Investigations on the Conditions for Hydrogenation of Fatty Oils with Polymer Anchored Pd-Phosphine Complexes

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ABSTRACT

Palladium chloride has been anchored to phosphinated, crosslinked polystyrene by substitution of the pyridine ligand in $Cl_2Pd(NC_5H_5)_2$ with the polymeric phosphine. By analytical and infrared studies of the prepared catalyst, it has been shown that the main species formed in the matrix is the half-substituted complex $Cl_2Pd(NC_5H_5)P$-PS (P-PS = polymeric benzyldiphenylphosphine). This polymer-bound palladium complex has been tested together with two other preparations, both of which are bisphosphine complexes, as catalysts for hydrogenation of soybean oil. The results show that the presence of the mixed phosphine-pyridine complex is necessary for catalytic activity under ambient conditions. The monoene fraction of the oil is hydrogenated very slowly, but the polyene fraction is reduced quickly. Relatively large amounts of *trans*-isomers are formed, however, in the reaction. It has been noted that the activation of the catalyst is coupled to a release of pyridine from the catalyst. It is proposed that after the release of pyridine, further reactions take place inside the polymer which cause the catalyst to be active under mild conditions.

INTRODUCTION

Since the pioneering work by Haag and Whitehurst (1), much research has been done on the attachment of homogeneous transition metal catalysts to insoluble supports. A number of recent reviews covering this topic have also been published (2-5). The main reason for heterogenizing a homogeneous transition metal catalyst is its easier handling, i.e., its removal, recovery and recycling.

For the homogeneous hydrogenation of unsaturated fatty acids, three types of complexes have been more thoroughly investigated (6). Bailar, Itatani and coworkers (7-10) have studied the X_2ML_2-type complexes (M = Ni, Pd, or Pt and L is a phosphine ligand). These complexes proved to be very selective for polyene hydrogenation. Frankel et al. have studied iron carbonyl complexes (11-14) and $Cr(CO)_3$-arene complexes (15-19) as catalysts. The Cr complexes have been shown to give very low *trans* content in the hydrogenated product.

The polyene selectivity of all these complexes and low concentration of *trans* products found for the Cr complexes are essential features of these catalysts that could conveniently be used to make products of specific quality. In spite of this, none of these complexes have had industrial application, mainly because of the great separation problem. However, by using polymer-anchored complexes as catalysts, one should be able to overcome the problem of separation and thereby take advantage of the high polyene selectivity and low *trans* formation, where such is found.

Evans et al. (20) has shown the possibility of immobilizing carbonyl complexes through CO-phosphine exchange. In this way, it should be possible to anchor $Fe(CO)_5$. Pittman et al. (21) have also synthesized polymer-bound $Cr(CO)_3$-arene complexes, but did not use them for fatty acid hydrogenation purposes. Awl et al. (22) have synthesized similar polymer-bound $Cr(CO)_3$-arene complexes and used these as catalysts in the hydrogenation of soybean oil and esters. Bruner and Bailar (23,24) have synthesized $PdCl_2$ and $PtCl_2$ bound to polymeric phosphine ligands and used these as catalysts for the hydrogenation of soybean oil methyl esters. We (25) have extended their work on $PdCl_2$ and found it to be a good catalyst for soybean oil hydrogenation. The polymer-bound $PtCl_2$ catalyst used by Bruner and Bailar (23,24) was found to give essentially the same hydrogenation behavior as the nonsupported catalyst. For the Pd-system, however, the situation is different (23,25). Marked differences between homogeneous and polymer-bound Pd-phosphine complexes are found. The essential features of these are summarized in Table I.

Differences between homogeneous and polymer catalysts in activity and selectivity have sometimes been noted (26,27). For the so-called Wilkinson catalyst, $ClRh(P\phi_3)_3$ (ϕ = phenyl), these differences are often explained in terms of the position of the phosphine dissociation equilibrium:

$$Cl\,Rh(P\phi_3)_3 \rightleftarrows Cl\,Rh(P\phi_3)_2 + P\phi_3$$

For other systems (28), the polymer ligand prevented an unfavorable aggregation of catalytic species and so increased the catalytic activity of the anchored complex compared to the homogeneous complex.

The reason for increased catalyst activity when $PdCl_2$ is anchored to a polymeric phosphine ligand is presumably not possible to find in terms of the already mentioned phosphine dissociation equilibrium or a hindered aggregation. Pittman et al. (29) have used polymer-bound palla-

TABLE I

Differences in Catalytic Behavior of Homogeneous and Heterogenized Pd Complexes

Characteristics	$Cl_2Pd(P\phi_3)_2$	Cl_2Pd bound to phosphinated polystyrene
Hydrogen pressure necessary for activity (atm)	35	1
Induction period	None	Yes, depending on temperature
Color change during hydrogenation	Remains yellow	Changes from light-yellow yellow to gray-green
Effect of cocatalyst addition ($SnCl_2$)	Essential for activity	Makes the catalyst inactive (1 atm H_2)
Effect of $P\phi_3$ addition	(No reports found)	Makes the catalyst inactive (1 atm H_2)

dium phosphine complexes to oligomerize 1,3-butadiene and noted the same color change as we do (see Table I). These authors ascribe this color change to the deposition of metallic Pd. However, the reduction to Pd metal was ruled out by Bruner and Bailar (24).

Under the reaction conditions we have used, monomeric $Cl_2Pd(PØ_3)_2$ has been found to be stable to reduction. If the change of the catalytic activity depends on the formation of metallic Pd in the matrix, this must derive its origin from species other than $Cl_2Pd(P\text{-}PS)_2$, (P-PS = polymeric benzyldiphenyl phosphine) within the matrix.

The aim of this work was to investigate the species formed when $PdCl_2$ is anchored to phosphinated polystyrene-divinyl benzene polymers. By this approach, we hoped to be able to learn about the possible formation of metallic Pd.

EXPERIMENTAL

Materials

Analytical-grade chemicals and solvents were used throughout this work without further purifications. Refined, bleached soybean oil was a gift from AB Karlshamns Oljefabriker. Chloromethylated polystyrene with 2% crosslinking and a chlorine content of 4-5% was purchased from Merck (Merrifield Harz).

$Cl_2Pd(NC_5H_5)_2$ was prepared by the standard procedure, i.e., treating a water solution of $PdCl_2$ with pyridine and recrystallizing the product from CH_2Cl_2/light petroleum mixture.

$Cl_2Pd(NC_5H_5)PØ_3$ was prepared by reacting $Cl_4Pd_2(PØ_3)_2$ with pyridine according to the procedure of Chatt and Venanzi (30).

Phosphination

The chloromethylated polymer was treated first with 1 N HCl, then with 1 N NaOH, and thereafter washed successively with water, methanol, 1:1 methanol/CH_2Cl_2, and finally with pure CH_2Cl_2 and dried at 80 C and 2 Torr for 24 hr. This dried polymer was made to react with a slight excess of $LiPØ_2$ generated from Li metal and $PØ_3$ (31) in THF (tetrahydrofuran) under N_2. After at least 24 hr, unreacted $LiPØ_2$ was hydrolyzed by the addition of ethanol. The polymer was recovered by filtration. It was then washed with water, ethanol and THF, and finally extracted in a Soxhlet apparatus with acetone for 6 hr and with CH_2Cl_2 for 18 hr before drying. Analysis of this polymer gave 1.8% P corresponding to 0.58 mmol P/g.

Catalyst Preparations

Catalyst 1. This was prepared by the procedure of Bruner and Bailar (23,24), i.e., exchanging an N-donor ligand with the polymeric phosphine ligand. As the N-donor ligand, we chose pyridine instead of benzonitrile. The procedure was: $Cl_2Pd(NC_5H_5)_2$ (2.1 g, 6.2 mmol) dissolved in CH_2Cl_2 was reacted under nitrogen with the phosphinated polystyrene (20 g, 11.6 mmol) for 24 hr at room temperature. The resulting yellow polymer was then collected by filtration and finally extracted with CH_2Cl_2 for 24 hr in a Soxhlet apparatus. Analysis gave 3.10% Pd and 0.33% N corresponding to 0.29 mmol Pd/g and 0.24 mmol N/g. The filtrate from the reaction was analyzed for released pyridine. Calculated (for a release of 2 mol pyridine/mol Pd incorporated in the polymer): 12.4 mmol; found: 7.8 mmol; difference: 4.6 mmol. This difference corresponds to 0.23 mmol pyridine still remaining on each gram of the prepared catalyst.

Catalyst 2. A solution of $Cl_2Pd(PØ_3)_2$ (0.70 g, 1 mmol) in CH_2Cl_2 (200 ml) was stirred at reflux under N_2 atmosphere with the phosphinated polymer (2 g, 1.2 mmol P) for 48 hr. This was then filtered and extracted as catalyst 1. Analysis of this preparation gave 1.36% Pd corresponding to 0.13 mmol Pd/g.

Catalyst 3. This catalyst was prepared by reacting catalyst 1 (2.0 g, 0.58 mmol Pd) with a solution of $PØ_3$ (0.16 g, 0.6 mmol) in CH_2Cl_2 (25 ml). After 12 hr treatment, the polymer was separated and extracted in the same way as catalyst 1. Analysis of this catalyst gave 1.20% Pd (0.11 mmol/g) and no measurable content of N. Analysis of the filtrate for released pyridine gave 0.48 mmol of pyridine. This value corresponds to 0.24 mmol pyridine/g catalyst 1.

Analytical Procedures

To analyze the amount of P and Pd in the polymer catalysts, the organic polymer had to be completely oxidized This was done with H_2SO_4 + H_2O_2 according to the following procedure: To 50 mg of finely ground polymer a few drops of concentrated sulfuric acid was added. After allowing the polymer to be thoroughly wetted by the acid, the sample was heated gently on an open flame until the polymer no longer floated, and was then cooled. When the mixture was cold, a few drops of hydrogen peroxide (30%) was added and the mixture heated on an oil bath at 80 C. The addition of hydrogen peroxide was continued until complete dissolution and discoloration of the solution occurred. The mixture was heated at 150 C overnight to remove traces of unreacted hydrogen peroxide.

Phosphorus was determined as phosphate. This was done spectrophotometrically by a molybdenum blue method, using ammonium molybdate and amidol as reagents (32). Analysis of phosphorus was done on phosphinated polymers before metal fixations. Palladium was determined by atomic absorption spectrometry.

Gas liquid chromatography (GLC) analysis of released pyridine in the filtrates from the catalyst preparations was done on a BDS column with octanol as internal standard. Coordinated pyridine was analyzed as elementary nitrogen (Microanalytical Laboratory, University of Lund).

Hydrogenations

All hydrogenations were performed on bleached, refined soybean oil at atmospheric pressure in an apparatus as depicted in Figure 1. The reactor was loaded with soybean oil and catalyst while a slow stream of nitrogen was maintained. The reaction vessel was heated and when the desired temperature was reached, the first sample was withdrawn (t=o) and the nitrogen gas was replaced by hydrogen. The hydrogen flow was kept at a fixed value. At regular time intervals, samples were withdrawn with a syringe.

The catalyst was separated from the oil by centrifuging the samples. After converting the oil samples to methyl esters, these were analyzed on a 6-ft SS SP-216 PS column using a PE F17 chromatograph equipped with flame ionization detection. *Trans* content was determined by IR spectroscopy (33).

RESULTS AND DISCUSSION

Catalysts

Ligand substitution according to Equation I

$$X_2ML_2 + 2\,PR_3 \rightleftarrows X_2M(PR_3)_2 + 2\,L \qquad [1]$$

(where L represents an N-donor ligand) is a convenient way to prepare palladium-phosphine complexes. When monomeric phosphine ligands such as triphenylphosphine are used, the equilibrium lies far to the right and substitution is

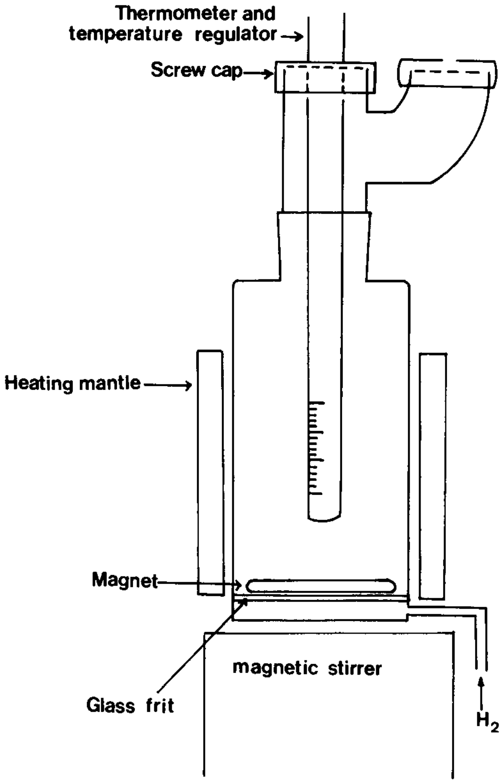

FIG. 1. Catalytic hydrogenation apparatus used.

quantitative.

This facile substitution reaction has also been applied to phosphinated styrene divinylbenzene polymers as ligands (24,25). Even in this case, the substitution seems to proceed according to Equation I as judged by the complete discoloration of the yellow solution when a stoichiometric ratio of Pd:P is used.

Substitution according to Equation I must be assumed to proceed as a two-step process with successive substitution of the N-donor.

$$X_2ML_2 \xrightarrow[-L]{+PR_3} X_2MLPR_3 \xrightarrow[-L]{+PR_3} X_2M(PR_3)_2 \qquad [II]$$

In an effort to explain the differences in catalytic behavior (Table I) between the homogeneous catalyst $Cl_2Pd(P\phi_3)_2$ and the polymer-anchored complex $Cl_2Pd(P\text{-}PS)_2$, we have investigated the substitution reaction in greater detail.

Catalyst 1

Analyses of the filtrate for displaced pyridine and total nitrogen clearly indicate that, with this polymer-phosphine ligand, the substitution is incomplete. The reaction does not proceed much further than corresponding to the first step in Equation II. The main species formed would thus have structure II proposed in Figure 2. The reason for formation of the half-substituted species II in Figure 2 is probably best explained in terms of the stability of species II and the separation and mobility of the phosphine groups in the matrix. An analog to the half-substituted species can be prepared and isolated by reacting a dimeric, chlorine-bridged phosphine complex with pyridine (see Experimental).

$$Cl_4Pd_2(P\phi_3)_2 + 2\,py \rightarrow 2\,Cl_2PdP\phi_3\,py \qquad [III]$$

This mixed pyridine-phosphine complex is stable and does not disproportionate to bisamine and bisphosphine complexes as do similar complexes with sulfur, selenium or tellurium.

In the styrene-divinyl benzene matrix, only ca. 10% of the benzene rings are substituted with phosphine groups. This means that the styrene chains have to bend to bring the phosphine groups closer together. If the repulsive energy that develops for steric reasons when the styrene chains bend is greater than the energy gained by substitution of the second pyridine ligand, the substitution is stopped after the first step in Equation II. Some of the phosphine groups are, however, located so that reaction according to Equation I also will occur. This can be seen by the ratio Pd/N = 1.21 > 1.

The analysis of catalyst 1 indicates that species I expected from Equation I is only formed to a minor extent. Instead, species II will be the major product in the matrix.

Catalyst 2

Catalyst 2 was prepared by reacting $Cl_2Pd(P\phi_3)_2$ with the polymeric phosphine ligand in CH_2Cl_2 (Equation IV).

$$Cl_2Pd(P\phi_3)_2 + n(P\text{-}PS) \rightarrow Cl_2Pd(P\phi_3)_{2-n}(P\text{-}PS)_n + n\,P\phi_3 \qquad [IV]$$

Although an excess of $Cl_2Pd(P\phi_3)_2$ was used, the equilibrium position for this reaction is such that only a small quantity of palladium was incorporated into the polymer. The palladium in this catalyst is, however, coordinated to two phosphines. From a comparison between catalysts 1 and 2, it should be possible to obtain some information about whether species II formed in catalyst 1 is responsible for the changed catalytic behavior.

Catalyst 3

This catalyst was prepared by treating catalyst 1 with $P\phi_3$, in hopes that the reaction V would proceed.

$$Cl_2Pd(\text{pyridine})\,(P\text{-}PS) + P\phi_3 \rightarrow Cl_2PdP\phi_3\,(P\text{-}PS) + \text{pyridine} \qquad [V]$$

This pyridine-triphenylphosphine exchange was, however, also followed by some Pd leaching from the polymer, probably due to the formation of $Cl_2Pd(P\phi_3)_2$. Therefore, the amount of palladium in this catalyst is lower than in catalyst 1. This Pd leaching is probably caused by a greater tendency of Pd to coordinate to $P\phi_3$ compared to P-PS. The basis for this suggestion is the result obtained upon synthesis of catalyst 2. The equilibrium position in the preparation of catalyst 2 (Eq. IV) is such that the left side is favored and a nearly equal amount of Pd is coordinated in catalysts 2 and 3.

In spite of these complications, the treatment of catalyst 1 with $P\phi_3$ results in a catalyst containing only bisphosphine complexes. (The amount of pyridine released upon $P\phi_3$ treatment 0.24 mmol/g equals the amount of pyridine calcd from N-elementary analysis of catalyst 1.) This $P\phi_3$

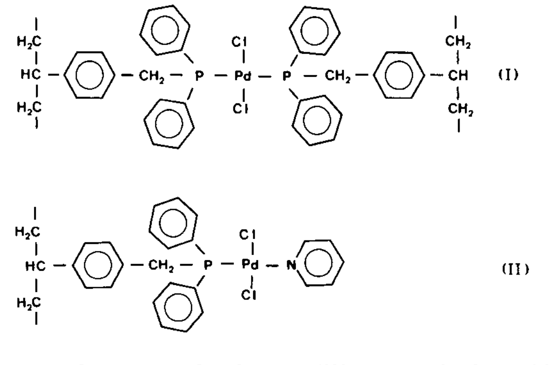

FIG. 2. Proposed structures for the two different species formed in the polymer matrix.

treatment gives yet another possibility for studying the catalytic effect of the phosphine-pyridine complex Cl_2Pd pyridine (P-PS) compared to the bis-phosphine complex.

IR Spectra

As further evidence for the formation of species II in the preparation of catalyst 1, IR spectra were recorded for all the prepared catalysts. The spectra of catalysts 2 and 3 show no peaks that cannot be identified in the spectra of either the matrix or $Cl_2Pd(P\O_3)_2$ in the region 4000-400 cm^{-1}.

In the spectra of catalyst 1, a weak shoulder at 1220 cm^{-1} is present (see Fig. 3). This signal corresponds to a very sharp peak at the same wavelength in the spectra of Cl_2Pd py($P\O_3$), that is not present in either the matrix or $Cl_2Pd(P\O_3)_2$ spectra. Also, in other regions of the spectra, significant similarities to the spectrum of Cl_2Pd py($P\O_3$) can be found. Therefore, this spectrum of catalyst 1 strengthens the evidence for formation of species II.

HYDROGENATIONS

The three different preparations were tested as catalysts for the hydrogenation of soybean oil. The same mild reaction conditions were used for these tests as previously used with polymer-bound $PdCl_2$ (25), i.e., atmospheric pressure and temperatures in the range of 80-140 C. Figure 4 shows the product composition as a function of time for the hydrogenation by catalyst 1. This pattern is very similar to that found by Bruner and Bailar (24) in their hydrogenation of soybean oil methyl ester in 50% methanol/50% benzene solution, i.e., a high selectivity is found for the formation of monoene as long as sufficient unreacted diene is present in the reaction mixture. However, one very serious drawback of this catalyst is the formation of large quantities of *trans* isomers. The curve representing *trans* isomers increases almost linearly and very closely follows the curve for the monoene fraction (Fig. 4). An alternative way to display the result from this hydrogenation is shown in Figure 5. This gives the product pattern at different iodine values and one notices that the triene fraction is completely hydrogenated at an iodine value of 102 whereas 37% of the diene fraction still is present. At the same time, the increase in saturates is negligible.

Catalysts 2 and 3, both of which contain only palladium coordinated to two phosphine ligands, have no hydrogenation activity at all under the conditions used. This is in line with the behavior of their monomeric analog $Cl_2Pd(P\O_3)_2$, which requires higher hydrogen pressure to be active. This difference in reactivity between catalyst 1 on the one hand and catalysts 2 and 3 on the other hand demonstrates the crucial influence of species II for catalytic activity under low hydrogen pressure. These findings may also explain why the addition of triphenylphosphine inhibits the catalytic activity of this type of catalyst (24). By displacing the pyridine ligand, the triphenylphosphine forms a complex like catalyst 3 with no hydrogenation activity under low hydrogen pressure.

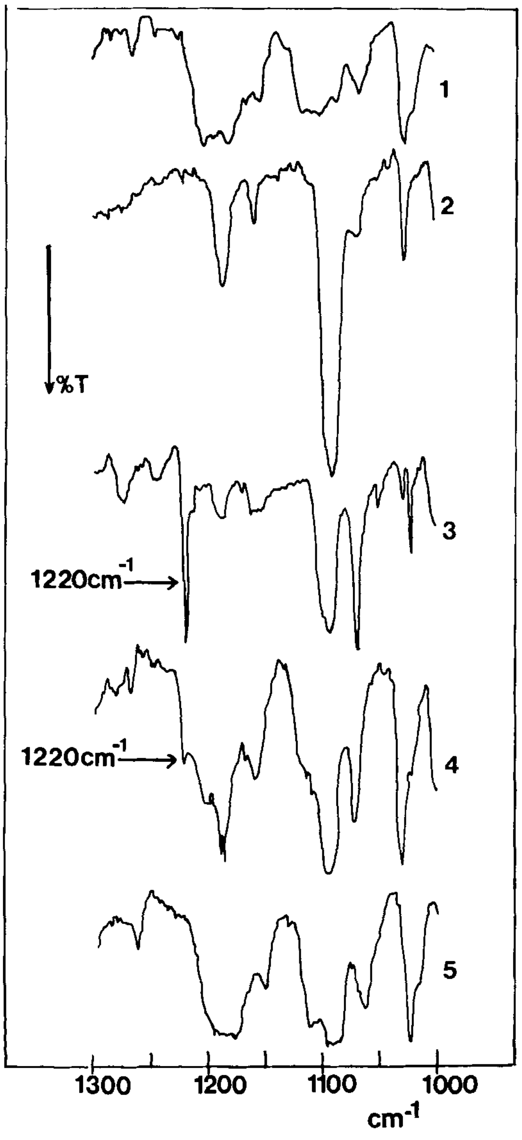

FIG. 3. IR-spectra in the region 1300-1100 cm^{-1} of 1: matrix; 2: $Cl_2Pd(P\O_3)_2$; 3: $Cl_2PdP\O_3NC_5H_5$; 4: catalyst 1; 5: catalyst 3.

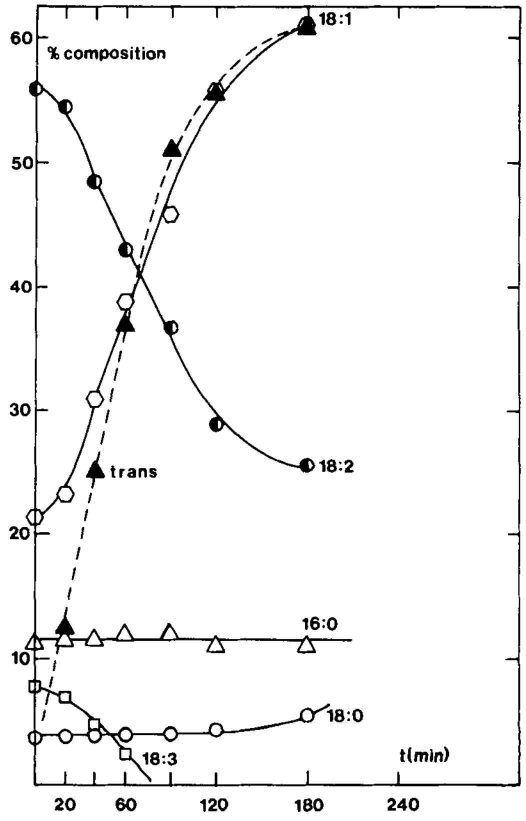

FIG. 4. Rate of hydrogenation of soybean oil with catalyst 1 (50.0 g soybean oil, 1.0 g catalyst 1, 140 C, 1 atm H_2).

Catalyst Activation

We have previously noted (25) a temperature-dependent activation period for catalysts prepared as catalyst 1. This activation is also coupled with the color change of the catalyst. In order to test the influence of the pyridine ligand in this activation, some hydrogenation experiments at different temperatures were done. The results from these experiments are shown in Figure 6.

Obviously, the hydrogenation activity (expressed as decrease in IV) is related to the release of pyridine from the catalyst. At 100 C, the pyridine loss is slow and there is a marked induction period, whereas at 140 C, the loss is faster and the catalyst is active at once.

By heating catalyst 1 to 80 C under vacuum (0.01 torr) no pyridine is lost. This probably means that the pyridine in this catalyst is not bound as a solvate in the axial positions. Instead, as suggested in species II, it is bound as one of the four ligands in the square, planar-coordinated palladium atom.

One way in which the pyridine might be lost from such a complex is by dimerization in the matrix.

$$2\ Cl_2Pd\ py(P\text{-}PS) \rightarrow Cl_4Pd_2\ (P\text{-}PS)_2 + 2\ py$$

An increase in temperature will increase the mobility of the polymer network and thus enhance this dimerization.

The findings of Bruner and Bailar (24) that no benzonitrile was present in the IR-spectra of their catalyst preparations support this suggestion of the formation of the chlorine-bridged species. The high phosphorus loading in the polymer used by Bruner and Bailar (24) and the low complex binding ability for benzonitrile compared to pyridine may have already caused the formation of the bridged complex at the synthesis stage. Another way in

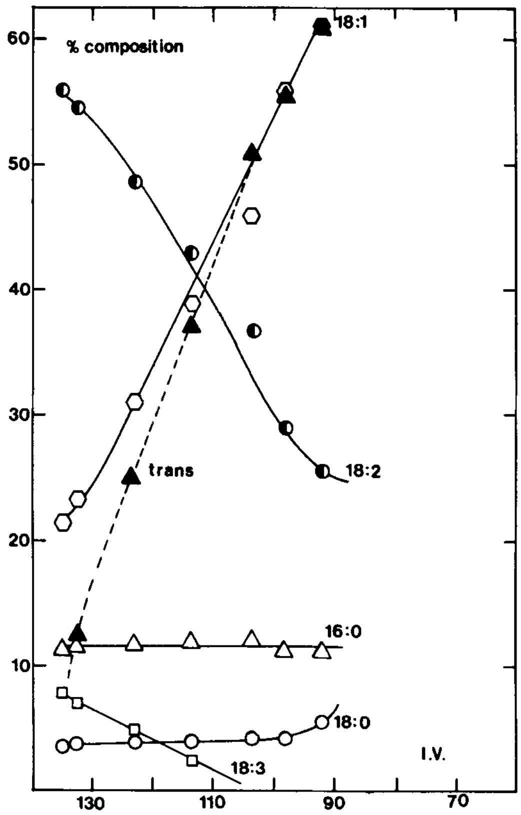

FIG. 5. Percent composition vs iodine value in the hydrogenation of soybean oil with catalyst 1 (50.0 g soybean oil, 1.0 g catalyst, 140 C, 1 atm H_2).

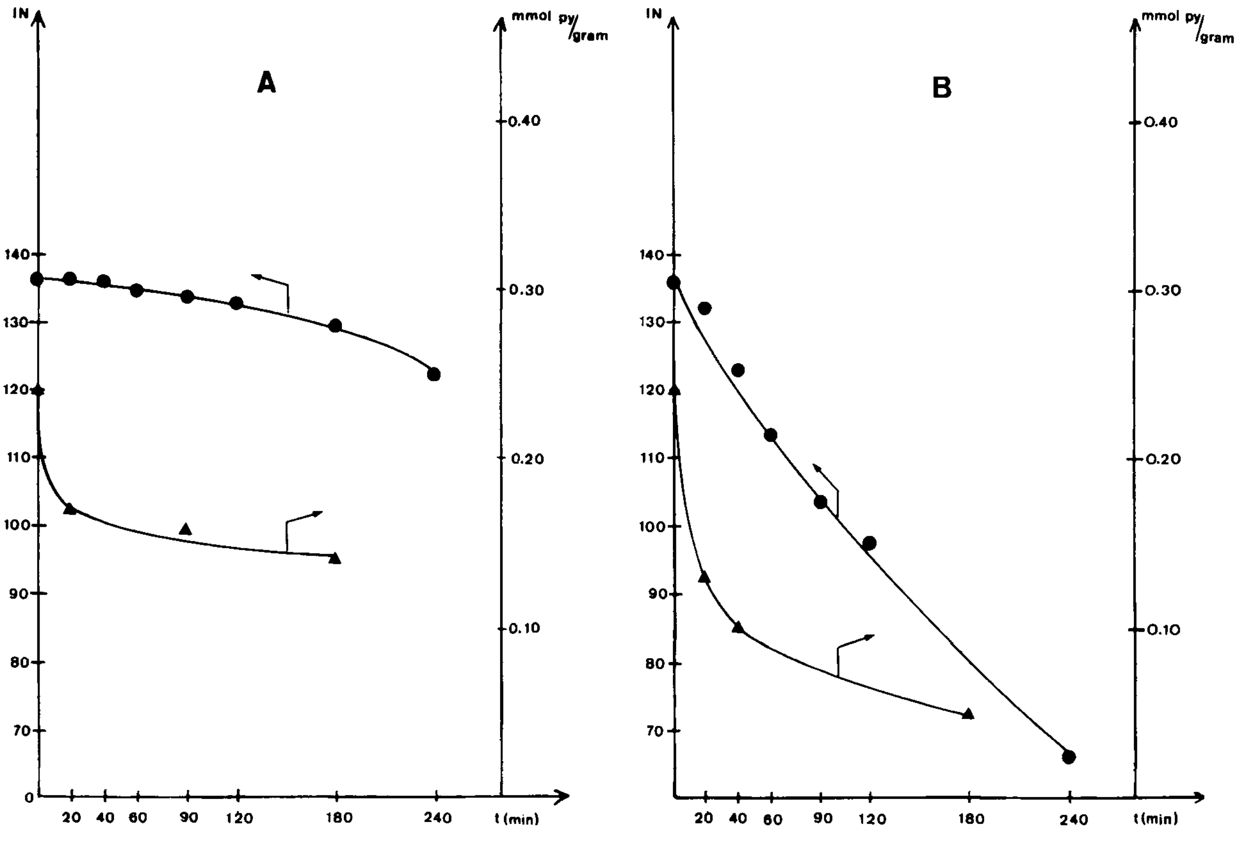

FIG. 6. Relationship between catalytic activity and the release of pyridine at two different temperatures: A, 100 C; B, 140 C (1 atm H_2, 50 g soybean oil, 1.0 g catalyst).

which pyridine might be released is by substitution with an olefin molecule.

$$Cl_2Pd\ pyridine(P\text{-}PS) + R_2\text{-}CH = CH\text{-}R_1 \rightarrow Cl_2Pd(R_2\text{-}CH = CH\text{-}R_1)\ (P\text{-}PS) + pyridine$$

Because of the color change noted during the activation, none of the proposed substitution products are likely to be the final stage in the activation (our catalyst is gray-green after hydrogenation; $Cl_4Pd_2(P\phi_3)_2$ is an orange-red complex and Pd olefin complexes are yellow). Instead, one can assume that further reactions cause the formation of the active species. This might well be Pd(0), as small metal particles or as zero valent Pd-phosphine clusters, because a monophosphine complex is probably not as resistant to reduction as a bisphosphine complex. At present, we are investigating this aspect and will report the results later.

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REFERENCES

1. Haag, W.O., and D.D. Whitehurst, German Patents 1,800,380 (1979); 1,800,371 (1979); and 1,800,379 (1979).
2. Michalska, Z.M., and D.E. Webster, Platinum Met. Rev. 18:65 (1974).
3. Bailar, J.C., Jr., Cat. Rev. Scr. Eng. 10:17 (1974).
4. Hartley, F.R., and P.N. Vezey, Adv. Organomet. Chem. 15:189 (1977).
5. Pittman, C.U., Jr., Polym. News 4:5 (1977).
6. Frankel, E.N., and H.J. Dutton, in "Topics in Lipid Chem.," Vol. 1, edited by F.D. Gunstone, Logos Press, London, 1970, p. 161.
7. Bailar, J.C., Jr., and H. Itatani, J. Am. Chem. Soc. 89:1592 (1967).
8. Itatani, H., and J.C. Bailar, Jr., Ibid. 89:1600 (1967).
9. Bailar, J.C., Jr., JAOCS 47:475 (1970).
10. Bailar, J.C., Jr., Platinum Met. Rev. 15:2 (1971).
11. Frankel, E.N., E.A. Emken and V.L. Davidson, J. Org. Chem. 30:2739 (1965).
12. Frankel, E.N., E.A. Emken, H.M. Peters, V.L. Davidson and R.O. Butterfield, Ibid. 29:3292 (1964).
13. Frankel, E.N., T.L. Mounts, R.O. Butterfield and H.J. Dutton, Adv. Chem. Ser. 70:177 (1968).
14. Frankel, E.N., H.M. Peters, E.P. Jones and H.J. Dutton, JAOCS 41:186 (1964).
15. Frankel, E.N., and F. Little, Ibid. 46:256 (1969).
16. Frankel, E.N., Ibid. 47:11 (1970).
17. Frankel, E.N., and R.O. Butterfield, J. Org. Chem. 34:3930 (1969).
18. Frankel, E.N., F.L. Thomas and J.C. Cowan, JAOCS 47:497 (1970).
19. Frankel, E.N., and F.L. Thomas, Ibid. 49:70 (1972).
20. Evans, G.O., C.U. Pittman, Jr., R. McMillan, R.T. Beach and R. Jones, J. Organomet. Chem. 67:295 (1974).
21. Pittman, C.U., Jr., B.T. Kim and W.M. Douglas, J. Org. Chem. 40:590 (1975).
22. Awl, R.A., E.N. Frankel, J.P. Friedrich and E.H. Pryde, JAOCS 55:577 (1978).
23. Bruner, H., and J.C. Bailar, Jr., Ibid. 49:533 (1972).
24. Bruner, H., and J.C. Bailar, Jr., Inorg. Chem. 12:1465 (1973).
25. Andersson, C., and R. Larsson, Chem. Script. 15:45 (1980).
26. Jacobsson, S., W. Clements, H. Hiramoto and C.U. Pittman, Jr., J. Mol. Cat. 1:73 (1975).
27. Pittman, C.U., Jr., and R.M. Hanes, J. Am. Chem. Soc. 98:5402 (1976).
28. Grubbs, R.H., C. Gibbons, L.C. Kroll, W.D. Bonds and C.H. Brubaker, Ibid. 95:2373 (1973).
29. Pittman, C.U., Jr., S.K. Wuu and S.E. Jacobson, J. Catal. 44:87 (1976).
30. Chatt, J., and L.M. Venanzi, J. Chem. Soc. 2787 (1955).
31. Kosolapoff, G.M., and L. Maier, "Organic Phosphorus Compounds," Vol. 1, Wiley, New York, 1972.
32. Method used at the Microanalytical Laboratory, University of Lund, Lund, Sweden.
33. "Official and Tentative Methods of the American Oil Chemists' Society," Vols. 1 & 2, 3rd Edition, 1973, AOCS, Champaign, IL, Method Cd 14-61.

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Flavor Perceptibility of Straight Chain, Unsaturated Aldehydes As a Function of Double-Bond Position and Geometry

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ABSTRACT

The mean threshold values for odor and taste of straight-chain mono- and diunsaturated aldehydes are determined in solutions of paraffin oil. The threshold values lie at low concentrations and display interesting odor and taste aspects. Special attention is given to the influence of chain length, double-bond position, number of double bonds and *cis/trans* geometry.

INTRODUCTION

In 1964, we published some data about the odor and taste of a number of saturated and unsaturated straight-chain aldehydes in paraffin solutions (1). An interesting pattern of odor and taste aspects was obtained if the threshold values were plotted as a function of the chain length within a homologous series or within a series of aldehydes having the same chain length and with none, one or two double bonds in the molecule.

Considering these results, we continued our study with straight-chain mono- and diunsaturated aldehydes. Special attention was given to chain length, double-bond position, number of double bonds and *cis/trans* geometry.

The data may prove valuable for researchers working on taste and odor aspects in fruits, oils, fats and other fields.

EXPERIMENTAL

The aldehydes were synthesized as described in the literature (2,3). The odor and taste threshold values were determined in spectroscopically pure (tasteless) solutions of paraffin oil according to Patton and Josephson (4). Duplicate determinations were done according to ref. 1.

RESULTS AND DISCUSSION

Table I gives a survey of the average threshold values for odor and taste, and flavor descriptions of the aldehydes synthesized. The alternating taste threshold values found earlier for the homologous *trans*-2-alkenals were also determined for the homologous series of alkenals with the iso-