

Kinetics and mechanisms of homogeneous catalytic reactions

Part 6. Hydroformylation of 1-hexene by use of $\text{Rh}(\text{acac})(\text{CO})_2/\text{dppe}$ [$\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$] as the precatalyst

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Abstract

A kinetic study of the homogeneous hydroformylation of 1-hexene to the corresponding aldehydes (heptanal and 2-methyl-hexanal) was carried out using a rhodium catalyst formed by addition of 1 equiv. of 1,2-bis(diphenylphosphino)ethane (dppe) to $\text{Rh}(\text{acac})(\text{CO})_2$ under mild reaction conditions (80 °C, 1–7 atm H_2 and 1–7 atm CO) in toluene; in all cases linear to branched ratios were close to 2. The reaction rate is first-order in dissolved hydrogen concentration at pressures below 3 atm, but independent of this parameter at higher pressures. In both regimes (low and high H_2 pressure), the initial rate was first-order with respect to the concentration of Rh and fractional order with respect to 1-hexene concentration. Increasing CO pressure had a positive effect on the rate up to a threshold value above which inhibition of the reaction was observed; the range of positive order on CO concentration is smaller when the total pressure is increased. The kinetic data and related coordination chemistry are consistent with a mechanism involving $\text{RhH}(\text{CO})(\text{dppe})$ as the active species initiating the cycle, hydrogenolysis of the acyl intermediate as the rate-determining step of the catalytic cycle at low hydrogen pressure, and migratory insertion of the olefin into the metal-hydride bond as rate limiting at high hydrogen pressure. This catalytic cycle is similar to the one commonly accepted for $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ but different from previous proposals for Rh-diphosphine catalysts.

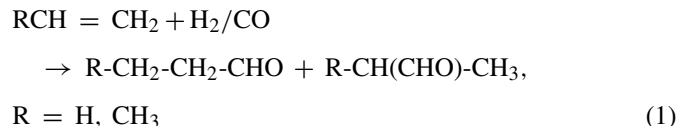
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1. Introduction

The hydroformylation of alkenes is a well-known synthetic tool for a wide range of organic molecules of high commercial value, as well as one of the largest scale applications of homogeneous catalysis in industry. The major capacity is based on the low-pressure oxo process (LPO) using phosphine-modified rhodium carbonyls as catalysts. LPO is used to convert light olefins (mainly C_2 and C_3) into C_3 and C_4 aldehydes by their reaction with syn-gas ($\text{CO} + \text{H}_2$) (Eq. (1)); these aldehydes are mainly converted to $\text{C}_{n>8}$ alcohols used in the manufacture of

polyvinyl chloride (PVC) plasticizers and detergents [1].



The most widely used ligand in LPO is triphenylphosphine and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is recognized as one of the most important catalysts for the homogeneous hydroformylation of alkenes. In recent years, new applications for high added-value intermediates for fine chemicals and pharmaceuticals have emerged in literature [2], e.g. the hydroformylation of styrene or its derivatives to obtain aryl propionaldehydes, which on subsequent oxidation can give aryl propionic acid derivatives (e.g. ibuprofen from *p*-isobutylstyrene). Van Leeuwen and Claver recently

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published a comprehensive review dealing with recent advances in homogeneous and biphasic hydroformylation of olefins with rhodium complexes, including kinetic and mechanistic aspects [3].

In spite of the industrial importance of olefin hydroformylation and the large number of publications in this field published over several decades, relatively few studies have been devoted to the kinetics of this reaction, and most of them involve $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ [4–9]; kinetic and mechanistic studies of hydroformylation with catalysts containing bulky phosphites [10,11], phosphine-phosphite [12] or diphosphites [13], 1,2,5-triphenyl-1H-phosphole [14] and triphenylarsine [15] as ligands have also been reported. Of particular relevance to the present work, hydroformylation by rhodium–diphosphine systems has been extensively studied over the years and reasonable catalytic cycles have been proposed [1,3,16]. A recent publication from the group of Claver on the mechanism of hydroformylation by rhodium–diphosphine catalysts [17a] and the book on Rh hydroformylation by Van Leeuwen and Claver published in 2000 [3] both point out that *the kinetics* of hydroformylation with these systems have not been discussed. Another review by Green et al. from 2004 [17b] summarizes the accumulated knowledge about hydroformylation mechanisms by rhodium–diphosphine catalysts, noting the influence of bite angles on the activity and selectivity, as well as the agreement of theoretical studies with previously proposed catalytic cycles; no mention is made of any previous study on the kinetics of hydroformylation by Rh–diphosphine systems.

In the present paper, we describe such a study of the hydroformylation of 1-hexene using as the precatalyst the system formed by addition of 1 equiv. of 1,2-bis(diphenylphosphine)ethane (dppe) to $\text{Rh}(\text{acac})(\text{CO})_2$ and propose a mechanism consistent with the kinetic data and with some related coordination chemistry. This mechanism is discussed in reference to previous mechanistic proposals for similar catalysts. In the accompanying subsequent paper of this series, a similar study is reported for the hydroformylation of 1-hexene by cationic complexes $[\text{M}(\text{COD})(\text{PPh}_3)_2]\text{PF}_6$, $\text{M} = \text{Rh}, \text{Ir}$.

2. Experimental

2.1. Instruments and materials

All manipulations were conducted with rigorous exclusion of air using Schlenck techniques. 1-Hexene was purified by distillation under reduced pressure. Solvents were purified by known procedures. $\text{Rh}(\text{acac})(\text{CO})_2$ was prepared by a published procedure [18]. NMR and IR spectra were recorded on a Bruker AM-300 spectrometer and a Shimadzu 8300 FT-IR instrument, respectively.

2.2. Procedure for kinetic measurements

Kinetic experiments were carried out in a high-pressure reactor, supplied by Parr Instruments, which was provided with an arrangement for sampling of liquid contents, automatic temperature and pressure control and variable stirrer speed. In a

typical experiment, a solution containing the catalyst, 1-hexene, *n*-heptane (as internal standard) and toluene as the solvent (to 30 mL total volume) was placed in the reactor. The solution was carefully deoxygenated by flushing with argon, stirring was commenced and the reactor was heated to the desired temperature. When the reaction temperature was reached, a mixture of CO and H_2 in the required proportion and pressure was introduced into the autoclave; this moment was taken as the zero time of the reaction. Each run was followed by taking liquid samples at regular intervals of time, and analyzing them by gas chromatography using a 610 Series UNICAM gas chromatograph fitted with a thermal conductivity detector and a 3 m 10% SE-30 on Supelcoport glass column, with helium as the carrier gas; the chromatograph was coupled to a UNICAM 4815 data system.

The supply of CO/H_2 from a high-pressure reservoir was maintained at constant pressure and molar ratio throughout the reaction. Each run was repeated at least twice in order to ensure reproducibility of the results. All the reactions were carried out for short periods of time to maintain the conversion in the liquid phase at no more than *ca.* 10% in order to perform a kinetic analysis based on the initial rate method [19]. The data for 1-hexene hydroformylation were plotted as molar concentration of the corresponding products *vs.* time yielding straight lines, which were fitted by conventional linear regression programs. Initial reaction rates were obtained from the corresponding slopes. The hydrogen and carbon monoxide concentrations in the reaction medium were calculated from solubility data reported in the literature [20].

2.3. Study of the interaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with each component of the catalytic mixture

2.3.1. Interaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with dppe

To a solution of $\text{Rh}(\text{acac})(\text{CO})_2$ (100 mg, 0.38 mmol) in benzene (10 mL) was added dppe (160 mg, 0.40 mmol) and the mixture was stirred vigorously under argon at room temperature producing a yellow solution, which was evaporated under vacuum to *ca.* one-third of its initial volume. A yellow precipitate was obtained by addition of *n*-pentane; it was washed with *n*-pentane and diethylether and dried *in vacuo*.

2.3.2. Interaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with dppe under *syn-gas*

$\text{Rh}(\text{acac})(\text{CO})_2$ (103 mg, 0.38 mmol) and dppe (160 mg, 0.40 mmol) in toluene (10 mL) were introduced in a Fischer–Porter reactor, charged with 5 atm of *syn-gas* and heated at 100 °C for 2 h; the resulting solution was dried under a stream of *syn-gas*.

2.3.3. Interaction of $\text{RhH}(\text{CO})_2(\text{dppe})$ with PPh_3

$\text{RhH}(\text{CO})_2(\text{dppe})$ was prepared *in situ* as described before but 1 equiv. of PPh_3 was further added (105 mg, 0.40 mmol). The resulting solution was dried under a stream of *syn-gas*. This reaction was also carried out in toluene- d_8 , the solution transferred to a NMR tube under a *syn-gas* atmosphere and immediately monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR.

Table 1

Effect of the total pressure of syn-gas on the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe

p (atm)	r_i ($\times 10^5$ M s ⁻¹)
1.4	2.56
2.8	5.30
4.1	10.20
6.9	24.72

Conditions: [cat] = 1.68×10^{-3} M, [S] = 0.51 M, 80 °C, $p(\text{CO})/p(\text{H}_2) = 1$, toluene; r_i : initial rate, l/b ratio = 2.0–2.6.

3. Results

3.1. Catalytic hydroformylation of 1-hexene

The system Rh(acac)(CO)₂/dppe is an efficient catalyst precursor for the hydroformylation of 1-hexene in toluene solution under moderate conditions of temperature and pressure (80 °C, 1–7 atm of syn-gas) yielding exclusively the corresponding aldehydes, heptanal and 2-methyl-hexanal; the linear to branched ratio (l/b) is practically constant (*ca.* 2) within the range of reaction conditions used in this work. The initial rate of 1-hexene hydroformylation was found to be independent of the speed of stirring in the range 500–800 rpm, indicating that the data obtained correspond to a kinetic regime and that mass transfer effects were negligible.

3.2. Kinetic investigation

The kinetics of the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe in toluene solution were studied by carrying out runs at different concentrations of catalyst, substrate, dissolved H₂, and dissolved CO at 80 °C. First of all, it was observed that the hydroformylation rate varied proportionally to the total syn-gas pressure in the range 1–7 atm, as shown in Table 1 and Fig. 1 and therefore the rest of the kinetic

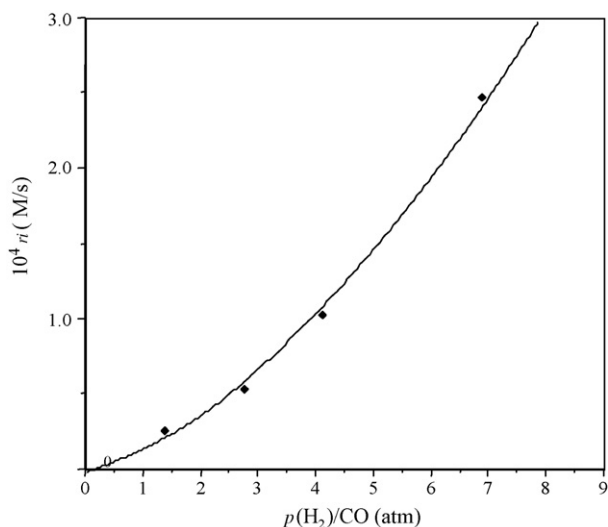


Fig. 1. Rate dependence on total syn-gas pressure for the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe. Conditions: [cat] = 1.68×10^{-3} M, [hex] = 0.51 M, 80 °C, toluene.

Table 2

Effect of the dissolved hydrogen concentration on the rate of the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe

p (atm)	[H ₂] ($\times 10^3$ M)	r_i ($\times 10^5$ M s ⁻¹)
1.0	5.0	2.52
1.4	6.3	5.30
2.4	10.1	9.97
3.5	13.9	15.49
4.1	16.6	16.81
4.8	19.2	15.58
5.5	21.8	15.42
6.1	23.9	16.00

Conditions: [cat] = 1.68×10^{-3} M, [S] = 0.51 M, [CO] = 8.8×10^{-3} M (1.4 atm), 80 °C, toluene; r_i : initial rate, l/b ratio = 2.0–2.6.

study was carried out within this pressure range. The variation of the initial hydroformylation rate at 80 °C was studied for several hydrogen concentrations, while the catalyst, substrate and CO concentrations were kept constant; these results are collected in Table 2 and in Fig. 2, where a typical saturation curve with respect to [H₂] is observed. This corresponds to an approximately first-order dependence at hydrogen pressures below 3 atm ($\log r_i = -1.5 + 1.2 \log [\text{H}_2]$, $r^2 = 0.98$), which tends to zero order at higher H₂ pressures ($\log r_i = -3.8 - 0.1 \log [\text{H}_2]$, $r^2 = 0.03$). In consequence, the rate dependence on the concentration of the other reactants was evaluated at three different values of [H₂]: low (1.4 atm, 6.3×10^{-3} M), intermediate (3.5 atm, 1.0×10^{-2} M), and high (6.1 atm, 2.4×10^{-2} M).

At low [H₂] (data in Table 3) the rate dependence with respect to [CO] yielded the “volcano-type” curve shown in Fig. 3, which indicates that the reaction is inhibited by CO above a threshold value of about 2.1 atm CO (1.3×10^{-2} M). At lower CO pressures the dependence was first-order ($\log r_i = -1.8 + 1.1 \log [\text{CO}]$, $r^2 = 0.99$), but it becomes of *inverse order* (-1.6) at higher CO pressures ($\log r_i = -6.9 - 1.6 \log [\text{CO}]$, $r^2 = 0.98$). Under the same con-

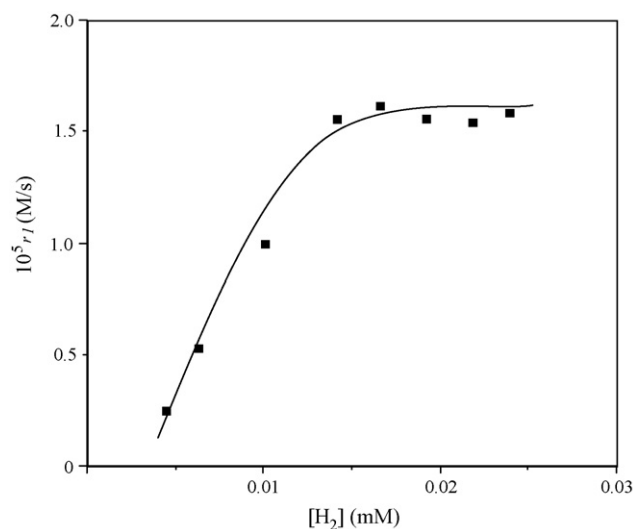


Fig. 2. Rate dependence on dissolved H₂ concentration for the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe. Conditions: [cat] = 1.68×10^{-3} M, [hex] = 0.51 M, [CO] = 8.8×10^{-3} M (1.4 atm), 80 °C, toluene.

Table 3
Kinetic data for the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe at low p(H₂)

[Rh] (× 10 ³ M)	[1-Hexene] (M)	p(CO) (atm)	[CO] (× 10 ³ M)	r _i (× 10 ⁵ M s ⁻¹)
1.68	0.51	0.7	4.4	2.11
1.68	0.51	1.0	6.6	3.87
1.68	0.51	1.4	8.8	5.30
1.68	0.51	1.7	10.9	6.84
1.68	0.51	2.1	13.2	8.28
1.68	0.51	2.8	17.6	7.48
1.68	0.51	3.5	22.0	6.14
1.68	0.51	4.1	26.4	4.11
1.68	0.51	5.5	35.3	2.36
0.64	0.51	1.4	8.8	1.66
1.29	0.51	1.4	8.8	3.59
2.54	0.51	1.4	8.8	7.43
3.24	0.51	1.4	8.8	10.52
1.68	0.13	1.4	8.8	2.24
1.68	0.27	1.4	8.8	3.93
1.68	0.59	1.4	8.8	6.54
1.68	0.67	1.4	8.8	6.85

Conditions: p(H₂) = 1.4 atm ([H₂] 6.3 × 10⁻³ M); T = 80 °C; solvent: toluene, r_i: initial rate, l/b ratio = 1.9–2.4.

ditions, the rate of hydroformylation shows a first-order dependence on rhodium concentration ($\log r_i = -1.3 + 1.1 \log [\text{Rh}]$, $r^2 = 0.99$), while it is of fractional order (0.7) with respect to the concentration of the alkene ($\log r_i = -4.0 + 0.7 \log [1\text{-hexene}]$, $r^2 = 0.99$).

Similarly, the results of the kinetics of the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe at intermediate hydrogen pressure (3.5 atm) (Table 4) proved to be approximately first-order with respect to [CO] at low pressures ($\log r_i = -1.8 + 1.1 \log [\text{CO}]$, $r^2 = 0.95$) while it tends to negative order at high CO pressures ($\log r_i = -6.9 - 2.1 \log [\text{CO}]$, $r^2 = 0.98$). The rate is also first-order in rhodium concentration ($\log r_i = -0.7 + 1.1 \log [\text{Rh}]$, $r^2 = 0.96$) and fractional order in substrate concentration ($\log r_i = -3.6 + 0.7 \log [1\text{-hexene}]$, $r^2 = 0.99$). At high hydrogen pressures, the results (not shown)

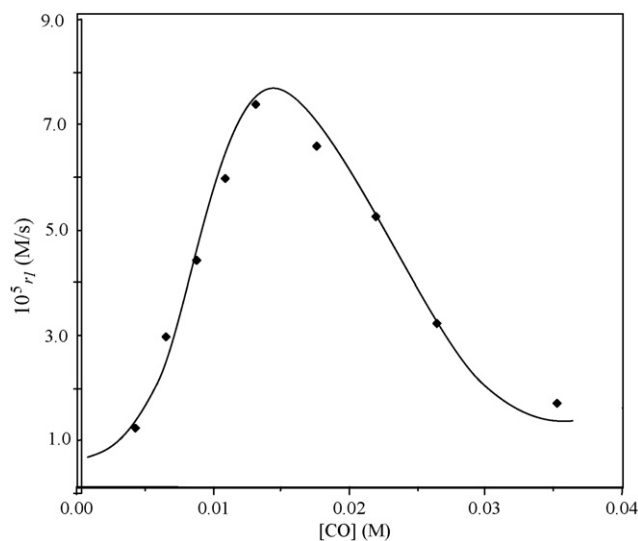


Fig. 3. Rate dependence on dissolved CO concentration for the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe at low hydrogen concentration (1.5 atm, 1.0 × 10⁻² M).

are rather similar to those found at the intermediate hydrogen concentration.

The linear to branched ratio (l/b) of the aldehydes formed was practically constant (between 2.0 and 2.6) and independent of the reaction conditions, except for the increment on the syn-gas and CO pressure where a slightly reduction of l/b ratio was observed.

3.3. Coordination chemistry related with 1-hexene hydroformylation

In order to complement the kinetic study of 1-hexene hydroformylation described above, the interaction of the catalyst precursor Rh(acac)(CO)₂ with each component of the catalytic mixture (*i.e.* dppe and syn-gas) was studied independently; the results are summarized in Scheme 1. The interaction of Rh(acac)(CO)₂ (**1**) with 1 equiv. dppe in benzene results in the evolution of CO and the formation of a yellow solution, from which a yellow solid was isolated whose IR spectrum showed no presence of carbonyl ligands. The ¹H and ³¹P{¹H} NMR spectra showed the presence of [Rh(dppe)₂]⁺ (**2**), formed as the acac salt, as the only phosphorus-containing species [58.8 ppm (d, ²J_{P-Rh} = 133 Hz)], together with the starting complex; this cationic bis(dppe) complex was initially reported by James and Mahahan in 1979 [21a]. On the other hand, when a solution of **1** reacted with 1 equiv. of dppe under syn-gas (4 atm), a yellow solution was obtained, from which a brown-yellow solid could be isolated. IR and NMR spectra indicate the presence of several species, among which [Rh(CO)(dppe)₂(μ-CO)₂] (**3**) could be identified by the signals in ³¹P{¹H} NMR at 41.5 and 40.3 ppm as part of a AA'A''A'''XX' spin system [21b]. We believe that this reaction initially produces RhH(CO)₂(dppe) (**A**) which easily decomposes to form, among other species, the dimer **3**; this latter compound is analogous to the one claimed by Wilkinson et al. [22] to be formed as a byproduct in the hydroformylation of 1-hexene catalyzed by RhH(CO)(PPh₃)₃ and more recently

Table 4

Kinetic data for the hydroformylation of 1-hexene catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2/\text{dppe}$ at intermediate $p(\text{H}_2)$

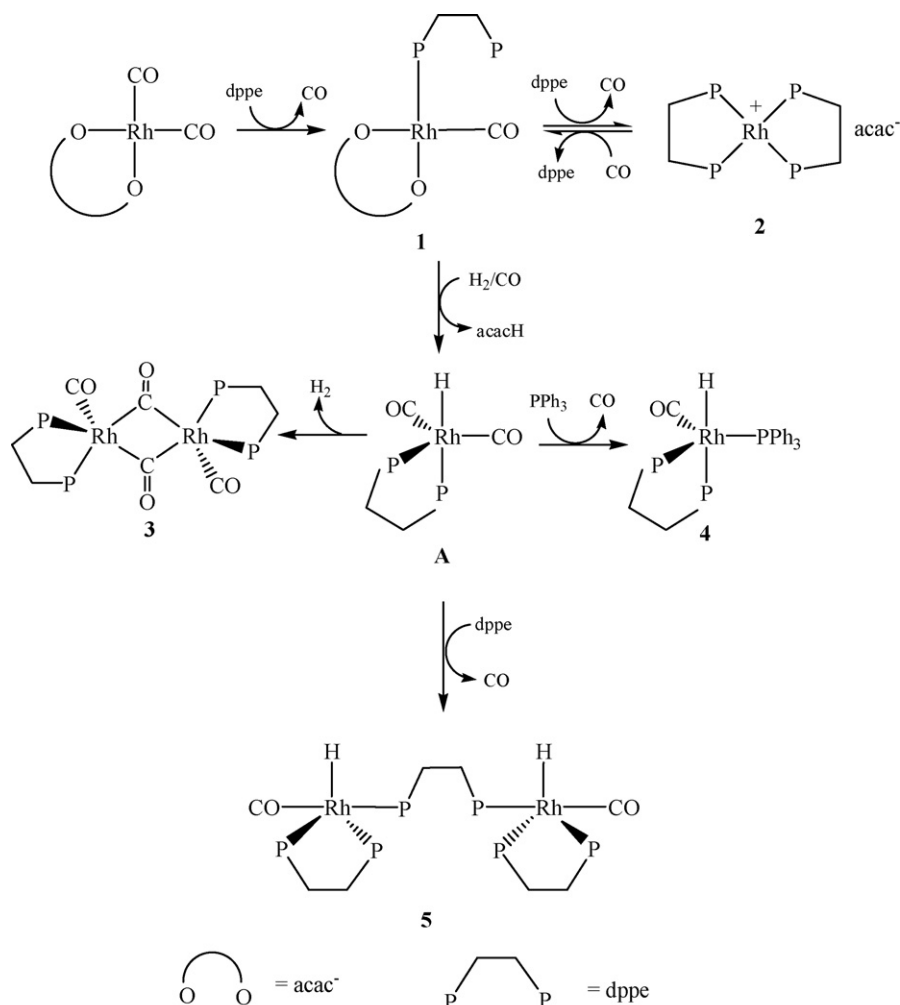
$[\text{Rh}] (\times 10^3 \text{ M})$	[1-Hexene] (M)	$p(\text{CO})$ (atm)	$[\text{CO}] (\times 10^3 \text{ M})$	$r_i (\times 10^5 \text{ M s}^{-1})$
1.68	0.51	0.7	4.4	3.80
1.68	0.51	2.8	17.6	18.00
1.68	0.51	3.5	22.0	24.80
1.68	0.51	4.1	26.4	18.90
1.68	0.51	4.8	30.9	12.40
1.68	0.51	1.4	8.8	15.50
2.07	0.51	1.4	8.8	20.00
2.66	0.51	1.4	8.8	26.40
3.27	0.51	1.4	8.8	40.70
1.68	0.27	1.4	8.8	10.40
1.68	0.40	1.4	8.8	13.00
1.68	0.59	1.4	8.8	17.50

Conditions: $p(\text{H}_2) = 3.5 \text{ atm}$ ($[\text{H}_2] 1.0 \times 10^{-2} \text{ M}$); $T = 80^\circ \text{C}$; solvent: toluene; r_i : initial, l/b ratio = 2.0–2.4.

observed by Bianchini et al. [4] by high pressure NMR spectroscopy.

Finally, in order to have more evidence for the presence of $\text{RhH}(\text{CO})_2(\text{dppe})$ in our reaction medium, we studied the interaction of a solution of **A** with 1 equiv. of PPh_3 in toluene- d_8 (under a stream of syn-gas), which produced a mixture of at

least four complexes: the dimeric complex **3**, which is the major species detected by $^{31}\text{P}\{^1\text{H}\}$ NMR and three hydride-containing species (detected by ^1H NMR), which were characterized as $\text{RhH}(\text{CO})_2(\text{dppe})$ (**A**, triplet of doublets at 8.3 ppm, $J = 54$ and 11 Hz), $\text{RhH}(\text{CO})(\text{dppe})(\text{PPh}_3)$ (**4**, broad triplet at 10.1 ppm) and $[\text{Rh}(\text{H})(\text{CO})(\text{dppe})]_2(\mu\text{-dppe})$ (**5**, triplet of doublets of dou-

Scheme 1. Stoichiometric reactions related with the hydroformylation of 1-hexene catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2/\text{dppe}$.

blets at 8.6 ppm, $J = 57$, 15 and 9 Hz); similar hydride species containing 1,3-bis(diphenylphosphino)propane (dppp) have been reported by James et al. [23]. The use of Rh-dppe-PPh₃ mixtures in hydroformylation catalysis has been reported before [16]. All these experiments lead us to propose that under the hydroformylation conditions, species **A** is the resting state of the catalyst; the cationic bis(diphosphine) rhodium complex (**2**) was discarded as the active species because of under syn-gas conditions this species must be transformed in **A**, as reported by the groups of Claver and van Leeuwen [24] for a similar rhodium system with (2*S*,4*S*)-bis(diphenylphosphine)pentane (BDPP) as the chelating phosphine ligand.

4. Discussion

Despite the fact that Rh-catalyzed hydroformylation is practiced successfully in industry and has been the object of intense studies for several decades, information on the kinetics of this reaction is still relatively scarce and often contradictory, mainly because these reactions are extremely sensitive to the experimental conditions employed. Most of the kinetic studies available have dealt with the Rh–PPh₃ system, for which the reaction has been generally found to be first-order with respect to olefin and rhodium concentration and zero order on hydrogen pressure, implying that the slow step is either the coordination of the substrate to Rh or the migratory insertion of the alkene into the Rh–H bond. However, the oxidative addition of hydrogen has been considered as the rate-determining step in other reports employing the same catalytic system under different reaction conditions on the basis of the acceleration of the hydroformylation rate observed upon increasing the hydrogen pressure [3–9]. Nevertheless this is considered by some authors [3] to be most likely an artifact due to the presence of inactive dimeric species which react with hydrogen to regenerate monomeric rhodium hydrides, thereby increasing the effective concentration of active rhodium in solution. It is claimed that under “standard” catalytic conditions (*i.e.* “industrial operating conditions” 70–120 °C, 5–25 atm CO, 5–25 atm H₂, *ca.* 1 mM Rh, 0.1–2 M alkene) the reaction is first-order in rhodium and alkene concentration, zero order in olefin and negative order in CO or phosphine concentrations [3]. Pioneering work by Cavalieri d’Oro [5] on the hydroformylation of propene reported a rate law:

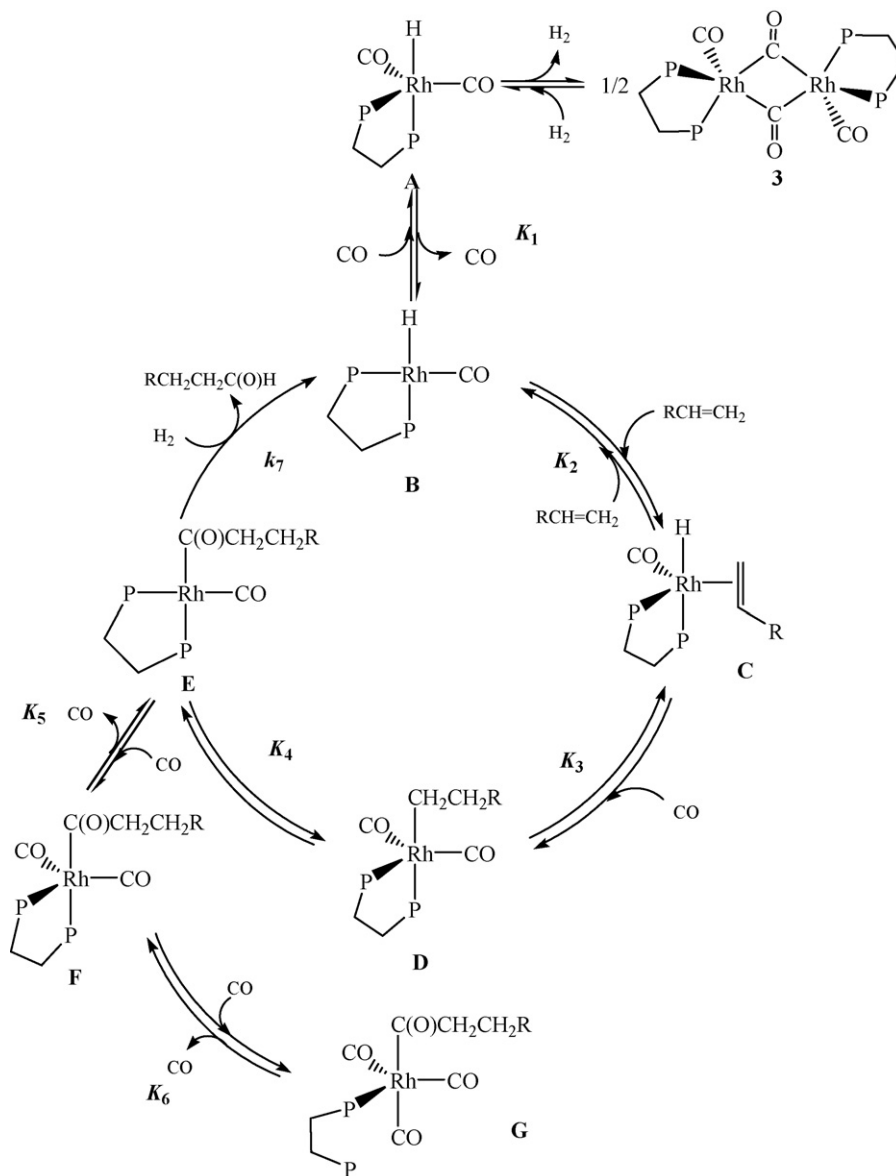
$$r = k[\text{alkene}]^{0.6}[\text{PPh}_3]^{-0.7}[\text{CO}]^{-0.1}[\text{Rh}]^1[\text{H}_2]^0$$

A detailed study has also been carried out with catalysts containing bulky phosphite ligands [10,11], which are characterized by the fact that only one phosphorus ligand is coordinated to rhodium; in this case, the rate is independent of the alkene concentration, first-order in hydrogen and rhodium concentrations and inverse first-order in CO pressure; the rate determining step is thought to be the hydrogenolysis of the acyl intermediate [11]. For bulky diphosphites the reaction exhibited a first-order dependence on alkene concentration, zero order in hydrogen pressure and negative order in CO pressure, consistent with an rds early in the catalytic cycle [13].

Our results can be accommodated by the mechanism depicted in Scheme 2 for the formation of the linear aldehyde (branched

isomer excluded for clarity), which in general terms is analogous to the commonly accepted cycle for the Rh–PPh₃ system [3,4]. It is known that Rh(acac)(CO)₂ (**1**) reacts with syn-gas in presence of an excess of PPh₃ to generate complexes RhH(CO)_{*x*}(PPh₃)_{4–*x*} ($x = 1, 2$) [6]. It is known that dppe prefers to bind as a chelate to one metal center, rather than bridge between two metals, which is the preferred bonding mode of other diphosphines with a longer chain between the phosphorus donor atoms [16b–d,21,25]. We propose that (**1**) reacts with 1 equiv. dppe under syn-gas to form RhH(CO)₂(dppe) (**A**); this species is unstable in absence of syn-gas to form the carbonyl-bridged dimer [Rh(CO)(dppe)]₂(μ-CO)₂ (**3**). Complex (**1**) is probably in equilibrium (K_1) with the 16-electron RhH(CO)(dppe) (**B**), which initiates the catalytic cycle (see Scheme 2). **B** reversibly coordinates the olefin (K_2) to produce RhH(CO)(olefin)(dppe) (**C**). Then, migratory insertion of the olefin into the metal hydride bond takes place (K_3) with the concomitant coordination of a CO molecule to yield Rh(CO)₂(alkyl)(dppe) (**D**); the reversibility of this reaction has been postulated in other works [8,15]. The insertion of CO into the Rh–alkyl bond of **D**, generates the unsaturated acyl species Rh(CO)(acyl)(dppe) (**E**) through K_4 . Finally, hydrogenolysis of (**E**) produces the aldehyde, and regenerates the catalytically active species (**A**), which re-starts the cycle. At high CO pressure, species **E** can reversibly coordinate CO to generate Rh(CO)₂(acyl)(dppe) (**F**) through K_5 , and a further CO ligand through K_6 , to form RhH(CO)₃(acyl)(dppe*) (**G**), by dissociation of one of the P-atoms of dppe.

Our results indicate that, depending on the dissolved hydrogen concentration, different rate-determining steps may be operating in this cycle. The first-order kinetics observed at low hydrogen pressure is consistent with the hydrogenolysis of the acyl intermediate **E** being the rds, whereas the zero order dependence on [H₂] at higher pressures points to a rds in the early stages of the cycle, most likely the migratory insertion of the olefin into the Rh–H bond. Hydroformylation is clearly first-order in rhodium concentration, irrespectively of the gas pressures employed. Claver et al. [17] reported a similar observation for the hydroformylation of styrene catalyzed by the rhodium/BDPP system and interpreted it in terms of dinuclear species not being involved in the rate-limiting step, which would result in fractional order with respect to metal concentration. Although we favor a similar explanation in our case, the implication of dinuclear species in the catalytic process cannot be definitively ruled out with the available data. On the other hand, the fractional kinetics observed as a function of substrate concentration may be the result of operating in the intermediate regime of a saturation kinetics, similarly to what was found by Cavalieri d’Oro et al. for the hydroformylation of propylene catalyzed by RhH(CO)(PPh₃)₃ [5]. Saturation kinetics in olefin hydroformylation catalyzed by this precursor have also been reported by Kiss et al. for ethene [6], and by Chaudhari et al. for 1-hexene [7], for 1-decene [8], and for 1-dodecene. Chaudhari et al. also have reported a zero order with respect to olefin for styrene hydroformylation catalyzed by the same precursor [9]. Finally, the inhibition of the rate of hydroformylation of 1-hexene at high CO pressures may be explained by the reactions occurring in the catalytic cycle of Scheme 2 (k_{-1} , k_5 and k_6) leading to inactive

Scheme 2. Catalytic cycle for the Rh(acac)(CO)₂/dppe-catalyzed 1-hexene hydroformylation.

coordinatively saturated polycarbonyl species, similarly to what has been reported for hydroformylation with RhH(CO)(PPh₃)₃ [5–9].

It is important to compare our catalytic cycle with earlier mechanistic proposals by workers from Celanese on closely related Rh–diphosphine systems [16c,d]. These workers found that the [diphosphine]:[Rh] ratio had a strong influence on the activity and selectivity of the reaction. The most selective systems for the production of linear aldehydes contained 2 or more equivalents of diphosphine and mechanistic studies were concentrated on those systems. The crucial species under such conditions are of the type HRh(CO)(P–P)(P–P*), where P–P represents a bidentate and P–P* a monodentate diphosphine, and the catalytic cycle derived from such species is substantially different from the one commonly accepted for PPh₃, where the key species contains only two phosphorus donors,

viz. HRh(CO)₂(PPh₃)₂. In contrast, our data indicate that if only one equivalent of diphosphine is used, HRh(CO)₂(P–P) is preferentially formed and in consequence, the mechanism is closely related to that of Rh–PPh₃. This illustrates well how sensitive the kinetics and mechanisms of hydroformylation are to seemingly small variations of the reaction conditions.

4.1. Rate expressions for the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)₂/dppe

According to the cycle described in Scheme 2, the rate law for the hydroformylation of 1-hexene with Rh(acac)(CO)₂/dppe, under conditions for which the hydrogenolysis of the acyl intermediate E is the rds, can be derived by applying the Equilibrium Approximation. Taking into account that the overall hydroformylation rate is given by the individual rate of this step, the

rate equation may be expressed as

$$r = k_7[\mathbf{E}][\text{H}_2] \quad (2)$$

Considering the equilibria involved between K_1 and K_6 and the mass balance for rhodium as $[\text{Rh}]_0 = [\mathbf{A}] + [\mathbf{C}] + [\mathbf{D}] + [\mathbf{F}] + [\mathbf{G}]$ (coordinatively saturated species which can be in significant concentrations under the catalytic reaction conditions), the rate expression becomes:

$$r = \frac{K_1 K_2 K_3 K_4 K_7 [\text{Rh}]_0 [\text{S}][\text{H}_2][\text{CO}]}{[\text{CO}] + (K_1 K_2 + K_1 K_2 K_3 [\text{CO}][\text{S}] + K_1 K_2 K_3 K_4 K_5 [\text{S}][\text{CO}]^2 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{S}][\text{CO}]^3)} \quad (3)$$

where S is the substrate (1-hexene). This rate law is consistent with our proposed mechanism for the hydroformylation of 1-hexene under low hydrogen pressures, indicating a first-order dependence on $[\text{H}_2]$ and $[\text{Rh}]$, first-order in CO at low pressure and negative order at high pressures and fractional order in olefin concentration; this rate law is also rather similar to that found by Chaudhari et al. for the hydrogenation of styrene catalyzed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ [9]. It is impossible with our data to further discuss the details of the hydrogenolysis step, which may be a concerted reaction or a two stage process involving the oxidative addition of hydrogen (rds) followed by reductive elimination of the product aldehyde. On the other hand, if the CO-promoted migration of hydride to the olefin (k_3) is considered as the (irreversible) rate-determining step, then the rate law becomes:

$$r = k_3[\mathbf{C}][\text{CO}] \quad (5)$$

By a similar procedure and considerations as described for the prior case, the rate expression becomes:

$$r = \frac{K_1 K_2 K_3 [\text{Rh}]_0 [\text{S}][\text{CO}]}{[\text{CO}] + K_1 K_2 [\text{S}]} \quad (6)$$

This expression is in accord with our proposed hydroformylation mechanism at higher hydrogen pressures. The negative order with respect to CO concentration at high pressure of this gas may be explained by the accumulation of species **F** and **G**, which are outside of the cycle under these reaction conditions and therefore should reduce and/or inhibit the rate of the reaction.

5. Conclusions

Our results indicate that the system $\text{Rh}(\text{acac})(\text{CO})_2/\text{dppe}$ is an efficient precatalyst for the homogeneous hydroformylation of 1-hexene under mild reaction conditions; the linear to branched ratio (*l/b*) of aldehydes formed was practically constant (between 2.0 and 2.6) and practically independent of the reaction conditions, except when the syn-gas and CO pressure were increased, where a slight reduction of the *l/b* ratio was observed. No isomerization or hydrogenation products were detected. The reaction was found to be extremely sensitive to experimental conditions, due to the existence of complex equilibria that influence the reaction rate and are controlled mainly by the concentrations of the gaseous reactants. Kinetic and mechanistic studies allowed us to propose the catalytic cycle depicted in Scheme 2, in which

$\text{RhH}(\text{CO})_2(\text{dppe})$ is the resting state and $\text{RhH}(\text{CO})(\text{dppe})$ is considered the active species. This mechanism is similar to the one generally accepted for Rh- PPh_3 catalysts but different from the one proposed for the Rh system containing 2 equiv. of dppe. The hydrogenolysis of the acyl intermediate or the migration of the olefin into the metal hydride bond are the rate determining steps at low and high hydrogen pressures, respectively. Under high CO pressures ($[\text{CO}]/[\text{H}_2] > 2$), the stable catalytically

inactive polycarbonyl species $\text{Rh}(\text{acyl})(\text{CO})_2(\text{dppe})$, and possibly $\text{Rh}(\text{acyl})(\text{CO})_3(\text{dppe}^*)$ are present in appreciable concentrations outside the productive cycle, which explains the high negative order of the reaction rate on $[\text{CO}]$ under these conditions.

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