Hydrogenation of Linolenate. VI. Survey of Commercial Catalysts[1]

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Abstract

A survey of commercially available hydrogenation catalysts has been made in a search for high-selectivity and low-isomerizing characteristics. Selectivity—the ratio of hydrogenation rates for linolenate to linoleate—was determined on a linoleate-linolenate equimixture under standardized conditions. Ratios of reaction rate constants for nickel catalysts at 140C ranged between 1.48 and 2.71; for palladium catalysts at 25C, 1.68 to 1.99; and for platinum catalysts at 25C, 1.33 to 1.61. *Trans* contents of ester mixtures reduced with these three metal catalysts ranged from 18.0 to 22.8, 16.7 to 20.5, and 6.3 to 8.4%, respectively. Although platinum catalysts produced the lowest isomerization, their selectivities were also low.

EVIDENCE exists that an improved, stabilized salad oil could be made from soybean oil by the elimination of linolenic acid containing glycerides (8). One approach is the conversion of linolenate to "linoleate" by selective hydrogenation. In this paper, selectivity means the preferential reduction of double bonds in linolenate compared with those in linoleate. For the hydrogenated oil to remain liquid at refrigerator temperature, hydrogenation must proceed with minimal formation of *trans* geometric isomers (2).

A survey was instigated to learn the range of selectivity and isomerization inherent in commercially available hydrogenation catalysts. Such a survey is necessary before undertaking research on catalysts' preparation and on the variables of time, temperature, pressure, and dispersion.

Experimental

Hydrogenation was performed in glass manometric equipment consisting of a 125-ml flask with a 24/40 ₸ joint attached through a capillary tube to a 50-ml gas burette and mercury leveling bulb. The flask, equipped with a side arm closed with a rubber serum cap, was immersed in a thermostatically controlled silicone oil bath. A magnetic stirrer supplied agitation.

Trilinolenin (7), trilinolein (10), methyl linoleate (12), and methyl linolenate (12) were prepared by countercurrent distribution.

In Table I are listed the commercially available platinum, palladium, and nickel catalysts used in this study. As indicated, catalysts differed not only in the metal, but also in the percentage of the metal and the type of carrier. Greatest variation in metal content was for the nickel catalysts, which ranged from 23 to 65%. Percentage of catalysts present (based on metal weight) varied according to metal; generally, 0.15% nickel; 0.05% palladium, and 0.4% platinum were used. Platinum and palladium catalysts were held at room temperature during hydrogenation; the nickel catalysts were used at 140C.

To begin the hydrogenation, the catalyst and a magnetic stirrer bar were placed in the flask, and the flask was attached to the manometer. Hydrogen at atmospheric pressure was used to flush and fill the equipment and also to saturate the catalyst. After the starting volume of hydrogen was read on the gas burette, an exact weight of the methyl ester sample (1 g) was introduced into the flask through the serum cap by means of a tared syringe and needle, and the stirrer was activated. Hydrogenation was continued until 0.5 mole of hydrogen per mole ester was absorbed (38.2 ml STP).

The derivation of equations for determining the ratio of hydrogenation rate constants for linolenate (Le) and linoleate (Lo) or the selectivity coefficient ($K = \frac{k_{Le}}{k_{Lo}}$) from kinetic considerations is detailed elsewhere (6). This method requires reducing an equal mixture of methyl linolenate and linoleate with 0.5 mole of hydrogen per mole ester, determining composition by gas chromatography, and calculating therefrom the ratio of reaction rates for the two esters. The volumes of hydrogen absorbed were measured to give, within the reading error of the gas burette, an iodine value of 172.4. Equivalent iodine values calculated from the chromatography data (Table IV) were 174.4 ± 4.0.

The percentage isomerization of *cis* to *trans* bonds was determined by infrared spectrophotometry with a Baird Atomic KM-1 instrument. Samples for infrared analysis were dissolved in carbon disulfide (2.5%

TABLE I

Catalyst Description and Isomerization Characteristics

No.	Description	Isomerization		
		Trans	Mean *Trans*	Statistical significance[a]
		%	%	
1	Platinum oxide	6.6 6.3	6.45	
2	5% Platinum on carbon	7.5 8.2	7.85	
3	5% Platinum on alumina	8.4 8.3	8.35	
4	5% Palladium on carbon powder	18.2 17.4	17.80	
5	47% Nickel on carbon	18.0 18.1	18.05	
6	23% Nickel in cottonseed flakes	18.2 18.4	18.30	
7	5% Palladium on alumina	20.5 16.7	18.60	
8	59% Nickel on kieselguhr	19.1 18.7	18.90	
9	25% Nickel in hardened oil	20.5 19.5	20.00	
10	65% Nickel on carbon	20.0 21.1	20.55	
11	25% Nickel (electrolytic) in cottonseed flakes	21.7 19.7	20.70	
12	40% Nickel on carbon	22.1 19.7	20.90	
13	30% Nickel in hardened oil	22.8 20.9	21.85	

[a] No significant difference exists between the mean values bracketed by lines.

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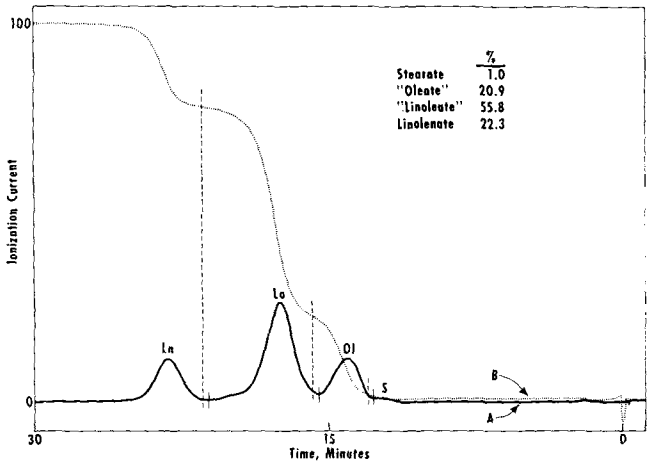

FIG. 1. Gas chromatogram of esters hydrogenated, (A) is the differential curve and (B) the integral curve.

w/v). Methyl elaidate was used as the standard for calculating the percentage isolated *trans* from the I.R. absorption at 10.36 μ.

Gas-liquid chromatographic analyses were obtained on a 4-ft by ¼-inch glass column packed with 10% polyvinyl acetate on Chromosorb and operated at 165C. Argon gas (flow, 33 ml/min) and a radium D ionization detector were also employed. A typical gas chromatographic curve of the hydrogenated mixture is shown in Figure 1 (Curve A), together with the electronically integrated curve (Curve B). The selectivity coefficient $K = \frac{k_{Le}}{k_{Lo}}$ was obtained from gas chromatographic data by reading the percentage composition of the hydrogenated sample from the integrated curve (Curve B, Figure 1):

	%
Stearate (S)	1.0
"Oleate" (Ol)	20.9
"Linoleate" (Lo)	55.8
Linolenate (Le)	22.3

Then

$$Ax = \frac{\%Le + \%Ol + \%S}{2} = \frac{22.3 + 20.9 + 1.0}{2} = 22.1$$

By referring to the graph of K *versus* $\overline{A_x}$ (6) one obtains a value for K = 2.05.

Results and Discussion

In hydrogenation studies, methyl esters have a distinct advantage over triglyceryl esters because gas-liquid chromatographic data can be obtained without further treatment of the methyl esters other than filtering out the catalyst. However, it is first necessary to identify reaction ratios and products for both during their hydrogenation (Table II). Analysis of variance (13) of the data of Tables I and IV, given in Table III, and application of Duncan's multiple

TABLE III

Analysis of Variance for Nickel, Palladium, and Platinum Catalysts Used to Hydrogenate Equimixture of Methyl Linolenate and Methyl Linoleate

Source	Sum of squares	Degrees freedom	Mean squares	F[a]	$F_{.05}$	$F_{.01}$
Percentage *Trans*						
Total variability	720.9601	25	.....	.....	.....	.....
Between replicates	4.2809	1	4,2809	4.5195	4.75	9.33
Between catalysts	705.3223	12	58.7769	62.0533	2.69	4.16
Within catalysts or error	11.366	12	0.9472	.....	.....	.....
Selectivity (K)						
Total variability	3.0223	25	.....	.....	.....	.....
Between replicates	.1316	1	.1316	8.8322	4.75	9.33
Between catalysts	2.7124	12	.2260	15.1678	2.69	4.16
Within catalysts or error	.1783	12	.0149	.....	.....	.....

[a] F designates the variance ratio.

range test (5) indicate that a difference in means of K between the methyl esters and the triglyceride must be greater than 0.3, and that a difference in means of percentage of *trans* must be greater than 2.4% to be significant at the 5% level. If one calculates the I.V.'s from chromatographic data and allows for the slightly lower hydrogen absorption of the methyl ester runs, mean K values and the mean percentage of *trans* values do not differ significantly between methyl linolenate and trilinolenin. Further, a detailed analysis of isomers from methyl linolenate and trilinolenin gave similar compositions on extensive countercurrent distribution and capillary gas chromatographic separation (11). Consequently, the determinations of K and percentage *trans* were carried out with confidence on a mixture of 50% methyl linoleate and 50% methyl linolenate. The triglycerides take 4 to 5 times as long to hydrogenate as the comparable methyl esters, as expected from the other observations dealing with the influence of viscosity on hydrogenation rate (1,4).

Tables I and IV contain the analytical data and the calculated results therefrom for the catalysts described in Table I. Nickel has a mean value of K = 2.0; palladium, 1.8; and platinum, 1.5. The nickel catalyst values for K ranged from 1.5 to 2.7; palladium, from 1.7 to 2.0; and platinum, from 1.3 to 1.6.

Anomalies in data exist. While palladium is much more active (hydrogenates at 25C) than nickel (hydrogenates at 140C), their selectivity is about the same (1.8 and 2.0, respectively). Platinum (1.5) at room temperature does not show the selectivity of either nickel or palladium.

The effect of the temperature perameter upon *trans* formation has been intensively studied for nickel catalyst No. 11. As will be described in a subsequent publication, temperature has been found to be a controlling factor in determining *trans* content but has little effect on selectivity ratio. Since hydrogenations

TABLE II

Hydrogenation of the Linoleate-Linolenate Mixture (5% Palladium-on-Alumina Catalyst)

Ester type	Temperature	Time	Le[a]	Lo	Ol	S	$\frac{k_{Le}}{k_{Lo}}$	Mean K	*Trans*	Mean *Trans*
	°C	*min.*	%	%	%	%			%	%
Methyl esters	24	17	20.1	60.7	19.2	0	2.8	.....	19.2	.....
	25	17	23.2	58.6	18.2	0	2.5	2.65	18.7	18.95
Triglycerides	25	76	15.2	61.1	23.2	0.4	2.8	.....	25.3	.....
	25	83	16.1	60.7	22.2	0.9	2.8	2.8	23.7	24.5

[a] Le = Linolenate, Lo = Linoleate, Ol = Oleate, S = Stearate.

with Pt and Pd catalysts were necessarily conducted at lower temperatures than with nickel, the lower *trans* contents observed for Pt catalysts may be due in part to the lower temperature of reaction.

Figure 2 shows a plot of K (selectivity) against isolated *trans*. A nearly random dispersion of the data is apparent when one compares the variety of catalysts under standardized conditions. The correlation coefficient for all data is 0.284; for nickel catalyst at 140C only, the coefficient is 0.304; neither coefficient is significant at the 5% level. In these experiments selectivity and isomerization are not significantly related.

Statistical evaluation of the amount of isomerization, measured as percentage *trans*, shows that variation due to catalysts is highly significant. The graphical representation of the application of Duncan's multiple range test to evaluation of these data is shown in Table I. No significant difference exists between the uppermost figure bracketed and the bracketed figures lower in the table. Significant differences do exist between the uppermost figure bracketed and unbracketed figures below it in the table. Thus catalyst No. 2 is not significantly different from catalyst No. 3 but is significantly different from all catalysts below in table, i.e., Nos. 4 through 13; No. 3 shows significantly different results from all catalysts below in table, i.e., Nos. 4 through 13. Differences in percentage of *trans* required for significance at the 5% level range from 2.120 to 2.381 units. Analysis shows therefore that percentage of *trans* for the three platinum catalysts is significantly lower than for either the two palladium or the eight nickel catalysts. Because the palladium catalysts distribute into the range of the nickel catalysts, they show no significant difference from the nickel.

Similarly, statistical evaluation of the selectivity data shows that variation due to catalysts is highly significant (Table IV). Differences in K required for

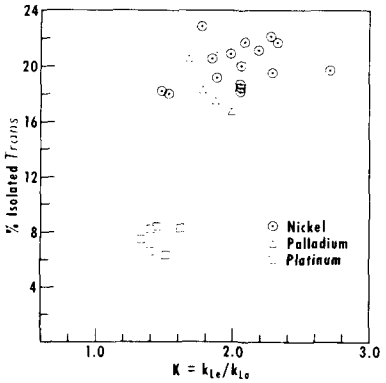

FIG. 2. A plot of selectivity ratio, K, to the percentage isolated *trans* in methyl esters for various hydrogenation catalysts.

significance at the 5% level range from 0.266 to 0.299 units. Again, analysis shows that the K for three platinum catalysts are significantly lower than for either the two palladium or 7 of the 8 nickel catalysts.

Zajew (14), studying the hydrogenation of linoleic containing oils, noted the same order of selectivity for platinum and palladium. Feuge (9) considered platinum and palladium to be relatively unselective, while present data places palladium in the same range with the nickel catalysts. Nickel catalysts have a range in selectivity nearly as wide as that of all the catalysts together. Bailey *et al.* (3) found also that the method of preparation for nickel catalysts could influence selectivity and degree of isomerization of the hydrogenated product. By comparing the order of listing of catalysts in Tables I and IV, one may discern a roughly parallel sequence.

The tremendous complexity of the catalytic hydrogenation reaction is indicated by these data. This very complexity also provides the hope that specific conditions of catalyst preparation may be found to accentuate selectivity and minimize *trans* formations.

TABLE IV
Selectivity Characteristics of Catalysts
(0.5 Mole Hydrogen Absorbed per Mole of Ester)

Catalyst	Temperature	Time	Le[a]	Lo	Ol	S	$K=\frac{k_{Le}}{k_{Lo}}$	Mean $K=\frac{k_{Le}}{k_{Lo}}$	Statistical significance
	C	min.	%	%	%	%			
2A Pt	25	20	30.9	47.8	15.0	6.3	1.33	1.365	
2B Pt	25	25	29.0	49.0	16.0	6.0	1.40		
1A PtO_2	25	36	28.0	48.8	17.6	5.6	1.39	1.45	
1B PtO_2	28	34	25.7	50.6	18.2	5.5	1.51		
5A Ni	140	48	25.8	50.9	21.2	2.1	1.53	1.505	
5B Ni	140	75	26.2	50.2	21.5	2.1	1.48		
3A Pt	24	23	30.3	49.6	16.5	3.6	1.44	1.525	
3B Pt	25	25	26.2	50.3	18.2	5.3	1.61		
4A Pd	26	36	27.0	53.5	17.8	1.7	1.78	1.825	
4B Pd	26	40	26.8	54.4	18.0	0.8	1.87		
7A Pd	25	17	26.1	52.6	20.6	0.7	1.68	1.835	
7B Pd	23	17	30.0	55.4	14.6	0	1.99		
13A Ni	140	5	25.3	53.4	21.3	0	1.77	1.880	
13B Ni	140	11	24.5	55.4	20.1	0	1.99		
8A Ni	140	6	25.1	54.4	20.4	0	1.89	1.970	
8B Ni	140	14	25.0	55.9	19.1	0	2.05		
6A Ni	140	42	22.3	55.8	20.9	1.0	2.05	2.050	
6B Ni	140	27	23.4	55.8	19.8	1.0	2.05		
9A Ni	140	16	25.1	54.2	19.9	0.8	1.85	2.070	
9B Ni	140	27	19.1	56.5	22.8	1.6	2.29		
10A Ni	140	39	22.7	55.9	20.4	1.0	2.06	2.125	
10B Ni	140	57	23.2	56.2	19.9	0.7	2.19		
12A Ni	140	7	22.5	57.5	20.0	0	2.28	2.185	
12B Ni	140	19	21.7	56.2	22.1	0	2.09		
11A Ni	140	28	20.2	56.9	21.1	1.7	2.33	2.520	
11B Ni	140	33	18.9	59.6	19.8	1.7	2.71		

[a] Le = Linolenate, Lo = Linoleate, Ol = Oleate, S = Stearate.

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Direct Determination of *Trans* Unsaturation in Triglycerides by Infrared Spectrophotometry

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Abstract

A differential infrared spectrophotometric method is described for the determination of *trans* unsaturation in fats. The method utilizes absorption at 965 cm^{-1}, due to the C–H out-of-plane deformation vibrations of *trans* unsaturated compounds. The method is rapid, accurate, and directly applicable to the determination of *trans* unsaturation in triglycerides. It is applicable to samples which contain low concentrations of *trans* acids (down to 2%) and also to samples with fatty acids of mixed chain length.

THE I.R. ABSORPTION BAND at 965 cm^{-1} of *trans* unsaturated compounds has been widely used in recent years for the quantitative determination of *trans* fatty acids and their derivatives (1,2,3). O'Connor (4) reported anomalous absorptivities in the case of glycerides containing very short chains and mixtures of short and long chain fatty acids. He considered that determination of *trans* unsaturated acids in triglycerides could at best be only partly quantitative until more spectra of pure triglycerides became available. Kaufmann (5) investigated, in addition, glycerides composed of medium and long chain saturated acids and reported "apparent *trans* contents" for these compounds. Similar anomalous results were reported by the Spectroscopy Committee of the A.O.C.S. (6), but at that time they still recommended that *trans* determinations be made on the triglycerides rather than risk isomerism by converting to methyl esters.

As a result of collaborative studies (7,8) this committee developed a method for the determination of *trans* unsaturation using a "baseline" type of background correction.

Firestone and De La Luz Villadolman (9) discuss the problems in the analysis of triglycerides and how they can be solved by the use of this A.O.C.S. procedure.

The problem of obtaining a correct analytical result is at least partly caused by the strong background absorption of the triglycerides. McDonald (10) and Cleverley (11) published differential techniques similar to the one described in this paper for the estimation of *trans* unsaturation in fatty acids and esters prepared from naturally occurring lipids. However, the analysis of triglycerides was not discussed.

In this study, the unwanted absorption was cancelled out by a differential technique, using in the reference beam a solution of a fully saturated triglyceride. The reference compounds should ideally be the test sample fully hydrogenated, but in practice negligible error is introduced provided that the chain lengths of the component fatty acids of the reference triglyceride are reasonably similar to those of the sample.

The method is particularly advantageous when working with small routine type instruments such as Perkin-Elmer Infracord Model 137 Spectrophotometer with fixed slit width and fixed scan speed program. With these instruments the method recommended by the Spectroscopy Committee is inaccurate because of the steeply sloping baseline.

A further advantage of the proposed method is that it is possible to analyze samples with *trans* acids content as low as 2%, whereas other published methods require that the sample be converted to the methyl ester if the *trans* acids content is below 15%. Samples containing fatty acids of mixed chain length can also be analyzed if part of the sample is fully hydrogenated and used in the reference beam of the spectrophotometer.

In addition to the determination of spectral data, it is necessary to know the iodine value of the sample to allow calculation of the trans acids content. This is not considered to be a limitation of the method, since this analytical constant is almost invariably required as part of any fat analysis program.

Experimental

Materials and Apparatus

Fully hydrogenated beef tallow stearin—saponification value 203; I.V. 0.25. This was prepared from beef tallow stearin by exhaustive hydrogenation using an oil-free nickel catalyst supported by kieselguhr.

Partially hydrogenated whale oil—saponification value 195; I.V. 57.5.

Peanut oil—saponification value 193; I.V. 93.0.

Secondary standard triglycerides—*trans* content 51.9% as trielaidate; I.V. 67.3. Supplied by R. T. O'Connor of the A.O.C.S. Spectroscopy Committee.

Carbon disulphide—Univar.

All spectra were plotted on a Perkin-Elmer Model 137 Infracord double beam spectrophotometer. A