

Vapor-Phase Hydrogenation of Methyl Linoleate in the Presence of a Supported Copper Catalyst

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ABSTRACT

Methyl linoleate was hydrogenated in the vapor phase in the presence of a copper-on-alpha alumina catalyst. The kinetics of the reaction could be formulated with a Eley-Rideal mechanism including the reaction between chemisorbed methyl ester and hydrogen in the gas phase. The absorption coefficients in the rate equation were based on separately performed adsorption studies recently reported.

INTRODUCTION

The intrinsic properties of a catalyst are closely related to its surface properties. These characteristics give the limits of attainable selectivity in a catalytic reaction. The effect of these surface properties is screened, however, in various ways owing to the presence of transport resistances giving rise to important gradients of concentration close to the outer surface and within the pores of the catalyst.

These complications are well known from the study of the hydrogenation of vegetable oils. It is rather difficult to begin a study of catalyst properties using such a complicated reaction system as that involved in fat hydrogenation. Many studies have therefore been performed with methyl esters of different fatty acids. However, this reaction system may also be too complicated to use in a basic study.

In the present and following papers, the properties of the catalyst were studied in vapor-phase hydrogenations of fatty acid methyl esters. The advantages and disadvantages of this technique are discussed by Lidelfelt (1). The aim of these studies is to shed new light on the selectivity property of the catalyst in order to understand the influence of various factors on the reaction mechanism. The first paper in the series concerns vapor-phase hydrogenation of methyl linoleate in the presence of a supported copper catalyst. The kinetics of this reaction has not previously been reported in the literature. Moreover, hydrogenation of methyl esters of fatty acids in the vapor phase has hitherto been of little interest (2).

EXPERIMENTAL

Hydrogenation

The hydrogenations were performed in a specially designed so-called gradient-free reactor. The reactor equipment and the measuring technique are discussed elsewhere (1). The reactor was a perfectly mixed type reactor, which means that the reaction rate can be calculated directly from the difference between the inlet and outlet reactant partial pressures according to the equation

$$r = q(p_{in} - p_{out})/RTW \quad [1]$$

where r = reaction rate, mol/s kg catalyst; q = volumetric flow rate, dm³/s; p_{in} , p_{out} = partial pressures of methyl linoleate in inflow and outflow of the reactor, respectively, in bar (1 bar = 0.9869 atm); R = 0.0831 bar dm³/mol K; T = temperature, K; and W = mass of catalyst, kg.

Equation 1 presupposes that the change in volume due to the reaction can be neglected. Moreover, the stoichiometric coefficient of the reactant is assumed to be equal to unity. All hydrogenations were performed in the presence of an excess of nitrogen. The reactor contained 160 pellets of catalyst, corresponding to 7.68 g of catalyst. The total volumetric gas flow rate was $q = 0.3 \times 10^{-3}$ dm³/s.

The methyl linoleate used was of analytical grade quality with a purity better than 99.9%.

Catalyst

The carrier of the catalyst was 4 × 2 mm alpha-Al₂O₃ cylinders with relatively low BET-surface area and low content of acid groups in order to minimize the tendency of cracking during the reaction. The catalyst preparation technique is described elsewhere (3).

The metal surface area was determined by hydrogen adsorption in a static vacuum apparatus. This method is well established for nickel but its suitability for copper seems to be disputable. The total metal content was measured by an atomic absorption spectrometer. The properties of the catalyst are given in Table I.

TABLE I

Properties of the Catalyst

BET surface	35 m ² /g
Metal content	0.1 %
H ₂ uptake	0.356 × 10 ⁻⁶ mol H/g
Dispersion	2.4 %
Pore volume	0.21 cm ³ /g
Average pore diameter	1200 Å

The influence of the pore transport was estimated by using methods developed by Roberts et al. (4). Relevant parameters in Roberts' method (Φ , E , and K_{PAS}) were estimated to be $\Phi = 0.01-0.16$, $E = 700-800$, and $K_{PAS} = -0.6-0.1$. These values showed that the pore transport is not a limiting step of the process. The value of E is out of the range calculated by Roberts due to the large difference between hydrogen and linoleate diffusivities and partial pressures. However, the effectiveness factor η is nearly independent of E when η is small and E is large and the graphs in (4) give acceptable estimates of the effectiveness factor.

Analysis

All analyses of the methyl esters were performed with an on-line gas chromatograph Perkin Elmer F11 using a Supelco 10% SP-2330 on 100/120 Chromosorb W 17 E 1-1851 column.

RESULTS AND DISCUSSION

Extent of the Study

Hydrogenations (35 runs) were performed at three different temperatures (147, 178, and 213 C) and at various hydrogen pressures between 0.04 and 0.13 bar and linoleate pressures ranging from 0.27 to 1.1 mbar in the inflow and 0.16 to 0.8 mbar in the outflow. Nitrogen was present in excess and the total pressure was 1 bar in all runs. The mixing was very intense so that the concentration differences across the film surrounding the outer surface of the catalyst may be neglected (1). The same is valid for the pore transport limitations discussed under Experimental.

Discrimination between Kinetic Models

In the separate study of the adsorption properties of methyl linoleate and methyl oleate on the catalyst used, Lidfelt (3) found that the methyl esters are relatively strongly adsorbed on the surface. Similar studies by Magnusson (5), where the formation of HD from protium (H_2) and deuterium (D_2) was studied in the presence of the same catalyst, showed that hydrogen was weakly adsorbed on the surface. From these observations it is obvious that hydrogenation of methyl linoleate may occur either between chemisorbed methyl linoleate and chemisorbed hydrogen or between chemisorbed methyl linoleate and hydrogen in the gas phase. Supposing Langmuir adsorption, where one active site on the surface takes part in the adsorption of methyl linoleate and supposing also the surface reaction controlling the process, three different rate equations may then be possible to describe the rate of the surface process.

I. The reaction between chemisorbed methyl linoleate and hydrogen in the gas phase is assumed to be the rate-determining step (so-called Eley-Rideal mechanism):

$$r = \frac{k_s K_{lin} P_{lin} P_{H_2}}{1 + K_{lin} P_{lin} + K_{ol} P_{ol}} \quad [2]$$

where r = rate of reaction, mol/s kg cat; k_s = rate constant of the surface reaction, mol/s kg cat; K_{lin} = adsorption equilibrium constant of methyl linoleate, bar^{-1} ; K_{ol} = adsorption equilibrium constant of methyl oleate, bar^{-1} ; and P_{lin} , P_{ol} , P_{H_2} = partial pressures of methyl linoleate, methyl oleate, and hydrogen, respectively.

II. The reaction between chemisorbed methyl linoleate and two chemisorbed hydrogen atoms is assumed to be the rate-determining step:

$$r = \frac{k_s K_{H_2} K_{lin} P_{H_2} P_{lin}}{(1 + K_{ol} P_{ol} + K_{lin} P_{lin})^2} \quad [3]$$

where K_{H_2} = adsorption equilibrium constant of hydrogen, bar^{-1} .

The adsorption term of hydrogen has not been included in the denominator of Equations 3 and 4, since this term is negligible compared to the other terms.

III. The reaction between chemisorbed methyl linoleate and one chemisorbed hydrogen atom giving a half-hydrogenated radical, is assumed to be the rate-determining step:

$$r = \frac{k_s \sqrt{P_{H_2} K_{H_2}} K_{lin} P_{lin}}{(1 + K_{ol} P_{ol} + K_{lin} P_{lin})^2} \quad [4]$$

The formation of a half-hydrogenated radical as an intermediate step in the hydrogenation was proposed as early as 1956 by Allen and Kiess (6) as a possible mechanism for the fat hydrogenation.

The rate of reaction was obtained from Equation 1 at each run. The partial pressures of the different components were easily calculated from the analysis of the outflow gas. The experimental result showed that the reaction order with respect to the hydrogen pressure was close to unity, thus excluding the reaction model III. The formation of the half-hydrogenated radical may not be a rate-determining step of the process. In discriminating between models I and II, the two rate equations were fitted to the experimental data using standard regression analysis without any weighting factors. Since the constants K_{lin} and K_{ol} are known from the adsorption study, referred to above (3), this fit was easily performed. The predicted rate of reaction according to the two models and the corresponding experimental values were then used as a basis for the calculation of the probability of the models according to a theory given by Box and Hill (7). Starting with the assumption that the two models have equal probability ($P_I = P_{II} = 0.5$) before the first hydrogenation, we found that after eleven runs at 147 C and 12 runs at both 178 C and 213 C, the probability for the rate model I was $P_I = 1.000$ in all the runs. The model including hydrogen from the gas phase is thus the most probable one of the three proposed models. It should, however, be noted that the reaction including adsorbed hydrogen may proceed simultaneously but at a much lower rate.

Estimation of the Rate Constant in Model I

Since model I has only one single parameter (k_s) to be estimated, the calculation seems to be rather easy. We should, however, realize that if the two constants K_{lin} and K_{ol} , obtained in the separate adsorption study, are not correctly determined, it is not possible to compensate this error effectively with only one adjustable parameter. A good estimation of k_s thus presupposes that the same adsorption conditions were prevailing in the hydrogenations as in the separate adsorption study.

Due to strong correlation between k_s and K_{lin} in model I, the regression analysis gives in the first place a value of $k_s K_{lin}$. The results of the kinetic study are given in Table II along with the values of the adsorption equilibrium constants used in the calculation.

Adequacy of Model I

The adequacy of the rate equation was tested with a residual analysis given in Figure 1, where the difference between experimental and predicted values of the reaction rate is plotted vs the predicted reaction rate. As seen from Figure 1, the residuals are randomly distributed along the axis of the predicted values, which means that the rate equation may be accepted from a statistical point of view. In an additional calculation, the equilibrium coefficients K_{ol} and K_{lin} were also fitted to the experimental values instead of being fixed. The rate constants were found to be $k_s \times 10^6 = 2.59, 9.78$ and $216 \text{ mol s}^{-1} \text{ kg}^{-1} \text{ bar}^{-1}$ at 147, 178, and 213 C, respectively. The difference between these values and the ones given in Table II is relatively small. A residual analysis of this calculation is given in Figure 2, showing a fit as good as that in Figure 1. This result strongly sup-

TABLE II

Rate Constant k_s for Vapor-Phase Hydrogenation of Methyl Linoleate in the Presence of a Supported Copper Catalyst

Number of experiments	Temperature (C)	$k_s K_{lin}$ mol s ⁻¹ kg ⁻¹ bar ⁻²	$k_s \times 10^6$ mol s ⁻¹ kg ⁻¹ bar ⁻¹	$K_{lin} \times 10^{-3}$ bar ⁻¹	$K_{o1} \times 10^{-3}$ bar ⁻¹
11	147	0.188 ± 0.011	1.71 ± 1.09	110 ± 70	207 ± 82
12	178	0.144 ± 0.013	9.69 ± 3.55	14.9 ± 5.3	19.5 ± 5.4
12	213	0.133 ± 0.072	60.5 ± 32.9	2.2 ± 0.4	2.0 ± 0.4

K_{lin} and K_{o1} are derived from separate adsorption measurements (3). All confidence limits are calculated at the 95% level.

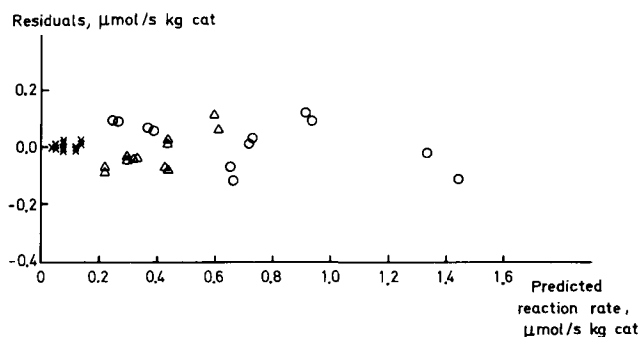


FIG. 1. Residuals vs predicted reaction rate when the adsorption equilibrium constants in the rate equation are calculated from independent adsorption measurements: X runs at 147 C, Δ runs at 178 C, ○ runs at 213 C.

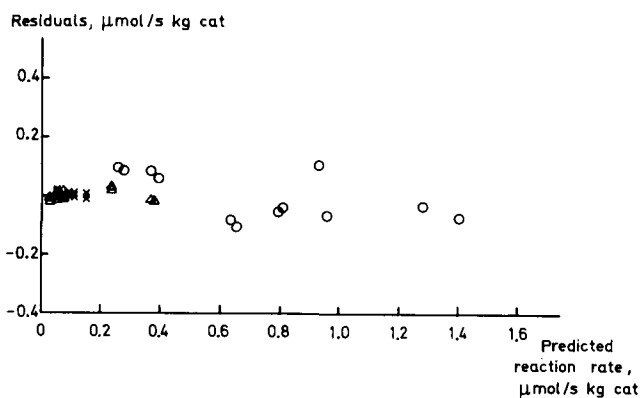


FIG. 2. Residuals vs predicted reaction rate when the adsorption equilibrium constants are calculated from the rate experiments: X runs at 147 C, Δ runs at 178 C, ○ runs at 213 C.

ports the fact that the rate equation may be accepted not only statistically, but also chemically.

Chemical Aspects of Model I

The values given in Table II were calculated for each temperature separately. The influence of temperature on k_s is plotted vs $1/T$. Figure 3 shows that the rate constant follows the Arrhenius law and the activation energy is calculated to be 92.1 ± 5.5 kJ/mol (with 95% confidence limits).

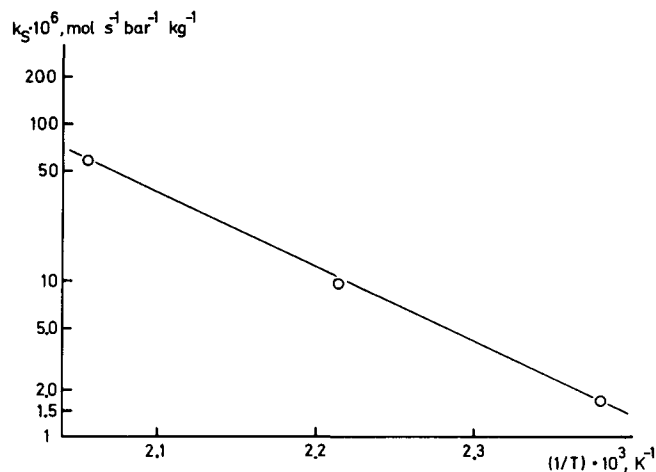


FIG. 3. The influence of temperature on the rate constants k_s .

No methyl stearate was formed in the hydrogenations of methyl linoleate, which confirms the well known fact that methyl oleate reacts very slowly in the presence of a copper catalyst. Since the result in Table II indicates that the surface coverage of methyl linoleate and methyl oleate is of the same order of magnitude, it is obvious that the different activity of copper with respect to methyl linoleate and methyl oleate in the hydrogenations may be explained by the fact that quite different reaction mechanisms are operating. Possibly, the hydrogenation of methyl linoleate contrary to that of methyl oleate includes the formation of a reactive intermediate with conjugated double bonds.

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