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Kinetics and mechanisms of homogeneous catalytic reactions Part 9. Hydroformylation of 1-hexene catalyzed by a rhodium system containing a tridentated phosphine

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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 by using a rhodium catalyst formed by the addition of 1 equiv. of 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to the complex $Rh(acac)(CO)_2$ under mild reaction conditions (80 °C, 2–10 atm of syn-gas) in toluene; linear to branched ratios (*l*/*b*) varied from 1.3 to 5.8, depending on the reaction conditions. The reaction rate is first order with respect to the concentration of Rh, fractional order with respect to 1-hexene concentration and zero order with respect to dissolved hydrogen concentration. Increasing the CO pressure up to a threshold value of 2.1 atm accelerates the reaction, further increments inhibit the reaction. Complex $RhH(CO)(\kappa^3$-triphos) was isolated and characterized by IR and NMR (^1H and $^{31}P\{H\}$). The kinetic data and related co-ordination chemistry are consistent with a mechanism involving $RhH(CO)(\kappa^2$-triphos) as the active species and the migratory insertion of the alkene into the metal–hydride bond as the rate limiting step. This catalytic cycle is rather similar to that proposed for $RhH(CO)(PPh_3)_3$ and for $RhH(CO)_2$(dppe); however, the presence of a triphos ligand co-ordinated in a κ^2 mode through the cycle resulted in *l*/*b* ratio higher than those obtained in systems containing bidentated phosphines.

1. Introduction

The hydroformylation of alkenes is an important synthetic tool for the production of a wide range of organic molecules of high commercial value, as well as one of the largest scale application of homogeneous catalysis in industry; in particular those based on the low-pressure oxo process (LPO) using triphenylphosphine-modified rhodium carbonyls as catalysts [1,2]. In recent years, other hydroformylation applications for high added-value intermediates for fine chemicals and pharmaceuticals have emerged in the literature [2,3].

In spite of the industrial importance of olefin hydroformylation and the large number of articles in this field published over several decades, relatively few studies have been devoted to the kinetics of this reaction, and most of them involve $RhH(CO)(PPh_3)_3$ [4–9]. Kinetic and mechanistic studies of hydroformylation with catalysts containing bulky phosphites [10,11], diphosphines [12,13], phosphine–phosphite [14] or diphosphites [15], 1,2,5-triphenyl-1H-phosphole [16] and triphenylarsine [17] as ligands have also been reported. Van Leeuwen and Claver [3] published a comprehensive review dealing with recent advances in homogeneous and biphasic hydroformylation of alkenes with rhodium complexes, including kinetic and mechanistic aspects. Of particular relevance to the present work, hydroformylation by rhodium–triphosphine systems has been little studied [18].

Continuing our research program on kinetics and mechanisms of homogeneous catalytic reactions such as hydrogenation [19] and hydroformylation [13,20], in the present paper we describe a study of the hydroformylation of 1-hexene using as the precatalyst the system formed by the addition of 1 equiv. of 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to the complex $Rh(acac)(CO)_2$ and propose a mechanism consistent with the kinetic data and with related co-ordination chemistry.

2. Experimental

2.1. Instruments and materials

All manipulations were conducted with rigorous exclusion of air using Schlenck techniques. 1-Hexene was purified by

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distillation under reduced pressure. Solvents were purified by known procedures. $Rh(acac)(CO)_2$ was prepared by a published procedure [21]. NMR and IR spectra were recorded on a Bruker AM-300 spectrometer and a Shimadzu 8300 FT-IR instrument, respectively. The products of the catalytic reactions were analyzed by gas chromatography using a 3300 Series VARIAN instrument fitted with a flame ionization detector (FID), a 2-m 20% SP-2100, 0.1% carbowax, 100/120 Supelcoport column and a VARIAN 4400 data system using *n*-heptane as an internal standard.

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 catalytic system, $Rh(acac)(CO)_2$ and triphos in a 1:1 molar ratio, 1-hexene, *n*-heptane (as an internal standard) and toluene (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.

The supply of CO/H_2 was from a high-pressure reservoir maintained a 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 [22]. The data for 1-hexene hydroformylation was plotted as molar concentration of the corresponding products versus 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 [23].

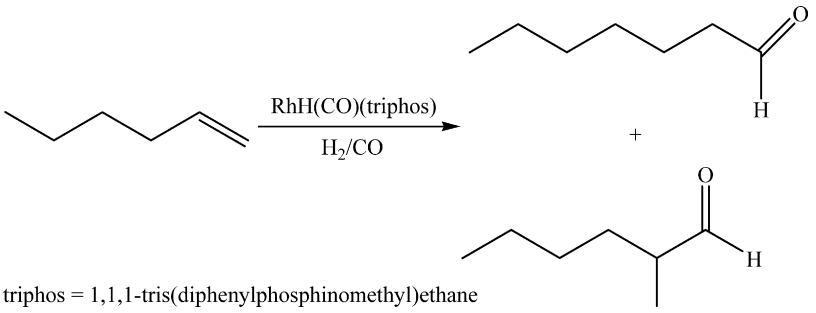
2.3. Study of the interaction of $Rh(acac)(CO)_2$ with triphos under syn-gas

$Rh(acac)(CO)_2$ (103 mg, 0.38 mmol) and triphos (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 to obtain a yellow solid. ^1H and $^{31}P\{^1H\}$ NMR of this compound were performed in a syn-gas saturated $CDCl_3$ solution. ^1H NMR ($CDCl_3$, 300 MHz, ppm): 7.42–6.46 (series of m, 30H), 2.10 (d, $^3J_{H-P}$ = 12.2 Hz, 6H), 1.43 (s, 3H), −8.23 (qd, $^2J_{H-P}$ = 34.7 and $^1J_{H-Rh}$ = 14.6 Hz, 1H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, ppm): d, 17.5 ppm, $^2J_{P-Rh}$ = 115.5 Hz.

3. Results and discussion

3.1. Catalytic hydroformylation of 1-hexene

The system $Rh(acac)(CO)_2$/triphos is an efficient catalyst precursor for the hydroformylation of 1-hexene in toluene solution under mild conditions of temperature and pressure (80 °C, 2–10 atm of syn-gas) yielding exclusively the corresponding aldehydes, heptanal and 2-methyl-hexanal (Eq. (1)), the linear to branched ratio (*l*/*b*) varying between 1.3 and 5.8 under 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 corresponds to a kinetic-controlled reaction regime and that mass transfer effects were negligible.



triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane (1)

3.2. Kinetic investigation

The kinetics of the hydroformylation of 1-hexene catalyzed by the $Rh(acac)(CO)_2$/triphos system in toluene solution was studied by carrying out runs at different concentrations of catalyst, substrate, dissolved H_2, and dissolved CO at 80 °C. First of all, it was observed that the hydroformylation rate increases in accord with a saturation curve with the total syn-gas pressure in the range 2–10 atm, as shown in Table 1 and Fig. 1; between 2.0 and 6.6 atm of syn-gas, the behavior of the reaction rate was rather linear [$-2.17 \times 10^{-5} + 2.12 \times 10^{-5}$ p(atm), r^2 = 0.99] and therefore the rest of the kinetic study was carried out within this pressure range. The initial rate data for this series of reactions is collected in Table 2. The results indicate that:

(1) The initial rate of hydroformylation shows a direct dependence on the rhodium concentration (entries 1–5). The plot of log r_i versus log[Rh] (log r_i = −1.3 + 1.1 log[Rh], r^2 = 0.99) shows a first-order dependence with regard to this parameter.

Table 1
Effect of the total pressure of syn-gas on the hydroformylation of 1-hexene catalyzed by $Rh(acac)(CO)_2$/triphos

p (atm)	10^5 r_i (M s^{-1})	*l*/*b* ratio
2.0	1.58 ± 0.08	2.8
2.6	4.27 ± 0.10	3.4
3.3	4.67 ± 0.07	3.8
4.6	7.22 ± 0.15	3.7
6.6	12.0 ± 0.41	4.7
10.0	15.1 ± 0.02	4.5

Conditions: [cat] = 1.67×10^{-3} M, [S] = 0.5 M, 80 °C, $p(CO)/p(H_2)$ = 1, toluene; r_i: initial rate.

Table 2
Kinetic data for the hydroformylation of 1-hexene catalyzed by the system $Rh(acac)(CO)_2$/triphos

Entry	10^3 [Rh] (M)	[S] (M)	p(CO) (atm)	10^2 [CO] (M)	$p(H_2)$ (atm)	10^3 [H_2] (M)	10^5 r_i (M s^{-1})	l/b Ratio
1	1.67	0.50	1.4	0.6	1.4	1.5	4.27 ± 0.10	3.4
2	2.08	0.50	1.4	0.6	1.4	1.5	5.56 ± 0.04	3.5
3	2.50	0.50	1.4	0.6	1.4	1.5	6.04 ± 0.10	2.8
4	2.90	0.50	1.4	0.6	1.4	1.5	7.59 ± 0.26	2.4
5	3.36	0.50	1.4	0.6	1.4	1.5	8.94 ± 0.23	1.3
6	1.67	0.32	1.4	0.6	1.4	1.5	3.15 ± 0.14	4.0
7	1.67	0.37	1.4	0.6	1.4	1.5	3.58 ± 0.13	4.2
8	1.67	0.43	1.4	0.6	1.4	1.5	3.91 ± 0.12	4.4
9	1.67	0.48	1.4	0.6	1.4	1.5	4.13 ± 0.13	4.5
10	1.67	0.53	1.4	0.6	1.4	1.5	4.29 ± 0.18	4.5
11	1.67	0.56	1.4	0.6	1.4	1.5	3.81 ± 0.18	4.6
12	1.67	0.64	1.4	0.6	1.4	1.5	2.43 ± 0.10	4.6
13	1.67	0.50	1.4	0.6	1.0	1.2	0.38 ± 0.02	3.1
14	1.67	0.50	1.4	0.6	2.8	3.3	4.17 ± 0.13	3.3
15	1.67	0.50	1.4	0.6	4.1	4.6	4.59 ± 0.20	3.1
16	1.67	0.50	1.4	0.6	5.5	6.4	4.27 ± 0.10	3.2
17	1.67	0.50	1.0	0.5	1.4	1.5	1.52 ± 0.04	1.5
18	1.67	0.50	2.1	0.9	1.4	1.5	4.39 ± 0.50	3.8
19	1.67	0.50	4.1	1.8	1.4	1.5	2.01 ± 0.04	5.4
20	1.67	0.50	5.5	2.5	1.4	1.5	1.41 ± 0.03	5.8

Conditions: T = 80 °C; solvent: toluene; r_i: initial rate.

(2) The rate of hydroformylation is of positive fractional order (0.7) with respect to the concentration of the alkene ($\log r_i = -4.0 + 0.7 \log$[1-hexene], $r^2 = 0.99$) until the concentration of 0.53 M (entries 1 and 6–10), beyond which the rate decreases on increasing the 1-hexene concentration (entries 11 and 12), which is usually attributed to a shift in the rate-determining step; similar results were reported for the $RhH(CO)(PPh_3)_3$ complex [7] and for its $AsPh_3$ analogue [17]. The fractional kinetics observed as a function of the substrate concentration (in the range 0.32–0.53 M) may be the result of operating in the intermediate regime of a saturation kinetics, similar to what was found by Cavalieri d'Oro et al. for the hydroformylation of propylene catalyzed by $RhH(CO)(PPh_3)_3$ [5]; saturation kinetics in alkene hydroformylation catalyzed by this precursor have also been reported by other authors [6–8] whereas zero order with respect to olefin have been reported by Chaudhari and coworkers [9] for the styrene hydroformylation with the same precatalyst.

(3) 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; the results (entries 1 and 14–16) showed a zero order with regard to the H_2 concentration ($\log r_i = -3.8 - 0.1 \log[H_2]$, $r^2 = 0.03$). However, at the hydrogen pressure of 1 atm (entry 13), it was found that the reaction rate decreased drastically.

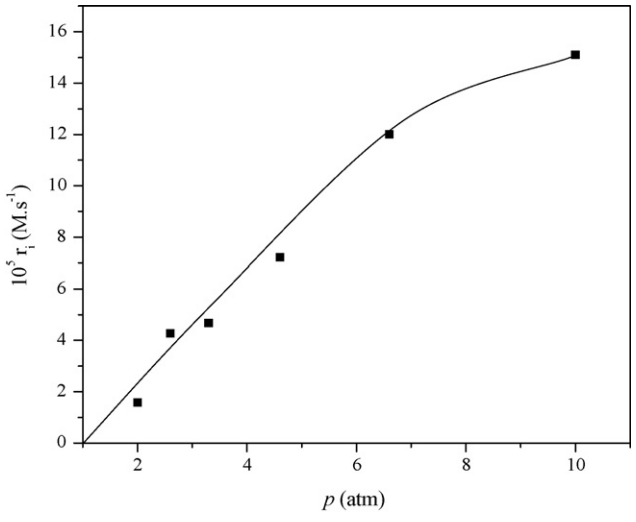


Fig. 1. Rate dependence on total syn-gas pressure for the hydroformylation of 1-hexene catalyzed by $Rh(acac)(CO)_2$/triphos. Conditions as in Table 1.

(4) The rate dependence with respect to [CO] yielded a "volcano-type" curve, 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 (entries 1, 17 and 18) the dependence was first order ($\log r_i = -1.8 + 1.1 \log$[CO], $r^2 = 0.99$), but it becomes of *inverse order* ($\log r_i = -6.9 - 1.6 \log$[CO], $r^2 = 0.98$) at higher CO pressures (entries 19 and 20). The inhibition of the rate of hydroformylation of 1-hexene at high-CO pressures may be explained by the reaction of some Rh species with CO occurring outside of the catalytic cycle leading to inactive co-ordinatively saturated polycarbonyl complexes, in accordance to what has been reported for hydroformylations with $RhH(CO)(PPh_3)_3$ [5–9] and $RhH(CO)_2$(dppe) [13].

(5) The linear to branched ratio (l/b) of the aldehydes formed varied substantially (between 1.3 and 5.8) with the reaction conditions applied. It was observed that the l/b ratio decreases with the Rh concentration, increases with substrate and CO concentrations and it is practically independent of the hydrogen concentration. These results differ substantially from those found for the $RhH(CO)(PPh_3)_3$ precatalyst [7] and its $AsPPh_3$ analogue [17], for which the l/b ratios decrease with precatalyst concentration and the CO and H_2 pressure and increase with the substrate concentration.

3.3. Co-ordination chemistry related with 1-hexene hydroformylation

In order to complement the kinetic study of the 1-hexene hydroformylation described above, the interaction of the catalyst precursor $Rh(acac)(CO)_2$ with the components of the catalytic mixture was studied. When a solution of $Rh(acac)(CO)_2$ reacted with 1 equiv. of triphos under syn-gas (4 atm) a yellow solution was obtained, from which a yellow solid could be isolated. This solid was characterized as $RhH(CO)(\kappa^3$-triphos) (**1**) based on the high-field signal in ^{1}H NMR (Fig. 2) as a quartet of doublets at −8.23 ppm ($^2J_{H-P}$ = 34.7 and $^1J_{H-Rh}$ = 14.6 Hz) and the $^{31}P\{^1H\}$NMR signal (d, 17.5 ppm, $^2J_{P-Rh}$ = 115.5 Hz); this hydride species has been reported by Ott et al. [24]. This experiment led us to propose that under the

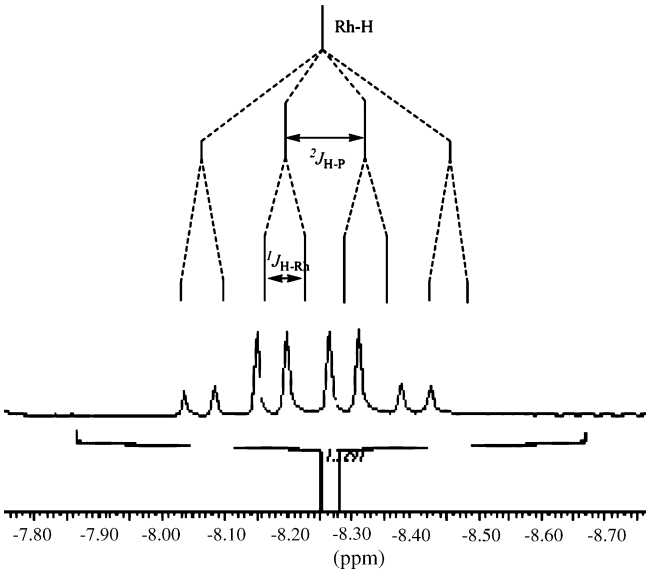


Fig. 2. High-field region of the ^{1}H NMR spectrum of the reaction between Rh(acac)(CO)$_2$ and triphos under hydroformylation conditions.

hydroformylation conditions, species **1** is the resting state of the catalyst.

3.4. Catalytic cycle for the hydroformylation of 1-hexene catalyzed by Rh(acac)(CO)$_2$/triphos

On the basis of experimental findings (kinetics and coordination chemistry studies), we propose the catalytic cycle depicted in Fig. 3 for the formation of the linear aldehyde (branched isomers excluded for clarity), which in general terms is analogous to the commonly accepted cycle for the Rh–PPh$_3$ [3–9] and Rh–dppe systems [13]. Rh(acac)(CO)$_2$ reacts with syn-gas in presence of one equivalent of triphos to generate complex RhH(CO)(κ^3-triphos) (**1**), which is considered the resting state of the catalytic process; it is well known that triphos ligand prefers to bind in a *facial* mode to the metal center. Complex **1** is probably in equilibrium (***K*$_1$**) with the 16-electron RhH(CO)(κ^2-triphos) (**A**), which initiates the catalytic cycle (see Fig. 3). Species **A** reversibly associates either a CO molecule (***K*$_2$**) to produce RhH(CO)$_2$(κ^2-triphos) (**B**), which is outside of the cycle or the olefin (***K*$_3$**) to produce RhH(alkene)(CO)(κ^2-triphos) (**C**). Then, a migratory insertion of the olefin into the metal–hydride bond of **C** takes place (***K*$_4$**) with the concomitant co-ordination of a CO molecule to yield Rh(alkyl)(CO)$_2$(κ^2-triphos) (**D**); this is considered the rate-determining step of the catalytic cycle. The insertion of CO into the Rh-alkyl bond of **D**, generates the unsaturated acyl species Rh(acyl)(CO)(κ^2-triphos) (**E**) through ***K*$_5$**. Finally, hydrogenolysis (***K*$_7$**) of **E** produces the corresponding aldehyde, and regenerates the catalytically active species (**A**), which restarts the cycle. At high-CO pressure, species **E** can reversibly coordinate other CO molecule to generate Rh(acyl)(CO)$_2$(κ^2-triphos) (**F**) through ***K*$_6$**.

According to the cycle described in Fig. 3, the rate law for the hydroformylation of 1-hexene with Rh(acac)(CO)$_2$/triphos can be derived by applying the equilibrium approximation. Taking into account that the overall hydroformylation rate is given by the individual rate of the rate-determining step, the rate equation may be expressed as

$$r = k_4[\mathrm{C}][\mathrm{CO}] \quad (2)$$

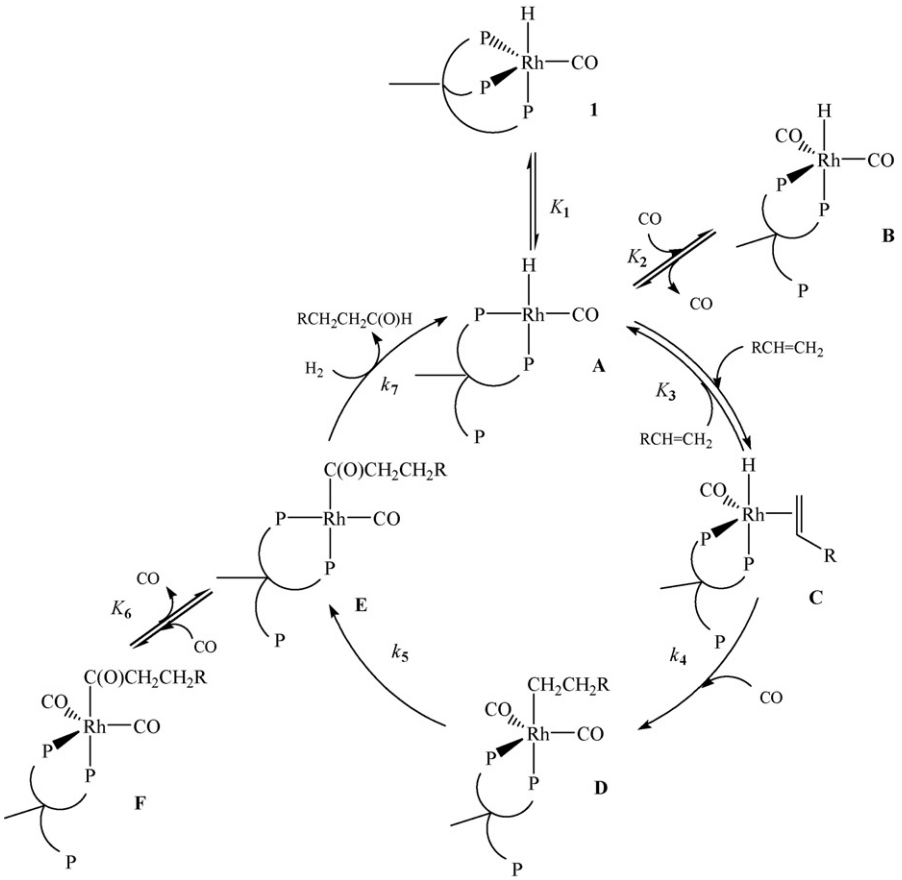


Fig. 3. Catalytic cycle for the Rh(acac)(CO)$_2$/triphos-catalyzed 1-hexene hydroformylation.

Considering the equilibria involved, K_1, K_2 and K_3, and the mass balance for rhodium as $[Rh]_o = [\mathbf{1}] + [\mathbf{A}] + [\mathbf{B}] + [\mathbf{C}]$, the rate expression becomes

$$r = \frac{K_1 K_3 K_4}{1 + K_1 + K_1 K_2 [CO] + K_1 K_3 [S]} [Rh]_o [S][CO] \quad (3)$$

where S is the 1-hexene substrate.

This expression explains the dependence of first order with respect to the catalyst concentration, the fractional order with respect to the substrate concentration and the positive order with respect to the carbon monoxide concentration at low-CO pressure. The negative order with respect to CO concentration at high pressure of this gas may be explained by the displacement of the equilibria K_2 and K_6 toward the species **B** and **F** under these reaction conditions; the accumulation of these species, which are outside of the catalytic cycle, should reduce and/or inhibit the rate of the reaction. The fact that at the hydrogen pressure of 1 atm (entry 13) the reaction rate decreased drastically, may be explained either by a change in the rate-determining step (the hydrogenolysis of the acyl intermediate **E** at low H_2 being the rds at low-H_2 pressure instead of the migratory insertion of the olefin into the metal–hydride bond of **C**), as reported by some of us [13,19] or 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, as proposed by some authors [3]. Finally, the fact that the *l*/*b* ratio increased with the CO pressure, contrary to that observed for the $RhH(CO)(PPh_3)_3$ precatalyst [7] and its $AsPPh_3$ analogue [17] may be explained by the presence of a triphos ligand co-ordinated in a κ^2 mode throughout the cycle, which could behave as a bulky bidentated phosphine.

4. Conclusions

Our results indicate that the system $Rh(acac)(CO)_2$/triphos 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 varied between 1.3 and 5.8 and it is dependent on the reaction conditions. Kinetic and mechanistic studies allowed us to propose the catalytic cycle depicted in Fig. 3, in which $RhH(CO)(\kappa^3$-triphos) is the resting state of the catalyst and $RhH(CO)(\kappa^2$-triphos), formed by dissociation of one of the phosphorous atoms of the triphos ligand, is considered the active species; the insertion of the alkene into the metal–hydride bond is the rate-determining step. This mechanism is similar to those generally accepted for $Rh–PPh_3$ and Rh–dppe catalysts. Under high-CO pressures ($[CO]/[H_2] > 2$), stable, catalytically inactive polycarbonyl species are present in appreciable concentrations outside the productive cycle, which explains the high-negative order of the reaction rate on [CO] under these conditions.

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