



## Carbonylation of 1-hexene catalyzed by *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) complexes in aqueous tetrabutylammonium hydrogensulfate solutions

Germán Gascón<sup>a</sup>, Marisol C. Ortega<sup>a,\*</sup>, José D. Suárez<sup>a</sup>, Alvaro J. Pardey<sup>a,\*</sup>, Clementina Longo<sup>b</sup>, Sergio A. Moya<sup>c</sup>

<sup>a</sup> Centro de Equilibrios en Solución, Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela

<sup>b</sup> Centro de Investigación y Desarrollo de Radiofármacos, Facultad de Farmacia, Universidad Central de Venezuela, Caracas, Venezuela

<sup>c</sup> Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile

### ARTICLE INFO

#### Article history:

Received 11 December 2007

Received in revised form 28 April 2008

Accepted 17 May 2008

Available online 28 May 2008

#### Keywords:

Rhodium complexes

1-Hexene

Hydrocarboxylation

Hydroformylation

Water–gas shift reaction

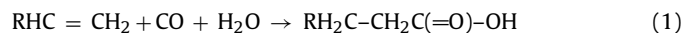
### ABSTRACT

In aqueous solution of tetrabutylammonium hydrogensulfate (N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub>), rhodium complexes like *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) (amine = pyridine, 4-picoline, 3-picoline, 2-picoline, 3,5-lutidine or 2,6-lutidine) promote the carbonylation of 1-hexene to heptanoic acid and heptanal under carbon monoxide atmosphere. Gaseous by-products (H<sub>2</sub> and CO<sub>2</sub>) from the catalysis of the water–gas shift reaction (WGS) are also observed. The catalytic activities for heptanoic acid and heptanal production depend on the nature of the coordinate amine to the rhodium center for [Rh] = 1 × 10<sup>-4</sup> mol, [1-hexene] = 0.05 mol, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), S/C = 500, P(CO) = 22 atm at 150 °C. Analyses of kinetic results for the Rh/4-picoline system (one of the more active and the most stable catalyst among tested) towards the carbonylation reaction for the organic products formation show a nonlinear dependence on total rhodium concentration and on N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> amount in the range of studies. The last result suggested that the salty medium stabilize the ionic Rh catalytic species formed under the reaction conditions, therefore enhancing the reactivity. The increase in P(CO) is accompanied by improvement in the catalytic activities of oxygenated products, then reaches a maximum and starts decreasing at higher P(CO). These data are discussed in terms of catalytic cycles bearing a common Rh–H catalytic species.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

The synthesis of oxygenated organic products by reaction of an olefinic substrate with CO and water (Eq. (1)) in the presence of transition metal complexes to give carboxylic acids (hydrocarboxylation reaction) is well known [1,2].



Some examples of carbonylation reactions promoted by homogeneous and immobilized rhodium [3–5], cobalt [6] and water soluble–palladium complexes [7] under CO/H<sub>2</sub>O have been reported.

A soluble ruthenium(II) complex *fac*-[Ru(CO)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(C(O)C<sub>2</sub>H<sub>5</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] using wet tetrabutylammonium hydrogensulfate salt under CO have demonstrated its applicability as catalyst for hydrocarboxylation and hydrocarbonylation of ethylene to propionic acid and to diethyl ketone and propanal, respectively [8].

As well, soluble cationic carbonylrhodium(I) complexes of pyridine and related ligands catalyzed the hydroformylation and oligomerization of CO/ethylene in aqueous tetrabutylammonium hydrogensulfate solutions [9]. It has been stated that the salty medium stabilize the catalytic species formed under the reaction conditions.

Continuing our work on carbonylrhodium(I) complexes of pyridine and related ligands dissolved in the salty medium of tetrabutylammonium hydrogensulfate, we report here the influence of the nature of the coordinated pyridine ligand as well as the effect of variations in reaction parameters on catalytic hydrocarboxylation and hydroformylation of 1-hexene in CO/water by these rhodium(I) complexes and the mechanistic implications.

### 2. Experimental

#### 2.1. Materials and instrumentation

Pyridine (py), methyl pyridines (2-picoline (2-pic), 3-picoline (3-pic), and 4-picoline (4-pic)) and dimethyl pyridines (3,5-lutidine (3,5-lut) and 2,6-lutidine (2,6-lut)) were obtained from Aldrich

\* Corresponding authors. Fax: +58 212 6051225.

E-mail addresses: [marisol.ortega@ciens.ucv.ve](mailto:marisol.ortega@ciens.ucv.ve) (M.C. Ortega), [alvaro.pardey@ciens.ucv.ve](mailto:alvaro.pardey@ciens.ucv.ve) (A.J. Pardey).

**Table 1**  
Carbonylation of 1-hexene in aqueous tetrabutylammonium hydrogensulfate catalyzed by the *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) complexes<sup>a</sup>

Amine (pK <sub>a</sub> ) <sup>b</sup>	[Heptanoic acid] <sup>c</sup> (mol × 10 <sup>-4</sup> )	[Heptanal] <sup>c</sup> (mol × 10 <sup>-4</sup> )	TF(heptanoic acid) <sup>c</sup> (yield %; selectivity %)	TF(heptanal) <sup>c</sup> (yield %; selectivity %)
Pyridine (5.27)	14	10	46 (2.9; 58)	31 (2.1; 42)
3-Picoline (5.52)	20	11	70 (4.2; 64)	35 (2.3; 36)
2-Picoline (5.97)	16	18	55 (3.3; 47)	64 (3.8; 53)
4-Picoline (6.00)	25	38	90 (5.2; 40)	139 (7.9; 60)
3,5-Lutidine (6.63)	34	7	131 (7.1; 83)	26 (1.5; 17)
2,6-Lutidine (6.75)	21	45	73 (4.4; 32)	161 (9.4; 68)

<sup>a</sup> [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), P(CO) = 22 atm at 150 °C for 7 h.

<sup>b</sup> From Ref. [13].

<sup>c</sup> TF(product) = [(mol of product)/((mol of Rh) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%.

and distilled over KOH. Water was doubly distilled. All gas mixtures He/H<sub>2</sub> (91.4%/8.6%, v/v), CO/CH<sub>4</sub> (95.8%/4.2%, v/v) and CO/CH<sub>4</sub>/CO<sub>2</sub>/H<sub>2</sub> (84.8%/5.1%/5.3%/4.8%, v/v) were purchased from BOC gases and were used as received. The complexes of the type *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) (amine = 4-pic, 3-pic, 2-pic, py, 3,5-lut or 2,6-lut) were synthesized and characterized as reported by Denise and Pannetier [10] and their IR spectra in chloroform demonstrated their identity and purity (two strong bands in the ν<sub>(CO)</sub> region at 2095 and 2020 cm<sup>-1</sup>). These complexes will be referred as Rh(amine)<sub>2</sub> complexes.

Gas samples analyses from catalysis and kinetics runs were performed as described in detail previously [11] on a Hewlett-Packard 5890 Series II programmable (ChemStation) gas chromatograph fitted with a thermal conductivity detector. The column employed was Carbosieve-B (80–100 mesh) obtained from Hewlett-Packard and using the He/H<sub>2</sub> mixture as the carrier gas. Analyses of liquid phase were done on a Buck Scientific 910 programmable gas chromatograph fitted with a HP-1 (methyl silicone gum, 50 m × 0.323 mm × 0.17 μm) column and flame ionization detector, and using He as the carrier gas.

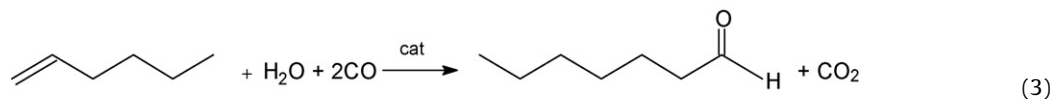
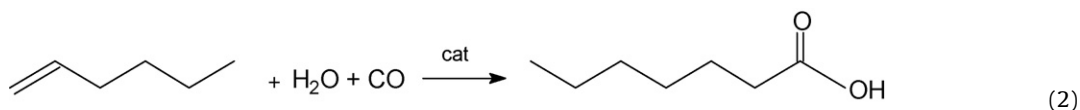
A Varian Chrompack 3800 programmable gas chromatograph fitted with a CP-Sil-8-CB (phenyldimethylpolysiloxane) (30 m × 0.250 mm) column using He as the carrier gas and a Varian Chrompack, Saturn 2000 mass selective detector were used to confirm the identity of the organic reaction

temperature-controlled heating device at typically 150 ± 1 °C and mechanically stirred (rpm = 650) for 7 h. These pressures and temperatures were chosen as an average from previously reported systems [11]. The CH<sub>4</sub> was used as internal standard to allow calculation of absolute quantities of CO consumed and H<sub>2</sub> and CO<sub>2</sub> produced. In addition, calibration curves were prepared periodically for CO, CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub>, and analyzing known mixtures checked their validities. Moreover, liquid samples were removed and analyzed by GC and GC-MS. Peak position of various reaction products were compared and matched with the retention times of authentic samples. The amounts of organic products were determined by using the response factor method for gas chromatographic analyses [12].

### 3. Results and discussion

#### 3.1. General aspects

The Rh(amine)<sub>2</sub> catalysts were investigated as precursors for the catalytic reactions of 1-hexene/CO in aqueous solution of tetrabutylammonium hydrogensulfate. These catalytic systems are known to be active for 1-hexene hydrocarboxylation Eq. (2) and hydroformylation Eq. (3), and the water–gas shift reaction (WGSR), Eq. (4). Also, traces (~1%) of products coming from isomerization of 1-hexene under catalysis conditions were observed.



products at the end of each run. Also the organic products were separated by column chromatography and analyzed by <sup>13</sup>C and <sup>1</sup>H NMR in a Jeol Eclipse 270 NMR spectrometer.

#### 2.2. Catalyst testing

Catalytic runs were carried out in a 250 mL mechanically stirred stainless steel Parr autoclave charged with a given amount ((1–30) × 10<sup>-5</sup> mol) of the *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) complex, variable amounts of 1-hexene (1.2–6.1 mL), 40 mL of water, variable amounts of tetrabutylammonium hydrogensulfate salt (2.4 (5.6 wt.%)–26.8 g (67 wt.%)) and pressurized with CO/CH<sub>4</sub> (22–57 atm) at 110–170 °C. The autoclave was placed in a

The relative extent of the competing catalytic reactions (Eqs. (2)–(4)) can be established by comparing the amounts of the products. The results are shown in Tables 1 and 2. Further control experiments show that activity toward the WGSR and the carbonylation of 1-hexene under CO was not observed when the mixture of an aqueous solution of tetrabutylammonium hydrogensulfate with 1-hexene was tested under similar experimental conditions in the absence of any of these Rh(amine)<sub>2</sub> catalysts.

#### 3.2. Hydrocarboxylation and hydroformylation catalysis

Table 1 summarizes the results of the catalytic carbonylation of 1-hexene by the Rh(amine)<sub>2</sub> complexes dissolved in aqueous solution of tetrabutylammonium hydrogensulfate under CO

**Table 2**WGSR in aqueous tetrabutylammonium hydrogensulfate catalyzed by the *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) complexes<sup>a</sup>

Amine (pK <sub>a</sub> ) <sup>b</sup>	[H <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	[CO <sub>2</sub> ] (total) (mol × 10 <sup>-4</sup> )	[CO <sub>2</sub> ] (WGSR) <sup>c</sup> (mol × 10 <sup>-4</sup> )	TF(H <sub>2</sub> ) <sup>d</sup>	TF(CO <sub>2</sub> ) <sup>d</sup>
Pyridine (5.27)	11	20	11	36	36
3-Picoline (5.52)	13	21	13	42	46
2-Picoline (5.97)	12	33	12	39	42
4-Picoline (6.00)	15	53	15	49	53
3,5-Lutidine (6.63)	14	25	14	44	51
2,6-Lutidine (6.75)	13	62	15	40	54

<sup>a</sup> [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), P(CO) = 22 atm at 150 °C for 7 h.<sup>b</sup> From Ref. [13].<sup>c</sup> [CO<sub>2</sub>](WGSR) = [CO<sub>2</sub>](total) – [CO<sub>2</sub>](hydroformylation).<sup>d</sup> TF(gas) = [(mol of gas)/(mol of Rh) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%.

atmosphere. <sup>1</sup>H NMR, GC and GC–MS analyses of the liquid phases allowed identifying heptanoic acid and heptanal as products coming from the 1-hexene hydrocarboxylation Eq. (2) and hydroformylation Eq. (3), respectively.

The reactivity toward heptanoic acid formation for this Rh(amine)<sub>2</sub> system proved also to be dependent on the nature of the heterocyclic nitrogen ligand coordinated to the rhodium center, for example the TF(heptanoic acid) (24 h<sup>-1</sup>) values for these carbonyl rhodium complexes followed the order: 3,5-lut (131) > 4-pic (90) > 2,6-lut (73) > 3-pic (70) > 2-pic (55) > py (46) under the same catalytic conditions. The results show the positive effect of amine basicity on the formation of the heptanoic acid (thermodynamic product), which increases with pK<sub>a</sub> augmentation of the amine ligand in absence of steric effect (present in the 2-picoline and 2,6-lutidine); namely, 3,5-lut displays the highest activity. However, reaction rates decreased markedly with increasing steric hindrance of the coordinated amine as shown by the lower activity of 2-picoline and in a lesser extent by the 2,6-lutidine. These results suggest a critical steric parameter, which can be viewed as the effect of competition for binding to the catalytic center, which is more affected by steric constraints than by electronic effects. Even that the TF(heptanal)/(24 h<sup>-1</sup>) values follow, in general, a similar tendency to the above described product, namely: 2,6-lut (161) > 4-pic (139) > 2-pic (64) > 3-pic (35) > py (31) > 3,5-lut (26), the steric constraints contrary to the observed for the heptanoic acid have small influence on the yield of the heptanal (kinetics product). The observed low TF(heptanal) (24 h<sup>-1</sup>) value for 3,5-lut lies on the high selectivity (83%) towards heptanoic acid production by this Rh(3,5-lut)<sub>2</sub> catalytic system.

Further the total yield of the principal products (heptanoic acid and heptanal) and their selectivity also depends on the nature of the amine ligand. For example, the 1-hexene conversion values follow the order: 2,6-lut (13.8%) > 4-pic (13.1%) > 3,5-lut (8.6%) > 2-pic (7.1%) > 3-pic (6.5%) > py (5.0%), being the Rh(2,6-lut)<sub>2</sub> and Rh(4-pic)<sub>2</sub> the most catalytic active systems towards carbonylation. Further, both Rh(2,6-lut)<sub>2</sub> and Rh(4-pic)<sub>2</sub> catalytic systems show a preferential selectivity towards the heptanal product, contrary to the observed for the Rh(3,5-lut)<sub>2</sub> catalytic system, which it shows a higher selectivity towards the heptanoic acid.

### 3.3. WGSR catalysis

The relationship between WGSR and olefin carbonylation catalysis under CO/H<sub>2</sub>O by transition metal complexes has been illustrated in the scientific literature [14]. All of these Rh(amine)<sub>2</sub>/aq. N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> systems, are also active for the catalysis of the WGSR under the conditions required for the catalytic carbonylation of 1-hexene. GC analyses of the gas phase of the catalytic runs allowed the identification of H<sub>2</sub> and CO<sub>2</sub> as sole gaseous products. The H<sub>2</sub> and certain amount of CO<sub>2</sub> come from the WGSR. Another portion of the CO<sub>2</sub> produced comes from the catalytic

hydroformylation of 1-hexene under CO/H<sub>2</sub>O, Eq. (3) and the total CO<sub>2</sub> mass balances both, Eqs. (3) and (4).

Additionally, a control experiment shows no WGSR activity in the absence of any of soluble Rh(amine)<sub>2</sub> compounds under similar reaction conditions. The results described in Table 2 show that TF(H<sub>2</sub>) values are almost similar, suggesting that the nature of the amine does not control WGSR rates in these systems. Similar results were observed in the catalytic hydroesterification and hydroformylation–acetalization of 1-hexene by *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) (amine = pyridine, 2-picoline, 3-picoline, 4-picoline, 3,5-lutidine or 2,6-lutidine) complexes dissolved in methanol under carbon monoxide atmosphere [11].

However, a different tendency was observed in the catalysis of the WGSR by *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) complexes dissolved in 80% aqueous pyridine or substituted pyridines. For example the TF(H<sub>2</sub>) decreased from 80 (24 h)<sup>-1</sup> for the 4-picoline system to 1 (24 h)<sup>-1</sup> for the 2,6-lutidine system under the following catalytic conditions: [Rh] = 10 mM, 10 mL of 80% aqueous amine under P(CO) = 0.9 atm at 100 °C. In those Rh(amine)<sub>2</sub>/aqueous amine systems the steric factor controls the rate of H<sub>2</sub> formation [15].

### 3.4. Kinetics studies

The following kinetics studies were made using the Rh(4-pic)<sub>2</sub> system despite the Rh(2,6-lut)<sub>2</sub> is the most active for the carbonylation reaction. The reason lies in the better stability of the *cis*-[Rh(CO)<sub>2</sub>(4-pic)<sub>2</sub>](PF<sub>6</sub>) complex in comparison to *cis*-[Rh(CO)<sub>2</sub>(2,6-lut)<sub>2</sub>](PF<sub>6</sub>), which tends to decompose in relatively short times on air.

For the Rh(4-pic)<sub>2</sub> system the effects of varying the carbon monoxide pressure, the temperature, rhodium concentration, the 1-hexene/Rh molar ratio and the tetrabutylammonium hydrogensulfate amount on WGSR and carbonylation of 1-hexene were studied.

#### 3.4.1. Effect of the carbon monoxide pressure

The effect of varying the CO pressure for the Rh(4-pic)<sub>2</sub> system is summarized in Table 3. Fig. 1 shows the plot of TF(heptanoic acid)/24 h, TF(heptanal)/24 h and TF(H<sub>2</sub>)/24 h values vs. P(CO). As can be inferred from Table 3 and Fig. 1, increase in P(CO) from 22 atm is accompanied by improvement in the TF(heptanoic acid)/24 h value, then reaches a maximum at P(CO) = 38 atm and starts decreasing at P(CO) ≥ 47 atm. Also, the TF(heptanal)/24 h values increase from 22 to 30 atm of CO and then decreasing at P(CO) > 38 atm. However, for the competitive WGSR, the TF(H<sub>2</sub>)/24 h values increase almost linear (from 35 to 88 (24 h)<sup>-1</sup>) in the carbon monoxide 22–57 (atm) range.

Accordingly, while the carbonylation reaction is disfavored at high P(CO), the opposite occurs with WGS reaction. These findings indicate that the catalytic activity for the carbonylation reaction

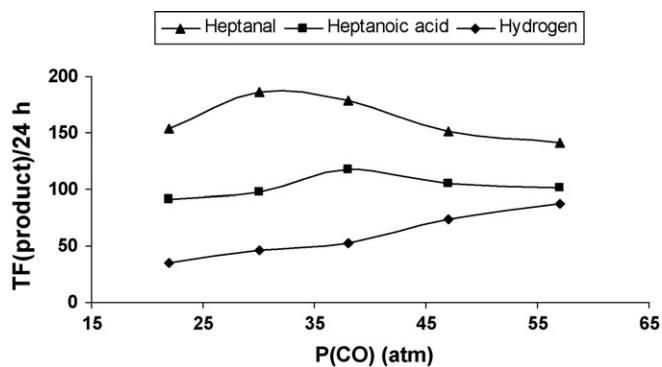
**Table 3**  
The effects of the carbon monoxide pressure variation on WGS and carbonylation of 1-hexene in aqueous tetrabutylammonium hydrogensulfate catalyzed by the *cis*-[Rh(CO)<sub>2</sub>(4-picoline)<sub>2</sub>](PF<sub>6</sub>) complex<sup>a</sup>

<i>P</i> (CO) (atm)	[CO <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	[H <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	TF(H <sub>2</sub> ) <sup>b</sup>	[HA] <sup>c</sup> (mol × 10 <sup>-4</sup> )	TF(HA) <sup>b,c</sup> (yield %; selectivity %)	[Heptanal] (mol × 10 <sup>-4</sup> )	TF(heptanal) <sup>b</sup> (yield %; selectivity %)
22	54	10	35	26	91 (18.4; 37)	44	154 (10.9; 63)
30	65	13	46	28	97 (22.2; 34)	53	186 (11.7; 66)
38	67	15	53	33	118 (21.3; 40)	51	179 (13.8; 60)
47	65	21	74	30	105 (18.0; 40)	43	151 (12.6; 60)
57	68	25	88	29	101 (16.7; 42)	40	141 (12.1; 58)

<sup>a</sup> [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), at 150 °C for 7 h.

<sup>b</sup> TF(product) = [(mol of product)/(mol of Rh) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%.

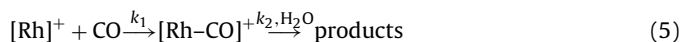
<sup>c</sup> HA: heptanoic acid.



**Fig. 1.** A plot of TF(product)/24 h vs. *P*(CO): heptanal (▲), heptanoic acid (■) and hydrogen (◆). Reaction conditions: [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), at 150 °C for 7 h. Lines drawn for illustrative purpose only.

does not follow a linear dependence on *P*(CO) in the range of 22–57 atm and suggest the formation of a less-active rhodium carbonyl species toward this type of reaction, at high CO pressure or reversible addition of CO before the rate determining for organic products formation.

The plot of TF(H<sub>2</sub>) values vs. *P*(CO) shown in Fig. 1, is almost linear, indicating that the reaction is first order in [CO] in the 22–57 atm range. Based on the first order in [CO] we suggest a possible mechanism for the WGS where the rate-limiting step (*k*<sub>2</sub>) is preceded by coordination of CO, e.g.



The WGS rate law for such behavior would be:

$$\text{rate} = k_1 k_2 P(\text{CO}) [\text{Rh}]_{\text{tot}} \quad (6)$$

where [Rh]<sub>tot</sub> = [Rh]<sup>+</sup> + [Rh-CO]<sup>+</sup> and *k*<sub>1</sub> includes the solubility of CO in the medium and *k*<sub>2</sub> the [solvent]. The above expression, Eq. (6)

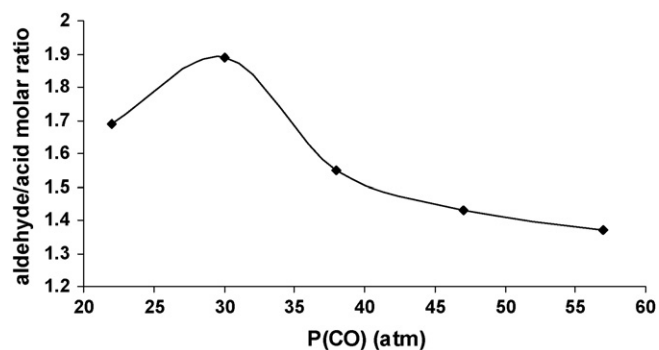
**Table 4**  
The effects of the temperature (*T*) variation on WGS and carbonylation of 1-hexene in aqueous tetrabutylammonium hydrogensulfate catalyzed by the *cis*-[Rh(CO)<sub>2</sub>(4-picoline)<sub>2</sub>](PF<sub>6</sub>) complex<sup>a</sup>

<i>T</i> (°C)	[CO <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	[H <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	TF(H <sub>2</sub> ) <sup>b</sup>	[HA] <sup>c</sup> (mol × 10 <sup>-4</sup> )	TF(HA) <sup>b,c</sup> (yield %; selectivity %)	[heptanal] (mol × 10 <sup>-4</sup> )	TF(heptanal) <sup>b</sup> (yield %; selectivity %)
110	26	3	11	12	42 (5.0; 36)	21	73 (8.8; 64)
130	48	5	18	18	64 (7.5; 30)	42	150 (17.6; 70)
140	57	9	32	22	78 (9.2; 32)	47	167 (19.7; 68)
150	54	10	36	26	91 (10.9; 37)	44	154 (18.4; 63)
170	47	25	90	21	77 (8.8; 48)	23	85 (9.6; 52)

<sup>a</sup> [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), *P*(CO) = 22 atm for 7 h.

<sup>b</sup> TF(product) = [(mol of product)/(mol of Rh) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%.

<sup>c</sup> HA: heptanoic acid.



**Fig. 2.** A plot of aldehyde/acid molar ratio vs. *P*(CO). Reaction conditions: [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), at 150 °C for 7 h. Line drawn for illustrative purpose only.

can be reduced to:

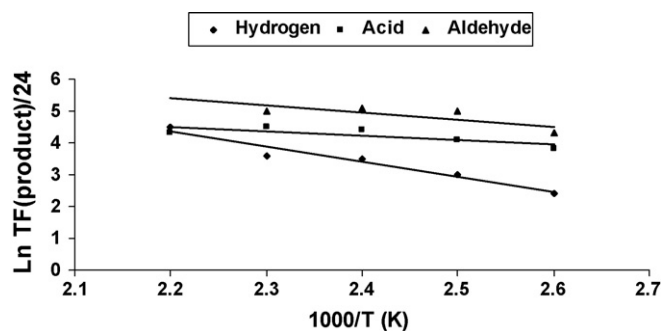
$$\text{TF}(\text{H}_2) = k_1 k_2 P(\text{CO}) \quad (7)$$

For this kinetics model plots of TF(H<sub>2</sub>) vs. *P*(CO) should be linear with slopes of *k*<sub>1</sub>*k*<sub>2</sub> and zero intercept. For example, the TF(H<sub>2</sub>) plot vs. *P*(CO) is linear with nearly a zero intercept value as predicted by Eq. (7). Further, by plotting Ln TF(H<sub>2</sub>) versus Ln *P*(CO) a slope with a value ca. 1 is observed.

Further, the selectivity between the organic products changes with the increase of the *P*(CO) in the 22–57 atm range (Fig. 2), namely the aldehyde/acid molar ratio increase from 1.69 (*P*(CO) = 22 atm) to 1.89 (*P*(CO) = 30 atm) reaching its maximum value at this CO pressure, then decreasing from 1.55 (*P*(CO) = 38 atm) to 1.37 (*P*(CO) = 57 atm), indicating that formation of the heptanoic acid (thermodynamic product) is favorable at CO pressure >30 atm.

### 3.4.2. Effect of the temperature

As shown in Table 4, varying the temperature from 110 to 150 °C, increases the production of heptanoic acid and for *T* = 170 °C



**Fig. 3.** The Arrhenius plot for heptanal (▲), heptanoic acid (■) and hydrogen (◆) production. Reaction conditions:  $[Rh] = 1 \times 10^{-4}$  mol, 1-hexene = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, 40 mL of water (2.2 mol); 2.4 g of  $N(C_4H_9)_4HSO_4$  (5.6 wt.%),  $P(CO) = 22$  atm for 7 h.

decreases its production. On the other hand, heptanal formation increases from 110 to 140 °C and then decreasing its production. The production of  $H_2$  increases almost linear in the 110–170 °C range.

To determine the activation parameters for the WGS and carbonylation reaction, the  $TF(\text{product})/24$  h values for the  $Rh(4\text{-pic})_2$  system were measured at various temperatures in the 100–170 °C range (Table 4) under  $P(CO) = 22$  atm. This pressure was chosen for security reason. Fig. 3 displays the  $\ln TF(\text{product})/24$  h values vs.  $1000/T$  plot for  $[Rh] = 1 \times 10^{-4}$  mol, [1-hexene] = 6.1 mL (0.05 mol), 1-hexene/Rh = 500, for 7 h. The Arrhenius plot for the  $H_2$  production is linear in the 100–170 °C range with an apparent activation energy of 37 kJ/molK. Further, the apparent activation energies obtained from the slope of the heptanal and heptanoic acid production reaction are 16 and 26 kJ/mol K, respectively, indicating that hydroformylation is kinetically favorable over hydrocarboxylation. At high temperatures the catalysis of the WGS by this  $Rh(4\text{-pic})_2$  is favorable. Accordingly, the WGS starts competing at a high extension with the carbonylation reactions causing a decrease of the organic products.

### 3.4.3. Effect of the 1-hexene/Rh molar ratio

The effect of varying the 1-hexene concentration on the  $(1-5) \times 10^{-2}$  mol range for the  $Rh(4\text{-pic})_2$  catalytic system is summarized in Table 5 and shown in Fig. 4. The  $TF(HA)$  increases from 51 ( $24 h^{-1}$ ) ([1-hexene] =  $1 \times 10^{-2}$  mol) and reaches a saturation point of about 91 ( $24 h^{-1}$ ) at higher 1-hexene/Rh molar ratio. Additionally, the  $TF(\text{heptanal})$  increases from 61 ( $24 h^{-1}$ ) (1-hexene/Rh = 150), reaching a maximum value of 154 ( $24 h^{-1}$ ) at 1-hexene/Rh = 240 and then decreases to 139 ( $24 h^{-1}$ ) at 1-hexene/Rh = 500 indicative of a reversible addition of 1-hexene to rhodium center on the 1-hexene/Rh (100–500) molar ratio range. Fig. 4 shows the plot of  $TF(\text{product})/24$  h vs. [1-hexene]/Rh molar ratio under 22 atm of CO at 150 °C and allows to visualize better this behavior.

**Table 5**

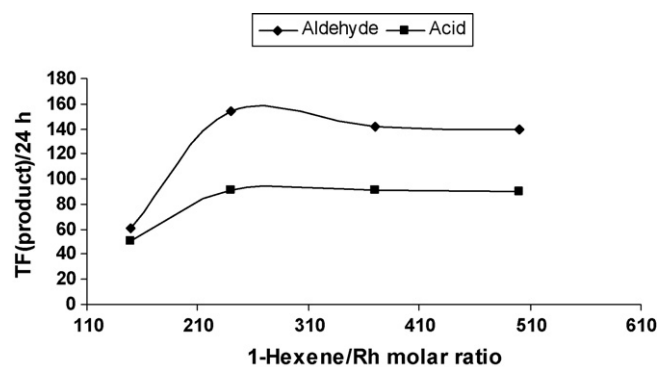
The effects of the 1-hexene/Rh molar ratio variation (S/C) on WGS and carbonylation of 1-hexene in aqueous tetrabutylammonium hydrogensulfate catalyzed by the  $cis\text{-}[Rh(CO)_2(4\text{-picoline})_2](PF_6)$  complex<sup>a</sup>

S/C	$[CO_2]$ (mol $\times 10^{-4}$ )	$[H_2]$ (mol $\times 10^{-4}$ )	$TF(H_2)^b$	$[HA]^c$ (mol $\times 10^{-4}$ )	$TF(HA)^{b,c}$ (yield %; selectivity %)	$[Heptanal]$ (mol $\times 10^{-4}$ )	$TF(\text{heptanal})^b$ (yield %; selectivity %)
150	19	2	7	14	51 (5.9; 45)	17	61 (7.1; 55)
240	54	10	35	26	91 (10.9; 37)	44	154 (18.4; 63)
370	51	12	42	26	91 (10.9; 39)	40	142 (16.7; 61)
500	53	12	42	25	90 (10.9; 40)	38	139 (15.9; 60)

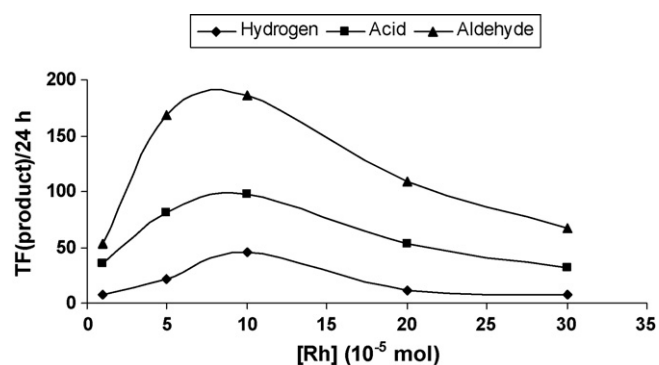
<sup>a</sup>  $[Rh] = 1 \times 10^{-4}$  mol, 1-hexene = 1.2–6.1 mL (0.01–0.05 mol), 40 mL of water (2.2 mol); 2.4 g of  $N(C_4H_9)_4HSO_4$  (5.6 wt.%),  $P(CO) = 22$  atm 150 °C for 7 h.

<sup>b</sup>  $TF(\text{product}) = [(\text{mol of product})/(\text{mol of Rh}) \times (\text{rt})] \times 24$  h, where (rt) = reaction time in hours. Experimental uncertainty <10%.

<sup>c</sup> HA: heptanoic acid.



**Fig. 4.** A plot of  $TF(\text{product})/24$  h vs. 1-hexene/Rh molar ratio: heptanal (◆) and heptanoic acid (■). Reaction conditions:  $[Rh] = 1 \times 10^{-4}$  mol, 1-hexene = 1.2–6.1 mL (0.01–0.05 mol), 40 mL of water (2.2 mol); 2.4 g of  $N(C_4H_9)_4HSO_4$  (5.6 wt.%),  $P(CO) = 22$  atm 150 °C for 7 h. Lines drawn for illustrative purpose only.



**Fig. 5.** A plot of  $TF(\text{product})/24$  h vs.  $[Rh]$ : heptanal (▲), heptanoic acid (■) and hydrogen (◆). Reaction conditions: 1-hexene = (0.3–9.0) mL, 1-hexene/Rh = 240, 40 mL of water (2.2 mol); 2.4 g of  $N(C_4H_9)_4HSO_4$  (5.6 wt.%),  $P(CO) = 30$  atm at 150 °C for 7 h. Lines drawn for illustrative purpose only.

### 3.4.4. Effect of the Rh concentration

Catalytic runs were carried out for a series of different rhodium concentrations over the range  $(1-30) \times 10^{-5}$  mol (Table 6). A typical run involved determination of  $TF/24$  h as a function of  $[Rh]$  in 5.6% aqueous tetrabutylammonium hydrogensulfate, [1-hexene]/Rh = 240 under  $P(CO) = 30$  atm at 150 °C (under this temperature, the 1-hexene conversion to carbonyl products reaches the highest value of 29.3% (Table 4)). The amount of 1-hexene was varied from 0.3 mL ( $2.4 \times 10^{-3}$  mol) at  $[Rh] = 1 \times 10^{-5}$  mol to 9.0 mL ( $72 \times 10^{-3}$  mol) at  $[Rh] = 30 \times 10^{-5}$  mol in order to keep the molar ratio 1-hexene/Rh = 240 in all runs. Fig. 5 shows the plot of  $TF(\text{product})/24$  h vs.  $[Rh]$ .

An increase in  $[Rh]$  from  $1 \times 10^{-5}$  mol further increased the  $TF(\text{product})/24$  h values, reaching a maximum at  $[Rh] = 10 \times 10^{-5}$  mol. The activity toward  $H_2$ , heptanoic acid

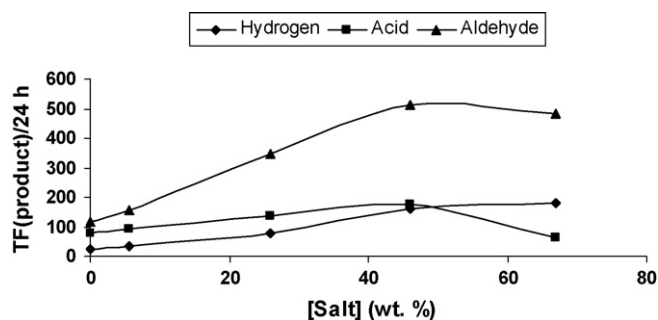
**Table 6**  
The effects of the rhodium concentration variation ([Rh]) on WGS and carbonylation of 1-hexene in aqueous tetrabutylammonium hydrogensulfate catalyzed by the *cis*-[Rh(CO)<sub>2</sub>(4-picoline)<sub>2</sub>](PF<sub>6</sub>) complex<sup>a</sup>

[Rh] (mol × 10 <sup>-5</sup> )	[CO <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	[H <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	TF(H <sub>2</sub> ) <sup>b</sup>	[HA] <sup>c</sup> (mol × 10 <sup>-4</sup> )	TF(HA) <sup>b,c</sup> (yield %; selectivity %)	[Heptanal] (mol × 10 <sup>-4</sup> )	TF(heptanal) <sup>b</sup> (yield %; selectivity %)
1	19	2	7	10	35 (40.0; 40)	15	53 (60.0; 60)
5	57	6	21	23	81 (19.1; 32)	48	168 (40.0; 68)
10	65	13	46	28	97 (11.7; 35)	53	186 (22.1; 65)
20	34	3	11	15	53 (3.1; 33)	31	109 (6.5; 67)
30	20	2	7	9	32 (1.3; 32)	19	67 (2.6; 68)

<sup>a</sup> 1-Hexene = (0.3–9.0) mL, 1-hexene/Rh = 240, 40 mL of water (2.2 mol); 2.4 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (5.6 wt.%), P(CO) = 30 atm at 150 °C for 7 h.

<sup>b</sup> TF(product) = [(mol of product)/(mol of Rh) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%.

<sup>c</sup> HA: heptanoic acid.



**Fig. 6.** A plot of TF(product)/24 h vs. [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub>]: heptanal (▲), heptanoic acid (■) and hydrogen (◆). Reaction conditions: [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 3 mL (0.024 mol), 40 mL of water (2.2 mol); 1-hexene/Rh = 240, P(CO) = 22 atm at 150 °C for 7 h. Lines drawn for illustrative purpose only.

and heptanal production starts decreasing at [Rh] > 10 × 10<sup>-5</sup> mol. These findings indicate that catalyst activity does not follow a linear dependence on [Rh] in the range of ((1–30) × 10<sup>-5</sup> mol) and suggest the intervention of less-active polynuclear species [16].

### 3.4.5. Effect of the tetrabutylammonium hydrogensulfate amount

A remarkable result related to the heptanoic acid and heptanal formations catalyzed by the Rh(4-pic)<sub>2</sub> system is observed when the concentration of the (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)<sub>4</sub>NHSO<sub>4</sub> salt was increased from 2.4 g (5.6 wt.%) to 80.0 g (67.0 wt.%) at 1-hexene/Rh = 240 molar ratio under 22 atm of CO at 150 °C. The 1-hexene/Rh = 240 molar ratio chosen in this study resulted the optimum value (see above) among studied. The total conversion of 1-hexene increases from 29.3% for [salt] = 5.6 wt.%, reaching a maximum value of 81.7% for [salt] = 46.0 wt.% and decrease to 63.8% for [salt] = 67.0 wt.% due to the observed diminution of the solubility of 1-hexene at high concentration of the (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)<sub>4</sub>NHSO<sub>4</sub> salt.

As observed in Table 7 and Fig. 6, the TF(heptanal)/24 h and TF(heptanoic acid)/24 h reach the highest values of 514 (yield of 60.9% and selectivity ca. 67% at 1-hexene total conversion of 81.7% in 7 h) and 176 (24 h)<sup>-1</sup> (yield of 20.8% and selectivity ca. 33%), respec-

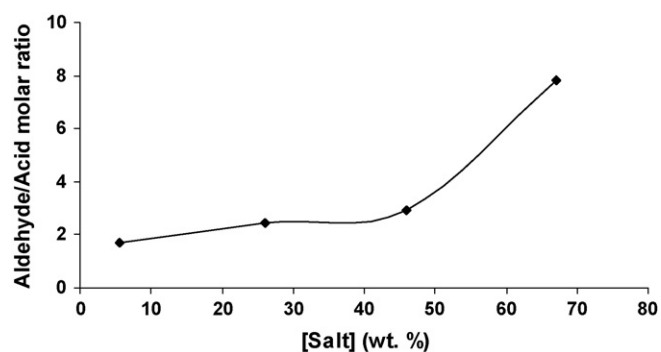
**Table 7**  
The effects of the tetrabutylammonium hydrogensulfate concentration ([salt]) variation on WGS and carbonylation of 1-hexene catalyzed by the *cis*-[Rh(CO)<sub>2</sub>(4-picoline)<sub>2</sub>](PF<sub>6</sub>) complex<sup>a</sup>

[Salt] (wt.%)	[CO <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	[H <sub>2</sub> ] (mol × 10 <sup>-4</sup> )	TF(H <sub>2</sub> ) <sup>b</sup>	[HA] <sup>c</sup> (mol × 10 <sup>-4</sup> )	TF(HA) <sup>b,c</sup> (yield %; selectivity %)	[Heptanal] (mol × 10 <sup>-4</sup> )	TF(heptanal) <sup>b</sup> (yield %; selectivity %)
0.0	41	7	24	22	77 (9.2; 40)	33	115 (13.8; 60)
5.6	54	10	35	26	91 (10.9; 45)	44	154 (18.4; 55)
26.0	121	21	76	40	139 (16.7; 37)	98	344 (40.8; 63)
46.0	198	45	162	50	176 (20.8; 33)	146	514 (60.9; 67)
67.0	182	50	180	15	62 (6.3; 41)	138	484 (57.5; 59)

<sup>a</sup> [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 3 mL (0.024 mol), 40 mL of water (2.2 mol); 1-hexene/Rh = 240, P(CO) = 22 atm at 150 °C for 7 h.

<sup>b</sup> TF(product) = [(mol of product)/(mol of Rh) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%.

<sup>c</sup> HA: heptanoic acid.



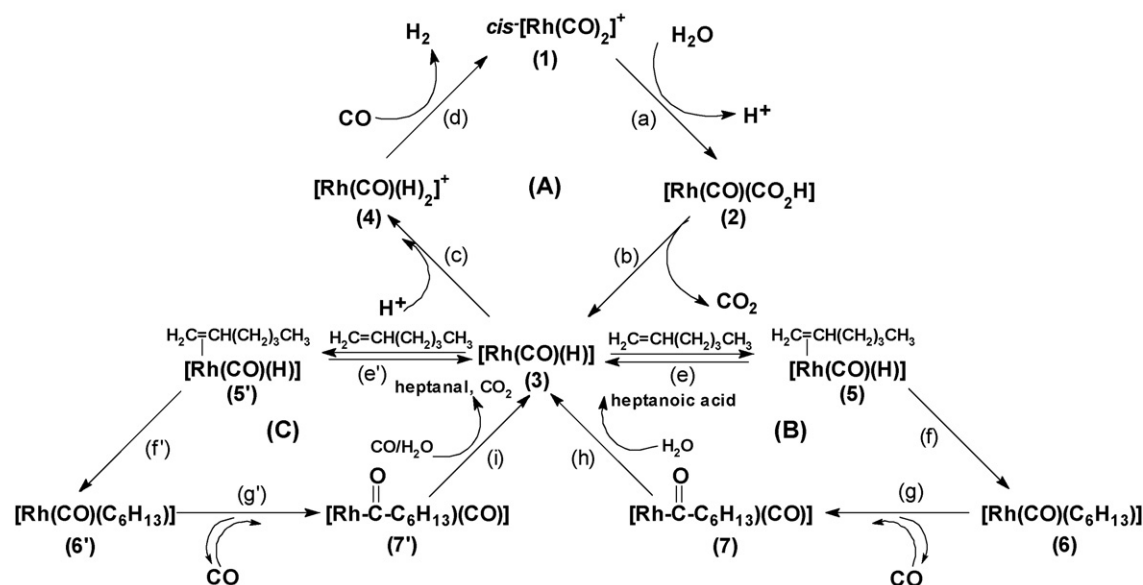
**Fig. 7.** A plot of aldehyde/acid molar ratio vs. [salt] ([N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub>]). Reaction conditions: [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 3 mL (0.024 mol), 40 mL of water (2.2 mol); 1-hexene/Rh = 240, P(CO) = 22 atm at 150 °C for 7 h. Line drawn for illustrative purpose only.

tively, at 46.0 wt.% of tetrabutylammonium hydrogensulfate. On the other hand, the TF(H<sub>2</sub>)/24 h increases from 35 ([salt] = 5.6 wt.%) to 180 ([salt] = 67.0 wt.%). These results suggest that the salty medium stabilizes the ionic Rh catalytic species formed under the reaction conditions, therefore enhancing the reactivity. Further, as shown in Fig. 7 the selectivity towards hydroformylation is favored over hydrocarboxylation on the 5.6–67.0 wt.% concentration range of (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)<sub>4</sub>NHSO<sub>4</sub>. Discussion of this behavior is described in Section 3.5.

Furthermore, the highest TF(heptanoic acid) = 169, TF(heptanal) = 573 and TF(H<sub>2</sub>) = 182 (24 h)<sup>-1</sup> values were achieved under optimal conditions, e.g., [Rh] = 1 × 10<sup>-4</sup> mol, 1-hexene = 3 mL, 1-hexene/Rh = 240, 40 mL of water (2.2 mol); 55.2 g of N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>HSO<sub>4</sub> (46 wt.%) and P(CO) = 38 atm at 150 °C for 7 h.

### 3.5. Mechanistic considerations

Scheme 1 illustrates a proposed mechanism for the WGS and the hydrocarboxylation and hydroformylation reaction of 1-hexene by Rh(4-pic)<sub>2</sub> system. The evaluation of the mechanism for H<sub>2</sub>,



Scheme 1. Proposed mechanism.

CO<sub>2</sub>, heptanoic acid and heptanal formation by this catalytic system under CO shows some key features:

First, previously has been reported that rhodium(I) *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) (amine = 4-picoline or pyridine) complexes in 80% aqueous amine, under 0.9 atm of CO at 100 °C, catalyzed the water gas shift reaction. Proposed mechanisms for these systems involve the formation of rhodium hydride intermediates, which were confirmed by *in situ* <sup>1</sup>H NMR spectroscopic studies [15].

Second, the H<sub>2</sub> turnover frequency in the presence of 1-hexene for the Rh(4-pic)<sub>2</sub> system (49 (24 h)<sup>-1</sup>) is lower than the WGSR activity (141 (24 h)<sup>-1</sup>) for the same system in the absence of 1-hexene under reaction conditions given in Table 1. Presumably in the former systems a reactive Rh–H intermediate is intercepted prior to H<sub>2</sub> formation by reaction with 1-hexene to generate a rhodium–olefin intermediate. Under CO/H<sub>2</sub>O conditions the latter would be expected to react further to give the observed organic products.

Third, studies of the variation of [Rh] also suggest the occurrence of active rhodium species having different nuclearity, under the catalytic conditions.

Fourth, the CO concentrations studies showed a linear dependence on [CO] for the WGSR and reversible addition of CO for the carbonylation reactions. Also, the carbonylation reactions showed a reversible dependence with respect to [1-hexene].

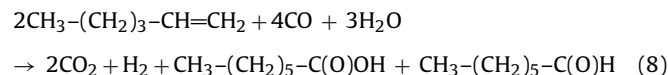
Given the above, the reaction mechanism depicted in Scheme 1 is proposed for WGSR and hydrocarboxylation and hydroformylation of 1-hexene catalyzed by mononuclear cationic Rh(I) species. In Scheme 1, the amine ligands of the intermediate rhodium are omitted for clarity. Three connected cycles account for the observed products. In cycle (A), the formation of H<sub>2</sub> via WGSR implies a nucleophilic attack by H<sub>2</sub>O on the coordinated CO of complex (1) to yield a hydroxycarbonylation complex [Rh(CO)(CO<sub>2</sub>H)] (2) and H<sup>+</sup> (step a). Elimination of CO<sub>2</sub> from the former complex gives the hydride [Rh(CO)(H)] complex (3) (step b), which upon protonation by H<sup>+</sup> (step c) forms the dihydride complex [Rh(CO)(H)<sub>2</sub>]<sup>+</sup> (4). Reductive elimination of H<sub>2</sub> (step d) assisted by CO coordination regenerates the starting *cis*-[Rh(CO)<sub>2</sub>]<sup>+</sup> complex (1) and closes the WGSR cycle.

Cycle (B) describes the formation of heptanoic acid which comes from *in situ* hydrolysis of the [Rh(CO)(acyl)] complex (7) (step h).

The Rh–acyl complex arises from the reversible coordination of 1-hexene to form the intermediate complex (5) (step e). Insertion of the olefin to the Rh–H bond (step f) [31] gives [C<sub>6</sub>H<sub>13</sub>Rh(CO)] (6). Then *cis*-migration of the C<sub>6</sub>H<sub>13</sub> group so formed to [Rh–CO] moiety assisted by the reversible CO coordination (step g) gives the [Rh(CO)(acyl)] complex (7). Formation of the hydride–rhodium complex (3) and production of heptanoic acid (step h) closes the catalytic cycle (B). The Lewis-acid promoted migratory-insertions of an alkyl group to a coordinated CO affording an acyl intermediate has been reported [17]. In our systems the presence of [(CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)<sub>4</sub>N](HSO<sub>4</sub>) considered as a mild Lewis-acid [18] should accelerate the formation of this key intermediate, increasing catalytic activity. Further, the results on Section 3.2 show the production of carbonyl products as a function of the pK<sub>a</sub> value of the coordinated amine. The electron-donating methyl groups on the pyridine ring should favor metal ion protonation of (7) facilitating [Rh(CO)(H)] (3) formation. Simultaneously, the nucleophilic attack by an OH<sup>-</sup> group over the electrophilic carbonyl carbon of acyl ligand facilitates heptanoic acid formation, hence increasing the hydrolysis reaction (step h).

Cycle (C) describes the formation of heptanal which comes from *in situ* hydrogenolysis of Rh–acyl complex (7') (step i). Hydrogenolysis of the Rh–acyl intermediate, which leads to heptanal formation, probably comes from *intra*-hydrogen transfer from Rh–H species [9] and/or by the H<sub>2</sub>, both formed via the WGSR (cycle A).

The overall reaction for products formation is (Eq. (8)):



Furthermore, the TF(heptanal) = 139 (24 h)<sup>-1</sup> value, for the “Rh(4-pic)<sub>2</sub>” system, is higher than the TF(heptanoic acid) = 90 (24 h)<sup>-1</sup> value, by a factor of 1.5 (Table 1). These results show, that termination step by hydrogenolysis of (6') affording heptanal (step h') is faster than termination step by hydrolysis of (6) affording heptanoic acid (step i), in spite of the fact that both products come from the same kind of intermediates, namely the Rh–acyl complex (7 and 7').

#### 4. Conclusions

In this study, heptanoic acid and heptanal were synthesized by a hydrocarboxylation and hydroformylation of 1-hexene, respectively. Both reactions were catalyzed by *cis*-[Rh(CO)<sub>2</sub>(amine)<sub>2</sub>](PF<sub>6</sub>) complexes in a salty medium of tetrabutylammonium hydrogensulfate. The electronic and steric effects of the coordinate amine can control all or some of these catalytic key steps.

It can be seen a remarkable increment on the organic products formation catalyzed by the Rh(4-pic)<sub>2</sub> system when the concentration of the tetrabutylammonium hydrogensulfate salt increased. The increment of the *P*(CO) favors the WGSR but disfavors the carbonylation reaction at *P*(CO) > 38 atm. The increment of the Rh content disfavors the WGSR and the carbonylation reaction suggesting the presence of active rhodium species having different nuclearity and activity. Our approach related to the use of salty medium can constitute another alternative reaction media to heptanoic acid and heptanal synthesis.

Finally, a catalytic scheme for the production of H<sub>2</sub>, CO<sub>2</sub>, heptanoic acid and heptanal bearing common Rh–H catalytic species is proposed.

#### Acknowledgments

The authors thank the CDCH-UCV (PG: 03.12.4957.2005) and the FONACIT (S1-2002000260) for funding. SAM thanks to Fondecyt-Chile (1085135).

#### References

- [1] P. Pino, F. Piacenti, M. Bianchi, in: I. Wender, P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls*, John Wiley, New York, 1968, p. 233.
- [2] G. Kiss, *Chem. Rev.* 101 (2001) 3435.
- [3] M. Kilner, N.J. Winter, *J. Mol. Catal. A* 112 (1996) 327.
- [4] M.M. Mdleleni, R.G. Rinker, P.C. Ford, *Inorg. Chim. Acta* 270 (1998) 345.
- [5] F. Hung-Low, G.C. Uzcátegui, J. Alvarez, M.C. Ortega, A.J. Pardey, C. Longo, *React. Kinet. Catal. Lett.* 84 (2005) 87.
- [6] A. Cabrera, P. Sharma, J.L. Garcia, L. Velazco, F.J. Perez, J.L. Arias, N. Rosas, *J. Mol. Catal. A* 118 (1997) 167.
- [7] G. Verspui, J. Feiken, G. Papadogianaskis, R.A. Sheldon, *J. Mol. Catal. A* 146 (1999) 299.
- [8] A.J. Pardey, A.B. Rivas, C. Longo, T. Funaioli, G. Fachinetti, *J. Coord. Chem.* 57 (2004) 871.
- [9] A.J. Pardey, C. Longo, T. Funaioli, G. Fachinetti, *Polyhedron* 23 (2004) 1677.
- [10] B. Denise, G. Pannetier, *J. Organomet. Chem.* 63 (1973) 423.
- [11] A.J. Pardey, G.C. Uzcátegui, F. Hung-Low, A.B. Rivas, J.E. Yáñez, M.C. Ortega, J. Alvarez, C. Longo, P. Aguirre, S.A. Moya, *J. Mol. Catal. A* 239 (2005) 205.
- [12] H.M. McNair, J.M. Miller, *Basic Gas Chromatography*, Wiley-Interscience, New York, 1997, Chapter 8.
- [13] K. Schofield, *Hetero-Aromatic Nitrogen Compounds*, Plenum Press, New York, 1967, pp. 146–148.
- [14] P.C. Ford, A. Rokicki, *Adv. Organometal. Chem.* 28 (1988) 139.
- [15] A.J. Pardey, P.C. Ford, *J. Mol. Catal.* 53 (1989) 247.
- [16] R.M. Laine, *J. Mol. Catal.* 14 (1982) 137.
- [17] S.B. Butts, E.M. Holt, S.H. Strauss, N.W. Alcock, R.E. Stimson, D.F. Shriver, *J. Am. Chem. Soc.* 101 (1979) 5864.
- [18] R.-H. Fan, X.-L. Hou, *Org. Biomol. Chem.* 1 (2003) 1565.