Selective Hydrogenation of Soybean Oil: XII. Trialkyl Aluminum-Copper Stearate Homogeneous Catalysts[1]

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ABSTRACT

The reaction of copper stearate with triethylaluminum (TEAL) formed a soluble catalyst that promoted the selective hydrogenation of the linolenyl groups in soybean oil. This homogeneous catalyst was more active than copper-chromite. The activity was enhanced by the addition of silica, alumina or titania. Ethyl alcohol accelerated the hydrogenation when it was added in small amounts and retarded hydrogenation when increased amounts were added. More active and, in some cases, more selective catalysts were formed when TEAL was replaced by trialkylaluminum compounds containing longer chain length in the alkyl groups. Among other organometallics tested, diethylmagnesium and diisobutylaluminum ethoxide formed catalysts with activity comparable to heterogeneous nickel catalysts. The linolenate selectivity of these homogeneous catalysts (K_{Le}/K_{Lo} = 2.8-5.2) was less than that obtained with copper-chromite (12-14), but greater than that of commercially used nickel catalysts (2). Isomerization, as measured by the percentage of *trans* isomers formed, was similar to that of heterogeneous copper catalysts (% *trans*/ΔIV = 0.6-0.7).

INTRODUCTION

Soybean oil, a leading vegetable oil in terms of consumption, contains 7-9% linolenic acid; flavor reversion has been attributed to its presence. Selective hydrogenation of linolenic acid in soybean oil is one of the most important ways of improving flavor stability of the oil (1). A common industrial practice in the U.S. is to partially hydrogenate soybean oil. Because commercially used nickel catalysts have a limited linolenic selectivity (K_{Le}/K_{Lo}) of about 2, soybean oil hydrogenated to an iodine value (IV) of 110 contains 3-4% linolenic acid (2). In contrast, hydrogenation with highly selective (K_{Le}/K_{Lo} = 13-15) copper-chromite and supported copper catalysts (3) to the same IV results in soybean oil containing no linolenic acid. However, use of these catalysts in industry is impeded due to their low activity.

Homogeneous catalysts might be more active and less susceptible to poisoning than their counterpart heterogeneous catalysts. The reaction of transition metal compounds with triethylaluminum (TEAL) formed a homogeneous catalyst for the hydrogenation of soybean methyl esters as well as pure methyl linoleate and methyl linolenate (4). More recently, Stern et al. (5) reported the hydrogenation of soybean oil with 30-50 ppm of soluble nickel catalyst. This level of catalyst is 6-10 times less than the amount of heterogeneous nickel catalyst usually used. A recent patent (6) issued to a group of French workers demonstrated the use of homogeneous copper catalyst to hydrogenate crude soybean oil at 175 C and 300 psi hydrogen pressure.

The work presented in this study resulted from our interest in increasing the activity of copper catalysts. Homogeneous copper catalysts were prepared with different aluminum alkyls and other organometallics to ascertain how different organometallics affected the selectivity and activity of soybean oil hydrogenation. The influence of supports such as silica, alumina and titania, and of oxygenated solvents such as ethanol and acetone, was also evaluated.

EXPERIMENTAL PROCEDURES

Materials

Refined and bleached soybean oil was obtained from commercial sources. Organometallics were purchased from Texas Alkyls (Deer Park, TX) as 15-25% solutions in heptane. Diethylmagnesium consisted of a mixture of diethylmagnesium and TEAL, because diethylmagnesium by itself is an insoluble solid. Copper stearate was purchased from ICN Pharmaceuticals Inc., Plainview, NY. Cab-O-sil, Alon-C and Cab-O-Ti (fumed silica, alumina and titania, respectively) were obtained from Cabot Corporation, Boston, MA.

Catalysts

Catalysts were prepared in situ in an inert atmosphere. Soybean oil (75 g) and copper stearate (0.743 g, 1.178 mmol) were placed in an Erlenmeyer flask provided with a magnetic stirrer and a side arm, which was sealed with a serum cap. Silica, alumina or titania (10 times the weight of copper) were added as required. Any dissolved air and moisture were expelled under pump vacuum at 80 C. The mixture was then placed under a blanket of nitrogen and, while stirring with a magnetic stirrer, 3 mL of 25% TEAL in heptane (4.7 mmol) was added through the serum cap on the side arm. The required amounts of solvents such as ethanol were added.

Hydrogenation

The oil containing the dissolved copper complex was transferred under pressure into a 150-mL magnetically stirred Magna-Dash autoclave, which was electrically heated to 170 C under nitrogen pressure. At the reaction temperature, the stirrer was stopped and nitrogen was vented to the atmosphere. Hydrogen (150 psi) was admitted from an external tank through a pressure regulator valve, and the pressure in the autoclave was maintained constant (150 psi hydrogen pressure and 15 psi nitrogen pressure) during the course of the reaction that started when the stirrer was turned on. Samples were withdrawn at intervals for analysis.

Analytical Methods

Hydrogenated soybean oil samples containing the dissolved copper complex were used directly for preparation of methyl esters. Methyl esters were prepared with sodium methoxide catalyst according to the method of Christopherson and Glass (7), which was modified by replacing petroleum ether with diethyl ether. Fatty acid composition was determined by gas-liquid chromatography with packed columns (EGSS-X), and the IV was calculated. The percentage of isolated *trans* was measured by comparing the infrared absorption of methyl esters at 10.36 μm with methyl elaidate standard. Selectivity ratios (K_{Le}/K_{Lo}) were determined by a digital computer assuming consecutive reactions; i.e., triene→diene→monoene→stearate (8).

RESULTS AND DISCUSSION

Effect of Aluminum-to-Copper Ratio

A series of hydrogenations was carried out with different

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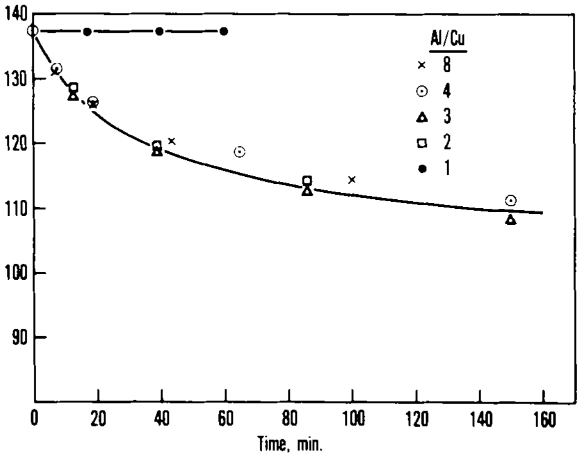

FIG. 1. Hydrogenation of soybean oil with TEAL-copper stearate complex: effect of Al/Cu ratio at 170 C, 60 psi and 0.1% copper.

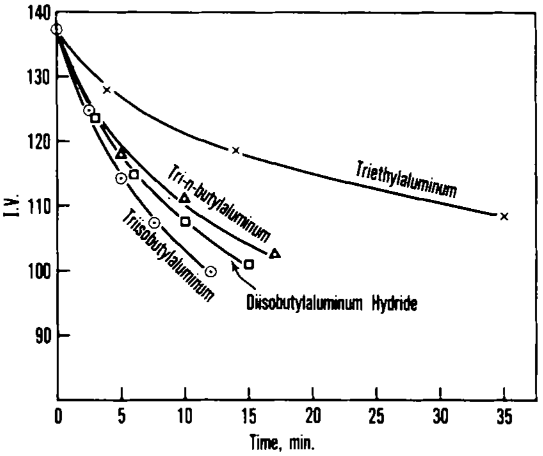

FIG. 2. Hydrogenation of soybean oil with organometallic-copper stearate complex: effect of alkyl groups at 170 C, 150 psi and 0.1% copper.

aluminum-to-copper ratios to ascertain the effect of TEAL on hydrogenation of soybean oil. The hydrogenation rate curves (IV vs time) for these experiments (Fig. 1) showed that, with 0.1% copper, a change in aluminum-to-copper ratio of between 2 and 8 had no effect. At an aluminum-to-copper ratio of 1, no soluble copper complex formed and no reaction occurred. Increasing the ratio to 2 resulted in a catalyst that was only partially soluble. but the reaction progressed normally. Soluble catalyst was formed at an aluminum-to-copper ratio of 3. A ratio of 4 was chosen for all further experiments except in the case of diethylmagnesium, for which the magnesium-to-copper ratio was in the range of 6-10. When the ratio of aluminum to copper varied between 2 and 8, there was no difference in the selectivity of the reaction or isomerization as measured by the percentage of *trans*-isomers formed per unit IV drop.

Effect of Organometallic Compounds

The progress of hydrogenation of soybean oil with different organometallics was shown by hydrogenation rate curves drawn in Figures 2 and 3. At 170 C and 150 psi hydrogen pressure, the IV dropped to 109 in 35 min with 0.1% copper activated by TEAL. All other organometallics except diethylaluminum ethoxide required 10 min or less to lower the IV to 110. Increasing the chain length of the alkyl groups had an accelerating effect. Triisobutylaluminum showed slightly better activity than tri-*n*-butylaluminum. Trihexyl-, trioctyl- and tridecylaluminums had similar activities. Diisobutylaluminum hydride, a strong reducing agent, dropped the IV to 101 in 15 min. Diethylaluminum ethoxide, which is formed by replacing one ethyl group in TEAL with an ethoxy group, is considerably more active than TEAL. Diethylmagnesium formed a more active catalyst than TEAL. Among other organometallics tested, triisobutylboron and diethylzinc did not form active catalysts with copper stearate.

Due to the high activity of soluble copper catalysts, the reaction with 0.1% copper was complete in 15 min or less. The concentration of copper was reduced to 0.025%, and the progress of hydrogenation for some typical catalysts is shown in Figure 4. With diisobutylaluminum hydride, the IV dropped to 110 in 75 min. A more active catalyst resulted with triisobutylaluminum that reduced the IV to 104 in 60 min. As with TEAL (Fig. 3), replacing one isobutyl group with an ethoxy group improved the catalyst activity considerably, with the IV dropping to 97 in 35

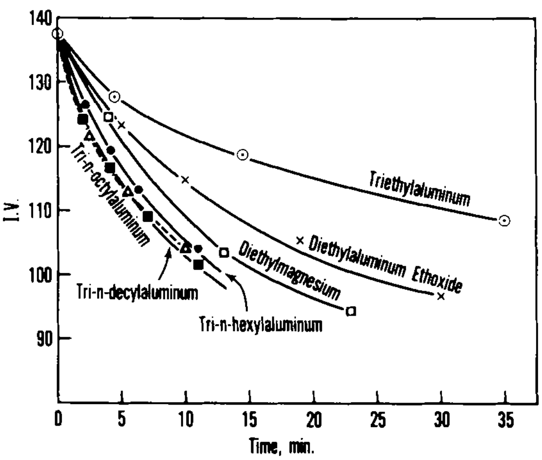

FIG. 3. Hydrogenation of soybean oil with organometallic-copper stearate complex: effect of alkyl groups at 170 C, 150 psi and 0.1% copper.

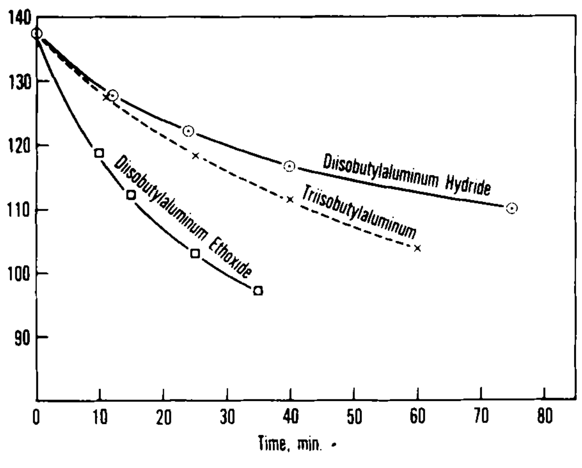

FIG. 4. Hydrogenation of soybean oil with organometallic-copper stearate complex at 170 C, 150 psi and 0.025% copper.

min. This catalyst is comparable in activity with heterogeneous nickel catalysts.

Effect of Additives

The activity of TEAL-copper stearate catalyst was improved considerably (Fig. 5) with the addition of alumina and only slightly with silica. The IV of soybean oil dropped to 100 in about 100 min with TEAL-copper stearate catalyst and in only 20 min with the inclusion of alumina. Both silica and alumina are commonly used as supports for heterogeneous catalysts because of their large surface area. In the present system where the catalyst is in solution, insoluble alumina is not expected to influence catalyst activity. Perhaps these additives adsorb some of the impurities in the oil which might otherwise poison the catalyst.

The effect of ethanol on hydrogenation rates with TEAL-copper stearate is most interesting. With 0.5% added ethanol, the activity is increased significantly. Addition of 1-2% ethanol, however, had the opposite effect. The hydrogenation of soybean oil virtually ceased with 5% ethanol. This anomalous behavior is due to the reaction of ethanol with TEAL. The lowest concentration used was just enough to replace one alkyl group with an ethoxy group to form diethylaluminum ethoxide which gave a better catalyst (Fig. 3) than TEAL with copper stearate. At higher concentrations of ethanol, all the alkyl groups in TEAL were replaced by ethoxy groups; apparently, this does not form an active catalyst. Acetone, which reacts with TEAL to form diethylaluminum isopropoxide, also improved catalyst activity (Fig. 5) but to a lesser extent than with ethanol.

These catalysts appear to be in solution and pass through a filter after hydrogenation except for a small amount of insoluble material which probably formed by decomposition. The suggestion (9) that colloidal metal is the active species in these catalyst systems was later disputed (10,11). There are no tests available to ascertain whether a catalyst is homogeneous. The observed reduction in the rate of hydrogenation with the addition of 1-2% alcohol can be used as an argument in favor of soluble catalysts, because if the active catalyst species were heterogeneous, then addition of alcohols should have, if any, a promoting effect (12-14).

As the hydrogenation was fast with 0.1% copper, the concentration of copper was reduced to 0.025%; the effect of additives on diethylmagnesium-copper stearate is shown in Figure 6. Addition of silica, titania or alumina improved the activity significantly; alumina was the most effective. The effect of ethanol on diethylmagnesium is similar to that of TEAL. The activity was increased significantly with the addition of 0.2% ethanol, which corresponded to 1 mol ethanol/mol of dimethylmagnesium. With 0.5% ethanol, which forms diethoxymagnesium, the reaction was almost stopped. The diethylmagnesium-copper stearate catalyst containing 0.2% ethanol was by far the most active of all catalysts studied. The IV dropped to 102 in 22 min with 0.025% copper. The activity of this catalyst compares favorably with heterogeneous nickel catalyst.

Fatty Acid Composition

A typical change in fatty acid composition during hydrogenation with diisobutylaluminum hydride-copper stearate complex is shown in Figure 7. Palmitate and stearate remained essentially constant, whereas triene and diene were reduced with a concomitant increase to monoene. The 75-min sample had a calculated IV of 110 and contained 0.6% linolenate. which is considerably lower than the 3%

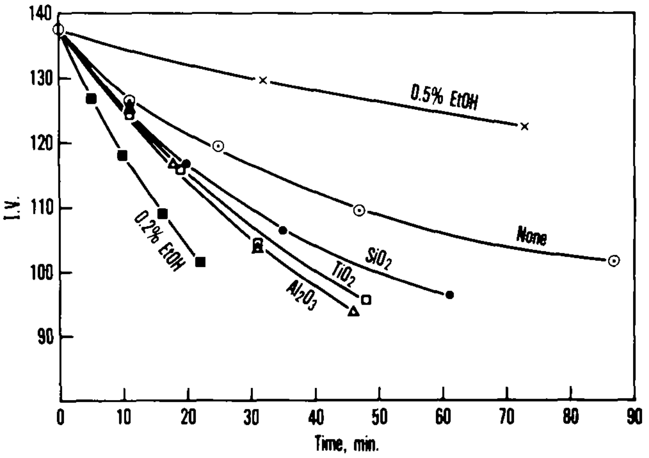

FIG. 6. Effect of additives on the hydrogenation of soybean oil with diethylmagnesium-copper stearate complex at 170 C, 150 psi and 0.025% copper.

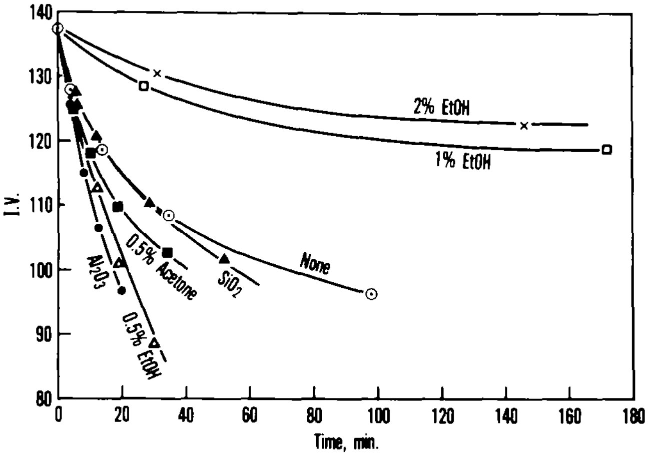

FIG. 5. Effect of additives on the hydrogenation of soybean oil with TEAL-copper stearate complex at 170 C, 150 psi and 0.1% copper.

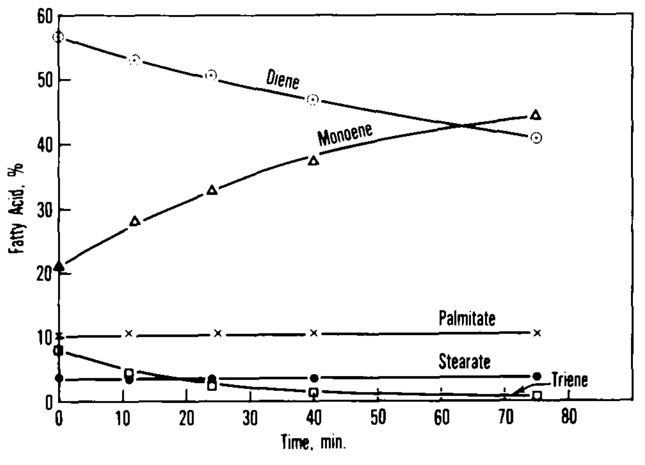

FIG. 7. Change in fatty acid composition during hydrogenation with diisobutylaluminum hydride-copper stearate complex at 170 C, 150 psi and 0.025% copper.

TABLE I

Selectivity and Isomerization with Organometallic-Copper Stearate Complexes

Organometallic compound	Selectivity		Isomerization
	K_{Le}/K_{Lo}	K_{Lo}/K_{Ol}	(% *trans*/ΔIV)
Triethylaluminum	3.3	13	0.65
Tri-*n*-butylaluminum	3.2	15	0.65
Triisobutylaluminum	2.8	25	0.64
Tri-*n*-hexylaluminum	3.2	14	0.66
Tri-*n*-octylaluminum	3.3	18	0.58
Tri-*n*-decylaluminum	3.3	26	0.71
Diisobutylaluminum hydride	5.2	∞	0.67
Diethylmagnesium	3.0	10	0.82
Diethylaluminum ethoxide	3.1	32	0.80
Diisobutylaluminum ethoxide	4.6	78	0.61
Triethylaluminum + ethanol	4.7	62	0.61
Triethylaluminum + Al_2O_3	3.5	32	0.65
Diethylmagnesium + Al_2O_3	2.9	22	0.81
Triethylmagnesium + SiO_2	3.7	15	0.67
Diethylmagnesium + SiO_2	3.1	21	0.82
Diethylmagnesium + TiO_2	2.8	19	0.79

normally found in soybean oil hydrogenated with nickel catalyst to the same IV (2).

Selectivity and Isomerization

The calculated selectivities for linolenate hydrogenation (K_{Le}/K_{Lo} = 2.8-5.2) with various organometallic catalysts (Table I) were considerably lower than the 12-13 obtained with copper chromite catalysts (15). The linoleate selectivities were also low (K_{Lo}/K_{Ol} = 13-78) with all homogeneous catalysts except diisobutylaluminum hydride-copper stearate, whereas copper chromite has infinite selectivity. This difference in selectivity behavior between homogeneous and heterogeneous catalysts suggests that they are different types of catalysts. The active agent in copper chromite catalysts was believed to be copper in the divalent state (16). Because of the highly reducing nature of the organoaluminum compounds, the homogeneous catalyst most likely has its copper in the zero valent state, which apparently is not as selective. The highest linolenate selectivity (5.2) was obtained with diisobutylaluminum hydride. All other organometallic-copper complexes had a selectivity of 3. Addition of ethanol appeared to improve linolenate selectivity. For example, the selectivity of TEAL improved from 3.3 to 4.7 upon addition of ethanol. Diisobutylaluminum ethoxide, which can also be prepared by the addition of ethanol to triisobutylaluminum, gave a linolenate selectivity of 4.6 vs 2.8 for triisobutylaluminum. Addition of silica, alumina and titania did not alter linolenate selectivity, but linoleate selectivity was somewhat higher (Table I).

Isomerization was measured as percentage *trans*/unit IV drop. By this criterion, most catalysts produced 0.6-0.7% *trans*/unit IV drop except diethylmagnesium, which gave a higher value of 0.8%.

Some of the catalysts described in this work have activity comparable with heterogeneous nickel catalysts. Low concentrations of copper (0.025%) effectively hydrogenated soybean oil. At the same time, these copper catalysts are more selective for the hydrogenation of linolenate than are nickel catalysts. Some of these homogeneous catalysts are, therefore, potentially useful in commercial hydrogenation of soybean oil. One disadvantage is the separation of product from the catalyst. A dilute acid wash removed the reddish brown color from the oil, indicating a probable process for catalyst removal. However, this involves an extra step in the processing of soybean oil.

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