

oleate. Using a dry-reduced, electrolytic nickel type of catalyst, hydrogenations were carried out at various catalyst concentrations, temperatures, and rates of hydrogen dispersion. Hydrogenations also were conducted with three other catalysts: the electrolytic nickel after poisoning with sulfur, palladium, and highly active Raney nickel. The reactions usually were stopped at an iodine value of about 50.

Of the several variables, temperature was found to have the most marked effect; as the temperature increased from about 90 to 200°C. the proportion of double bonds remaining in the 9-position decreased from about 74 to 17%. Increasing the amount of catalyst and decreasing the rate of hydrogen dispersion increased the amount of migration of the double bonds. In some hydrogenated samples, double bonds were found in the 6- through 14-positions.

Under comparable conditions the palladium catalyst produced more positional isomers than did the electrolytic nickel catalyst. Sulfur poisoning apparently had no effect on the distribution of the double bonds.

With all catalysts except the Raney nickel the percentages of double bonds found in the 7- and 8-positions generally were approximately equal to those found in the 11- and 10-positions, respectively. Because double bonds hydrogenate more rapidly as their distance from the ester group increases, it appears that more double bonds actually migrated away from than toward the ester group.

With the Raney nickel catalyst, which was used at 30°C., end-products were produced which contained more 7- and 8- than 10- and 11-isomers.

The amount of *trans* isomers formed was not proportional to either the degree of hydrogenation or the amount of migration of the double bonds.

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Selectivity in the Hydrogenation of Oleic-Linoleic Acid Oils with Commercial Nickel Catalysts

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LATEST DEVELOPMENTS in the assay of fatty acid mixtures by paper chromatography of Kaufmann and of Seher (1, 2) have given us an opportunity to review some of Bailey's (3) theories on the selectivity of the hydrogenation of oleic-linoleic acid oils.

The works of Swicklik *et al.* (4) and Vandenhoeve (5) have already proved that hydrogenations of oleic and linoleic acid derivatives will not always follow pure first-order kinetics. It has been shown that a hydrogenation may start with an initial period during which the reaction rate is near zero order, and unless these initial periods are of the same length for simultaneous hydrogenations of oleic and linoleic acid derivatives, the constancy of the relative reaction rate coefficients, as stated by Bailey, cannot be upheld.

In our investigations we have hydrogenated sesame oil and studied the influence of temperature and catalyst self-poisoning. We have shown that the initial periods are not of the same length for the oleic and linoleic oil components. Moreover we have found that during the period of first-order kinetics a change in

temperature has the same influence on the hydrogenation rate coefficients of the oleic and linoleic acid esters, which means that the activation energy per hydrogenated double bond is independent of the acid.

When working with self-poisoned catalysts, the hydrogenation of the last 10% of linoleic acid proved to be no easier than the hydrogenation of oleic acid. We believe that this was due to isomerization in connection with such catalysts.

In the following, the terms oleic acid and linoleic acid stand for all types of C₁₈-monoenoic and C₁₈-di-enoic acids, respectively.

Experimental

Procedure. In order to be able to extract samples at well-defined intervals during the hydrogenations we chose to make the experiments at atmospheric pressure by using a simple glass apparatus. The latter consisted of a vertical, cylindrical vessel with the dimensions h = 15 cm. and d = 5 cm., into which hydrogen was injected through a fritted-glass plate placed at the bottom. There was no other agitation

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than that caused by the hydrogen dispersion. The rate of flow of the hydrogen was kept constant at two liters a minute. The required temperature was maintained by immersing the hydrogenation vessel into an oil bath with thermostat.

All hydrogenations were carried out with the same sesame oil. Before each run the oil was warmed up for half an hour under a steady flow of hydrogen. The point when the catalyst mixed with a small quantity of oil was added marked the beginning of a hydrogenation. Two catalysts were used. One was a normal commercial nickel-guhr catalyst, the other a nickel catalyst of the same type which has been self-poisoned by use in the hydrogenation of marine oils. Before the experiments the latter was rinsed in about 10 times its weight of sesame oil. Both catalysts were added in quantities corresponding to those used in practice.

Analytical. The procedure described in references 1, 2 was followed very closely with a single addition. In order to insure the best possible equilibrium between the two phases on the paper, the impregnated strip was washed for 24 hrs. with the mobile phase, using the descending chromatographic technique. The paper strip was then dried for half an hour at room temperature, and the samples were applied in the usual way.

The chromatographic assays provide us with the relative molar composition of the samples with respect to stearic acid, oleic and palmitic acid, and linoleic acid. An additional determination of the iodine value enables us to distinguish between oleic and palmitic acid.

The fact that the palmitic acid content of the oil is not influenced by the course of the hydrogenation may be utilized for a determination of the linoleic acid content as soon as the common palmitic acid content is known. When this is the case, it is sufficient to calculate the ratio between stearic acid and oleic plus palmitic acid, and then to use the known palmitic acid content to find percentage of saturated acids, which, together with the iodine value, gives the linoleic acid content. Such an indirect determination is

TABLE I
Hydrogenations with a Normal Nickel-Guhr Catalyst

Operating conditions	Hydrogenation time (hrs.)	S % stearic	O % oleic	L % linoleic
Hydrogenation No. 1.....	0	7	40	43
Temperature 125°C.....	3	10	48	32
Catalyst concentration.....	6	14	61	15
0.25% Ni.....	8	22	57	11
Atmospheric pressure.....	10	26	58	6
High dispersion.....	13	25	65	2
	23½	41	49	0
Hydrogenation No. 2.....	0	7	40	43
Temperature 150°C.....	1½	11	57	22
Catalyst concentration.....	3	19	64	7
0.25% Ni.....	5	31	59	-5
Atmospheric pressure.....	7	45	45	0
High dispersion.....	9¾	57	33	-1
	14¼	68	22	-5
Hydrogenation No. 3.....	0	7	40	43
Temperature 175°C.....	½	8	51	31
Catalyst concentration.....	1	12	62	16
0.25% Ni.....	2	24	58	8
Atmospheric pressure.....	4	50	38	2
High dispersion.....	8	81	9	2
	12½	86	4	3
Hydrogenation No. 4.....	0	7	40	43
Temperature 200°C.....	¼	10	49	31
Catalyst concentration.....	½	11	60	19
0.25% Ni.....	1	19	67	4
Atmospheric pressure.....	2	46	44	-3
High dispersion.....	4	78	11	1
	6	82	8	0

TABLE II
Hydrogenations with a Self-Poisoned Nickel-Guhr Catalyst

Operating conditions	Hydrogenation time (hrs.)	S % stearic	O % oleic	L % linoleic
Hydrogenation No. 5.....	0	7	40	43
Temperature 125°C.....	2	8	38	44
Catalyst concentration.....	5	8	46	36
1.0% Ni.....	10	9	58	23
Atmospheric pressure.....	16½	11	68	11
High dispersion.....	23	15	63	12
	40	18	62	10
Hydrogenation No. 6.....	0	7	40	43
Temperature 150°C.....	1	9	42	39
Catalyst concentration.....	3	9	62	19
1.0% Ni.....	5½	11	68	11
Atmospheric pressure.....	8	14	67	9
High dispersion.....	12	17	64	9
	22	25	55	10
Hydrogenation No. 7.....	0	7	40	43
Temperature 175°C.....	½	8	48	34
Catalyst concentration.....	1	8	60	22
1.0% Ni.....	2½	12	65	13
Atmospheric pressure.....	5	15	66	9
High dispersion.....	9	17	68	5
	15	22	64	4
Hydrogenation No. 8.....	0	7	40	43
Temperature 200°C.....	½	7	60	23
Catalyst concentration.....	1	7	72	11
1.0% Ni.....	2	9	75	6
Atmospheric pressure.....	3½	13	71	6
High dispersion.....	6	20	62	8
	10	23	62	5

of particular value when the percentage to be obtained has become so small that the corresponding spot on the paper can no longer provide an accurate measurement, but since it is absolutely certain that all the assays should have given the same percentage of palmitic acid, a calculation based on a common well-determined palmitic acid percentage may also increase the accuracy in general. We took advantage of this fact in our final calculations. The common palmitic acid content was found as the average value of the results of all the assays in which the linoleic spot was still accurately detectable, and this value, which was furthermore checked by gas-liquid chromatography, was used in a final correction of all the results.

Results and Discussion

Tables I and II show the results of hydrogenations with a normal and a self-poisoned commercial nickel catalyst, respectively.

In connection with the hydrogenations of the linoleic components the natural logarithm ($\ln L$) of the direct results ($\% L$) is the most suitable derivative function to calculate since in the case of first-order kinetics we have

$$\frac{dL}{dt} = -K_L L; \ln L = -K_L t$$

An attempt to illustrate the course of hydrogenations of the oleic components proves to be more complicated because the oleic acid concentration not only decreases because of conversion to stearic acid but also increases as a result of linoleic acid hydrogenation. It seems reasonable to measure the hydrogenation of oleic acid by the increase in the stearic acid concentration ($dO = -dS$), which means that for first-order kinetics we have

$$\frac{dS}{dt} = K_O O$$

A change from infinitesimal to measurable intervals transforms this equation to

$$\frac{\Delta S}{\Delta t} = K_O \bar{O}$$

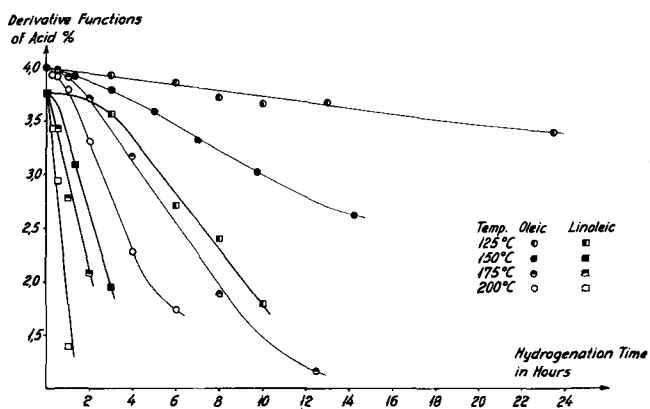


FIG. 1. Hydrogenations with a normal nickel-guhr catalyst (0.25% Ni).

where \bar{O} represents the average oleic acid concentration in the given time-interval. The term $-\frac{\Delta S}{\bar{O}}$ thus corresponds to $\frac{dL}{L}$ which means that $-\sum \frac{\Delta S}{\bar{O}}$ can be used as a suitable analogue to $\ln L$. Consequently we have chosen $\ln 55 - \sum \frac{\Delta S}{\bar{O}}$ as the derivative function for the hydrogenations of the oleic components. The term $\ln 55$ in this expression represents 55% O, which is an approximate common average for all hydrogenations of $\frac{O_{\text{initial}} + O_{\text{max}}}{2}$, the latter having arbitrarily been chosen to correspond to the initial linoleic concentration. In this way we have obtained for both acids directly comparable derivative functions and curves.

The derivative functions, which are given in Figures 1 and 2, show that each hydrogenation can be divided into an initial period with increasing rate coefficient, an intermediate period with a constant rate coefficient, and, in most cases, a final period with decreasing rate coefficient.

The initial periods show the same general course, independent of catalyst self-poisoning. In case of the linoleic hydrogenations the initial periods are most pronounced at 125°C., still distinct at 150°C., hardly visible at 175°C., and at 200°C. they vanish altogether. The hydrogenations of the oleic components also show decreasing initial periods with increasing tempera-

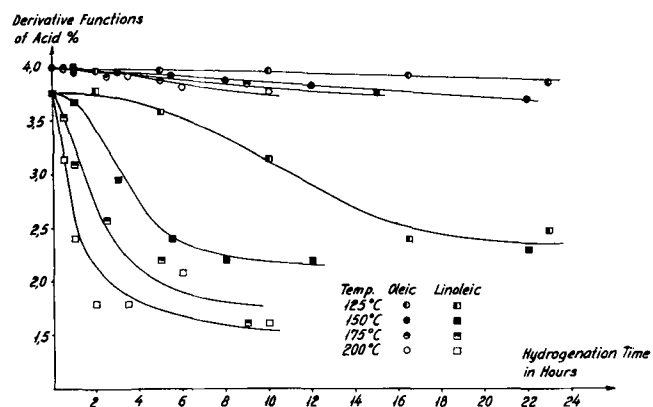


FIG. 2. Hydrogenations with a self-poisoned nickel-guhr catalyst (1.0% Ni).

ture. However in this case the initial periods are longer than the corresponding linoleic periods, at least when the normal catalyst is used. When hydrogenating with self-poisoned catalyst at temperatures below 175°C., the over-all oleic reaction rates are so small that it is no longer possible to distinguish between initial and intermediate periods. These differences in the duration of the initial periods, depending on the acid, show that lack of hydrogen saturation, as stated by Vandenhuevel (5), cannot be the only cause of initial zero-order kinetics. When compared with the following intermediate periods, in which a change in temperature seems to have no influence on the ratio between the linoleic and the oleic reaction rate coefficients, they also give the only explanation why a rise in temperature will increase selectivity.

The intermediate periods are characterized by pure first-order kinetics. Their rate coefficients are determined on the basis of Figures 1 and 2. According to the Arrhenius equation, $\ln K = \ln A - \frac{E}{RT}$, a graphical representation of $\ln K$ plotted against the reciprocal Kelvin temperature will be a straight line with the slope $-\frac{E}{R}$. Such a graphical correlation is shown in Figure 3. It may be seen that with the prevailing analytical error it is not possible to distinguish between the activation energies in the various cases.

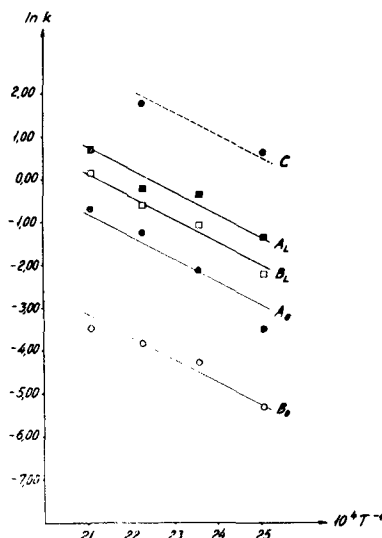


FIG. 3. Graphically estimated first-order rate coefficients. (A_L) Hydrogenation of linoleic components, normal catalyst, 0.25% Ni; (A_O) hydrogenation of oleic components, normal catalyst, 0.25% Ni; (B_L) hydrogenation of linoleic components, self-poisoned catalyst, 1.0% Ni; (B_O) hydrogenation of oleic components, self-poisoned catalyst, 1.0% Ni; (C) hydrogenation of triolein, Swicklik *et al.*

This means that the affinity of hydrogen to a double bond is practically independent of the acid and of catalyst self-poisoning. The differences between the hydrogenation rate coefficients of the oleic and the linoleic acids and the differences between the ratios of these two rate coefficients, depending on the state of the nickel catalyst, are thus caused by differences between the corresponding frequency factors. From the slopes of the straight line in Figure 3 the common activation energy per hydrogenated double bond can be determined to be approximately 10 kcal.

Figure 3 also shows two values of oleic hydrogenation rate coefficients which have been taken from the investigations of Swicklik and co-workers (4) (Table I) on the assumption that the first three results in Hydrogenation No. 3 are also due to an initial period. The corresponding experiments were carried out with 0.4% Ni, a hydrogen pressure of 65 lbs., vigorous agitation, and high hydrogen dispersion. Even though these conditions are quite different from ours, the results nevertheless show the same activation energy with a marked change in the frequency factor.

The final periods are independent of the catalyst only when oleic hydrogenations are examined, in which case they cannot be correlated with any common acid percentage. Hydrogenations of the linoleic components follow different patterns, depending on the state of the nickel. While, when hydrogenating with 0.25% fresh Ni, first-order kinetics can be observed down to linoleic percentages below 5%, the corresponding hydrogenations with 1% self-poisoned Ni seem to stop at about 10% linoleic acid. The experiments illustrated in Figure 4 were made in order to examine the stagnation of the linoleic hydrogenations. They were divided into five stages. (A) Sesame oil was hydrogenated with 1% self-poisoned Ni at 175°C. for 5 hrs. (B) What was left of the oil from stage (A) when samples had been drawn was doubled up with a fresh portion of sesame oil and hydrogenated for another 5 hrs. (C) A new portion of sesame oil was hydrogenated with 1% self-poisoned Ni at 175°C. for 6 hrs. After removal of the catalyst by filtration, what was left of this oil was divided into two equally large parts: (D) one part was hydrogenated in the same way as in stage (C) with a new portion of self-poisoned catalyst; (E) the other part was hydrogenated with 0.25% fresh Ni. On the basis of Figure 4 we draw the following conclusion. The decreasing hydrogenation rate coefficients cannot be caused by progressive catalyst poisoning since, after

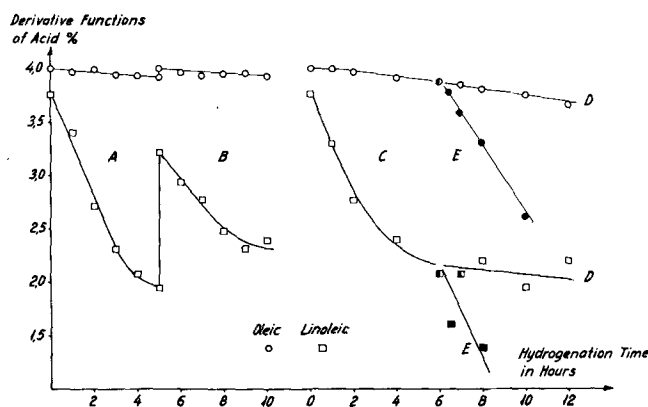


FIG. 4. Various hydrogenations to investigate the linoleic stagnation. (A) Hydrogenation with 1.0% self-poisoned Ni, 175°C.; (B) A continued after addition of fresh oil; (C) hydrogenation under the same conditions as A; (D) C continued after renewal of the 1.0% self-poisoned Ni; (E) C continued after exchange of the self-poisoned catalyst with 0.25% normal Ni.

an addition of fresh oil, the hydrogenation resumes what would have been its original rate, the reduced catalyst concentration taken into consideration. Once the final linoleic period has begun, the hydrogenation as a whole can best be characterized by assuming that the catalyst can no longer distinguish between linoleic and oleic components, and this applies whether fresh or self-poisoned nickel is used for further hydrogenations. We believe that these results are due to an isomerization of the linoleic acid.

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A Critical Study of the Oxidation Methods for the Determination of Glyceride Composition of Fats^{1,2}

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THE OXIDATION OF FATS with permanganate in acetone was proposed by Hilditch and Lea (9,15) for the estimation of trisaturated glycerides (GS₃).⁴ Kartha (21-23) carried out this oxidation in the presence of excess (3-6%) acetic acid and developed a method for the determination of the glyceride type of composition of natural fats by sep-

arating magnesium salts of azelao-glycerides. The results obtained for the glyceride type of composition of many natural fats by Kartha's method are different from those obtained by Hilditch's crystallization method (12), and the theories put forward by these two investigators (13,24) for the glyceride distribution in fats on the basis of these results also differ widely (10,11,14,24,28,36,41,42). Both the oxidation methods of Hilditch and Lea and Kartha are based on the assumptions that the unsaturated acids in the unsaturated glycerides (GS₂U, GSU₂, and GU₃) are cleaved and that the resultant azelao-glycerides are not hydrolyzed during the oxidation and the subsequent separation procedures.

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⁴ Abbreviations used are as follows: G, glyceryl radical; S, saturated acid or radical containing 16 or more carbon atoms; U, unsaturated acid radical; O, oleic acid radical; L, linoleic acid radical; A, azelaic acid radical; and S^o, oxygenated saturated acid radical (incomplete oxidation product of oleic acid).