• TECHNICAL

Studies on Conjugated Hydrogenation: Nickel Catalyst with Alcohols

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Abstract

Studies have been made on the conjugated hydrogenation of peanut and safflower oils using nickel catalyst and with alcohols as hydrogen donors. Peanut oil was reduced with ethyl alcohol to a final iodine value of 64–71 and the reaction is selective because little saturated acid is formed but some linoleic acid is retained. When the same oil is reduced with isopropyl or secondary butyl alcohols an iodine value of ~ 25 is reached while all linoleic acid has disappeared. With safflower oil and isopropyl alcohol an iodine value of ~ 46 is reached and the reaction is selective since all linoleic acid has disappeared. Thus the amount of monoene retained depends on initial unsaturation of the oil when a secondary alcohol is used as hydrogen donor.

Introduction

CONJUGATED HYDROGENATION refers to the hydrogenation process in which hydrogen is not supplied in the gaseous form but is contributed by a hydrogen donor, generally an alcohol which is dehydrogenated to a carbonyl compound. The liberated hydrogen is transferred to the double bond without appearing in the vapor phase. The process has so far been investigated only by Russian workers (1–5), who claim selectivity and preferential production of oleins from triglyceride oils. Further it is apparent from the reports that oils cannot be hydrogenated by this method below an iodine value of 64 to 70 with ethyl and propyl alcohols as hydrogen donors. Secondary alcohols are considered superior to primary alcohols as hydrogen donors.

The present investigation, part of which has been reported in a short communication (6), deals with the effect of a) concentration of catalyst, b) temperature, c) different amounts of hydrogen donor, d) using secondary alcohols in place of primary alcohols. In a series of experiments, refined and bleached peanut and safflower oils were used as hydrogen acceptors with nickel catalyst and in the presence and absence of ethyl alcohol (absolute), isopropyl and secondary butyl alcohols (E. Merck, Germany) as hydrogen donors.

Experimental

Hydrogenations were carried out in a high pressure shaking autoclave (Chas. W. Cook & Sons Ltd., England) provided with electrical heating and automatic temperature control. The shaking speed of the autoclave was 147 movements per minute.

Rufert nickel catalyst containing 25% Ni (Harshaw Chemical Company) was used as catalyst in amounts of 1% Ni and 0.5% Ni in reference to the oil used. The reactions were carried out at 200C, 225C and 250C with nitrogen gas in the head space during the hydrogenation and samples were withdrawn at regular intervals. The products were freed from catalyst by filtration aided by Hyflosupercel. Alcohol, carbonyl compounds and water were removed by a stream of N_2 under water vacuum at water bath temperature.

Methods of Analysis

Ultraviolet and infrared spectrophotometry were used for analysis and supplemented by gas-liquid chromatography.

cis-Linoleic acid was estimated by the method of Hilditch et al. (7) with a Beckman quartz spectrophotometer, model DU. The method does not distinguish strictly *cis* and *trans* dienes. Therefore the values are probably somewhat high for *cis, cis* linoleic acid, but low for total diene content.

The *trans* isomers were determined in an infrared spectrophotometer, Model 21 (Perkin-Elmer Corporation). The samples were dissolved in CS_2 and the percentages of *trans* double bonds expressed as methyl elaidate. In some experiments *trans* isomers were determined by the lead salt method of Cocks et al (8).

The results from some spectral tests were checked by GLC and the results were not markedly different. A Beckman GC-2 apparatus with thermal conductivity detector was used with a ¼ in. × 10 ft aluminum column containing 20% β-cyclodextrin acetate on Gas-Chrom P, 30–60 mesh. The temperature was 236C and the flow rate of He was 57 ml/min (9).

The slip points of the hydrogenated samples were determined by the capillary slip method (10) which is the same as that described by Mehlenbacher (10).

Results

The reaction conditions and the analytical data of the hydrogenated products are given in Tables I, II, III and IV.

Total oleic acid designates all the isomeric monoenoic acid.

TABLE I

Analytical Data of Hydrogenated Products from Peanut Oil and Ethyl Alcohol; 50 g Oil; 8.5 g Ethyl Alcohol; 1% Ni; 135–145 psig; 225C

Period of hydrogenation	Iodine value (Wijs' 0.5 hr)	Linoleic % UV	Oleic (Total) % Calcd. from UV & IV	Saturated % by difference	*trans*-isomer by IR %
0	93.6	27.5	52.7	19.8	......
1	76.7	12.9	65.1	22.0	11.0
2	74.6	20.9	66.7	22.4	12.0
3	74.5	20.7	66.7	22.6	12.8
4	72.6	8.8	67.7	23.5	16.3
5	71.3	7.6	68.8	23.6	16.5
50 g oil; 8.5 g ethyl alcohol 0.5% Ni; 135–145 psig; 225C					
0	93.6	27.5	52.7	19.8	......
1	81.6	17.2	61.2	21.6	7.3
2	79.4	13.2	64.2	22.6	10.3
3	76.7	10.9	66.5	22.6	12.7
4	76.2	10.6	66.2	23.2	13.0
5	74.7	8.9	67.7	23.4	16.0
6	73.9	7.8	68.3	23.9	16.0

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TABLE II

Analytical Data of Hydrogenated Products from Peanut Oil and Ethyl Alcohol; 50 g Oil; 8.5 g Ethyl Alcohol; 1% Ni; 165–175 psig; 250C

Period of hydrogenation, hr	Iodine value (Wijs' 0.5 hr)	Linoleic % UV	Oleic (Total) % Calcd. from UV & IV	Saturated % by difference	*trans* isomers by Pb-salt %
0	93.6	27.5	52.7	19.8	.....
1	71.8	9.9	67.6	22.5	7.7
2	67.4	5.7	71.2	23.1	12.0
3	67.1	5.7	71.2	23.1	8.6
4	67.1	5.7	71.2	23.1	6.9
5	64.2	2.7	74.0	23.3	9.9
50 g oil; 8.5 g ethyl alcohol; 0.5% Ni; 165–175 psig; 250C					
0	93.6	27.5	53.7	19.8	......
1	77.7	18.0	59.9	22.1	1.2
2	73.3	11.3	66.4	22.3	4.6
3	72.0	10.9	66.4	22.7	8.4
4	70.2	9.4	65.6	25.0	8.4
5	68.4	8.4	66.5	25.1	5.9
6	67.5	7.2	65.5	27.3	8.7

Discussions

The earlier observations (1,2,5) of a final iodine value between 64 to 71 were confirmed with peanut oil and ethyl alcohol as hydrogen donor. The higher value was reached at temperatures <250C and the pressures <165 psig while at higher temperature and higher pressure the hydrogenation apparently goes somewhat further.

However, it has been observed that when peanut oil is hydrogenated at 200C with 1% nickel, the final iodine value by prolonged hydrogenation is 80 instead of 70. This finding contradicts that of Lyubarskii (1) who stated that the final iodine value is reached irrespective of temperature by increasing the time of reaction.

The effect of temperature in augmenting the rate of reaction is confirmed. From Tables I and II it is apparent that the catalyst concentration has considerable effect on the rate although almost the same fatty acid composition is reached.

The conjugated hydrogenation reaction is rather selective when a primary alcohol, i.e., ethyl alcohol is used as hydrogen donor until the final iodine value is reached. Very little saturated acid is produced while reduction of linoleic acid takes place. At 225C, 1% Ni saturated acids are increased from 19.8% to 23.6% and that linoleic acid is decreased from 27.5% to 7.5% (Table I). At 250C, 1% Ni saturated acids are increased from 19.8% to 23.3% and linoleic acid is decreased from 27.5% to 2.7% (Table II).

It appears that conjugated hydrogenation is always accompanied by geometrical isomerization and thus resembles ordinary hydrogenation by gaseous hydrogen. Table I shows that heating peanut oil with ethyl alcohol at 225C with 1% Ni after 5 hr reduces the iodine value by $\sim$ 23 units while the amount of *trans* isomer is 16.5%. In an experiment without alcohol but with otherwise equal conditions under nitrogen the amount of *trans* isomer is 2% (Pb-salt method) after 5 hr.

When the conjugated hydrogenation is carried out at 200C with 1% Ni, the reduction of iodine value is $\sim$13 units and the amount of *trans* isomers (IR) is 1.9% after 5 hr. These observations illustrate that the rate of *trans* isomer formation increases with temperature as does the rate of hydrogenation.

Further, from Table I it is evident that when the conjugated hydrogenation is carried out at 225C with 0.5% Ni, the amount of *trans* isomers is 16% after 6 hr. Therefore, temperature has a greater effect on the formation of *trans* isomers than has the catalyst concentration. By analogy with the gaseous hydrogenation reaction (11,12), one might expect that increased temperature when giving rise to more *trans* isomer also gives rise to more positional isomers in conjugated hydrogenation. It seems that a hydrogenation-dehydrogenation mechanism is more predominant at higher than at lower temperature. It might be expected that in conjugated hydrogenation positional isomerization of the double bond is less than with ordinary hydrogenation.

It is seen from the results that at a particular point a constant iodine value is reached despite excess of hydrogen donor. This value is not changed when using alcohol in 100% excess over the theoretical amount required for reduction of all the double bonds. At a particular temperature and concentration of nickel catalyst a ratio of alcohol-carbonyl compound is reached and cannot be further changed. Rush et al. (2) showed that the catalyst can be reactivated when changing the gas in the closed system and they assume that the catalyst has been poisoned by CO resulting from the decomposition of carbonyl compounds.

From the data on Table III it is seen that with isopropyl alcohol as hydrogen donor the iodine value is reduced from 93.3 to 36.2 within 15 min, i.e., much faster and further than with ethyl alcohol. The final iodine value of 24.7 is reached after 4 hr.

This behavior is a substantial departure from that of a primary alcohol like ethyl and *n*-propyl alcohol and points to the easy removal of hydrogen from the secondary alcohol under the condition of the reaction. The same was observed with secondary-butyl alcohol in place of isopropyl alcohol, i.e., the difference in the molecular weight of the secondary alcohols did not change the final value.

When using isopropyl alcohol all linoleic acid is reduced within 15 min and the value of oleic acid is reduced by 15.7% while the saturated acids increased by 40.7%. A considerable portion of linoleic acid has been converted to saturated acids. Although the rate of hydrogenation is vary rapid in the beginning it slows down to approach the final value asymptotically. In this respect conjugated hydrogenation with secondary alcohol resembles that with primary ones and the reason may be the same.

Results obtained from conjugated hydrogenation of safflower oil with isopropyl alcohol are shown in Table IV. A reduction in iodine value by 75.6 units

TABLE III

Analytical Data of Hydrogenated Products Obtained from Peanut Oil and Isopropyl Alcohol; 40 g Oil; 8.5 g Isopropyl Alcohol; 1% Ni; 180–190 psig; 250C

Period of hydrogenation, hr	Iodine value (Wijs' 0.5 hr)	Linoleic % UV	Oleic (Total) % Calcd. from UV & I.V.	Saturated % by difference	*Trans*-isomer by IR %	Slip point (C)
0.0	93.3	25.0	57.7	17.3	......	......
0.25	36.2	......	42.0	58.0	22.4	50.3
1.0	35.6	......	41.3	58.7	21.8	51.0
2.0	32.1	......	38.7	61.3	20.2	49.5
3.0	28.0	......	32.5	67.5	16.9	54.0
4.0 [a]	24.7	......	28.1	71.9	14.2	53.5

[a] *No further changes after 4 hr.*

TABLE IV

Analytical Data of Hydrogenated Products from Safflower Oil and Isopropyl Alcohol; 40 g Oil; 13.5 g Isopropyl Alcohol; 1% Ni; 250–270 psig; 250C

Period of hydrogenation hr	Iodine value (Wijs' 0.5 hr)	Linoleic % UV	Oleic (Total) % Calcd. from UV & I.V.	Saturated % by difference	*Trans* isomer by Pb-salt %	Slip point (C)
0	144.4	74.5	12.9	12.6		
0.25	68.8	0.2	77.7	22.1	26.6	38.5
1	64.6	0.1	73.9	26.0	27.5	38.5
2	53.5	0.1	61.1	38.8	22.9	40.0
3	54.1	0.1	63.1	36.8	21.9	39.7
4 [a]	45.6	Negligible	51.8	48.2	19.0	41.0

[a] No further change after 4 hr.

takes place within 15 min. The rate of the overall reduction is higher than with the less unsaturated peanut oil. The reaction becomes slower after 15 min and the final iodine value of ~45.6 is reached within 4 hr.

Within the fast initial period of reduction linoleic acid disappears virtually completely while oleic acid increases from 12.9% to 77.7%. A relatively small increase of saturated acids from 12.6% to 22.1% is observed. At this point reduction of safflower oil seems to be more selective than that of peanut oil. It appears that with increased unsaturation of the hydrogen acceptor and a secondary alcohol as hydrogen donor the reaction becomes more selective. In a more general comparison of conjugated hydrogenation one can state that for an oil rich in linoleic acid and reduced with isopropyl alcohol the selectivity is comparable to that of a less unsaturated oil using a primary alcohol as hydrogen donor.

The data on the slip points of the samples are given in Tables III and IV. They are a rough measure to the extent of geometrical and positional isomerization in the partially hydrogenated products.

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