Hydrogenation of Soybean Oil with Cationic Rh(I)-Phosphine Complexes as Catalysts – Para-Toluene Sulfonate and Sulfonated Styrene Resins as Counterions

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ABSTRACT

A cationic rhodium(I) complex, viz. Rh NBD diphos$^+$ 4-CH_3-$C_6H_5SO_3^-$ [NBD = norbornadiene, diphos = $(C_6H_5)_2$ P-CH_2-CH_2-$P(C_6H_5)_2$], has been used as a homogeneous catalyst for the hydrogenation of soybean oil in acetone solution. This complex acts almost in the same way as the corresponding ones with ClO_4^- or PF_6^- as counterions, i.e., it gives high polyene selectivity and low formation of *trans* isomers. Because of the somewhat stronger basic character of the p-toluene-sulfonate ion compared with the perchlorate and hexafluorphosphate ions, the relative proportion of reaction via the so-called monohydride path is larger in the present case. When the ionic complex, Rh NBD diphos$^+$, is bound to a solid support, e.g., to the anionic sites of sulfonated polystyrene resins, a nearly total lack of catalytic activity is observed. Possible reasons for these effects are discussed in terms of π-arene-metal binding and covalent coordination of the sulfonate group.

INTRODUCTION

The rather unique properties of cationic rhodium complexes, e.g., NBD Rh L_2^+ X^- where NBD = norbornadiene, L = tertiary phosphine and X = ClO_4^- or PF_6^-, as catalysts for the hydrogenation of olefins are now well documented (1-4). These types of complexes have shown high polyene selectivity and a low formation of *trans* isomers in the hydrogenation of fatty acid methyl esters (5) and triglycerides (6). For practical applications, however, the catalysts must be separated easily from the reaction mixture and also easy to reuse. This possibly can be achieved by using one of the techniques to bind transition metal complexes to solid carriers that have been reported in recent years. This can be done via covalent (7-9) or ionic interactions (10-12). Attempts to immobilize the present type of complexes to phosphinated polystyrene resins also have been published (13-15). These matrix-bound complexes tend, however, to be unstable under hydrogenation conditions and are reduced to the metallic state (15-16).

To improve catalyst stability, Neuberg (17) has developed a silica-bound chelating bisphosphine ligand. The complexes prepared with this new ligand are reported (17) to be active and stable with essentially the same characteristics as those of the homogeneous analog.

In the present communication we report our attempts to use a matrix-bound counterion, O-X^-, to immobilize the cationic complex. The ion X^- chosen for this study was the sulfonate group -R-SO_3^- in commercially available anion exchangers.

A preliminary study was carried out in a homogeneous stystem with p-toluenesulfonate as the anion. During the course of this work a brief note (18) on similar studies was reported.

EXPERIMENTAL

Two different substrates were tested, 1-hexene and soybean oil. Analytical and hydrogenation procedures were the same as reported previously (6).

Preparation of Rhodium Complexes

Rh NBD diphos$^+$ 4-$CH_3C_6H_4SO_3^-$ was prepared by reacting Rh NBD acetylacetonate (acac) with p-toluene sulfonic acid (1 equ.) and subsequently with diphos (1 equ.) in tetrahydrofuran solution (19). An orange-red crystalline compound precipitated when diethylether (Rh = 13.4%) was added. To prepare the polymer-bound complex, the following procedure was used. The strongly acid macroreticular resin, Amberlyst XN-1010 (surface area 540 m^2/g, ion exchange capacity 3.3 meq/g), was purified by washing with NaOH (1 M) , HCl (1 M), distilled water, acetone and toluene in this order. It was extracted with methanol for 18 hr and dried under vacuum (1 torr, 50 C) for 6 hr. Rh NBD diphos$^+$ ClO_4^- (150 mg) in acetone solution was then reacted with the resin (500 mg). These amounts correspond to a ratio -RSO^3H/Rh of 8/1, i.e., one is not making use of the full ion exchange capacity. In this way a complete decoloration of the acetone solution was reached, yielding a gel with 3.6% Rh.

RESULTS AND DISCUSSION

Homogeneous System

In a hydrogenation experiment with the complex Rh NBD diphos$^+$ $-$-4-CH_3-C_6H_4-SO_3^-, the product composition is shown as a function of the iodine value in Figure 1. This pattern is qualitatively the same as that found previously (6) with the complex Rh NBD diphos$^+$ ClO_4^- and triethylamine added, i.e., a very low increase in stearate and a rather high increase in *trans* and conjugated isomers with decreasing iodine value. This result is probably an effect of the basicity of the p-toluene sulfonate group in acetone media. By its proton affinity (eq. 3) the sulfonate ion shifts the equilibrium 2 towards the monohydride side.

$$\text{NBD Rh diphos}^+ + H_2 \rightarrow \underset{\text{(I)}}{\text{Rh diphos } H_2^+} \qquad [1]$$

$$\underset{\text{(I)}}{\text{Rh diphos } H_2^+} \rightleftarrows \underset{\text{(II)}}{\text{Rh diphos H}} + H^+ \qquad [2]$$

$$-RSO_3H \rightleftarrows RSO_3^- + H^+ \qquad [3]$$

The monohydride (II) is known to be an effective catalyst of hydrogenation and isomerization (1). The presence of this complex will, therefore, produce hydrogenated as well as isomerized products as found.

Addition of $HClO_4$ (3 equ.) to the same reaction mixture as above results in a different product pattern (Fig. 2). In this case the amount of undesirable products, e.g., *trans* and conjugated isomers, is reduced considerably. Probably the added acid shifts equilibria 2 and 3 to their left-hand side. Therefore, a reaction via the dihydride Rh diphos H_2^+ occurs, giving lower amounts of isomerized products. Even in this case, however, the monohydride complex is probably also operating, but to a much lower extent.

Heterogeneous System

We now turn to the case where the sulfonate group is bound to an organic polymer. The position of the equi-

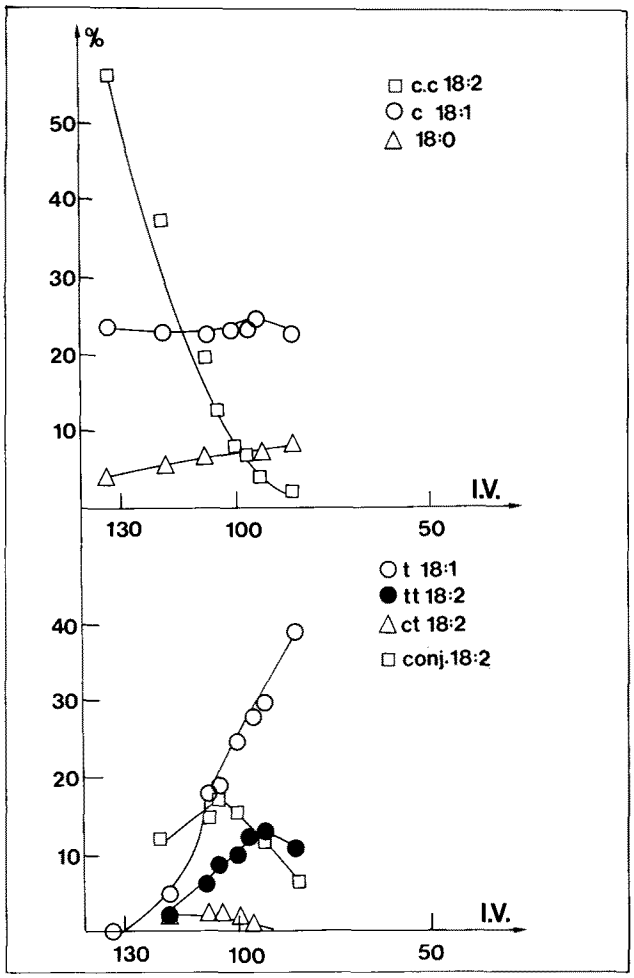

FIG. 1. Product composition at different iodine values in the hydrogenation of soybean oil (1.0 mL) with Rh NBD diphos$^+$ 4-CH_3-C_6H_4-SO_3^- (58 mg) as catalyst. Methyl linolenate (7.8%) in the starting oil was not detected further as reaction progressed. Acetone solution (9 mL), total pressure 1 atm. and temperature T = 31 C. No additives.

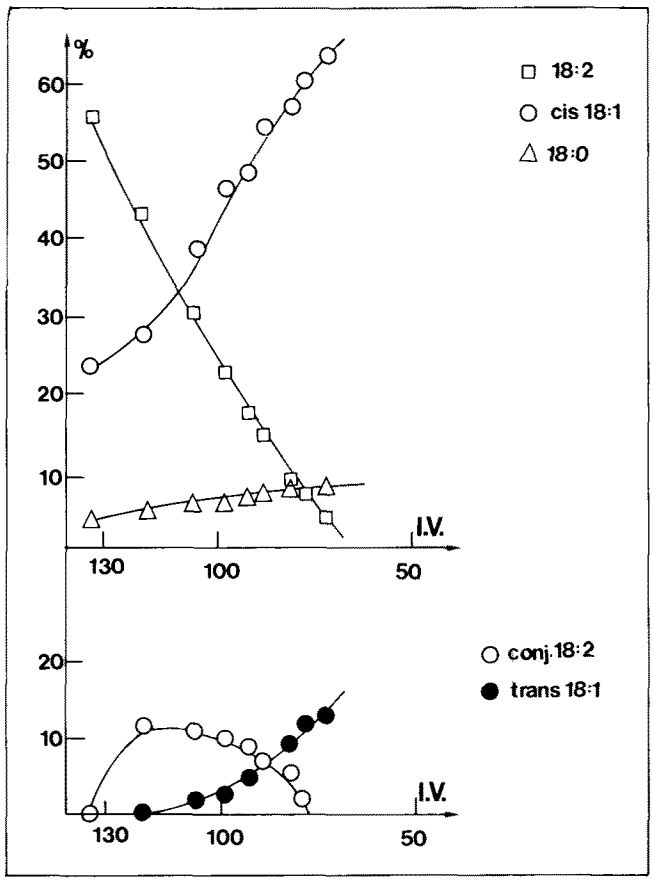

FIG. 2. Product composition at different iodine values with $HClO_4$ added to the reaction mixture. Conditions as in Figure 1; [$HClO_4$] = 20 mM.

librium in eq. 2 can then be controlled by having only a part of the available sulfonate groups in the gel exchanged for the rhodium complex, whereas the main part is in the acidic form (eq. 3). Hence, controlling the extent of isomerization should be possible. One must, however, be careful not to protonate all the sulfonate groups in the resin. This would make the electrostatic binding of the positive Rh-complex impossible.

For the reasons given above we have used acidic groups in the resin, i.e., a high sulfonate to rhodium ratio. All catalysts prepared in this way were found to be inactive for soybean oil hydrogenations. The only case where very low activity has been observed is for the hydrogenation of 1-hexene.

Because the small-sized substrate 1-hexene also gives a very low rate of reaction compared with the homogeneous counterpart (1), the lack of activity observed for soybean oil samples is probably not caused by mass transport limitations inside the polymer gel. The main difference between the homogeneous system NBD Rh diphos$^+$ -p-toluensulfonate and its heterogeneous counterpart is the ratio of Rh to sulfonate groups and π-arene groups. In the homogeneous system, one arene group and one sulfonate group occurs for every rhodium atom whereas in the heterogeneous system, the R-SO_3/Rh ratio is 8 and the arene/Rh ratio is even greater. These groups might have a greater possibility in the heterogeneous system to block the metal center and result in an inactive complex. Evidence for sulfonate coordination via oxygen binding to rhodium has been published recently (18,20). We, too, have observed during the present study that the addition of excess p-toluensulfonic acid to the homogeneous system inhibits its catalytic activity completely. π-Arene coordination to rhodium also is well documented (4,21-22).

Results from the present investigations on the homogeneous and the matrix-bound systems indicate that if the ionic binding approach is to be applied successfully non-aromatic polymers with ionic groups less basic than the sulfonate group must be used.

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