Articles

Kinetics and Mechanism of the Regioselective Homogeneous Hydrogenation of Quinoline Using $[Rh(COD)(PPh_3)_2]PF_6$ as the Catalyst Precursor

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The kinetics and mechanism of the regiospecific homogeneous hydrogenation of quinoline (Q) to 1,2,3,4-tetrahydroquinoline (THQ) using $[Rh(COD)(PPh_3)_2]PF_6$ (1) as the catalyst precursor in toluene solution under mild reaction conditions have been studied. The experimentally determined rate law is $r_i = k_{cat}[Rh][H_2]^2$, where $k_{cat} = 50 \pm 6\ M^{-2}\ s^{-1}$ at 370 K; the corresponding activation parameters are $\Delta H^{\ddagger} = 9 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -27.0 \pm 0.3$ eu, and $\Delta G^{\ddagger} = 19.1 \pm 0.3$ kcal mol^{-1}. Complex 1 was shown to react rapidly with Q to yield $[Rh(COD)(PPh_3)(Q)]PF_6$ (2) at room temperature and $[Rh(COD)Q_2]PF_6$ (4) in boiling toluene; complex 4 was also isolated almost quantitatively from the catalytic runs. Reaction of 1 with H_2 followed by interaction with Q at room temperature produces $[Rh(PPh_3)_2Q_2]PF_6$ (3). These findings indicate that 4 is the catalytically active species and are consistent with a mechanism involving a rapid and reversible hydrogenation of one coordinated Q in 4 to dihydroquinoline (DHQ), followed by a rate-determining reduction of this intermediate to yield THQ. A catalytic cycle accounting for these results is postulated.

Introduction

The regioselective homogeneous hydrogenation of heteroaromatic compounds has attracted attention in recent years, both because of its potential synthetic applications and as a model for some elementary steps in heterogeneous catalytic processes.

Quinoline (Q) and its derivatives are commonly used as substrates in model studies of hydrodenitrogenation (HDN), a reaction of prime importance in the petroleum and coal industries. It is known that HDN of this type of compound requires hydrogenation of the nitrogen-containing ring prior to removal of the heteroatom from the polynuclear frame.[1] Thus it is of interest to gain a fundamental understanding of such selective hydrogenation reactions.

Fish and co-workers have carried out extensive studies on the homogeneous hydrogenation of N-heteroaromatics by use of ruthenium and rhodium complexes, which provide much practical information, as well as a fairly complete mechanistic picture of this reaction.[2] We have also reported that a variety of Ru, Os, Rh, and Ir complexes are capable of efficiently catalyzing the regioselective hydrogenation of Q and benzothiophene under moderate reaction conditions.[3] Other catalytic systems which effect this transformation under diverse reaction conditions have been described.[4]

One important aspect of this chemistry which has been hitherto essentially neglected is the kinetics of the hydrogenation process, in contrast to detailed studies carried out for other substrates such as olefins,[5] acetylenes,[6] aldehydes,[7] ketones,[8] polynuclear aromatic hydrocar-

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(1) Kwart, H.; Schuit, G. C. A.; Gates, B. C. G. *J. Catal.* **1980,** *61,* 128. Laine, R. M. *Catal. Rev.—Sci. Eng.* **1983,** *25,* 459. Schulz, H.; Schon, M.; Rahman, N. M. In *Studies in Surface Science and Catalysis*; Cerveny, L., Ed.; Elsevier: Amsterdam, 1986; Chapter 6.

(2) (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982,** *104,* 5234. (b) Fish, R. H. *Ann. N.Y. Acad. Sci.* **1983,** *415,* 292. (c) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *J. Org. Chem.* **1984,** *49,* 4500. (d) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *Organometallics* **1985,** *4,* 1743. (e) Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics* **1991,** *10,* 54. (f) Baralt, E.; Smith, S. J.; Hurwitz, J.; Horváth, I.; Fish, R. H. *J. Am. Chem. Soc.* **1992,** *114,* 5187.

(3) (a) Sánchez-Delgado, R. A.; González, E. *Polyhedron* **1989,** *8,* 1431. (b) Sanchez-Delgado, R. A. In *Advances in Catalyst Design*; Grazian, M., Rao, C. N. R., Eds.; World Scientific Publishing Co.: Singapore, 1991; p 214. (c) Sánchez-Delgado, R. A.; Herrera, V.; Rincón, L.; Andriollo, A.; Martín, G. Submitted for publication.

(4) Jardine, I.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1970,** 626. Derecsenyl, T. T.; Vermeulen, T. *LBL Rept* **1979,** *No. 9777. Chem. Abstr.* **1980,** *93,* 188 929. Lynch, T. J.; Banah, M.; McDougall, M.; Kaesz, H. D.; Porter, C. R. *J. Mol. Catal.* **1982,** *17,* 109.

(5) (a) Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973,** 629. (b) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1977,** *2,* 65. (c) Halpern, J.; Riley, D. P.; Chan, A. C. S.; Pluth, J. J. *J. Am. Chem. Soc.* **1977,** *99,* 8056. (d) Chan, A. C. S.; Halpern, J. *J. Am. Chem. Soc.* **1980,** *102,* 838. (e) Halpern, J. *Inorg. Chim. Acta* **1981,** *50,* 11.

(6) (a) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989,** *111,* 7431–7437. (b) Esteruelas, M. A.; López, A. M.; Oro, L. A.; Pérez, A.; Schulz, M.; Werner, H. *Organometallics* **1993,** *12,* 1823.

(7) Rosales, M.; González, A.; Alvarado, Y.; Rubio, R.; Andriollo, A.; Sánchez-Delgado, R. *J. Mol. Catal.* **1992,** *75,* 1.

(8) (a) Halpern, J.; Linn, D. E. *J. Am. Chem. Soc.* **1987,** *109,* 2969. (b) Halpern, J. *Pure Appl. Chem.* **1987,** *59,* 173.

0276-7333/93/2312-4291$04.00/0

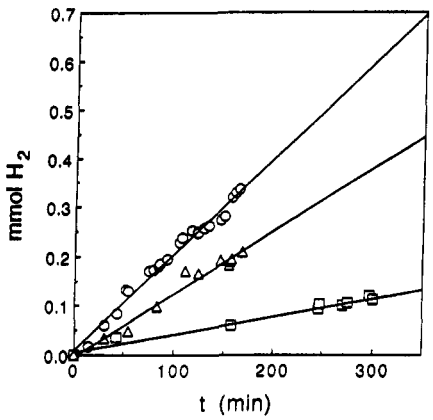
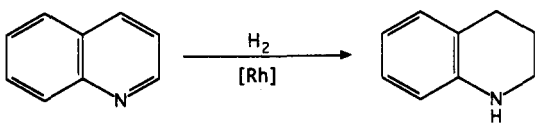


Figure 1. Hydrogenation of Q to THQ by complex 1: some examples of hydrogen uptake measurements at different catalyst concentrations. [Q] = 8.5×10^{-2} M; [H_2] = 4.1×10^{-3} M; [Rh] = (□) 1.0×10^{-4} M, (△) 1.6×10^{-4} M, (○) 3.9×10^{-4} M; solvent = toluene; V_{tot} = 50 mL; T = 370 K.

bons,[8,9] and benzothiophene.[3c] This paper describes such a kinetic study of the regioselective reduction of Q using $[Rh(COD)(PPh_3)_2]PF_6$ (1) (COD = 1,5-cyclooctadiene) as the catalyst precursor; this, together with some relevant coordination chemistry, leads us to propose a mechanism for the catalytic process.

Results

Kinetics of Quinoline Hydrogenation. In a previous paper, we reported that a series of Ru, Os, Rh, and Ir complexes are capable of effecting the selective hydrogenation of Q to 1,2,3,4-tetrahydroquinoline (THQ) (eq 1)



(1)

under moderate reaction conditions (423 K, 30 atm of H_2). The most active catalyst precursor of that group turned out to be complex 1, which runs at a rate of about 200 turnovers/h for several hours without any apparent deactivation under those conditions.[3] This is of considerable interest for potential organic synthesis applications, but no mechanistic information concerning this system is available up to now.

We have found that complex 1 also functions effectively as a catalyst precursor for the hydrogenation of Q to THQ in toluene solution under much milder conditions (370 K and atmospheric or subatmospheric pressure of H_2), which makes it an ideal candidate for the detailed kinetic investigation we report in this paper. The homogeneity of the reaction was established by well-known methods.[10]

Initial rates were determined by following the H_2 pressure drop as a function of time. Some representative examples of catalytic runs at different catalyst concentrations are shown in Figure 1. Although no deactivation was observed even at relatively high conversions (up to *ca.* 60–70%), we have used our data at conversions below 10% in order to perform a kinetic analysis based on the initial rates method. Under these conditions, the reaction follows a pseudo-zero-order rate law, according to eq 2, where $k_{obs} = k_{cat}[Q]^x[H_2]^y$.

$$-d[Q]/dt = k_{obs}[Rh] \quad (2)$$

Table I. Kinetic Data for the Hydrogenation of Quinoline Catalyzed by $[Rh(COD)(PPh_3)_2]PF_6$[a]

10^4[Rh] (M)	10^2[Q] (M)	10^3[H_2] (M)	P(H_2) (atm)	T (K)	$10^7 r_i$ (M s^{-1})
3.0	3.1	4.1	1.01	370	1.87 ± 0.03
3.1	5.1	4.1	1.01	370	2.05 ± 0.01
3.0	8.5	4.1	1.00	370	2.35 ± 0.01
3.0	11.8	4.0	0.98	370	2.11 ± 0.02
3.2	16.9	4.1	0.99	370	1.92 ± 0.02
1.0	8.5	4.1	0.99	370	0.61 ± 0.03
1.6	8.5	4.1	1.01	370	1.58 ± 0.03
2.3	8.5	4.1	1.00	370	2.15 ± 0.02
3.6	8.5	4.1	1.01	370	2.87 ± 0.02
3.9	8.5	4.0	0.98	370	3.26 ± 0.02
3.1	8.5	3.1	0.76	370	1.16 ± 0.03
3.1	8.5	3.5	0.85	370	1.82 ± 0.01
3.0	8.5	4.5	1.10	370	3.18 ± 0.02
3.1	8.5	4.9	1.19	370	4.21 ± 0.02
3.1	8.5	3.8	0.92	332	0.38 ± 0.02
3.0	8.5	4.0	0.96	351	0.93 ± 0.01
3.0	8.5	4.0	0.98	361	1.44 ± 0.02

[a] r_i = initial rates; solvent = toluene.

Values for initial rates under different reaction conditions are collected in Table I. A plot of log d[THQ]/dt vs log [Rh] (Figure 2) yields a straight line of slope 1.0, in agreement with a first-order rate dependence on catalyst concentration.

The results of varying the concentration of the substrate while all other concentrations were kept constant (Table I) show that the rate of the catalytic process is independent of the substrate concentration (x = 0).

On the other hand, a plot of log d[THQ]/dt vs log [H_2] (Figure 3) yields a straight line of slope 1.98, which correlates well with a second-order rate dependence on hydrogen concentration.

In conclusion, the rate law for the homogeneous hydrogenation of Q to THQ is

$$-d[Q]/dt = k_{cat}[Rh][H_2]^2 \quad (3)$$

The value of the catalytic rate constant at 370 K was calculated from eq 3: $k_{cat} = 50 \pm 6$ M^{-2} s^{-1}.

The effect of temperature on the rate constant was studied in the range 332–370 K for concentrations of Q at 8.5×10^{-2} M, catalyst at 3.0×10^{-4} M, and dissolved hydrogen at 4.0×10^{-3} M. Within the range of conditions used, the variation of the solubility of hydrogen with temperature is negligible. An Arrhenius plot allowed us to evaluate the activation energy E_a, the frequency factor A, the extrapolated value of the rate constant at 298 K, and the values of enthalpy, entropy, and free energy of activation (calculated from the equations $\Delta H^* = E_a - RT$, $\Delta S^* = R \ln(hA/e^3kT)$, and $\Delta G^* = \Delta H^* - T\Delta S^*$, respectively); these values are collected in Table II.

Hydrogenation of Dihydroquinoline (DHQ). Since the only detected product of the hydrogenation of Q as described above is THQ, we have also investigated the hydrogenation of the intermediate product DHQ. Reduction of quinoline with $LiAlH_4$ (see Experimental Section) produces a mixture of 1,2- and 1,4-dihydroquinoline. The results of hydrogenating such a mixture using $[Rh(COD)Q_2]PF_6$ as the catalyst precursor are shown in

(9) (a) Landis, C. R.; Halpern, J. *Organometallics* **1983**, *2*, 840. (b) Halpern, J.; Fordyce, W. A.; Wilczynski, R. *J. Organomet. Chem.* **1985**, *296*, 115.

(10) (a) Crabtree, R.; Anton, D. R. *Organometallics* **1983**, *2*, 855. (b) Sánchez-Delgado, R. A.; Andriollo, A.; Puga, J.; Martín, G. *Inorg. Chem.* **1987**, *26*, 1867.

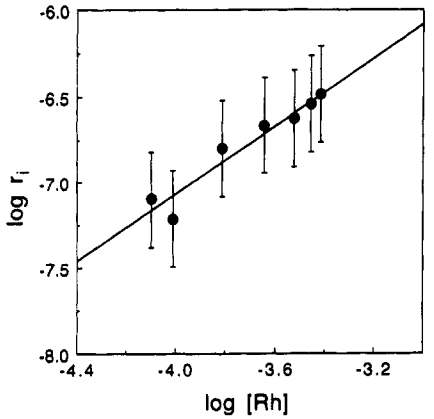


Figure 2. Hydrogenation of Q to THQ by complex 1: rate dependence on catalyst concentration. Conditions are as in Table I.

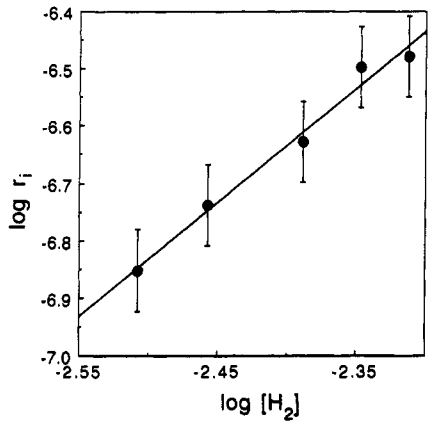


Figure 3. Hydrogenation of Q to THQ by complex 1: rate dependence on hydrogen concentration. Conditions are as in Table I.

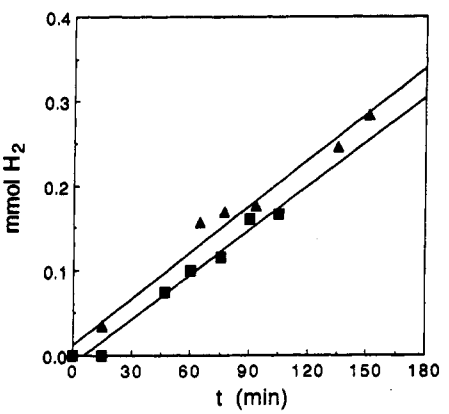


Figure 4. Hydrogen uptake measurements in the hydrogenation of (▲) quinoline and (■) DHQ to THQ by complex 4. [Rh] = 3.0×10^{-4} M; [substrate] = 8.5×10^{-2} M; [H_2] = 4.0×10^{-3} M; solvent = toluene; V_{tot} = 50 mL; T = 373 K.

Figure 4 in comparison with a similar run for the hydrogenation of Q. We note that the reaction profiles are remarkably similar; the initial rate of hydrogenation of DHQ (2.92×10^{-7} M s^{-1}) and the corresponding k_{obs} (0.97×10^{-3} s^{-1}) are very close to the rate of hydrogenation (3.03×10^{-7} M s^{-1}) and k_{obs} (1.08×10^{-3} s^{-1}) for Q under the same reaction conditions, which has important mechanistic implications (*vide infra*).

Coordination Chemistry of 1. In order to gain further insight into the catalytic cycle, we have studied some relevant aspects of the coordination chemistry of complex 1, as summarized in Scheme I.

Table II. Activation Parameters for the Hydrogenation of Quinoline Catalyzed by $[Rh(COD)(PPh_3)_2]PF_6$

E_a	10 ± 1 kcal mol^{-1}	$\Delta H^{\ddagger}$	9 ± 1 kcal mol^{-1}
A	2.67×10^7	$\Delta S^{\ddagger}$	−27.0 ± 0.3 eu
k_{cat} (298 K)	1.7 ± 0.5 M^{-2} s^{-1}	$\Delta G^{\ddagger}$	19.1 ± 0.3 kcal mol^{-1}

When complex 1 and Q are allowed to react in CH_2Cl_2 under N_2 at room temperature, an almost immediate color change from orange to yellow is observed. Addition of Et_2O after 30 min produced high yields of air stable orange crystals of complex 2. IR, NMR, and analytical data (see Experimental Section) are consistent with the rapid displacement of one phosphine ligand by a Q molecule, according to eq i in Scheme I. This cation of 2 was previously prepared by Oro and co-workers[11] by displacement of a Q ligand of $[Rh(COD)Q_2]ClO_4$ by triphenylphosphine and characterized by elemental analysis and IR spectroscopy.

If the reaction is carried out under an atmosphere of hydrogen, the same cation of 2 is obtained. This is interesting in that complex 1 is known to react rapidly with H_2 in the absence of Q to form the dihydride $[Rh(H)_2(PPh_3)_2(solv)_2]^+$ by hydrogenation of COD.[12] Our results indicate that phosphine displacement by Q occurs more rapidly than the reaction with hydrogen, yielding complex 2, which is inert toward hydrogenation of COD under those conditions.

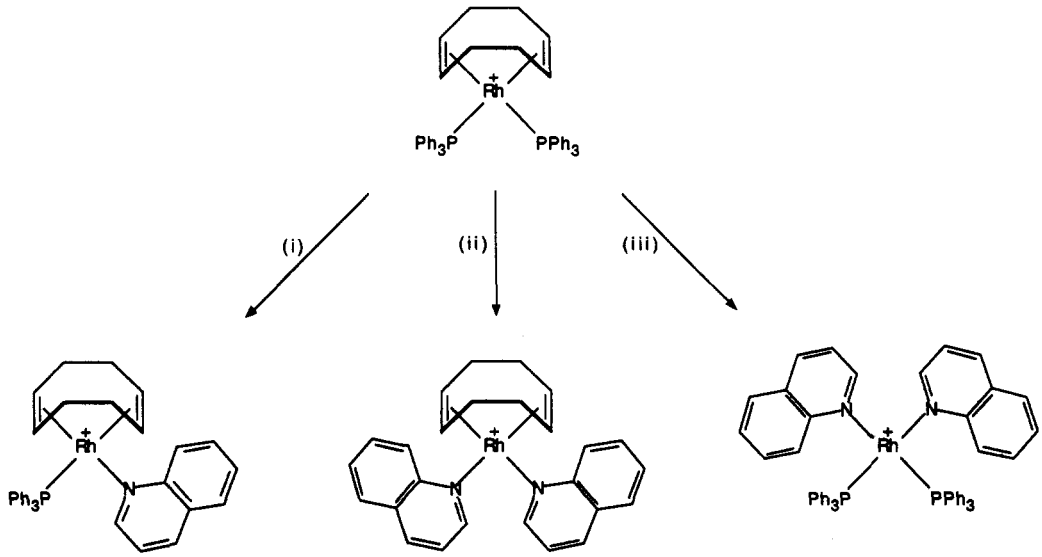
When, on the other hand, complex 1 is allowed to react with H_2 in acetone to form $[Rh(H)_2(PPh_3)_2(Me_2CO)_2]^+$ and an excess of Q is *subsequently* added, the color of the solution correspondingly changes from orange to pale yellow and finally bright yellow. Addition of Et_2O gave good yields of complex 3, characterized by spectroscopic and analytical data (see Experimental Section) as $[Rh(PPh_3)_2Q_2]PF_6$ (3); this compound is produced either by loss of molecular hydrogen or by hydrogenation of coordinated acetone or of one molecule of incoming Q (reaction iii, Scheme I). It is unlikely, however, that complex 3 is of any importance in our catalytic cycle, since in our experimental procedure complex 1 and Q are always put in contact *before* hydrogen is introduced into the system.

When 1 and Q are *refluxed* in toluene for 3 h under N_2 or H_2, a different yellow solid 4 is obtained on cooling the mixture to room temperature. The ^1H NMR spectrum of 4 shows only the signals corresponding to Q and COD but no peaks assignable to triphenylphosphine or metal hydrides; this, together with IR and analytical data, confirms the stoichiometry $[Rh(COD)Q_2]PF_6$ (reaction ii, Scheme I). The cation of this complex has been previously prepared by Oro and co-workers by reaction of $[Rh(COD)_2]ClO_4$ with the appropriate amount of Q.[11a] More interestingly, complex 4 was also isolated essentially quantitatively from our catalytic runs, and we therefore postulate this to be a stable intermediate directly involved in the catalytic cycle. Further support for this idea comes from the fact that when pure complex 4 was introduced as the catalyst precursor, instead of the phosphine derivative, the hydrogenation rates were essentially iden-

(11) (a) Usón, R.; Oro, L. A.; Garralda, M. A.; Claver, C.; Lahuerta, P. *Transition Met. Chem. (London)* **1979**, *4*, 55. (b) Usón, R.; Oro, L. A.; Claver, C.; Garralda, M. A. *J. Organomet. Chem.* **1976**, *105*, 365.

(12) (a) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.

Scheme I. Reactions of Complex 1[a]



[a] Key: (i) Q, CH_2Cl_2 at 25 °C, 30 min; (ii) Q, refluxing toluene, 3 h; (iii) H_2, acetone, 40 min, then Q, 30 min at 25 °C.

tical to those obtained for 1; addition of small amounts of phosphine to solutions of 4 did not affect the catalysis.

We also studied the interaction of 1 and of 4 with H_2 in the presence of excess THQ and in the absence of Q, which led to extensive decomposition to Rh metal. Furthermore, no H–D exchange in either the aromatic or the aliphatic rings of THQ was observed in these reactions when D_2 was used instead of H_2. These combined results indicate that THQ is not a good ligand for Rh in these complexes, in contrast with the $Cp^*Rh(NCMe)_3^{2+}$ system reported by Fish[2f] and in accord with the fact that no deactivation was apparent even at high conversions in this and in our previous work[3] with this system.

Discussion

Mechanism of Quinoline Hydrogenation. From the coordination chemistry reported above, we conclude that the catalyst precursor 1 is transformed during the reaction into complex 4 which is the species entering the catalytic cycle. Our kinetic data may then be interpreted in terms of the following set of reactions, in accord with the experimentally determined rate law (ions of the PF_6 salts given):

$$\underset{4}{[Rh(COD)Q_2]^+} + H_2 \overset{K_4}{\rightleftharpoons} \underset{5}{[Rh(COD)(Q)(DHQ)]^+} \quad (4)$$

$$\underset{5}{[Rh(COD)(Q)(DHQ)]^+} + H_2 \xrightarrow{k_5} \underset{6}{[Rh(COD)(Q)]^+} + THQ \quad (5)$$

$$\underset{6}{[Rh(COD)(Q)]^+} + Q \xrightarrow{k_6} \underset{4}{[Rh(COD)Q_2]^+} \quad (6)$$

If the mechanism is thought of as a series of consecutive reactions involving a pre-equilibrium largely displaced to the left (eq 4), the concentration of 5 should be low and the application of the steady-state approximation leads to

$$d[5]/dt = k_4[4][H_2] - k_{-4}[5] - k_5[5][H_2] = 0$$

and therefore

$$[5] = k_4[4][H_2]/(k_{-4} + k_5[H_2])$$

The rate of formation of THQ may be expressed as

$$d[THQ]/dt = k_5[H_2][5]$$

and thus

$$d[THQ]/dt = k_5[H_2]\{k_4[4][H_2]/(k_{-4} + k_5[H_2])\}$$

If the rate-determining step is the hydrogenation of DHQ, then $k_{-4} \gg k_5$ and the term $k_5[H_2]$ may be neglected, leading to

$$d[THQ]/dt = k_5K_4[4][H_2]^2$$

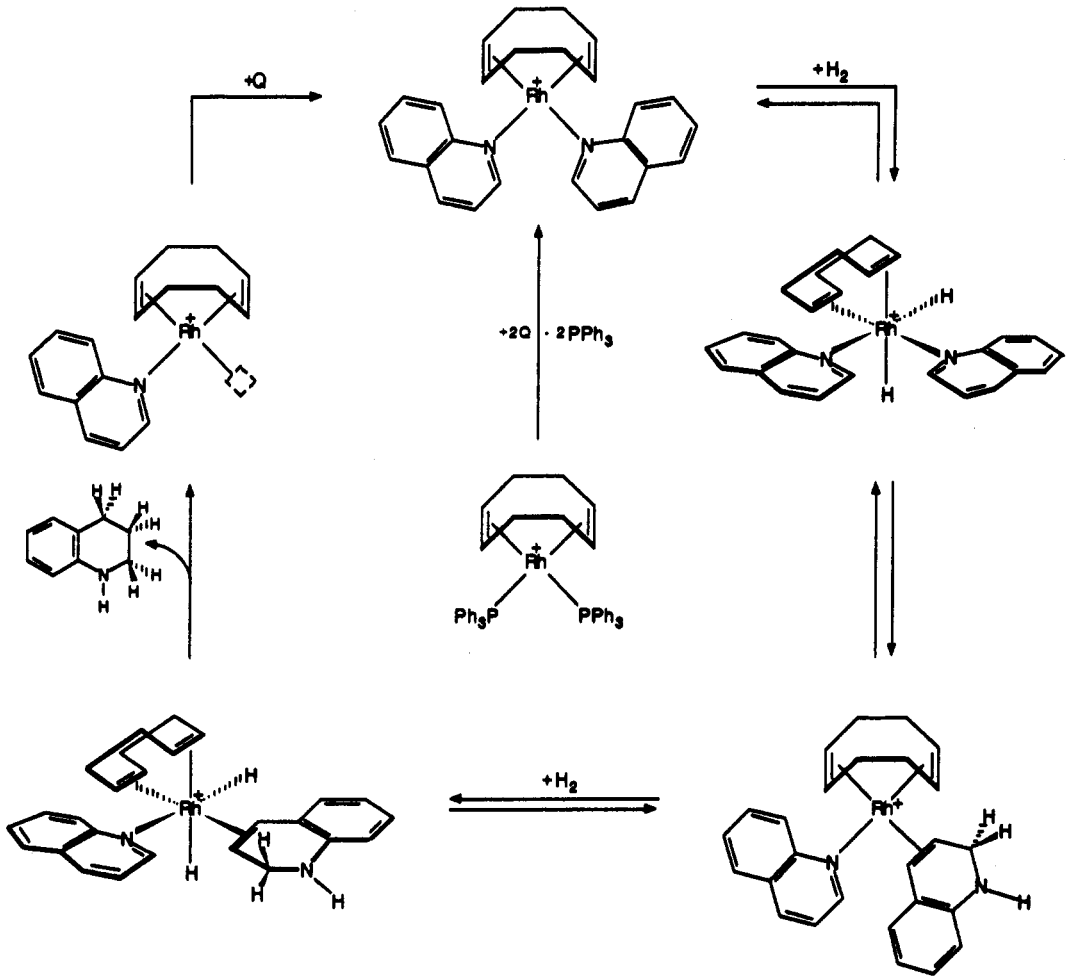
which is identical to our experimental rate law, if $k_{cat} = k_5K_4$.

This mechanism implies that under the reaction conditions Q is rapidly and reversibly hydrogenated to DHQ. The overall hydrogenation kinetics should then be determined by the rate of hydrogenation of this partially hydrogenated intermediate to the fully reduced ring in THQ. This proposal is in agreement with what is commonly accepted to occur on catalytic surfaces prior to C–N bond scission in HDN[1] and with recent results of Fish which clearly demonstrate the reversibility of this first hydrogenation taking place at the C=N bond of Q.[2f]

The results of our experiments using DHQ as the substrate confirm this hypothesis, as the rate of DHQ hydrogenation is identical to that of the overall reduction of Q. Since our DHQ was actually a mixture of 1,2- and 1,4-dihydroquinoline, these findings may be reasonably interpreted in two ways: (i) both isomers of DHQ are hydrogenated at approximately the same rate, which is the rate-determining step for the overall hydrogenation of Q, or (ii) the isomer mixture reacts rapidly with the rhodium catalyst via C=C bond migration and dehydrogenation to produce the equilibrium concentrations of 4 and 5, the latter containing only coordinated 1,2-DHQ.

Although the intimate details of each step involved in our mechanism have not been elucidated, Scheme II shows a sequence of events likely to be taking place during a hydrogenation cycle. Catalysis commences by N-binding of Q to the Rh center. Activation of molecular hydrogen

Scheme II. Proposed Mechanism for the Regioselective Hydrogenation of Q to THQ Catalyzed by Complex 1



probably occurs by oxidative addition to Rh(I) to yield the 18-electron Rh(III) intermediate $[Rh(COD)(H)_2Q_2]^+$, possibly via a Rh(I) η^2-hydrogen complex $[Rh(COD)(\eta^2\text{-}H_2)Q_2]^+$; a related iridium complex containing η^2-H_2 and benzoquinoline has been reported.[13] 1,2- or 1,4-transfer of the hydrides would produce coordinated 1,2- or 1,4-DHQ. Although we cannot distinguish between these possibilities with our experimental evidence, all literature precedents would tend to favor the formation of 1,2-DHQ by a reversible hydrogenation of the C=N bond of Q; therefore only this possibility is represented in the scheme, for the sake of simplicity. At this point, the Rh cation probably migrates to form a η^2 complex with the C=C bond of DHQ. Further oxidative addition of dihydrogen, followed by consecutive hydride transfers to the C=C bond, produces THQ, which decoordinates to leave an empty site which will be rapidly occupied by a new Q molecule to restart the cycle.

This mechanism agrees in essence with the one recently proposed by Fish using $[(C_5Me_5)Rh(NCMe)_3]^{2+}$ as the catalyst precursor,[2f] although some important differences become apparent. Fish and co-workers start with a Rh(III) precursor and invoke dicationic intermediates containing C_5Me_5- and one or more H^- (or D^-) ligands, besides the quinoline or partially hydrogenated quinoline bonded to the metal; this suggests that in their case Rh has to go through oxidation states higher than 3 at some points in the cycle, which is unusual. In our case, we start with a Rh(I) complex and go through the cycle using only Rh(I)/Rh(III) couples formed by standard oxidative addition–reductive elimination processes.

This difference in oxidation states also accounts for the difference in the final step proposed for each mechanism. The Cp^*Rh^{2+} fragment has 12 electrons and displays a strong affinity for arenes; migration of the hydrogenated substrate toward a π-bonded arene form, followed by displacement of η^6-THQ by η^1(N)-Q in $Cp^*Rh(\eta^6\text{-}L)^{2+}$ (L = Q, THQ) is proposed as the step that liberates the hydrogenated product and restarts the catalytic cycle; both complexes have been properly characterized by Fish. Further support for the intermediate containing η^6-bonded THQ was provided by the observation of H–D exchange of the aromatic protons of the hydrogenated heterocycle. In our case, we have demonstrated that THQ does not bind effectively to the Rh center and does not undergo H–D exchange upon interaction with D_2 gas in the presence of 1 or 4; we therefore postulate that THQ decoordinates from the metal as soon as it is formed, leaving behind the 14-electron fragment $[Rh(COD)(\eta^1(N)\text{-}Q]^+$; this 14-electron species is not capable of binding arenes in an η^6 fashion but instead takes up an additional η^1(N)-Q ligand to attain a 16-electron Rh(I) structure and restart the cycle.

Conclusions

We have found that $[Rh(COD)Q_2]PF_6$ (formed by hydrogenation of $[Rh(COD)(PPh_3)_2]PF_6$ in the presence

(13) Crabtree, R. H.; Lavin, M.; Beneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

of quinoline) efficiently catalyzes the specific hydrogenation of the heterocyclic ring in Q under mild reaction conditions. The experimentally determined rate law for this process and some related coordination chemistry are consistent with a mechanism involving a rapid and reversible partial hydrogenation of $[Rh(COD)Q_2]PF_6$ to $[Rh(COD)(Q)(DHQ)]PF_6$, followed by a rate-determining reduction of this intermediate to yield the fully hydrogenated heterocycle in free THQ.

Experimental Section

Instruments and Materials. FTIR spectra (in KBr disks) were obtained with a Nicolet 5DXC spectrometer. NMR spectra were recorded on Bruker AM-250 and AM-300 instruments. Elemental analyses were performed by the Analytical Services of the LCC-CNRS (Toulouse). Solvents of analytical grade were distilled from appropriate drying agents immediately prior to use; Q was distilled under reduced pressure over sodium hydroxide; other commercially available reagents were purified by standard procedures or used without further purification. Hydrogen was purified by passing through two columns in series containing CuO/Al_2O_3 and $CaSO_4$, respectively. DHQ was synthesized by reducing Q with $LiAlH_4$ in diethyl ether and characterized by its UV–vis spectrum.[14] This procedure actually produces an approximately 1:1 mixture of 1,2- and 1,4-dihydroquinoline, as shown by NMR spectroscopy. $[Rh(COD)(PPh_3)_2]PF_6$ was prepared by a published procedure.[15] The apparatus for the catalytic runs has been previously described in detail by us.[10b]

Procedure for Kinetic Measurements. In a typical experiment, a solution of the catalyst and the substrate in toluene was placed in a glass reactor fitted with a reflux condenser kept at 0 °C. The reactor was sealed with Apiezon wax to a high-vacuum line, and the solution was carefully deoxygenated by three freeze–pump–thaw cycles; hydrogen was admitted at this point to the desired pressure, an electric oven preheated to the required temperature was placed around the reactor, and magnetic stirring was immediately commenced. The reaction was followed by measuring the hydrogen pressure as a function of time.

The conversion of reactants in the catalytic reactions was generally (although not necessarily) kept below 10% (*ca.* 5–20 turnovers) in order to use the initial rates method in our calculations. The measured $\Delta P(H_2)$ values were converted to millimoles of THQ produced, taking into account the reaction stoichiometry. The data were plotted as molar concentration of the product as a function of time, yielding straight lines. Initial rates were then obtained from the corresponding slopes. All straight lines were fitted by use of conventional linear regression software to $r^2 > 0.98$. Concentrations of dissolved hydrogen were calculated using solubility data reported by Brunner.[16]

Interaction of 1 with Q To Yield 2 or 4. To a solution of 1 (0.15 g, 0.17 mmol) in CH_2Cl_2 (30 mL) was added Q in excess (1.0 mL, 8.5 mmol), and the mixture was stirred at room temperature under nitrogen for 30 min, after which a color change from orange to pale yellow was observed. The volume of solvent was then reduced to about 50% under a nitrogen stream, and diethyl ether was added until the solution became turbid; on standing, an orange crystalline solid (2) deposited, which was filtered off, washed with diethyl ether, and dried under vacuum. The same results were obtained when the whole procedure was carried out under hydrogen instead of nitrogen. Yield: 89%. Anal. Calcd for $C_{35}H_{34}NF_6P_2Rh$: C, 56.4; H, 4.6; N, 1.9. Found: C, 55.9; H, 4.6; N, 1.9. IR: ν(P–F) 840 cm^{-1}. ^1H NMR (250 or 300 MHz, δ): PPh_3, 7.4–7.2 (m), COD, C*H* (AA′) 3.91 (br), C*H* (BB′), 4.98 (br), 4.64 (br), CH_2 1.91–2.86 (m); Q, H(2)–H(8) 8.81 (d, J = 4.2 Hz), 7.55 (t, J = 8.3 Hz), 8.18 (J = 8.3 Hz), 7.82 (J = 8.3 Hz), 7.69 (d, J = 8.0 Hz), 7.86 (t, J = 7.8 Hz), 9.23 (d, J = 8.1 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, δ) PPh_3, 133.92, 133.77, 131.31, 131.29, 129.18, 128.61; COD, *C*H (A) 81.21 (d, J(C–Rh) = 11.3 Hz), *C*H (A′) 83.25 (d, J(C–Rh) = 12.0 Hz), *C*H (BB′) 101.41 (dd, J(C–Rh) = 10.7 Hz, J(C–P) = 7.2 Hz), 106.67 (dd, J(C–Rh) = 10.7 Hz, J(C–P) = 7.2 Hz), CH_2 33.68 (s), 30.85 (s), 30.29 (s), 28.71 (s); Q, C(2)–C(10) 152.84 (s), 122.67 (s), 138.98 (s), 129.89 (s), 128.86 (s), 131.89 (s, C7 and C8), 146.99 (s) 129.89 (s); $^{31}P\{^1H\}$ NMR (121.5 MHz, δ) 21.73 (d, J(P–Rh = 153 Hz). When the reaction was carried out in refluxing toluene under nitrogen or hydrogen for 3 h, a fine yellow powder (4) precipitated after cooling to room temperature; it was filtered off, washed with pentane, and dried in vacuum. Yield: 90%. Anal. Calcd for $C_{26}H_{26}N_2F_6PRh$: C, 51.0; H, 4.2; N, 4.6. Found: C, 49.9; H, 4.4; N, 4.2. IR: ν(P–F) 840 cm^{-1}. ^1H NMR (250 or 300 MHz, δ) COD, C*H* (AA′) 4.12 (br), C*H* (BB′) 4.45 (br), CH_2 2.50 (m); Q H(2)–H(8) 9.24 (d, J = 4.4 Hz), 7.38 (t, J = 7.1 Hz), 8.23 (J = 7.4 Hz), 7.86 (J = 7.2 Hz), 7.73 (d, J = 7.2 Hz), 8.15 (d, J = 8.2 Hz), 10.07 (d, J = 8.5 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, δ) COD, *C*H (AA′) 85.11 (d, J(C–Rh) = 12.5 Hz), *C*H (BB′) 87.18 (d, J(C–Rh) = 12.3 Hz), CH_2 31.95, 30.15; Q, C(2)–C(10) 153.39 (s), 122.23 (s), 139.13 (s), 129.72 (s), 128.65 (s), 131.49 (s, C7 and C8), 147.17 (s), 129.59 (s).

Interaction of $[Rh(H)_2(PPh_3)_2(Me_2CO)_2]^+$ with Q. Hydrogen was bubbled through a solution of 1 (0.1 g, 0.11 mmol) in acetone (20 mL) for 40 min, during which the solution changed color from orange to pale yellow. Q was subsequently added in excess (3.0 mL, 25.4 mmol), and the mixture was stirred at room temperature under nitrogen for 30 min, after which a color change from pale yellow to bright yellow was observed. The volume of solvent was reduced to about 50% under vacuum, and diethyl ether was added until the solution became turbid; on standing, a yellow crystalline solid precipitated, which was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 76%. Anal. Calcd for $C_{54}H_{44}N_2F_6P_3Rh$: C, 63.0; H, 4.3; N, 2.7. Found: C, 62.7; H, 4.4; N, 2.6. IR: ν(P–F) 840 cm^{-1}. ^1H NMR (250 or 300 MHz, δ): PPh_3, 7.80–6.98 (m); Q, H(2)–H(8) 9.61 (d, J = 4.3 Hz), 7.70 (d, J = 7.2 Hz), 9.28 (d, J = 7.5 Hz), 8.90 (d, J = 7.3 Hz), 8.01 (d, J = 7.4 Hz), 8.98 (d, J = 8.1 Hz), 10.38 (d, J = 8.4 Hz). No signals corresponding to COD or metal hydrides were detected.

Interaction of 1 and 4 with THQ and D_2. A solution containing complex 1 or 4 (0.2 mmol) and excess THQ (0.5 mL) in toluene (50 mL) was placed in a stainless steel autoclave which was flushed and subsequently pressurized with D_2 (1 bar) and heated to 370 K for 24 h. After cooling and venting, the suspension obtained containing mainly Rh metal was filtered through Florisil, the solvent was removed under vacuum, and THQ was analyzed for H–D exchange by ^1H NMR.

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(14) Rosenmund, K. W.; Zymalkowski, F. *Chem. Ber.* **1953**, *86*, 37.
(15) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.
(16) Brunner, E. *J. Chem. Eng. Data* **1985**, *30*, 269.