•*Technical*

Positional Isomers Formed During the Hydrogenation of Methyl Oleate[1]

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THE FORMATION of positional isomers during the hydrogenation of oleic acid and its esters has been regarded as a fact almost since the process of hydrogenating oils was discovered. In 1913 Lewkowitsch (13) suggested that the iso-oleic acid formed during the hydrogenation of oleic acid was a positional isomer. At a later date Moore (14) examined ethyl oleate which had been partially hydrogenated with the aid of palladium and nickel catalysts and concluded that some of the residual double bonds occurred in the 11- and possibly 10-position of the fatty acid groups. Hilditch and Vidyarthi (11) reported that the partial hydrogenation of methyl oleate yielded some iso-oleic acid groups having double bonds in the 8- and 10-positions. Subsequently others have offered additional evidence that migration of the double bond does occur. However evidence as to the proportions of double bonds involved and the distances of their migrations along the carbon chain was obtained only recently. Boelhouwer *et al.* (4) published data on the migration of double bonds during the hydrogenation of methyl oleate, elaidinate, and petroselinate. As an extension of this investigation, Knegtel *et al.* (12) developed additional data on the migration of double bonds during the hydrogenation of methyl oleate. In both investigations hydrogenation was carried out at about 180°C., and 3% by weight of a 20% nickel-on-kieselguhr catalyst was used. Allen and Kiess (2) investigated the migration of double bonds during the hydrogenation of oleic acid, elaidic acid, and methyl oleate. Only one type of catalyst, reduced nickel formate, was employed. A single hydrogenation was carried out with each compound and samples were withdrawn at various iodine values. Apparently no one has investigated the effect of the operating conditions on the migration of double bonds during the hydrogenation of oleic acid or oleates. The only investigation which might be considered to be even remotely in this category was carried out in our laboratory with cottonseed oil, a product which contains about 25% oleic acid among its component fatty acids (5).

The purpose of the present investigation was to obtain data on the shift of double bonds during the catalytic hydrogenation of methyl oleate under various operating conditions. A single preparation of methyl oleate was employed. The varied operating conditions were temperature, rate of hydrogen dispersion, type of catalyst, and catalyst concentration.

Experimental

Materials. The methyl oleate was prepared from a commercial pecan oil of good quality.

To convert the pecan oil into mixed methyl esters, 4,000 g. of it were added to 900 g. of absolute methanol, which previously had been treated with 14.0 g. of sodium. The methanolysis was allowed to proceed for 2 hrs. at 50°C. Then the product was washed successively with dilute acetic acid and water. Mixed esters were dried and passed through a pot still. The distilled esters were crystallized from acetone, once at −60°C., once at −37°C., and twice again at −60°C. The crystallization at −37°C. was carried out by using 10 ml. of acetone per 1 g. of esters while those at −60°C. were carried out by using 15 ml. per 1 g. All proportions were based on the original weight of the methyl esters. In the −37°C. crystallization the precipitate was discarded; in the −60°C. crystallizations the filtrates were discarded. The methyl oleate from the crystallizations was redistilled to obtain a final yield of 1,650 g. with an iodine value of 83.0 (theoretical, 85.6), a linoleate content of 0.13%, and a *trans* isomer content of 0.0%. Propyl gallate in the amount of 0.01% was added as an antioxidant.

The electrolytic nickel catalyst, which was used in most of the hydrogenations, was a commercial product of the supported type prepared by dry reduction. It was obtained from the Girdler Company. The hard fat in which the catalyst had been suspended by the manufacturer was removed before each hydrogenation.

The W-5 nickel catalyst was prepared essentially according to the method of Adkins and Billica (1). This catalyst, which is a suspension of Raney nickel in ethanol, is claimed to have a very high activity.

The palladium catalyst, which was obtained from Baker and Company Inc., was of the carbon-supported type and contained 10% by weight of the metal.

The sulfur-poisoned nickel catalyst was prepared by the procedure of Ziels and Schmidt (17). Nine grams of sulfurated oil, prepared by reacting 5 g. of sulfur and 500 g. of refined cottonseed oil for 2 hrs. at 95°C., followed by another 2 hrs. under nitrogen at 180°C., was mixed with 500 g. of fresh cottonseed oil and electrolytic nickel catalyst containing 25 g. of nickel. This mixture was hydrogenated to an iodine value of 86. The sulfur-poisoned nickel catalyst was removed by filtration.

Hydrogenation Apparatus and Procedure. The hydrogenations were carried out in a glass vessel 28 mm. in diameter and 200 mm. long. The top of the vessel was fitted with a 29/42 standard taper joint, the upper part of which was equipped with hydrogen inlet and outlet tubes and a thermocouple well. The hydrogen inlet tube and thermocouple well extended to near the bottom of the vessel. The rate of gas dispersion was varied by using two different inlet tubes. One was equipped with a small, flat, fritted-glass disk (good dispersion) while the other was drawn down to a relatively small diameter (poor dispersion).

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TABLE I

Operational and Analytical Data on the Hydrogenation of Methyl Oleate

Run No.	Hydrogenation conditions				Hydrog. time, min.	Iodine value	*Trans* isomers, wt. %	*Trans* bonds,[a] %	Composition of dicarboxylic acids obtained on oxidation of acyl groups, mol %								
	Temp., °C.	Catalyst		Hydrog. dispersion rate					C_6[b]	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
		Conc., %	Type														
1	90[c]	0.2	Ni	Low	857	54.5	13.5	21.2	0.0	2.0	11.9	74.5	11.5	0.0	0.0	0.0	0.0
2	110	0.2	Ni	High	148	49.7	22.8	39.3	0.0	5.9	15.7	62.0	13.6	2.8	0.0	0.0	0.0
3	170	0.2	Ni	High	28	49.8	40.3	69.3	0.0	11.0	17.5	23.3	19.1	9.6	7.2	6.6	5.6
4	200	0.2	Ni	High	21	49.2	39.1	68.0	2.1	13.6	16.7	16.7	16.7	11.5	8.4	6.7	7.5
5	170	0.8	Ni	High	25	50.0	41.0	70.2	0.0	10.3	15.3	16.1	16.5	11.6	9.1	8.7	12.4
6	170	0.2	Ni	Low	44	48.6	39.6	69.7	3.5	10.7	18.3	17.9	17.9	14.2	9.4	5.7	2.4
7	170	0.2	Pd	High	23	48.4	38.5	68.1	4.9	9.9	10.9	12.7	18.0	13.7	11.7	9.7	8.5
8	170	0.2	Ni+S[d]	High	63	50.6	40.9	69.2	0.0	12.5	21.8	23.7	18.7	13.3	5.9	4.2	0.0
9[e]	30	3.4	W-5 Ni	High	65	32.7	13.3	34.8	0.0	16.6	16.1	54.4	9.6	3.8	0.0	0.0	0.0
10[e]	30	3.4	W-5 Ni	High	45	52.1	13.9	22.8	0.0	10.7	17.3	62.8	9.3	....	....	....	....
Original methyl oleate						83.0	0.0	0.0	0.0	1.7	7.8	90.6	0.0	....	....	....	....

[a] Based on the total number of *cis* and *trans* bonds.
[b] A portion of the C_6 dibasic acid was lost during the analysis.
[c] Temperature varied within ±10°C. as required to maintain reasonable rate of reduction.
[d] Nickel poisoned with sulfur.
[e] A 25-ml. solution of methyl oleate and ethanol, 1:1 by wt., was hydrogenated. Catalyst concentration was calculated on a methyl oleate basis.

The sample to be hydrogenated was heated electrically. Manipulation of the voltage control and the depth of the glass vessel in the heating mantle permitted temperature control to within ±1°C.

Hydrogen was passed through the sample at a rate of approximately 425 ml./min. by means of a Sigma pump and suitable connections and bypass lines. Excess hydrogen was recycled. The rate of flow and the amount of hydrogen absorbed were measured, respectively, by a rotometer and by the loss of volume in a small gas-holder. Good mixing of the ester and catalyst was ensured under all conditions by the rate of gas flow.

To make a run, 25 g. of methyl oleate and the desired amount of catalyst were placed in the glass vessel; and the entire system, including the sample, was thoroughly flushed with hydrogen. The sample was then heated to the proper temperature, and the reaction was started. When the predetermined amount of hydrogen had been removed from the gas holder, the flow was stopped, the sample was cooled to about room temperature, and the catalyst was removed by filtration. Each sample was stored under hydrogen in a refrigerator until analyzed.

Methods of Analysis. The analytical techniques employed to determine the positions of the double bonds have been described previously (5) and can be summarized as follows:

A 2-g. portion of each hydrogenated sample was dissolved in 100 ml. of ethyl acetate, cooled to −5°C., and ozonized, using 6–7% ozone in oxygen, until the reaction was complete, as judged by the effect of the spent gas on a potassium iodide solution. Then 10 ml. of 30% hydrogen peroxide were added to the ozonides, the mixture was refluxed for 1 hr., and the solvent was removed by evaporation under nitrogen.

The resulting product was refluxed for 1 hr. with a 10% excess of alcoholic potassium hydroxide. Then the ethanol was evaporated under nitrogen while the volume was kept constant by the addition of water. The ethanol-free soap solution was acidulated, the fatty and dibasic acids were extracted with ethyl ether, and the ether was evaporated. The residual mixture of mono- and dibasic acids was dissolved in 200 ml. of a 5% tert-amyl alcohol-in-chloroform solution, and 5-ml. portions were analyzed on each of two types of chromatographic columns, using modifications of the techniques described by Higuchi *et al.* (10) and Corcoran (6).

The percentages of C_6 through C_{10} dibasic acids were determined with a column of silicic acid mixed with a citrate buffer (25 g. of acid plus 18.75 ml. of 1 *M* citrate of pH 5.40). Percentages of C_{11} through C_{14} dibasic acids were determined by using a column of special silicic acid mixed with a glycine buffer (25 g. of acid plus 16.5 ml. of 2 *M* glycine of pH 8.50). Both columns were eluted first with chloroform, then with solutions of butanol in chloroform in which the concentration of butanol was increased progressively.

Trans isomers were determined by a modification (8) of the infrared spectrophotometric method of Swern *et al.* (16).

Results and Discussion

General Considerations. The unhydrogenated methyl oleate was found on analysis to have 7.8% of its double bonds in the 8-position of the fatty acid chain (Table I). Somewhat similar analyses have been encountered by other investigators and attributed either to a limited migration of the double bonds during the preparation of the oleic acid (2) or to the presence of 8-octadecenoic acid in the glycerides of some natural fats (3). The percentage of double bonds in the 8-position of the methyl oleate represented in Table I does not appear to be the result of a faulty method of analysis. Cottonseed oil analyzed by the same procedures yielded only the C_9 dibasic acids.

The mole percentages of the dibasic acids (Table I) are estimated to be reproducible to within about 3 percentage units. In calculating the mole percentages, the titrations for each peak of the titration curves were corrected by subtracting the blank titrations. Titrations between peaks were disregarded. By this procedure the combined acidity of the individual components eluted from the columns equaled 90 to 110% of the amount of the acidity to be expected on the basis of a titration of the original mixture of fatty and dibasic acids.

The percentages of the C_6 dibasic acid represented in Table I are lower than the actual percentages of double bonds in the 6-position. Tests indicated that the ether extraction of the acidulated soap solutions, as described above, did not remove all of the C_6 dibasic acid. Because the percentages of C_6 dibasic acid found were small, this failure to extract it completely did not have a significant effect on the relative proportions of the C_7–C_{14} dibasic acids found. No difficulty was encountered in extracting the C_7 dibasic acid.

Each hydrogenation was essentially a zero-order reaction, that is, the decrease in iodine value was

directly proportional to the reaction time. However this reaction order was not attributable to the same operating variable in each hydrogenation. From the data in Table I it appears that temperature was the rate-determining factor in two hydrogenations. The type of catalyst or rate of hydrogen dispersion appeared to be responsible in others.

Effect of Operating Conditions on Extent of Migration. Hydrogenation Runs 1 through 4 (Table I) show the effect of temperature on the migration of the double bonds. Run 1 can be included in the comparison because the reaction time, 857 min., was so long that the rate of hydrogen dispersion had no significant effect on the course of the reaction, a conclusion which is supported by a comparison of Runs 3 and 6. The pattern of distribution of double bonds in the samples of hydrogenated methyl oleate from Runs 1 through 4 is also shown in Figure 1.

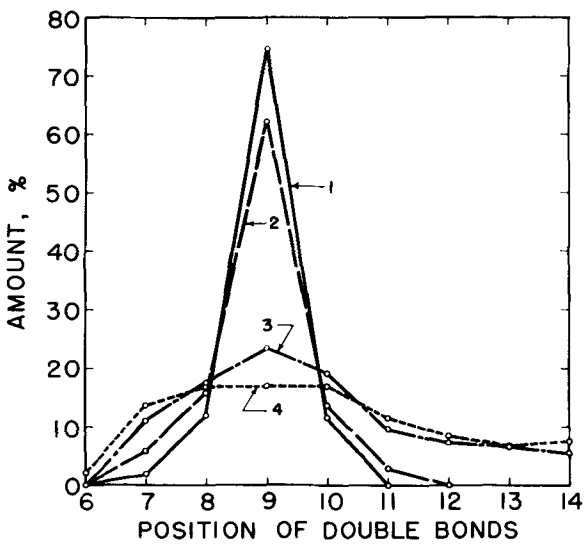

FIG. 1. Distribution of double bonds at different hydrogenation temperatures: 90°C., 1; 110°C., 2; 170°C., 3; 200°C., 4. Curve numbers refer to run numbers in Table I.

As the temperature was increased progressively from about 90°C. to 200°C., the proportion of residual double bonds in the 9-position at an iodine value of approximately 50 decreased from 74.5 to 16.7%. As the temperature increased, double bonds were found at increasing distances away from the 9-position; and at 200°C. they were found spread from the 6- through 14-positions. Some double bonds probably migrated beyond these positions, but this could not be established by the method of analysis employed.

The temperature of 90°C. was the practical lower limit at which the electrolytic nickel catalyst could be employed. The W-5 nickel catalyst was active at the much lower temperature of 30°C. As will be discussed below, its mode of action was apparently different, and runs made with it cannot properly be considered as part of the series made to determine the effect of temperature. Nevertheless it is interesting to note that an hydrogenation carried out at 30°C. with nickel catalyst still produces a sizable migration of double bonds.

The data from Runs 1 through 4 should provide some information as to the degree to which the migration of double bonds in oleic acid-containing triglycerides can be controlled under plant conditions by varying the temperature. Most of the temperature ranges used for Runs 1–4, the catalyst, and the concentration of catalyst are encountered in commercial practice. However it must be remembered that under a given set of conditions the double bond in methyl oleate isomerizes faster and more extensively than does the double bond in the oleoyl group of an ordinary triglyceride.

By comparing the data from Runs 3 and 5, information can be obtained on the effect of catalyst concentrations. Increasing the catalyst concentration from 0.2 to 0.8% lowered the proportion of residual double bonds in the 9-position from 23.3 to 16.1% and increased slightly the proportions of double bonds in the 10 and higher positions. Increasing the catalyst concentration decreased, from 28 min. to 25 min., the reaction time required to reach an iodine value of approximately 50, indicating that in both runs the hydrogenation system was well supplied with catalyst and that the rate of dispersion of hydrogen in the oil largely controlled the reaction rate. However it is doubtful that other catalyst concentrations would have produced greatly different patterns of distribution of the double bonds. Catalyst concentration is generally recognized to be less effective than temperature as a tool for changing the properties of a hydrogenated oil.

The effect of rate of hydrogen dispersion on the pattern of distribution of the double bonds can be determined from Runs 3 and 6. The low rate of hydrogen dispersion, Run 6, resulted in a lower percentage of residual double bonds in the 9-position and in the migration of some double bonds to the 6-position. The high rate of hydrogen dispersion apparently did not produce double bonds in the 6-position.

Comparison of Runs 3, 7, and 8 reveals the effect of three types of catalysts on the patterns of distribution of the residual double bonds. From Runs 3 and 8 it is evident that poisoning the electrolytic nickel catalyst with sulfur had practically no effect on the pattern of distribution even though the hydrogenation time was increased from 28 min. to 63 min. Use of the palladium catalyst in place of electrolytic nickel did produce a difference in the pattern of distribution. The percentage of residual double bonds in the 9-position decreased from 23.3 to 12.7, and the double bonds arranged themselves more or less evenly among the 7- through 14-positions. A relatively large percentage was found in the 6-position.

The behavior of the three catalysts is not quite in agreement with that observed when the same catalysts were used under similar conditions in the hydrogenation of methyl linoleate (7). With the latter compound the three catalysts produced essentially the same pattern of distribution of double bonds.

Hydrogenation Runs 9 and 10, which were carried out with the W-5 nickel catalyst, yielded products which differed in at least one respect from those obtained in the other eight runs carried out with the electrolytic nickel, sulfur-poisoned nickel, and palladium catalysts. In Runs 9 and 10 those double bonds which migrated moved mostly to the 7- and 8-positions. Because the presence or absence of ethanol was found in another hydrogenation (7) to have no effect on the movement of double bonds, it might be concluded at this time that the unique behavior was caused by the catalyst.

Direction of Migration of Double Bonds. Earlier investigators have come to the conclusion that during the hydrogenation of methyl oleate the migration of

double bonds takes place equally in both directions from the 9-position. Allen and Kiess (2) found that percentages of the 7- and 8-isomers always equalled, respectively, the percentages of the 11- and 10-isomers. As hydrogenation proceeded, the proportion of each of the 7- through 11-isomers approached 20%. Knegtel *et al.* (12) also agreed that migration proceeded equally in both directions. Their conclusion was based on a determination of the percentages of double bonds in the 6- through 12-positions of samples hydrogenated progressively to an iodine value of 48.1. This conclusion regarding the direction of movement undoubtedly was correct under the experimental conditions which were described, provided it was limited to the residual double bonds found after hydrogenation. If a very precise method of determining the positions of all double bonds were available, it might be possible to show that the residual double bonds found after hydrogenation are seldom distributed equally on both sides of the original position.

The fact is generally accepted that as a double bond is moved farther away from the ester or carboxyl group its rate of hydrogenation increases. Pigulevskiĭ and Antamonov (15) apparently were the first to offer experimental proof when they prepared 2-, 3-, 6-, and 9-octadecenoic acids and with their aid demonstrated that the rate of hydrogenation increased with the distance of the double bond from the carboxyl group. Evidence is also available that, under at least some of the operating conditions represented in Table I, the preferential reduction of the outer bonds should occur to a measurable and significant degree. Similar experiments with hydrogenating methyl linoleate (7) showed that the percentage of double bonds remaining in the original 9-position exceeded significantly in a number of instances the percentage remaining in the original 12-position. Consequently the finding that, in the hydrogenated samples obtained in Runs 1 through 8 (Table I) the percentage of double bonds in the 7- and 8-positions generally equalled the percentage in the 10- and 11-positions, must mean that the amount of migration during hydrogenation was not equal in both directions and that the greater number of double bonds actually migrated away from the ester group.

It might be noted that the preferential hydrogenation of the double bonds farthest from the ester group would ensure most of the double bonds eventually migrating away from the ester group even if the direction of migration of the individual bonds in the different positions were purely a matter of chance.

There is other evidence that in Runs 1 through 8 the greater number of double bonds migrated away from the ester group. The original methyl oleate contained 7.8% of the 8-isomer. Hence, if the percentage of the 7- and 8-isomers generally equalled the percentage of 10- and 11-isomers after hydrogenation, the double bonds could not have migrated equally in each direction.

In hydrogenation Runs 9 and 10, which were carried out with the W-5 modification of the Raney nickel catalyst, the 7- and 8-isomers definitely exceeded the amounts of 10- and 11-isomers in the end products. However this does not necessarily mean that in these two runs the greater proportion of double bonds migrated toward the ester group. It is not known to what degree each of the different isomers was hydrogenated.

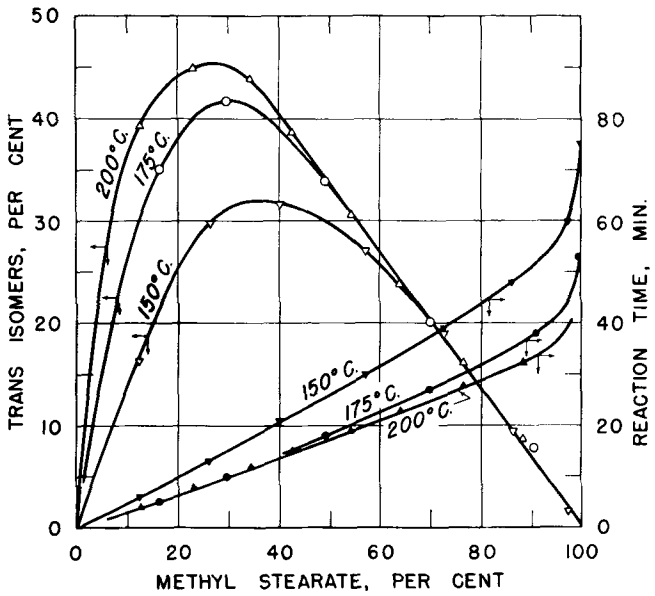

FIG. 2. Effect of temperature on the formation of *trans* isomers during the hydrogenation of methyl oleate with 0.25% electrolytic nickel catalyst and good dispersion of hydrogen (9).

Trans Isomers. The hydrogenation conditions which have been found to cause an increase in the formation of positional isomers also have been found to cause an increase in the formation of geometrical isomers (9). Geometrical isomerization, like positional isomerization, usually occurs at a rapid rate. The rates at which *trans* isomers are formed during the hydrogenation of methyl oleate have been measured under operating conditions similar to those employed in the present investigation; the same electrolytic nickel catalyst and a similar hydrogenation apparatus were employed (9). Data from this earlier investigation are shown graphically in Figure 2.

The straight line portions of the *trans* isomers *vs.* methyl stearate curves represent the region in which the ratio of *trans* to *cis* isomers has reached equilibrium; and the proportion of *trans* isomers present is 67%, based on the total amount of unsaturated esters present. Also Allen and Kiess (2) have shown that each positional isomer formed during the hydrogenation of methyl oleate contains 67% *trans* bonds. With this background the proportions of *trans* isomers found in Runs 1 through 10 are readily explained.

In most of the hydrogenated samples the *cis-trans* isomerization had reached equilibrium when the hydrogenation was stopped at an iodine value of about 50, which iodine value corresponds to the formation of about 40% methyl stearate. Hence the proportion of *trans* bonds was approximately 67%.

In the low-temperature hydrogenations, Runs 1, 2, 9, and 10, equilibrium never was reached. In these runs the proportions of *trans* isomers found were not proportional to the degree of hydrogenation or the amount of positional isomers found. The proportions of *trans* and positional isomers could not be correlated because varying proportions of the original *cis* bonds in the 9-position also were converted to *trans* bonds.

Summary

To obtain information on the influence of the operating variables on the migration of double bonds during the hydrogenation of the oleoyl group, a series of experiments was carried out with purified methyl

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 Vandenheuvel (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 C_{18}-monoenoic and C_{18}-dienoic 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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