



Influence of an additional gas on the rhodium-catalyzed hydroformylation of olefins

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

An additional gas such as dinitrogen, argon or xenon, present in the reaction medium in high concentration, affects the hydroformylation of cyclohexene, hex-1-ene or styrene in the presence of $\text{RhHCO}(\text{PPh}_3)_3$. The rate of hydroformylation of cyclohexene decreases as the amount of the additional gas increases: this effect may be attributed to a competition between the additional gas and one of the reagents, alkene, hydrogen or carbon monoxide for a coordinative unsaturated site available on the catalytically active intermediates. An analogous behaviour is shown when a terminal olefin (hex-1-ene or styrene) is hydroformylated in the presence of a low pressure of xenon. On the contrary, a very high pressure of dinitrogen or argon is required to show a decrease of the initial rate of the hydroformylation of the same terminal olefins. Finally, there is no or a slightly positive influence of a high pressure of helium or methane on the initial rate of the hydroformylation of the above reported olefins. This behaviour may be explained assuming an interaction between the additional gas and the rhodium catalyst.

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1. Introduction

The use of phosphine modified rhodium carbonyl offers many advantages over cobalt system in alkene hydroformylation [1–3]. Rhodium complexes are much more active for the oxo reaction and secondary reactions such as hydrogenation and aldolization are always low, usually below 1%. Furthermore, the pressure and temperature required for the hydroformylation are relatively lower than the Co-based process.

The regioselectivity of the Rh-catalyzed reaction can be improved with the use of an excess of free phosphine in solution [1–4] and the phosphine ligand affects dramatically the stereochemistry of the products. Pittman and coworkers [5,6] report a higher selectivity when a homogeneous catalyst was supported on polymers.

The mechanism of the reaction with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ has been proposed by Wilkinson and coworkers [1–3] many years ago and lots of publications still today deal with this reaction which is very important from an industrial and economical point of view [7]. By the use of computational techniques [8–11] and new spectroscopic methods, such as high pressure NMR [12–15], further insight on the

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catalytically active species and their role in the catalytic cycle have been proposed. A new mechanism was suggested through experimental [16–18] and theoretical data [19]. The associative step proposed by Wilkinson and coworkers [1–3] appears unlikely because it involves a 20-electron six-coordinate rhodium complex which is unfavourable from an electronic and a steric point of view. The new studies [19] suggest a dissociative mechanism with formation of two possible intermediates: $\text{RhH}(\text{CO})_2(\text{PPh}_3)$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_2$. The first complex is considered the key intermediate while the *trans* phosphine ligands present in the second complex may inhibit the activation of the olefin. The catalytic cycle involves four possible rate determining steps (RDS): (a) olefin insertion into the catalytically active $\text{RhH}(\text{CO})_2(\text{PPh}_3)$, (b) carbonyl insertion to give the corresponding acyl derivative, (c) oxidative addition of hydrogen to the acyl intermediate and (d) the reductive elimination of the aldehyde [15,19,20].

The last two steps are not elucidated up to now and the presence of a dihydrogen rhodium complex as the initial step of dihydrogen activation have not been considered as an intermediate.

As established by several reports such as the work of Sacco and Rossi [21], dinitrogen and dihydrogen are in competition in the $\text{Co}(\text{H}_2)\text{H}(\text{PR}_3)_3/\text{Co}(\text{N}_2)\text{H}(\text{PR}_3)_3$ system. In addition, the complexes with dinitrogen are usually more stable than the corresponding complex containing dihydrogen [22,23]. These facts suggest the use of an additional gas such as dinitrogen as an interesting way to collect evidences if a dihydrogen complex is an intermediate of the catalytic cycle of the hydroformylation. The additional gas is not involved in the thermodynamic of the process, but it can affect the rate of the reaction itself, because dinitrogen competes with dihydrogen, or eventually with alkene and/or carbon monoxide for the coordination to the metal. As a consequence, the initial rate of the reaction decreases because the concentration of the catalytically active intermediate is reduced.

The behaviour of cobalt-catalyzed hydroformylation in the presence of an additional gas was previously reported [24–27] and in this paper we examine if an analogous influence is present in the rhodium-catalyzed hydroformylation.

2. Experimental

2.1. Instruments

GC analyses were performed using a gas-chromatograph Shimadzu GC-14A equipped with packed columns, connected with a Shimadzu model C-R4A integrator and a GC instrument for capillary columns Perkin-Elmer model 8320. All instruments have FID detectors. The following columns were used: a packed (2 m) polypropylenglycol column (“PPG” LB-550-X 15% supported on Chromosorb W) to analyse the hydroformylation products of hex-1-ene and cyclohexene; a capillary column filled with $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ (50 m, i.d.: 0.32 mm) to analyse the residual olefins present after the hydroformylation of hex-1-ene; a packed (2 m) free fatty acids phase column (“FFAP” 5% supported on Chromosorb G-AW-DMCS) to analyse the reaction mixture of the hydroformylation of styrene.

The identity of the products was confirmed by GC-MS analysis using a Shimadzu instrument QP5050A equipped with a capillary column SPTM-1 (30 m, i.d.: 0.25 mm, film thickness: 0.1 μm).

Quantitative analyses of isomeric compounds were performed assuming that all products have the same response factors.

2.2. Materials

Hex-1-ene, Aldrich reagent grade, was eluted through neutral Al_2O_3 and distilled under dinitrogen before use, bp = 337 K. Toluene C. Erba reagent grade was refluxed over sodium and distilled under dinitrogen before use. Cyclohexene Fluka reagent grade, was treated as hex-1-ene, bp = 356 K. Styrene, Aldrich reagent grade, was eluted through neutral Al_2O_3 and distilled under vacuum before use, bp = 333 K/100 mm Hg. Triethylamine was distilled under dinitrogen and stored on KOH pellets.

The catalyst $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ was prepared as described in the literature [28]. Its purity was checked by IR and NMR spectroscopies and by elemental analysis.

Helium (99.998%), methane (99.998%), dinitrogen (99.996%), argon (99.998%), carbon monoxide (99.90%) and hydrogen (99.85%) were supplied

by Sol, xenon (99.997%), and were available from Rivoira.

2.3. Procedure

The hydroformylation experiments were performed in a stainless steel rocking autoclave, 25.4 ml capacity, capable of withstanding a pressure of 400 MPa, electrically heated with a temperature control (± 1 K). Pressures were measured with a transducer with an accuracy of ± 0.1 MPa (transducer model Z Absolute, Sensotec).

A toluene solution of the catalyst and the olefin was prepared in a sample tube under dinitrogen. This solution was introduced by suction in the autoclave and then carbon monoxide was pressurized up to 1.5 MPa. The autoclave was rocked and heated at the prefixed temperature, then hydrogen up to a total pressure of 3.0 MPa and the additional gas up to the required pressure was rapidly introduced into the autoclave, which was then rocked for the prefixed time.

At the end of the hydroformylation, the autoclave was rapidly cooled by immersion into water. Gases were evacuated and the yellow solution was analysed by GLC to determine the conversion of the olefin.

Olefin hydrogenation was always below 1%.

Working with xenon, a different procedure was used: the solution of the catalyst and olefin in toluene was introduced in the autoclave by suction, then the autoclave was filled with xenon at room temperature. Carbon monoxide of 1.5 MPa was introduced and the system heated at the prefixed temperature, then 1.5 MPa of hydrogen was added. The amount of xenon was determined by the weight difference of the cylinder. The subsequent procedure was identical to the one reported above.

3. Results and discussion

The influence of an increasing amount of an additional gas such as helium, dinitrogen, argon, xenon or methane on the rate of hydroformylation of cyclohexene, hex-1-ene and styrene is reported. The experiments were usually carried out introducing the additional gas immediately after carbon monoxide and dihydrogen. Xenon, as additional gas was introduced in a different sequence (see Section 2) due to its different characteristics.

3.1. Cyclohexene hydroformylation

The presence of an increasing amount of dinitrogen (Table 1), decreases the reaction rate as reported for

Table 1
Hydroformylation of alkenes in the presence of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$

| Alkene | Additional gas | Pressure of additional gas (MPa) | | | | | | | | |
|--------------------------|-----------------|----------------------------------|------|------|------|------|------|-------------------|------|------|
| | | 0 | 12.5 | 25 | 50 | 75 | 100 | 110 | 140 | 180 |
| Cyclohexene ^a | N ₂ | 0.32 | n.d. | 0.31 | 0.27 | 0.26 | 0.24 | n.d. | n.d. | n.d. |
| Cyclohexene ^a | Ar | 0.32 | n.d. | 0.30 | 0.24 | 0.18 | 0.17 | n.d. | n.d. | n.d. |
| Cyclohexene ^a | He | 0.32 | n.d. | 0.40 | 0.41 | 0.43 | 0.49 | n.d. | n.d. | n.d. |
| Cyclohexene ^a | CH ₄ | 0.32 | n.d. | 0.31 | 0.29 | 0.28 | 0.30 | n.d. | n.d. | n.d. |
| Hex-1-ene ^b | N ₂ | 0.67 | 0.71 | 1.11 | 1.12 | 1.13 | 1.10 | 1.15 | 1.19 | 1.09 |
| Hex-1-ene ^b | Ar | 0.67 | 1.08 | 1.05 | 1.07 | 1.05 | 0.76 | 0.54 | n.d. | n.d. |
| Hex-1-ene ^b | He | 0.67 | n.d. | 0.63 | 0.65 | 0.66 | n.d. | n.d. | n.d. | n.d. |
| Styrene ^c | N ₂ | 0.30 | n.d. | 0.40 | 0.49 | 0.49 | n.d. | 0.51 ^d | n.d. | n.d. |
| Styrene ^c | Ar | 0.30 | n.d. | 0.41 | 0.47 | 0.50 | 0.43 | 0.39 ^d | n.d. | n.d. |
| Styrene ^c | He | 0.30 | n.d. | 0.29 | 0.28 | 0.33 | n.d. | n.d. | n.d. | n.d. |

Influence of an additional gas on the initial rate (mmol/h). Toluene: 5.0 ml, $p(\text{CO}) = p(\text{H}_2) = 1.5$ MPa, initial rate = mol. aldehyde formed/reaction time.

^a $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 18.30 mg (0.02 mmol), cyclohexene: 405 μl (4.0 mmol), T : 373 K, reaction time: 4 h.

^b $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 7.500 mg (0.0082 mmol), hex-1-ene: 490 μl (4.0 mmol), T : 323 K, reaction time: 3 h.

^c $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 7.500 mg (0.0082 mmol), styrene: 230 μl (1.99 mmol), T : 313 K, reaction time: 3 h.

^d Pressure of the additional gas: 120 MPa.

the hydroformylation of the same olefin in the presence of $\text{Co}_2(\text{CO})_8$ [24–26]. Using argon, under the same experimental conditions (Table 1), an analogous behaviour is shown.

These data may be explained through a competitive influence of the additional gas with dihydrogen or alkene for a coordinatively unsaturated place available in the catalytically active intermediates.

On the contrary, the hydroformylation of cyclohexene under an increasing pressure of helium shows an increase of the initial rate from 0.32 to 0.49 mmol/h. This behaviour is surprising, but it has been reported in other reactions where the activation volume is negative [29]. In our case, these data can be explained with a rate determining step involving the coordination of one of the reactants (olefin, hydrogen, etc.) to the transition metal and this step involves a negative volume of activation.

Methane does not show any influence on the conversion of the olefin. In these tests, the physical effect of an increase of initial rate due to the high pressure of the methane is overcome by the dilution of the solution due to the gas dissolved in toluene. As a consequence there is no effect of methane on the initial rate of the reaction. In agreement with this hypothesis, the solubility of methane in toluene is much higher than helium [30,31] and the dilution of the solution due to the methane dissolved in the solvent is high, especially when a high pressure of this gas is employed.

Xenon shows a strong decreasing effect on the initial rate of hydroformylation (Table 2) even if its pressure is low. This behaviour may be ascribed to the better ability of xenon to interact with the metal owing to its lower ionisation potential [32], in comparison with the other additional gases above reported. Furthermore, these data are not affected by the high pressure of the additional gas, as evidenced for helium, and consequently the influence of xenon is more evident.

The strong inhibition observed with xenon is also reported for the hydroformylation of cyclohexene catalysed by $\text{Co}_2(\text{CO})_8$ [23–25] or $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$ [27].

3.2. Hex-1-ene hydroformylation

Hex-1-ene is hydroformylated in softer conditions than cyclohexene because it is a terminal olefin and

Table 2
Hydroformylation of cyclohexene in the presence of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$

| Alkene | Xe (g) | $p(\text{Xe})^a$ (MPa) | Initial rate ^b (mmol/h) | Initial rate reduction ^c (%) |
|--------------------------|--------|---------------------------|---------------------------------------|--|
| Cyclohexene ^d | 0 | 0 | 0.32 | 0 |
| Cyclohexene ^d | 5.1 | 2.0 | 0.30 | 6 |
| Cyclohexene ^d | 33 | 4.8 | 0.11 | 66 |
| Hex-1-ene ^e | 0 | 0 | 0.67 | 0 |
| Hex-1-ene ^e | 2.2 | 2.0 | 0.62 | 7 |
| Hex-1-ene ^e | 5.9 | 3.4 | 0.55 | 18 |

Influence of xenon on the initial rate. Toluene: 5.0 ml, $p(\text{CO}) = p(\text{H}_2) = 1.5$ MPa.

^a Partial pressure of xenon.

^b Initial rate = mol. aldehyde formed/reaction time.

^c Initial rate reduction = (initial rate in the absence of xenon) – (initial rate observed)/(initial rate in the absence of xenon).

^d $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 18.30 mg (0.02 mmol), cyclohexene: 405 μl (4.0 mmol), T : 373 K, reaction time: 4 h.

^e $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 7.500 mg (0.0082 mmol), hex-1-ene: 490 μl (4.0 mmol), T : 323 K, reaction time: 3 h.

it is more reactive in the hydroformylation [1–3]. Due to these considerations, the reaction was carried out at 323 K, with a higher substrate/catalyst ratio (480 instead of 200) and a shorter reaction time (3 h).

The hydroformylation of hex-1-ene under a high pressure of dinitrogen (Table 1), in the range 0–25 MPa show a linear increment of the reaction rate. A further increase of dinitrogen pressure, from 25 to 140 MPa does not show any influence of the initial rate. A slight decrease of the initial rate is shown at the higher pressures tested (180 MPa).

Argon shows the same behaviour of dinitrogen when the pressure of the additional gas is lower than 75 MPa. Working with a higher argon pressure, the initial rate decreases as the pressure of the additional gas increases. The different characteristics of the two gases and their different solubilities in toluene require different pressures to show the same behaviour.

The presence of helium, in the same range of pressures, does not affect the initial rate of hex-1-ene hydroformylation.

Finally, xenon shows a negative effect on the initial rate of the hydroformylation of hex-1-ene. A low pressure of xenon (2.0–3.4 MPa) shows an effect analogous to that above reported with a high pressure of argon (80–105 MPa) (Tables 1 and 2).

3.3. Styrene hydroformylation

The hydroformylation of styrene is affected by the presence of an additional gas and the results are analogous to those reported above using hex-1-ene: argon or dinitrogen increases the reaction rate in the range 0–75 MPa, above these values the presence of argon causes a decrease of the initial rate, while the negative influence of dinitrogen is not evidenced in same range of pressures (Table 1).

Helium, on the other hand, does not show any appreciable change of the initial rate of the reaction (Table 1).

3.4. Discussion

The results above reported may be explained through an interaction of the coordinatively unsaturated rhodium species involved in the hydroformylation with some of the additional gases present (dinitrogen, argon or xenon). As a consequence, the catalyst was partially subtracted to the catalytic cycle decreasing the initial rate of the reaction.

Complexes of transition metals with noble gases have been identified in solid matrix by UV/Vis, EPR and IR spectroscopy [33,34]. Unsaturated transition metal complexes are able to coordinate noble gases through σ -donation as theoretically demonstrated by Perutz and Turner [35]. Finally, the X-ray crystal structure of $[\text{AuXe}_4^{2+}][\text{Sb}_2\text{F}_{11}^-]_2$ has been reported [36].

To verify the hypothesis of an interaction between the catalyst and an additional ligand, we have carried out the hydroformylation of styrene in the presence of an increasing amount of triethylamine, which can act as a weak ligand for an unsaturated rhodium complex. In this case also the initial rate of the hydroformylation decreases with an increasing concentration of the base (Table 3).

Furthermore, we have evidenced that an increasing amount of dinitrogen decreases the initial rate of hex-1-ene isomerization catalysed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (Table 4) as previously reported for the isomerization of hex-1-ene in the presence of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ [37].

These data support the hypothesis of a competition between dinitrogen and alkene for the coordination to an unsaturated rhodium complex. However, because

Table 3

Hydroformylation of styrene in the presence of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$

| NEt_3/Rh (molar ratio) | Initial rate ^a (mmol/h) | Initial rate reduction ^b (%) |
|---|---------------------------------------|--|
| 0 | 0.24 | 0 |
| 10 | 0.23 | 4 |
| 20 | 0.21 | 12 |
| 30 | 0.20 | 17 |

Influence of triethylamine on the initial rate. $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 7.500 mg (0.082 mmol), styrene: 230 μl (1.99 mmol), toluene: 25.0 ml, $p(\text{CO}) = p(\text{H}_2) = 1.5$ MPa, T : 313 K, reaction time: 4 h.

^a Initial rate = mol. aldehyde formed/reaction time.

^b Initial rate reduction = (initial rate in the absence of xenon) – (initial rate observed)/(initial rate in the absence of xenon).

the initial rate of hex-1-ene isomerization is approximately double the rate of hydroformylation (Tables 1 and 4), the formation of a π -complex between the catalyst and the olefin cannot be assumed as the rate determining step in the hydroformylation of hex-1-ene. Probably the formation of an acyl complex or the dihydrogen activation may be the RDS of this reaction. In a recent paper [38], Van Leeuwen and coworkers reported that the RDS for the hydroformylation of oct-1-ene is the oxidative addition of dihydrogen to the acylrhodium intermediate. On the contrary, using cyclohexene, the RDS involves the coordination of the olefin to a rhodium hydride complex. The effect of the additional gas could be related to the different kinetics evidenced for terminal and internal olefins: the interaction of the additional gas with rhodium, affecting the initial rate, takes place in a different step of the hydroformylation.

Table 4

Isomerization of hex-1-ene in the presence of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$

| $p(\text{N}_2)$ (MPa) | Initial rate ^a (mmol/h) | Initial rate reduction ^b (%) |
|-----------------------|---------------------------------------|--|
| 0 | 1.20 | 0 |
| 18 | 1.22 | 2 |
| 56 | 0.98 | 18 |
| 102 | 1.04 | 13 |

Influence of dinitrogen on the initial rate. Reaction conditions: $\text{RhH}(\text{CO})(\text{PPh}_3)_3$: 7.500 mg (0.0082 mmol), hex-1-ene: 490 μl (4.0 mmol), toluene: 5.0 ml, T : 323 K, reaction time: 3 h.

^a Initial rate = mol. aldehyde formed/reaction time.

^b Initial rate reduction = (initial rate in the absence of xenon) – (initial rate observed)/(initial rate in the absence of xenon).

4. Conclusion

The influence of an additional gas in the reaction medium may be tentatively explained through weak interactions between the transition metal and a substrate (alkene or hydrogen) through “non-classical” interactions involving energy lower than a chemical bond [39,40].

Helium and methane does not give any interactions with transition metals, so they do not affect the initial rate. The low and positive influence observed in some cases using these gases may be ascribed to a physical effect connected with the high pressure employed.

Argon, dinitrogen and xenon, showing a coordinating ability, when present in high concentration, reduce the initial rate of olefin hydroformylation confirming a competition between these gases and a substrate for a coordinatively unsaturated position of the rhodium catalyst.

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