Selective Hydrogenation Catalyzed by Polymeric Palladium and Platinum Complexes[1]

ABSTRACT

An organic polymer containing a diphenylbenzylphosphine functional group, combined with $PtCl_2$ or $PdCl_2$, gives a heterogeneous hydrogenation catalyst which is analogous to the homogeneous catalysts $PtCl_2(P\phi_3)_2$ and $PdCl_2(P\phi_3)_2$.In the hydrogenation of soybean methyl ester, this catalyst is highly selective, the products being monoene and diene, with almost no increase in the content of saturated ester.

For some years the U.S. Department of Agriculture has supported an extensive search for a catalyst, for the selective hydrogenation of the polyunsaturated components of soybean oil, that will not increase the proportion of saturated fats. Although several transition metal complexes have been found to be highly selective homogeneous catalysts (1), the commercial application of these systems has been limited by the expense of catalyst recovery.

Recently there has been considerable interest in the preparation of polymeric analogs of known homogeneous catalysts in the hope that these compounds would have the limited solubility of a polymer and yet retain the catalytic activity of the monomer (2). In the work reported in this paper, an organic polymer containing diphenylbenzylphosphine functional groups was prepared from a polystyrene and used as a ligand in the synthesis of dichloroplatinum (II) and palladium (II) complexes. The resultant compounds are analogs of $PtCl_2(PPh_3)_2$ and $PdCl_2(PPh_3)_2$, which have been shown to be selective homogeneous hydrogenation catalysts in the presence of $SnCl_2$(3). Similar rhodium (I) polymers have been shown to be effective catalysts for nonselective hydrogenation (4-6) and for hydroformylation of olefins.

The polymeric ligand was prepared by the reaction of sodium diphenylphosphide with a chloromethylated copolymer of styrene and divinylbenzene by the method of Haag and Whitehurst (7). The inability to analyze for oxygen in the presence of phosphorous complicated the elemental analysis of the phosphine polymers. If all the material not accounted for by the C, H, P and Cl analyses is assumed to be oxygen, the empirical formula for this compound is $C_{48}H_{49}O_3ClP_2$. A stirred suspension of this ligand in dry degassed acetone was refluxed under nitrogen for 2 days with a 10% excess of $PtCl_2(\phi CN)_2$ or $PdCl_2(\phi CN)_2$ to form the desired metal complexes (8). Since this preparation involved reaction at a liquid-solid interface, the amount of metal incorporated into the polymer varied with each synthesis. The empirical formula for one platinum system was $C_{48}H_{49}O_3ClP_2 \cdot (PtCl_2)_{0.505}$, but for the palladium complex the metal uptake was as high as $C_{48}H_{49}O_3ClP_2 \cdot (PdCl_2)_{0.851}$. The nujol mull IR spectra of the metal complexes show one band which is not present in the phosphine ligand itself. This band occurs at 351 and at 339 cm^{-1} for the palladium and the platinum polymers, respectively, and corresponds to the metal-halogen stretching frequency observed in $PtCl_2(PR_3)_2$ and $PdCl_2(PR_3)_2$ complexes (9).

The $C_{48}H_{49}O_3ClP_2 \cdot (PdCl_2)_{0.851}$ complex proved to be an active, selective hydrogenation catalyst with soybean methyl ester. Using 85 mg catalyst and 2 ml unsaturated ester (mole ratio of palladium-olefin = 1.02×10^{-3}) in methylene chloride at 550 psi of hydrogen and 25 C, all of the triene component was reduced after 4 hours. In methanol the catalyst activity is greatly increased. After 3 hr in methanol at 25 C and 1 atm of hydrogen, even though the catalyst-olefin ratio was halved, all of the triene and most of the diene were reduced, and some saturate was formed. In order to regain selectivity in the hydrogenation, it was necessary to dilute the alcohol with an equal volume of benzene.

Catalyst activity parallels the amount of palladium in the complex (Table I). When the value of n was below 0.524, it became necessary to increase the reaction temperature to obtain a significant reduction within 3 hr. At higher reaction temperatures (>90 C), less hydrogenation was observed. Black metallic particles found in the recovered polymer suggest that the loss in activity at higher temperatures must have been the result of extensive decomposition of the catalyst.

The platinum phosphine polymer did not function as a hydrogenation catalyst below 150 C in the absence of $SnCl_2 \cdot 2H_2O$. In the presence of the $SnCl_2 \cdot 2H_2O$ (Sn/Pt 10:1), selective hydrogenation occurred readily at 150 C

TABLE I

Catalytic Hydrogenation of 2 ml Soybean Methyl Ester in 70 ml Methylene Chloride Using 85 mg $P \cdot (PdCl_2)_n$ Catalyst Under 550 psi Hydrogen for 3 hr[a]

$P \cdot (PdCl_2)_n$			Composition of Product			
n	Palladium, mmoles	Temperature, C	Saturate	Monoene	Diene	Triene
0.851	0.0785	25	15.1	53.4	30.3	1.1
0.600	0.0581	25	14.0	38.8	44.3	2.9
0.524	0.0517	25	13.5	31.8	50.2	4.5
0.507	0.0501	70	13.6	68.9	17.7	---
0.490	0.0486	70	14.6	40.5	40.5	4.4
0.406	0.0410	70	14.1	28.8	52.0	5.1

[a] Substrate was 14.2% saturate, 22.3% monoene, 56.2% diene and 7.0% triene.

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[1] A preliminary report based on a portion of the Ph.D. thesis of H.S. Bruner.

TABLE II

The Hydrogenation of Three Samples of Soybean Methyl Ester with Each of Two Single 85 mg Samples of Metal-Polymer Catalyst in Methylene Chloride at 550 psi Hydrogen[a]

Catalyst	Per cent composition of product				
	Saturate	Monoene	Diene	Conjugated diene	Triene
$C_{48}H_{49}ClO_3P_2 \cdot (PtCl_2)_{0.505}$[b]					
First hydrogenation run	14.5	37.8	28.3	20.1	—
Second hydrogenation run	14.9	26.8	38.3	18.5	1.6
Third hydrogenation run	13.8	26.6	39.2	18.4	2.0
$C_{48}H_{49}ClO_3P_2 \cdot (PdCl_2)_{0.507}$[c]					
First hydrogenation run	13.6	68.9	17.7	—	—
Second hydrogenation run	14.6	34.0	46.7	—	4.7
Third hydrogenation run	14.8	35.2	45.9	—	4.3

[a] Initial composition was 14.2% saturate, 22.3% monoene, 56.2% diene and 7.0% triene.

[b] Reactions at 150 C for 6 hr with 226 mg $SnCl_2 \cdot 2H_2O$.

[c] Reactions at 70 C for 3 hr.

and 600 psi of hydrogen. After 6 hr in methylene chloride, all of the triene fraction was reduced without the formation of saturate. The isomerization of the diene fraction to form conjugated diene was also observed under these conditions. The similar palladium-tin system decomposed below 150 C and was then catalytically inactive.

Both catalysts may be recovered by filtration and reused many times, although the platinum system requires the addition of fresh $SnCl_2 \cdot 2H_2O$ for each reaction. As shown in Table II, a slight loss of catalytic acitivity is observed after the first recovery of catalyst, but no further losses occur on subsequent reactions. The analytical data and IR spectrum of the palladium complex are unchanged after several catalytic reactions. The platinum compound is recovered considerably altered, but the data are not consistent with any structure analogous to known products of similar reactions between $SnCl_2 \cdot 2H_2O$ and platinum halide complexes.

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Alkali Isomerization of Linoleate Isomers: Characterization of Products

ABSTRACT

Geometrical isomers of methyl linoleate were reacted with alakli, and the resulting conjugated isomers were separated into *trans,trans*; *cis,trans*; and *cis,cis* fractions. The position of double bonds in the various fractions was determined by reductive ozonolysis. *trans*-9,*trans*-12-Isomer of linoleate formed *trans,trans*- and *cis,trans*-conjugated dienes, whereas *cis*-9,*trans*-12- and *trans*-9,*cis*-12-isomers in addition formed *cis,cis*-conjugated dienes. The formation of the products is in accordance with the theoretical predictions. During conjugation *trans* double bonds shifted to form a *trans* bond preferentially. During conjugation of *cis*-9,*trans*-12- and *trans*-9,*cis*-12-linoleate isomers, the *cis* double bond shifted preferentially over the *trans* double bond. A small amount of diene not conjugated was probably a geometrical and positional isomer of the starting material.

Methylene-interrupted double bonds in polyunsaturated fatty acids undergo rearrangement to conjugated double bonds not only during hydrogenation and autoxidation, but also during treatment with alkali. Similar conjugated products might be produced by the three methods. Nichols et al. (1) characterized products from alkali-isomerized linoleic acid. On theoretical grounds they also formulated rules to predict products from geometrical isomers of linoleic acid; however these products have not been thoroughly characterized (2) to test the validity of these rules.

Methyl *trans*-9,*trans*-12-octadecadienoate (*t,t*-Lo) was prepared by the procedure of Harlow et al. (3). Final

TABLE I

Composition of Products from Alkali Isomerization of Linoleate Isomers

Linoleate isomer	Weight %			
	Unconjugated diene	*trans, trans*- Conjugated diene	*cis trans*- Conjugated diene	*cis,cis*- Conjugated diene
trans-9,*trans*-12	5	56	39	0
cis-9,*trans*-12	4	56	28	12
trans-9,*cis*-12	4	55	29	12