

# Influence of an additional gas on the hydroformylation of cyclohexene with $\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2$

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Received 6 December 2000; accepted 28 February 2001

Dedicated to Prof. Brian James, University of British Columbia (Canada) on the occasion of his 65th Birthday.

## Abstract

The influence of an additional gas on the hydroformylation of cyclohexene in the presence of  $\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2$  has been tested.

The rate of the hydroformylation is reduced by the presence of an appropriate amount of dinitrogen, argon or xenon as additional gas. The conversion decreases as the pressure of the additional gas increases. Helium, on the other hand, does not show any influence.

These results are in agreement with the previous data reported for the hydroformylation of the same olefin in the presence of  $\text{Co}_2(\text{CO})_8$  even if the entity of the reduction of the reaction rate is now less evident. The reduced influence of the additional gas may be attributed to the more severe conditions necessary to perform the reaction or to the higher stability of the catalytic system.

The analogy between these two catalytic systems is confirmed by the comparable influence displaced by the additional gas. This influence on the reaction rate may be attributed, on a molecular basis, to a competition among the additional gas and dihydrogen and/or olefin to a coordinatively unsaturated place on the catalytically active complex. The formation of an additional gas containing complex reduces the concentration of the active cobalt intermediate available for the catalysis and, as a consequence, the hydroformylation rate.

These data are not sufficient to identify the step of the catalytic process influenced by the presence of the additional gas, however, indicate the involvement of a dihydrogen or an olefin containing complex in the rate determining step of the hydroformylation.

The formation of a cobalt complex containing an additional gas as ligand (dinitrogen, argon or xenon) in the conditions required to perform the hydroformylation is supported by these experiments. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydroformylation; Cobalt carbonyl; Dinitrogen; Argon; Xenon

## 1. Introduction

Hydroformylation or oxo synthesis is the term usually adopted to indicate the reaction between alkene,

$\text{CO}$  and  $\text{H}_2$  to give carbonylic compounds, generally aldehydes or ketones. When speaking of hydroformylation we refer to the synthesis of aldehydes, high yields of ketones are formed only in particular reaction conditions. The reaction was discovered by Roelen in 1938 [1] and it is nowadays important by an industrial point of view. Aldehydes are in fact intermediates for the syntheses of carboxylic acids, alcohols, aldols

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or amines. These products may be employed as raw materials for the synthesis of solvents, polymers, plastifiers, detergents or many other products.

The usually employed catalysts are Co or Rh complexes. Rhodium compounds show higher activity and selectivity than cobalt but are expensive. On the contrary cobalt complexes are cheaper but less regioselective; to improve their regioselectivity cobalt modified catalysts have been developed in some instances [2]. Trialkyl- and triaryl-phosphines are the ligands usually employed, because their synthesis is easy and cobalt complexes containing these ligands show a high regioselectivity even if their catalytic activity is not very high. Several studies have been performed using these cobalt modified catalysts and the influence of the phosphine is generally attributed to the steric hindrance of the cobalt complex, favouring the insertion of the formyl group on the terminal carbon of the starting olefin [2–7].

Among the phosphine substituted cobalt catalysts the most used is  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$ , usually employed in the presence of free phosphine. It is synthesized starting from  $\text{Co}_2(\text{CO})_8$  and tributylphosphine [3]. The mechanism usually accepted to explain the catalytic activity of  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$  [2] in the hydroformylation of olefins is analogous to that one reported for  $\text{Co}_2(\text{CO})_8$ : the hydride  $\text{HCo}(\text{CO})_3(\text{PBu}_3)$  is considered the active catalyst that reacts with the olefin to form an alkylcobalt complex [4]. The presence of tributylphosphine having a high steric hindrance improves the regioselectivity of the catalyst giving a large amount of the linear alkylcobalt carbonyls [4]. The acylcobalt carbonyl is formed through a subsequent CO insertion and, in the following step, it is hydrogenolyzed giving the aldehyde and the starting  $\text{HCo}(\text{CO})_3(\text{PBu}_3)$ . The dihydrogen activation is one of the unsolved step in the hydroformylation of olefins in the presence of cobalt catalysts. Dihydrogen is involved in the reaction with  $\text{Co}_2(\text{CO})_6\text{L}_2$  ( $\text{L} = \text{CO}, \text{PBu}_3$ ) to give  $\text{HCo}(\text{CO})_3\text{L}$  and in the hydrogenolysis of the acylcobalt carbonyls to restore  $\text{HCo}(\text{CO})_3\text{L}$  and to give the aldehyde (Scheme 1). To collect evidence if dihydrogen is activated through the formation of a dihydrogen cobalt complex, Piacenti and coworkers [8,9] carried out the hydroformylation of cyclohexene catalyzed by  $\text{Co}_2(\text{CO})_8$  in the presence of dinitrogen, an additional gas which is proved to be able to form cobalt complexes more stable than the corresponding

dihydrogen complexes [10]. In the conditions tested, the hydroformylation of cyclohexene is drastically reduced giving an indication that dihydrogen cobalt complexes or an analogous olefin cobalt complex is involved in the rate determining step of the reaction. The additional gas is not involved in the thermodynamic of the reaction, but it influences the rate of the hydroformylation because it forms, in the reaction conditions tested, a cobalt complex unable to react with olefin or dihydrogen [8,9]. In other words, dinitrogen competes with olefin or dihydrogen to an unsaturated position on the catalytic specie, thus, reducing the amount of cobalt complex available for the catalytic cycle (Scheme 1).

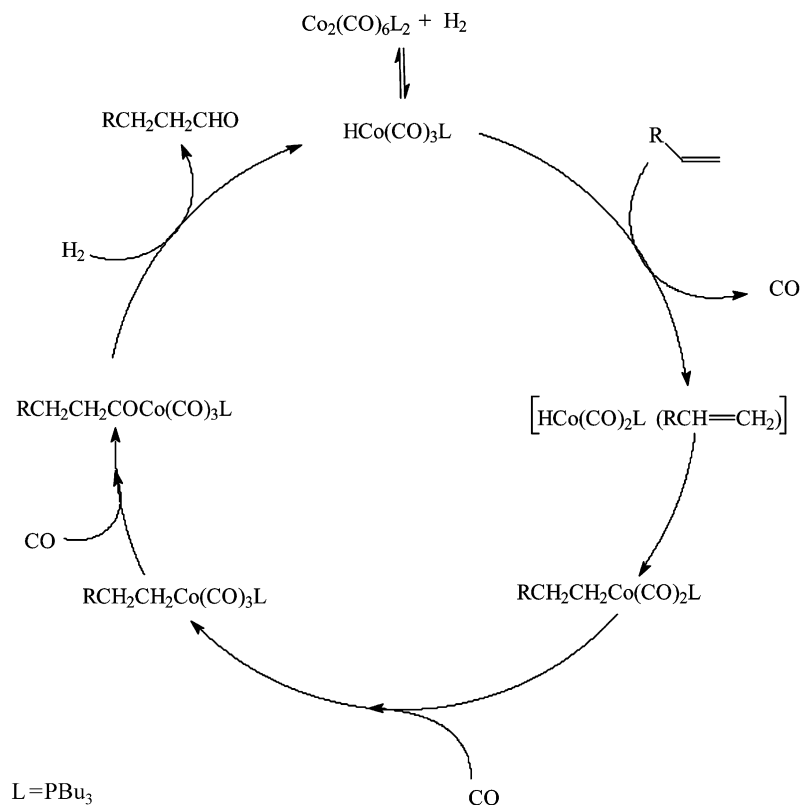
The influence of an additional gas on the rate of the hydroformylation is also shown in the presence of argon and xenon [8,9]. If the same explanation may be claimed, a cobalt complex containing one of these gases is formed.

Using the methodology previously reported for the hydroformylation of olefins in the presence of  $\text{Co}_2(\text{CO})_8$  and an additional gas we have tested, if the same reaction, catalyzed by  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$ , is also affected by the presence of an additional gas, such as dinitrogen, argon or xenon, in consideration of the analogies reported for these two catalytic systems.

## 2. Results

The hydroformylation of cyclohexene catalyzed by  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$ , has been tested evaluating the conversion of the olefin in isochronous experiments carried out in the presence of an increasing pressure of the additional gas. Each experiment was repeated three times and the mean value is reported. Cyclohexene was employed as substrate because it cannot isomerize and only one alkyl- and acylcobalt intermediate are formed. As a consequence only one aldehyde is obtained, thus, avoiding the problems connected with the formation of isomeric aldehydes. Finally the data collected may be correlated with those reported using  $\text{Co}_2(\text{CO})_8$  as catalytic precursor.

1,2,4-Trimethylbenzene was employed as solvent, due to its characteristics of aromatic solvent. Its high vaporization enthalpy ( $\Delta H_v = 44.8 \text{ kJ mol}^{-1}$  at  $169.3^\circ\text{C}$ ) [11] is an indication of its low ability to coordinate a transition metal. This property of the



Scheme 1.

solvent is important in consideration of the low energy involved in the interaction between dihydrogen and a transition metal.

All tests were carried out using a  $p(\text{H}_2)$  of 50 bar and a  $p(\text{CO})$  of 5 bar with a molar ratio  $\text{Co}_2(\text{CO})_6$  ( $\text{PBu}_3$ )<sub>2</sub>/cyclohexene of 1:40 and 1,2,4-trimethylbenzene as solvent. A low pressure of CO was chosen to avoid the displacement of the coordinated phosphine. The reaction temperature initially chosen was 150°C with a reaction time (r.t.) of 8 h.

The reaction products were identified by gas chromatographic analysis (GC) using appropriate standards and their identification was confirmed by GC–MS analysis (Tables 1–4).

## 2.1. Influence of an additional gas

### 2.1.1. Nitrogen

The rate of hydroformylation of cyclohexene has been tested at the reaction temperature (150°C) usually

adopted to carry out this reaction using phosphine modified catalysts. After 8 h (Table 1) the conversion of the olefin was very high (more than 96%) and the influence of dinitrogen was very low. The conversion of cyclohexene into cyclohexanecarboxaldehyde was reduced from 23.7 to 21.0% when the dinitrogen pressure was increased from 0 to 1000 bar. Several products were formed: cyclohexane due to the hydrogenation of the alkene, cyclohexylmethanol from the hydrogenation of the aldehyde, and cyclohexylmethyl formate by carbonylation of the alcohol. As a consequence the interpretation of the data was very difficult.

Adopting r.t. of 5 h, the catalytic activity was always high (cyclohexene conversion 94.4%) (Table 1) and considerable amount of alkane (12.0%), alcohol (35.3%) and cyclohexylmethyl formate (11.3%) were formed. The influence of dinitrogen on the olefin conversion was, however, more evident. The conversion decreased to 87.5% in the presence of 518 bar of dinitrogen. The amount of aldehyde was, however, almost

Table 1  
Hydroformylation of cyclohexene in the presence of dinitrogen as additional gas<sup>a</sup>

$p(\text{N}_2)$ (bar)	Conversion (%)	$T$ (°C)	r.t. (h)	Reaction products, yield (%)			
				Cyclohexane	Cyclohexane-carboxyaldehyde	Cyclohexylmethylformate	Cyclohexylmethanol
0	34.7	130	3	4.9	28.6	0.0	1.2
232	28.2	130	3	3.8	23.0	0.0	1.4
532	27.6	130	3	3.3	23.0	0.0	1.3
749	27.0	130	3	3.4	22.8	0.0	0.8
1073	25.8	130	3	3.6	20.8	0.0	1.4
0	89.3	150	3	13.4	37.7	6.5	31.7
524	71.4	150	3	11.0	35.9	6.8	17.7
0	94.4	150	5	12.0	35.8	11.3	35.3
518	87.5	150	5	14.3	34.5	14.2	24.6
1002	77.7	150	5	13.6	33.9	14.1	16.2
0	96.8	150	8	14.9	23.7	22.6	35.6
506	96.0	150	8	14.6	23.7	23.0	34.7
805	97.6	150	8	15.8	22.4	25.0	34.4
1000	97.7	150	8	14.9	21.3	25.1	36.3

<sup>a</sup> 1,2,4-Trimethylbenzene: 7 ml; cyclohexene: 0.79 mmol (64.9 mg);  $\text{Co}_2(\text{CO})_6(\text{PBU}_3)_3$ : 0.020 mmol (14.0 mg);  $p(\text{CO})$ :  $5 \pm 1$  bar at room temperature;  $p(\text{H}_2)$ :  $50 \pm 2$  bar at reaction temperature.

Table 2  
Hydroformylation of cyclohexene in the presence of helium as additional gas<sup>a</sup>

$p(\text{He})$ (bar)	Conversion (%)	Reaction products, yield (%)		
		Cyclohexane	Cyclohexanecarboxyaldehyde	Cyclohexylmethanol
0	34.7	4.9	28.6	1.2
259	43.1	5.0	36.1	2.0
523	40.5	5.0	34.1	1.4
750	40.3	5.4	34.2	0.8
953	44.1	5.8	36.8	1.5

<sup>a</sup> 1,2,4-Trimethylbenzene: 7 ml; cyclohexene: 0.79 mmol (64.9 mg);  $\text{Co}_2(\text{CO})_6(\text{PBU}_3)_3$ : 0.020 mmol (14.0 mg);  $p(\text{CO})$ :  $5 \pm 1$  bar at room temperature;  $p(\text{H}_2)$ :  $50 \pm 2$  bar at 130°C;  $T$ : 130°C; r.t.: 3 h.

Table 3  
Hydroformylation of cyclohexene in the presence of argon as additional gas<sup>a</sup>

$p(\text{Ar})$ (bar)	Conversion (%)	Reaction products, yield (%)		
		Cyclohexane	Cyclohexanecarboxyaldehyde	Cyclohexylmethanol
0	34.7	4.9	28.6	1.2
265	31.7	3.8	26.8	1.1
500	25.4	3.4	20.9	1.1
823	23.7	4.2	18.2	1.3
1003	23.9	2.8	20.1	1.0

<sup>a</sup> 1,2,4-Trimethylbenzene: 7 ml; cyclohexene: 0.79 mmol (64.9 mg);  $\text{Co}_2(\text{CO})_6(\text{PBU}_3)_3$ : 0.020 mmol (14.0 mg);  $p(\text{CO})$ :  $5 \pm 1$  bar at room temperature;  $p(\text{H}_2)$ :  $50 \pm 2$  bar at 130°C;  $T$ : 130°C; r.t.: 3 h.

Table 4  
Hydroformylation of cyclohexene in the presence of helium or xenon as additional gas<sup>a</sup>

Additional gas		Conversion (%)	Reaction products, yield (%)		
<i>p</i> (He) (bar)	Xenon (g)		Cyclohexane	Cyclohexanecarboxyaldehyde	Cyclohexylmethanol
18	0	50.4	6.8	40.1	3.5
0	4.1	42.3	4.6	35.9	1.8

<sup>a</sup> 1,2,4-Trimethylbenzene: 7 ml; cyclohexene: 0.79 mmol (64.9 mg); Co<sub>2</sub>(CO)<sub>8</sub>(PBU<sub>3</sub>)<sub>3</sub>: 0.020 mmol (14.0 mg); *p*(CO): 5 ± 1 bar at room temperature; Xe or He was introduced at r.t.; *p*(H<sub>2</sub>): 50 ± 2 bar at 130°C; *T*: 130°C; r.t.: 3 h.

unchanged while the alcohol formed was reduced from 35.3 (*p*(N<sub>2</sub>) = 0 bar) to 24.6% (*p*(N<sub>2</sub>) = 518 bar).

Even reducing r.t. to 3 h the conversion remained always high (89.3%, Table 1). The influence of dinitrogen was more evident than in the previous tests. The byproducts were formed in a low amount, especially cyclohexylmethyl formate (7.3%, Table 1) but the conversion was high to perform kinetic evaluations.

With the aim to reduce the alkene conversion, the hydroformylation was carried out at 130°C with r.t. of 3 h the conversion of cyclohexene was 34.7%. The hydrogenation of alkene was low (4.9%), and also the hydrogenation of the cyclohexanecarboxyaldehyde was negligible (cyclohexylmethanol 1.2%) while cyclohexylmethyl formate was absent. These conditions were chosen as appropriate for our investigation. In fact, in these conditions the main reaction is the olefin hydroformylation and a minimum hydrogenation of the substrate and of the aldehyde takes place.

The data collected using different pressures of the additional gas are reported in Table 1. Working in the presence of 232 bar of dinitrogen the cyclohexene conversion was 28.2%. Increasing the dinitrogen pressure up to 1023 bar the conversion was progressively reduced up to 25.8%. The amount of cyclohexanecarboxyaldehyde is affected by the presence of dinitrogen, while the amount of cyclohexane and cyclohexylmethanol was very low and almost unchanged (cyclohexane 0.1–1.5% and cyclohexylmethanol 0.1–0.6%).

As previously reported, in the presence of 1000 bar of dinitrogen at 100°C, the gas dissolved in the solvent increases the volume of the solution of 1.4 ml [9,11]. To evaluate the influence of an increasing amount of solvent due to the gas dissolved in it, the cyclohexene hydroformylation was carried out at 130°C using 8.4 ml of solvent, instead of 7.0 ml. The conversion of the alkene is reduced of less than 1%. We conclude

that the reduction of the hydroformylation rate cannot be attributed to the increment of the volume of the solution.

The influence of the additional gas on the rate of the reaction may be ascribed, as reported for the hydroformylation catalyzed by Co<sub>2</sub>(CO)<sub>8</sub>, to a competition between dinitrogen and dihydrogen (and/or the olefin) for an unsaturated coordination site of the catalyst. The dinitrogen complex, thus, formed reduces the amount of the cobalt complex available for the catalytic reaction because the dinitrogen cobalt complex, in the condition adopted, is unable to perform the hydroformylation.

### 2.1.2. Helium

The hydroformylation of cyclohexene carried out in the reaction conditions adopted when dinitrogen was used, but in the presence of 256, 523, 750 and 935 bar of helium does not show any effect. The conversion of cyclohexene and the composition of the products remain almost unchanged (Table 2) in agreement with the first ionization potential of helium (24.87 eV) [12], that is with its inability to act as a ligand.

These data exclude that the negative influence of dinitrogen may be attributed to an influence of the high pressure on the transition state because, in the other way, the same effect must be present using helium or dinitrogen as additional gas.

### 2.1.3. Argon

The influence of argon has been tested using the same reaction conditions adopted in the test performed in the presence of dinitrogen. The data obtained are reported in Table 3. The conversion of cyclohexene is reduced to 31.7% using 265 bar of argon and progressively down up to 23.9% with an argon pressure of 1003 bar, in agreement with the data obtained using Co<sub>2</sub>(CO)<sub>8</sub> [8] as catalyst. Argon apparently shows a

higher negative influence than dinitrogen on the rate of the hydroformylation. It must, however, be noticed that the solubility of argon is higher than that of dinitrogen [13], and also that the fugacities of these two gases are different [11].

#### 2.1.4. Xenon

Using xenon, a cryogenic gas, a lightly different procedure has been adopted. The hydroformylation of cyclohexene in the presence of  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$  and xenon shows a behaviour analogous to those above reported for dinitrogen and argon. The data obtained (Table 4) show that in the presence of 31.2 mmol of xenon the conversion of cyclohexene is reduced from 50.4 to 42.3%. As a consequence the amount of aldehyde as well as the hydrogenated products cyclohexane and cyclohexylmethanol are reduced.

### 3. Discussion

The data obtained stress once again the analogy between the mechanism of the hydroformylation of olefins in the presence of  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$  and  $\text{Co}_2(\text{CO})_8$ . The influence of an additional gas on the rate of the hydroformylation of cyclohexene with  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$  is analogous to that one reported for the same reaction catalyzed by  $\text{Co}_2(\text{CO})_8$ : the additional gas ( $\text{N}_2$ , Ar or Xe) reduces the rate of hydroformylation using these two catalytic systems but in the case of  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$  (Tables 1–4) the entity of the reduction is lower.

These data confirm that the additional gas influences a reaction performed with a catalytic system different from  $\text{Co}_2(\text{CO})_8$  and in more severe reaction conditions. The influence of  $\text{N}_2$ , Ar or Xe may be rationalized on molecular bases as reported for the hydroformylation of cyclohexene in the presence of  $\text{Co}_2(\text{CO})_8$ . A cobalt complex containing one of the above mentioned gas is formed and in the reaction condition tested, this new complex is not involved in the catalytic cycle of the hydroformylation.

The following data are reported in the literature [3] on the reactivity of the phosphine substituted cobalt complexes involved in the catalytic cycle (Scheme 1):

1.  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$  reacts with  $\text{H}_2$  giving  $\text{HCo}(\text{CO})_3(\text{PBu}_3)$  at  $120^\circ\text{C}$  in the presence of a low pressure of CO.

2.  $\text{HCo}(\text{CO})_3(\text{PBu}_3)$  reacts with an olefin at  $120^\circ\text{C}$  in the presence of 10 atm of CO giving  $\text{RCOCo}(\text{CO})_3(\text{PBu}_3)$ .
3.  $\text{RCOCo}(\text{CO})_3(\text{PBu}_3)_3$  reacts with CO at room temperature to give  $\text{RCOCo}(\text{CO})_3(\text{PBu}_3)$ .
4.  $\text{RCOCo}(\text{CO})_3(\text{PBu}_3)$  reacts with  $\text{H}_2$  giving RCHO at  $15^\circ\text{C}$  and  $p(\text{H}_2)$  of 20 atm.

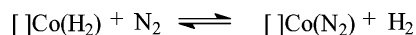
Taking into account these data, the reaction of the alkylcobalt complex with CO (3) or the reaction of the acyl intermediate  $[\text{RCOCo}(\text{CO})_3(\text{PBu}_3)]$  with hydrogen (4) cannot be influenced by the presence of an additional gas due to the very mild conditions necessary to perform these reactions. The influence of an additional gas may indicate the formation of  $\text{HCo}(\text{CO})_3(\text{PBu}_3)$  from  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$  (1), or the step involved in the olefin activation (2) as the rate determining step.

This suggestion is different from that reported for  $\text{Co}_2(\text{CO})_8$  as catalytic system in agreement with the different reactivity of the complexes involved.

The lower influence of the additional gas on the rate of the hydroformylation carried out in the presence of  $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$ , if correlated with that reported using  $\text{Co}_2(\text{CO})_8$ , may be attributed to the different rate determining step and as a consequence, to the different activation energy required. Furthermore the catalytic precursor is more stable and less reactive than  $\text{Co}_2(\text{CO})_8$  and the lower influence of the additional gas may be also ascribed to the high temperature required to perform the hydroformylation that reduces the amount of the additional gas in the solution.

These data confirm the involvement of a labile intermediate, such as a dihydrogen and/or an olefin cobalt complex in the catalytic cycle of the hydroformylation. The additional gas, dinitrogen for instance, shift the dihydrogen coordinated to cobalt to form a dinitrogen complex as reported by Sacco and Rossi [10], that it is not involved in the hydroformylation (Scheme 2).

These experiments may be considered as a different way to evidence labile intermediates involved in a catalytic cycle. Furthermore the data collected provide a strong indication that even in the drastic conditions tested there is an interaction between  $\text{N}_2$ , Ar



Scheme 2.

and Xe with a phosphine substituted cobalt complex analogous to that one reported for  $\text{Co}_2(\text{CO})_8$ . These data may be, therefore, considered as an indication of new transition metal complexes containing xenon as ligand that may be added to those reported in the last years [14–17].

#### 4. Experimental

The GC analyses were performed using a Perkin-Elmer Autosystem chromatograph equipped with a FID detector and a computer Perkin-Elmer Nelson GC Plus. A PPG packed column (“polypropylenglycol” LB-550-X on Chromosorb W at 15%), length 2 m, i.d. 1/8 in. was employed. In consideration of the similarity of the products the correction factors were not applied. The reproducibility of the GC analyses was higher than 0.2%.

The IR spectra were collected using an FT-IR Perkin-Elmer mod. 1760-X instrument connected with a PC using the Spectrum 2000 software. Liquid products or solutions were analyzed using a sample cell, thickness 0.1 mm, KBr or  $\text{CaF}_2$  windows.

The NMR spectra were recorded using a Varian VXR 300 operating at 299.944 MHz for  $^1\text{H}$ , at 75.429 MHz for  $^{13}\text{C}$  and at 121.421 MHz for  $^{31}\text{P}$  NMR. The  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were acquired using a broad band decoupler. Sample were dissolved in the appropriate deuterated solvents. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are reported in parts per millions (ppm), referred to TMS as external standard;  $\text{H}_3\text{PO}_4$  85% in  $\text{H}_2\text{O}$  was employed as external reference for  $^{31}\text{P}$  NMR spectra, signals at low field of the reference are reported as positive.

The GC-MS spectra were collected using a Shimadzu GC-17A chromatograph equipped with a capillary column SP<sup>TM</sup>-1 30 m, i.d. 0.25 mm having a stationary phase of 0.1  $\mu\text{m}$ , connected with a mass detector Shimadzu mod. QP5050 and a computer.

Elemental analyses were performed with a Perkin-Elmer mod. 240 C instrument by the Department of Organic Chemistry of the University of Florence.

Reactor: the experiments were carried out in a special stainless steel reactor, inner volume 24.5 ml, tested to a total pressure of 4000 bar. The vessel was equipped with a high pressure Nova Swiss valve used for the introduction of gases and solution. An

electrically heated oven was employed, the temperature was regulated using a Pt100 indicator that measure the temperature of the solution contained in the autoclave with an accuracy of  $\pm 1^\circ\text{C}$ . The autoclave was rocked through an oscillation of the oven containing the autoclave. The pressure was determined through a transducer (Sensotec, model Z Absolute) with an accuracy of  $\pm 1$  bar. The data of the experimental conditions adopted, the amount of reagents, catalyst and solvent are reported in tables. The amount of reagents were chosen to avoid relevant variation of the pressure adopted in the various tests.

$\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2$ : prepared according to Piacenti et al. [3], recrystallized by *n*-hexane had mp 121–122°C. IR spectra is in agreement with that one reported in the literature [3].

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) shows signals at  $\delta$ : 1.56 (m, 12H,  $\text{PCH}_2\text{CH}_2$ ), 1.26–1.19 (pq, 6H,  $\text{CH}_2\text{CH}_3$ ), 0.82 ppm (t, 9H,  $\text{CH}_3$ ,  $^3J_{\text{H-H}} = 7.3$  Hz).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ) shows signals at  $\delta$ : 203.6 (pt, CO), 29.3 (m,  $\text{CH}_2\text{CH}_3$ ), 26.0 (s,  $\text{PCH}_2\text{CH}_2$ ), 24.2 (m,  $\text{PCH}_2$ ), 13.5 ppm (s,  $\text{CH}_3$ ).

$^{31}\text{P}$  NMR shows a singlet at  $\delta$ : 55.3 ppm.

Cyclohexylmethyl formate: in a round bottom flask, in a nitrogen atmosphere, 4.56 g (39.93 mmol) of cyclohexylmethanol, 4.25 g (92.33 mmol) of formic acid, 0.1 ml of  $\text{H}_2\text{SO}_4$  at 96% (1.86 mmol) and 15 ml of toluene was introduced. The solution was heated at reflux temperature for 2 h than cooled and after the usual working up dried on  $\text{Na}_2\text{SO}_4$ . After distillation at reduced pressure 2.65 g (20.65 mmol, yield 51.7%) of cyclohexylmethyl formate having bp  $60^\circ\text{C}/7$  mmHg were collected.

The IR spectrum (neat), in the 3200–800  $\text{cm}^{-1}$  region, shows characteristic bands at 2929 (vs), 2854 (s), 1729 (vs), 1450 (m), 1378 (w), 1176 (s)  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows signals at  $\delta$ : 8.0 (s, 1H, HCOO), 3.9 (d, 2H,  $\text{CH}_2\text{O}$ ,  $^2J_{\text{H-H}} = 13.2$  Hz), 1.6 (m, 6H, CH, cyclohexyl), 1.1 ppm (m, 5H, CH, cyclohexyl).

The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) shows signals at  $\delta$ : 161.3 (1C, HCOO), 69.1 (1C,  $\text{CH}_2\text{O}$ ), 37.2 (1C,  $\text{CHCH}_2\text{O}$ ), 29.7 (2C,  $\text{CH}_2$ , cyclohexyl), 26.4 (1C,  $\text{CH}_2$ , cyclohexyl), 25.8 ppm (2C,  $\text{CH}_2$  cyclohexyl).

The GC-MS spectrum shows fragments at  $m/z$ : 96 (9)  $[\text{C}_7\text{H}_{12}]^+$ , 82 (3)  $[\text{C}_6\text{H}_{10}]^+$ , 81 (30)  $[\text{C}_6\text{H}_{11}]^+$ , 68 (16)  $[\text{C}_5\text{H}_8]^+$ , 67 (34)  $[\text{C}_5\text{H}_7]^+$ , 55 (100)  $[\text{C}_4\text{H}_7]^+$ , 41 (51)  $[\text{C}_3\text{H}_5]^+$ .

Cyclohexene: Fluka product, purified through elution on  $\text{Al}_2\text{O}_3$  column then distilled under nitrogen, had bp  $83^\circ\text{C}$  and a GC purity of 99.9%. 1,2,4-Trimethylbenzene was refluxed on Na for 3 h, then distilled under nitrogen; had bp  $167^\circ\text{C}$  [18].

Nitrogen from Sol Centro purity 99.996%; argon from Sol Centro purity 99.998%; xenon from Rivoira purity 99.997%; helium from Sol Centro purity 99.998%. Other reagents were commercial products and used without further purification.

#### 4.1. Hydroformylation of cyclohexene

The following procedure was adopted for the hydroformylation of cyclohexene in the presence of dinitrogen, argon or helium: the catalyst was placed in a stainless steel autoclave in which a nitrogen atmosphere was present. The vessel was sealed and the gas evacuated. A solution of the olefin in 1,2,4-trimethylbenzene was prepared in a Schlenk tube and introduced in the autoclave by suction, then CO up to 5 bar was added. The reactor was rocked and heated; when the solution reached the prefixed temperature the autoclave was stopped and hydrogen up to a total pressure of 55 bar was introduced (hydrogen partial pressure 50 bar) and then, rapidly, the additional gas up to the required pressure. Only few minutes were necessary to perform these two last operations. Subsequently the reactor was rocked for the established time, then rapidly cooled at room temperature. The gases were vented and the solution analyzed by GC to evaluate the conversion of cyclohexene. The following GC conditions were employed: the column was kept at  $50^\circ\text{C}$  for 5 min then heated up to  $100^\circ\text{C}$  at a rate of  $2^\circ\text{C min}^{-1}$  and kept at this temperature for 35 min, then heated at a rate of  $5^\circ\text{C min}^{-1}$  up to  $110^\circ\text{C}$  and kept at this temperature for 10 min.

Cyclohexane, cyclohexene, 1,2,4-trimethylbenzene, cyclohexanecarboxyaldehyde, cyclohexylmethyl formate and cyclohexylmethanol were separated and their amount quantified by the area of the corresponding chromatographic peaks.

The tests in the presence of xenon were carried out using a different procedure because this is a cryogenic gas. After the introduction of the solution containing the olefin and the catalyst, liquid xenon was added at room temperature from a cylinder, then CO up to 5 bar at r.t. The amount of xenon introduced was

evaluated weighting the xenon cylinder before and after the introduction of this gas in the autoclave. The reactor was heated at  $130^\circ\text{C}$  then the appropriate amount of hydrogen was introduced. The subsequent steps were identical to those above reported when the other additional gases were used. The data in the presence of xenon were correlated with a reference test in the presence of helium, carried out using the same procedure. The results of the hydroformylation of cyclohexene are reported in Tables 1–4. The mean value of three tests was reported.

#### Acknowledgements

The authors wish to thank the University of Florence and the Ministero della Ricerca Scientifica e Tecnologica (MURST), Programmi di Ricerca Scientifica di Notevole Interesse Nazionale, Cofinanziamento MURST 2000–2001, for financial support.

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