Selective Hydrogenation of Soybean Oil. II. Copper-Chromium Catalysts

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Abstract

Soybean oil was partially hydrogenated at 170 and 200C with 0.5 and 0.1% copper-chromium catalysts, respectively. The reaction proceeded selectively at both temperatures, although selectivity was better at the lower temperature. Both commercial and laboratory-prepared catalysts reduced the linolenic acid to less than 1% and with selectivity ratios (K_{Le}/K_{Lo}) ranging from 6 to 13. Since stearate did not increase, linoleate selectivity (K_{Lo}/K_{Ol}) was extremely high. About 80% or more of the original linoleic acid remained in the hydrogenated products as measured by the alkali-isomerization method. More conjugated dienes were formed at 200 than at 170C.

Introduction

THE DEVELOPMENT of certain flavors in edible soybean oil has been attributed to the presence of linolenate (5). Consequently a more stable oil should be obtained by selectively hydrogenating the linolenate. Considerable attention therefore has been given to finding a suitable selective catalyst. Part I of this series (7) reported that among a variety of sodium borohydride-reduced metal salts, copper-chromium mixtures formed the most selective catalysts for the hydrogenation of linolenate in soybean oil; however, low temperatures (150C), high amounts of catalyst (2% metal) and small samples (1 ml) were employed in those investigations.

This report covers the hydrogenation of 300-ml samples of soybean oil at moderate pressures with commercial and laboratory-prepared catalysts at 170 and 200C with 0.5 and 0.1% catalysts, respectively.

Experimental

Catalysts

Catalysts G-13 (53% CuO; 39% Cr_2O_3), G-22 (42% CuO; 40% Cr_2O_3; 12% BaO), T-953 (40.1% Cu; 31.6% Cr; 3.7% Cd), and T-970 (experimental sample containing 36.6% Cu, 32.7% Cr and 6.2% Mn) were furnished by Girdler Catalysts, Chemetron Corporation, Louisville, Ky.

Catalysts Cu-1106P (40% CuO, 47% Cr_2O_3, 10% BaO) and Cu-0202P (82% CuO, 17% Cr_2O_3) were furnished by he Harshaw Chemical Company, Cleveland, Ohio.

Catalysts were also prepared in the laboratory by three different procedures described below:

a) *Urea Precipitation.* This procedure is similar to that of Pass et al. (9). First, 6.057 g copper nitrate and 1.361 g chromium nitrate (Cu/Cr = 9) were dissolved in 250 ml water and then 250 ml of an aqueous solution containing 14 g urea was added. After the mixture was heated on a steam bath for 3 hr, the resulting dark-green precipitate was filtered, washed thoroughly with distilled water, dried at 110C and ground to a fine powder. Heating the 2.72 g of green powder to 350C in a muffle furnace yielded 2.17 g of black powder.

b) *Sodium Borohydride Reduction.* To a 250-ml solution containing 4.038 g copper nitrate and 0.907 g chromium nitrate (Cu/Cr = 9) was slowly added 100 ml of a 5% sodium borohydride solution. The solution was stirred magnetically and nitrogen bubbled through the solution. One hour after the addition of the borohydride, the precipitate was separated by filtration, washed thoroughly with distilled water and dried at 110C. This catalyst (1.57 g) was heated to 350C in a muffle furnace for 1 hr before use.

c) *Copper-Exchanged Molecular Sieve.* About 3 g of Linde molecular sieve 13 X was exchanged with copper by stirring for 72 hr in 30 ml of a solution containing 2 g copper nitrate. During the day the temperature of the stirred solution was maintained at 45C. After the supernatant was removed by filtration, the exchanged material was washed thoroughly with distilled water. The copper-exchanged sieve was placed in 30 ml water and then reacted with 1 g of sodium borohydride in 20 ml water. After 2 hr the catalyst was filtered, washed thoroughly with distilled water and dried at 110C. Before use the catalyst was heated to 350C in a muffle furnace for 1.5 hr.

Hydrogenation

Hydrogenations were carried out in a Parr apparatus equipped with a gas dispersion agitator of the design described by Beal and Lancaster (2). Usually 300 ml refined and bleached soybean oil and the appropriate amount of catalyst were charged into the bomb. It was then flushed with nitrogen by bubbling the gas through the oil and venting at the top. While being heated, the oil and the catalyst were stirred (1700 rpm) and kept under reduced pressure with an oil pump. When the proper temperature was attained, hydrogen gas was admitted from an external reservoir and maintained at 30 psi by means of a pressure-reducing valve. The extent of reaction was followed from the pressure drop in the external reservoir. After the desired amount of hydrogen was taken up, the oil was cooled to room temperature and filtered through Celite.

The analytical methods employed have been described previously (7). A Perkin-Elmer 621 grating infrared spectrophotometer was used for determining *trans* isomers.

Results and Discussion

The analytical data for soybean oil hydrogenated at 170C with different catalysts are shown in Table I. All the catalysts tested were considered moderately active under the conditions employed, and hydrogenation was complete in about 1 hr or less. All the hydrogenated products contained 1% or less linolenic acid as measured by the alkali-isomerization method. The gas-liquid chromatographic (GLC) analyses gave higher values for triene since *cis,trans* conjugated dienes interfere with determination of linolenate (7). Countercurrent distribution (CCD) analyses were performed on the methyl esters of some of these hy-

TABLE I

Hydrogenation of Soybean Oil with Copper-Chromium Catalysts
(Catalyst, 1.5 g; oil, 300 ml; temperature, 170C; pressure, 30 psi)

Catalyst	Reaction time, min	Fatty acid composition, % GLC				IV (calcd.)	*trans*, %	Conj. diene, % (UV)	Alkali isomerization		Selectivity K_{Le}/K_{Lo}
		M[a]	D	T[b]	*trans,trans* conj. diene				Le, %	Lo, %	
None	....	26.0	52.5	7.3	0.0	132.4	0	0	7.3	47.3	......
G-13	65	37.8	45.1	1.8	1.2	117.4	9.2	0.9	0.3	40.5	11.7
G-22	72	36.3	47.3	1.6	0.8	118.7	8.9	1.0	0.5	37.9	12.4
Cu-0202P	79	37.9	45.5	1.6	0.5	116.5	8.3	0.8	0.6	40.4	10.3
Cu-1106P	36	37.7	45.7	1.5	0.9	117.1	8.6	1.1	0.3	41.0	12.2
T-953	38	35.1	47.3	2.2	1.0	119.6	6.6	1.6	1.2	38.4	9.5
T-970	45	35.9	47.8	1.0	0.8	117.7	8.9	1.1	0.5	41.4	13.0
Cu-Cr (urea precipitation)	49	35.9	47.1	1.8	1.0	118.9	7.5	0.8	0.7	40.8	11.4
Cu-Cr (sodium borohydride reduction)	63	37.1	45.9	1.8	0.8	117.5	9.3	1.0	0.4	36.9	11.9

[a] Abbreviations: M, monoene; D, diene; T, triene; Le, linolenate; Lo, linoleate.
[b] Also includes *cis,trans* conj. diene.

drogenated products (8). The results are in agreement with the alkali-isomerization values. Further, in the triene fractions (free of interfering conjugated dienes) isolated by CCD, the GLC and alkali-isomerization values for triene were nearly equal. Consequently we are reasonably certain that the alkali-isomerization method is a true measure of the unreacted linolenate in these hydrogenated products.

From the fatty acid composition of the initial and hydrogenated soybean oils, selectivity ratios (K_{Le}/K_{Lo}) were determined with an analog computer by assuming consecutive reactions, Triene → Diene → Monene (3), and by using triene values obtained by alkali isomerization. The selectivity ratios of Table I for different copper-chromium catalysts vary from 9.5 to 13.0. These values are considerably higher than for any other catalyst so far reported. The selectivity ratio of 11.9 for the borohydride-reduced catalyst is lower than the previously reported (7) value of 14 which was obtained at 150C when alkali-isomerization values for triene were used. As seen from Table II, the selectivity ratio for the same catalyst dropped to 10.0 when hydrogenation was carried out at 200C. Evidently increasing the temperature of hydrogenation decreases selectivity towards linolenate. Because stearate was not formed under these conditions, the selectivity towards linoleate (K_{Lo}/K_{Ol}) must be extremely high.

The linoleate in the hydrogenated products as measured by alkali-isomerization method amounted to about 80% or more of the original linoleate. The *cis,trans* and *trans,trans* isomers of linoleate are also partly conjugated under the conditions of this procedure (6). Diene fractions isolated by CCD from some of the hydrogenated products contained no more than 5% isolated *trans*; hence, the interference by geometrical isomers must be small. Positional isomers of methylene interrupted dienes formed from linolenate will, in part, be conjugatable.

Soybean oil hydrogenations at 200C are shown in Table II. A comparison with Table I indicates that selectivity towards linolenate is lowered by increasing the temperature. Although *trans* isomer formation does not increase appreciably, the amount of conjugated dienes formed is more than doubled at the higher temperature.

Copper, when exchanged on a molecular sieve, performed as well as a copper-chromium catalyst. In our previous experience (7) copper alone did not form a stable catalyst. Apparently the molecular sieve must protect copper in some way as yet unexplained. This phenomenon is being investigated further.

At a hydrogenation temperature of 170C all catalysts, except urea-precipitated copper-chromium catalyst, gave products which formed trace amounts of solids when stored for 24 hr at 7C. Soybean oil hydrogenated with urea-precipitated catalyst remained clear at 7C and formed only trace amounts of solids at 0C. All the oils hydrogenated at 200C formed some solids at 7C. When soybean oils hydrogenated at 170C were subjected to the AOCS cold test (1), only the products from the two laboratory-prepared catalysts and from commercial Cu-0202P remained clear in ice for 5.5 hr. All the other products became turbid.

A copper-on-guhr catalyst reportedly hydrogenates soybean oil selectively (4). The hydrogenations by DeJonge et al. were carried out with 0.2% copper at 185C and 5 atmospheres hydrogen pressure. When we analyzed their GLC data by the analog computer method (3), we found selectivity ratios of 7 to 9.5. A comparison with Table I shows that all the catalysts under our conditions gave higher selectivity ratios. If conjugated dienes were present in their products, triene values by alkali isomerization would be expected to be lower than the triene values by GLC and their selectivities would be higher. However, no conjugated dienes were reported in their analyses of hydrogenated products.

These laboratory results and chemical analyses suggest that copper-containing catalysts may meet the commercial requirements for producing a flavor-stabilized liquid soybean cooking oil. Such selective

TABLE II

Hydrogenation of Soybean Oil with Copper-Chromium Catalysts
(Catalyst, 0.3 g; oil, 300 ml; temperature, 200C; pressure, 30 psi)

Catalyst	Reaction time, min	Fatty acid composition, % GLC				IV (calcd.)	*trans*, %	Conj. diene, % (UV)	Alkali isomerization		Selectivity K_{Le}/K_{Lo}
		M	D	T[a]	*trans,trans* conj. diene				Le, %	Lo, %	
None	....	22.7	54.4	8.0	0.0	134.7	0	0	8.1	51.9	....
G-22	110	31.6	50.1	2.6	1.6	123.5	9.0	2.3	1.7	45.2	9.2
Cu-0202P	64	34.9	45.3	3.0	2.1	120.0	9.5	2.0	1.7	42.3	6.2
T-970	68	35.2	46.8	2.3	1.3	119.6	10.5	1.7	1.4	40.0	6.9
Cu-Cr (urea precipitation)	60	34.3	47.3	2.7	1.6	121.3	9.9	2.4	1.1	42.6	8.7
Cu-Cr (sodium borohydride reduction)	17	34.8	47.0	2.0	1.9	119.9	8.1	3.5	0.7	42.0	10.0
Copper-exchanged molecular sieve 13X	18	36.4	45.7	1.9	1.7	118.4	11.5	2.8	0.5	40.7	10.0

[a] Also includes *cis,trans* conj. diene.

catalysts reduce the linolenate content of soybean oil below 1% at an iodine value of over 115. They increase the *trans* content of the liquid oil much less than does a nickel catalyst, and they do not increase saturates. If the prooxidant effect of any catalysts that may remain in the oil can be overcome, it would be possible to produce more stable liquid soybean oil that would not require winterization.

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