Conjugation of Polyunsaturated Fats: Methyl Linoleate With Tris(triphenylphosphine) Chlororhodium[1]

W.J. DeJARLAIS and **L.E. GAST**, Northern Regional Research Laboratory[2],
Peoria, Illinois 61604

ABSTRACT

Tris(triphenylphosphine) chlororhodium in methanol produces nearly 95% conjugated dienes from methyl linoleate. The dienes are principally *cis,trans-* and *cis,cis*-conjugated. Since deuterium is introduced into the products when deuterated methanol is the solvent, a dihydride complex is the probable intermediate. The reaction is sluggish in chloroform, possible because the dihydride cannot easily form. The catalyst is activated in chloroform with hydrogen. Since no reduction occurs in the absence of hydrogen, hydrogenation likely occurs by hydrogenolysis of the alkyl complex of the dihydride olefin rather than a transfer of both hydrogens from the hydride complex.

INTRODUCTION

Osborn and coworkers (1) described the hydrogenation of olefins with tris(triphenylphosphine) chlororhodium ($RhClL_3$). The active hydrogenation catalyst had the formula $H_2RhCl[(C_6H_5)_3P]_2$ (H_2RhClL_2) formed from $RhClL_3$ by the elimination of one molecule of triphenylphosphine and addition of two hydrogen atoms. Although some isomerization of hexanes was noted under hydrogenation conditions, none occurred with $RhClL_3$ under nitrogen in benzene-hexane solution at 25 C for 24 hr.

Biellmann and Jung (2) reported that $RhClL_3$ in the presence of H_2 isomerized the double bond of damsin rather than reducing it. They suggested that H_2RhClL_2 was the intermediate since no isomerization occurred with $RhClL_3$ in ethanol in the absence of H_2. When the deuterium analog of H_2RhClL_2 was used in equivalent amounts, the isomerized olefin contained only about one deuterium atom. They suggested that isomerization takes place through an alkyl metal sigma-bonded intermediate similar to Cramer and Lindsey's proposal (3).

Birch and Subba Rao (4) observed that certain vinyl ethers containing 1,4-dienyl groups were conjugated by $RhClL_3$ in refluxing $CHCl_3$. In benzene the reaction was slower.

Because of our interest in the conjugation of polyunsaturated fats, we have studied the action of $RhClL_3$ on methyl linoleate (hereafter referred to merely as linoleate).

RESULTS AND DISCUSSION

Birch and Subba Rao refluxed the substrate in chloroform with 1% to 2% $RhClL_3$, presumably in air. In air we found no conjugation produced by refluxing linoleate with 2% $RhClL_3$ in chloroform. Nor was conjugation produced by reaction under N_2 (Table I, Run 1) in 2 hr. However, after 10 hr a small amount of conjugation developed (Table I, Run 8). Osborn and coworkers (1) noted that $RhClL_3$ forms complexes with oxygen readily and that careful degassing of solvents was required to obtain the correct molecular weight of $RhClL_3$. We found that either by pulling a vacuum briefly and adding more catalyst (Table I, Runs 5 and 6) or by sweeping the linoleate solution with N_2 for 1 hr before the addition of catalyst (Table I, Run 7) partial conjugation resulted.

We found methanol to be a useful reaction medium. The results of treating linoleate with two different concentrations of $RhClL_3$ at 65 C in methanol are shown in Figures 1 and 2. Since the disappearance of linoleate practically stops after 4 hr, $RhClL_3$ may well be converted by then to a catalytically inactive form such as the dimer, $Rh_2Cl_2[(C_6H_5)_3P]_4$, which is not active as a hydrogenation catalyst (1). When solid $RhClL_3$ was added to a deoxygenated methanol solution of linoleate, a more active catalyst is obtained than when an equivalent amount of

TABLE I

Conjugation of Methyl Linoleate (1 g) in Chloroform (10 ml) With $RhClL_3$ Under N_2 at 65 C

Run	Amount catalyst, mg	Reaction time, hr	Yield of conjugated dienes, %[a]	Comments
1	20	2	Nil	---
2	20	2	Nil	Pull vacuum on solution before catalyst added
3	20	2	Nil	As Run 2
4	20	4	Nil	As Run 2
5	40	4 + 2	21	Add 20 mg catalyst to Run 4, heat 2 hr
6	40	4 + 6	49	Run 5 continued
7	20	10	35	Sweep with N_2 1 hr before catalyst solution added
8	20	10	44	---

[a] Determined by gas chromatography.

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[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

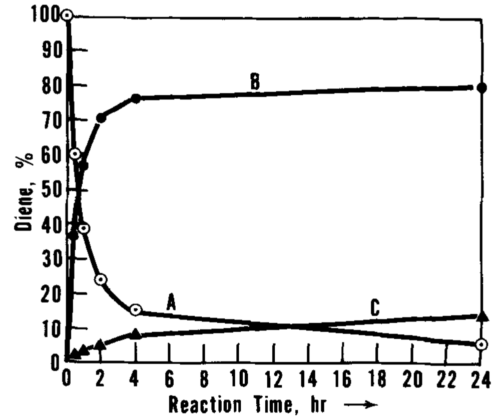


FIG. 1. Reaction of methyl linoleate (1 g) and $RhClL_3$ (20 mg) in methanol (10 ml) at 65 C. Solid catalyst method. A, Nonconjugated diene; B, *cis,trans-* and *cis,cis*-Conjugated diene; C, *trans,trans*-Conjugated diene.

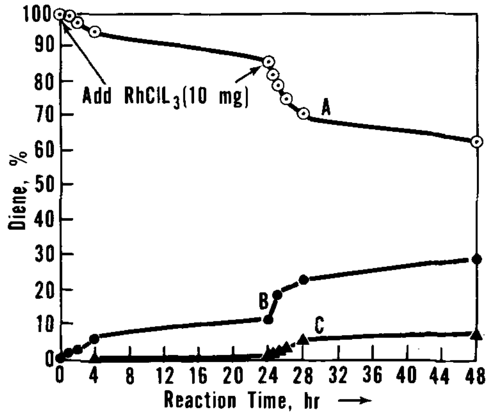


FIG. 3. Reaction of methyl linoleate (1 g) and $RhClL_3$ in methanol (10 ml) at 65 C. Solution catalyst method. A, Nonconjugated diene; B, *cis,trans-* and *cis,cis*-conjugated diene; C, *trans,trans*-conjugated diene.

$RhClL_3$ is added as a chloroform solution. Thus in 24 hr with 2% by weight catalyst, the conjugated diene yield when the catalyst is added as a chloroform solution is ca. 60-75% of the yield with the solid catalyst. Twenty milligrams $RhClL_3$ does not completely dissolve in 10 ml of methanol and 1 g linoleate even after 24 hr at 65 C; whereas 10 mg in the same solution dissolves in 24 hr. Perhaps the greater amount of $RhClL_3$ gives a higher conversion because the solid $RhClL_3$ is able to supply an active catalyst to the system continuously. Solid $RhClL_3$ is not catalytic as shown in experiments in which methanol is replaced by *n*-butylcarbitol. $RhClL_3$ appears nearly insoluble in *n*-butylcarbitol at 65 C. When a mixture of 10% *n*-butylcarbitol in methanol is used, the yield of conjugated dienes obtained in 24 hr at 65 C is 49% vs. near 95% in methanol only.

Figure 3 suggests that not all the oxygen is removed from the system by bubbling nitrogen through the methanol solution of linoleate before adding the catalyst. Data in Figure 3 were obtained by initiating the reaction with a solution of 10 mg of $RhClL_3$ in chloroform (0.5 ml of solution) and then by adding a second 10 mg of $RhClL_3$ in chloroform (0.5 ml of solution) after 24 hr. The rate of reaction achieved following the first catalyst addition was much less than that following the second catalyst addition.

$RhClL_3$ is almost insoluble in higher alcohols. However, these alcohols may be used if chloroform is present to dissolve the catalyst. For example, linoleate can be conjugated with $RhClL_3$ in isopropanol when $RhClL_3$ is added in a chloroform solution (1 ml) (Fig. 4). If the solid catalyst method is used with higher alcohols, little if any of the catalyst dissolves and a low level of conjugation is achieved (ca. 4% in 24 hr at 65 C in isopropanol).

If the reaction proceeds through H_2RhClL_2 as indicated by Biellmann and Jung (2), then a priori the greater degree of activity in methanol than in chloroform is due to the greater ease with which H_2RhClL_2 is formed, i.e., the greater ease of getting hydrogen from methanol. However, one of the products of such a reaction would be formaldehyde:

$$\begin{aligned} &RhCl[(C_6H_5)_3P]_3 + 2CH_3OH \rightarrow \\ &RhCl[(C_6H_5)_3P]_2(CH_3OH)\cdot H_2 \\ &+ P(C_6H_5)_3 + CH_2O \qquad [1] \end{aligned}$$

Formaldehyde might well poison the catalyst via the aldehyde reaction described by Osborn and coworkers (1):

$$\begin{aligned} &RhCl[(C_6H_5)_3P]_3 + CH_2O \rightarrow \\ &RhCl[(C_6H_5)_3P]_2(CO) + H_2 + (C_6H_5)_3P \qquad [2] \end{aligned}$$

The carbonyl complex is extremely stable and catalytically inactive (5). The addition of formaldehyde even in massive amounts (3000 times that required to neutralize the catalyst) did not destroy the activity of the catalyst for conjugation. For example, the experiment of Figure 4 was repeated and after 1 hr of reaction 0.5 ml of 37% formalin

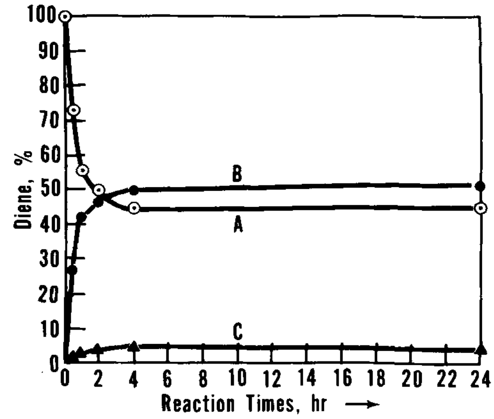


FIG. 2. Reaction of methyl linoleate (1 g) and $RhClL_3$ (10 mg) in methanol (10 ml) at 65 C. Solid catalyst method. A, Nonconjugated diene; B, *cis,trans* and *cis,cis*-conjugated diene; C, *trans,trans*-conjugated diene.

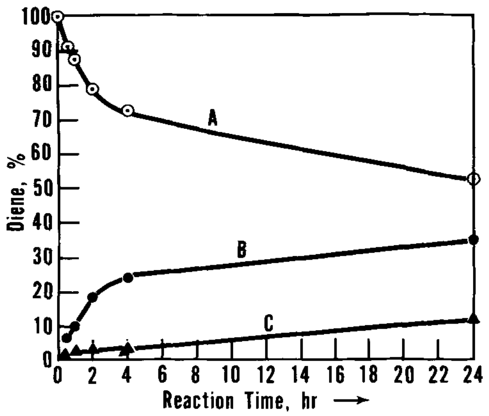


FIG. 4. Reaction methyl linoleate (1 g) and $RhClL_3$ (20 mg) in isopropanol (9 ml) at 65 C. Solution catalyst method (1 ml $CHCl_3$ solution). A, Nonconjugated diene; B, *cis,trans-* and *cis,cis*-conjugated diene; C, *trans,trans*-conjugated diene.

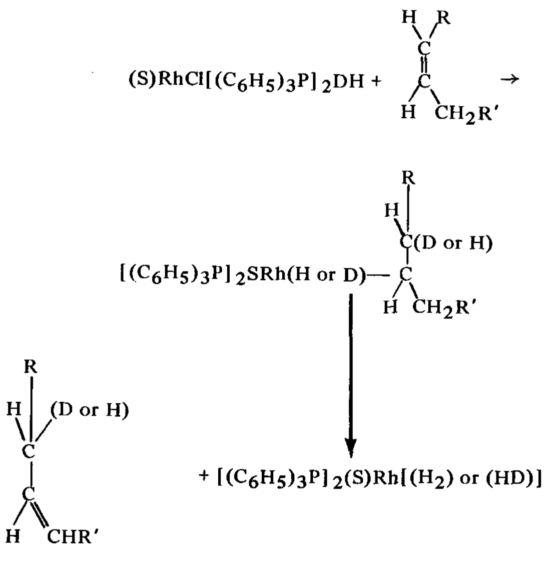
was added. Conjugation was 33% after 24 hr, compared with 47% in the absence of formalin.

In Figure 5 and 6 are plotted respective runs in methanol and chloroform under hydrogen. In methanol reduction continues after an apparently constant level of nonconjugated dienes is reached. After 6 hr nonconjugated diene in chloroform under H_2 (Fig. 6) has decreased to 39%, whereas under N_2 about 51% remained at this reaction time. However, hydrogenation is also more active in methanol than in chloroform. Our results indicate that little, if any, reduction occurs in the absence of hydrogen and thus are not in agreement with the suggestion of Osborn and coworkers (1) or Biellmann and Jung (2) that H_2RhClL_2 transfers its hydrogen to the olefin via the metal alkyl complex and then reforms by reaction with hydrogen. We infer that H_2RhClL_2 forms the metal-alkyl complex, as they have suggested, but undergoes hydrogenolysis to form the reduced olefin and regenerates the dihydride in the presence of hydrogen, but in its absence produces isomerization only. A similar hydrogenolysis of a platinum-carbon bond has been proposed (6).

When the conjugation of linoleate is carried out in CH_3OD with $RhClL_3$ for 4 hr at 65 C, about 1.9, 0.5 and 0.3% (all ± 0.1%)of the product molecules contain one, two and three deuterium atoms, respectively, based on the mass spectrum. In this reaction there were ca. 155 moles of linoleate per mole of $RhClL_3$. A transfer of one deuterium atom to one linoleate molecule per $RhClL_3$ molecule would yield 0.65% of the molecules carrying one deuterium. Since the deuterium content indicates a transfer of about 3.88% on a basis of one deuterium atom per molecule, the complex probably exchanges with CH_3OD via Equation 4. The overall reactions are:

$$\begin{gathered}RhCl[(C_6H_5)_3P]_3 + CH_3OD \rightarrow \\ (S)RhCl[(C_6H_5)_3P]_2DH + CH_2O + (C_6H_5)_3P \\ S = CH_3OD \text{ or } CH_3OH \end{gathered} \qquad [3]$$

$$\begin{gathered}CH_3OD + (S)RhCl[(C_6H_5)_3P]_2DH \rightleftharpoons \\ (S)RhCL[(C_6H_5)_3P]_2D_2 + CH_3OH\end{gathered} \qquad [4]$$



[5]

In this sample the overall conversion to conjugated dienes was 59%. This percentage indicates a conversion of nearly 88 molecules of linoleate to conjugated molecules per molecule of $RhClL_3$. Therefore, while there is evidence for reaction 4 its relative importance is minor.

We also showed that the rhodium catalyst reacts with a pure conjugated fatty ester to give a mixture of conjugated *cis-trans* and some nonconjugated isomers. When $RhClL_3$ was reacted with methyl 9,11-*trans,trans*-octadecadienoate in methanol at 65 C for 1 hr, there was formed 2.0% of nonconjugated dienes and 2.6% conjugated *cis,trans*- and *cis,cis*-conjugated dienes.

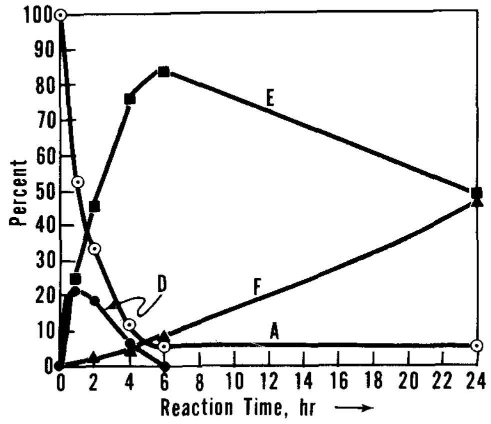


FIG. 5. Reaction methyl linoleate (1 g) and $RhClL_3$ (20 mg) in methanol (10 ml) under H_2 (1 atm) at 65 C. Solution catalyst method. A, Nonconjugated diene; D, conjugated dienes; E, monoenes; F, stearate.

EXPERIMENTAL PROCEDURES

Pure methyl linoleate was obtained from The Hormel Institute. Tris(triphenylphosphine) chlororhodium was purchased from Alfa Inorganics, Inc.

All isomerizations were carried out under a nitrogen atmosphere at 65 C in a three-necked flask fitted with reflux condenser, nitrogen bubbler tube, mercury-valve seal and septum-sealed neck for sampling and reagent addition. The catalyst solutions were prepared by weighing the catalyst into a vial and sealing the vial with a rubber septum. The vial was swept with nitrogen by passing the gas in one hypodermic needle and out through another. The required amount of deoxygenated chloroform was then added with a syringe to form the catalyst solution. When the catalyst solution method was used, a methyl linoleate solution was swept with nitrogen 1 hr at 65 C before addition of the catalyst by syringe. When the solid catalyst method was used, the catalyst was suspended in a small beaker over the solution of methyl linoleate. After passing nitrogen through the solution 1 hr, the catalyst was caused

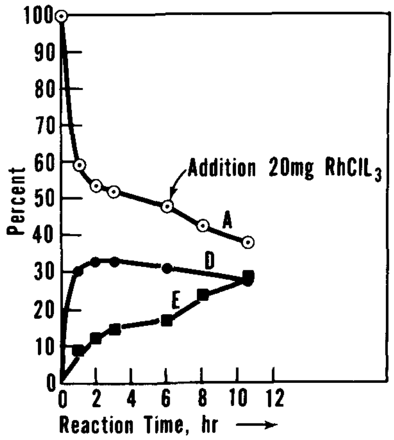


FIG. 6. Reaction methyl linoleate (1 g) and $RhClL_3$ (20 mg + 20 mg added later) in chloroform (10 ml) under H_2 (1 atm) at 25 C. Solution catalyst method. A, Nonconjugated diene; D. conjugated dienes; E, monoenes.

to fall into the solution. The products were isolated following partitioning between hexane and water. The products were determined by gas chromatography on a 10 ft X 1/8 in. 10% EGSS-X column in a Model 1625C Aerograph Gas Chromatograph. Methyl stearate was used as an internal standard.

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