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HOMOGENEOUS CATALYTIC REDUCTION OF BENZALACETONE WITH CARBON MONOXIDE AND WATER

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Summary

The selective hydrogenation of benzalacetone to the corresponding saturated ketone $PhCH_2CH_2COCH_3$ with CO and water as the hydrogen source is catalyzed by $[Rh(diene)L_2]^+$ complexes (diene = 1,5-cyclooctadiene or norbornadiene; L_2 = mono- or bidentate phosphorous ligands) and by rhodium and iridium carbonyls. The effects of these catalysts in the water gas shift reaction are also reported.

Introduction

Various types of transition metal compounds, such as metal carbonyls [1], carbonyl clusters [2], potential carbonyl precursors [3], platinum(II)/tin(II) systems [4], low valent platinum complexes [5] are known to be active catalysts for the water gas shift reaction (WGSR) in homogeneous phase:

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

This reaction is thermodynamically favoured by the relatively low temperature at which these systems operate, but the activity does not appear to be as high as it must be for any practical applications.

In the presence of metal carbonyls the system $CO + H_2O$ has also been used usefully as source of hydrogen for the reduction of organic compounds, e.g. aldehydes to alcohols [6] and aromatic nitrocompounds to the corresponding amines [7], and for the hydroformylation of olefins [8]. These catalysts however are reported to behave differently in oxosynthesis ($CO + H_2$) and in Reppe reaction conditions ($CO + H_2O$) [9]; for the latter $Fe(CO)_5$ is quite active whereas it is a poor hydroformylation catalyst [10,11].

We have previously reported [3] that WGSR is catalyzed by $[Ir(diene)L_2]^+$ complexes (L_2 = mono- or bidentate ligands having phosphorus or nitrogen as donor atom) in various solvents. The catalytic activities we found for these compounds are roughly similar to those reported for catalysts prepared in situ by reaction of $MCl_3 \cdot 3H_2O$ (M = Rh, Ir) with bipyridyl or phenanthroline derivatives [12]. We

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have now investigated the behaviour in the WGSR reaction of $[Rh(diene)P_2]^+$ complexes [diene = 1,5-cyclooctadiene (COD) or norbornadiene (NBD); P_2 = bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$: dpe; $n = 3$: dpp) and *cis*-$Ph_2PCHCHPPh_2$ (dpet), or monodentate phosphines: PPh_3, $PMePh_2$ and PPh_3S (m-monosulfonated triphenylphosphine [27])]. We have also studied the reduction of $PhCH{=}CHCOCH_3$ to $PhCH_2CH_2COCH_3$ catalyzed by the same complexes using $CO + H_2O$ system as hydrogen source; the reduction of this ketone under similar conditions catalyzed by the carbonyl clusters $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$ is also reported.

Results and discussion

The results obtained for WGSR are reported in Table 1. The reaction was carried out in dioxane/water mixture or in water. In the former case, the system $[Rh(COD)P_2]^+$ is not very sensitive to ligand variation, but the activity of $[Rh(COD)(PPh_3S)_2]^-$ in water varies with the pH. For this system the initial pH was buffered at various values (Table 1, runs 19–27) but the pH changed during the reaction and could not be kept in the basic or neutral range, probably because of the

TABLE 1

CATALYSIS OF THE WATER GAS SHIFT REACTION BY RHODIUM COMPLEXES [a]

Run	Catalyst	P_{CO}	CO/cat.	Cycles h^{-1}	Notes
1	$[Rh(COD)dpe]^+$	10	2500	2.5	
2	$[Rh(COD)dpe]^+$	20	5000	5.5	
3	$[Rh(COD)dpe]^+$	30	7500	6.5	
4	$[Rh(COD)dpe]^+$	30	7500	8	Reaction temperature 180°C
5	$[Rh(COD)dpe]^+$	10	1250	1	Cat. conc. 10^{-3} *M*
6	$[Rh(COD)dpe]^+$	10	1250	2.5	$MeOH/H_2O = 3$, cat. conc. 10^{-3} *M*
7	$[Rh(COD)dpp]^+$	10	2500	2	
8	$[Rh(COD)dpp]^+$	20	5000	6	
9	$[Rh(COD)dpp]^+$	30	7500	9	
10	$[Rh(COD)dpet]^+$	10	2500	1	
11	$[Rh(COD)dpet]^+$	20	5000	5	
12	$[Rh(COD)dpet]^+$	30	7500	6.5	
13	$[Rh(COD)(PPh_3)_2]^+$	10	2500	1	
14	$[Rh(COD)(PPh_3)_2]^+$	20	5000	2.5	
15	$[Rh(COD)(PPh_3)_2]^+$	30	7500	6	
16	$[Rh(COD)(PPh_2Me)_2]^+$	10	2500	2	
17	$[Rh(COD)(PPh_2Me)_2]^+$	20	5000	7.5	
18	$[Rh(COD)(PPh_2Me)_2]^+$	30	7500	14.5	
19	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	11	In water. Not buffered
20	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	7	Buffered at pH = 11
21	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	7	Buffered at pH = 10
22	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	3.5	Buffered at pH = 8
23	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	6	Buffered at pH = 6
24	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	18	Buffered at pH = 4
25	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	64	Buffered at pH = 3
26	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	127	Buffered at pH = 2
27	$[Rh(COD)(PPh_3S)_2]^-$	30	37500	7	Buffered at pH = 1

[a] Reaction conditions: 155°C. Catalyst concentration: 5×10^{-4} *M*; 10^{-4} *M* in runs 19–27. Solvent: Dioxane/water (3/1) in runs 1–18, water in runs 19–27.

number of reactions in which OH^- is involved.

$CO + OH^- \rightarrow HCO_2^-$

$CO_2 + OH^- \rightarrow HCO_3^-$

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

Our results indicate that the catalytic activity is independent of the initial pH in the range 6–11, but becomes sensitive to pH in the acidic range, reaching a maximum value at pH = 2 (127 cycles h^{-1}) and then decreasing sharply at pH = 1.

Rhodium and iridium phenanthroline systems were found to be particularly active in the pH range 6–10 [12], and this is consistent with nucleophilic attack of OH^- on the coordinated carbon monoxide being an important step.

The conversion of protons to hydrogen:

$MH + H^+ \rightleftharpoons M^+ + H_2$

could play a role in WGSR in our case, accounting for the greater activity found in acidic medium using $[Rh(COD)(PPh_3S)_2]^-$ as catalyst. On the other hand, it is known that the catalytic activity for WGSR does not require basic solutions in the case of rhodium [13] and ruthenium [14] compounds, which are, in fact, much more active in the presence of acid. The mechanism of WGSR however, is far from clear. Stable water adducts formed by oxidative addition assisted by basic solvents such as pyridine were proposed in the case of $RhH(PPr_3^i)_3$ as catalyst.

Transition metal complexes which promote WGSR are also used as catalysts in the reduction of several organic compounds with CO and H_2O as the source of hydrogen. They usually show low catalytic activity, unless some additives such as

TABLE 2

REDUCTION OF $PhCH{=}CHCOCH_3$ VIA WATER GAS SHIFT REACTION CATALYZED BY RHODIUM COMPLEXES [a]

Run	Catalyst	T (°C)	% Conversion (h)	Cycles h^{-1}	Solvent
1	$[Rh(PPh_3)_3Cl]$	155	39 (3)	129	Dioxane/water 9/1
2	$[Rh(PPh_3)_3Cl]$	155	84 (3)	280	Ethanol/water 95/5
3	$[Rh(PPh_3)_3Cl]$	155	51 (3)	172	Ethanol/water 994/6
4	$[Rh(COD)dpe]^+$	155	14 (3)	47	Dioxane/water 9/1
5	$[Rh(COD)Cl]_2$	155	46 (4)	116	Dioxane/water 9/1
6 [b]	$[Rh(COD)Cl]_2$	155	92 (1.5)	613	Dioxane/water 9/1
7	$[Rh(COD)Cl]_2$	145	78 (3)	261	Ethanol/water 95/5
8	$[Rh(COD)Cl]_2$	145	96 (3)	319	Ethanol/water 9/1
9	$[Rh(COD)Cl]_2$	108	31 (5)	63	Ethanol/water 9/1
10 [c]	$[Rh(COD)Cl]_2$	108	58 (5)	115	Ethanol/water 9/1
11 [c]	$[Rh(COD)Cl]_2$	108	77 (5)	141	Ethanol/water 9/1
12 [c]	$[Rh(COD)Cl]_2$	108	79 (5)	143	Ethanol/water 9/1
13	$[Rh(COD)(PPh_3S)_2]^-$	145	85 (5)	170	Ethanol/water 9/1
14	$[Rh(COD)(PMePh_2)_2]^+$	145	90 (5)	180	Ethanol/water 9/1
15	$[Rh(COD)dpe]^+$	145	40.5 (5)	81	Ethanol/water 9/1
16	$[Rh(NBD)dpe]^+$	145	40 (5)	80	Ethanol/water 9/1

[a] Reaction conditions: Catalyst concentration: 10^{-4} *M*; p_{CO} 30 atm, substrate/catalyst = 1000; [b] Ethylenediamine added (en): en/cat = 10. [c] KOH added: run 10: KOH/cat = 10, run 11: KOH/cat = 50, run 12: KOH/cat = 100.

KOH, amines, or tin chloride are present. For example $Rh_6(CO)_{16}$ is much more active in the presence of diamines for WGSR [18] and in the reduction of aldehydes by the $CO + H_2O$ system [19].

In Table 2 are summarized the results for the hydrogen transfer from CO/H_2O system to $PhCH{=}CHCOCH_3$ to the saturated ketone catalyzed by rhodium complexes. Addition of ethylenediamine to $[Rh(COD)Cl]_2$ in dioxane/water mixture enhances the catalytic activity of the system, the number of cycles h^{-1} rising from 116 to 613 (runs 5 and 6, Table 2).

The reaction is faster if ethanol is present, which may be related to the possibility of hydrogen transfer from the alcohol catalyzed by rhodium complexes (run 3, Table 2); several transition metal compounds have been shown to catalyze the reduction of α,β unsaturated ketones by hydrogen transfer from a variety of alcohols [20].

In Table 3 are listed results for the reduction of $PhCH{=}CHCOCH_3$ to the corresponding saturated ketone using $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$ as catalysts. The rhodium is more active than the iridium system, and in both cases there is some hydrogen transfer from the alcohol. The activity of $Rh_6(CO)_{16}$ in ethanol is practically the same as in ethanol/water mixture (Table 3, runs 1,2), whereas it is higher in isopropanol (run 9, Table 3). In contrast, $Ir_4(CO)_{12}$ is more active when water is present (runs 11, 12, Table 3). It is clear that the presence of alcohol leads to an important increase in the catalytic activity (Table 3, runs 11,13). When triphenylphosphine and/or base are added the rate is lowered, and this can be explained in terms of formation of new complexes in solution. In the presence of base, for

TABLE 3

REDUCTION OF $PhCH{=}CHCOCH_3$ USING $Rh_6(CO)_{16}$ AND $Ir_4(CO)_{12}$ AS CATALYSTS

$Rh_6(CO)_{16}$: $[Rh_6] = 10^{-4}$ *M*, substrate/rhodium = 1000,
T 145°C, p_{CO} 30 atm,
reaction time 5 h.

Run	%Conversion	$NaOH/Rh_6$	PPh_3/Rh_6	Solvent
1	74	–	–	EtOH
2	77	–	–	$EtOH/H_2O = 9$
3	87	–	1	$EtOH/H_2O = 9$
4	29	–	6	$EtOH/H_2O = 9$
5	24	–	12	$EtOH/H_2O = 9$
6	26	–	60	$EtOH/H_2O = 9$
7	43	60	–	$EtOH/H_2O = 9$
8	18	60	1	$EtOH/H_2O = 9$
9	98	–	–	i-PrOH
$Ir_4(CO)_{12}$:	$[Ir_4] = 10^{-4}$ *M*, substrate/iridium = 1000, *T* 155°C, p_{CO} 30 atm, reaction time 23 h.			
10	22	–	–	Ethoxyethanol
11	28 (5 h)	–	–	$EtOH/H_2O = 9$
12	12	–	–	EtOH
13	0.5	–	–	$Dioxane/H_2O = 9$
14	38	–	–	i-PrOH

example, various equilibria involving $Rh(CO)_{16}$ could give $Rh_6(CO)_{15}H^-$, $Rh_6(CO)_{15}^{2-}$ and others [22].

Finally, in the absence of water, carbon monoxide prevents the reduction of the catalyst to metal.

Experimental section

Chemicals

Ethanol was used without further purification, while the other solvents were distilled before use (dioxane over sodium) and stored under an inert atmosphere. Benzalacetone was recrystallized from ethanol.

$[Rh(1,5\text{-cyclooctadiene})L_2]^+$ [24], $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ [25] and $Rh(PPh_3)_3Cl$ [26] were prepared by published methods. PPh_3S (m-monosulfonated triphenylphosphine) was synthesized as described by Chatt et al. [27].

$[Rh(1,5\text{-COD})(PPh_3S)_2]^- Na^+$ was prepared by slight modification of reported method [24]. $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$ were purchased from the Strem Chemicals.

Procedure

Two autoclaves (190 and 100 ml) were used. The reaction solutions were prepared outside the autoclave, in a stream of carbon monoxide, and then loaded into it. The reagents were added as follows: CO was bubbled into the deareated solvent for 15 min, then the catalyst was dissolved and after 15 more min benzalacetone was added. The analyses were performed on a DANI 3400 gaschromatograph equipped with a thermal conductivity detector. A Porapak Q column with argon as carrier gas was used for the gas analyses, and a C20M column with helium as carrier was used to monitor the reduction of benzalacetone.

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