Bull Soc Chim Fr (1995) 132, 815-823
© Elsevier, Paris

Simple kinetics of the catalysis of the hydroformylation of olefins by a rhodium phosphane complex: catalysis of the hydroformylation of styrene by the rhodium-1,2,5-triphenyl-1*H*-phosphole system. Kinetically deduced involvement of a 14-electron bis(1,2,5-triphenyl-1*H*-phosphole)rhodium intermediate

Christian Bergounhou, Denis Neibecker*, Régis Réau

Laboratoire de chimie de coordination du CNRS, Unité No 8241, liée par convention à l'université Paul-Sabatier et à l'Institut national polytechnique, 205, route de Narbonne, 31077 Toulouse Cedex, France

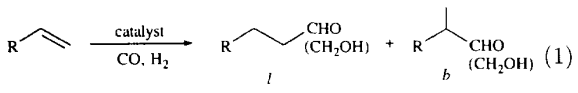
(received 21 December 1994, accepted 1 June 1995)

Summary – The kinetics of the hydroformylation of styrene have been studied using the complex $Rh(CO)Cl(TPP)_2$ **4** (TPP = 1,2,5-triphenyl-1*H*-phosphole) as a catalyst precursor. This is one of the rare rhodium-based catalytic systems that is not sensitive to the phosphorus/rhodium ratio. The rate of hydroformylation was found to follow the expression $R = K$ [styrene][**4**]pH_2pCO^{-1}, which is the first simple rate equation to be reported for a rhodium phosphane catalyst. The reaction orders are consistent with a mechanism including i) dissociation of carbon monoxide from a $HRh(CO)_2(TPP)_2$ complex formed outside the catalytic cycle during an induction period; ii) the involvement of a 14-electron acylrhodium intermediate $RCORh(TPP)_2$ **10**; and iii) a rate-determining step involving oxidative addition of hydrogen to **10**. The existence of a catalytic intermediate such as **10** can be used to rationalize the results of the hydroformylation of functionalized olefins.

hydroformylation / rhodium / phosphole / kinetics / mechanism

Introduction

The hydroformylation of olefins involves the addition of hydrogen and carbon monoxide to produce aldehydes or alcohols (eq 1).



(1)

Since its discovery at the end of the 1930s, this reaction has been extensively investigated and developed into extremely important industrial processes accounting for some 6 million tons of hydroformylation products per year. The reaction is catalyzed by a wide range of metal complexes, the most important being those of cobalt and rhodium. Until the 1970s, hydroformylation was carried out with cobalt catalysts under rather drastic conditions (110–180°C, 200–300 bar), the selectivity in linear aldehyde (*l*, eq 1) being around 80% in the case of propene. Higher selectivities for linear products have been achieved by adding a phosphorus ligand to the original cobalt system or by using rhodium phosphane catalysts. These rhodium-modified systems can be active under ambient conditions and give selectivities for linear aldehydes greater than 90% [1-3]. Throughout the extensive research dealing with the optimization of the reaction parameters and the tailoring of the catalyst, two main fields have emerged.

First, many studies have been devoted to the hydroformylation of functionalized olefins to widen the use of hydroformylation as a synthetic tool. Important advances have been achieved in the last ten years and, for example, styrene, ethyl acrylate and vinyl acetate are now efficiently hydroformylated [4]. Asymmetric hydroformylation is also making progress and recently ee's up to 95% have been reported [5-7].

The second important concern is the understanding of the hydroformylation mechanism; this continues to be a subject of great debate [8a]. The mechanism of the hydroformylation catalyzed by rhodium phosphane complexes has received much attention due to the growing importance of the rhodium-based systems [8b,c]. Most published reports deal with rhodium triphenylphosphine catalysts which are used in industrial propene hydroformylation [8d]. Some complexes thought to be involved in the catalytic process have been isolated or modeled [9], and many labeling experiments have been very useful for a better understanding

* Correspondence and reprints

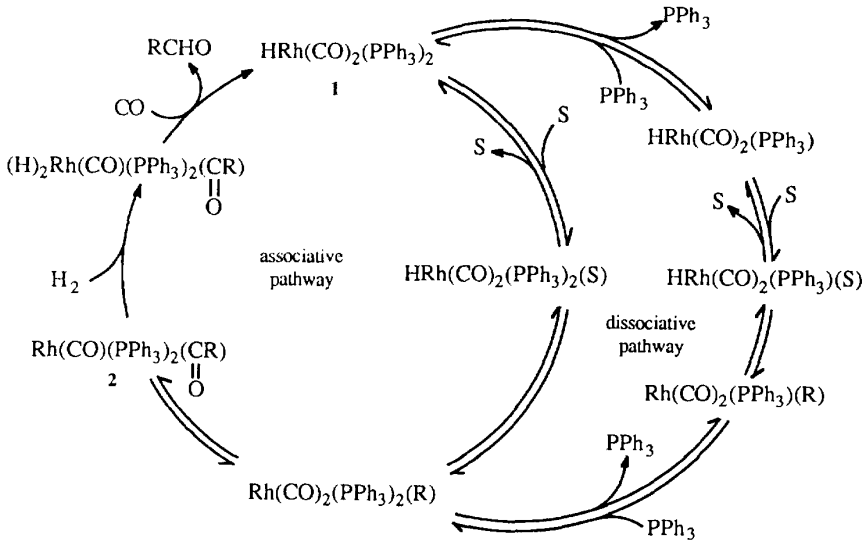


Fig 1. Mechanism proposed by Wilkinson *et al*, for the catalysis of the hydroformylation of alkenes by the rhodium triphenylphosphine system (S = substrate; R = linear or branched alkyl).

of the reaction mechanism [10]. However, a complete step-by-step mechanism has not yet been found.

Following their pioneering kinetic studies, Wilkinson *et al* [11] suggested a hydroformylation mechanism based on competitive associative and dissociative pathways, which is quite similar to the Heck and Breslow mechanism for cobalt-catalyzed hydroformylation [12]. Under hydroformylation conditions, the rhodium hydride complex $HRh(CO)_2(PPh_3)_2$ **1** is readily formed. This complex either coordinates the olefin to generate a formally 20-electron intermediate (associative pathway) or first dissociates a phosphane ligand before it activates the substrate (dissociative pathway) (fig 1).

The associative pathway is thought to be more selective than the dissociative pathway since it involves diphosphane complexes which are more sterically congested and possess a higher hydridic character than monophosphane complexes. The competition between these two routes explains the enhanced linear aldehyde selectivity that is observed with an excess of phosphane, dissociation from **1** being prevented. However, the associative pathway violates the 18-electron rule since it involves a 20-electron intermediate. Although 20-electron complexes are not rare, the 20-electron olefin intermediate could, in this case, be circumvented by a reversible hydride migration to CO or by a four-center addition step (like hydroboration). Wilkinson *et al* assumed that the rate-determining steps for the two routes is hydrogen addition to the acylrhodium complexes **2**.

The different elementary steps of these early mechanisms are commonly accepted but both the nature of the main active species and the rate-determining step are still under dispute. Initially, several authors suggested a second dissociative pathway initiated by carbon monoxide dissociation from **1** leading to the active species $HRh(CO)(PPh_3)_2$ **3** [13, 14]. This hypothesis has been confirmed by *in situ* infrared spectroscopic studies. Moser *et al* thus proposed that complex **3** is involved in the main catalytic pathway and that the rate-determining step is its formation, *ie* the carbon monoxide dissociation from **1** [15].

In 1982, Unruh *et al* showed that species containing three phosphorus ligands may be active in the rhodium-catalyzed hydroformylation [16]. This feature has been corroborated recently by Bianchini *et al* [17]. Furthermore, to explain the influence of the hydrogen/carbon monoxide ratio on the branched/linear aldehyde ratio, Unruh *et al* suggested that hydrogen activation is the rate-determining step for the catalytic route producing the linear aldehyde, while alkylrhodium formation is the rate-determining step for the catalytic route giving the branched product.

Since all the complexes $HRh(CO)_n(PPh_3)_{4-n}$ are thought to be active, the hydroformylation mechanism could be based on at least eight catalytic cycles [8b]. Each reaction parameter influences the relative concentration of the catalytic intermediates, the reaction rate and, perhaps, the rate-determining step [16]. Several kinetic studies have been performed with the aim of clarifying the mechanism of the catalysis of hydroformylation by rhodium phosphane complexes [11c, 18-22], but they are not satisfactory since i) they cover a limited range of conditions; ii) the orders with respect to substrate, catalyst, hydrogen, and carbon monoxide are often fractional; and iii) the linear aldehyde selectivity changes with the reaction parameters. Consequently, the established rate expressions are complicated and do not give crucial information on the detailed mechanism.

We previously reported that 1,2,5-triphenyl-1*H*-phosphole (TPP) gives rise to catalytic systems that hydroformylate a broad range of substrates similar to the PPh_3 system, and that TPP is a more efficient ligand than PPh_3 for the rhodium-catalyzed hydroformylation of 1-hexene [23], styrene [24] and ethyl acrylate [25] under mild conditions. The study of the influence of the TPP/Rh ratio performed either with 1-hexene or styrene revealed that the Rh-TPP system leads to a unique active species containing exactly only two TPP ligands for which we proposed the formula

$HRh(CO)_x(TPP)_2$ (x = 1, 2) [26]. Thus we had found a simplified rhodium phosphane catalytic system and anticipated a simpler reaction mechanism than that of systems involving association/dissociation equilibria of triphenylphosphine. The results of a complete kinetic study of the catalysis of hydroformylation by the Rh-TPP system are reported here.

Experimental section

GC analyses were performed on an Intersmat IGC 120 gas chromatograph fitted with a flame ionization detector. All solvents were carefully dried, distilled and stored according to literature procedures. Similarly, all reagents were stored under argon after distillation or recrystallization. All the gases were high quality gases (argon U, CO N2O and H_2 U), from l'Air Liquide. 1,2,5-Triphenylphosphole was supplied by F Mathey [27], or synthesized according to a published procedure [28]. Triethylamine (Janssen Chimica, 99%) and styrene (Fluka, > 99%) were distilled just before use from potassium hydroxide and calcium hydride, respectively. The catalyst precursor $Rh(CO)Cl(TPP)_2$ **4** was prepared according to the reported method [23].

Apparatus

All the experiments were carried out in a home-made apparatus which consists of an autoclave and a control unit allowing the regulation of the autoclave pressure and the measurement of the consumption of syngas from a reservoir (fig 2). The pressure was regulated *via* an electric signal given by a pressure transducer connected to the autoclave. This signal manipulated an electrovalve which controlled the syngas flow (Brooks 5838N). A second pressure transducer measured the pressure drop in the reservoirs (15 and 40 cm^3) thermostated at 25°C and thus allowed the monitoring of syngas consumption. The peculiarity of this apparatus lay in the use of differential pressure transducers (Foxboro 843 DP). The high pressure part (0–20 bar scale) of the transducer used for volume measurements was connected to the syngas reservoir and the low-pressure part to a reference reservoir. The high pressure part (0–5 bar) of the differential pressure transducer used for pressure regulation was also connected to this reference reservoir and its low pressure part to the autoclave. This system allowed experiments at absolute pressures between 0 and 80 bar with the same accuracy and the same sensitivity over the entire scale. The deviation in autoclave pressure was less than ±0.2% for a hydrogen flow of 2 000 mL per hour.

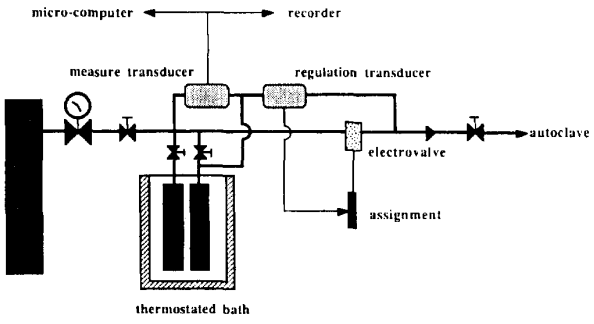


Fig 2. Schematic representation of the control unit.

The differential transducer measuring the gas consumption in the reservoirs delivered a voltage of 2 to 10 V, corresponding to a pressure drop of 20 bar. The acquisition data board of the microcomputer Apple IIe was made up of a digitizer that converted the analog signal into a number between 2 000 and 10 000. The acquisition program plotted, in real time, the intensity of the signal (which is proportional to the amount of syngas consumed) as a function of time. The random noise of the crude data was reduced using the method of Savitzky and Golay [29]. We selected a treatment on seven points, which represents a compromise between the quality of the measurements and their processing time. The data-processing software analyzed up to 1 000 data points and then computed the syngas consumption and the number of moles of reactants transformed, as a function of time. The accuracy of the measurements (within 1%) was checked by GC analysis of the reaction mixture at the end of each kinetic run. This software also permitted the determination of the reaction order by automatically plotting the curves [styrene] = f(t), Ln([styrene]$_0$/[styrene]) = f(t) and 1/[styrene] = f(t).

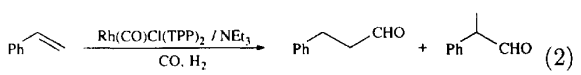
Hydroformylation experiments

The hydroformylation of styrene was performed in a home-made 100 mL Teflon-coated stainless steel autoclave equipped with a magnetic stirrer, a safety valve, a ball valve for the introduction of liquids and an argon/gas inlet-outlet valve and linked to the apparatus described in figure 2.

In a typical run, $Rh(CO)Cl(TPP)_2$ **4** (31.7 mg, 0.04 mmol) was placed in the autoclave which was then closed. The atmosphere was replaced by argon and a toluene solution (47 mL) containing triethylamine (0.06 mL, 0.8 mmol) was introduced through the ball valve. This valve was closed and the autoclave was pressurized with CO and H_2 (20 bar; 1/1) and heated to 40°C for 10 min. Styrene (2.8 g, 27 mmol) was then injected (the total volume of the reaction mixture was 50 mL) and the gas consumption monitored. At the end of the experiment, the autoclave was cooled to 0°C. The reaction products were collected under argon into a Schlenk tube with toluene and analyzed by GC (3 m × 1/8″ column, 10% carbowax 20 M on chromosorb 80–100 mesh working at 180°C and N_2 as carrier gas (flow-rate 1.8 $L.h^{-1}$) with hexadecane as an internal standard for the aldehyde analysis and working at 80°C, 0.8 $L.h^{-1}$ flow-rate of N_2 for the ethylbenzene analysis).

Results

The kinetic study of the catalysis of hydroformylation by the Rh-TPP system was performed with styrene (eq 2) under reaction conditions for which no hydrogenation of the substrate occurs [24]. This ensures that the reaction rate can be followed by monitoring the syngas consumption. In all but one experiment, the selectivity for the formation of the branched aldehyde remained constant giving around 85% of hydratropaldehyde (2-phenylpropanal), **5**. Since we had previously shown that the active species contains two TPP ligands, we used the readily available complex $Rh(CO)Cl(TPP)_2$ **4** as a catalyst precursor. As usual, an excess of triethylamine was added to remove the hydrochloric acid produced



(2)

during the formation of the active rhodium hydride species [8b, 11a].

Since mass transfer restriction may occur [18], the effect of agitation speed on the hydroformylation rate was studied. Beyond 500 rpm the reaction rate was independent of agitation speed. All the experiments were performed at 1 000 rpm to be sure that the reaction is not under diffusion control.

The hydroformylation rate depends on substrate and rhodium concentrations, hydrogen and carbon monoxide partial pressures and temperature. The determination of the influence of concentrations and pressures leads to the rate law, while studying the influence of the temperature gives the experimental activation energy and the preexponential factor. We have studied the reaction with the *constant initial concentration method* consisting of varying the initial concentration of one reactant keeping the other concentrations constant. The plot of the integrated rate equation was used to determine the reaction order *vs* time (which is 1 in all runs except obviously when $pH_2 \neq pCO$), the apparent rate constant k_{obs} and the extrapolated initial rate. At time zero, the change in the initial rate R_0 depends only on the change of initial concentration of the reactant A studied. Thus, the initial order with respect to styrene, rhodium, hydrogen and carbon monoxide can be obtained by plotting $\mathrm{Ln}R_0$ *vs* $\mathrm{Ln}[A]_0$. The measurement of the initial gas consumption is difficult since the reaction was started by injecting the substrate. However after 2 min (corresponding to a styrene conversion of 5%), a stationary regime is obtained, and the consumption decreases regularly with time up to a styrene conversion of 95%. It is thus possible to extrapolate to time-zero to determine the initial gas consumption which affords the initial rate. In all runs, the standard conditions were those described in the *Experimental section*, the values of the parameter being studied being varied accordingly.

Effect of styrene concentration on the reaction rate

This study was carried out by varying the initial styrene concentration from 0.19 to 0.70 $mol.L^{-1}$. For each run, the plot of $Ln([styrene]_0/[styrene])$ *vs* time indicates that the order with respect to time is 1 (fig 3).

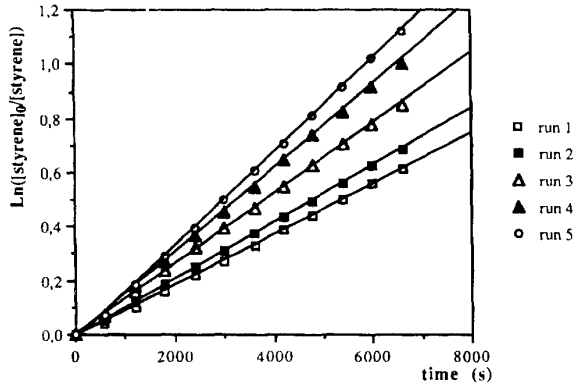


Fig 3. Determination of the styrene order with respect to time.

The rate expression is:

$$R = -\mathrm{d}[\mathrm{styrene}]/\mathrm{d}t = k_{obs}\,[\mathrm{styrene}] \qquad (3)$$

The apparent rate constant k_{obs} includes the effect of all the other variables which are kept constant. Surprisingly, k_{obs} varies with the styrene initial concentration $[styrene]_0$ (table I).

Table I. Effect of the initial styrene concentration on the reaction rate.

Run	$[Styrene]_0$ ($mol.L^{-1}$)	5 (%)	Yield (%)	$10^5 R_0$ ($mol.L^{-1}.s^{-1}$)	$10^4 k_{obs}$ (s^{-1})
1	0.70	85	89	6.7	0.95
2	0.54	84	86	5.7	1.05
3	0.37	85	85	4.7	1.28
4	0.26	85	94	4.0	1.54
5	0.19	85	96	3.3	1.74

The initial order with respect to styrene concentration is determined by plotting Ln R_0 *vs* Ln $[styrene]_0$ as shown in figure 4.

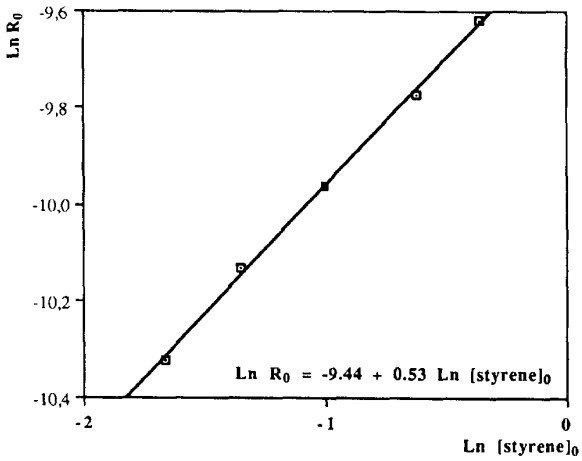


Fig 4. Determination of the initial order with respect to styrene.

These data lead to the following initial rate expression:

$$R_0 = k_1[\mathrm{styrene}]_0^{0.53},\ k_1 = \exp(-9.44) = 8.0 \times 10^{-5}(\mathrm{mol.L^{-1}})^{0.47}.\mathrm{s}^{-1} \qquad (4)$$

Comparison of eq 3 and 4 gives a relationship between k_{obs} and k_1:

$$R_0 = k_{obs}[\mathrm{styrene}]_0 = k_1[\mathrm{styrene}]_0^{0.53} \qquad (5)$$

The rate equation becomes:

$$R = 8.0 \times 10^{-5}[\mathrm{styrene}]_0^{-0.47}[\mathrm{styrene}] \qquad (6)$$

Effect of the concentration of **4** *on the reaction rate*

The influence of rhodium concentration on rate was studied for concentrations of the precursor complex **4** varying from 4×10^{-4} to 16×10^{-4} mol.L^{-1}, the Et_3N/Rh ratio [23] being maintained at 10 (table II).

Table II. Effect of the concentration of **4** on the reaction rate.

Run	10^4[**4**] (mol.L^{-1})	**5** (%)	Yield (%)	$10^5 R_0$ (mol.L^{-1}.s^{-1})	$10^4 k_{obs}$ (s^{-1})
6	4	85	50	2.7	0.51
2	8	84	86	5.7	1.05
7	12	84	84	8.4	1.56
8	16	84	99	10.9	2.02

As shown in figure 5, the initial reaction rate shows a first-order dependency on the catalyst concentration.

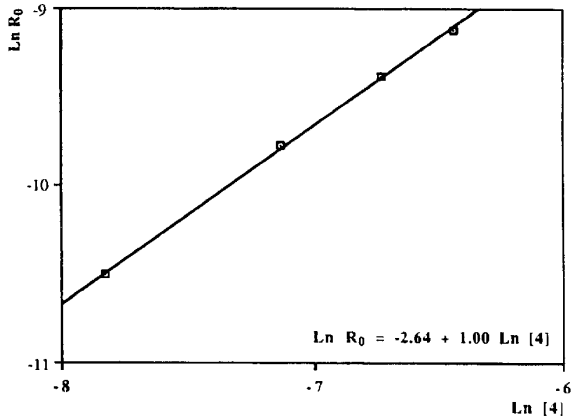


Fig 5. Determination of the initial order with respect to **4**.

Since $R_0 = k_2$ [**4**], eq 5 gives $k_2 = k_1[\text{styrene}]_0^{0.53}$ [**4**]$^{-1}$ with $k_2 = \exp(-2.64) = 0.071$ s^{-1} (fig 5). The rate equation becomes:

$$R = k_3[\text{styrene}]_0^{-0.47}[\text{styrene}]\,[\mathbf{4}] \qquad (7)$$

For each run $R = k_{obs}$[styrene] then $k_3 = k_{obs}$ [styrene]$_0^{0.47}$[**4**]$^{-1}$ (see table III). The mean value calculated from table III is $k_3 = 0.099 \pm 0.005$ (mol.L^{-1})$^{-0.53}$ s^{-1}.

Table III. Determination of the constant k_3.

run	[styrene]$_0$ (mol.L^{-1})	10^4[**4**] (mol.L^{-1})	$10^4 k_{obs}$ (s^{-1})	k_3 [(mol.L^{-1})$^{-0.53}$.s^{-1}]
1	0.70	8	0.95	0.095
2	0.54	8	1.05	0.098
3	0.37	8	1.28	0.100
4	0.26	8	1.54	0.102
5	0.19	8	1.74	0.100
6	0.54	4	0.51	0.095
7	0.54	12	1.56	0.097
8	0.54	16	2.02	0.095

Effect of hydrogen and carbon monoxide partial pressure on the reaction rate

Preliminary studies on the influence of the hydrogen/carbon monoxide ratio led us to suggest that in the case of 1-hexene [23], the orders with respect to hydrogen and carbon monoxide are 1 and −1, respectively. This hypothesis was confirmed by the lack of influence of the total pressure on the catalytic activity up to 80°C when the hydrogen/carbon monoxide ratio is 1:1 [23]. Thus, instead of keeping one partial pressure constant and studying the influence of the other, we decided to investigate directly the influence of the hydrogen/carbon monoxide ratio on the reaction rate for a total pressure of 20 bar (table IV).

Table IV. Effect of the hydrogen/carbon monoxide ratio on the reaction rate.

Run	pH_2/pCO	**5**[a] (%)	$10^5 R_0$ (mol.L^{-1}.s^{-1})
9	2/1	72	11.1
2	1/1	84	5.7
10	1/2	85	3.2

[a] Selectivity determined at the end of the experiments.

The initial rate is directly proportional to the hydrogen/carbon monoxide ratio, confirming the hypothesis that the orders with respect to hydrogen and carbon monoxide are 1 and −1, respectively (fig 6).

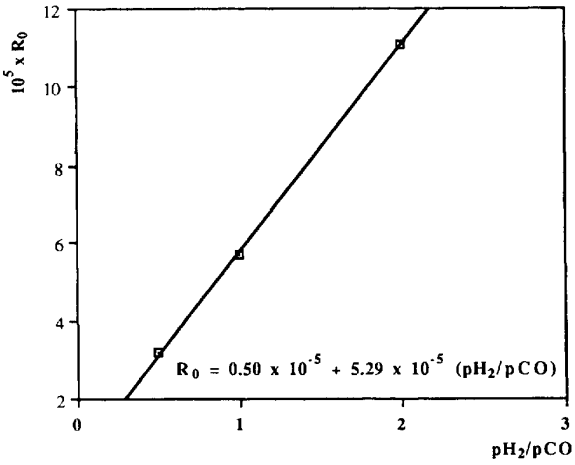


Fig 6. Influence of the hydrogen/carbon monoxide ratio on the initial rate.

The values for k_{obs} are obviously not available from these experiments since the H_2/CO ratio rapidly deviates from the original value after a few catalytic cycles. However, the initial rate is given by eq 8.

$$R_0 = k_4 pH_2/pCO, k_4 = 5.29 \times 10^{-5} \text{ mol.L}^{-1}\text{.s}^{-1} \qquad (8)$$

The reaction rate is, as expected from eq 8, independent of the total pressure when the hydrogen/carbon monoxide ratio is 1:1 (table V).

Table V. Influence of the total pressure on the catalytic activity for a hydrogen/carbon monoxide ratio H_2/CO of 1:1.

Run	Total pressure (bar)	5 (%)	Yield (%)	$10^5 R_0$ (mol.L^{-1}.s^{-1})	$10^4 k_{obs}$ (s^{-1})
11	10	82	80	5.7	1.05
2	20	84	86	5.7	1.05
12	30	85	85	5.8	1.07

Thus, the rate equation for styrene hydroformylation catalyzed by the Rh-TPP system is:

$$R = -\mathrm{d}[\text{styrene}]/\mathrm{d}t = k_3[\text{styrene}]_0^{-0.47}[\text{styrene}][\mathbf{4}]pH_2/pCO$$

Effect of temperature on the reaction rate

The rate dependency on temperature obeys the Arrhenius law between 30 and 60°C (table VI).

Table VI. Influence of the temperature on the reaction rate.

Run[a]	$10^5 R_0$ (mol.L^{-1}.s^{-1})	T (K)	$10^4 k_{obs}$ (s^{-1})
13	0.22	304	0.41
2	5.7	313	1.05
14	11.2	324	2.07
15	22.3	333	4.13

[a] $[\text{styrene}]_0 = 0.54$ mol.L^{-1}; $[\mathbf{4}] = 8.10^{-4}$ mol.L^{-1}

The experimental activation energy E_a and preexponential factor k_0 are obtained from the plot of Ln k_{obs} *vs* $1/T$. A linear regression (fig 7) gives the equation Ln k_{obs} = Ln $k_0 - E_a/RT$ with $E_a = 65.2 \pm 1.3$ kJ.mol^{-1} and $k_0 = 7.3 \times 10^6$s^{-1}.

It is of interest to note that the linear/branched aldehyde ratio remains constant in the temperature range studied.

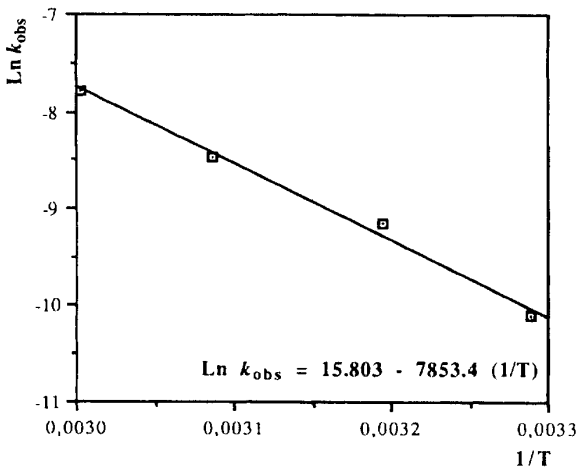


Fig 7. Influence of the temperature on the rate constant.

Discussion

Rate law

In contrast to rhodium triphenylphosphine systems [7, 18, 19], no critical concentration of the catalyst or dramatic variation of the linear/branched aldehyde ratio was observed for hydroformylation catalysis using the Rh-TPP system. This result is consistent with the proposal that the Rh-TPP system leads to a unique active species. The reaction order with respect to catalyst precursor is 1 (table II), and, even at low catalyst concentrations, the hydroformylation rate decreases linearly with respect to substrate concentration, indicating that the concentration of the active species remains constant throughout each experiment.

The reaction order with respect to substrate is 1 (fig 3) but, surprisingly, the apparent rate constant depends on the initial substrate concentration (table I). In the case of the catalysis of hydroformylation by the rhodium triphenylphosphine complex, a kinetic equation including the initial substrate concentration has previously been reported but not explained [18]. Furthermore, the observation made by Wilkinson *et al* [11c] that an increase in the alkene concentration leads to an asymptotic value of the reaction rate can perhaps be explained by a rate law where the initial substrate concentration appears with a negative order. However, in our case as well as in the above-cited works, it is not possible to rationalize the observations without further experiments.

The reaction orders with respect to hydrogen and carbon monoxide are 1 and −1, respectively (table IV). This result is confirmed by the non-influence of the total pressure on the reaction rate (table V). For any given hydrogen/carbon monoxide ratio no hydrogenation of styrene occurred. For the highest hydrogen partial pressure, the branched aldehyde selectivity slightly decreased (run 9 *vs* 2 and 10). Similar catalytic behavior was previously observed with 1-hexene as substrate [23], but no conclusion could be drawn since the selectivity was determined at the end of the experiment, *ie* when the H_2/CO ratio had changed considerably.

The rate equation for styrene hydroformylation catalyzed by the Rh-TPP system is:

$$R = -\mathrm{d}[\text{styrene}]/\mathrm{d}t = 0.099[\text{styrene}]_0^{-0.47}[\text{styrene}][\mathbf{4}](pH_2/pCO) \quad (9)$$

The experimental activation energy is lower than those found for the rhodium triphenylphosphine systems [3, 18, 19]; this is as expected since the Rh-TPP system is a more efficient hydroformylation catalyst than the Rh-PPh_3 system [23-26].

Thus, for the first time, a simple and complete kinetic equation for rhodium phosphane-catalyzed hydroformylation is described. Apart from the term $[\text{styrene}]_0^{-0.47}$, the orders with respect to substrate, catalyst, hydrogen and carbon monoxide are integers.

Mechanism

A hydroformylation cycle implies the reaction of four constituents: the rhodium hydride, the substrate, carbon monoxide and hydrogen. The reaction order −1

with respect to carbon monoxide can only be explained by dissociation of carbon monoxide from an intermediate *before* the rate-determining step. Thus, we propose that the active rhodium hydride formed during the induction period is the complex $HRh(CO)_2(TPP)_2$ **6**. This complex is the starting point of a catalytic cycle (fig 8) which is in agreement with the kinetics described above: (1) dissociation of carbon monoxide from **6** to give the 16-electron intermediate $HRh(CO)(TPP)_2$ **7**; (2) coordination of the substrate; (3) formation of the alkylrhodium complex **9**; (4) formation of the acylrhodium complex **10**; and (5) reaction of the latter with dihydrogen in a rate-determining step. Steps (1) to (3) are proposed to be equilibria since we have shown that the same catalytic system is able to isomerize 1-hexene [23]. The formation of acylrhodium species under hydroformylation conditions has been experimentally demonstrated for both phosphine-modified and unmodified rhodium systems [14, 30]. What was not clear until very recently was whether the formation of the aldehyde from the acyl complex occurs *via* a reaction with dihydrogen and/or *via* a reaction with a rhodium hydride species. Recent findings indicate that the aldehyde-forming step proceeds *via* a direct reaction of an acyl complex with dihydrogen [31]. The present kinetic study is also in agreement with such a proposal since the reaction order with respect to rhodium is 1. The actual mechanism of the reaction of dihydrogen with the acyl complex is however unknown. It could occur through σ-bond metathesis or through oxidative addition. In light of the results reported for the reactions of an iridium analogue of a rhodium hydroformylation catalyst [9], we favor the oxidative addition mechanism.

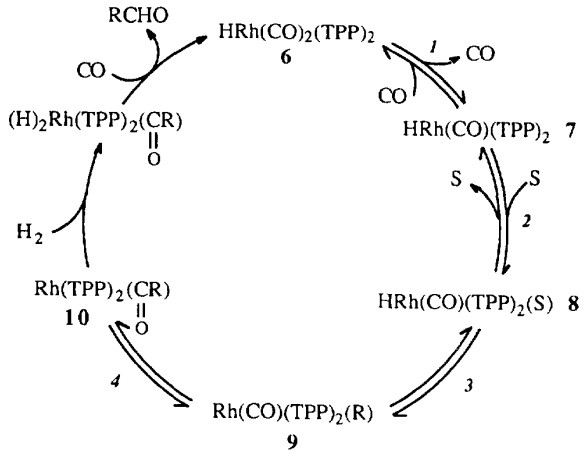


Fig 8. Proposed mechanism for the catalysis of the hydroformylation of styrene by the Rh-TPP system (S = substrate; R = linear or branched alkyl).

We tried to verify the formation of some of the intermediates in the proposed catalytic cycle. Unfortunately, all attempts to prepare a rhodium hydride from **4** or to isolate rhodium complexes from hydroformylation media failed since the catalytic system is not stable in the absence of syngas. We did obtain preliminary indications of the behavior of **4** under hydroformylation conditions but in the absence of styrene, by performing experiments in a glass pressure reactor. The yellow catalyst precursor **4** is not soluble in toluene at 40°C in the absence of syngas. Intake of 10 bar of syngas causes the formation of a clear cognac-colored solution in less than 5 min. Preliminary spectroscopic studies (IR, NMR) of these solutions show the formation of mixtures of a labile rhodium hydride, characterized as $HRh(CO)_2(TPP)_2$ **6**, and CO-bridged dinuclear complexes [32]. These results indicate that although **4** is fully consumed, only some of it forms a rhodium hydride, at least under the above-mentioned reaction conditions.

The catalytic species proposed in the mechanism depicted in figure 8 are all conventional except for the acylrhodium complex **10**, which is the key intermediate since it precedes the rate-determining step. This unsaturated, tricoordinate, 14-electron complex may be stabilized by interactions between the ligand and the metal center as described below. TPP is a congested phosphane [23] which exhibits a high electronic delocalization due to the conjugation of the phenyl groups and the intracyclic system [33]. These specific stereoelectronic properties should place the rhodium atom in a protecting 'cage', alleviating its electron deficiency. Thus, we propose the geometry depicted in figure 9 for complex **10**.

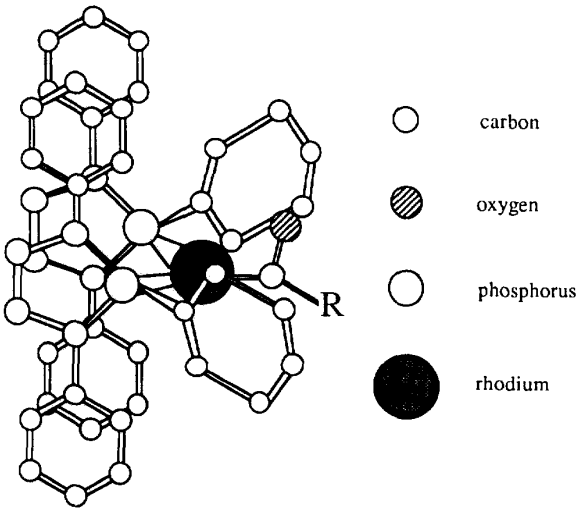


Fig 9. Proposed geometry for intermediate **10**.

Complexes in which aromatic–aromatic interactions (π-stacking) lead to similar structures have been obtained with 5-phenyldibenzophosphole [34], which is the only other phosphole with such high electronic delocalization [35]. Theoretical support for structures such as these has recently been reported for intermediates in platinum-catalyzed hydroformylation [36].

The idea that an intermediate such as **10** is active in the catalytic cycle can also be used to rationalize the results obtained during hydroformylation of 1-hexene [23] or vinylarenes [24]. We observed that 3,4-dimethylphosphole ligands do not promote efficient rhodium-catalyzed hydroformylation of 1-hexene and

styrene. These phospholes are much more basic but less congested than TPP [23]. Furthermore, due to the nature of the phospholyl substituents, no electronic delocalization is expected. Thus, these phospholes cannot stabilize intermediates similar to **10** and lead to relatively inactive catalytic systems. The 1,2,3,4,5-pentaphenylphosphole possesses the required electronic properties but does not have the steric properties required to stabilize intermediates such as **10**, since the presence of phenyl groups in positions 3 and 4 gives rise to too much congestion. TPP is a unique ligand since both its steric and electronic properties allow the stabilization of intermediate **10**.

Figure 9 also shows that the acyl group may adopt a special orientation to minimize steric repulsions and/or favor electronic interactions. For example, during the course of the styrene hydroformylation, the branched acyl moiety may be favored by aromatic–aromatic interactions between the acyl phenyl substituent and the 2-phenyl group of each TPP, leading to the observed branched selectivity. In the case of the 4-isobutylstyrene hydroformylation, the perturbation introduced by the 4-(isobutyl) substituent is weak since in complex **10** this substituent is far from the rhodium coordination sphere, eventually leading to a similar branched aldehyde selectivity [24]. However, in the case of 3-phenoxystyrene, an intermediate such as **10** might be more stable than in the case of styrene and 4-isobutylstyrene, due to further interactions between the phenoxy phenyl group and the TPP phenyl groups. This may account for a 6% increase in the branched aldehyde selectivity [24].

Conclusion

Simple kinetics for the catalysis of the hydroformylation of olefins by a rhodium phosphane complex are reported for the first time. These results were obtained with a catalytic system which is active for a wide range of substrates with very different electronic and steric properties and led us to propose a mechanism involving the unsaturated, 14-electron intermediate **10**. The formation of such an intermediate can explain the experimental results observed during the use of phospholes as ligands in the hydroformylation of α-olefins. On the basis of our results, it seems likely that similar intermediates may also occur in the catalysis of the hydroformylation of olefins by the rhodium triphenylphosphine system.

Acknowledgments

The authors wish to thank the Centre National de la Recherche Scientifique (CNRS) for financial support and the Société Nationale des Poudres et Explosifs (SNPE) for financial support and for a fellowship to RR They are also grateful to L Rosenberg for her editorial assistance. Helptul discussions with F Mathey (Ecole Polytechnique, Palaiseau), S Lecolier (SNPE) and I Tkatchenko (CNRS, Institut de Recherches sur la Catalyse, Villeurbanne) are also gratefully acknowledged.

References

1 Cornils B, *New Syntheses with Carbon Monoxide*, Falbe J, Ed Springer, 1980, p 1

2 Tkatchenko I *Comprehensive Organometallic Chemistry*, Wilkinson G, Stone FGA, Abel EW, Eds, Pergamon, Oxford, 1982, Vol 8, p 115

3 Collman JP, Hegedus LS, Norton JR, Finke RG, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, 1987

4 a) Botteghi C, Ganzerla R, Lanarda M, Moretti G, *J Mol Catal* (1987) 40, 129
b) Neibecker D, Réau R, *Angew Chem Int Ed Engl* (1989) 28, 500
c) Amer I, Alper H, *J Am Chem Soc* (1990) 112, 3674
d) Alper H, Zhou JQ, *J Org Chem* (1992) 57, 3729
e) Cuny GD, Buchwald SL, *J Am Chem Soc* (1993) 115, 2066
f) Kwok TJ, Wink DJ, *Organometallics* (1993) 12, 1954

5 Botteghi C, Paganelli S, Schionato A, Marchetti M, *Chirality* (1991) 3, 355 and references therein

6 Sakai N, Mano S, Nozaki K, Takaya H, *J Am Chem Soc* (1993) 115, 7033

7 Arena CG, Nicolo F, Drommi D, Bruno G, Faraone F, *J Chem Soc Chem Commun* (1994), 2251

8 a) Stille JK, *Comprehensive Organic Synthesis*, Trost BM, Fleming I, Semmelhack MF, Eds, Pergamon, Oxford, 1991; Vol 4, p 913
b) Tolman CA, Faller JW, *Homogeneous Catalysis with Metal Phosphine Complexes*, Pignolet LH, Ed, Plenum, New-York, 1983, p 81
c) Broussard ME, Juma B, Train SG, Peng WJ, Laneman SA, Stanley GG, *Science* (1993) 260, 1784
d) Weissermel K, Arpe HJ, *Industrial Organic Chemistry*, VCH, Weinheim, 1993, p 123

9 Deutsch PP, Eisenberg R, *Organometallics* (1990) 9, 709 and references therein

10 a) Consiglio G, Morandini F, Haelg P, Pino P, *J Mol Catal* (1990) 60, 363
b) Uccello-Barretta G, Lazzaroni R, Settambolo R, Salvadori P, *J Organomet Chem* (1991) 417, 111 and references therein

11 a) Evans D, Osborn JA, Wilkinson G, *J Chem Soc* (1968) A, 3133
b) Yagupski G, Brown CK, Wilkinson G, *J Chem Soc* (1970) A, 1392
c) Brown CK, Wilkinson G, *J Chem Soc* (1970) A, 2753

12 Heck RF, Breslow DS, *J Am Chem Soc* (1961) 83, 4023

13 Jardine FH, *Polyhedron* (1982) 1, 569

14 Brown JM, Kent G, *J Chem Soc Perkin Trans II* (1987) 1597

15 Moser WR, Papile CJ, Brannon DA, Durwell RA, Weiniger SJ, *J Mol Catal* (1987) 41, 271

16 a) Unruh JD, Christenson JR, *J Mol Catal* (1982) 14, 19
b) Unruh JD, Christenson JR, Hughes OR, Young DA, *Catalysis of Organic Reaction*, Moser WR, Ed, Dekker, New-York, 1981; p 309

17 Bianchini C, Meli A, Peruzzini M, Vizza F, Fujiwara Y, Jintoku T, Taniguchi H, *J Chem Soc Chem Commun* (1988), 299

18 Royo M, Melo F, Manrique A, Oro L, *Transition Met Chem* (1982) 7, 44

19 Deshpande RM, Chaudhari RV, *Ind Eng Chem Res* (1988) 27, 1996

20 Cavalieri d'Oro P, Raimondi L, Pagani G, Montrasi G, Gregoro G, Andreetta A, *Chim Ind (Milan)* (1980) 62, 572

21 Strohmeier W, Michel M, *Z Phys Chem* (1981) 124, 23

22 van Rooy A, Orij EN, Kamer PCJ, van den Aardweg F, van Leeuwen PWNM, *J Chem Soc Chem Commun* (1991) 1096

23 a) Neibecker D, Réau R, *J Mol Catal* (1989) 53, 219
b) Neibecker D, Réau R, *J Mol Catal* (1989) 57, 153
24 Neibecker D, Réau R, Lecolier S, *J Org Chem* (1989) 54, 5208
25 Neibecker D, Réau R, *New J Chem* (1991) 15, 279
26 Bergounhou C, Neibecker D, Réau R, *J Chem Soc Chem Commun* (1988) 1370
27 Mathey F, *Chem Rev* (1988) 88, 429
28 Lukas B, Roberts RMG, Silver J, Wells AS, *J Organomet Chem* (1983) 256, 103
29 Savitzky A, Golay MJF, *Anal Chem* (1964) 36, 1627
30 a)Garland M, Pino P *Organometallics* (1991) 10, 1693
b) Fyhr C, Garland M, *Organometallics* (1993) 12, 1753
31 Jongsma T, Challa G, van Leeuwen PWNM, *J Organomet Chem* (1991) 421, 121
32 Bergounhou C, Neibecker D, to be published
33 Mathey F, *Top in Phosphorus Chem* (1980) 10, 1
34 Affandi S, Nelson JH, Alcock NW, Howarth OW, Aleya EC, Sheeldrick GM, *Organometallics* (1988) 7, 1724
35 Hjortkjaer J, Dueholm H, De Mello PC, *J Mol Catal* (1987) 39, 79
36 Castonguay LA, Rappé AK, Casewit CJ, *J Am Chem Soc* (1991) 113, 7177