The effect of water on the rhodium-catalyzed carbonylation of isopropylallylamine

Ricardo Gomes da Rosa [*], José Daniel Ribeiro de Campos, Regina Buffon

Instituto de Química-Unicamp, P.O. Box 6154, 13083-970 Campinas-SP, Brazil

Abstract

The effects of the presence of water on the rhodium-catalyzed carbonylation of isopropylallylamine were studied as a function of the following parameters: reaction temperature; water content; presence of phosphines; solvent polarity and presence of bulky ions. It turned out that the reaction is strongly dependent on the temperature and that water seems to behave both as a source of hydrogen and as a ligand in the active species. The phosphine ligands showed no effect since in the presence of water they were all converted to their corresponding oxides. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The rhodium/phosphine-catalyzed carbonylation of allylamines in the presence of hydrogen leads to γ-lactams in good yields [1]. Although hydrogen is not required for the lactam formation, its presence [2] as well as the addition of other sources of hydride such as $NaBH_4$ [3], allows for the reaction to be carried out under milder conditions. Recently, we reported on the effects of the chelating angle formed between diphosphines and the rhodium atom, as well as of the nature of the alkyl group attached to the nitrogen atom, on the activity and selectivity of the catalytic system in this reaction [4]. When the susbtrate was isopropylallylamine, a competition between the ''carbonylation'' (leading to *N*-isopropylbutyrolactam, Scheme 1) and the ''hydroformylation'' (leading to *N*-isopropylpyrroline and *N*-isopropylpyrrolidine, Scheme 2) pathways were observed [4]. Here we report our results obtained using water instead of hydrogen, under water gas shift (WGS) conditions. Our main goal was to improve the selectivity to carbonylation products: the addition of water would be expected to inhibit the hydroformylation pathway since formation of both pyrroline and pyrrolidine involves a dehydration step (Scheme 2). On the other hand, the WGS conditions would provide the hydrogen

* Corresponding author. Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio Grande do Sul (UFRGS), P.O. Box 15003, 91501-970 Porto Alegre-RS, Brazil. Fax: +55-51-319-1499.

E-mail address: rgomes@if.ufrgs.br (R.G. da Rosa).

Scheme 1.
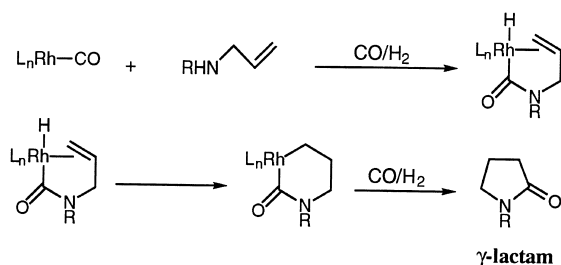
needed to the formation of the catalytic intermediates [2].

2. Experimental

2.1. Materials

Isopropylallylamine [5] and RhCl(CO)(PPh$_3$)$_2$ [6] were prepared as described in the literature. Solvents (THF, toluene and cyclohexane) were distilled over Na/benzophenone under an argon atmosphere. Water was distilled and degassed just before use.

2.2. Catalytic experiments

The catalytic experiments were performed in a stainless steel 300-ml Parr reactor under 20 bar (CO or CO/H$_2$ = 4/1). The reaction temperature was kept at 70°C or 100°C and the solution was stirred at 300 or 500 rpm, for 24 h. In a typical experiment, 0.038 mmol of RhCl(CO)(PPh$_3$)$_2$ was added to the reactor, followed by 7.6 mmol of isopropylallylamine, 500 mg of cyclooctane (internal standard) and 30 ml of THF/H$_2$O (390 mmol of water). The reactor was closed and purged with CO, pressurized to 20 bar and heated at 100°C. The products were analysed through an HP-5890 II gas chromatograph equipped with a gas flame ionization detector and an HP 5 capillary column (30.0 m × 0.25 mm).

^{31}P NMR analyses were carried out on a Bruker AC 300P spectrometer at 121 MHz us-

ing H$_3$PO$_4$ as reference and C$_6$D$_6$ as the solvent.

Infrared spectra were recorded on a Nicolet 520-FT spectrometer (128 scans) with a resolution of 4.0 cm^{-1}.

3. Results and discussion

In our previous work, 70°C was established as the optimal temperature for carbonylation of allylamines under CO/H$_2$ [2,4]. Since we were replacing H$_2$ by water, some experiments with two catalytic systems were carried out in order to evaluate the effect of temperature on the catalytic activity and selectivity to the desired product (Table 1). When the temperature was raised from 70°C to 100°C a marked increase in conversion was observed for both systems. This is in agreement with a WGS reaction, which is known to require higher temperatures, around 100°C [7]. Even when the selectivity decreased (in the presence of RhCl(CO)(PPh$_3$)$_2$), the yield in γ-lactam was higher. Since conversions reached ∼ 100% already at 100°C, this temperature was considered to be high enough because a further increase would certainly have a deleterious effect on the selectivity.

When hydrogen was replaced by water the effect of the phosphines on the selectivity to lactam was completely suppressed (Table 2). This result can be ascribed to the oxidation of those ligands (Table 3) giving rise to a common
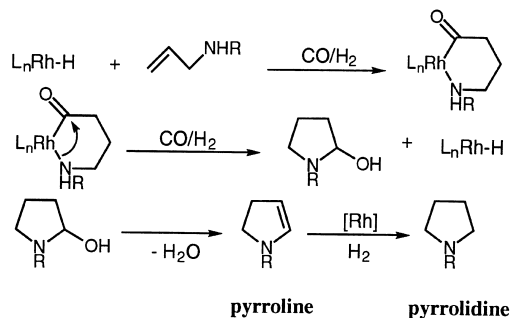
Scheme 2.

Table 1

Influence of the reaction temperature on the carbonylation of isopropylallylamine[a]

Catalytic system	Temperature (°C)	Conversion (%)	Selectivity[b] to lactam (%)
$RhCl(CO)(PPh_3)_2$	70	23	100
$RhCl(CO)(PPh_3)_2$	100	100	61
1,4-Diphos/$RhCl_3 \cdot 3H_2O$	70	32	0
1,4-Diphos/$RhCl_3 \cdot 3H_2O$	100	95	45

[a] Reaction conditions: 0.038 mmol Rh; $[PPh_3]/[Rh] = 2$; 752 mg (7.6 mmol) isopropylallylamine; 500 mg cyclooctane (internal standard); $P_{CO} = 20$ bar; THF + $H_2O = 30$ ml, 23 v/v% H_2O; 300 rpm; 24 h.

[b] Other products: isopropylamine, *n*-propylisopropylamine, isopropylpropenylamine, *N*-propylideneisopropylamine. 1,4-diphos = 1,4-diphenylphosphinebutane.

catalytic species. In the case of diphosphines/ $RhCl_3 \cdot 3H_2O$ systems, the improvement on the selectivity to lactam was clearly due to a decrease on the formation of hydroformylation products. In the absence of phosphines, $RhCl_3 \cdot 3H_2O/H_2$ gave a low conversion and a very low selectivity to lactam in contrast with the good results (activity and selectivity) obtained with $RhCl_3 \cdot 3H_2O$ under CO/H_2O. In the latter case, the selectivity to lactam was even better than that obtained in the presence of phosphines under CO/H_2. The results of Table 2 also suggest that water behaves both as a source of H_2 (WGS reaction) and as a ligand in the active species, replacing the phosphine ligands which are necessary in the absence of water. Other considerations about results described in Table 3 are: (i) no signals of oxides were observed in the samples taken from solutions of reactions performed under CO/H_2,

confirming that water was responsible for the oxidation; (ii) with 0.3 v/v% water a PPh_3 signal was still observed, suggesting that there was still some $RhCl(CO)(PPh_3)_2$ in the reaction solution. Using 2.3 v/v% water, all PPh_3 ligands in the $RhCl(CO)(PPh_3)_2$ were converted to the oxide.

Table 4 shows the influence of the water content in both conversion and selectivity to lactam. It is clear that up to 2.3 v/v% the increase in water concentration led to an increase on the catalytic activity. In the case of $RhCl_3 \cdot 3H_2O$, the selectivity was significantly affected only at water concentrations ≥ 1.5 v/v%, reaching a maximum of 75% with 23 v/v%. For the $RhCl(CO)(PPh_3)_2$ system, the conversion observed at 0.3 v/v% water was significantly higher than that obtained with $RhCl_3 \cdot 3H_2O$. At this water content some $RhCl(CO)(PPh_3)_2$ is still present (see above),

Table 2

Effects of the replacement of H_2 by H_2O on the carbonylation of isopropylallylamine[a]

1,2-diphos = 1,2-diphenylphosphineethane; 1,3-diphos = 1,3-diphenylphosphinepropane.

Catalytic system	H_2[b,c]			H_2O[c,d]	
	Conversion (%)	Lactam (%)	Hydroformylation products (%)	Conversion (%)	Lactam (%)
$RhCl_3 \cdot 3H_2O$	15	10	0	91	75
$RhCl(CO)(PPh_3)_2$	100	59	33	100	61
$P(OPh_3)/RhCl_3 \cdot 3H_2O$	84	44	0	90	43
1,2-Diphos/$RhCl_3 \cdot 3H_2O$	100	39	41	95	50
1,3-Diphos/$RhCl_3 \cdot 3H_2O$	97	24	43	96	55
1,4-Diphos/$RhCl_3 \cdot 3H_2O$	100	9	20	98	45

[a] Reaction conditions as in Table 1.

[b] $P = 20$ bar ($CO/H_2 = 4/1$); 30 ml THF; 70°C.

[c] Other products: isopropylamine, *n*-propylisopropylamine, isopropylpropenylamine, *N*-propylideneisopropylamine.

[d] 100°C.

Table 3
^{31}P{^{1}H} NMR analyses of the reaction solutions[a]

Catalytic system	$\delta\ ^{31}$P (m; J(Hz))[b]		
	H$_2^c$[c]	H$_2$O[d]	P = O[e]
RhCl(CO)(PPh$_3$)$_2$	29.6 (d; 128.4)	26.6 (s)[f]	26.0 (s)
RhCl(CO)(PPh$_3$)$_2$		29.7 (d; 128.4)[g]	
		26.9 (s)	
1,2-Diphos/RhCl$_3$ · 3H$_2$O	36.0 (d; 109.0)	33.1 (s)	34.2 (s)
1,3-Diphos/RhCl$_3$ · 3H$_2$O	24.0 (d; 124.5)	32.3 (s)	33.9 (s)
1,4-Diphos/RhCl$_3$ · 3H$_2$O	23.0 (d; 124.0)	32.7 (s)	33.6 (s)

[a] Spectra were recorded after addition of C$_6$D$_6$ to the reaction solutions. Reaction conditions as in Table 1.
[b] m = multiplicity.
[c] Reaction temperature: 70°C.
[d] Reaction temperature: 100°C.
[e] The samples were prepared by addition of H$_2$O$_2$ to the C$_6$D$_6$ solutions of the corresponding phosphines.
[f] 2.3 v/v% water.
[g] 0.3 v/v% water.

but there would not be enough water to generate a reasonable concentration of active species with RhCl$_3$ · 3H$_2$O. At 2.3 v/v% water, both precursors seem to converge to the same catalytic species as they lead to almost the same conversions and selectivities. Moreover, yields (conversion × selectivity in lactam) obtained at 23.0 v/v% are 68% and 61% for RhCl$_3$ · 3H$_2$O and RhCl(CO)(PPh$_3$)$_2$, respectively. The promoting effect of water is clear when we compare results obtained with the RhCl$_3$ · 3H$_2$O system with and without water: at 0.3 v/v% water the conversion was twice that obtained without water. This result together with those shown in Table 2 for RhCl$_3$ · 3H$_2$O/H$_2$ and discussed above

strongly suggests that water is needed as a ligand.

In order to evaluate the influence of the solvent polarity on the catalytic behavior of these systems, cyclohexane and toluene were also tested as solvents (Table 5). With cyclohexane no conversion was observed (under CO/H$_2$). The same result was obtained when using a toluene/water biphasic system and RhCl$_3$ · 3H$_2$O/TPPTS as a catalyst precursor. TPPTS appears not to have any particular effect on the catalytic activity (see Table 5, fourth row, and Table 4, first row, for comparison), but it is clear that THF has an important role on the formation of the active species. This effect should be related to the fine tuning of the solution polarity, required for the formation and

Table 4
Effect of the water content on the carbonylation of isopropylallylamine[a]

Catalytic system	H$_2$O (v/v%)	Conversion (%)	Lactam (%)
RhCl$_3$ · 3H$_2$O	23.0	91	75
	2.3	100	49
	1.5	67	48
	1.0	54	38
	0.3	35	36
	0.0	17	33
RhCl(CO)(PPh$_3$)$_2$	23.0	100	61
	2.3	95	40
	0.3	61	53

[a] Reaction conditions as in Table 1; THF + H$_2$O = 30 ml; reaction temperature: 100°C.

Table 5
Influence of the solvent on the carbonylation of isopropylallylamine

Catalytic system	Conversion (%)	Lactam (%)
RhCl(CO)(PPh$_3$)$_2$ /THF[a]	100	59
RhCl(CO)(PPh$_3$)$_2$ /cyclohexane[a]	0	0
RhCl$_3$ · 3H$_2$O + TPPTS/toluene + water[b]	0	0
RhCl$_3$ · 3H$_2$O + TPPTS/THF + water[c]	90	65

[a] P = 20 bar (CO/H$_2$ = 4/1); T = 70°C.
[b] Toluene + water = 30 ml; 50 v/v % water.
[c] THF + water = 30 ml; 23 v/v % water. TPPTS = sodium salt of tris(3-sulfonatophenyl)phosphine tetrahydrate.
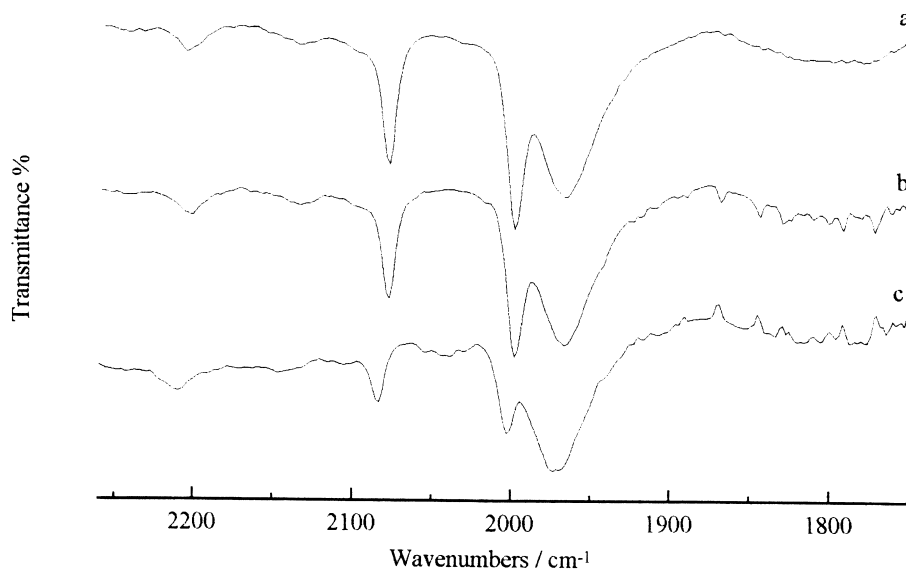
Fig. 1. FT-IR spectra of the reaction solutions: (a) D_2O, 4 h; (b) H_2O, 4 h; (c) H_2O, 24 h. Water content: 0.6 v/v.%. Other reaction conditions as stated in Table 1.

stabilization of the active species which could not be provided by either toluene or cyclohexane [8,9]. It has been shown that complexes like $[trans\text{-}Rh(CO)(S)L_2]^+[OH]^-$, where S = solvent and L = ligand or substrate, could be involved in WGS reactions [8]. If a rhodium cationic species were indeed formed it might be stabilized by the presence of a bulky anion which would lead to a negative effect on the reaction kinetic. In order to evaluate such a hypothesis some experiments were carried out using a bulky anion $[BPh_4]^-$. However, the only effect observed in the presence of $[BPh_4]^-$ (up to $[BPh_4]^-/[Rh] = 30$) was an increase in the concentration of isomerization products, leading to a decrease in selectivity to γ-lactam. This result suggests that the active species in the rate-determining step does not correspond to an ionic species as supposed above, but should have some polar character as indicated by the effect of the solvent. Perhaps high-pressure in situ IR experiments together with electric-conductivity measurements could provide a deeper knowledge on the actual nature of the catalytic intermediates.

On the other hand, hydride species could also be formed through an amine-assisted nucleo-

philic attack of a water molecule on a coordinated carbonyl ligand. Infrared studies of the reaction solutions, employing H_2O or D_2O, failed to give any evidence for such a hydride formation (Fig. 1): bands at 2077, 1998 and 1966 cm^{-1} could all be assigned to terminal carbonyl stretching since none of them was shifted (nor had its intensity affected) in the presence of D_2O (ν_{M-H} is expected around 2000 cm^{-1} [10]). According to the relative intensity of these bands after 4-h and 24-h reaction time, a time-dependent isomerization from
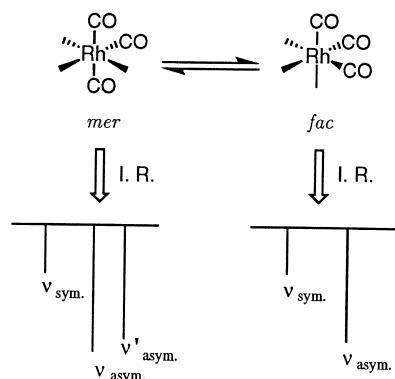
Scheme 3.

a mer- to a fac-tricarbonylrhodium(I) species seems to take place (Scheme 3). Although there are several examples of rhodium hydride complexes in the literature, the non-observation of a hydride species in our case does not rule out its presence as an intermediate in the catalytic cycle. This failure can be explained by the lack of stabilizing ligands, such as phosphines, in the rhodium coordination sphere.

4. Conclusions

This work describes for the first time the successful replacement of hydrogen and phosphorated ligands by water in the rhodium-catalyzed carbonylation of alkylallylamines to produce γ-lactams, which is, to our knowledge, the easiest way ever reported for the synthesis of such valuable products. The reaction of *N*-isopropylallylamine with CO/H_2O at 100°C in the presence of $RhCl_3 \cdot x H_2O$ ([substrate]/[Rh] molar ratio = 200) gives 100% conversion with 75% of γ-lactam formation, while that carried out with CO/H_2 gives only 15% conversion with 10% yield. An increase in both conversion and selectivity to lactam could be ascribed to the suppression of the hydroformylation pathway. A further enhancement in the selectivity was prevented by the water-induced hydrogenation–isomerization side reactions.

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