

# Catalytic Isomerization of Safflower Oil with Rhodium Complexes

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Cationic rhodium (I) complexes of the type  $[(\text{NBD})\text{RhL}_2]^+ \text{ClO}_4^-$  (NBD, norbornadiene; L, triphenyl phosphine or diphenyl phosphino ethane) have been studied as catalysts for the isomerization of methyl linoleate and safflower oil. The catalysts gave very good yields of conjugated products with both oil and methyl linoleate. Isomerization could be carried out under very mild conditions (55–65 C, 1 atm  $\text{N}_2$ ). Although the catalyst undergoes transformation in the course of the reaction, it maintains its catalytic activity. In fact, the catalysts isolated from the reaction with safflower oil were recycled with practically no loss of activity.

The hydrogenation of vegetable oils has many industrial applications because it results in materials with new properties and of increased value and utility. Although heterogeneous catalysts are commonly employed, there also are many examples of hydrogenation with homogeneous catalysts (1–7). However, compared to hydrogenation, there have been fewer studies on isomerization of oils (8–13). Conjugated oils are important industrially because of their improved drying property. In this paper we describe the use of cationic rhodium complexes as catalysts for the isomerization of safflower oil and methyl linoleate (14).

The properties of cationic rhodium complexes as hydrogenation catalysts have been studied extensively by Schrock and Osborn (15–17). The catalytic activity of these complexes for hydrogenation of dienoic fatty esters and soybean oil has been reported recently (18–20). However, to the best of our knowledge, no attempt has been made to use these complexes as isomerization catalysts with oils. A fundamental problem in homogeneous catalysis is the separation of catalysts at the end of the reaction. The cationic rhodium complexes are particularly attractive in this regard because of the ease with which they can be separated from a nonpolar substrate, either by extraction with a polar solvent immiscible with the oil layer or by precipitation on addition of a nonpolar solvent.

## EXPERIMENTAL

Methyl linoleate of 89% purity was supplied by Acme Chemicals (Bombay, India). The impurities in this were methyl oleate (10%) and methyl palmitate (1%). The cationic rhodium complexes  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]\text{ClO}_4$  and  $[\text{Rh}(\text{NBD})(\text{DPPE})]\text{ClO}_4$  were synthesized by previously published procedures (16) (NBD, norbornadiene; COD, 1,5-cyclooctadiene, and DPPE, diphenyl phosphino ethane). The catalytic experiments were carried out with dry and degassed solvents under a  $\text{N}_2$  atmosphere. In a typical experiment with safflower oil, 30 mg of  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]\text{ClO}_4$  (0.037 mmol) were refluxed with 2.5 g of safflower oil in an acetone/methanol mixture (90:10, v/v) under  $\text{N}_2$  for 16 hr. At the end of the reaction, the solvent was removed and the catalyst was precipitated from

the oil by addition of pentane. The catalyst was isolated by filtration, and isomerized oil was obtained by removing pentane from the filtrate. The extent of isomerization was determined by gas liquid chromatography (GLC) using a Pye-Unicam 204 instrument with a 10% EGSS-X column. Methyl palmitate present in the starting material served as an internal standard. Lack of change in the percentage of methyl palmitate in the reaction indicated there was no polymerization. For GLC analysis, the oil recovered at the end of the reaction was converted to methyl ester by refluxing with sodium in dry methanol. The same procedure was followed in experiments with methyl linoleate except that no further conversion to methyl ester was necessary. In all experiments with  $[\text{RhH}_2\text{L}_2\text{S}_2]^+$  (L,  $\text{PPh}_3$  or DPPE; S, solvent), the catalyst was first generated in situ by passing  $\text{H}_2$  before safflower oil or methyl linoleate was added.

## RESULTS AND DISCUSSION

*Isomerization of methyl linoleate.* The results of isomerization of methyl linoleate with different rhodium complexes are summarized in Table 1. Analysis of the products showed that the conjugated dienes produced were a mixture of *cis-trans*, *cis-cis* and *trans-trans* isomers.

As can be seen from Table 1, no isomerization was produced with  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$  in neat acetone, and the presence of some alcohol was necessary for the reaction to take place. This indicates that the active catalytic species is not the starting complex but some other species that is derived from it in situ in alcoholic solvents. A possible explanation is that in these  $[\text{Rh}(\text{Diene})\text{L}_2]^+$  complexes (diene, NBD or COD; L,  $\text{PPh}_3$  or DPPE), norbornadiene or cyclooctadiene gets hydrogenated by transfer hydrogenation from the alcoholic solvent and is thereby removed from the coordination sphere of the rhodium metal. This helps to create the coordinative unsaturation or solvent coordination at the metal center that is necessary for catalytic action. In one experiment, norbornane was detected by GLC to be formed in almost quantitative amounts on refluxing  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$  in MeOH under  $\text{N}_2$ . The difference in catalytic activity of  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$  and  $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]^+$  presumably is due to the difference in the rate at which they undergo transfer hydrogenation. There have been examples of transfer hydrogenation from alcohols by Rh(I) complexes (21).

We also have synthesized in situ  $[\text{RhH}_2(\text{PPh}_3)_2\text{S}_2]^+$  separately, as reported by Schrock and Osborn (16). This was done by passing  $\text{H}_2$  through a methanol solution of  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$ , when the color changed sharply from yellow-orange to pale yellow. This solution was then used for isomerization of methyl linoleate under  $\text{N}_2$ . With preformed  $[\text{RhH}_2(\text{PPh}_3)_2\text{S}_2]^+$ , the reaction was found to proceed much faster and was complete in only two hr. We also synthesized  $[\text{RhH}_2(\text{PPh}_3)_2\text{S}_2]^+$  in  $\text{CH}_2\text{Cl}_2$  or acetone and could carry out isomerization of methyl linoleate in these solvents under  $\text{N}_2$ . This clearly confirmed that the role of alcohol was to generate the active catalytic species from the  $[\text{Rh}(\text{diene})\text{L}_2]^+$  precursor. The similarity in the isomer distribution of conjugated dienes produced from methyl

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## ISOMERIZATION OF SAFFLOWER OIL

TABLE 1

Activity of Rhodium Complexes for Isomerization of Methyl Linoleate

Catalyst precursor	Solvent	Conversion (%)	<i>cis-trans</i> conjugated diene (%)	<i>cis-cis</i> conjugated diene (%)	<i>trans-trans</i> conjugated diene (%)
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+a</sup>	MeOH	79.3	42.0	23.4	12.2
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+b</sup>	(CH <sub>3</sub> ) <sub>2</sub> CO	nil	—	—	—
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+b</sup>	(CH <sub>3</sub> ) <sub>2</sub> CO-MeOH (95:5)	27.6	10.6	10.7	3.5
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+c</sup>	Cyclohexanol	91.2	39.9	23.2	17.3
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+c</sup>	Isopropanol	93.0	39.0	26.2	17.7
[Rh(COD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+a</sup>	MeOH	40.5	16.5	17.1	4.4
[RhH <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> S <sub>2</sub> ] <sup>+d</sup>	MeOH	86.0	45.0	24.2	15.8
[Rh(NBD)(DPPE)] <sup>+a</sup>	MeOH	76.0	39.0	22.6	13.9

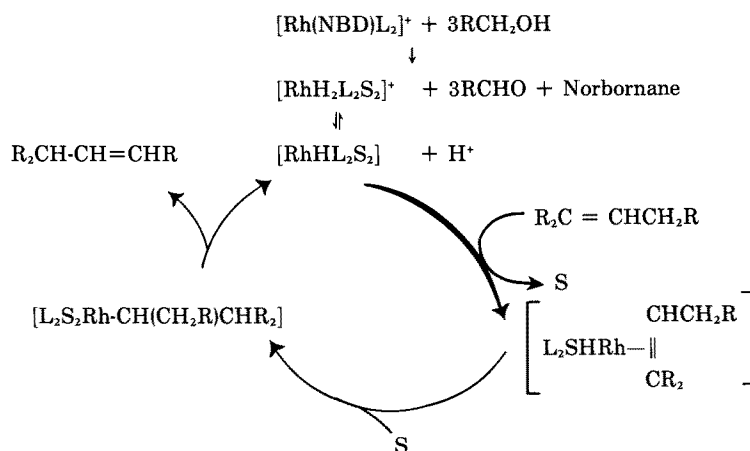
<sup>a</sup>Reaction was carried out under N<sub>2</sub> at 65 C for 5 hr.<sup>b</sup>Reaction was carried out under N<sub>2</sub> at reflux temperature for 5 hr.<sup>c</sup>Reaction was carried out at 80 C for 5 hr.<sup>d</sup>Reaction was carried out at 65 C for 2 hr.

FIG. 1. Proposed mechanism for the isomerization of methyl linoleate.

linoleate with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>S<sub>2</sub>]<sup>+</sup> point to a common catalytic intermediate in both cases. The kinetics of isomerization with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>S<sub>2</sub>]<sup>+</sup> was studied in MeOH by monitoring the disappearance of starting methyl linoleate. A long induction time ca. three hr was observed with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> at the beginning, followed by rapid disappearance of methyl linoleate, the rate of which was the same as that with [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>S<sub>2</sub>]<sup>+</sup>. This further suggests that a common catalytic intermediate is involved with both catalysts. The formation of monoenes, which provide evidence for transfer hydrogenation of methyl linoleate from the solvent, was negligible in all cases.

It was reported earlier that one of the reasons for the low rate of activity of [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub> for hydrogenation of soybean oil is, perhaps, the formation of the complex [Rh(diene)<sub>2</sub>PPh<sub>3</sub>]<sup>+</sup> in situ (20), which reacts with H<sub>2</sub> only very

slowly. Schrock and Osborn have suggested the use of chelating ligands like diphenyl phosphino ethane (DPPE) to prevent the formation of such diolefin complexes (18). To determine whether the isomerization reaction can be made to proceed faster than with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, we have synthesized [Rh(NBD)(DPPE)]<sup>+</sup> and used it for isomerization of methyl linoleate. However, no significant difference in the rate of isomerization or isomer distribution of the conjugated diene was observed between [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Rh(NBD)(DPPE)]<sup>+</sup> catalysts. This clearly shows that diolefin complexes of the [Rh(diene)<sub>2</sub>PPh<sub>3</sub>]<sup>+</sup> type are not formed to any appreciable extent with a bulky olefin like methyl linoleate. The isomerization with [Rh(NBD)L<sub>2</sub>]<sup>+</sup> is perhaps best explained by the mechanism proposed in Figure 1.

The isomerization activity of [RhHL<sub>2</sub>S<sub>2</sub>] species has been reported earlier (15).

TABLE 2

Activity of Rhodium Complexes for Isomerization of Safflower Oil

Expt. number	Catalyst precursor	Reaction time (hr)	Conversion (%)	<i>cis-trans</i> + <i>cis-cis</i> conjugated diene (%) <sup>f</sup>	<i>trans-trans</i> conjugated diene (%)
1	[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+a</sup>	16	95.8	82.7	7.1
2	Recycled from expt. 1 <sup>a</sup>	16	94.9	80.4	14.1
3	[RhH <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> S <sub>2</sub> ] <sup>+a,b</sup>	5	85.2	77.3	8.0
4	Recycled from expt. 3 <sup>a,c</sup>	5	93.0	74.4	11.9
5	Recycled from expt. 3 <sup>a,d</sup>	5	29.9	25.5	2.5
6	[RhH <sub>2</sub> (DPPE)S <sub>2</sub> ] <sup>+a,e</sup>	4	76.3	74.5	1.8

<sup>a</sup>Reaction was carried out in acetone/methanol mixture (90:10, v/v) at reflux temperature under N<sub>2</sub>.

<sup>b</sup>Catalyst was generated in situ from [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> by passing H<sub>2</sub> for 30 min.

<sup>c</sup>Recycled catalyst was first activated by passing H<sub>2</sub> for 1 hr.

<sup>d</sup>No activation of the recycled catalyst was carried out.

<sup>e</sup>Catalyst was generated in situ from [Rh(NBD)(DPPE)]<sup>+</sup> by passing H<sub>2</sub> for 30 min.

<sup>f</sup>Resolution of *cis-trans* and *cis-cis* isomers was not possible.

*Isomerization of safflower oil.* In the isomerization reactions with safflower oil, a mixture of acetone/methanol (90:10, v/v) was used as the solvent to ensure complete miscibility with the oil. The results are summarized in Table 2.

One interesting difference in the isomerization results for methyl linoleate and safflower oil was the much lower amount of *trans-trans* conjugated diene that was formed with oil. Presumably this is due to steric factors which play a major role with a sterically crowded triglyceride like safflower oil. As can be seen from Expt. 1 in Table 2, the isomerization of safflower oil with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> proceeds much more slowly compared to methyl linoleate, again due to steric reasons. In experiments with oil, we have isolated the catalyst at the end of the reaction to check its catalytic activity on recycling. This was done by removing the solvent at the end of the reaction and adding pentane when the catalyst precipitated out. The catalyst was then isolated by filtration and recycled for further experiments. It was concluded from NMR and elemental analysis of the recovered catalyst (Expt. 1, Table 2) that the starting complex [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> had undergone transformation in the course of the reaction. The efficiency of recovery based on rhodium estimation by atomic absorption was 95%. This recovered catalyst was recycled as shown in Expt. 2 in Table 2. It was found that the drop in catalytic activity on recycling was negligible.

As pointed out earlier, isomerization of safflower oil with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> was rather slow. In order to speed up the reaction, we generated [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>S<sub>2</sub>]<sup>+</sup> in situ by bubbling H<sub>2</sub> through a solution of [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> for 30 min. Safflower oil was then added to this solution and refluxed under N<sub>2</sub>. It was found that isomerization proceeded much faster, and the reaction was almost complete in five hr. In this case also, we isolated the catalyst at the end of the reaction as before and checked its activity on recycling. The recycle experiments in this case were done in two ways. In one experiment (Expt. 4, Table 2), we reactivated the catalyst by bubbling H<sub>2</sub> for one hr before adding the oil and changing over to N<sub>2</sub>. In the other

case (Expt. 5, Table 2), no prior activation with H<sub>2</sub> was done. As can be seen from Table 2, the catalytic activity on recycling was much higher in the case where reactivation with H<sub>2</sub> was done. It is possible that in reaction with oil, [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>S<sub>2</sub>]<sup>+</sup> is degraded due to the formation of a stable complex through the olefinic double bonds of oil. In fact, the NMR spectra of the recovered catalyst in this case did show the presence of triglyceride moiety. Reactivation with H<sub>2</sub> may help remove the bound triglyceride and regenerate the starting catalytically active species. It is to be noted that no such activation was necessary for recycled [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (Expt. 2, Table 2), which maintained very good catalytic activity. This indicates that, in contrast to methyl linoleate, the active catalytic species derived from [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>S<sub>2</sub>]<sup>+</sup> in isomerization reactions with oil are different. Similar catalytic activity also was observed with [RhH<sub>2</sub>(DPPE)S<sub>2</sub>]<sup>+</sup> (Expt. 6, Table 2). However, recovery of the catalyst at the end of the reaction proved to be much more difficult than with [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>S<sub>2</sub>]<sup>+</sup>.

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## Study of Thermal Oxidation of Thin Film of Trilinolein by Thermogravimetric Analysis

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The thermal oxidation of thin film of trilinolein has been investigated. The amounts of thermal decomposition products and polymerization products were determined using vacuum thermogravimetric analysis (vacuum TGA). It was found that the thermal oxidation decomposition and polymerization occurred in at least the outermost 120  $\mu$  of trilinolein films heated at 200 C for 4 min. In addition, it was found that the thermal polymerization is markedly affected by the nature of sample pans.

In recent years, the thermal oxidation reactions of oil during storage and thermal treatment have been investigated extensively, and a number of papers on the subject have been published (1-7). Although most studies have been carried out by using bulk phase rather than thin film phase of oil, studies on the thin film of oil are very limited (8-10). In addition, in the case of cooking and lubrication, the oil generally is used as a thin film phase. Therefore, the study of thermal oxidation reaction of thin film is of particular importance.

On the other hand, it is well known that the thermal oxidation reaction of oil occurs at the oil surface and is influenced by the nature of the utensil. Such surface reactions are difficult to monitor by conventional experimental methods. The suitable surface analytical techniques were not commonly available at the time these studies were carried out. Thus, we have used a modified vacuum thermogravimetric analysis (vacuum TGA) to investigate the thermal oxidation reaction of thin film.

In this study, attempts were made to investigate the thermal oxidation decomposition and polymerization of thin film of trilinolein by vacuum TGA.

### EXPERIMENTAL

**Materials.** 1,2,3-Tri-[(*cis,cis*)-9,12-octadecadienoyl]-*rac*-glycerol (Trilinolein, purity 99%) was obtained from

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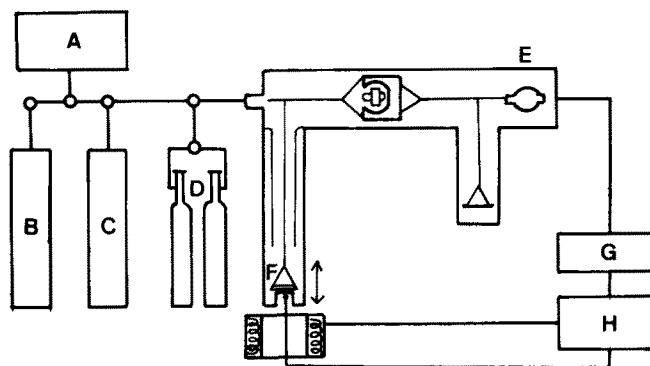


FIG. 1. Schematic diagram of apparatus. A, Ionization vacuum gauge; B, rotary pump; C, diffusion pump; D, gas cylinder; E, detector; F, sample pan; G, recorder; H, thermal controller.

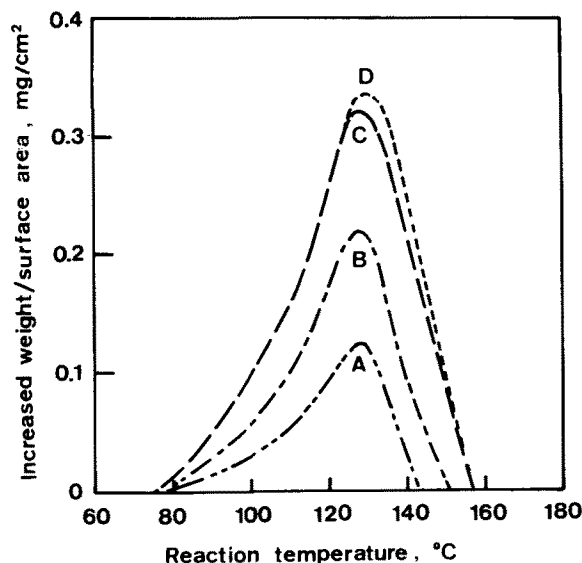


FIG. 2. Thermogravimetric curve of trilinolein in air. Film thickness: A, 90  $\mu$ ; B, 230  $\mu$ ; C, 410  $\mu$ ; D, 780  $\mu$ .

Sigma Chemical Co. (St. Louis, Missouri) and was used without purification.

**Apparatus.** A Shimadzu TB-20 electric microthermo-balance equipped with a modified chamber for measuring thermal decomposition products and thermal