# The Role of Hydrogen in the Selectivity
# of Vapor-Phase Hydrogenation of Methyl Linoleate

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## ABSTRACT

Methyl linoleate was hydrogenated in the vapor phase in the presence of a nickel on alpha-alumina catalyst. A reaction mechanism was proposed to explain the fact that the selectivity is influenced by the hydrogen pressure. A rate equation was derived based on the mechanism and the rate constant was evaluated from kinetic experiments. The adsorption coefficients in the rate equation were based on separately performed adsorption studies recently published.

## BACKGROUND TO THE STUDY

It is well known that the hydrogen concentration plays an important role in fat hydrogenation selectivity. Low concentration of hydrogen is known to give high selectivity, whereas high concentration will result in low selectivity. Applied to the hydrogenation of linoleic acid in glycerides, this means that the amount of oleic acid, elaidic acid, and other monoenoic acids formed during the hydrogenation decreases with increasing hydrogen concentration. This selectivity phenomenon does not seem to be completely elucidated and therefore it may be difficult to find the best catalyst composition, pore size distribution and particle size with respect to selectivity.

From a kinetic point of view, the different influence of hydrogen on the hydrogenation of linoleic acid and oleic acid was, in early papers, attributed to rate constants, dependent on the hydrogen concentration. Thus, the rate equation did not explicitly include any factor describing the influence of hydrogen pressure or concentration. In more recent work, the hydrogen concentration was included in the rate equation, and the reaction order with respect to hydrogen was evaluated. The influence of hydrogen on the selectivity could then be described as a difference in the reaction orders with respect to hydrogen between linoleic acid hydrogenation and oleic acid hydrogenation.

This description of the influence of the hydrogen concentration rather correlates data than explains the phenomenon. Various attempts have been made to explain the role of hydrogen as a selectivity factor. These attempts can be divided into two main groups.

In the first group, the different influence of hydrogen in the two consecutive hydrogenation reactions originates from different properties of the surface reactions. This means that the reaction mechanism might be quite different for hydrogenation of linoleic acid and oleic acid. It also follows from this explanation that it should be possible to change the hydrogen influence on the selectivity by changing the surface composition of the catalyst (1).

In the second group of explanations, it was possible to show that a slow diffusional transport in porous catalysts may result in a hydrogen-dependent selectivity. The hydrogen influence in this case may be altered by a simple change in the pore size of the catalyst (2).

There are additional physical steps not yet discussed in connection with fat hydrogenation, which may influence

the selectivity in a similar way as the pore diffusion. It is known (3) from other gas-liquid processes, occurring in the presence of a finely divided solid catalyst, that an enhanced absorption of the gas component was obtained owing to the fact that very small catalyst particles penetrated the diffusion liquid film surrounding the gas bubbles. The process in this film is thus no longer a pure physical transport step but is coupled with the chemical reaction on the catalyst surface. If the fraction of finely divided catalyst and its activity are high, the chemical reaction will proceed exclusively in this diffusion film. This extreme variant may be promoted if the equilibrium solubility of the gas component is low (3). It is obvious that this type of complication is also possible in fat hydrogenation. It is furthermore obvious that the selectivity, for the same reasons as for the pore transport limited process, may be influenced by the hydrogen concentration. A possible way to decrease the influence of hydrogen concentration on the selectivity is then to choose a particle size much larger than the diffusion film thickness.

In the present study, methyl linoleate was hydrogenated in the vapor phase in the presence of a supported nickel catalyst. The reaction condition chosen made it possible to eliminate the interaction of limiting physical steps.

Since the kinetic measurements were performed in a so-called perfectly mixed reactor giving the rate of reaction very directly, this reaction equipment may be suitable for obtaining precise kinetic information concerning the chemical reaction steps. Complementary knowledge of the adsorption properties of the reactants on the present catalyst (4), as well as of the kinetics of the hydrogenation of methyl oleate (5), was necessary to interpret the results.

## PREVIOUS WORK

Important contributions to the reaction mechanism of fat hydrogenation have been made by Blekkingh (6) and by Allen and Kiess (7) among others, who introduced the theory of the half-hydrogenated radical (often referred to as the Horiuti-Polanyi mechanism [8]) as a possible explanation of the isomerization reactions. This mechanism was found by Frankel and Dutton (9) to have been proposed already by Hilditch and Vidyarthi (10). Hilditch (11) was also the first one to assume that selective hydrogenation of dienoic and trienoic acid glycerides was attributed to the formation of conjugated double bonds as an intermediate (see also 6, 7, 12, 13). In addition to these theories, it is generally accepted that the adsorption on the catalyst increases with an increasing number of double bonds in the fatty acid, thus providing explanation of the fact that dienoic acids are hydrogenated in preference to monoenoic acids.

There are only a few papers concerning the influence of hydrogen concentration in fat hydrogenation from a mech-

anistic point of view. Hashimoto et al. (14) evaluated experimental results from Eldib and Albright (15) and from Wisniak and Albright (16) on cottonseed oil hydrogenations. They found the reaction to be half order with respect to hydrogen in the hydrogenation of linoleic acid and first order in the subsequent hydrogenation of oleic acid. From these findings, they tried to formulate a rate equation based on the half-hydrogenated radical mechanism. Hashimoto suggested the same reaction mechanism to be valid for both linoleic acid hydrogenation and oleic acid hydrogenation. It is thus interesting to note that this assumption may result in different reaction orders with respect to hydrogen for the two reactions.

The possibility of explaining the hydrogen effect by the influence of a slow diffusion step has attracted more interest. Hell et al. (2) showed that the presence of a slow pore diffusional transport may give rise to a hydrogen dependent selectivity. The surface reaction rate was supposed to be first order with respect to hydrogen in the two consecutive reactions. The apparent difference in reaction orders due to slow pore transport was found to be at the most 0.45.

Hell based his study on a simple power rate equation. A more sophisticated study was performed by Tsuto et al. (17), who found that decreased selectivity with increasing hydrogen concentration may be explained by a combined effect of nonequilibrium adsorption and a slow pore transport.

## 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 (5). 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 oleate (5). 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 $0.86 \cdot 10^{-3}$ mol H/kg catalyst.

### Chemicals and Analyses

Methyl linoleate, 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

### Extent of the Study

In all, 69 runs were performed at three temperatures, 148, 180, and 214 C and at methyl linoleate pressures from 0.012 to 0.54 mbar, methyl oleate pressures up to 0.85 mbar, hydrogen pressures from 0.5 to 55 mbar in an excess of nitrogen. All pressures refer to the conditions in the reactor. The total pressure was 1 bar (equal to 0.987 atm).

### Influence of Hydrogen Pressure on the Selectivity

It is seen from the results in Table I that the hydrogen effect on the selectivity, well known from fat hydrogenation practice, also characterizes the vapor-phase hydrogenation of methyl linoleate. Since transport-limiting steps are eliminated, it may be concluded that this property really is an intrinsic property referred to the surface chemistry of the process. In Table I, the differential selectivity, S, is defined as the ratio between the rate of methyl linoleate hydrogenation and methyl oleate hydrogenation (18).

### Reaction Order with Respect to Hydrogen

It was found in a recent study of methyl oleate hydrogenation (5) that the reaction order with respect to hydrogen was higher than unity and increased with increasing temperature. From the selectivity properties found above in the hydrogenation of methyl linoleate, the corresponding reaction order for the hydrogenation of methyl linoleate is expected to be lower. From Figure 1, it is also seen that the reaction order in question is less than unity at 148 and 180 C and increases with increasing temperature.

### Proposal of a Reaction Mechanism

In proposing a reaction mechanism for the hydrogenation of methyl linoleate, it is necessary to refer first to the mechanism for the hydrogenation of methyl oleate. The very high reaction order with respect to hydrogen found in

**TABLE I**

Influence of Hydrogen Pressure on the Differential Selectivity (S) in Hydrogenation of Methyl Linoleate

| Temperature (C) | Linoleate (mbar) | Oleate (mbar) | Hydrogen (mbar) | $r_{lin}$ $\dfrac{\mu\ mol}{s\ kg\ cat}$ | $r_{ol}$ $\dfrac{\mu\ mol}{s\ kg\ cat}$ | $S = \dfrac{r_{lin}}{r_{ol}}$ |
|---|---|---|---|---|---|---|
| 148 | 0.019 | 0.083 | 1.86 | 2.54 | 0.33 | 7.7 |
|  | 0.022 | 0.085 | 1.24 | 2.46 | 0.20 | 12.3 |
| 180 | 0.12 | 0.63 | 22.1 | 11.75 | 2.25 | 5.2 |
|  | 0.15 | 0.63 | 13.8 | 10.42 | 0.84 | 12.4 |
| 214 | 0.12 | 0.62 | 41.3 | 8.56 | 1.11 | 7.7 |
|  | 0.13 | 0.63 | 28.6 | 7.94 | 0.57 | 13.9 |
|  | 0.15 | 0.62 | 20.0 | 7.59 | 0.37 | 20.5 |

FIG. 1. Reaction order with respect to hydrogen in methyl linoleate hydrogenation in vapor phase at different temperatures. The confidence limits are at the 95% level.

methyl oleate hydrogenation was proposed (5) to be explained by a reaction mechanism, where the rate-determining step consists of the reaction between a half-hydrogenated methyl oleate radical and two hydrogen atoms. Both the species were assumed to be adsorbed on the surface of the catalyst. It is most probable that methyl linoleate forms a similar adsorbed half-hydrogenated radical. In addition to this radical formation on the surface, it is obvious that methyl oleate and methyl linoleate are also directly adsorbed on the nickel surface.

Contrary to hitherto accepted opinion, recent adsorption studies showed (4) that methyl oleate and methyl linoleate are about equally adsorbed on the nickel surface. There are also indications (5) that the adsorbed hydrogenated radical of methyl oleate is more readily formed than the adsorbed methyl oleate on the nickel surface. It is therefore reasonable to assume that methyl linoleate behaves in the same way with respect to a preferable formation of the adsorbed radical. Despite these similarities in the adsorption properties of the two methyl esters, methyl linoleate was shown to react more rapidly than methyl oleate, especially at low hydrogen pressure. This result indicates that there may exist an alternative and more favorable reaction path for methyl linoleate. It is reasonable to assume that methyl linoleate adsorbed on nickel sites is transformed, with the assistance of adjacent adsorbed hydrogen, to adsorbed methyl linoleate containing conjugated double bonds. This compound thereafter reacts with adsorbed hydrogen forming adsorbed methyl ester of monoenoic acid, which desorbs or reacts further forming a half-hydrogenated radical. The parallel hydrogenation of methyl linoleate via the formation of a half-hydrogenated radical may proceed at the same rate as the hydrogenation of the methyl ester of the monoenoic acid, since the same mechanism is operating. This path of hydrogenation may be neglected compared to the one including the conjugated double bond. This was obvious from the facts that the selectivity in methyl linoleate hydrogenation is of the magnitude of 10 and that the reaction order with respect to hydrogen is much lower than 1.5 found in the hydrogenation of methyl oleate (5). At high hydrogen pressure or low temperature corresponding to nonselective conditions, the

direct hydrogenation of the adsorbed half-hydrogenated radical of methyl linoleate may instead be the rate-determining reaction.

From the discussion above, the reaction mechanism of methyl linoleate hydrogenation may be formulated according to the following scheme.

Hydrogen is dissociatively adsorbed on nickel sites (s) according to

$$2s + H_2 \rightleftharpoons 2H{\cdot}s, \quad K_{H_2} \qquad [1]$$
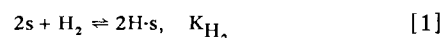
Owing to the fact (5), that methyl oleate and methyl linoleate are adsorbed on the nickel catalyst with about the same bonding strength, it is reasonable to assume that only one carbon double bond is involved in the adsorption of methyl linoleate. The adsorption of methyl linoleate (Lin) is therefore assumed to include only one active nickel site giving

$$Lin + s \rightleftharpoons Lin{\cdot}s, \quad K_{lin} \qquad [2]$$
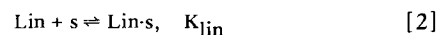
The conjugation may proceed rapidly in the presence of adsorbed hydrogen. This reaction may be written:

$$Lin{\cdot}s + n(H{\cdot}s) \rightarrow Lin(conj){\cdot}s + n(H{\cdot}s) \qquad [3]$$
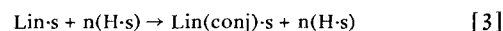
where Lin(conj) corresponds to conjugated methyl linoleate. The number (n) of participating hydrogen atoms is not known. The formation of conjugated methyl linoleate may possibly goes through a half hydrogenated radical which is omitted in Equation 3.

The hydrogenation of methyl linoleat may then proceed according to

$$Lin(conj){\cdot}s + 2H{\cdot}s \rightarrow Ol{\cdot}s + 2s, \quad k_l \qquad [4]$$
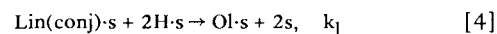
This reaction may proceed in more than one step. The observed reaction order with respect to hydrogen was found to be less than unity and approached this value on increasing the temperature to ca. 220 C. In order to obtain this kinetic behavior, the rate-determining step must include two adsorbed hydrogen atoms and Equation 4 formally fullfil this requirement. It should be pointed out that methyl linoleate may also react directly to methyl stearate via a shunt reaction. The extent of this shunt reaction was estimated by comparing the total rate of methyl stearate formation with the rate of this formation from methyl esters of monoenoic acids calculated from kinetic data of hydrogenation of methyl oleate given in a recent paper (5), with corrections for the influence of the competitive adsorption of methyl linoleate. It was obvious from this calculation that the shunt reaction can be neglected under the reaction conditions in the present study.

The adsorbed methyl ester of monoenoic acid (Ol·s) formed in reaction 4 is in equilibrium with this methyl ester in the gas phase according to
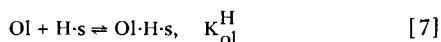
$$Ol{\cdot}s \rightleftharpoons Ol + s, \quad K_{ol} \qquad [5]$$
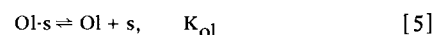
or reacts further with one adsorbed hydrogen atom giving the half hydrogenated radical according to

$$Ol{\cdot}s + H{\cdot}s \rightarrow Ol{\cdot}H{\cdot}s \qquad [6]$$

The equilibrium between the monoenoic acid methyl ester in the gas phase and the adsorbed radical may, moreover, be written:

$$Ol + H \cdot s \rightleftharpoons Ol \cdot H \cdot s, \quad K_{ol}^{H} \qquad [7]$$

The corresponding equilibrium for methyl linoleate is subsequently

$$Lin + H \cdot s \rightleftharpoons Lin \cdot H \cdot s, \quad K_{lin}^{H} \qquad [8]$$

The equilibrium between conjugated methyl linoleate in the gas phase and adsorbed on the nickel surface was not considered, since the partial pressure of this compound was not easily determined with sufficient accuracy. This equilibrium was therefore assumed to lie far towards the adsorbed form.

The hydrogenation of the half-hydrogenated radical $Ol \cdot H \cdot s$ was, moreover, found to be written (5):

$$Ol \cdot H \cdot s + 2H \cdot s \rightarrow St + H \cdot s + 2s, \quad k_s \qquad [9]$$
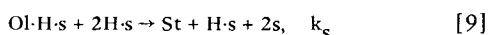
where methyl stearate (St) was found not to adsorb on the nickel surface. The corresponding hydrogenation of $Li \cdot H \cdot s$ was assumed to be slow in comparison to reaction 4 as mentioned above.

The rate equations were derived under the assumption that steps 4 and 9 are rate determining, that Langmuir adsorption theory may be applied, that hydrogen does not compete with the methyl esters for the active sites (the methyl esters compete mutually), and that steady state conditions are at hand.

The rate of methyl linoleate hydrogenation was thus derived to be

$$r_{lin} = \frac{k' \, p_{lin} \, p_{H_2}}{(1 + K_{lin} \, p_{lin} + K_{ol} \, p_{ol})(1 + \sqrt{K_{H_2} \, p_{H_2}})^2} \qquad [10]$$

where $r_{lin}$ = rate of methyl linoleate hydrogenation, and $k' = K_{lin} \, K_{H_2} \, k_l$. The meaning of the three constants may be clear from the reaction scheme. Upper case letters stand for equilibrium constants and lower case letters for rate constants. $p_{lin}$, $p_{ol}$, $p_{H_2}$ = pressures of methyl linoleate, methyl esters of monoenoic acids and hydrogen, respectively.

The rate of hydrogenation of methyl esters of monoenoic acids may be derived to be

$$r_{ol} = \frac{k'' \, p_{ol} \, p_{H_2}^{3/2}}{(1 + K_{ol}^{H} \, p_{ol} + K_{lin}^{H} \, p_{lin})(1 + \sqrt{K_{H_2} \, p_{H_2}})^3} \qquad [11]$$

where $r_{ol}$ = rate of hydrogenation of methyl esters of monoenoic acids, and $k'' = k_s \, K_{ol}^{H} \, K_{H_2}^{3/2}$.

As may be seen from Equation 10, the rate of methyl linoleate hydrogenation will be first order with respect to hydrogen at high temperature, since $K_{H_2}$ in the denominator decreases at increasing temperature. At low temperature the limiting reaction order will be zero. The corresponding values for hydrogenation of methyl esters of monoenoic acids will be 1.5 at high temperature and zero at low temperature. The derived rate equations thus explain the hydrogen effect on the selectivity and also fulfill the

requirements for explaining the temperature dependence of the reaction order with respect to hydrogen.

## Estimation of Kinetic Parameters

There are only two parameters, $k'$ and $K_{lin}^{H}$, to be estimated in the reaction model represented by Equations 10 and 11. The constants $k''$ and $K_{ol}^{H}$ have already been estimated in a recent kinetic study of methyl oleate hydrogenation (5), and the equilibrium constants $K_{lin}$, $K_{ol}$ and $K_{H_2}$ were determined in separate adsorption studies with the same catalyst as in the present study (4, 19). The rate of reaction was easily calculated since the kinetic study was performed in a perfectly mixed reactor. The constants $k'$ and $K_{lin}^{H}$ were then directly calculated with an ordinary regression analysis. The calculation was performed separately for each temperature. The results are given in Table II. From this table it is seen that the precision is acceptable for most of the constants. The confidence limits are calculated at the 95% level which is rather high with regard to the fact that the reaction mechanism proposed includes some approximations.

The results in Table II confirm the well known fact that methyl linoleate hydrogenates more rapidly than methyl esters of monoenoic acids. This higher reaction rate does not depend on a higher surface coverage with respect to methyl linoleate but is a kinetic property. This conclusion is based on the fact that the ratio between the rate constants $k_l/k_s$ is high (equal to 29 at 148 C and 350 at 214 C, cf. ref 5) and that the adsorption equilibrium constants $K_{lin}$ and $K_{ol}$ are of the same order of magnitude (Table II).

It is also seen (Table II, and ref. 3) that $K_{lin}^{H}$ and $K_{ol}^{H}$ are ca. 100 times $K_{lin}$ and $K_{ol}$, which indicates that the adsorbed radicals are much more readily formed than are the adsorbed methyl esters. The adsorbed radical is of secondary importance, however, in the methyl linoleate hydrogenation as was discussed above.

The temperature dependence of $k_l$ and $K_{lin}^{H}$ is shown in Figures 2 and 3. The activation energy for the hydrogenation of methyl linoleate was calculated to be $E_L = (90.9 \pm 9.6)$ kJ/mol. This activation energy is much higher than the activation energy for the hydrogenation of methyl oleate, $E_S = (28.4 \pm 3.2)$ kJ/mol, found recently (5). The large value of $E_L$ means that the selectivity in methyl linoleate hydrogenation increases with increasing temperature. This is in agreement with the experience from fat hydrogenation. It is difficult at the present stage of the study to explain the large difference in the activation energy of the two consecutive hydrogenation reactions.

From the temperature dependence of $K_{lin}^{H}$ given in Figure 3, the enthalpy is calculated to be $-\Delta H_{lin}^{H} = (77.3 \pm 10.6)$ kJ/mol, which is of the same order of magnitude as the corresponding enthalpy for $K_{ol}^{H}$ $[-\Delta H_{ol}^{H} = (67.3 \pm 41)$ kJ/mol] (5).

## Accuracy of the Estimated Parameters

In addition to the estimation of the precision of the parameters, it is necessary to check their accuracy and the validity of the reaction model by a residual analysis. From Equations 10 and 11, we find that there is only one single parameter ($k'$ in Equation 10 and $K_{lin}^{H}$ in Equation 11) in each equation to be estimated, the other being fixed from separate experiments. This means that it may be rather difficult to fit the rate equations to the experimental data.

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**TABLE II**

Kinetic Parameters in Rate Equations for Hydrogenation of Methyl Linoleate and Methyl Esters of Monoenoic Acids in Vapor Phase

| Number of experiments | Temperature (C) | k' (mol s⁻¹ kg⁻¹ bar⁻²) | $K_{lin}^H \times 10^{-3}$ (bar⁻¹) | $K_{lin} \times 10^{-3}$ (bar⁻¹) | $k_l \times 10^3$ (mol s⁻¹ kg⁻¹) | $K_{ol} \times 10^{-3}$ (bar⁻¹) | $K_{H_2}^a$ (bar⁻¹) | $K_{ol}^H \times 10^{-3 \, a}$ (bar⁻¹) |
|---|---|---|---|---|---|---|---|---|
| 24 | 148 | 67.3 ±13.1 | 57.3 ±37.8 | 1.20 ±0.28 | 0.198 ±0.103 | 1.33 ±0.38 | 284 ±120 | 25.1 ±15.6 |
| 24 | 180 | 14.6 ± 1.5 | 11.3 ± 6.8 | 0.161 ±0.034 | 1.06 ±0.45 | 0.228 ±0.067 | 85.5 ±30 | 4.1 ±2.1 |
| 21 | 214 | 2.83 ±0.81 | 3.31 ± 4.20 | 0.026 ±0.006 | 6.62 ±3.58 | 0.044 ±0.018 | 16.8 ±6.7 | 2.3 ±1.7 |

$K_{lin}$ and $K_{ol}$ are derived from separate adsorption measurements (4). All confidence limits are calculated at the 95% level.
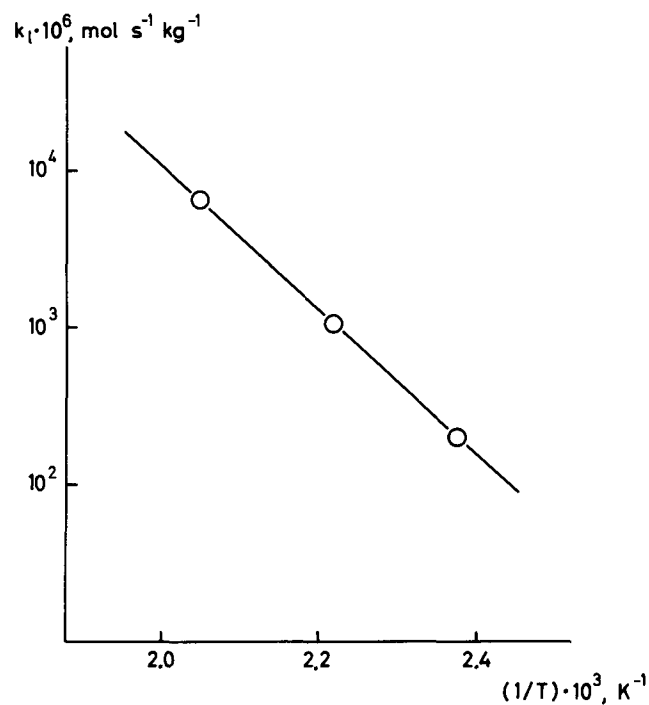aFrom ref. 5.



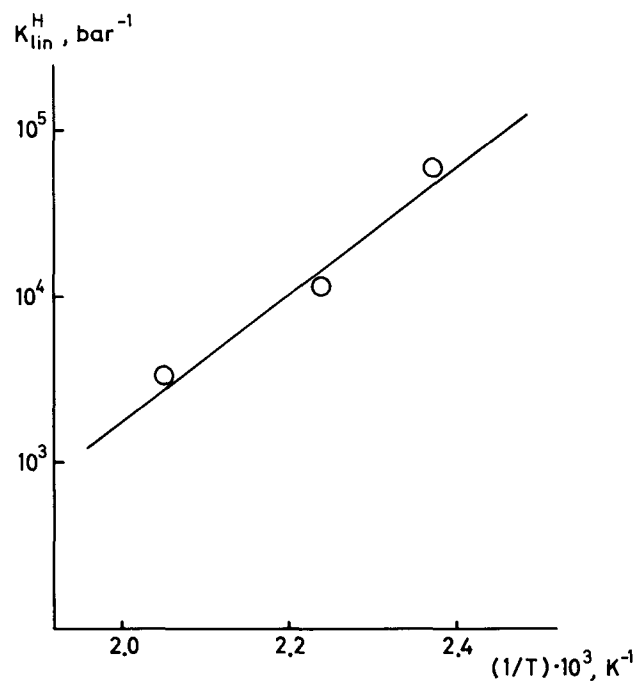FIG. 2. The rate constant $k_I$ for methyl linoleate hydrogenation vs 1/T.



FIG. 3. The equilibrium constant $K_{lin}^H$ for formation of adsorbed half hydrogenated methyl linoleate radical vs 1/T.

As also seen from the residual plot in Figure 4, the residuals, i.e., the difference between observed reaction rate and predicted reaction rate, are scattered. Scattering increases at high reaction rate. This distribution of the residuals may be explained by a possible lack of accuracy of $K_{H_2}$ since this constant was determined at a very low pressure (vacuum conditions and clean surface) compared to that in the kinetic experiments.

If the value of $K_{H_2}$ is biased, this may be difficult to compensate for with only one variable parameter to fit the equation. In this connection, it may be mentioned that the other equilibrium constants were determined at conditions very similar to those prevailing during the hydrogenation.

## Discrimination between Rival Reaction Models

It is often very difficult to discriminate between different reaction models based on kinetic measurements only. The most frequently used method is to first design the experiments according to the Box-Hill method (20) or some variant of this method and thereafter to apply the Williams-Kloot test (21, 22) when analysing the result. Owing to several experimental restrictions in the present investigation, it was not possible to use the Box-Hill method effectively in designing the experiments. On the other hand, the Williams-Kloot test was easily applied.

There are some possible alternative reaction mechanisms to be considered in the present study, the most interesting being the alternative where the adsorption of hydrogen competes with the methyl esters for the active sites. According to some authors (23), this competition does not seem so probable due to the great difference in the molecular size, but it is still being discussed by others. If the methyl esters compete with hydrogen for the active sites, the denominator of Equation 10 will change to

$$(1 + K_{lin} P_{lin} + K_{ol} P_{ol} + \sqrt{K_{H_2} P_{H_2}})^3$$

The corresponding change of the denominator of Equation 11 will give

$$(1 + K_{ol}^H P_{ol} + K_{lin}^H P_{lin}) (1 + K_{lin} P_{lin} + K_{ol} P_{ol} + \sqrt{K_{H_2} P_{H_2}})^3$$

A discrimination between the two models with the Williams-Kloot test gave

$$\lambda = -0.36 \pm 0.70 \ (95\% \text{ confidence limits}),$$

where $\lambda$ is a key test parameter (cf. ref. 22).

The result may be interpreted in the following way. For a $\lambda$ value of 0.5 the competitive model (hydrogen competes with the methyl esters) should be true, whereas a $\lambda$ value of $-0.5$ favors the noncompetitive model. The result found shows that the noncompetitive model is the most probable one of these two alternatives. The probability for the competitive model may be calculated to be less than 1%.

The reaction between hydrogen in the gas phase and an adsorbed reactant is often assumed to be the rate-determining step in hydrogenations. This alternative model, however, will result in a first-order kinetics with respect to the hydrogen pressure for the hydrogenation of methyl linoleate. The first-order dependence is, moreover, not affected by the temperature and can therefore not be an acceptable model in the present study.
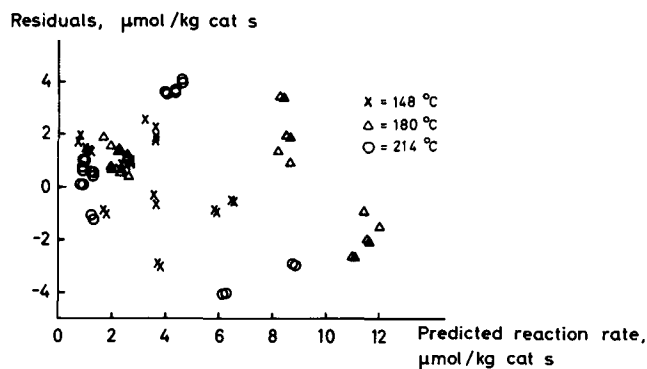


FIG. 4. Residuals vs predicted reaction rate.

An additional possible model of certain interest is the one where the adsorption of hydrogen is the rate-determining step. This model results in a reaction rate which among other things is not dependent on the partial pressure in the methyl ester. This is not in accordance with the results in the present study.

REFERENCES

1. Bond, G.C., and P.B. Wells in Advance in Catalysis and Related Subjects, vol. 15, Academic Press, edited by D.D. Eley, H. Pines and P.B. Weiz, New York, 1964, p. 91.
2. Hell, M., L.E. Lundqvist and N.-H. Schöön, Acta Polytech. Scand. Chem. Ser. 100: No. 3 (1971).
3. Alper, E., B. Wichtendahl and W.-D. Deckwer, Chem. Eng. Sci. 35:217 (1980).
4. Lidefelt, J.-O., JAOCS 60:593 (1983).
5. Lidefelt, J.-O., J. Magnusson and N.-H. Schöön, JAOCS 60:603 (1983).
6. Blekkingh, J.J.A., Disc. Faraday Soc. No 8:200 (1950).
7. Allen, R.R., and A.A. Kiess, JAOCS 33:355 (1956).
8. Horiuti, J., and M. Polanyi, Trans. Faraday Soc. 30:1164 (1934).
9. Frankel, E.N., and H.J. Dutton, in Topics in Lipid Chemistry, vol. 1, edited by F.D. Gunstone, Logos Press Limited, London, 1970, p. 161.
10. Hilditch, T.P., and N.L. Vidyarthi, Proc. Roy. Soc. 122A:552 (1929).
11. Hilditch, T.P., Nature 157:586 (1946).
12. Feuge, R.O., E.R. Cousins, S.P. Fore, E.E. Dupré, and R.T. O'Connor, JAOCS 30:454 (1953).
13. Coenen, J.W.E., and H. Boerma, Fette, Seifen, Anstrichm. 70:8 (1968).
14. Hashimoto, K., K. Muroyama, K. and S. Nagata, JAOCS 48: 291 (1971).
15. Eldib, I., and L.F. Albright, Ind. Eng. Chem. 49:825 (1957).
16. Wisniak, J., and L.F. Albright, Ibid. 53:375 (1961).
17. Tsuto, K., P., Harriott and K.B. Bischoff, Ind. Eng. Chem. Fundam. 17:199 (1978).
18. The Working Party, Chemical Reaction Engineering of the EFChE, Chem. Eng. Sci. 35:2065 (1980).
19. Magnusson, J., J. Catal. (submitted for publication) (1982).
20. Box, G.E.P., and W.J. Hill, Technometrics 9:57 (1967).
21. Williams, E.J., and N.H. Kloot, Aust. J. Appl. Sci. 4:1 (1953).
22. Mezaki, R., and J.R. Kitrell, Can. J. Chem. Eng. 44:285 (1966).
23. Wells, P.B., in Surface and Defect Properties of Solids, vol. 1, The Chemical Society, Senior Reporters M.W. Roberts and J.M. Thomas, London, 1972.