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In situ high pressure FT-IR spectroscopy on alkene hydroformylation catalysed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and $\text{Co}_2(\text{CO})_8$

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Abstract

Catalytic hydroformylation of olefins has been carried out in a HP FT-IR cell using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ catalytic precursor. A different behaviour was noticed between a terminal (hex-1-ene) and an internal alkene (cyclohexene) and different rate-determining steps of the catalytic cycle have been hypothesised. The hydroformylation of hex-1-ene has also been tested in the presence of $\text{Co}_2(\text{CO})_8$ as catalyst. In this case, only the catalytic precursor is evidenced by HP FT-IR. Finally, the influence of an additional gas (helium, nitrogen or argon) in the reaction medium was evaluated: a high pressure of argon or nitrogen affects the initial rate of the reaction as shown by a decrease of the rate of the aldehyde formation.

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1. Introduction

Hydroformylation is a well known synthetic tool for the preparation of a wide range of organic molecules of high commercial value [1]. It is one of the most important applications of homogeneous catalysis in an industrial process and gives aldehydes as the main product that may be subsequently transformed in alcohols or acids. In this reaction the mechanism of hydrogen activation is not completely clarified, even if many researches are devoted to its elucidation. In this paper, we have tried to get direct evidences on this step through in situ HP FT-IR technique. NMR spectroscopy is also an useful tool for in situ studies and an investigation has been reported by Bianchini et al. [2]. This last technique, however, requires a catalyst concentration usually two orders of magnitude higher than that employed in cata-

lytic reactions, to obtain a satisfactory signal-to-noise ratio (e.g., 10–100 mM instead of 0.1–1 mM employed in catalytic experiments). Furthermore, the low sensibility of this technique may not evidence species present in low concentration. The different concentrations employed may also affect the equilibria among the catalytic species present in the medium [3]. Finally, the volume of the gas above the solution is often too small when the reaction is carried out in a NMR sample tube and mass transfer is usually too low; as a result, the conditions are quite different from those adopted in a reactor vessel. The in situ study of reaction mechanism in a stirred high pressure FT-IR spectroscopy cell can be a complementary technique.

Some of us studying the hydroformylation of cyclohexene catalysed by $\text{Co}_2(\text{CO})_8$ (1) in the presence of nitrogen, argon or xenon as an additional gas have proposed that the activation of hydrogen takes place through a dihydrogen cobalt complex [4,5]. In fact, the initial rate of the hydroformylation decreases when the pressure of the additional gas rises. Similar results have

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also been obtained in the cyclohexene hydroformylation catalysed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (**2**) [6], while in the hex-1-ene hydroformylation in the presence of (**2**), a very high pressure of argon or nitrogen is required to obtain a reduction of the initial rate. These results have been explained assuming that the formation of a dihydrogen transition metal complex is involved for dihydrogen activation in the course of hydroformylation. In the presence of nitrogen as an additional gas, the dihydrogen complex is shifted towards a dinitrogen complex and consequently part of the catalyst is subtracted to the catalytic cycle. According to these hypotheses, a competition between dinitrogen and dihydrogen for a vacant site of the coordination sphere of a ruthenium diporphirine complex with the formation of the dinitrogen complex has been reported by Collman et al. [7]. An analogous behaviour was also reported by Sacco and Rossi [8] for cobalt complexes.

Taking into account these results, it may be interesting to follow the rhodium or cobalt-catalysed hydroformylation by in situ HP FT-IR spectroscopy in a stirred high pressure cell in order to point out the role played by the above mentioned additional gases.

2. Results and discussion

2.1. $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (**2**) catalysed hydroformylation

The HP FT-IR spectra were collected by increasing the complexity of the system: (a) a toluene solution of the catalyst (**2**), (b) a toluene solution of (**2**) in the presence of carbon monoxide, (c) a toluene solution of (**2**) in the presence of carbon monoxide and hex-1-ene, (d) a toluene solution of (**2**) in the presence of hex-1-ene, carbon monoxide, hydrogen (hydroformylation conditions), and (e) all experiments were repeated under a high pressure of an additional gas (He, N_2 or Ar).

2.1.1. Behaviour of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (**2**)

The FT-IR spectrum of a toluene solution of (**2**) shows, after 30 min, a new band at 1968 cm^{-1} which is attributed to $[\text{Rh}(\text{CO})(\text{PPh}_3)_2]_2$ (**3**) in agreement with the known behaviour [9,10]. It is in fact reported that (**2**) dissolved in dried benzene under inert atmosphere is slowly transformed into (**3**).

The same experiments carried out in the presence of a high pressure of an additional gas (helium, nitrogen or argon), heating the solution up to 323 K, do not show any differences of the HP FT-IR spectra: new species were not evidenced in the presence of an additional gas up to a pressure of 1200 bar.

2.1.2. Behaviour of (**2**) with carbon monoxide

When a toluene solution of (**2**) was pressurised with 30 bar of CO at 298 K, the absorptions at 2008 and

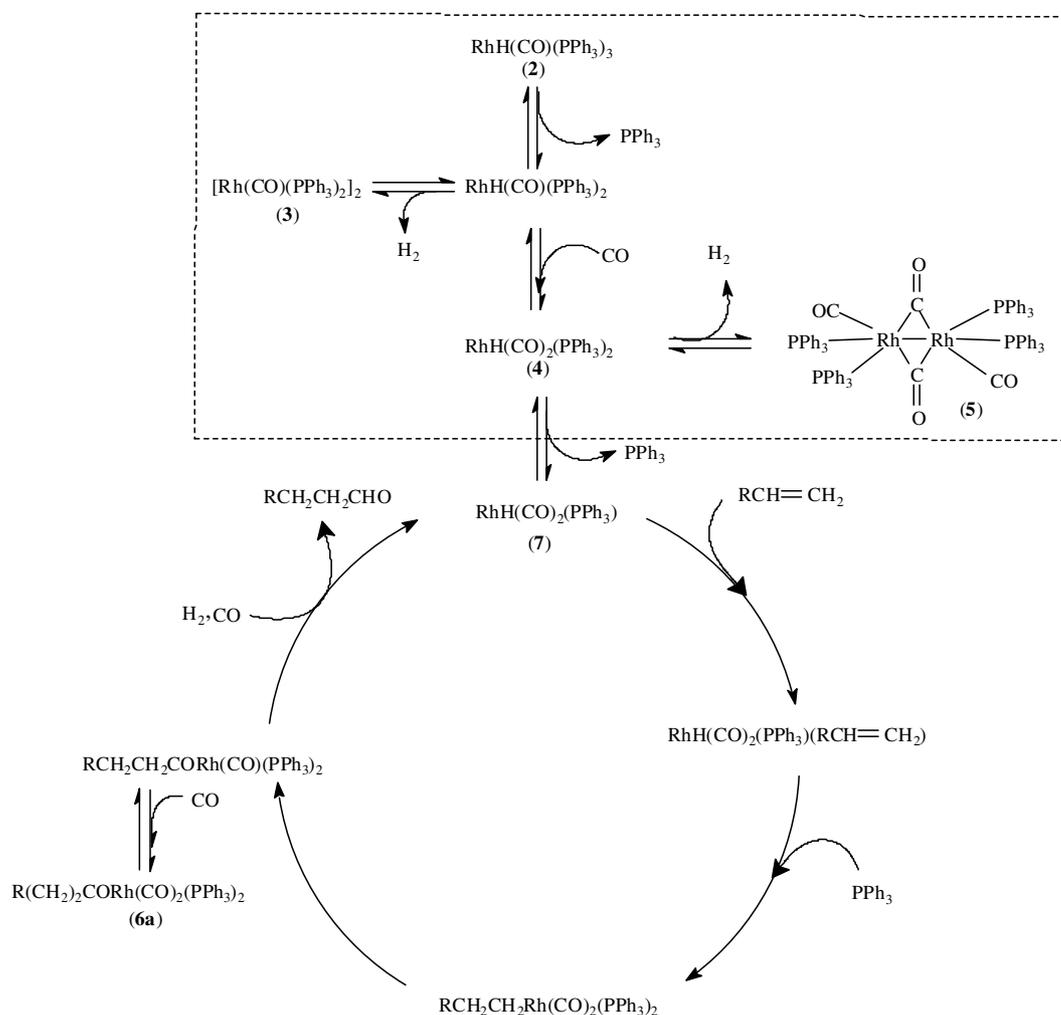
1926 cm^{-1} characteristic of (**2**) were replaced by new peaks at 2041, 1981 and 1945 cm^{-1} . These bands can be attributed to $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ (**4**) in agreement with the data reported in the literature [11]. Moser et al. synthesise (**4**) under syngas conditions and attribute the absorption at 2041 cm^{-1} to Rh–H stretching and the other peaks to Rh–CO stretchings, evaluating that the two CO groups are *cis*. Evans et al. [12] confirm these attributions to the products of the reaction of (**2**) with carbon monoxide. A trigonal-bipyramidal structure has been attributed to (**4**) and this complex may exist in solution as a mixture of two isomers in equilibrium with a rapid interconversion of one into the other through a pseudorotation mechanism. Van Leeuwen et al. [13], studying the rhodium catalyst (**2**) in the oct-1-ene hydroformylation by in situ IR spectroscopy, report four peaks (2041 , 1994 (sh), 1981 and 1943 cm^{-1}) attributed to an isomeric mixture of (**4**). They assume that the four bands are due to CO stretchings because the rhodium hydride band is too weak to be observable.

In our experiment, the peak at 1981 cm^{-1} is broad and after few minutes a shoulder at 1994 cm^{-1} and a weak band at 2026 cm^{-1} are formed, attributable to terminal carbonyl stretchings, while a new band at 1790 cm^{-1} of medium intensity may be ascribed to the stretching of the bridging CO. The new bands present after pressurisation with carbon monoxide are attributable to the presence of (**3**) and $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]_2$ (**5**), this last product is formed due to the absence of hydrogen. In Scheme 1, the equilibria among the species present in solution are reported in the dashed box.

The same experiments have been repeated in the presence of a high pressure of helium or argon. No observable changes in the IR spectra have been detected.

2.1.3. Reaction of (**2**) with hex-1-ene and carbon monoxide

The acyl complexes $\text{RCORh}(\text{CO})_2(\text{PPh}_3)_2$ (**6**) (linear (**6a**) and branched (**6b**)) were synthesised through the following procedure. A toluene solution of the catalyst (**2**) and the olefin was prepared at room temperature in a Schlenk tube, and transferred into the high pressure infrared cell. The vessel was pressurised with CO (30 bar) and the FT-IR spectrum showed, in the 2100 – 1700 cm^{-1} region, the presence of (**4**) (bands at 2040, 1980, and 1943 cm^{-1}) and (**5**) (bands at 2026, 1996, and 1790 cm^{-1}) in low concentration. After few minutes, the spectrum was appreciably modified: the peaks at 2040 and 1943 cm^{-1} were weaker, that is the concentration of (**4**) was reduced. New absorptions were present at 2054 (w), 2027 (w), 1998 (s), and 1978 cm^{-1} . A broad absorbance was also present at 1676 cm^{-1} that is in the region characteristic for the acyl group stretching [14], so it could be assigned to the linear and branched acyl complexes $\text{RCH}_2\text{CH}_2\text{CORh}(\text{CO})_2(\text{PPh}_3)_2$ (**6a**) and $\text{RCH}(\text{CH}_3)\text{CORh}(\text{CO})_2(\text{PPh}_3)_2$ (**6b**). This last



Scheme 1. Catalytic cycle of the hydroformylation of alkenes catalysed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (2).

peak is asymmetric, with a maximum at 1676 cm^{-1} and a shoulder shifted to a lower frequency (about 5 cm^{-1}), see Fig. 1. The peak at 1676 cm^{-1} may be attributed to the linear acyl, while the shoulder is ascribed to the branched acylrhodium intermediate.

This result is in agreement with previous IR [14,15] and NMR [2] studies performed in the course of the hydroformylation: (2) reacts with CO and the alkene to form the acyl complexes (6) (linear and branched).

In our conditions, a high concentration of dimer (5) was also present because the experiments were performed in the absence of free triphenylphosphine in solution. The equilibria among the species present were partially shifted towards the Rh(0) dimer (see Scheme 1, dashed box).

An NMR study [16] on the structure of the acyl rhodium complexes showed that the RCO groups occupy an axial position and the two CO groups are, respectively, *cis*, so the bands observed at 1999 and 1979 cm^{-1} are attributable to the two equatorial CO groups of (6).

Finally, we have performed the same HP FT-IR experiments in the presence of an additional gas (helium, nitrogen or argon) in order to evidence its role on the rate of this reaction. No additional bands were evidenced in the HP FT-IR spectra using a pressure of the additional gas up to 1200 bar.

2.1.4. Reaction of (2) with hex-1-ene and syngas (hydroformylation conditions)

In the reaction of hex-1-ene with CO in the presence of (2), a high amount of Rh(0) dimer (5) was present, however, after hydrogen addition the intensity of the peaks characteristic of the rhodium dimer (5) and rhodium hydride (4) rapidly decreases and it is possible to evidence a broad band with a shoulder at 1678 cm^{-1} attributable to the acyl group of the complexes (6) (linear and branched, see Fig. 1).

These data are in agreement with those reported by Bianchini et al. [2] for the hex-1-ene hydroformylation catalysed by (2). ^{31}P NMR and ^1H NMR show the presence of the hydride (4) and acyl intermediates (6a) and

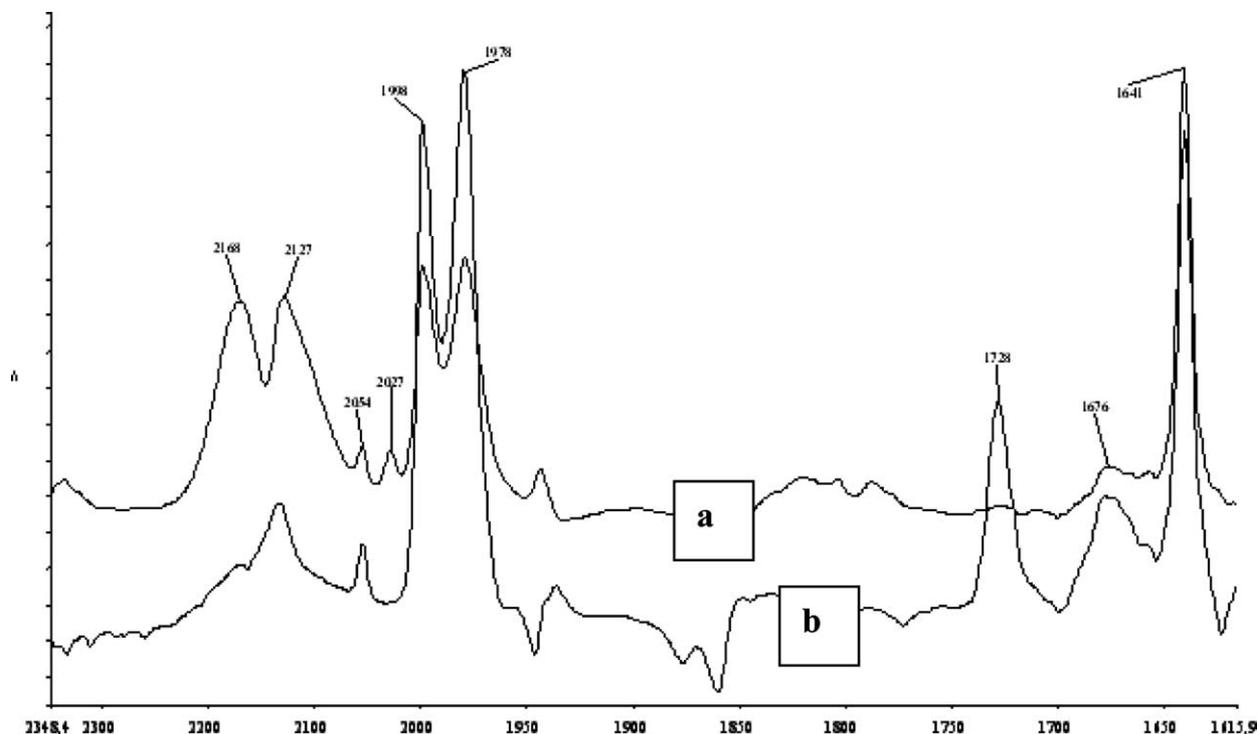


Fig. 1. In situ HP FT-IR spectra of: (a, grey line) syntheses of the acyl intermediates (linear and branched) $\text{RCORh}(\text{CO})_2(\text{PPh}_3)_2$ and (b, black line) hydroformylation of hex-1-ene catalysed by $\text{RhHCO}(\text{PPh}_3)_3$. (a) Reaction conditions: $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 25 mg (0.0272 mmol), hex-1-ene: 150 μl (1.2 mmol), toluene: 1.7 ml, $p(\text{CO})$, T : 323 K, reaction time: 3 h. (b) The same reaction conditions, plus hydrogen $p(\text{H}_2)$: 30 bar.

(6b) in reaction conditions analogous to those employed by us.

The same experiments performed in the presence of an additional gas do not show any change in the FT-IR spectra: new rhodium species were not detected, however the peaks of aldehydes are increasing in the course of the reaction, confirming that the reaction takes place.

2.1.5. Reaction of (2) with cyclohexene and syngas (hydroformylation conditions)

The spectra recorded during the reaction showed the presence of aldehydes, the alkene, the dimer (5) and the hydride complex (4) (Fig. 2). The IR pattern does not show any evidences of the presence of acyl rhodium complexes: as a consequence, (4) may be considered the intermediate before the transition state of the reaction. This observation suggests the coordination of cyclohexene to the rhodium hydride species as the rate determining step. This hypothesis is in agreement with the low reactivity of cyclohexene with respect to hex-1-ene in the hydroformylation [17]. A higher activation energy may be required for cyclohexene coordination to rhodium hydride due to the steric requirements of the cyclic olefin. If we remember that we are working in the absence of free triphenylphosphine, we may suggest that the hydride (4) loses a PPh_3 ligand giving the $\text{RhH}(\text{CO})_2(\text{PPh}_3)$ (7) species, which is reported to be the active intermediate involved in the coordination of the olefin to give in a following step the alkyl complex (Scheme 1).

As a conclusion, we observe acylrhodium compounds (6) as the rhodium complexes formed during the hydroformylation of hex-1-ene and $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ (4) as the complex present in the course of the hydroformylation of cyclohexene.

These data confirm that CO insertion into an alkylrhodium complex is always very fast and it is not possible to observe the alkylrhodium complexes during the hydroformylation of olefins.

Cyclohexene hydroformylation catalysed by (2) was carried out also in the presence of 500 bar of nitrogen or argon as an additional gas. The increase of the aldehyde concentration in the course of the reaction was followed by HP FT-IR. It is observed that the rate of the cyclohexene hydroformylation is reduced by the presence of an additional gas, confirming the behaviour previously reported for the same reaction performed in an autoclave. The initial rate of cyclohexene hydroformylation decreases as the pressure of the additional gas rises, however the FT-IR spectra show the same intermediates observed without any additional gas.

2.2. Dicobalt octacarbonyl (1) catalysed hydroformylation

2.2.1. Behaviour of $\text{Co}_2(\text{CO})_8$ (1)

The behaviour of the catalyst (1), that dissolved in toluene and transferred into the HP FT-IR cell, was

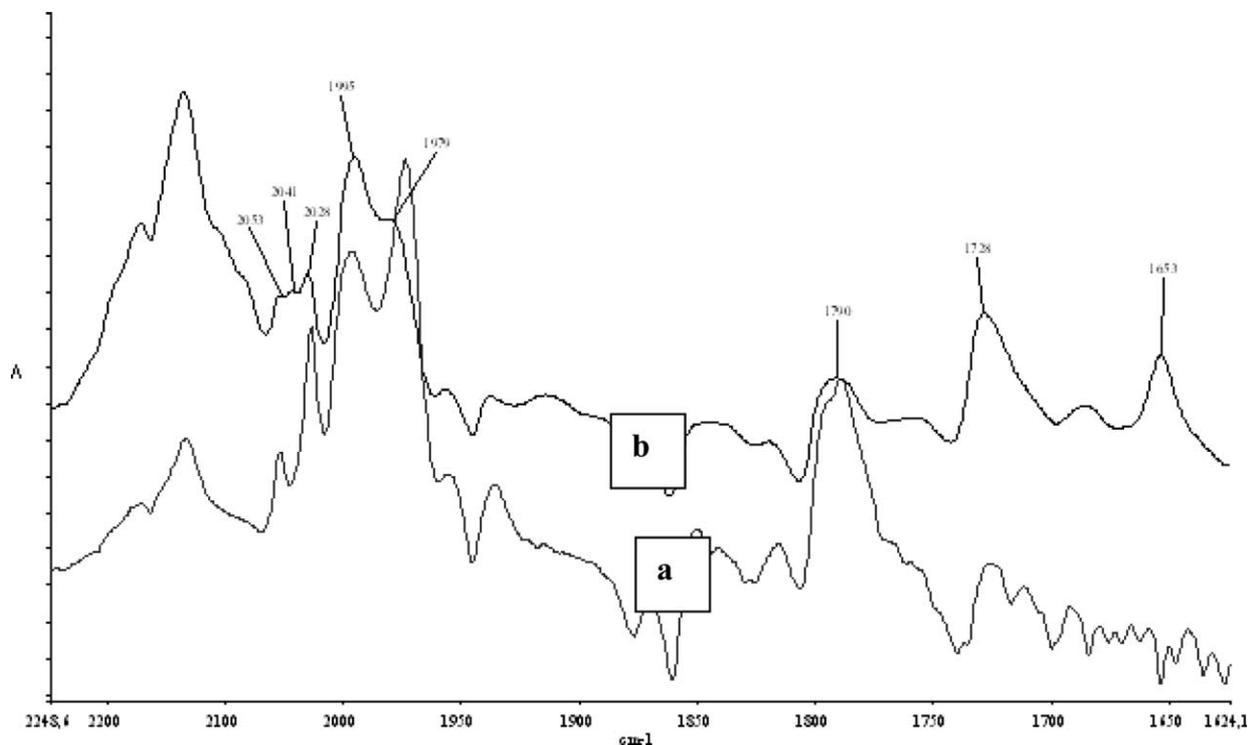


Fig. 2. In situ HP FT-IR spectra of: (a, black line) reactivity of $\text{RhHCO}(\text{PPh}_3)_3$ with CO and (b, grey line) cyclohexene hydroformylation catalysed by $\text{RhHCO}(\text{PPh}_3)_3$. (a) Reaction conditions: $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 25 mg (0.0272 mmol), toluene: 1.7 ml, $p(\text{CO})$, T : 323 K, reaction time: 4 h. (b) The same reaction conditions, plus cyclohexene: 50 μl (0.493 mmol), and hydrogen $p(\text{H}_2)$: 30 bar.

tested. The solution was heated up to 323 K, that is the temperature used for the hydroformylation. The IR pattern shows a gradual increase of the bands characteristic of $\text{Co}_4(\text{CO})_{12}$ (**8**) [18] and a slow decrease of the absorbances due to (**1**) [19]. The decrease of the absorption of (**1**) at 2070 cm^{-1} is reported in Fig. 3 as a function of the reaction time.

The same reaction was repeated in the presence of 500 bar of nitrogen or argon and the intensity of the

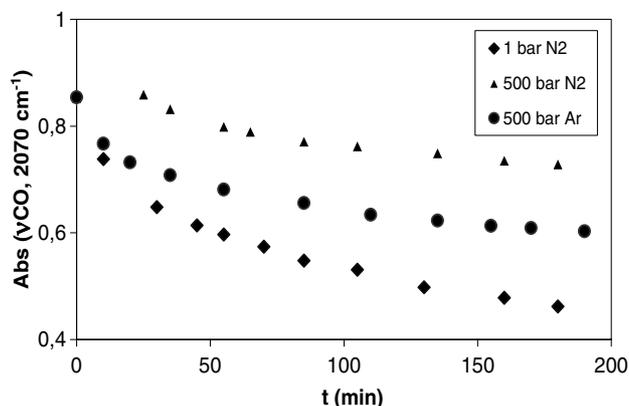


Fig. 3. Influence of a high pressure of nitrogen or argon on the initial rate of the transformation of $\text{Co}_2(\text{CO})_8$ (**1**) into $\text{Co}_4(\text{CO})_{12}$ (**8**). The ν_{CO} of $\text{Co}_2(\text{CO})_8$ at 2070 cm^{-1} was monitored. Reaction conditions: $\text{Co}_2(\text{CO})_8$: 8 mg (0.0234 mmol), Toluene: 4 ml, T : 323 K.

absorption at 2070 cm^{-1} is reported. The initial rate of the transformation of (**1**) into (**8**) is reduced by the presence of a high pressure of argon as an additional gas (Fig. 3).

The same reaction performed under CO (1 bar) shows a lower rate of the transformation of (**1**) into (**8**) as reported by Ungvary and Markò [20].

2.2.2. Reaction of (**1**) with hex-1-ene and syngas (hydroformylation conditions)

The hydroformylation of hex-1-ene in the presence of (**1**) and syngas was performed at the same temperature (323 K) of the rhodium complex (**2**), but using a low substrate/catalyst ratio because (**1**) is less active than (**2**).

The IR pattern observed during the hydroformylation of hex-1-ene in the presence of (**1**) shows the presence of the catalytic precursor, the olefin and the aldehydes. No other intermediates have been evidenced during the course of the reaction by in situ FT-IR spectroscopy. The bands of other possible cobalt species may be hidden by the very strong and broad bands of the catalytic precursor in the carbonyl stretching region.

The hex-1-ene hydroformylation experiments catalysed by (**1**) were repeated in the presence of a high pressure of argon up to 1200 bar. The same intermediates observed during the reaction carried out in the absence of an additional gas have been evidenced through FT-

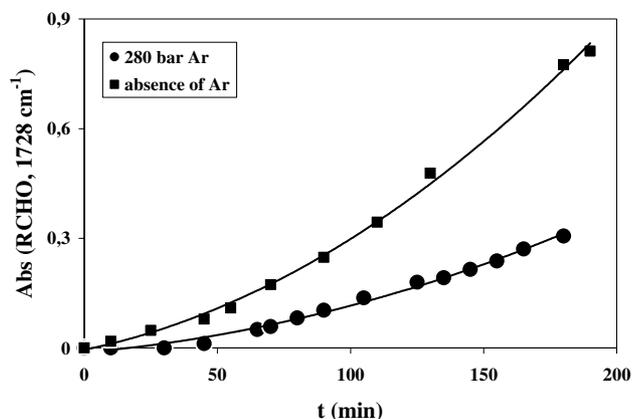


Fig. 4. Hex-1-ene hydroformylation catalyzed by $\text{Co}_2(\text{CO})_8$ (**1**). Influence of argon (280 bar) as additional gas. Reaction conditions: $\text{Co}_2(\text{CO})_8$: 8.500 mg (0.0249 mmol); hex-1-ene: 50 μl (0.4 mmol); Toluene: 1.7 ml; $p(\text{CO})$: 70 bar, $p(\text{H}_2)$: 85 bar, T : 323 K.

IR experiments,¹ however, as shown in Fig. 4, the rate of the reaction is lower when argon is present. These data confirm the behaviour previously reported for cyclohexene hydroformylation: the initial rate of the reaction catalysed by (**1**) is reduced by the presence of an additional gas such as nitrogen or argon [4a,5].

3. Conclusion

The data collected by HP FT-IR spectroscopy do not show any direct evidence of an interaction between nitrogen or argon with the catalytic species. Probably, the interaction of the transition metal complex with nitrogen or argon can cause a very small frequency shift of the residue carbonyl ligands. Furthermore, the carbonyl bands of the complexes involved in the catalytic hydroformylation are quite broad, consequently it is not possible to appreciate any small changes, if present.

In the hydroformylation of olefins catalysed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (**2**), different rhodium complexes have been evidenced, as a function of the type of olefin tested. Employing hex-1-ene, the species present in high concentration is the acylrhodium complexes, while using cyclohexene as the substrate, the rhodium hydride com-

plex (**4**) has been shown. An analogous behaviour has already been observed by Mirbach [21] in the oct-1-ene and cyclohexene hydroformylation catalysed by $\text{Co}_2(\text{CO})_8$ (**1**) by in situ FT-IR spectroscopy. They have observed the acyl species during the hydroformylation of terminal olefins, while the cobalt hydride $\text{CoH}(\text{CO})_4$ (**9**) was present during the hydroformylation of internal alkenes, in this last case the concentration of the acylcobalt complex was not detectable.

Our data collected on the rhodium catalysed hydroformylation of terminal olefin suggest the hydrogenolysis of the acylrhodium complex as the rate determining step. However, in the presence of internal olefins, the slowest step of the catalytic cycle is the reaction of the rhodium hydride complex with cyclohexene. The hydrogenolysis of an acyl rhodium complex is hypothesised by many authors as the rate determining step of the hydroformylation of terminal olefins, using different techniques [22]. The kinetics rate reported by Cavalieri d'Oro et al. [23] for the rhodium catalysed hydroformylation of propene in the presence of a strong excess of free phosphine (molar ratio phosphine/catalyst = 300) depends on olefin and phosphine concentration, but these data were collected in conditions very far from those adopted by us. Finally, our results are in agreement with the kinetic data reported by Van Rooy et al. [24] in oct-1-ene and cyclohexene hydroformylation catalysed by rhodium catalyst, even if a bulky phosphite is employed by these authors as ancillary ligand.

4. Experimental

4.1. General information

All operations were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was dried over sodium and distilled before use.

$\text{Co}_2(\text{CO})_8$ (**1**) [25] and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (**2**) [26] were prepared according to established methods.

4.2. Equipment

A new general purpose high pressure FT-IR cell was constructed at the EPFL-Lausanne [27]. All materials in contact with the solution are chemically inert and non metallic PTFE, PCTFE and Viton seals were employed. To study the influence of dissolved gases and to assure a saturation and a constant homogeneous concentration of the gases in the solution, the cell was provided with an external permanent magnet that moves an internal magnet linked to the mixer.

The HP FT-IR cell was equipped with CaF_2 windows having a diameter of 10 mm and a thickness of 17 mm in order to support a pressure of 2000 bar. The optical path was 0.1 mm.

¹ The hydrogenolysis of an acylcobalt intermediate in the presence of an additional gas has been investigated. The butanoylcobalt tetracarbonyl has been synthesised from $\text{NaCo}(\text{CO})_4$ and propanoyl chloride, then the hydrogenolysis of this intermediate in the presence of a high pressure of argon or nitrogen has been tested: the initial rate of the hydrogenolysis decreases as the amount of an additional gas (nitrogen or argon) increases. This kinetic behaviour (P. Frediani, unpublished results) is analogous to that reported in the hydroformylation of olefins. These data are in agreement with the hypotheses that the hydrogenolysis of the acyl intermediates is the rate determining step of the hydroformylation.

The sample was kept in isothermal conditions using a cryostat, temperature measurements were performed on the fluid of the cryostat and on the IR cell with a Pt100 device.

The high pressure cell was placed in a Perkin–Elmer 2000 FT-IR spectrometer. The resolution was set to 4 cm^{-1} for all spectroscopic measurements. A diagram of the experimental setup was shown in [27].

The data were elaborated using a Perkin–Elmer SPECTRUM 2000 IR data handling software for Windows.

4.3. *In situ* spectroscopic studies

All experiments were performed in a similar way. Toluene (1.5 ml) was transferred into the cell and a spectrum was recorded as a blank. The toluene was replaced by a toluene solution of the catalyst and the alkene, prepared using the Schlenk technique, was introduced in the HP FT-IR cell. Finally, the required gases were added up to the prefixed pressure and the system heated up to the required temperature. HP FT-IR spectra were collected in the range 4000–900 cm^{-1} .

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