PHOSPHINERHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

XV *. HYDROGENATION OF KETONES WITH PPh₃-CONTAINING RHODIUM CATALYSTS

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Summary

Wilkinson-type complexes containing PPh₃ ligands and modified by Et₃N can be successfully used as catalysts for the homogeneous hydrogenation of ketones. The reaction is first order in substrate and rhodium and the rate does not depend on the partial pressure of hydrogen. Excess of the ligand ($PPh_3/Rh > 3$) does not inhibit the reduction. The reaction between $HRh(PPh_3)_3$ and the ketone is regarded as the rate-determining step, and this is followed by a fast reaction with H_2. The activity of the catalyst is not very sensitive to the structure of the substrate.

Introduction

Several phosphinerhodium complexes were tested as catalysts for ketone hydrogenation, but only few of them proved to be active under atmospheric pressure [1–4]; triarylphosphine-containing derivatives (except for the $[RhCl(C_8H_{12})(PPh_3)]/NaBH_4/KOH$ system [5]) were found to be inactive. However, as we have shown earlier [6], even these complexes can be activated by adding triethylamine, which transforms the $Rh(PPh_3)_3Cl$ catalyst or the PPh₃-containing rhodium complexes prepared in situ into hydridorhodium(I)phosphine species [7]. These catalyze the reduction of different dialkyl-, alkylaryl-, diaryl- and cyclic ketones with acceptable reaction rates under mild conditions (50°C, 1 bar).

In this paper we present kinetic data for the $[Rh(NBD)Cl]_2/PPh_3/Et_3N$ catalytic system and some additional results obtained in hydrogenation of ketones with different structures.

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* For part XIV see ref. 9.

TABLE 1

HYDROGENATION OF ACETOPHENONE WITH RHODIUM CATALYSTS CONTAINING PPh$_3$ [a]

Catalyst	Rh/P/N	$10^5 r_i$ [b] $(M\,s^{-1})$
Rh(PPh$_3$)$_3$Cl	1/3	0
Rh(PPh$_3$)$_3$Cl/Et$_3$N	1/3/5	2.98
[Rh(NBD)Cl]$_2$/PPh$_3$	1/3.2	0
[Rh(NBD)Cl]$_2$/PPh$_3$/Et$_3$N	1/3.2/5	3.47
[Rh(NBD)Cl]$_2$/PPh$_3$/Et$_3$N	1/2.2/5	0.96
[Rh(NBD)(PPh$_3$)$_2$]ClO$_4$/Et$_3$N	1/2/5	1.1
[Rh(NBD)(PPh$_3$)$_2$]ClO$_4$/PPh$_3$/Et$_3$N	1/3.2/5	3.9
HRh(PPh$_3$)$_4$	1/4	3.85
[Rh(NBD)Cl]$_2$/PPh$_3$/Et$_3$N	1/4/5	3.57

[a] 50°C, 1 bar H$_2$, 10 mmol acetophenone and 0.05 mmol Rh in 4 ml benzene/methanol = 1/1. [b] Initial rate.

Results and discussion

Preliminary results collected in Table 1 show that in the presence of Et$_3$N both Wilkinson-type systems and ionic catalysts are active for the hydrogenation of acetophenone. The complex HRh(PPh$_3$)$_4$ is also active in the absence of Et$_3$N.

In general, a benzene/methanol mixed solvent was used. It was found that increasing the amount of the methanol increased the reaction rate, but some benzene was necessary to dissolve the rhodium complexes (Fig. 1). The influence of Et$_3$N on
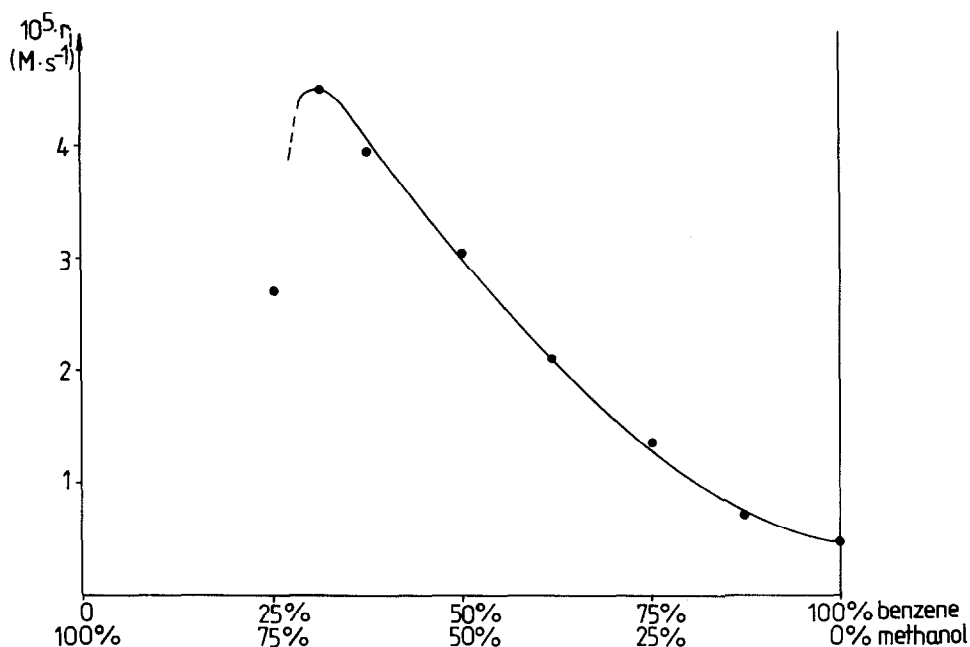

Fig. 1. Initial rate (r_i) as a function of the benzene/methanol ratio; reaction conditions: 50°C, 1 bar H$_2$; 10 mmol ketone and 0.05 mmol Rh in 4 ml benzene/methanol; Rh/P/N = 1/3.2/5.
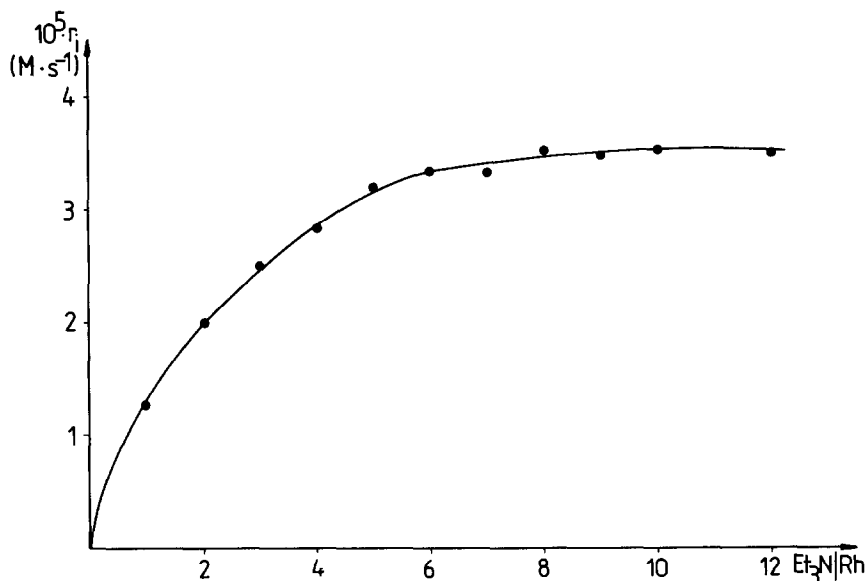
Fig. 2. Influence of the Et_3N/Rh ratio on the initial rate of hydrogenation; reaction conditions: 50°C, 1 bar H_2; 10 mmol ketone and 0.05 mmol Rh in 4 ml benzene/methanol = 1/1; Rh/P = 1/3.2.

the rate is shown in Fig. 2. It can be seen that the presence of Et_3N is essential, and the highest activities are obtained at $Et_3N/Rh \geq 5$. The saturation-type curve in Fig. 2 suggests there is actually an equilibrium such as eq. 1, which has to be shifted to the right in order to transform most of the Rh into the catalytically more active HRh^I species:

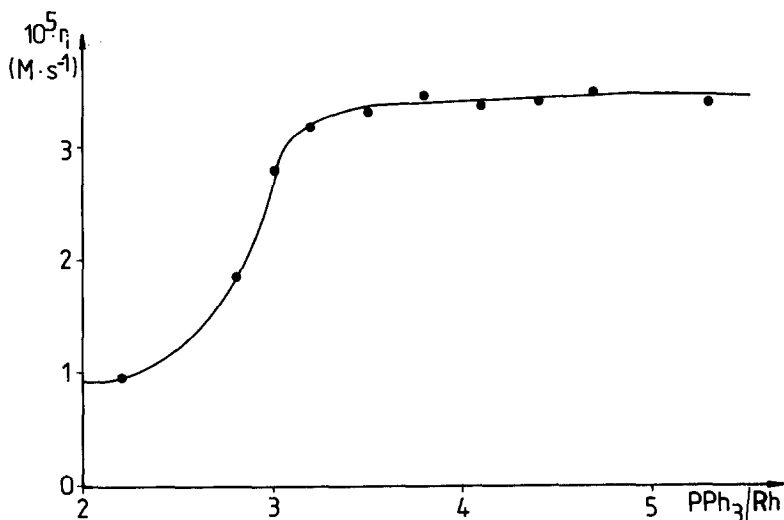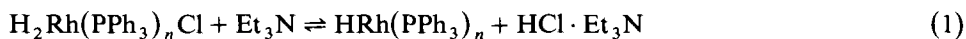$$H_2Rh(PPh_3)_n Cl + Et_3N \rightleftharpoons HRh(PPh_3)_n + HCl \cdot Et_3N \qquad (1)$$

Fig. 3. Initial rate of hydrogenation as a function of the PPh_3/Rh ratio; reaction conditions: 50°C, 1 bar H_2; 10 mmol ketone and 0.05 mmol Rh in 4 ml benzene/methanol = 1/1; Rh/N = 1/5.

TABLE 2

INITIAL RATES OF ACETOPHENONE HYDROGENATION AND THE OBSERVED RATE CONSTANTS AT VARIOUS INITIAL CONCENTRATIONS AND TEMPERATURES (Solvent: benzene/methanol = 1/1)

[Rh] (M)	[PhCOMe] (M)	P_{total} (mbar)	Temp. (°C)	$10^5 r_i$ $(M\,s^{-1})$	$10^3 k_{obs}$ $(M^{-1}\,s^{-1})$
0.003	2.00	983	50	0.7	1.1
0.006	2.00	985	50	1.54	1.28
0.008	2.00	985	50	2.09	1.31
0.012	2.00	980	50	3.21	1.33
0.015	2.00	985	50	3.77	1.26
0.02	2.00	985	50	5.24	1.31
0.025	2.00	983	50	6.48	1.3
0.03	2.00	983	50	7.55	1.26
0.035	2.00	985	50	8.98	1.28
0.01	0.33	985	50	0.5	1.6
0.01	0.66	983	50	0.96	1.45
0.01	1.00	990	50	1.3	1.3
0.01	1.33	979	50	1.7	1.3
0.01	1.66	984	50	2.2	1.3
0.01	2.00	985	50	2.5	1.3
0.01	2.33	988	50	2.84	1.22
0.01	2.66	985	50	3.48	1.31
0.01	3.00	976	50	3.77	1.26
0.01	2.00	825	50	2.63	1.32
0.01	2.00	867	50	2.61	1.3
0.01	2.00	908	50	2.74	1.37
0.01	2.00	955	50	2.8	1.4
0.01	2.00	1039	50	2.92	1.46
0.01	2.00	1068	50	2.66	1.33
0.01	2.00	1105	50	2.8	1.4
0.01	2.00	1221	50	2.76	1.38
0.01	2.00	1312	50	2.79	1.39
0.01	2.00	1355	50	2.75	1.37
0.01	2.00	1394	50	2.87	1.43
0.01	2.00	985	45	2.35	1.17
0.01	2.00	981	40	1.7	0.85
0.01	2.00	989	35	1.23	0.61
0.01	2.00	986	30	0.87	0.44

As shown in Fig. 3, an increase of the PPh_3/Rh from 2 to 4 increases the activity of the catalytic system. This is a rather unusual phenomenon in the case of transition metal phosphine complex catalysts, which are usually inhibited by an excess of the ligand. The increase in activity is accompanied by a significant lightening of the reaction mixture from dark brown to yellow. This observation and the shape of the curve in Fig. 3 suggest that the catalytically active species contains three PPh_3 ligands, does not readily coordinate a fourth PPh_3 ligand, and is transformed into catalytically less active clusters if it loses one of its three PPh_3 ligands. This situation is depicted in eq. 2:

$$\left[HRh(PPh_3)_2\right]_n \underset{}{\overset{PPh_3}{\rightleftharpoons}} HRh(PPh_3)_3 \underset{}{\overset{PPh_3}{\rightleftharpoons}} HRh(PPh_3)_4 \qquad (2)$$

To obtain some additional information about the mechanism of ketone hydrogenation with this catalytic system, kinetic measurements were carried out at constant Et_3N/Rh (5/1) and constant PPh_3/Rh (3.2/1) ratios. The results are listed in Table 2. The initial rate of acetophenone hydrogenation was found to be first order in substrate and rhodium, and zero order in hydrogen. Based on these results and those obtained with varying Et_3N and PPh_3 concentrations (see above), we suggest the following schematic mechanism for this catalytic hydrogenation:
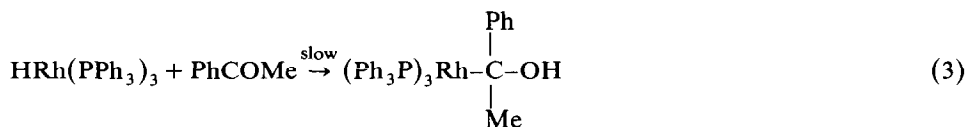
$$HRh(PPh_3)_3 + PhCOMe \overset{slow}{\rightarrow} (Ph_3P)_3Rh-\underset{\underset{Me}{|}}{\overset{\overset{Ph}{|}}{C}}-OH \qquad (3)$$

TABLE 3

HYDROGENATION OF VARIOUS KETONES WITH THE $[Rh(NBD)Cl]_2/PPh_3/Et_3N$ CATALYTIC SYSTEM [a]

Ketone	$10^6\, r_i$ [b] $(M\,s^{-1})$	Conversion (%) [c]
Acetone	4.1	38.1
2-Butanone	1.9	14.7
4-Methyl-2-pentanone	2.5	21.5
3-Methyl-2-pentanone	2.3	19.6
3,3-Dimethyl-2-butanone	0.9	8.3
2-Heptanone	2.2	18.5
4-Phenyl-2-butanone	3.7	43.4
Phenyl-2-propanone	3.6	40.8
1,1-Diphenyl-2-propanone	4.3	32.8
Acetophenone	6.7	70.6
Phenoxy-2-propanone	5.9	41.5
1-Acetonaphthone	11.5	83.4
2-Acetonaphthone	7.7	52.1
4-Methyl acetophenone	5.5	62.3
4-Ethyl acetophenone	5.1	54.6
4-t-Butyl acetophenone	4.2	51.3
4-Fluoroacetophenone	4.0	40.0
4-Methoxy acetophenone	6.8	67.2
4-Hydroxy acetophenone	8.4	77.8
2-Methyl acetophenone	4.7	46.7
2-Hydroxy acetophenone	1.8	17.0
2,4-Dimethyl acetophenone	4.3	50.7
2,4-Dimethoxy acetophenone	5.6	62.3
Propiophenone	5.7	39.6
Valerophenone	5.0	48.3
1-Phenyl-1-octanone	6.1	50.6
3-Pentanone	1.3	11.7
3-Heptanone	2.6	25.7
Cyclopentanone	6.9	53.2
Cyclohexanone	8.3	54.0
4-t-Butylcyclohexanone	10.2	74.3
Benzophenone	6.4	54.7

[a] 50°C, 1 bar H_2; 1 mmol ketone and 0.025 mmol Rh in 5 ml benzene/methanol = 3/7; Rh/P/N = 1/3.2/5. [b] Initial rate. [c] Reaction time 6 h.

TABLE 4

HYDROGENATION OF AMINO KETONES WITH [Rh(NBD)Cl]$_2$ + PPh$_3$ CATALYST[a]

Ketone	Et$_3$N/Rh	$10^6 r_i$[b] (M s^{-1})	Conversion[c] (%)
4-Dimethylamino-2-butanone	5	5.1	49.8
4-Dimethylamino-2-butanone	–	5.4	53.5
α-NEt$_2$-acetophenone	5	4.1	39.3
α-NEt$_2$-acetophenone	–	4.2	41.4
α-NEt$_2$-p-Me-acetophenone	–	3.9	37.1
α-NEt$_2$-p-Et-acetophenone	–	3.8	35.4
α-NEt$_2$-p-i-Pr-acetophenone	–	2.8	27.2
α-N(Bu^n)$_2$-acetophenone	–	3.7	33.6
N-Benzyl-4-piperidone	–	4.8	61.9

[a] For reaction conditions see Table 3, footnote a. [b] Initial rate. [c] Reaction time 6 h.

$$(Ph_3P)_3Rh-\underset{\underset{Me}{|}}{\overset{\overset{Ph}{|}}{C}}-OH + H_2 \overset{fast}{\rightarrow} (Ph_3P)_3RhH + PhCH\underset{OH}{\overset{|}{}}Me \qquad (4)$$
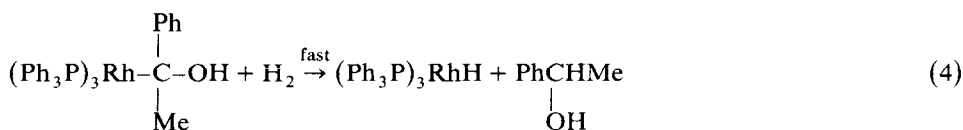
Such a mechanism is in accordance with the observed kinetic eq. 5:

$$-\frac{d(PhCOMe)}{dt} = k_{obs}[PhCOMe][Rh] \qquad (5)$$

Obviously both of the steps 3 and 4 are actually more complex, and at least two other intermediates may be involved in the catalytic cycle (a π-complex of the ketone preceeding the σ-alkyl intermediate and a Rh^{III} dihydride formed initially in the reaction of this alkyl derivative with H$_2$) but since no direct information is available about such details further discussion would be unjustified.

Measurement of the rates at various temperatures (30–50°C, see Table 2) gave the following activation parameters: $\Delta H^* = 50.1$ kJ mol^{-1} and $\Delta S^* = -34.3$ e.u. The large negative entropy of activation is consistent with the proposal that the bimolecular step 3 is rate-determining.

The [Rh(NBD)Cl]$_2$/PPh$_3$/Et$_3$N catalyst system was successfully used for the hydrogenation of a wide range of ketones. The results listed in Table 3 reveal, that all the second order rate constants fall practically within one order of magnitude, a remarkably narrow range. In general, dialkyl ketones are somewhat less reactive than aromatic ketones, and surprisingly even benzophenone (which is not readily hydrogenated by Osborne's catalyst [1]) can be hydrogenated quite easily.

Our catalytic system is also suitable for the hydrogenation of aminoketones [8] under ambient conditions (Table 4), but in this case addition of Et$_3$N is not necessary. In these reaction mixtures the substrate itself acts as the base which is required for the formation of the active catalyst (eq. 1).

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