Isomerization During Hydrogenation of Soap. I. Potassium Oleate

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Abstract

Potassium oleate in slightly alkaline solution was hydrogenated for up to 7 hr with Rufert nickel catalyst at 150C and 20 kg/sq cm pressure. With 1% catalyst, the iodine value dropped by 12 units in the first hour, and only slightly thereafter. With 2% catalyst there was a drop of 24 units in iodine value in the first hour, a steady state for the next 3 hr, and a second sharp drop of 30 units prior to the seventh hour. Samples of fat hydrogenated over 1% catalyst for 3 hr and 7 hr respectively were analyzed by gas-liquid chromatography, the *cis* and *trans* monoenes were separated by argentation thin-layer chromatography, and the positional isomers in each were determined by oxidation of the total fraction to dicarboxylic acids, which were then estimated by GLC.

Apart from double-bond saturation during the first 3 hr of hydrogenation, extensive double-bond migration yielded 23.5% of *trans* 8- to 13-monoene, accompanied by small amounts only of positional *cis* monoenes other than the starting material. After 7 hr of hydrogenation, extensive *cis* to *cis* isomerization occurs, accompanied by less *cis* to *trans* shift; the *cis*:*trans* ratio for each monoene consequently tended toward 1:1. The results are explained on the sorption mechanism of hydrogenation and suggest that soap hydrogenation, involving catalyst poisoning, may represent a magnified version of normal fat hydrogenation.

Introduction

THOUGH TRACES OF SOAP are catalyst poisons in hydrogenating fatty oils, hydrogenation of soap solutions of unsaturated fatty acids under slightly alkaline conditions by using Raney nickel catalysts has occasionally been recorded (1–3), especially in Japan (4–8). Catalyst concentration is comparatively high (1–2%), and the pressure has ranged from 2–50 kg/sq cm. Preliminary experiments showed that even the alkali-refining soapstocks from peanut and cottonseed oils could be hydrogenated into more saturated products, which would be in greater demand than the originals for soapmaking. Since the nature of soap hydrogenation is not known, hydrogenation of potassium oleate and linoleate was systematically studied.

Formation of both positional and geometric isomers during hydrogenation of oleic acid, its esters, or its glyceride is now well documented (9). Under the mild hydrogenation conditions used in hardening for edible purposes, Feuge and Cousins (10) demonstrated migration of the double bond in oleate to all positions from carbon 6 to 14. For each isomer the ratio of the *cis* to *trans* form was believed to be 1:2. In later work Allen and Kiess (11) and Allen (12) showed an equal migration of the double bond to either adjacent carbon during hydrogenation of *cis* 6-, 9-, and 12-monoenes, and to lesser extents to other carbons. Using improved analytical techniques, Scholfield et al. (13) and Subbaram and Youngs (14) showed that migration to *trans* forms was considerably greater than to *cis* forms; the *cis*:*trans* ratio varied between 1:4 and 1:7 for individual newly-formed positional isomers.

The pattern of hydrogenation of potassium oleate and the nature of the *cis* and *trans* monoenes present at two selected time intervals are presented in this paper. A similar study of potassium linoleate hydrogenation will follow.

Materials and Methods

Potassium Oleate

Oleic acid was prepared from olive oil mixed acids by two adductions with urea, the first to remove saturates and the second to leave linoleate in the solubles (15). Distillation of the methyl esters gave methyl oleate (bp 178–180C/4 mm, I.V. 85.3), which was saponified with ethanolic potash and the solvent was removed.

Dibasic acids (C_5–C_{13}), used for GLC, were either commercial or laboratory-prepared samples. Various combinations of dimethyl sebacate and azelate were employed for prior standardization of GLC quantitation.

Hydrogenation

Potassium oleate (140 g) was charged into a 2-liter stainless steel autoclave with an up-and-down magnetic stirrer. Samples could be drawn at intervals without interrupting the hydrogenation. The hydrogenation conditions were based on preliminary work. Potassium hydroxide (7 g, 5 N) was added to the soap to give a 5% excess of alkali, followed by 140 ml of water, 7 g kieselguhr as catalyst support, and finally 5.6 g Rufert nickel catalyst (25% Ni, Harshaw Chemical Company, U.S.A.) to give a catalyst concentration of 1%. Electrolytic hydrogen (99.9%) was employed, and hydrogenation was carried out at 150C and 20 kg/sq cm for a total period of 7 hr. A similar run with 2% catalyst was also conducted. Samples were drawn at various time-intervals and their I.V. was determined as acids. Isolated *trans* bonds were determined on a Perkin-Elmer Model 221 Infrared Spectrophotometer by the AOCS tentative method (16), by using methyl elaidate as the primary calibration standard.

Column Chromatography (17)

Silica gel (BDH, chromatographic grade, ground to 100–200 mesh) was impregnated with an aqueous solution of silver nitrate (50% w/v). The product (30 g) was packed by slurrying in a column (18 mm I.D.) to give a column length of 34 cm. The hydrogenated material, after conversion to methyl esters (ca. 250 mg), was applied and eluted successively with 15% benzene in light petroleum to remove saturates, 30% to remove *trans* monoenes, and 45% to remove *cis* monoenes. Fractions were monitored by thin-layer chromatography on microplates coated with argentated silica gel (18).

Oxidation

Methyl esters of the total hydrogenated material and of the separated total *cis* and *trans* monoenes were each oxidized with permanganate-periodate (19). Typically, 25 mg of monoene in 5 ml of tertiary butanol was added to a solution of the oxidant (7 ml) in 12 ml of water and 8.5 ml of tertiary butanol. The contents were stirred for 3 hr at 60–65C and, at the end of the reaction period, acidified with hydrochloric acid and decolorized with sodium bisulfite. Tertiary butanol was removed by blowing with nitrogen on a water bath. The contents were saturated with sodium chloride, and the dicarboxylic acids were isolated with chloroform, esterified with diazomethane, and analyzed by GLC.

Gas-Liquid Chromatography

An F&M Model 720, dual-column, temperature-programmed GLC unit with a thermal conductivity detector, was used. For monocarboxy methyl ester analysis, a column (8-ft. $\frac{3}{16}$-in. I.D.), packed with supported polyester (20% diethyleneglycol succinate on Chromosorb W 40–60 mesh), was employed under the following conditions: chart speed 0.5-in./min, injection port 300C, detector block 280C, hydrogen flow rate 60 ml/min, attenuation 4, isothermal at 205C. Esters of the dicarboxylic acids which were obtained by oxidation were analyzed on a silicone column (SE 30, 2-ft) as follows: chart speed 0.5-in./min, injection port 230C, detector block 220C, hydrogen flow rate 60 ml/min, attenuation 4, temperature programming from 130–180C at 5C/min. Peak areas were measured by triangulation, and calculated compositions were converted from weight to mole percentages.

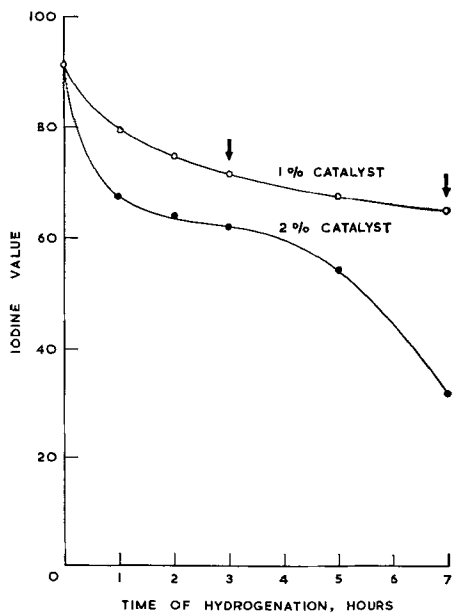

FIG. 1. Reduction of iodine value with progressive hydrogenation of potassium oleate at two catalyst levels. Arrows show samples used for detailed analysis.

TABLE I

Iodine Values (as Acids) of Hydrogenated Potassium Oleate on Dry Weight of Soap

Catalyst concentration on the dry weight of soap, % Ni	Time of hydrogenation in hours					
	0	1	2	3	5	7
1.0	91.3	79.2	74.6	71.2	67.4	64.6
2.0	91.3	67.1	63.8	62.0	54.1	31.2

Results and Discussion

Alteration in Unsaturation

Change of I.V. with time of hydrogenation for both catalyst concentrations is shown in Figure 1. Analytical data are recorded in Table I. Hydrogenation with 1% catalyst brought about a reduction in I.V. by about 12 units during the first hour. Thereafter the I.V. dropped gradually and became more or less constant after 5 hr. Catalyst poisoning is perhaps responsible since the hydrogenation could be resumed if fresh catalyst were added (not shown in figure).

With 2% catalyst the first hour saw a reduction of 20 units in the I.V., which then kept steady for the next 2 hr. Thereafter there was a second fall in I.V. to a value of 31 after 7 hr. Thus, at this higher catalyst concentration, the poisoning is temporary.

To examine the positional isomers which were formed, the products of the hydrogenation of potassium oleate with 1% nickel catalyst for 3 hr and 7 hr were resolved on a chromatographic column into saturates, *trans* monoenes, and *cis* monoenes. The monoenes were each oxidized, and the resulting dicarboxylic acids were analyzed as esters by GLC. The relative proportions of these corresponded to the proportions of the positional isomers present. Thus the components of the *cis* and *trans* monoenes were determined for the two hydrogenated samples.

Potassium Oleate Hydrogenated for Three Hours

The top half of Table II gives the analytical data, calculated as mole percentages, for the original fat, hydrogenated fat (3 hr), and its *cis* and *trans* monoene constituents. Both absolute and incremental values are given. The proportions of saturates obtained by GLC, and of *trans* monoenes by infrared

TABLE II

Isomerization of Potassium Oleate During Hydrogenation. Analysis of Dicarboxylic Acid Products of Oxidation of *cis* and *trans* Monoenes

Product	I.V.	Satd. acids % mole	Composition of Dicarboxylic Acids, Carbon Chain-Length													
			Absolute values, % mole							Increments, % mole						
			7	8	9	10	11	12	13	7	8	9	10	11	12	13
Starting material																
Oleate	91.3	4.0	....	1.5	95.5	.....	3.0	....	....	....	1.4	91.7	.....	2.9	....	....
3-hr Hydrogenated product																
Total	71.2	26.8	....	5.2	77.5	9.2	4.6	2.1	1.4	....	3.8	56.8	6.7	3.4	1.5	1.9
cis Fraction (49.7%)	.....	.....	....	2.4	91.1	3.5	3.0	....	....	....	1.2	45.3	1.7	1.5	....	....
trans Fraction (23.5%)	.....	.....	....	9.3	50.6	22.2	10.0	4.7	3.2	....	2.2	11.9	5.2	2.4	1.1	0.7
7-hr Hydrogenated product																
Total	64.6	37.5	3.8	14.3	39.0	21.2	12.9	5.6	3.2	2.4	9.0	24.3	13.2	8.1	3.5	2.0
cis Fraction (30.2%)	.....	.....	2.0	15.4	44.6	20.4	10.4	4.5	2.7	0.6	4.6	13.5	6.2	3.1	1.4	0.8
trans Fraction (32.3%)	.....	.....	4.8	15.4	30.2	25.1	15.7	5.8	3.0	1.6	5.0	9.7	8.1	5.0	1.9	1.0

analysis, agreed to within 2% with the actual weights of the fractions eluted from the argentated silicic acid column. The original oleic acid was analyzed by GLC and oxidation to 92% of *cis* 9-monoene, 4% saturates, and small amounts of other *cis* monoenes (8- and 11-).

The I.V. drop of ca. 20 units in 3 hr is clearly caused by the formation of about 26% of saturated acids. The totals of *cis* and *trans* isomers for each double-bond position are usually within 0.5% of the total proportion, determined on the hydrogenated material as a whole. This supports the accuracy of the various steps in the method of analysis employed, viz., separation on a silver nitrate-impregnated silica gel column, oxidation of total *cis* monoene and *trans* monoene fractions, conversion of dicarboxylic acids to esters with diazomethane, and analysis of the esters by GLC.

Apart from saturation, the other change as a result of hydrogenation is the formation of *trans* fatty acids. The percentage of the *cis* 9-isomer has only been reduced by about 4 units in the first 3 hr of hydrogenation. In the *trans* monoene acids that were created in the same period however, only half the material consists of the *trans* 9-ethenoid isomer; the remaining half consisted of other positional isomers ranging from *trans* 8- to *trans* 13-monoenes. Formation of positional and geometrical isomers during hydrogenation is currently best explained by Blekkingh's theory (20), whereby unsaturated fatty molecules are adsorbed on the catalyst surface where they encounter dissociated hydrogen atoms, giving rise to half-saturated free radicals. These may be released either after total saturation or with formation of a double bond either in the original or in an adjacent position; the preferred configuration is the *trans* form of lower energy. In the present instance the sorption of potassium oleate on the catalyst during the first 3 hr clearly appears to favor the release of the adsorbed material (in which no hydrogenation takes place) in the *trans* form, with a marked tendency to a shift of double bond. In other words, in the early stages of hydrogenation, apart from saturation of double bonds, new *cis* compounds are hardly formed, and the new double bonds created are mostly *trans* and in widely scattered locations. This is illustrated by the *cis* and *trans* ratios at the various double-bond positions, which are as follows:

Double-bond position	Approximate *cis*:*trans* ratio
8	1:4
9	1:0.5
10	1:6
11	1:3
12	only *trans* product
13	only *trans* product

The only exception to a high ratio in favor of the *trans* isomer is for 9-monoene. This is, of course, the original starting-material, which, being initially in considerable excess, will obviously require a longer time, whatever the mechanism, for conversion to the *trans* form.

Potassium Oleate Hydrogenated for Seven Hours

Results are presented in the lower half of Table II. During the next 4 hr under hydrogenating conditions, there is only a small change of 6.6 units in the I.V., which can be accounted for by an increase of saturated acids by about 10.7%.

The rates of hydrogenation of *cis* and *trans* monoenes are generally believed to be equal (21). By assuming this and considering the 2:1 ratio of *cis* to *trans* monoene, it will be noted that 7.2% of *cis* and 3.5% of *trans* monoenes will have been converted to saturated acids. In the *cis* fraction the 3-hr *cis* content of 49.7% mole has come down to 30.2%, a difference of 19.5% mole. If 7.2% of this has been saturated, the remaining 12.3% mole of *cis* will have been converted into the *trans* form. The increase actually noted in total *trans* acid content during these 4 hr of hydrogenation is 8.8%, which implies that, at this stage of the hydrogenation, *cis* forms are more easily converted to saturated acids than *trans* forms. Indeed it would appear that, of the 10.7% of the saturated acids newly produced, 8.8% has come from the *cis* fraction and only 1.9% from the *trans* fraction. The 8.8% of *cis* converted to *trans* is almost wholly the abundant *cis* 9-isomer.

Comparison of the 3-hr and 7-hr hydrogenation data shows that the transformation of this isomer, i.e., the *cis* 9-monoene, occurs in two directions. The 8.8% which is converted to *trans* goes not merely to *trans* 9-monoene but to other isomers which range from the *trans* 7- to the *trans* 13-monoene. This *cis* to *trans* change, accompanied by extensive double-bond shift, is thus a further continuation of the process which already took place in the first 3-hr hydrogenation period. An even greater part of the *cis* 9-isomer than is converted to *trans* is however transformed to other *cis* fractions; the double-bond shift occurs all the way from the *cis* 7-isomer to the *cis* 13-isomer. This type of isomerization was almost imperceptible in the first 3 hr of hydrogenation but is the major change during this stage. A consequence of these two changes, *viz.*, extensive *cis* to *cis* isomerization and rather less *cis* to *trans* isomerization, is that the *cis*:*trans* ratios now stand as follows:

Double-bond position	Approximate *cis*:*trans* ratio
7	1:2.5
8	1:1
9	1:0.66
10	1:1.2
11	1:1.5
12	1:1.3
13	1:1

These ratios are in marked contrast to the high ratios in favor of *trans* which occurred in the 3-hr hydrogenation. There appears to be a distinct movement towards a *cis*:*trans* ratio fairly close to 1:1. For obvious reasons the original *cis* 9-isomer has not yet achieved this equilibrium but has progressed toward doing so from the 3-hr situation, where the ratio was 1:0.5. Subbaram and Youngs (14) pointed out that, in the usual type of selective hydrogenation to produce edible shortenings, the *cis*:*trans* ratios at the end for various positional isomers ranged from 1:3 to 1:6, corresponding to the present 3-hr soap hydrogenation.

Mechanism of Hydrogenation of Soap

All the data are consistent with the normal sorption and desorption mechanism of heterogeneous catalytic hydrogenation, which thus appears to be operative in the hydrogenation of soap also. In the present instance the high ratios of the *trans* compared to *cis* forms for each positional isomer is particularly noteworthy. Poisoning of catalyst by soap is a well-known effect. The extensive isomerization shows that the poisoned catalyst still appears to be able to adsorb and desorb soap molecules. Its ability to hydrogenate double bonds is reduced, suggesting that it has lost its ability to dissociate hydrogen molecules into atoms. Although in the earlier stages, i.e., before poisoning, considerable *cis* to *trans* double bond migration occurs,

the poisoned catalyst appears to favor the release of the adsorbed material in the *cis* form of higher energy rather than in the *trans* form of lower energy. This is an observation which agrees well with the known fact that, in normal fat hydrogenation, when partly-spent poisoned catalysts are re-used, the formation of *trans* acids is less than when a fresh catalyst is employed (22). The other feature of soap hydrogenation, *viz.*, extensive *cis* double bond migration, may also apply when spent catalysts are used in fat hydrogenation, but data to check this are not available in the literature. In fact, soap hydrogenation may represent a magnified version of normal fat hydrogenation in which catalyst poisoning occurs gradually.

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