



# Kinetics and mechanisms of homogeneous catalytic reactions. Part 14. Hydroformylation of 1-hexene with formaldehyde catalyzed by a cationic bis(diphosphine)rhodium complex<sup>☆</sup>



Merlín Rosales<sup>a,\*</sup>, Homero Pérez<sup>a</sup>, Federico Arrieta<sup>a</sup>, Rodolfo Izquierdo<sup>a</sup>,  
Cristhina Moratinos<sup>a</sup>, Pablo J. Baricelli<sup>b</sup>

<sup>a</sup> Universidad del Zulia (L.U.Z.), Facultad Experimental de Ciencias, Departamento de Química, Laboratorios de Química Inorgánica, de Química Teórica y Computacional y de Química Inorgánica Teórica, Maracaibo, Venezuela

<sup>b</sup> Universidad de Carabobo (UC), Facultad de Ingeniería, Centro de Investigaciones Químicas, Valencia, Venezuela

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## ABSTRACT

Complex  $[\text{Rh}(\kappa^2\text{-P,P-dppe})_2]\text{acac}$  (**1a**)<sub>acac</sub>, dppe: 1,2-bis(diphenylphosphino)ethane) showed to be a highly efficient precatalyst for the hydroformylation of 1-hexene with formaldehyde under relatively mild reaction conditions (353–403 K) in 1,4-dioxane as the solvent; the corresponding C<sub>7</sub> aldehydes were obtained in linear to branched ratios (**I/b**) close to 2. A kinetic study for this reaction lead to the experimentally determined rate law:  $r_f = \{K_1 k_2 / (1 + K_1 [\text{CH}_2\text{O}])\} [\text{Rh}][\text{C}_6\text{H}_{12}][\text{CH}_2\text{O}]$  [ $K_1 = (1.47 \pm 0.04) \text{M}^{-1}$  and  $k_2 = (0.47 \pm 0.01) \text{M}^{-1} \text{s}^{-1}$  at 373 K]. The experimental activation parameters for the overall reaction were also calculated [ $E_a = (20.1 \pm 0.9) \text{kcal mol}^{-1}$ ,  $\Delta H^\ddagger = (19.5 \pm 0.9) \text{kcal mol}^{-1}$ ,  $\Delta S^\ddagger = (-9.3 \pm 0.5) \text{cal K}^{-1} \text{mol}^{-1}$  and  $\Delta G^\ddagger = (22 \pm 2) \text{kcal mol}^{-1}$ ]. The kinetic study together with results on coordination chemistry performed with **1a** and with the BF<sub>4</sub> salt of its iridium analogue,  $[\text{Ir}(\kappa^2\text{-P,P-dppe})_2]\text{BF}_4$  (**1b**)<sub>BF4</sub>, as well as theoretical DFT-calculations allowed us to propose a mechanism for this reaction. The catalytic cycle involves the reversible oxidative addition of formaldehyde to **1a** to yield  $[\text{Rh}(\text{H})(\text{CHO})(\kappa^2\text{-P,P-dppe})_2]^+$ , followed by the insertion of the olefin into the Rh–H bond to generate  $[\text{Rh}(\text{alkyl})(\text{CHO})(\kappa^2\text{-P,P-dppe})_2]^+$ , which is considered as the **rds** of the process [ $E_{a2} = (23.9 \pm 0.8) \text{kcal mol}^{-1}$ ]; the cycle is completed by the reductive elimination of the aldehydes to regenerate **1a** and restart the cycle.

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## 1. Introduction

The Rh-catalyzed olefin hydroformylation under a CO/H<sub>2</sub> mixture (henceforth referred as syn-gas) is a well-known synthetic tool for a wide range of organic molecules and one of the largest scale industrial application of homogeneous and aqueous–biphasic catalysis [1]. In recent years, new applications of this reaction to obtain high value intermediates for fine chemicals and pharmaceuticals are emerging in the literature [2]. Research on kinetics of this reaction catalyzed by  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  [3],  $\text{RhH}(\text{CO})(\text{AsPh}_3)_3$  [4], and other rhodium systems containing phosphites [5], phospholes [6], diphosphines [7], diphosphites [8], phosphine-phosphite [9] and

triposphine [10] have been published; they have shown that the syn-gas hydroformylation is a very complex reaction due to the existence of various equilibria, which depend on the concentration of the reactants (H<sub>2</sub>, CO and free phosphine ligands).

Another way to carry out this reaction is by the use of formaldehyde instead of syn-gas, a particular case of the hydroacylation reaction [11]. Furthermore, it has several advantages over the traditional method: (a) it enables the reaction to occur under atmospheric pressure of an inert gas, (b) it does not require high-pressure equipments, and (c) it avoids the use of lethal carbon monoxide. In spite of these advantages, the hydroformylation of olefins with formaldehyde had been poorly investigated [12]. Indeed, in 1999, Seok et al. [13] reported that  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  was an active precatalyst for the hydroformylation with formaldehyde of olefins containing oxygen at the β position to the carbon–carbon double bond (allyl alcohol, acrolein and methylacrylate); however, simple olefins, such as propylene, 1-hexene and styrene, were poorly hydroformylated. On the other hand, some of us

<sup>☆</sup> In memory of Professor Roberto Sanchez-Delgado.

\* Corresponding author.

E-mail addresses: [merlinrosalesaiz@gmail.com](mailto:merlinrosalesaiz@gmail.com), [merlin2002@cantv.net](mailto:merlin2002@cantv.net) (M. Rosales).

have reported that the hydroformylation of 1-hexene and other  $C_6$  olefins as well as allyl alcohol using formaldehyde as syn-gas substitute can be catalyzed by rhodium-phosphine system, being  $[Rh(\kappa^2-P,P-dppe)_2]acac$  (**1a**)<sub>acac</sub>; dppe:  $Ph_2P(CH_2)_2PPh_2)_2$ , 1,2-bis(diphenylphosphino)ethane) the most active precatalyst; this system can be an efficient catalytic precursor either for both simple olefins and for those molecules containing oxygen at the  $\beta$  position to the carbon-carbon double bond [14].

More recently, Morimoto et al. [15] reported a highly linear regioselective hydroformylation of 1-alkenes using formaldehyde to give aldehydes by using of rhodium catalysts with two type of diphosphine: Rh/binap [binap: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] for formaldehyde decomposition to give syn-gas and Rh/xantphos [xantphos: 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene] for olefin hydroformylation. In addition, Taddei et al. [16] showed that this reaction may be accelerated under microwave dielectric heating. Other recent works on the reaction of olefins, dienes and acetylenes with formaldehyde have been also reported [17], which lead us to think that formaldehyde is an excellent surrogate of syn-gas for the hydroformylation of olefins. Beller et al. [18] have published a comprehensive review dealing with recent advances on alkene carbonylation reactions performed without the use of carbon monoxide, including the hydroformylation of olefins with formaldehyde.

Continuing our research program on kinetics and mechanisms of homogeneous catalytic reactions, in the present paper we report the data obtained from experimental kinetic and coordination chemistry studies as well as Density Functional Theory (DFT) calculations of the hydroformylation of 1-hexene with formaldehyde by using **1a**)<sub>acac</sub> as precatalyst. To the best of our knowledge, there are not previous reports in the open literature of the kinetics of the hydroformylation of olefins by using formaldehyde.

## 2. Experimental

### 2.1. Instruments and materials

All manipulations and reactions were performed under rigorous exclusion of air using a vacuum line, an argon-filled Schlenk line or an argon-filled glovebox. 1-Hexene (B.D.H. Laboratory Reagents) was purified by distillation at reduced pressure and the solvents were distilled from appropriate drying agents, immediately prior to use.  $CDCl_3$  and THF- $d_8$  (Aldrich) were dried using activated molecular sieves. Formaldehyde was generated *in situ* in the reaction medium from paraformaldehyde. Complex **1a**)<sub>acac</sub> was prepared by published procedures [14a] from  $Rh(acac)(CO)_2$  [19]. The IR spectra of the complexes (in KBr disk) were recorded on a Shimadzu 8300 FT-IR instrument.  $^1H$  and  $^{31}P\{^1H\}$  NMR spectra were recorded on a Bruker AM-300 spectrometer; chemical shift are expressed in p.p.m. upfield from  $Me_4Si$  and  $H_3PO_4$ , respectively.

### 2.2. General procedure for kinetic runs

The reactions were carried out in a Parr Instrument high-pressure reactor, which was provided with an arrangement for sampling of liquid contents in order to take reaction mixture aliquots at regular intervals of time, besides of automatic temperature, pressure and variable stirrer speed controls. In a typical run, a solution of the catalyst, 1-hexene, formaldehyde, cycloheptane as internal standard (1.0 mL, 8.3 mmol) and 1,4-dioxane (total volume 30 mL) was placed in the reactor. The solution was carefully deoxygenated with argon and charged with this gas at atmospheric pressure, and the reactor was heated to the desired temperature; the reaction was monitored by using GC (3300 Series VARIAN with a flame ionization detector fitted to a 2 m 20% SP-2100 on a 0.1%

carbowax 100/120 Supelcoport column, using  $N_2$  as carrier gas). Calibration was made with cyclohexane as the internal standard. Each reaction was repeated at least twice in order to ensure reproducibility of the results.

### 2.3. Kinetic calculations

All the kinetic runs were carried out at low conversions (in the range of 5–10%) in order to perform a kinetic analysis based on the initial rate method [20]. The data of the catalytic reactions were plotted as total molar concentration of the products (heptanal and 2-methyl-hexanal) versus time yielding straight lines, which were fitted by conventional linear regression programs ( $r^2 > 0.95$ ); initial rates of the reaction ( $r_i$ ) were obtained from the corresponding slopes. The orders of the different components of the reaction (catalyst, substrate and formaldehyde) were determined from the slope of the plot of the logarithm of  $r_i$  versus logarithm of the corresponding reagent concentration.

### 2.4. Coordination chemistry related with the hydroformylation of 1-hexene with formaldehyde

#### 2.4.1. Interaction of **1a**)<sub>acac</sub> with formaldehyde

This reaction was carried by reaction of **1a**)<sub>acac</sub>, which was formed *in situ* as reported in a prior work [14a], with a ten-fold excess of formaldehyde (112 mg, 4 mmol) under reflux for 1 h; the solution was evaporated until dryness and the solid was washed with *n*-pentane. This reaction was also followed by *in situ*  $^{31}P\{^1H\}$  NMR using an 1:1 mixture of 1,4-dioxane and THF- $d_8$  as the solvent.

#### 2.4.2. Synthesis of $[Ir(\kappa^2-P,P-dppe)_2]BF_4$ (**1b**)<sub>BF<sub>4</sub></sub>)

$[Ir(\mu-Cl)(COE)_2)_2$  [21] (178 mg, 0.2 mmol), dppe (320 mg, 0.8 mmol) and benzene (15 mL) were placed under reflux for 2 h. The resulting solution was evaporated under vacuum, dissolved in 1,4-dioxane (10 mL) and  $NaBF_4$  (10 mg, 0.4 mmol) was added; the solution was heated for 1 h. The solvent was removed until dryness and the product was washed with methanol and *n*-pentane and dried in vacuum. Yield: 70%. IR (KBr disk):  $1080\text{ cm}^{-1}$  (vs,  $\nu_{B-F}$ );  $^1H$  NMR ( $CDCl_3$ , 298 K, 300 MHz),  $\delta = 7.4\text{--}7.2$  (m, Ph, 40H) and 2.1 ppm (br s,  $CH_2-P$ , 8H);  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 298 K, 121 MHz)  $\delta = 48.1$  ppm (s).

#### 2.4.3. Reaction of **1b**)<sub>BF<sub>4</sub></sub> with formaldehyde: synthesis of *cis*- and *trans*- $[Ir(H)_2(\kappa^2-P,P-dppe)_2]BF_4$

**1b**)<sub>BF<sub>4</sub></sub> (195 mg, 0.2 mmol) and a ten-fold excess of formaldehyde (56 mg, 2 mmol) were dissolved in 1,4-dioxane as the solvent (10 mL) and the reaction mixture was placed under reflux for 2 h. The solution was evaporated under vacuum to about 1/4 of its initial volume and the product was precipitated by addition of *n*-pentane, filtered and dried in vacuum. Yield: 80%. IR (KBr disk):  $2090$  and  $2080\text{ cm}^{-1}$  (m,  $\nu_{Ir-H}$ ),  $1080\text{ cm}^{-1}$  (vs,  $\nu_{B-F}$ );  $^1H$  NMR ( $CDCl_3$ , 298 K, 300 MHz):  $\delta = 8.5\text{--}6.9$  (m, Ph, 40H), 2.3 (m,  $CH_2-P$ , 8H),  $-10.5$  (quint,  $^2J(H-P) = 15$  Hz, Ir-H),  $-11.8$  ppm (dm,  $^2J(H-P) = 112$  Hz, Ir-H);  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 298 K, 121 MHz):  $\delta = 38.9$  (s), 32.9 (t,  $^2J(P-P) = 7$  Hz) and 21.1 ppm (t,  $^2J(P-P) = 7$  Hz); elemental analysis calcd (%) for  $IrC_{52}H_{50}BF_4P_4$ : C 57.94, H 4.68; found: C 58.12, H 4.59.

### 2.5. Computational details

All the calculations were carried out with the Gaussian-09 (G09) [22] computational package by using the hybrid functional M06L [23] of Density Functional Theory (DFT) combined with the effective core potential (ECP) LanL2DZ for Rh and P [24] and the extended basis set 6-31+G(d,p) for C, H and O were used [25]. Minimum energy structures (MES) and transition states (TS) calculations for all rhodium species involved in the catalytic cycle

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