A Simplified Horiuti-Polanyi Scheme for the Hydrogenation of Triacylglycerols

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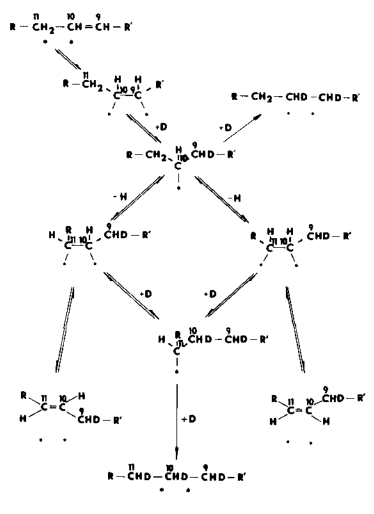
A simplification of the Horiuti-Polanyi reaction scheme for the hydrogenation of triacylglycerols taking into account saturation and *cis-trans* isomerization of double bonds and neglecting their positional isomerization is presented. From the comparison of experimental and calculated kinetic runs, the rate constants of individual reaction steps are obtained and the effects of hydrogen flow, hydrogen dispersion, oil unsaturation and catalyst quality on the rate constants are examined. Criteria for comprehensive characterization of the processes occurring in the course of hydrogenation, i.e., saturation and isomerization indices, are proposed.

KEY WORDS: *cis-trans* Isomerization, hydrogenation, kinetics, mechanism, rate constants, saturation, triacylglycerols.

Partial hydrogenation of triacylglycerols is an established and mature industry. Despite this, large gaps exist in the knowledge of the basic hydrogenation mechanism, obviously owing to its complexity. Horiuti and Polanyi (1) first proposed a mechanism for the hydrogenation of oleic acid catalyzed with a nickel catalyst (Scheme 1). The mechanism includes absorption of a double bond on the nickel catalyst, formation of the half-hydrogenated intermediate, formation of the saturated compound as well as positional and *cis-trans* isomerization of double bonds in fatty acids. The individual reaction steps are mostly reversible. Scheme 1 leaves aside such processes as dissolution and diffusion of hydrogen into the bulk of oil, adsorption of hydrogen on the catalyst surface, diffusion of oil to the catalyst, etc., which are not chemical reactions, but which can considerably affect the kinetics of hydrogenation.



Scheme 1. Horiuti-Polanyi reaction scheme for the hydrogenation of oleic acid on nickel catalyst.

The original Horiuti-Polanyi reaction scheme involves 18 rate constants. To quantitatively analyze such a complex scheme and obtain reliable values of rate constants is an almost unsolvable task. Numerous attempts presented extensively in reference 2 have been made to describe the hydrogenation by simpler kinetic schemes. In this paper an alternative kinetic scheme based on the simplification of the Horiuti-Polanyi mechanism is proposed. The scheme allows for hydrogenation and *cis-trans* isomerization of double bonds; positional isomerization is neglected. By the simultaneous treatment of the kinetic runs for iodine value and *trans*-isomer content, the rate constants of individual reaction steps are obtained. The effects of flow rate of hydrogen, hydrogen dispersion, oil unsaturation and catalyst quality on the rate constants of individual kinetic steps are examined.

EXPERIMENTAL PROCEDURES

Refined, bleached and deodorized olive, sunflower and linseed oils with iodine values of 85.2, 130.8 and 191.0, respectively, were used for hydrogenations catalyzed with two commercial nickel catalysts: NYSEL DM3 with Ni content 25% by wt. (Harshaw Chemie, The Netherlands), and STZ with 13.6% Ni by wt. (Ustí nad Labem, Czechoslovakia). The fatty acid compositions of oils determined by Christopherson and Glass (3) are given in Table 1.

Hydrogenations were carried out in two 250-mL glass reactors with free outlet of unreacted hydrogen. The reactors differed in hydrogen distribution. In the first type, hydrogen was introduced through a tube with inner diameter of 3 mm situated at the bottom of the vessel so that the dispersion of hydrogen was poor. In the other type, with good dispersion, hydrogen was finely dispersed by bubbling it through the sintered glass bottom. A charge of 200 g of oil was used for each run, the content of the reactor was agitated by bubbling hydrogen. The flow rate of hydrogen was 75 and 135 L h^{-1}.

The oil sample was thermostatted at 180°C. After the oil reached this temperature, the catalyst was added in a concentration of 0.1% Ni/oil by wt. Hydrogenations were carried out to nearly zero iodine values and oil samples were taken from the reactor at chosen time intervals. The iodine values of filtered samples were determined by the Hanuš method (4). The *trans* isomer content was determined using a SPECORD 71 IR spectrometer (Carl Zeiss, Jena, Germany) according to the standard AOCS methods (5).

Theoretical. The simplification of the Horiuti-Polanyi reaction mechanism is based on the assumptions that the adsorption on and desorption of double bonds from the catalyst surface are not the rate-limiting steps, and that hydrogen chemisorption is so rapid that its equilibrium is not affected by the hydrogen consumption in the course

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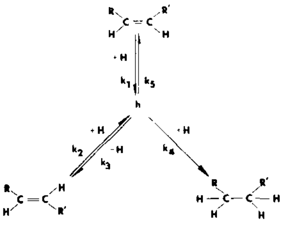
TABLE 1

Fatty Acid Composition of Oils

Oil	Palmitic acid % by wt.	Stearic acid % by wt.	Oleic acid % by wt.	Linoleic acid % by wt.	Linolenic acid % by wt.
Olive	9.1	2.4	78.7	9.8	—
Sunflower	6.6	3.3	24.2	65.9	—
Linseed	5.2	2.6	18.2	16.3	57.7



Scheme 2. Simplified Horiuti-Polanyi reaction scheme.

of hydrogenation. Scheme 1 shows that the isomerization and saturation of double bonds are not independent, both reactions start from the half-hydrogenated intermediate. Taking the neglect of positional isomerization into account, the Horiuti-Polanyi mechanism can be reduced to the form as shown in Scheme 2.

The simplified reaction scheme contains only five rate constants. It can be described by the following set of kinetic equations:

$$dc_1/dt = - k_1c_1 + k_5h \qquad [1]$$

$$dc_2/dt = k_3h - k_2c_2 \qquad [2]$$

$$dc_3/dt = k_4h \qquad [3]$$

where c_1 is the concentration of *cis* double bonds, c_2 is that of *trans* double bonds, c_3 means the concentration of saturated bonds formed in the course of hydrogenation, h is the concentration of the half-hydrogenated intermediate and t stands for time. The concentration of the half-hydrogenated state can be expressed by the material balance:

$$h = c_1^o - c_1 - c_2 - c_3 \qquad [4]$$

where c_1^o is the concentration of double bonds before hydrogenation (it is assumed that the oil contains solely *cis* double bonds before hydrogenation).

In calculations it is necessary to manipulate with concentrations expressed in homogeneous units. Their expression in the moles of bonds (*cis*-double, *trans*-double and saturated) *per* 100 g oil seems to us to be appropriate. As trielaidin contains three *trans* double bonds, the concentration c_2 is given as

$$c_2 = 3 \times (\%TI)/M \qquad [5]$$

where %TI is the *trans* isomers content expressed in percent of trielaidin and M = 885.5 g mol-1 is the molar weight of trielaidin. The concentration of saturated bonds formed in the course of hydrogenation can be calculated from the iodine values which indicate the advance of oil saturation:

$$c_3 = (IV_o - IV)/M(I_2) \qquad [6]$$

where IV_o is the iodine value at the time t=0, IV is the iodine value at time t and $M(I_2)$ = 253.8 g mol-1 is the molar weight of iodine.

The set of differential kinetic equations [1] through [3] is solved numerically by the fourth-order Runge-Kutta method for the initial conditions $c_1^o=IV_o/M(I_2)$, $c_2^o=0$, $c_3^o=0$ at the time t=0. The rate constants are obtained from kinetic runs by minimizing the sums of squares of deviations between the calculated and experimental concentrations c_2 and c_3. The minimization is carried out by the simplex method (6); the minimization parameters are the values of the rate constants. Preliminary calculations showed that in all cases but one, the value of the rate constant k_5 was lower by about four orders than the other constants, thus indicating that the formation of the half-hydrogenated intermediate from a *cis* double bond can be treated as a simple first-order reaction. Therefore, it is put k_5=0 and the sum of squares is minimized with respect to the rate constants k_1, k_2, k_3 and k_4. The accuracy of iodine value determination is higher than that of the determination of *trans* isomers content. For this reason, in calculations the statistical weight of 2 is assigned to the kinetic curve c_3 and the weight of 1 to the curve c_2.

RESULTS AND DISCUSSION

The experimental kinetic curves of iodine value and of *trans* isomer content are presented in Figures 1 to 4. These experimental results were recalculated using equations [5] and [6], and the rate constants were obtained from these transformed experimental data by the nonlinear least-squares method. The results of the calculations are given in Tables 2-4. The agreement reached between experimental and calculated curves is good, which points out that the simplified Horiuti-Polanyi mechanism given by Scheme 2 adequately describes both oil saturation and *cis-trans* isomerization in the course of hydrogenation. Comparison of experimental and calculated kinetic runs for a case, which is neither the best nor the worst one, is illustrated in Figure 5.

The simplified reaction scheme follows the leading idea of the original Horiuti-Polanyi mechanism that the isomerization and saturation of oil start from the half-hydrogenated intermediate. None of the schemes reviewed in reference 2 takes into account the existence of the

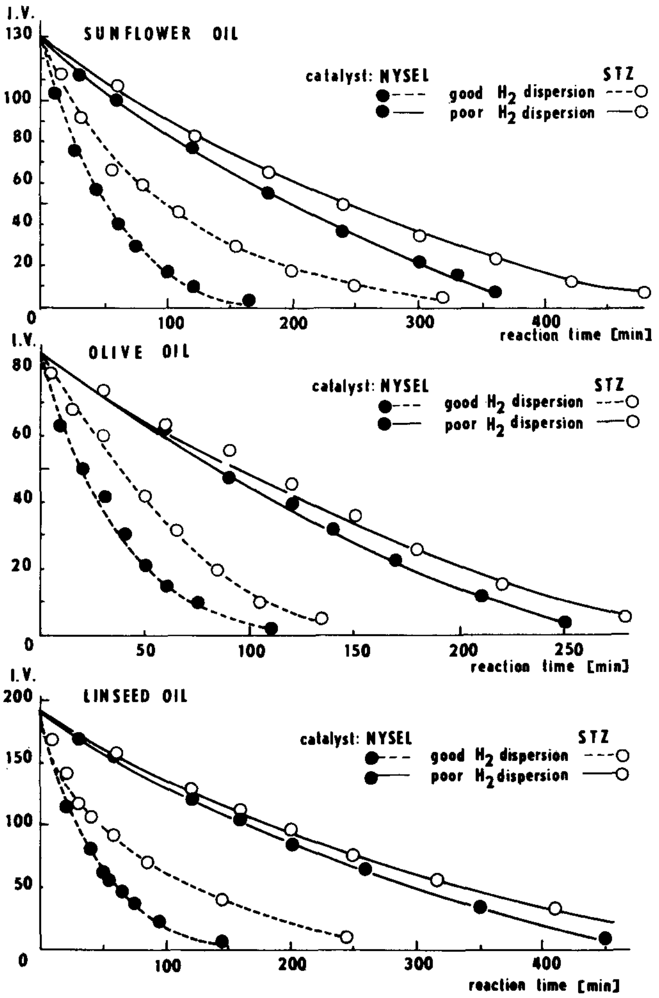


FIG. 1. Dependence of iodine value on the reaction time for hydrogen flow rate 135 L/hr.

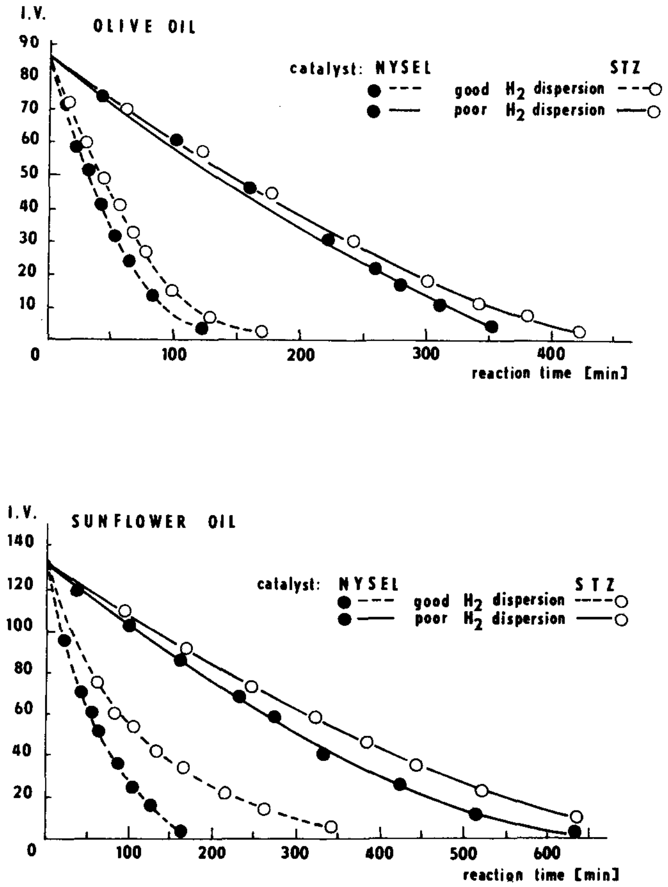


FIG. 2. Iodine value as a function of reaction time for hydrogen flow rate 75 L/hr.

intermediate. Interpretation of our rate constants is thus clearer since they do not involve such a number of effects as the global rate constants (2).

The reactions in Scheme 2 are pseudo-unimolecular, the rate constants implicitly involve the concentration of hydrogen chemisorbed on the catalyst surface. Consequently, their values should depend on the saturation of oil with hydrogen. The values of k_1, k_2 and k_4 should increase and k_3 should decrease with increasing hydrogen concentration in the bulk of oil. As can be seen from Tables 2-4, the values of rate constants hold this predicted trend for increasing hydrogen flow as well as for better hydrogen dispersion. The effect of dispersion is more pronounced, which is in agreement both with our observations and published results (7,8).

The values of rate constants offer the possibility to introduce criteria for a more comprehensive characterization of the process of hydrogenation. An important characteristic is the rate of double bonds saturation. As it is obvious from Scheme 2, this rate depends mainly on the partial rates of the half-hydrogenated intermediate formation and of the intermediate saturation. The greater the rate constants k_1 and k_4 are, the more rapid hydrogenation is. Hence, the saturation index, s, given as the product of both constants, provides quantitative estimation of the sensitivity of oil to hydrogenation:

$$s = k_1 k_4 \qquad [7]$$

The formation of *trans* isomer proceeds rapidly if the rate constant k_3 is great and rate constants k_2 and k_4 are small. Then, the isomerization index, i, allows us to see the tendency of oil to isomerize:

$$i = k_3/(k_2 k_4) \qquad [8]$$

This coefficient is an analogy of the specific isomerization index which gives the number of isomerized double bonds per a hydrogenated bond (9,10). However, the specific hydrogenation index is a function of the conversion of hydrogenation (10); an advantage of the isomerization index expressed by equation [8] is that it is constant. From Tables 2-4 it can be seen that s increases and i decreases when the concentration of hydrogen in the oil is higher. Again, the results show much greater influence of hydrogen dispersion than that of the flow rate of hydrogen on the rate of hydrogenation.

For the same regimes of hydrogenation, the rate constants depend on oil unsaturation. In the series olive-sunflower-linseed oils the values of k_1, k_2 and k_3 decrease and k_4 remains constant or increases slightly, the index s decreases and i increases. Obviously, the reason for these

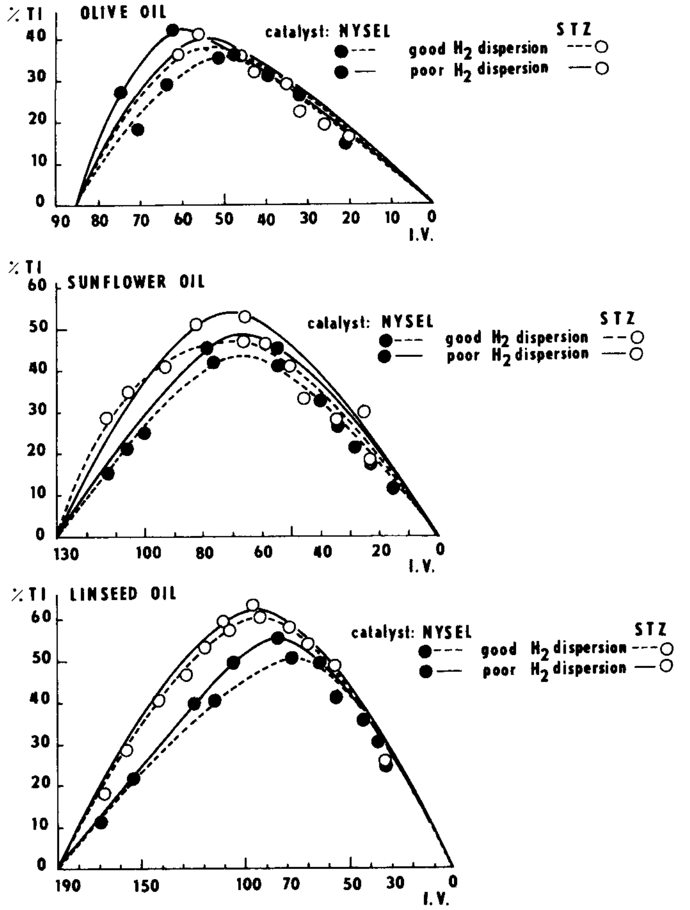


FIG. 3. *trans* Isomer content for the hydrogen flow rate 135 L/hr.

alterations lies in the fact that the original Horiuti-Polanyi mechanism has been found for monoenoic, i.e, oleic acid. From the oils studied here, only olive oil is monoenoic, sunflower oil includes mostly dienoic and linseed oil trienoic fatty acids (Table 1). In the presence of nickel catalyst, the C=C bonds in polyenoic acids are hydrogenated consecutively, not simultaneously. The double bonds approach the catalyst surface gradually, one by one, which is manifested in the mentioned decrease of reaction constants in comparison with the monoenoic oil when the experimental data are treated using Scheme 2. As it is obvious from the values of

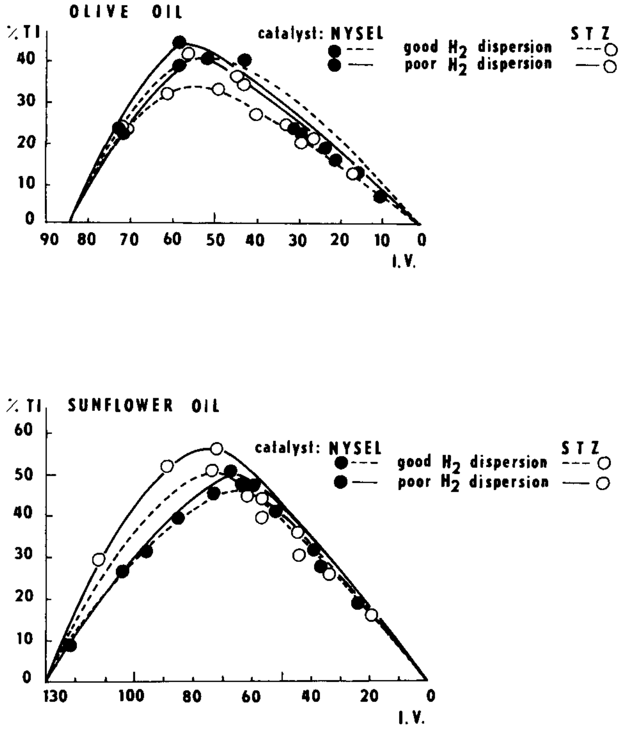


FIG. 4. *trans* Isomer content for the hydrogen flow rate 75 L/hr.

isomerization indices, the polyenoic oils exhibit greater tendency to isomerize. It is obviously due to a greater number of reaction paths leading to the decay of the half-hydrogenated state to *trans* acids.

The values of the rate constants enable us to look into the catalyst activity. From the experiments it has been found that the catalyst NYSEL is more active than STZ. Tables 2–4 show that the constants k_1 and k_2 are greater for NYSEL than for STZ, the constants k_3 and k_4 have no unambiguous trend. This leads to the conclusion that the catalyst activity is determined mainly by the rate of formation of the half-hydrogenated state. It is a matter of course that this rate implicitly involves the diffusion and adsorption of oil on the catalyst surface. Accordingly, any process of the diffusion, oil adsorption and the half-hydrogenated intermediate formation can be decisive for the catalyst activity. The fact that the activity is not determined by the rate constant k_4 indicates that the

TABLE 2

Rate Constants of Hydrogenation of Olive Oil

Catalyst	H_2 flow rate (L/hr)	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	k_4 (min^{-1})	Satur. index	Isomer. index
STZ	75[a]	1.15 E-2	1.01 E-1	4.16 E-1	4.42 E-2	5.14 E-4	93.1
STZ	75[b]	3.64 E-2	1.36 E-1	3.39 E-1	9.52 E-2	3.47 E-3	26.2
STZ	135[a]	1.67 E-2	8.48 E-2	3.13 E-1	5.45 E-2	9.11 E-4	67.6
STZ	135[b]	4.01 E-2	1.16 E-1	3.39 E-1	1.09 E-1	4.44 E-3	26.8
NYSEL	75[a]	1.38 E-2	9.72 E-2	4.17 E-1	4.59 E-2	6.36 E-4	93.4
NYSEL	75[b]	6.44 E-2	1.26 E-1	3.33 E-1	1.08 E-1	6.98 E-3	24.5
NYSEL	135[a]	2.28 E-2	1.28 E-1	3.12 E-1	4.84 E-2	1.10 E-3	62.0
NYSEL	135[b]	1.24 E-1	2.71 E-1	2.38 E-1	6.49 E-2	8.02 E-3	13.5

[a] Poor dispersion of hydrogen.
[b] Good dispersion of hydrogen.

TABLE 3

Rate Constants of Hydrogenation of Sunflower Oil

Catalyst	H_2 flow rate (L/hr)	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	k_4 (min^{-1})	Satur. index	Isomer. index
STZ	75[a]	6.64 E-3	2.59 E-2	2.87 E-1	6.92 E-2	4.59 E-4	160.6
STZ	75[b]	9.47 E-2	3.44 E-2	4.37 E-2	2.13 E-2	2.02 E-3	59.6
STZ	135[a]	1.06 E-2	2.92 E-2	2.28 E-1	7.08 E-2	7.51 E-4	110.4
STZ	135[b]	3.47 E-2	2.28 E-2	1.18 E-1	9.19 E-2	3.19 E-3	56.3
NYSEL	75[a]	6.55 E-3	8.57 E-2	4.34 E-1	4.89 E-2	3.20 E-4	103.4
NYSEL	75[b]	4.85 E-2	5.69 E-2	1.36 E-1	8.34 E-2	4.04 E-3	28.6
NYSEL	135[a]	1.25 E-2	2.43 E-2	6.49 E-2	3.63 E-2	4.54 E-4	73.5
NYSEL	135[b]	6.90 E-2	4.76 E-2	1.23 E-1	1.04 E-1	7.21 E-3	24.7

[a] Poor dispersion of hydrogen.
[b] Good dispersion of hydrogen.

TABLE 4

Rate Constants of Hydrogenation of Linseed Oil

Catalyst	H_2 flow rate (L/hr)	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	k_4 (min^{-1})	Satur. index	Isomer. index
STZ	135[a]	7.29 E-3	1.56 E-2	3.11 E-1	7.52 E-2	5.48 E-4	265.4
STZ	135[b]	3.83 E-2	1.78 E-2	9.82 E-2	1.12 E-1	4.27 E-3	49.4
NYSEL	135[a]	7.63 E-3	1.75 E-2	1.25 E-1	9.13 E-2	6.97 E-4	78.4
NYSEL	135[b]	4.66 E-2	3.88 E-2	2.24 E-1	2.84 E-1	1.32 E-2	20.4

[a] Poor dispersion of hydrogen.
[b] Good dispersion of hydrogen.

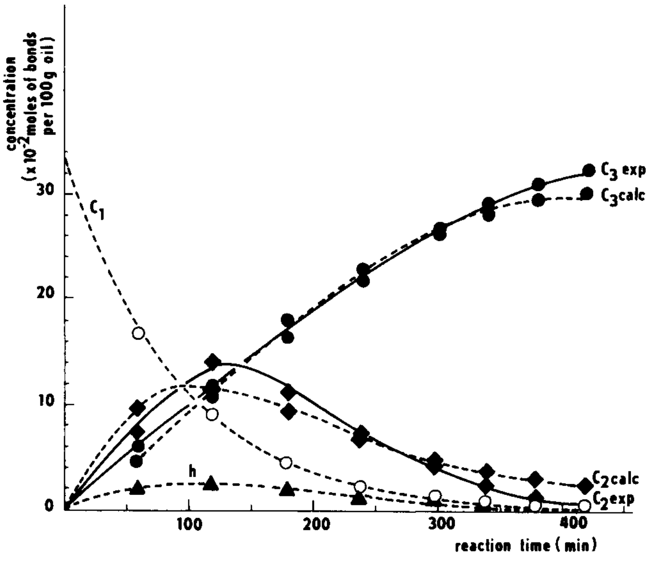


FIG. 5. Experimental and calculated concentrations of saturated and isomerized double bonds in the hydrogenation of olive oil with STZ catalyst, hydrogen flow rate 75 L/hr, poor dispersion of hydrogen.

assumption of equilibrium chemisorption of hydrogen is correct.

The results presented here demonstrate that the reduced Horiuti-Polanyi scheme is suitable for the description of oil hydrogenation. The main contribution of Scheme 1 is that it makes it possible to analyze the influence of reaction conditions on the rate constants of individual reaction steps and offers the possiblity of quantitative description and computer simulation of the process.

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