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A detailed kinetic and mechanistic study of the regioselective hydrogenation of quinoline to 1, 2, 3, 4-tetrahydroquinoline catalyzed by $[Os(H)(Cl)(CO)(PPh_3)_3]$

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Abstract

The complex $[OsH(Cl)(CO)(PPh_3)_3]$ is an efficient and regioselective precatalyst for the hydrogenation of the nitrogen-containing ring of quinoline (Q), under mild reaction conditions (125 °C and 4 atm H_2). A detailed kinetic study of this reaction led to the rate law: $r = \{K_1k_2/(1 + K_1[H_2])\}[Os][H_2]^2$ ($K_1 = 522\ M^{-1}$ and $k_2 = 5.45 \times 10^{-2}\ M^{-1}s^{-1}$ at 125°C). The active species is the hydrido-quinoline complex $[MHCl(CO)(NC_9H_7)(PPh_3)_2]$. The catalytic cycle involves a reversible partial hydrogenation of the coordinated quinoline to yield the 1,2-dihydroquinoline (DHQ) species, followed by the rate-determining second hydrogenation of the DHQ ligand, which yields a THQ derivative; the substitution of THQ by a new molecule of Q regenerates the active species and restarts the catalytic cycle. Activation parameters were found for both the overall catalytic reaction (Ea = 83 $kJmol^{-1}$, $\Delta H^{\neq} = 80\ kJmol^{-1}$, $\Delta S^{\neq} = -331\ JK^{-1}mol^{-1}$ and $\Delta G^{\neq} = 179\ kJmol^{-1}$) and for the determining step of the mechanism (Ea = 99 $kJmol^{-1}$, $\Delta H^{\neq} = 97\ kJmol^{-1}$, $\Delta S^{\neq} = -39\ JK^{-1}mol^{-1}$ and $\Delta G^{\neq} = 108\ kJmol^{-1}$). The experimental findings together with a theoretical study allowed us to propose a detailed catalytic cycle containing each elementary step.

Key words: Homogeneous catalysis; hydrogenation; osmium; ruthenium; quinoline.

Un estudio cinético y mecanístico detallado de la hidrogenación regioselectiva de quinolina a 1, 2, 3, 4-tetrahidroquinolina catalizada por $[Os(H)(Cl)(CO)(PPh_3)_3]$

Resumen

El complejo $[OsHCl(CO)(PPh_3)_3]$ es un precatalizador eficiente y regioselectivo para la hidrogenación del anillo nitrogenado de la quinolina, bajo condiciones moderadas de reacción (125°C and 4 atm H_2). Un estudio cinético detallado de esta reacción conllevó a la expression de velocidad: $v = \{K_1k_2/(1 + K_1[H_2])\}[Os][H_2]^2$ ($K_1 = 522\ M^{-1}$ y $k_2 = 5.45 \times 10^{-2}\ M^{-1}s^{-1}$ at 125°C). La especie activa del proceso es el complejo hidruro-quinolina $[MHCl(CO)(NC_9H_7)(PPh_3)_2]$. El ciclo catalítico

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involucra una hidrogenación parcial reversible del ligando quinolina para producir una especie conteniendo un ligando 1,2-dihidroquinolina (DHQ), seguida por la hidrogenación del ligando DHQ, determinante de la velocidad de reacción, la cual produce un derivado conteniendo una tetrahidroquinolina (THQ) coordinada; la sustitución del ligando THQ por una nueva molécula de Q regenera la especie activa y restablece el ciclo catalítico. Los parámetros de activación (Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$ y $\Delta G^{\neq}$) fueron calculados tanto para la reacción catalítica global (Ea = 62 $kJmol^{-1}$, $\Delta H^{\neq} = 59$ $kJmol^{-1}$, $\Delta S^{\neq} = -136$ $JK^{-1}mol^{-1}$ and $\Delta G^{\neq} = 100$ $kJmol^{-1}$) como para el paso determinante de la reacción (Ea = 99 $kJmol^{-1}$, $\Delta H^{\neq} = 97$ $kJmol^{-1}$, $\Delta S^{\neq} = -39$ $JK^{-1}mol^{-1}$ and $\Delta G^{\neq} = 108$ $kJmol^{-1}$). Los resultados experimentales, conjuntamente con un estudio teórico, permitió proponer un ciclo catalítico detallado para esta reacción, conteniendo cada uno de los pasos elementales del proceso.

Palabras clave: Catálisis homogénea; hidrogenación; osmio; rutenio; quinolina.

Introduction

The hydrogenation of the heterocyclic ring of quinoline and other polynuclear heteroaromatic nitrogen compounds is an area of considerable interest because it is related to the industrially important hydrodenitrogenation (HDN) process. Heavy petroleum, tar sands, oil shale and coal derived liquids are alternative sources for synthetic fuels; however, they contain high levels of organic nitrogen (up to 20%). In the HDN process, the nitrogen content of the various fuel products derived from coal and petroleum is minimized by removing it as ammonia. This process is essential to reduce NO_x emissions upon burning of fuels, and also to avoid deactivation or poisoning of *e.g.* hydrotreating or hydrocracking catalysts by nitrogen compounds. HDN catalysis is generally carried out over sulfided $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, or NiW/Al_2O_3 under rather severe hydrogenation conditions (350-500°C and 1500-3000 psi H_2) (1). However, it has been reported that sulfides of ruthenium, osmium, rhodium and iridium show the highest activity of all the *d*-block elements for the hydrotreating process (2).

Kinetic, mechanistic and thermodynamic studies have established that hydrogenation of the N-containing aromatic ring occurs prior to C-N bond cleavage; for instance, in the HDN of quinoline (Q), reduction to 1, 2, 3, 4-tetrahydroquinoline (THQ) takes place first, followed by hydrogenolysis of the C-N bonds to produce 3-phenylpropylamine and finally propylbenzene + NH_3 (3) as may be observed in Figure 1.

Homogeneous modeling of heterogeneous catalytic reactions by use of well-defined metal complexes can help in the understanding of specific steps of the reaction mechanisms. This has been extensively used in hydrodesulfurization (HDS) (4) but HDN model

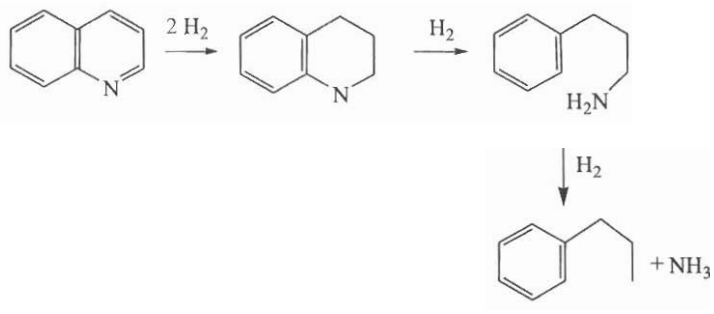


Figure 1. Proposed mechanism of hydrodenitrogenation of quinoline.

studies using coordination or organometallic complexes are scarce; modeling work has primarily focused on the coordination of N-heterocyclic compounds on mononuclear metal centers, on the homogeneous catalytic hydrogenation of N-aromatic compounds and on C-N bond activation (4-6).

Nevertheless, there are relatively few examples of homogeneous catalysts for the hydrogenation of this type of compounds. Some Ru-, Os-, Rh- and Ir- complexes such as $[RuHCl(PPh_3)_3]$ (7), $[RhCl(PPh_3)_3]$ (8), $[Rh(\eta^5\text{-}Cp^*)(NCMe)_3]^{2+}$ (9), $[M(COD)(PPh_3)_2]^+$ (10, 11), $[M(COD)(PPh_3)(NCPh)]^+$ and $[M(COD)(NCPh)_2]^+$ (12) (M = Rh or Ir and COD = 1,5-cyclooctadiene), $[Rh(DMAD)(triphos)]PF_6$ (DMAD = dimethylacetylendicarboxylate, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) [5b] as well as the systems M(Tp) and M(Tp*) (13), where M = Ru, Rh, Ir, Tp = tris(pyrazolyl)borate and Tp*= tris(3,5-dimethyl-pyrazolyl)borate, have been found to catalyze the reduction of quinoline and related compounds. In all these cases only the reduction of the heterocyclic ring was observed. However, Borowski *et al.* (14) reported the regioselective hydrogenation of the non-heterocyclic rings of quinoline, isoquinoline and acridine by using $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (Cy = cyclohexyl) as the precatalyst. Recently, Fujita et al. [15] reported the transfer hydrogenation of Q to THQ catalyzed by a ruthenium-cyclopentadienyl precatalysts using 2-propanol as a hydrogen source.

We have published a series of kinetic and mechanistic studies of the hydrogenation of the heterocyclic ring of quinoline and other heteroaromatic nitrogen compounds such as 5,6- and 7,8-benzoquinoline, acridine and indole catalyzed by ruthenium and osmium cationic complexes of the type $[MH(CO)(NCMe)_2(PPh_3)_2]BF_4$ (16-20). Now, we report a detailed kinetic and mechanistic investigation of the hydrogenation of quinoline by use of the neutral osmium complex $[OsHCl(CO)(PPh_3)_3]$ (1), including the determination of the rate and the equilibrium constants of some of the elementary steps of the catalytic cycle.

Materials and methods

1. Instruments and materials

All manipulations were conducted with rigorous exclusion of air using a high vacuum line, an argon-filled Schlenck line and/or an argon-filled glovebox. Q were dried over KOH and purified by distillation at reduced pressure. Solvents were purified by known procedures. H_2 was dried by passing through a column containing $CaSO_4$. Complex **1** was prepared by published procedure (21) and modified by some of us (19). ^1H and $^{31}P\{^1H\}$ N.M.R. 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. Procedure for kinetic and catalytic runs

The details regarding the apparatus used and the reaction procedure for the catalytic runs and kinetic experiments are similar to those reported earlier (16, 20). In a typical experiment a solution of the precatalyst, quinoline and xylene as the solvent (50 mL total volume) was placed in the reactor. The solution was carefully deoxygenated, a preheated oil bath was placed around the reactor and the magnetic stirring commenced. When the system reach the thermal equilibrium, hydrogen was admitted into the evacuated system to the desired pressure; this point was taken as zero time for the reaction. The reaction was followed by measuring the hydrogen pressure drop as a function of time and by using gas chromatography. The data for hydrogenation of Q were plotted as molar concentration of the product (THQ) *versus* time yielding straight lines, which were fitted by conventional linear regression programs. Initial rates of the reaction were obtained from the corresponding slopes.

Each reaction was repeated at least twice in order to ensure reproducibility of the results. In the kinetic experiments, the percentage of hydrogenation was restricted to 5 - 10% in order to perform a kinetic analysis based on the initial rate method (22). At the end of the catalytic runs, the composition of the reaction mixture was analyzed by means of a 610 Series UNICAM gas chromatograph fitted with a thermal conductivity detector and a 3 m 10% SE-30 on Supelcoport glass column using helium as carrier gas; the chromatograph was coupled to a UNICAM 4815 data system.

The hydrogen concentrations in xylene solution under the reaction conditions were calculated from the data reported in the literature (23, 24).

3. Coordination chemistry

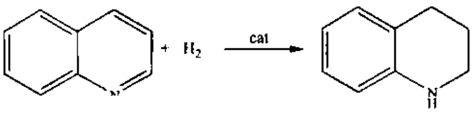
To a solution of complex **1** (104 mg, 0.1 mmol) in benzene (10 cm^3) was added quinoline (0.5 cm^3, 4.2 mmol), and the mixture was stirred vigorously under reflux for 1 h, giving a pale yellow solution, which was evaporated under vacuum to *ca.* one-third of its initial volume. A precipitate was obtained by addition of n-pentane, which was washed with pentane and diethylether and then dried *in vacuo*. ^1H N.M.R. ($CDCl_3$, 298 K): 9.6-7.1 p.p.m. (series of multipletes, Q and PPh_3); -6.9 ppm ($^2J_{H\text{-}Ptrans}$ = 90 Hz, $^2J_{H\text{-}Pcis}$ = 25 Hz, Os-H of complex **1**, -13.5 and -14.9 ppm (s, $^2J_{H\text{-}Pcis}$ = 20 Hz, Os-H of [$OsHCl(CO)(NC_9H_7)(PPh_3)_2$]).

4. Teorethical studies

All calculations were carried out at the semiempirical level, SCF-CNDO/2 in a similar way to that described by some of us in a previous paper (25).

Results and Discussion

The regioselective reduction of Q to give exclusively THQ under mild conditions (130°C and 4 bar H_2) in xylene solvent Eq. [1] was efficiently carried out by using the complex [$OsHCl(CO)(PPh_3)_3$] [**1**] as the precatalyst. Hydrogenation of the benzene ring of Q does not take place to any detectable extent during the hydrogenation runs.



[1]

All the reaction mixtures were homogeneous solutions with no evidence of metallic components. However, the homogeneity of the reaction was further established by the method of addition of mercury; when the hydrogenation reactions were carried out in presence of liquid mercury, no effect on the initial rate was observed. This results together with the high reproducibility of the results, confirmed that the catalytic reactions were truly homogeneous (26).

Finally, the hydrogenation of Q catalyzed by complex **1** was investigated in a range of speed of stirring (750-1300 rpm). The initial rates of hydrogenation were found to be independent of stirring speed; these results show that the rate data were in the kinetic regime and mass transfer effects were negligible.

1. Kinetic investigation of the hydrogenation of Q catalyzed by [$OsHCl(CO)(PPh_3)_3$]

In order to gain further insight on the hydrogenation of Q catalyzed by the complex [$OsHCl(CO)(PPh_3)_3$] [**1**] in xylene as the solvent, detailed kinetic studies were carried out by following the hydrogen pressure drop at different catalyst concentrations, substrate and dissolved hydrogen at constant temperature. The initial rate data for the Q hydrogenation catalyzed by this osmium complex are collected in Table 1. The results indicate that:

1. The initial rate of hydrogenation of quinoline shows a direct dependence on the osmium concentration (entries 1-6). The plot of log r_i *versus* log [Os] (log r_i = -3.2 + 1.0 log [Os]) indicates first-order behavior with respect to catalyst concentration.

Table 1

Kinetic data for the reduction of Q catalyzed by $[OsHCl(CO)(PPh_3)_3]$. Initial rates (r_i), xylene solvent.

Entry	T (K)	10^3[Os] (M)	[Q] (M)	pH_2, (atm)	$10^2[H_2]$ (M)	$10^7 r_i$ (Ms^{-1})
1	403	0.4	0.1	4.1	1.9	3.08 ± 0.02
2	403	0.6	0.1	4.1	1.9	4.74 ± 0.01
3	403	0.8	0.1	4.1	1.9	6.06 ± 0.02
4	403	1.0	0.1	4.1	1.9	7.85 ± 0.03
5	403	1.2	0.1	4.1	1.9	8.90 ± 0.02
6	403	1.4	0.1	4.1	1.9	10.58 ± 0.03
7	403	1.0	0.6	4.1	1.9	7.87 ± 0.04
8	403	1.0	0.8	4.1	1.9	7.77 ± 0.04
9	403	1.0	1.2	4.1	1.9	7.90 ± 0.03
10	403	1.0	1.4	4.1	1.9	7.72 ± 0.04
11	403	1.0	0.1	1.0	0.5	1.72 ± 0.08
12	403	1.0	0.1	1.4	0.6	2.57 ± 0.04
13	403	1.0	0.1	1.8	0.8	4.08 ± 0.04
14	403	1.0	0.1	2.8	1.2	5.12 ± 0.03
15	403	1.0	0.1	4.8	2.2	8.58 ± 0.20
16	403	1.0	0.1	5.5	2.5	11.20 ± 0.07
17	393	1.0	0.1	4.1	1.9	4.04 ± 0.02
18	413	1.0	0.1	4.1	1.9	10.20 ± 0.01
19	423	1.0	0.1	4.1	1.9	16.80 ± 0.05

2. The initial rate of the hydrogenation of quinoline is independent of the amount of substrate in the concentration range studied for this reaction (entries 4 and 7-10).
3. The dependence of the hydrogenation reaction with respect to dissolved hydrogen concentration is of a fractional order between first and second order; at hydrogen pressure below 1.6 atm (entries 11-13), the order with respect to this parameter was close to 2 ($\log r_i = -2.8 + 1.7 \log [H_2]$), whereas at higher pressure (entries 4 and 14-16) was found to be close to first order ($\log r_i = -4.2 + 1.1 \log [H_2]$). In recent works, it has been found a second order dependence of the Q reduction rate with respect to the hydrogen concentration has been found at low hydrogen pressure; however, at hydrogen pressure above 1 atm., the dependence with respect to hydrogen concentration tends toward first order (16, 20). The fractional kinetics as a function of hydrogen concentration observed in the present work (between 1.0 and 5.5 atm) may be the result of operating in the intermediate regime of this kind of kinetics.

In view of the above observations, the catalytic hydrogenation of Q by using $[OsHCl(CO)(PPh_3)_3]$ as the precatalysts proceeds according to the rate law:

$$r = \frac{a}{b + c[H_2]}[Os][H_2]^2 \qquad [2]$$

This rate expression ($k_{cat} = a/(b + c[H_2])$) is similar to that found for the hydrogenation of quinoline using cationic ruthenium and osmium complexes $[MH(CO)(NCMe)_2(PPh_3)_2][BF_4]$ as precatalysts (16, 20).

2. Coordination chemistry related with the catalytic hydrogenation of Q

In order to gain further understanding of the mechanisms of the regioselective hydrogenation of quinoline, the reaction of the neutral osmium complex **1** with the components of the catalytic mixture was carried out, with the aim of isolating or detecting some intermediates of the reaction. It was not possible to obtain simple products in a pure form from these reactions, as they all seem to involve rapid equilibria between closely related labile species, which is usually expected from a highly active catalytic system.

However, our previous studies of the reactivity of the ruthenium cationic complexes $[MH(CO)(NCMe)_2(PPh_3)_2]BF_4$ with Q in the presence and in absence of H_2, allowed us to identify the main species. The reaction of **1** with quinoline in benzene under reflux gives a yellow solution from which a pale yellow solid could be isolated by addition of diethylether. The ^1H- and $^{31}P\{^1H\}$ N.M.R. spectra of this solid showed the presence of three distinct species, the starting complex **1** (50 %) and two isomeric forms of the monosubstituted complex $[OsHCl(CO)(Q)(PPh_3)_2]$ (**2**). The ^1H-N.M.R. spectra show in the high field range, a doublet of triplets at -6.9 ppm ($^2J_{H\text{-}Ptrans}$ = 90 Hz, $^2J_{H\text{-}Pcis}$ = 25 Hz) corresponding to the complex **1**, and two triplets at -13.5 and -14.9 ppm ($^2J_{H\text{-}Pcis}$ = 20 Hz), consistent with two species containing osmium-hydride in *cis* position with respect to two equivalent phosphine ligands. The presence of these two triplets may be explained trough the formation of two isomers: one containing the hydrido ligand *trans* to the quinoline and other with these two ligands in a mutually *cis* position (Figure 2). Similar ruthenium isomers with acetonitrile and cyclohexylamine have been reported by Sánchez-Delgado et al (27) and by some of us (28), respectively. The presence of these two isomers was also corroborated by the presence of two singlets at 19.3 and 17.1 p.p.m. in the $^{31}P\{^1H\}$ N.M.R. spectrum. These data are consistent with octahedral structures involving mutually *trans* phosphines and the hydride *cis* to the carbonyl ligand in one of the isomers and traus in the other one, the other two positions are occupied by one quinoline and one chloride ligand.

On the other hand, complex **1** also reacts with THQ in benzene to form a yellow solution from which a pale yellow precipitate was isolated. Unfortunately, this solid decomposes immediately when dissolved in $CDCl_3$ and its ^1H- and $^{31}P\{^1H\}$ N.M.R. show only small amounts of starting material. We believe that in this reaction the hydrido-tetrahydroquinoline complex $[OsHCl(CO)(NC_9H_{11})(PPh_3)_2]$ may be formed, similar to the THQ and THiQ complexes $[MH(CO)(NC_9H_{11})(PPh_3)_2]BF_4$ (M = Ru, Os), which were isolated or detected by some of us (16, 20).

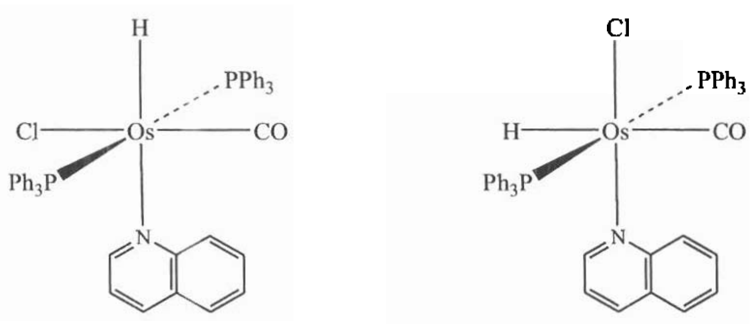


Figure 2. Isomers of the complex $[OsHCl(CO)(Q)(PPh_3)_2]$.

3. Mechanistic aspects of the hydrogenation of Q

On the basis of our experimental findings presented above, we propose a catalytic cycle in which complex **1** is quickly transformed by reaction with Q into the active species OsHCl(CO)(Q)(PPh_3)$_2$, **2**, which is postulated as the initial species entering the catalytic cycle. The cycle is constituted by the sequence of reactions shown in Figure 3, which involved a reversible partial hydrogenation of complex **2** to produce the 1,2-dihydroquinoline species [OsHCl(CO)(NC_9H_9)(PPh_3)$_2$] [**3**], followed by the rate determining second hydrogenation transforming the DHQ ligand into THQ to yield [OsHCl(CO)(NC_9H_{11})(PPh_3)$_2$] [**4**]; the substitution of the THQ ligand of **4** by a new molecule of Q regenerates the active species **2** and restarts the catalytic cycle.

According to these mechanisms, the rate law for the reduction of Q can be derived by applying of the Equilibrium Approximation, which may be expressed as

$$r = \frac{K_1 K_1}{1 + K_1 [H_2]} [Os][H_2]^2 \qquad [3]$$

This theoretical rate law is in good accord with the experimental finding Eq. [1] with a = K_1k_2, b = 1 and c = $K_1[H_2]$, and explains the fractional order dependence found for the reaction rate with respect to H_2 concentration.

Equation [3] can be inverted and reorganized as:

$$\frac{[Os]}{r} = \frac{1}{K_1 k_2 [H_2]^2} + \frac{1}{k_2 [H_2]} \qquad [4]$$

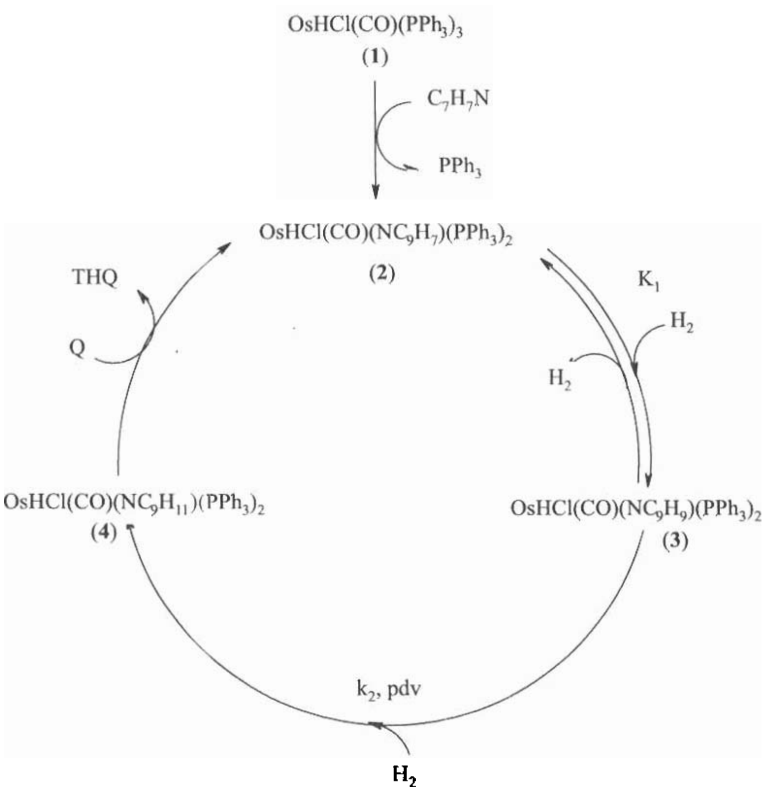


Figure 3. Mechanism of quinoline hydrogenation catalyzed by [OsHCl(CO)(PPh_3)$_3$].

A plot of [Os]/r *versus* the reciprocal of H_2 concentration was fitted to a quadratic type function and through the Levenberg-Marquardt method. In this way the values of K_1 (522 M^{-1}) and k_2 (5.45 x 10^{-2} $M^{-1}s^{-1}$) were obtained (Figure 4). The value of the rate constant and equilibrium one are in good agreement with the rate data obtained in the kinetic study.

4. Effect of temperature on the hydrogenations of Q

In order to calculate the activation parameters, the effect of the temperature on the rate constant was studied for the hydrogenation of Q at high hydrogen pressure (4.1 atm), where the kinetic regime with respect to the hydrogen concentration is near to first order. The plot of ln k_{cat} *versus* 1/T(K) yielded a straight line (Figure 5), from which the activation energy (Ea) and the frequency factor (A) were evaluated. The extrapolation of the straight line to 298 K allowed us to determine the rate constant at this temperature. These parameters and the values of enthalpy, entropy and free energy of activation (calculated from the usual relationships: $\Delta H^{\neq} = Ea - RT$; $\Delta S^{\neq} = R \ln(hA/e^{n}K_{B}T)$, n = 3; $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$) are listed in Table 2.

The activation parameters for the hydrogenation of Q catalyzed by the osmium precatalyst are higher than that found for the hydrogenation of Q by using the cationic Ru and Os complexes, $[MH(CO)(NCMe)_2(PPh_3)_2]BF_4$. The large negative activation entropy obtained for Q hydrogenation supports a highly ordered transition state leading to catalytic hydrogenation.

On the other hand, in order to determine the values of K_1 and k_2 at two other different temperatures (393 and 423 K), a series of catalytic runs was carried out varying the dissolved hydrogen concentration at each temperature; the results are shown in Table 3 (entries 1-6 at 393K and 7-12 at 413K). Making use of Eq. [4], the values of K_1 and k_2 were determined; these values are shown in Table 4. A plot of ln k_2 *versus* 1/T

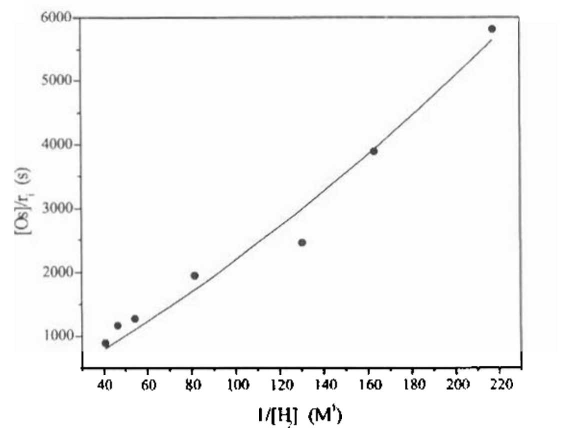


Figure 4. Plot of [Os]/r versus 1/[H_2] for the hydrogenation of quinoline catalyzed by $[OsHCl(CO)(PPh_3)_3]$.

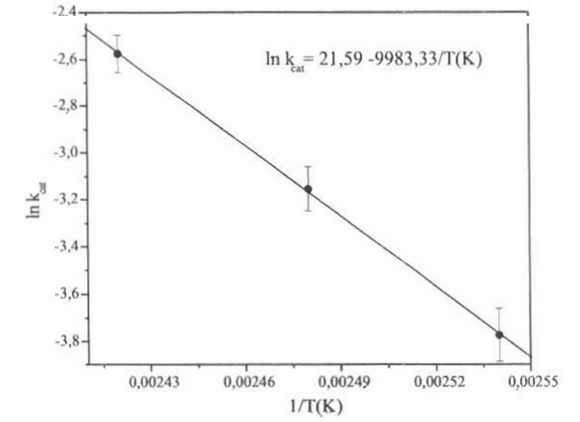


Figure 5. Arrhenius plot for the hydrogenation of quinoline catalyzed by $[OsHCl(CO)(PPh_3)_3]$.

Table 2
Activation parameters for the hydrogenation of Q catalyzed by $[OsHCl(CO)(PPh_3)_3]$.

Parameter	Value
Ea	**(83 ± 1) kJ mol^{-1}**
A	3.6 x 10^{6} $M^{-1}s^{-1}$
k_{cat} (298 K)	5.9 x 10^{-5} $M^{-1}s^{-1}$
$\Delta H^{\ddagger}$	(59 ± 1) kJ mol^{-1}
$\Delta S^{\ddagger}$	-(136 ± 3) $JK^{-1}mol^{-1}$
$\Delta G^{\ddagger}$	(100 ± 4) kJ mol^{-1}

Table 3

Efect of the hydrogen concentration on the reduction of Q catalyzed by $[OsHCl(CO)(PPh_3)_3]$ at 393 and 413 K. Initial rates (r_i), xylene solvent

Entry	T (K)	10^3 [Os] (M)	[Q] (M)	pH_2 (atm)	10^2 $[H_2]$ (M)	10^7 r_i (Ms^{-1})
1	393	1.0	0.1	2.1	0.9	1.80 ± 0.05
2	393	1.0	0.1	2.8	1.2	2.03 ± 0.11
3	393	1.0	0.1	3.4	1.5	3.44 ± 0.03
4	393	1.0	0.1	4.1	1.9	4.04 ± 0.13
5	393	1.0	0.1	4.8	2.0	5.44 ± 0.24
6	393	1.0	0.1	5.5	2.3	5.30 ± 0.13
7	423	1.0	0.1	1.4	0.6	3.21 ± 0.05
8	423	1.0	0.1	1.7	0.8	5.00 ± 0.21
9	423	1.0	0.1	2.8	1.3	10.50 ± 0.05
10	423	1.0	0.1	3.4	1.6	11.70 ± 0.04
11	423	1.0	0.1	4.1	1.9	14.60 ± 0.01
12	423	1.0	0.1	4.8	2.2	16.50 ± 0.02

Table 4

Value of K_1 and k_2 at different temperatures.

T (K)	K_1(M^{-1})	k_2 ($M^{-1}s^{-1}$)
393	226	2.84 x 10^{-2}
403	522	5.45 x 10^{-2}
413	112	1.24 x 10^{-2}

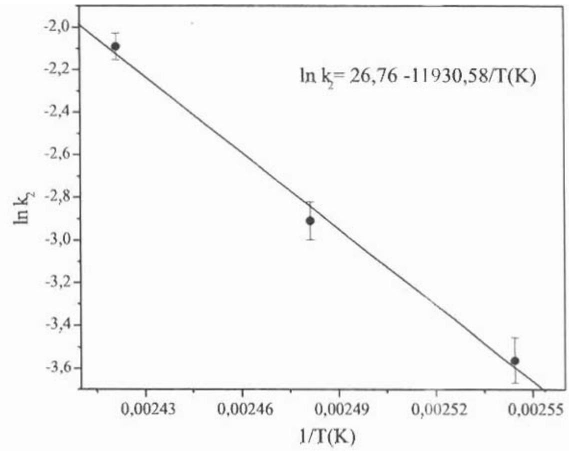


Figure 6. Arrhenius plot for the second step of the hydrogenation of quinoline catalyzed by $[OsHCl(CO)(PPh_3)_3]$.

Table 5

Activation parameters for the rate-determining step of the hydrogenation of Q catalyzed by $[OsHCl(CO)(PPh_3)_3]$.

Parameter	Value
Ea	(99 ± 2) kJ mol^{-1}
A	4.4 x 10^{11} $M^{-2}s^{-1}$
k_{cat} (298 K)	1.7 x 10^{-6} $M^{-2}s^{-1}$
$\Delta H^{\ddagger}$	(97 ± 2) kJ mol^{-1}
$\Delta S^{\ddagger}$	-(39 ± 1) $JK^{-1}mol^{-1}$
$\Delta G^{\ddagger}$	(108 ± 4) kJ mol^{-1}

(Figure 6) allowed us to calculate the energy activation value of the second step of the catalytic process (Ea_2) and the other activation parameters of this elementary step; the values are shown in Table 5.

If the limit cases of the expression rate was considered Eq. [3], *i.e.* at low and high H_2 pressure, it was possible to extract interesting conclusions. At low hydrogen concentration, the rate law comes given by Eq. [5] and [6]:

$$r = k_{cat}[Os][H_2]^2 \qquad [5]$$

$$K_{cat} = K_1 k_2 = \frac{k_1}{k_{-1}} k_2 \qquad [6]$$

The logaritm form of Eq. [6] (making use of the direct and inverse constants, k_1 and k_{-1}) yield:

$$\ln k_{cat} = \ln k_1 - \ln k_{-1} + \ln k_2 \qquad [7]$$

Substituing each one of the terms of the k´s by the corresponding Arrhenius expression, Eq. [7] can be transform in:

$$A - \frac{Ea\,cat}{RT} = in\left(A_1 - A_{-1} + A_2\right) - \frac{Ea_1 - Ea_1 + Ea_2}{RT}$$

of which $Ea_{cat} = Ea_1 - Ea_{-1} + Ea_2$.

Similarly, at high hydrogen concentration, through the law rate law ($r = k_2[Os][H_2]$) it may be deduced that $Ea = Ea_2$.

In conclusion, the activation energy calculated under the close first order kinetic regimen on the hydrogen concentration must be approximately equal to that found for the rate-determing step. As the Ea_{cat} = (83 ± 2) kJ/mol and Ea_2 = (99 ± 2) kJ/mol, it can be supposed that the activation energy for the forward reaction of the first elementary step (Ea_1) is smaller than the one for the reverse reaction one (Ea_{-1}), in c.a 16 KJ/mol (4 kcal/mol). Therefore, a qualitative diagram of energy of the hydrogenation process may be proposed, which is represented in Figure 7.

5. Theoretical investigation of the mechanism of quinoline hydrogenation catalyzed by OsHCl(CO)(Q)(PPh3)2

For further support of our catalytic cycle proposal, semiempirical SCF-CNDO/2 calculations were also employed to study this mechanism using Ru as the metal instead of Os and PH_3 instead of PPh_3. Similar to the calculations carried out on the mechanism of $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$-catalyzed quinoline hydrogenation, the main results of the theoretical investigation on $[RuHCl(CO)(PH_3)_3]$ indicate that:

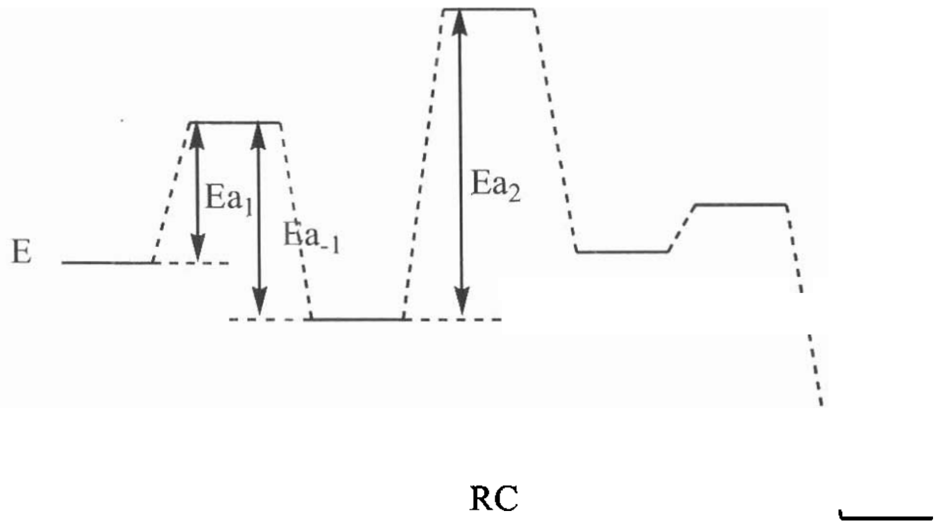


Figure 7. Qualitative energy diagram for the hydrogenation of quinoline catalyzed by $[OsHCl(CO)(PPh_3)_3]$ (Ea_1: activation energy of the forward reaction of the first addition of dihydrogen; Ea_{-1}: activation energy of the reverse reaction of the first addition of dihydrogen; Ea_2: activation energy of the second addition of dihydrogen).

1. The active species of the cycle is the species [RuHCl(CO)(NC$_9$H$_7$)(PH$_3$)$_2$] containing the hydride and quinoline ligands in a mutually *cis* position and the hydride close to the C(2) of Q.
2. In the first step of the cycle, the hydride ligand of the active species migrates to the C(2) of Q ligand to form the unsaturated species [RuCl(CO)(NC$_9$H$_8$)(PH$_3$)$_2$] which contains a monohydroquinolinide ligand (NC$_9$H$_8$) prior to the first addition of H$_2$.
3. The first hydrogenation occurs through heterolytic activation of dihydrogen, where the proton goes to the N of the monohydroquinolinide ligand and the hydride is bound to the metal center, generating the hidrido-dihydoquinoline species [RuHCl(CO)(NC$_9$H$_9$)(PH$_3$)$_2$].
4. The DHQ ligand, initially bonded trough the nitrogen atom, changes its coordination to a η^2-C(3),C(4) mode, which is necessary to reduce this double bond.

Additionally, our new theoretical study indicates that the hydride ligand of the complex [RuHCl(CO)(NC$_9$H$_9$)(PH$_3$)$_2$] migrates to C(3) forming the unsaturated species [RuCl(CO)(C$_9$H$_{10}$N)(PH$_3$)$_2$]. Oxidative addition of hydrogen produces a dihydrido species [Ru(H)$_2$Cl(CO)(C$_9$H$_{10}$N)(PH$_3$)$_2$], which by reductive elimination of THQ generates

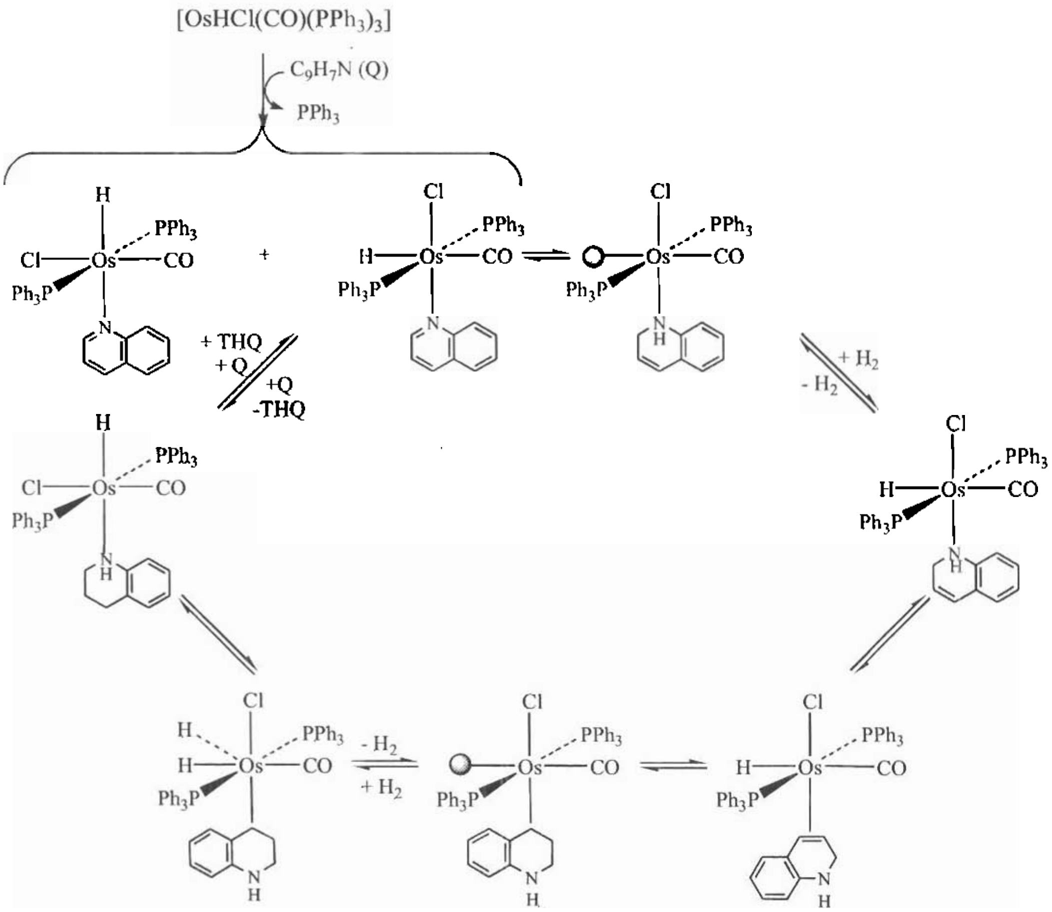


Figure 8. Detailed catalytic cycle of the [OsHCl(CO)(PPh$_3$)$_3$]-catalyzed quinoline hydrogenation.

[$RuHCl(CO)(NC_9H_{11})(PH_3)_2$], containing the THQ ligand (NC_9H_{11}) bonded through the nitrogen atom. Finally, substitution of the THQ ligand by a new molecule of Q regenerates the active species and restarts the cycle (28).

On the basis of our experimental findings (kinetic and coordination chemistry studies) and our the theoretical SCF-CNDO/2 calculations, a detailed catalytic cycle of quinoline hydrogenation catalyzed by [$OsHCl(CO)(PPh_3)_3$] is proposed in Figure 8.

Conclusions

The regioselective reduction of Q to give exclusively THQ under mild conditions (130°C and 4 bar H_2) in xylene solvent was efficiently carried out by using the complex [$OsHCl(CO)(PPh_3)_3$] [**1**] as the precatalyst. A detailed kinetic study allowed us to determine the equilibrium constant (K_1) and the rate-determining step constant (k_2) at various temperatures, and concomitantly the activation parameters of the overall reaction and of the rate-determining step. An analysis of the experimental results (kinetics and coordination chemistry studies) together with theoretical calculations provides insights into the mechanism of the homogeneous hydrogenation of Q to THQ catalyzed by [$OsHCl(CO)(PPh_3)_3$], which contributes to the understanding of the catalytic hydrogenation of nitrogen compounds which is considered the first step of the HDN process.

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