant k_s vs 1/T.

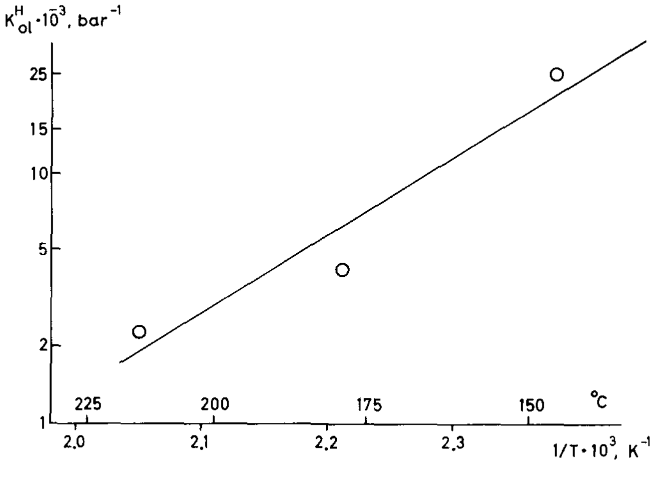

FIG. 5. The equilibrium constant K_{01}^{H} vs 1/T.

tion rate vs the hydrogen pressure were checked at first hand. As can be seen from Figure 3, there is a certain trend of the residuals. It is obviously rather difficult to predict correct values with rate Equation 6 at large values of p_{H_2}. The explanation (cf. Table I and Fig. 1) is that the experimentally found reaction order with respect to hydrogen was higher than 1.5 at the highest temperature. The limiting value of the reaction order was 1.5 in rate Equation 6 and it is therefore reasonable to assume that the predicted values are too low at high hydrogen pressure. It is possible to formulate an alternative reaction model giving a limiting reaction order of 2.0. This model presupposes that the adsorbed half-hydrogenated radical reacts with hydrogen adsorbed on effective sites. This reaction model was, however, rejected for chemical reasons.

The temperature dependence of k_s and K_{01}^{H} was calculated from Figures 4 and 5, respectively, which show that these dependencies agree well with the Arrhenius and van't Hoff laws. The activation energy E and the enthalpy of formation of the half-hydrogenated methyl oleate radical were estimated according to a weighted linear least squares regression calculation giving $E = (26.5 \pm 0.9)$ kJ/mol and $-\Delta H_{01}^{H} = (67.3 \pm 41)$ kJ/mol. The limits are 95% confidence limits.

The equilibrium constant K_{01}^{H} adsorption of the half-hydrogenated methyl oleate radical given in Table II may be compared with the adsorption equilibrium constant K_{01} for the adsorption of methyl oleate. From a recent study by Lidefelt (17), the value of this constant was found to be K_{01}: 1.34×10^3, 0.27×10^3, and 0.06×10^3 bar^{-1} at 148, 180 and 214 C, respectively. These values may be compared with the values 25.1×10^3, 4.1×10^3 and 2.3×10^3 bar^{-1} for K_{01}^{H} at the corresponding temperatures. It is obvious from equilibrium considerations that methyl oleate is more readily adsorbed as a half-hydrogenated radical than as methyl oleate. Comparing the adsorption enthalphy of methyl oleate given by Lidefelt (17) ($-\Delta H_{01} = (75 \pm 6)$ kJ/mol) with the adsorption enthalpy of the adsorbed half-hydrogenated radical, we find that they are of the same order of magnitude.

It may finally be noted that the activation energy is rather low. We intend to discuss this circumstance in more detail in connection with the results from a similar study concerning the hydrogenation of methyl linoleate to be published.

ACKNOWLEDGMENT

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