The Kinetics of the Hydrogenation of Triglycerides

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A SURVEY of the literature to 1941 shows that considerable confusion existed concerning the kinetics of fatty oil hydrogenation. Up to that time two conflicting views were held. Armstrong and Hilditch (1), Richardson and co-workers (14), and Lebedev and co-workers (11) believed that the reaction was linear. On the other hand, Ueno (18), Thomas (17), and Holomboe (10) supported a monomolecular type reaction. However in no case were the data quite satisfactory.

In the past 10 years the study of the kinetics of fatty oil hydrogenation has gained some impetus and clarification by the work of Bailey and Fisher (2), Zinovev (21), and Eisi and Hiroshi (7). By assuming the existence of affinity constants as a measure of the relative rates of absorption of hydrogen by the components of a mixture, Bailey and Fisher obtained some affinity constants which gave good correlation with the experimental data for the hydrogenation of a series of linseed, cottonseed, and soybean oils. Zinovev by hydrogenating oils containing high percentages of glycerol trioleate and Eisi and Hiroshi by hydrogenating oleic acid found that the hydrogenation proceeded by a monomolecular reaction and that the velocity constants were small. Zinovev further stated that the activity of a given nickel catalyst, expressed by his rate constants, increased during the reaction.

In view of this latter work it appeared that the hydrogenation of oils may occur by a monomolecular reaction. However work on more simple molecules is needed to substantiate these conclusions.

The purpose of this investigation was to determine the course and the rate of hydrogenation of such a simple molecule, namely triolein, under varying conditions of temperature and pressure and to determine the rate laws for the disappearance of the original reactant, the production and disappearance of the intermediate, and the production of the completely saturated product.

Materials

Highly purified oleic acid was prepared from virgin grade olive oil by saponification of the oil followed by esterification with methanol in the presence of sulfuric acid. The crude methyl oleate prepared in this manner was fractionally distilled and then freed of saturated methyl esters and polyunsaturated methyl esters by two crystallizations from acetone at —25°C., followed by three crystallizations from acetone at —55°C. The crystallized methyl oleate was then saponified and the oleic acid fractionally distilled. This procedure, which is a simplification of that described by Brown and Shinowara (5), yielded an oleic acid having a Wijs iodine value of 89.7-90.1 (theoretical 89.9); melting point of 13° to 14°C. (reported 13.5°C) and a refractive index at 50°C. of 1.4487 (reported 1.4487). It was stored in a sealed glass ampule under dry nitrogen and kept at low temperature to prevent oxidation prior to use.

The triolein was prepared from the highly purified oleic acid by a modification of the method of Wheeler, Riemenschneider, and Sando (20). This modification entailed the use of dry carbon dioxide as the source of agitation rather than dry nitrogen as suggested by the previous authors. It was found that, by using dry carbon dioxide, the reaction mixture acquired less discoloration. This procedure yielded a triolein which, after crystallization from acetone at —45°C. and molecular distillation, had an iodine value of 86.0 (theoretical 86.1); melting point of 4.2° to 4.5°C. (reported 4.7°C.); refractive index at 40°C. of 1.4620 (reported 1.4620); saponification equivalent of 295.2 (theoretical 294.9); percentage of free fatty acid of 0.18 (theoretical 0.0); and was free of peroxides. This was also stored in sealed glass ampules at low temperature prior to use.

Trielaidin was prepared by a modified procedure which Daubert (6) used to prepare dielaidyl-monosaturated triglycerides. Elaidyl chloride (3.03 moles) was added slowly to a mixture of absolute glycerol (1.0 mole) anhydrous quinoline (3.03 moles) and 45 ml. of absolute chloroform. The contents were swirled until the solution became homogeneous, and the mixture was warmed at 60°C. for one hour and then kept at room temperature for 24 hours. The reaction product was dissolved in ethyl ether and washed and dried. The trielaidin was purified by eight crystallizations from anhydrous acetone (10 ml. acetone per gram solute) at —10°C. and three crystallizations from a 50-50 mixture of ethyl ether and ethyl alcohol. The final product had an iodine value of 86.1 (theoretical 86.1); a melting point of 41.4°C. to 41.9°C. (reported 41.5°C.); and was free of peroxides.

Tristearin was obtained by crystallization of completely hydrogenated triolein from anhydrous chloroform. The tristearin prepared in this manner had an iodine value of 0.0 (theoretical 0.0), a melting point of 72.3° to 72.6°C. (reported 72.5°C.).

Hydrogenation Apparatus and Procedure

Those hydrogenations which were performed at pressures greater than atmospheric pressure were done in a Parr No. 4501 medium pressure hydrogenation unit. This consists essentially of a vertical, cylindrical stainless steel vessel, designed for operations at moderate pressure and provided with a motor-driven stirrer of the propellor type. Hydrogen from an ordinary commercial cylinder was injected into the hydrogenation unit through an adjustable reducing value, which served to maintain a constant pressure on the system. The temperature of the oil was measured by means of a Copper-Constantan thermocouple. Heat was supplied by means of a built-in heating element controlled by a variac connected to a constant-voltage regulator. Cooling was provided by a copper cooling coil placed in the outer jacket of the apparatus. Although temperature control was entirely manual, it was found possible to maintain the temperature within ± 0.5°C.

The hydrogenation conducted at atmospheric pressure was done in an apparatus similar to that employed by Feuge and co-workers (8). This consisted of a 500-ml. three-necked, round-bottom flask immersed in a constant temperature oil bath. The flow of hydrogen into the sample was kept constant by a special pressure regulator attached to the hydrogen cylinder. The temperature was maintained constant (± 0.5°C.) by adjusting the depth to which the reaction flask was immersed in the oil bath. A high degree of dispersion was maintained by bubbling the hydrogen at a fairly rapid rate through the inlet tube, which consisted of a coarse porosity, fritted-glass cylinder, 12 mm. in diameter and 10 mm. high.

In every case the initial charge of triolein was 200 g., and the catalyst used was a commercial nickel catalyst of the supported type suspended in a hardened fat (Harshaw Ni-OSOlF). Samples of 7 to 8 g. were withdrawn at time intervals and stored under anhydrous chloroform and dry nitrogen before the catalyst was removed. After removal of the catalyst and the chloroform each sample was analyzed with respect to total unsaturation, total saturation, and the percentage of *trans* isomer as triglyceride.

Total unsaturation and hence the progress of the hydrogenation was determined by a modified Wijs procedure (9) used to determine iodine values. The percentage of saturated component was determined by a modified Bertram Alkaline Permanganate Oxidation method (3). Since this method involved the determination of the saturated component as stearic acid, the percentage of stearic acid found was divided by 0.9573 to convert the percentage of saturated component to a triglyceride basis.

The percentage of *trans* component was determined by the infrared spectrophotometric method of Swern and co-workers (16), using carbon disulfide as a solvent.

All spectra were obtained on a Perkin-Elmer infrared spectrophotometer Model 12B, using a sodium chloride prism and a 0.255-mm. slit width. All measurements were made by the quantitative differential method, that is, measurement of carbon disulfide solution of the triglycerides against pure carbon disulfide.

The specific extinction coefficients at 966.8 cm.$^{-1}$ (10.3 microns) were used in calculating the proportions of *trans* isomer in the hydrogenated product and were determined by a method described by Shreve *et al.* (15). The values of the specific extinction coefficients at 966.8 cm.$^{-1}$ for the pure triglycerides were: triolein, 0.103; trielaidin, 0.531, and tristearin, 0.071.

In calculating the amount of *trans* component in a hydrogenated sample the following equation was used:

$$\%\ \text{TRANS} = \frac{100\ (K_{ob} - K_cY - K_sZ)}{K_t - K_c}$$

where K_{ob} is the extinction coefficient for the hydrogenated sample, K_c is the extinction coefficient for triolein, K_s the extinction coefficient for tristearin, K_t the extinction coefficient for trielaidin, Y is the total weight fraction of *cis* plus *trans* octadecenoic components in the mixture and Z is the weight fraction of tristearin calculated from Bertram oxidation.

The percentage of *cis* component was determined by difference. The results of the individual hydrogenations are given in Table I.

TABLE I

Hydrogenation of Triolein

Operating conditions	Hydrogen			Total *cis* (A) percentage	Total *trans* (B) percentage	Total saturated (C) percentage
	Sample no.	Time mins.	Iodine value			
Hydrogenation No. 1	0	0	86.0	100.0	0.0	0.0
Temperature 125°C.	1	15	80.0	87.1	7.0	5.9
Pressure 65 lb. gauge	2	30	71.7	78.5	6.7	14.8
Catalyst						
Concentration 0.4% Ni	3	60	38.6	40.5	6.3	53.2
High dispersion	5	75	25.8	30.4	3.0	66.6
Agitation 1725 r.p.m.	5	105	9.3	15.0	0.0	85.0
	6	120	6.0	10.8	0.0	89.2
Hydrogenation No. 2	1	2	84.5	95.7	0.8	3.5
Temperature 175°C.	2	5	82.2	91.0	4.4	4.6
Atmospheric pressure	3	15	76.5	66.9	22.2	10.9
Catalyst						
Concentration 0.4% Ni	4	30	67.7	39.6	39.0	21.4
High dispersion	5	40	62.2	28.5	42.9	28.6
Good agitation	6	50	55.4	22.9	42.5	34.6
	7	60	49.1	17.5	39.9	42.6
	8	90	31.2	10.4	25.8	63.8
	9	105	22.5	7.6	18.6	73.8
	10	120	14.1	4.8	11.5	83.7
	11	135	6.4	4.2	4.7	91.1
Hydrogenation No. 3	1	2	79.6	84.3	8.5	7.2
Temperature 175°C.	2	5	70.5	54.7	27.5	17.8
Pressure 65 lb. gauge	3	10	55.4	25.6	38.8	35.6
Catalyst	4	15	40.8	13.5	33.2	53.3
Concentration 0.4% Ni	5	20	27.8	8.9	23.4	67.7
High dispersion	6	25	17.2	6.6	14.6	78.8
Agitation 1725 r.p.m.	7	30	9.8	4.0	8.2	87.8
	8	40	2.6	1.8	1.9	96.3

Discussion

The course of the catalytic hydrogenation of monoethenoic acids and triglycerides is still not completely known; hence it was decided to assume a mechanism general enough to include as special cases all mechanisms that seem reasonable under the assumption that only three chemical species are involved in the reaction. The mechanism proposed for the catalytic hydrogenation of triolein is similar to the one proposed by Mazume (12) in 1928 for the hydrogenation of methyl oleate. The reactions for the mechanism proposed for triolein may be illustrated as follows:

$$\begin{tikzcd} A \arrow[r, shift left, "k_1"] \arrow[rr, bend right, "k_3"'] & B \arrow[l, shift left, "k_4"] \arrow[r, "k_2"] & C \end{tikzcd} \tag{I}$$

where A, B, and C represent the *cis* component, the *trans* component, and the saturated component, respectively; and k_1, k_2, k_3, k_4 are the rate constants.

The above mechanism may be criticized on the grounds that it has been shown (13) that octadecenoic acids hydrogenate at different rates depending on the position of the double bond. However other investigations (12, 19), have failed to show that such is the case in a hydrogenation reaction where one or more such acids may be present or formed during the reaction. It might be further stated that to show conclusively that isomeric octadecenoic acids or triglycerides hydrogenate at different rates, one would have to analyze for each isomer independently. At present no accurate quantitative method is available to make such an analysis. Therefore in the mechanism proposed it is assumed that the rate of hydrogenation of all *cis* components is approximately the same and likewise for all *trans* components.

The rate laws which are assumed to apply to the proposed mechanism are expressed by the following differential equations:

$$dA/dt = -(k_1 + k_3)A + k_4 B, \tag{1}$$

$$dB/dt = -(k_2 + k_4)B + k_1 A, \tag{2}$$

$$dC/dt = k_3 A + k_2 B, \tag{3}$$

where A, B, and C are the percentages of *cis, trans,* and saturated components respectively.

The solution of the differential equations (1), (2), and (3) is

$$A = c_1 e^{m_1 t} + c_2 e^{m_2 t}, \tag{4}$$

$$B = \frac{k_1 c_1 e^{m_1 t}}{m_1 + k_2 + k_4} + \frac{k_1 c_2 e^{m_2 t}}{m_2 + k_2 + k_4}, \tag{5}$$

$$C = 100 - (A + B), \tag{6}$$

where

$$m_1 = \frac{-b + \sqrt{b^2 - 4c}}{2},$$

$$m_2 = \frac{-b - \sqrt{b^2 - 4c}}{2},$$

and where

$$b = k_1 + k_2 + k_3 + k_4,$$

$$c = (k_1 + k_3)(k_2 + k_4) - k_1 k_4.$$

The rate laws given above apply to a homogeneous system; since catalytic hydrogenation is a heterogeneous reaction, one might expect that the rate constants as expressed in the rate laws might be a function of the extent of the reaction. This would imply that the effectiveness of the catalyst is a function of the composition of the reacting system. The rate laws thus could be modified by considering the rate constants to be a function of the reaction time. The simplest modification of the rate laws in this direction is to assume that all rate constants are affected in the same way by the catalyst and that they are linear functions of the reaction time. The rate constants would then be expressed as follows:

$$k_i = k_{0i}(1 + \alpha t) \qquad i = 1, 2, 3, 4 \tag{7}$$

where α is a constant which expresses the rate of change of the effectiveness of the catalyst. Differential equations (1), (2), and (3) would then become

$$dA/dt = -(k_{01} + k_{03})(1 + \alpha t)A + k_{04}(1 + \alpha t)B, \tag{8}$$

$$dB/dt = -(k_{02} + k_{04})(1 + \alpha t)B + k_{01}(1 + \alpha t)A, \tag{9}$$

$$dC/dt = k_{03}(1 + \alpha t)A + k_{02}(1 + \alpha t)B. \tag{10}$$

If one lets

$$(1 + \alpha t)\,dt = d\theta,$$

then

$$\theta = t + \frac{\alpha t^2}{2}. \tag{11}$$

Equations (8), (9), and (10) now become

$$dA/d\theta = -(k_{01} + k_{03})A + k_{04} B, \tag{12}$$

$$dB/d\theta = -(k_{02} + k_{04})B + k_{01} A, \tag{13}$$

$$dC/d\theta = k_{03} A + k_{02} B. \tag{14}$$

The solution of differential equations (12), (13), and (14) is

$$A = c_1 e^{m_{01}(t+\alpha t^2/2)} + c_2 e^{m_{02}(t+\alpha t^2/2)} \tag{15}$$

$$B = \frac{k_{01} c_1 e^{m_{01}(t+\alpha t^2/2)}}{m_{01} + k_{02} + k_{04}} + \frac{k_{01} c_2 e^{m_{02}(t+\alpha t^2/2)}}{m_{02} + k_{02} + k_{04}} \tag{16}$$

$$C = 100 - (A + B), \tag{17}$$

where m_{01} and m_{02} are as previously defined with k_{0i} replacing k_i.

Since zero time was taken at the instant hydrogen was admitted into the reaction mixture, it necessarily follows that there must be an induction period corresponding to the time required for hydrogen to diffuse to the catalyst and become active. A correction for this induction period can be made by taking for the initial conditions the experimentally determined percentage of A and B at some time, $t = t_0$; where t_0 is a time slightly greater than the induction period. The induction period must be determined experimentally for each set of reaction conditions.

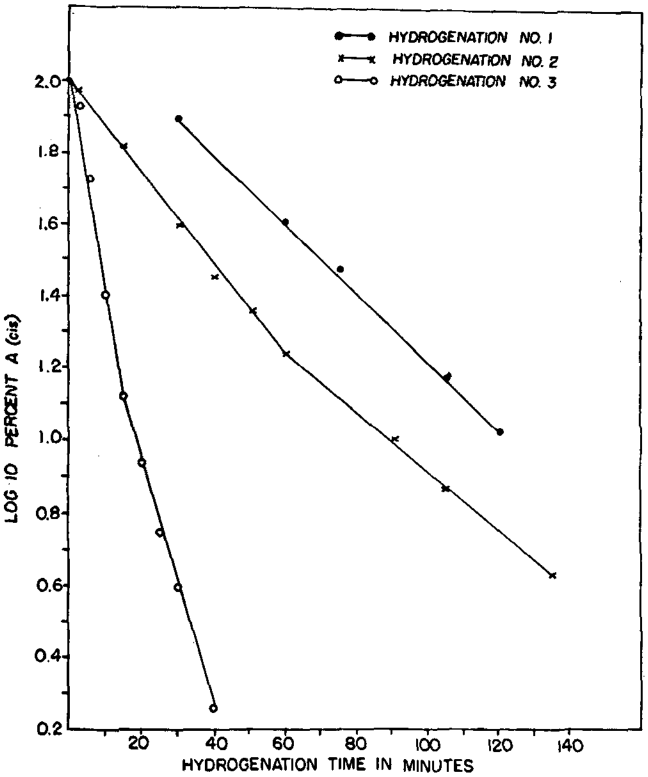

FIG. 1. Logarithm of the percentage of A *(cis)* as a function of the hydrogenation time.

Figure 1 gives curves showing the logarithm of the percentage of A *(cis)* as a function of the time for the three hydrogenations. The straight line which occurs for Hydrogenation No. 1 after an induction period (about 18 minutes as indicated by Figure 2) means that k_4 is small enough to be neglected and that A disappears according to a first-order reaction. Therefore in this case equations (15), (16), and (17) become

$$A = c_1 e^{-(k_{01}+k_{03})(t+\alpha t^2/2)} \tag{18}$$

$$B = c_2 e^{-k_{02}(t+\alpha t^2/2)} + \frac{k_{01} c_1 e^{-(k_{01}+k_{03})(t+\alpha t^2/2)}}{-(k_{01} + k_{03}) + k_{02}} \tag{19}$$

$$C = 100 - (A + B). \tag{20}$$

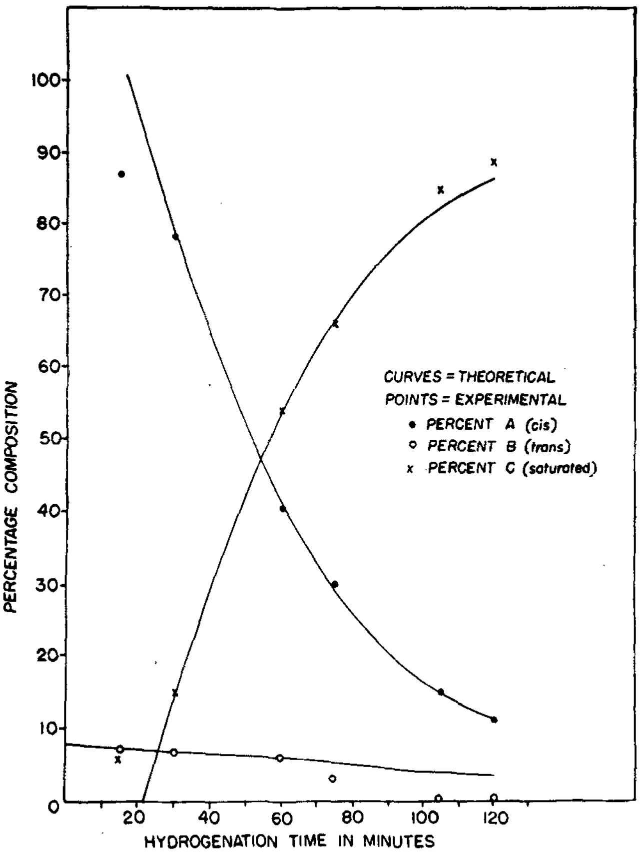

FIG. 2. Comparison of theory with experimental results for Hydrogenation No. 1.

The deviation from a straight line of the other two curves in Figure 1 shows that for Hydrogenations No. 2 and No. 3 k_4 cannot be neglected and the disappearance of A does not follow first-order kinetics.

The comparison of theory with experiment is shown in Figures 2, 3, and 4. The value of the various constants used in the equations were determined by a method of successive approximations and are given in Table II. The final values of k_{01}, k_{02}, k_{03}, k_{04}, c_1, c_2, and a which were chosen were in all cases those which gave the apparent best fit of the experimentally determined A curve. Although this did not necessarily give the best possible over-all fit of the experimental data, it was a means of being consistent and allowed for easier interpretation of the deviation between theory and experiment.

Although exact fits for the curve representing the percentage of *trans* component as a function of time were not obtained by the simple theory treated here, these fits could, in principle, be improved to any desired extent by suitable modification of equation (7).

TABLE II

Values of Constants

Hydrogenation number	k_{01} $\times 10^{-2}$ min.$^{-1}$	k_{02} $\times 10^{-2}$ min.$^{-1}$	k_{03} $\times 10^{-2}$ min.$^{-1}$	k_{04} $\times 10^{-2}$ min.$^{-1}$	a $\times 10^{-2}$	c_1	c_2
1[a]	0.01	1.0	2.2	0	0	151.76	9.94
2[b]	2.4	0.6	0.5	1.0	2.2	30.10	76.03
3[b]	9.1	2.5	3.7	3.5	9.0	24.96	85.25

[a] For equations 18, 19, and 20.
[b] For equations 15, 16, and 17.

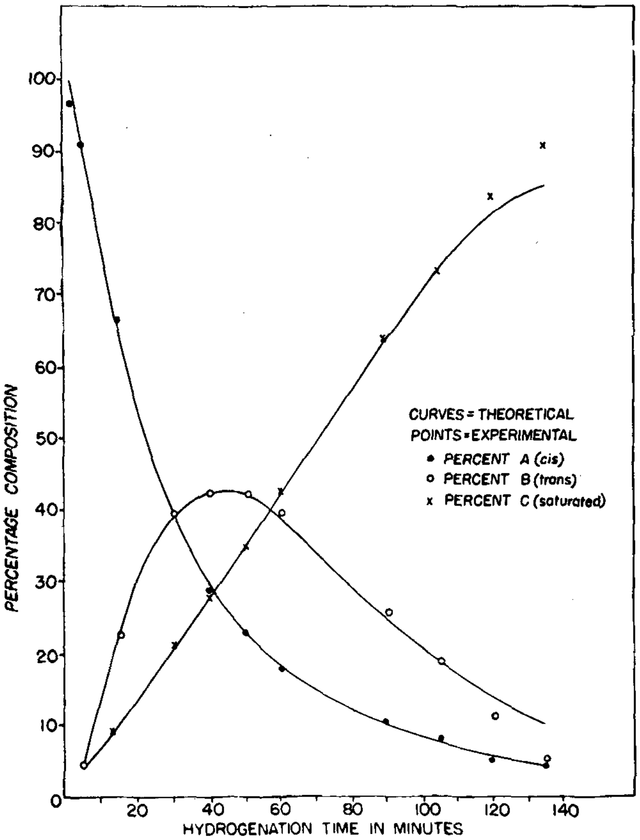

FIG. 3. Comparison of theory with experimental results for Hydrogenation No. 2.

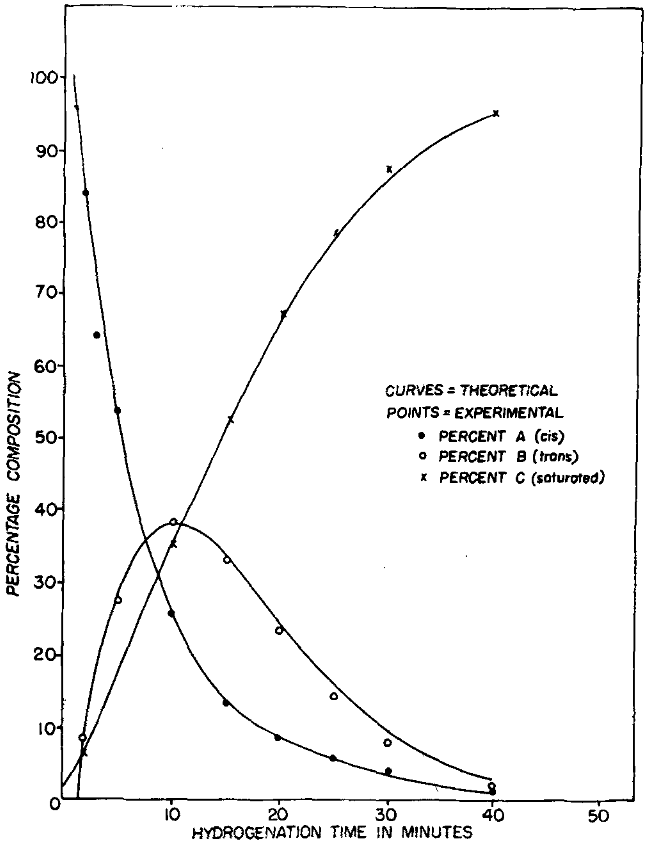

FIG. 4. Comparison of theory with experimental results for Hydrogenation No. 3.

Such a modification would be to include higher powers of *t* in the expressions for k_2 or k_4 or both. It would not be sufficient merely to modify equation (7) by using one value of α in k_1 and k_3 and a second value of α in k_2 and k_4. This would not give, for higher values of *t*, the proper curvature to the curve which expresses the percentage of *trans* component as a function of time. Although the modification suggested above is simple in principle, it would introduce into the rate laws governing the proposed mechanism new constants, the exact values of which would be of little theoretical interest at this time.

Previous investigators (4, 8) have stated that equilibrium conditions exist between *cis* and *trans* isomeric fatty acids or esters in those cases where *trans* isomers are formed in fairly high amounts during a hydrogenation. However the basis for this conclusion is not entirely clear. According to the mechanism assumed in this study such an equilibrium would require the percentage of *trans*/percentage *cis* $= k_1/k_4$. It will be noted that in Hydrogenation No. 2 this relationship is satisfied within experimental error between 18% *cis* and 5% *cis* where percentage *trans*/percentage *cis* $= 2.4$; $k_1/k_4 = 2.4$. Likewise in Hydrogenation No. 3 equilibrium conditions exist from 14% *cis* to 4% *cis* where percentage *trans*/percentage *cis* $= 2.5$; $k_1/k_4 = 2.6$.

From the curves for A as a function of the time the induction periods are found to be 18 min., 2 min., and 1 min. for Hydrogenations No. 1, No. 2, and No. 3, respectively.

Summary

Highly purified oleic acid was prepared from virgin grade olive oil and converted into a highly purified synthetic triolein by a direct esterification procedure. The triolein was hydrogenated at varying temperatures and pressures in the presence of nickel and a number of samples were withdrawn for analysis at carefully noted time-intervals.

The kinetics of the catalytic hydrogenation of triolein was analyzed. A mechanism was proposed for the course of the reaction involving three chemical species and the rate laws governing this mechanism were developed. The mechanism proposed along with the postulation that the effectiveness of the catalyst, as expressed by the term α, increases as the reaction proceeds was in theory sufficient to explain the experimental data. The reaction was first-order at a temperature of 125°C.; however at higher temperatures the reaction was found to be somewhat more complex. The kinetic study substantiated the existence of an equilibrium between *cis* and *trans* isomers over part of the reaction.

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Application of High-Speed Centrifugation to Studies of Plastic Spreads[1]

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DEVELOPMENT of plastic spreads frequently requires knowledge of the proportion and composition of the component solid and liquid phases. In principle it should be possible to separate a plastic spread for analysis by sedimentation into its solid and liquid phases since they generally differ in density by slightly more than 0.1 g./ml. Mohr and Baur-Kiel (4) tried to centrifugally separate the solids and liquid phases of butter in order to obtain a direct measure of the proportion of solid component. Only limited separation was achieved because of the comparatively weak centrifugal field produced in the centrifuge of conventional type which they used. By using the higher centrifugal field attainable in an ultracentrifuge (5, 6), we have separated butter, and, in addition, margarine, shortening, lard, and global edible spread (3) more completely into their solid and liquid components. In this work rates of separation of oil and solid phases were determined in an analytical ultracentrifuge and limiting values found for the proportion of solids separable under various experimental conditions. Although extensive phase separation occurred, complete oil-free solid sediments were not obtained; hence this method did not yield directly the solids content of the plastic spreads. Partial separation of the component phases also was achieved in a preparative ultracentrifuge and mate-

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