

Hydrogenation and Isomerization of Soybean Oil with Perchloratocarbonylbis-(triphenylphosphine)rhodium (I)

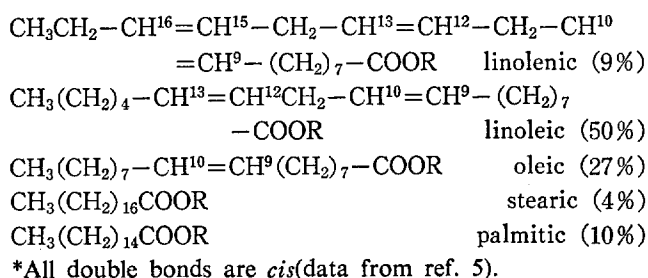
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It has been found that $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ catalyzes the hydrogenation and isomerization of soybean oil at room temperature under the atmospheric pressure of hydrogen. The hydrogenation occurs at the olefinic groups to produce saturated groups leaving the ester groups intact, and the isomerization converts $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ units to conjugated dienes and the dienes separated by more than two $-\text{CH}_2-$ groups. The rate of the hydrogenation is faster than that of the isomerization.

Introduction

Soybean oil is known to be a mixture of glycerine esters of unsaturated carboxylic acids (linolenic, linoleic, and oleic acid) and saturated carboxylic acids (stearic and palmitic acid) (see below), and most widely used in manufacturing oleomargarines, salad dressings, salad oils and other foods.



Linolenic ester, one of the major components of soybean oil, has a poor flavor which could be removed by the selective hydrogenation of $-\text{CH}^{16}=\text{CH}^{15}-$ group in the linolenic ester. Accordingly, the hydrogenation of soybean oil has been of interest in the field of homogeneous catalysis which shows better selectivities in general than the heterogeneous counterpart does.

The hydrogenation of soybean oil has been investigated with various catalytic systems: FeCl_3 and LiAlH_4 in tetrahydrofuran,¹ $\text{Cr}(\text{acac})_3$ and $\text{Al}(\text{i-bu})_3$ in decalin (acac = acetylacetonate group, i-bu = isobutyl group),² $\text{K}_3\text{Co}(\text{CN})_5$,³ $\text{Cr}(\text{C}_5\text{H}_5)(\text{CO})_3$,⁴ $\text{Pt}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_3)\text{Cl}$ ⁵ and $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$.⁶ Among these catalytic systems, Wilkinson's catalyst, $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ has been most thoroughly studied for the hydrogenation and isomerization of olefins.⁷⁻⁹ It has been well established that $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ shows the catalytic activities because one of $\text{P}(\text{C}_6\text{H}_5)_3$ readily dissociates from $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ to produce the catalytically active three coordinated $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_2$ which readily reacts with an olefin to form olefin complex, $\text{Rh}(\text{olefin})\text{Cl}(\text{P}(\text{C}_6\text{H}_5)_3)_2$.⁷⁻⁹

We have recently found that $\text{M}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ ($\text{M} = \text{Rh}$,¹⁰ Ir ¹¹) catalyze the hydrogenation¹⁰ and oligomerization^{10,11} of unsaturated nitriles. These catalytic activities have been expected by the fact that ClO_4 group in $\text{M}(\text{ClO}_4)-$

$(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ is so labile that the catalytically active unsaturated nitrile complexes, $[\text{M}(\text{unsaturated nitrile})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ could readily be formed by the reaction of $\text{M}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ with unsaturated nitriles.¹⁰⁻¹² Accordingly, it would be interesting to compare the catalytic activities of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ with those of $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$.

In this paper, we wish to report the hydrogenation and isomerization of soybean oil with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ at room temperature under the atmospheric pressure of hydrogen.

Results and Discussion

Figure 1 shows the rate of hydrogenation of soybean oil with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$. It is seen that the rate slowly decreases after ca. 40 hours and becomes very slow since. The hydrogen uptake levelled off after four days of catalysis at 25°C under the atmospheric pressure of hydrogen. The hydrogenation product (beige-white solid at room temperature) was isolated (see Experimental), and its infrared spectrum is shown in Figure 2.

The strong absorption band at 1740 cm^{-1} is due to the CO groups of soybean oil. This observation suggests that the hydrogenation occurs at the olefinic groups leaving CO groups in soybean oil intact, which is also confirmed by the ¹H-NMR spectral measurements (see text below). Infrared spectrum of soybean oil shows very weak absorption bands due to C=C stretching vibrational modes at ca. 1640 cm^{-1} where the hydrogenation product soybean oil shows practically no absorption bands in its infrared spectrum (see Figure 2).

In another experiment, the catalytic hydrogenation was followed by measuring the ¹H-NMR spectrum of the reaction mixture during the catalysis. Figure 3 shows the ¹H-NMR spectrum of soybean oil (before the catalysis) with the assignments of the protons whose ratio was closely watched during the hydrogenation. The ratio of $H_A : H_B : H_C : H_D : H_E$ in Figure 3 is determined to be 2.67 : 1.00 : 1.44 : 4.33 : 21.8. It has been found that the intensities of H_B , H_D and H_E remain practically unchanged during the catalysis while those of H_A and H_C (relatively to those of the remaining protons (H_B , H_D and H_E)) decrease during the catalysis. (It has

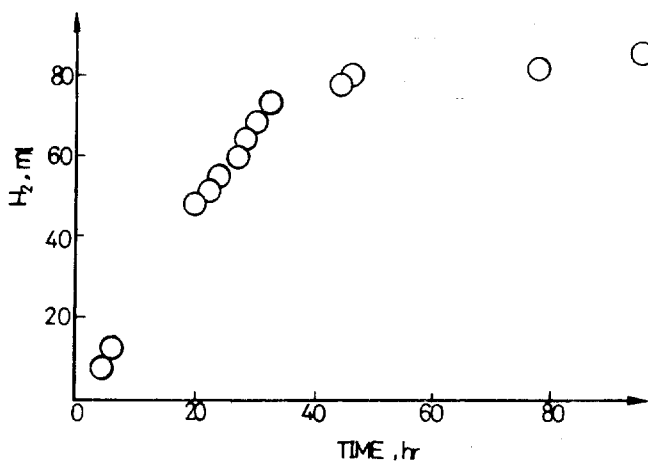


Figure 1. Hydrogen uptake by the reaction system of soybean oil (1.0 ml) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (0.2 g, 0.26 mmole) in chlorobenzene (10 ml) under hydrogen (P_{H_2} + vapor pressure of the solution = 1 atm.) at 25°C .

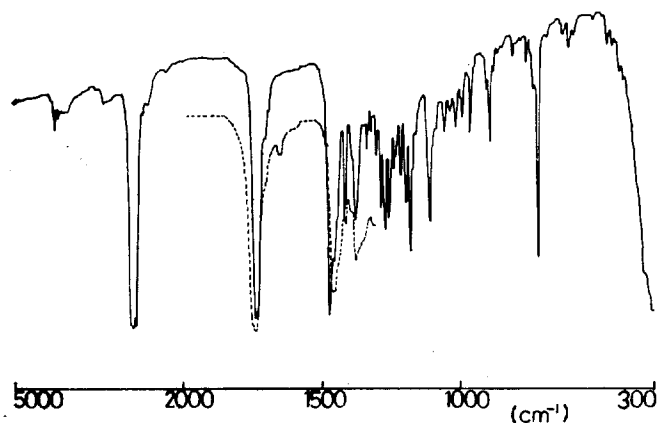


Figure 2. Infrared spectra of the hydrogenation product of Soybean oil (beige-white solid) in Nujol mull (solid line) and soybean oil (dotted line).

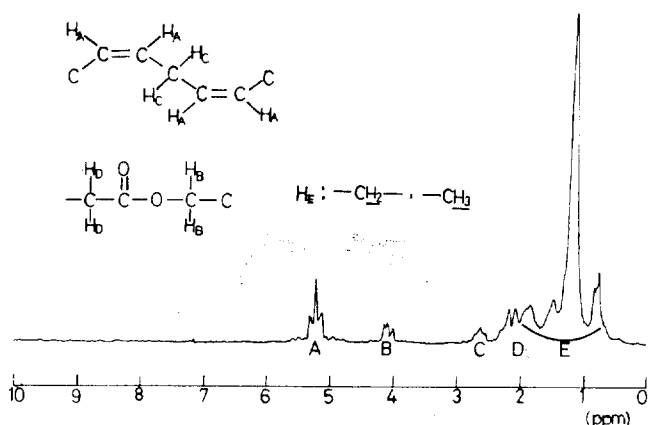


Figure 3. $^1\text{H-NMR}$ spectrum of soybean oil in CCl_4 at 25°C . Relative to TMS. $H_A : H_B : H_C : H_D : H_E = 2.67 : 1.00 : 1.44 : 4.33 : 21.8$.

been noticed that the intensity of H_E slightly increases after prolonged period of the catalysis.) It has also been found that the ratio of H_A/H_B slowly decreases while the ratio of H_C/H_B decreases relatively fast during the catalysis (see

Table 1 and Figure 4 which is the $^1\text{H-NMR}$ spectrum of the reaction mixture after 20 hours of the catalysis showing $H_A : H_B : H_C : H_D : H_E$ being 3.25 : 1.00 : 0.57 : 4.33 : 23.0). These $^1\text{H-NMR}$ spectral changes during the catalysis clearly suggest the followings: (1) the hydrogenation occurs at the olefinic groups in soybean oil leaving the ester groups intact, (2) the positional isomerization of the double bonds from $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(-\text{CH}_2-$: H_C at 2.6 ppm) to the dienes separated by more than two methylene groups such as $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=(\text{---}\text{CH}_2-$: H_E at 0.5 ~ 2.0 ppm) and to the conjugated dienes such as $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ (very weak signals appear at ca. 6 ppm after prolonged period of catalysis (see Figure 4)) also occurs, and (3) the rate of the isomerization is faster than that of the hydrogenation.

The protons at $-\text{CH}^{16}=\text{CH}^{15}-$ of the linolenic ester in soybean oil would be less than 7% of the whole olefinic protons in soybean oil. It is seen in Figure 4 and Table 1 that more than 7% of the olefinic protons (H_A) in soybean oil disappeared during the catalytic hydrogenation. Therefore, it might be said that the hydrogenation does not occur selectively at $-\text{CH}^{16}=\text{CH}^{15}-$ group of the linolenic ester in soybean oil.

Many catalytic systems with transition metal complexes have been known to catalyze the hydrogenation of terminal olefins more rapidly than that of inner olefins.¹² It is yet to be determined, however, whether the hydrogenation of soybean oil by $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ at 25°C under the atmospheric pressure of hydrogen proceeds faster at $-\text{CH}^{16}=\text{CH}^{15}-$ group of the linolenic ester than that at the other olefinic groups in soybean oil.

In order to obtain information on the catalysis, rhodium complex has been isolated from the reaction mixture of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and soybean oil under hydrogen at 25°C (see Experimental) and examined. Infrared spectrum of the isolated product is identical with that of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$. From many catalytic systems for hydrogenation of olefins have been isolated only olefin-free metal complexes which had been originally added into the catalytic systems as the precursors of the actual catalysts.⁷⁻⁹ It is, therefore, uncertain whether the actual catalytic species in our catalytic system is $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ itself or/and the Rh complex containing a soybean oil molecule. Further investigation for the nature of the catalysis is being carried out.

TABLE 1: The Ratio of the Protons in Soybean Oil During the Catalytic Hydrogenation of Soybean Oil (1.0 ml in $\text{C}_6\text{H}_5\text{Cl}$ (10 ml)) with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (0.015 g, 0.02 mmole) under Hydrogen (P_{H_2} + Vapor Pressure of the Solution = 1 atm) at 25°C . See Figure 3 for the Assignments of the Protons

Reaction time h	Ratio				
	H_A	H_B	H_C	H_D	H_E
0	2.67	1.00	1.44	4.33	21.8
20	2.33	1.00	0.57	4.33	23.0
54	1.67	1.00	0.1	4.33	24.2
95	1.06	1.00	0.1	4.33	24.5

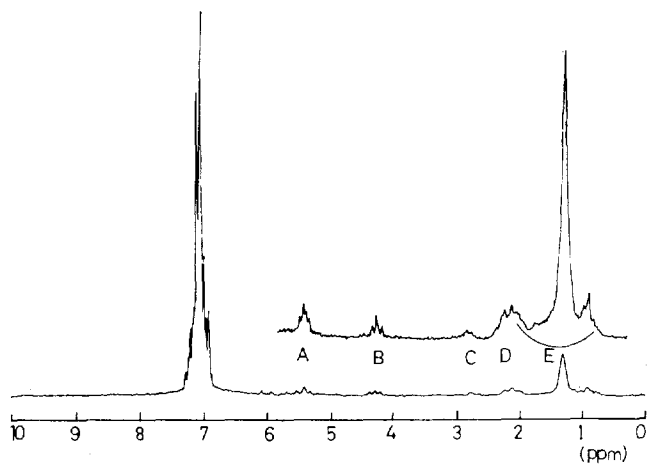


Figure 4. $^1\text{H-NMR}$ spectrum of the reaction mixture (soybean oil (1.0 ml) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (0.15 g, 0.2 mmole) in chlorobenzene, multiplet at ca. 7 ppm (10 ml)) under the catalytic conditions (at 25°C under hydrogen (P_{H_2} + vapor pressure of the solution = 1 atm) after 20 hours of catalysis. H_A : H_B : H_C : H_D : H_E = 2.33: 1.00: 0.57: 4.33: 23.0. Relative to TMS.

Experimental

Infrared and $^1\text{H-NMR}$ spectra were recorded on a Shimadzu Infrared Spectrophotometer (Model IR-440) and Varian 60 MHz spectrometer (Model EM-360A), respectively. Solvents were dried and distilled before use. $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ was prepared by the literature method.¹³ High purity N_2 and H_2 were purchased from Dong Yang Argon Co., Ltd.

Soybean Oil. Healthy and clean soybeans (150 g) were crushed into small flakes, placed into hexane (250 ml) in a 500 ml round bottom flask at room temperature under nitrogen, and refluxed for 48 hours. The reaction mixture was cooled to room temperature under nitrogen and filtered to obtain the pale yellow filtrate. Then the solvent (hexane) was distilled off on a rotary evaporator, and 25 ml of pale yellow soybean oil was obtained.

Hydrogen Uptake Measurements. $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (0.2 g, 0.26 mmole) and soybean oil (1.0 ml) in 10 ml of chlorobenzene were introduced into a 100 ml round bottom flask connected to a standard vacuum system under nitrogen. The yellow solution was evacuated with stirring in water bath maintained at 25°C . Hydrogen was introduced into the whole system designed for gas volume change measurements, which is composed with the followings: (a) the reactor in which the solution of soybean oil and the catalyst was placed, (b) a manometer to measure the pressure of the reaction system, (c) a gas burette partly filled with mercury to measure the volume change of H_2 gas during the catalysis, (d) a mercury reservoir connected to the gas burette by a long (75 cm) and flexible teflon tube, and (e) a large gas

container (2.0 l) connected with a stopcock to refill the consumed H_2 at intervals. During the catalysis, the mercury reservoir was moved up and down to adjust the pressure of the reaction system to 1 atm. (under which the catalysis was followed) and the mercury level in the gas burette was read to record the H_2 volume consumed by the catalysis (see Figure 1). After four days of catalysis, the solvent (chlorobenzene) was distilled off under vacuum at 25°C and beige-white solid (mixture of the hydrogenation product of soybean oil and the catalysis) was obtained. Acetone (20 ml) was added to this beige-white solid to dissolve the metal complexes and unreacted soybean oil, and the acetone-insoluble hydrogenation product was obtained by filtration. The beige-white hydrogenation product (solid at 25°C) was 0.8 g.

$^1\text{H-NMR}$ Spectral Measurements During the Catalysis. Chlorobenzene (10 ml) solution of soybean oil (1.0 ml) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (0.015 g, 0.02 mmole) was stirred under hydrogen (P_{H_2} + vapor pressure of the solution = 1 atm) at 25°C on a standard vacuum system. A portion (2.0 ml) of the reaction mixture was taken at intervals during the catalysis for $^1\text{H-NMR}$ spectrum measurement. After 4 days of catalytic hydrogenation, hexane (20 ml) was added into the reaction mixture (6 ml) to result in precipitation of yellow solid (Rh complexes) which was isolated by filtration, dried in vacuum and weighed (0.08 g).

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