

CHEMISTRY OF METAL HYDRIDES

XXIII *. CATALYTIC HYDROGENATION OF OLEFINS USING *trans*-PtH(NO₃)(PEt₃)₂ AS CATALYST

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Summary

trans-PtH(NO₃)(PEt₃)₂ was found to be an active catalyst for the hydrogenation of olefins. While it is active towards both internal and terminal olefins, it is not effective towards olefins with electron-withdrawing substituents. The hydrogenation is most effective when conducted in methanol at 60°C and 600 psi. The factors affecting this catalytic hydrogenation are investigated and mechanisms discussed, including the unique role of methanol as solvent.

Introduction

The catalytic hydrogenation of olefins has been extensively studied [1], particularly with rhodium and iridium catalysts. Such catalysts may contain a variety of ligands, although rarely has it been possible to examine in detail the relative influence of different ligands on catalytic activity. Studies of the effect of variations in the Group V donor ligand, L, on the catalytic activity of RhClL₃ have been reviewed by James [1]. For few other transition metals are similar studies possible. A variety of platinum-containing species, often in combination with tin(II) chloride, have been used as hydrogenation catalysts. Since platinum forms extensive series of complexes with a wide variety of ligands, such systems provide an excellent opportunity to explore further the influence of ligands on catalytic activity, as well as to understand the role of tin(II) chloride as co-catalyst.

It is generally believed [2] that one of the key steps in the catalytic cycle is the insertion reaction such as that depicted in eq. 1.



* For part XXII see ref. 20.

However, at least for platinum, this reaction is very slow and requires rather vigorous conditions (e.g. 95°C and 80 atm) [3]. Attempts have been made to improve the system and thus far two approaches have been successful: (i) Replacement of Cl⁻ by a strong π acceptor such as SnCl₃⁻. Thus, the reaction of eq. 1 when conducted in the presence of 1 mol% of SnCl₂, establishes equilibrium within 30 min at 25°C and 1 atm [4]. (ii) Replacement of Cl⁻ by a labile ligand such as acetone [5] or NO₃⁻ [6,7]. The reaction of PtH(NO₃)(PEt₃)₂ with ethylene has been found to be almost instantaneous [7]. Subsequent studies have shown that these two types of insertion reactions proceed via rather different mechanisms. The former involves the formation of a five-coordinated intermediate, PtH(SnCl₃)(PEt₃)₂(C₂H₄) [8], while the latter involves a four-coordinated intermediate PtH(C₂H₄)(PEt₃)₂⁺ [9,10]. Since many organic substrates have been catalytically hydrogenated using *cis*-PtCl₂(PPh₃)₂ [11] or PtHCl(PPh₃)₂ [12] with SnCl₂ as co-catalyst [13], it seemed worthwhile to investigate the activity of PtH(NO₃)(PEt₃)₂ as hydrogenation catalyst. Such results are reported in this paper and subsequently we will describe the effect of various ligands on this and related catalytic species.

Results and discussion

Choosing the hydrogenation conditions

The results of the catalyzed hydrogenation of various organic substrates using the nitrate complex as catalyst are summarized in Tables 1 and 2. Inspection of Table 1 for the hydrogenation of cyclohexene reveals that hydrogenation is most efficient when carried out at elevated temperature (60°C) and high pressure (600 psi H₂), and in methanol as solvent. These conditions are similar to those typi-

TABLE 1
CATALYTIC HYDROGENATION OF VARIOUS ORGANIC SUBSTRATES USING $\text{PtH}(\text{PEt}_3)_2\text{NO}_3$ (0.02 mmol) AS CATALYST IN MeOH (2 ml)

Substrate	Conditions			Product \downarrow	Turnover number ^d
	Temperature (°C)	Pressure (psi)	Time (h)		
Cyclohexene	25	58	21	Cyclohexane	7
Cyclohexene	25	600	40	Cyclohexane	51
Cyclohexene	60	600	16	Cyclohexane	86
Cyclohexene	25	600	20	Cyclohexane	6 ^a
Cyclohexene	60	600	17	Cyclohexane	19 ^b
Cyclooctene	66	600	21	Cyclooctane	>150
1,5-COD	66	600	19	Cyclooctane	6
1,5-Hexadiene	25	1000	24	Hexane	0
1,5-Hexadiene	62	600	9	Hexane	>150
Norbornene	60	600	11	Norbornane	>150
Norbornadiene	60	600	11	Norbornane	>150
(CHCOOCH ₃) ₂	60	600	10	Norbornane	0
CH ₂ =CHCN	60	600	18	p ^c	
CH ₂ =CHCOOCH ₃	60	600	13	p ^c	
Styrene	60	600	4	Ethyl benzene	460

^a In CH₂Cl₂. ^b In benzene. ^c p = polymerization. ^d Mole ratio of the hydrogenated substrate to catalyst.

TABLE 2

CATALYTIC HYDROGENATION OF HEXENES (3 mmol) USING $\text{HPt}(\text{PEt}_3)_2\text{NO}_3$ (0.02 mmol) AS CATALYST IN MeOH , 60°C , 600 psi H_2 , 4 h

Substrates	Products (%)				
	Hexane	1-Hexane	<i>trans</i> -2-Hexene	<i>cis</i> -2-Hexene	<i>trans</i> -3-Hexene
1-Hexene	56	<1	30	7	6
<i>trans</i> -2-Hexene	44	0	42	9	5
<i>trans</i> -3-Hexene	34	0	29	8	29

cally used with the $\text{PtCl}_2(\text{PPh}_3)_2\text{-SnCl}_2 \cdot 2\text{H}_2\text{O}$ system [12,14,15]. Under these conditions, in the absence of organic substrate, $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ undergoes some decomposition. After 20 h, 20% of $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ can be recovered together with another hydride-containing species, the elemental analyses of which conform to the empirical formula $\text{H}_3\text{Pt}_2(\text{PEt}_3)_4\text{NO}_3$. We are currently investigating the structure of this compound, but, importantly, it shows no catalytic activity towards hydrogenation. Thus, the catalytic activity of $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ is decreased, if it is first allowed to decompose under the hydrogenation condition and then introduced to the organic substrate (styrene). The decomposition product, therefore, is not the active catalyst.

Versatility of the catalyst

The results of the catalytic hydrogenation of various isomers of hexene are summarized in Table 2. The nitrate complex catalyzes the hydrogenation of terminal as well as internal olefins. The catalytic activity in terms of turnover numbers decreases in the order of 1-hexene > *trans*-2-hexene > *trans*-3-hexene. This ability of the nitrate complex to catalyze the hydrogenation of internal olefins is in marked contrast to the $\text{PtCl}_2(\text{PPh}_3)_2\text{-SnCl}_2$ system, which exhibits no catalytic activity towards internal olefins. This difference is probably a reflection of the smaller steric constraint in the insertion reaction for the nitrate complex (4-coordinated) as compared with that for the $\text{SnCl}_2\text{-PtCl}_2(\text{PPh}_3)_2$ system (5-coordinated). The hydrogenation of olefins in both systems is accompanied by extensive isomerization [14], mainly to the thermodynamically more stable *trans*-2-hexene. Cyclohexene was hydrogenated even at room temperature and low H_2 pressure (58 psi) (Table 1), but the rate of hydrogenation is significantly increased by raising the reaction temperature to 60°C and the pressure to 600 psi.

The hydrogenation of a monoene is generally easier than the hydrogenation of the corresponding diene. For example, in the hydrogenation of 1,5-cyclooctadiene, after 19 h, only 6 catalytic cycles were obtained (Table 1). Under similar conditions, cyclooctene is hydrogenated readily. A high reaction temperature is also necessary for the hydrogenation of dienes. Although there is no hydrogenation of 1,5-hexadiene at room temperature, complete hydrogenation is attained at 62°C .

Olefins with electron-withdrawing substituents are difficult to hydrogenate. Thus, there is little hydrogenation of acrylonitrile or methyl acrylate, but exten-

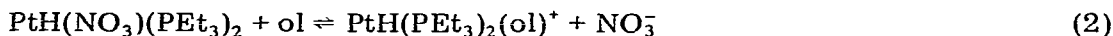
sive polymerization occurs. Again, this is in contrast to the $\text{PtCl}_2(\text{PPh}_3)_2\text{—SnCl}_2$ system, which catalyzes the ready hydrogenation of acrylonitrile [14].

The hydrogenation of styrene is particularly efficient, and we have therefore used it as a model substrate to investigate the mechanism of this catalytic hydrogenation reaction. The hydrogenation of styrene was carried out at 60°C , 600 psi H_2 , and after 4 h, the product was analyzed. The turnover number obtained gives the relative rate. Since the relative rates so obtained are only semi-quantitative, the results reflect only the gross mechanistic features of the system.

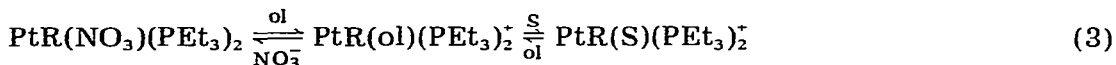
Mechanistic studies

Effect of solvent

The rate of hydrogenation depends markedly on the solvent used (Table 3). It increases by a factor of 7 in changing the solvent from acetone to methanol and by a factor of 20 in changing from methylene chloride to methanol. Generally, the formation of metal hydride is the rate-determining step in the catalytic hydrogenation cycle [1], but this oxidative addition reaction of H_2 with the metal species, has a relatively non-polar transition state and hence has little dependence on solvent. Thus, the rate of reaction of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with H_2 increases by a factor of 2 when the solvent is changed from benzene to dimethylformamide [16]. The large solvent effect observed in our present study is suggestive of a much more complex mechanism. It is possible that methanol provides another source of H_2 *. However, this is ruled out by the observation that under a N_2 atmosphere, the nitrate complex is inactive as a catalyst, whereas in H_2 , the number of catalytic cycles attained is greater than 150 (Table 3). A second possible explanation for the solvent effect observed is that the insertion reaction of olefin with the nitrate complex requires the displacement of the nitrate ligand by the olefin to form a cationic intermediate [10].



In less polar solvents, reaction 2 becomes so slow that it now becomes rate determining. If this is the case, the rate of hydrogenation should become even slower on addition of NO_3^- ion, a characteristic feature of the insertion reaction [10]. However, in the presence of a 10-fold excess of $n\text{-Bu}_4\text{NNO}_3$, the hydrogenation rate increases by a factor of 2 in acetone and of 6 in CH_2Cl_2 . A further increase to a 50-fold excess of nitrate increases the hydrogenation rates even further. While this effect of added NO_3^- is inconsistent with a mechanism involving insertion as the rate-determining step, it is consistent with the mechanism having oxidative addition of H_2 as the slow step. $\text{PtPhCl}(\text{PEt}_3)_2$ has been observed to react with H_2 at room temperature and atmospheric pressure to yield the corresponding hydride, $\text{PtHCl}(\text{PEt}_3)_2$ [3]. This reaction presumably proceeds via a platinum(IV) intermediate, $\text{PtPhH}_2\text{Cl}(\text{PEt}_3)_2$ [1]. In the reaction mixture, equilibria 3 exist **, so that addition of NO_3^- ion forces the equilibrium



* Alcohol acts as a hydride source has been observed in $\text{PtCl}_2(\text{PPh}_3)_2\text{—SnCl}_2 \cdot 2 \text{H}_2\text{O}$ system [12].

** Equilibria 3 for $\text{R} = \text{H}$, $\text{ol} = \text{CH}_2=\text{CHCOOCH}_3$, $\text{S} = \text{MeOH}$ have been observed and determined [10].

TABLE 3

CATALYTIC HYDROGENATION OF STYRENE USING $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$ (0.02 mmol) AS CATALYST AT 600 psi H_2 , 60°C, 4 h

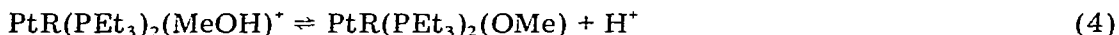
Solvent	$[\text{Bu}_4\text{NNO}_3]/[\text{Pt}]$	$[\text{HClO}_4]/[\text{Pt}]$	$[\text{Base}]^c/[\text{Pt}]$	Turnover number
MeOH	0	0	0	460
Acetone	0	0	0	67
CH_2Cl_2	0	0	0	21
MeOH ^a	0	0	0	0
MeOH ^b	0	0	0	>150
Acetone	10	0	0	120
CH_2Cl_2	10	0	0	128
CH_2Cl_2	50	0	0	215
MeOH	0	1	0	256
MeOH	0	0	1	600
MeOH	20	0	0	232

^a 58 psi N_2 , 12 h, 60°C. ^b 58 psi H_2 , 12 h, 60°C. ^c Base = *p*-nitroaniline.

towards the nitrate complex. Since the oxidative addition reaction of H_2 with the metal species involves a change in the oxidation state in the metal, it is extremely sensitive to the amount of electron density at the metal centre, and therefore sensitive to the type of ligands present. As the nitrate ligand is a better electron donor than styrene or solvent, this accounts for the faster rate of hydrogenation in the presence of added NO_3^- .

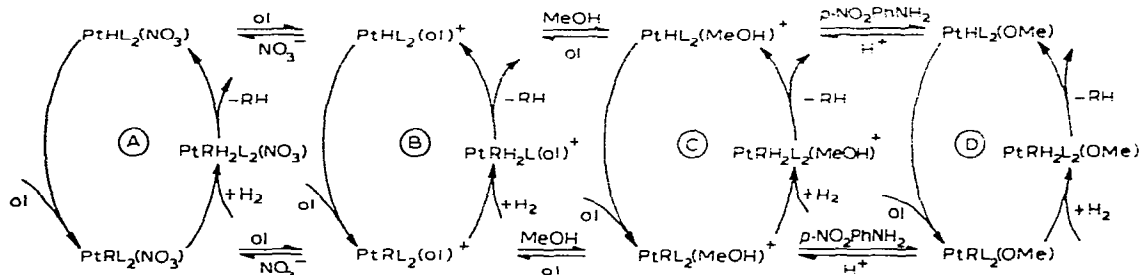
Effect of added acid and base in methanol

The marked rate enhancement of the catalytic hydrogenation of styrene in methanol, compared with the rates in acetone or methylene chloride, suggests that methanol plays a unique role. This is further indicated by the observations (a) that, in methanol, the hydrogenation rate is inhibited by added nitrate ion in contrast to the enhancements observed in acetone and CH_2Cl_2 , and (b) that, in methanol also, the rate of hydrogenation is again inhibited by the addition of 1 equivalent of HClO_4 , but is enhanced by 1 equivalent of base (*p*-nitroaniline). Equilibrium 4, in explaining these observations, provides a basis for the unique role of methanol.

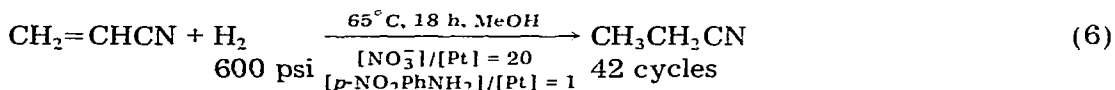
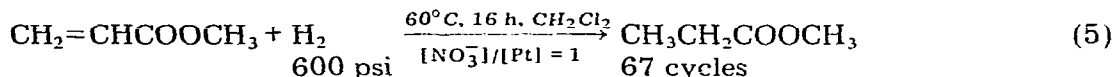


The addition of *p*-nitroaniline does not result in the removal of the hydride ligand attached to the metal, as has been observed in other cationic catalytic hydrogenation systems [17]. This is evidenced by the observation that on addition of 1 equivalent of *p*-nitroaniline to a methanolic solution of $\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2$, the Pt-H NMR signal at 36.5 ppm diminished, but was readily restored by addition of 3 equivalents of *n*- Bu_4NNO_3 to the solution. Hydroxides and methoxides are known to form stable complexes with platinum(II) [18,19]. The high electron density donated by the methoxide ligand enables the complex to undergo oxidative addition reaction with H_2 more readily, accounting for the unusually fast rate of hydrogenation in methanol and also for the effect of added NO_3^- , base and acid. The various hydrogenation pathways are summarized in Scheme 1. In methanol, D is the most effective route, while in CH_2Cl_2 and ace-

SCHEME 1



tone, A is the most effective pathway. The difficulty encountered in hydrogenating activated olefins and dienes can be attributed to the dominance of the relatively inactive intermediates in B. One might expect by introducing NO_3^- and/or base to the system, that activated olefins might also be hydrogenated. Indeed, this is found to be the case:



Experimental

trans-PtH(NO₃)(PEt₃)₂ was prepared by the method of Chatt and Shaw [3] and recrystallized from hexane. The olefins were distilled before use. Methanol was Fisher spectro-grade and was used without further purification. Hydrogen gas was from Matheson and was 99.99% pure.

Typical hydrogenation experiment

10.0 mg (0.02 mmol) of PtH(NO₃)(PEt₃)₂ were dissolved in 2 ml of MeOH in a glass tube (~80 ml volume) containing a teflon coated magnetic stirring bar. 2.30 ml of styrene (20 mmol) were then introduced. The glass tube was placed in a stainless steel autoclave, which was flushed with H₂ three times, pressurized to 600 psi, and then placed in a thermostatted water bath at 60°C. The contents were stirred vigorously (magnetically) for 4 h. The products were analyzed by ¹H NMR or GLC. When NMR was used, the turnover number was calculated based on the integration of the methyl group of the ethyl benzene and the phenyl group of both ethyl benzene and styrene. GLC analysis was performed with a Varian Aerograph model 700 equipped with a 1/4" × 32' Carbowax column, 60–80 mesh on Chromosorb W, with column temperature at 180°C. Both methods agreed to within 10%.

For analyses of hexenes, the same column was used with column temperature at 38°C and helium flow rate 100 ml/min.

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