Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 781–785 **781**
DOI: 10.1021/ic901808t

Base-Catalyzed Insertion of Dioxygen into Rhodium−Hydrogen Bonds: Kinetics and Mechanism

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Received September 10, 2009

The reaction between molecular oxygen and rhodium hydrides $L(OH)RhH^+$ ($L = (NH_3)_4$, *trans*-L^1, and *cis*-L^1, where L^1 = cyclam) in basic aqueous solutions rapidly produces the corresponding hydroperoxo complexes. Over the pH range $8 < pH < 12$, the kinetics exhibit a first order dependence on $[OH^-]$. The dependence on $[O_2]$ is less than first order and approaches saturation at the highest concentrations used. These data suggest an attack by OH^- at the hydride with $k = (1.45 \pm 0.25) \times 10^3\ M^{-1}\ s^{-1}$ for *trans*-$L^1(OH)RhH^+$ at 25 °C, resulting in heterolytic cleavage of the Rh−H bond and formation of a reactive Rh(I) intermediate. A competition between O_2 and H_2O for Rh(I) is the source of the observed dependence on O_2. In support of this mechanism, there is a significant kinetic isotope effect for the initial step, $L^1(OH(D))RhH(D)^+ + OH(D)^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} L^1(OH(D))Rh^I + H(D)_2O$, $k_{1H}/k_{1D} = 1.7$, and $k_{-1H}/k_{-1D} = 3.0$. The activation parameters for k_1 for *trans*-$L^1(OH)RhH^+$ are $\Delta H^‡ = 64.6 \pm 1.3\ kJ\ mol^{-1}$ and $\Delta S^‡ = 40 \pm 4\ J\ mol^{-1}\ K^{-1}$.

Introduction

Dioxygen reacts with transition metal hydrides in both aqueous and organic solvents to yield hydroperoxo metal complexes. Such reactions have been directly observed for the hydrides of, for example, platinum,[1,2] palladium,[3,4] cobalt,[5] and rhodium.[6−10] Several mechanisms have been proposed, including direct insertion[3] by hydrogen atom abstraction and intramolecular rearrangement of the metal−HOO entity,[11] radical chain reactions,[1,2,9,12,13] reductive elimination of HX from Pd(II) to generate Pd(0) followed by the reaction with O_2,[4] and several variants of these and related mechanisms, as recently summarized.[4,14]

This type of chemistry plays an important mechanistic role in aerobic oxidation of organic substrates catalyzed by transition metal complexes.[4,6,14−17] In oxidations catalyzed by palladium,[18,19] oxygen insertion into the metal hydride bond has been postulated as a key step that generates the hydroperoxide. Iridium(III)-catalyzed oxidation of alcohols with molecular oxygen also generates an Ir(III) hydroperoxide as intermediate.[20] Hydroperoxides have been proposed to be involved in the oxidation of cyclopentene to cyclopentanone catalyzed by dichlorobis(*N*,*N*-diethylacetamide)palladium(II)[18] and in palladium(II) acetate-catalyzed oxidation of terminal alkenes.[21] Palladium peroxides have been shown to transfer an oxygen atom to terminal alkenes through a five-membered intermediate in peroxy-palladation,[22] again supporting the involvement of metal hydroperoxides in the catalytic oxidation of olefins with O_2.

The reaction of rhodium hydrides with dioxygen has been used in our laboratory in the past as a convenient preparative route to rhodium hydroperoxides.[23−25] At pH ≥ 11 in O_2-saturated solutions, the reaction is instantaneous and

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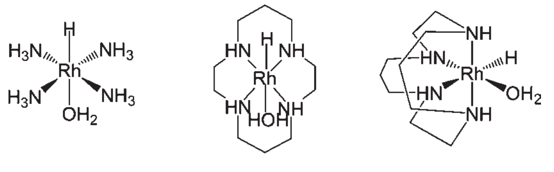
(1) Look, J. L.; Wick, D. D.; Mayer, J. M.; Goldberg, K. I. *Inorg. Chem.* **2009**, *48*, 1356–1369.
(2) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900–11901.
(3) Denney, M. C.; Smythe, N. A.; Cetto, K. L.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 2508–2509.
(4) Konnick, M. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 5753−5762 and references therein.
(5) Thyagarajan, S.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2001**, 2198–2199.
(6) Bakac, A. *Dalton Trans.* **2006**, 1589–1596.
(7) Roberts, H. L.; Symes, W. R. *J. Chem. Soc., A* **1968**, 1450.
(8) Gillard, R. D.; Heaton, B. T.; Vaughan, D. H. *J. Chem. Soc., A* **1970**, 3126.
(9) Endicott, J. F.; Wong, C.-L.; Inoue, T.; Natarajan, P. *Inorg. Chem.* **1979**, *18*, 450–454.
(10) Cui, W.; Wayland, B. B. *J. Am. Chem. Soc.* **2006**, *128*, 10350–10351.
(11) Keith, J. M.; Muller, R. P.; Kemp, R. A.; Goldberg, K. I.; Goddard, W. A.; Oxgaard, J. *Inorg. Chem.* **2006**, *45*, 9631–9633.
(12) Bakac, A. *J. Am. Chem. Soc.* **1997**, *119*, 10726–10731.
(13) Bakac, A. *J. Photochem. Photobiol., A* **2000**, *132*, 87–89.
(14) Popp, B. V.; Stahl, S. S. *Chem.*—*Eur. J.* **2009**, *15*, 2915–2922.
(15) Bakac, A. *Coord. Chem. Rev.* **2006**, *250*, 2046–2058.
(16) Fulmer, G. R.; Muller, R. P.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2009**, *131*, 1346–1347.
(17) Schlangen, M.; Schwarz, H. *Helv. Chim. Acta* **2008**, *91*, 379–386.
(18) Takehira, K.; Hayakawa, T.; Orita, H. *Chem. Lett.* **1985**, 1835–1838.
(19) Hosokawa, T.; Murahashi, S. *Acc. Chem. Res.* **1990**, *23*, 49–54.
(20) Jiang, B.; Feng, Y.; Ison, E. A. *J. Am. Chem. Soc.* **2008**, *130*, 14462–14464.
(21) Nishimura, T.; Kakiuchi, N.; Onoue, T.; Ohe, K.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1915–1918.
(22) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387–5390.
(23) Pestovsky, O.; Bakac, A. *Inorg. Chem.* **2002**, *41*, 3975–3982.
(24) Vasbinder, M.; Bakac, A. *Inorg. Chim. Acta* **2008**, *361*, 3193–3198.
(25) Vasbinder, M. J.; Bakac, A. *Inorg. Chem.* **2007**, *46*, 2921–2928.

Chart 1. Structures of Some Hydridorhodium Dications Used in This Work



$(NH_3)_4(H_2O)RhH^{2+}$ *trans*-$L^1(H_2O)RhH^{2+}$ *cis*-$L^1(H_2O)RhH^{2+}$

produces the hydroperoxides $L(OH)RhOOH^+$ (L = $(NH_3)_4$, *trans*-L^1, and *cis*-L^1) in ~80% yield. The ligand structures are shown in Chart 1. The complexes $(CN)_4(H_2O)RhH^{2-}$ and *trans*-$(OH)(en)_2RhH^+$ (en = ethylenediamine) also have been reported to engage in similar reactions.[7,8] Qualitative observations suggested[8] an attack by hydroxide ion at the hydride to generate rhodium(I) followed by the reaction with dioxygen and water to form the final product. Although plausible, this mechanism has never been confirmed.

In addition to the thermal reactions, hydroperoxides also can be generated from the hydrides by photochemical oxidation.[9,13] UV irradiation of $(NH_3)_4(H_2O)RhH^{2+}$ in oxygen-saturated acidic aqueous solutions[9] yielded $(NH_3)_4(H_2O)RhOOH^{2+}$ by a free radical mechanism utilizing Rh(II) and superoxorhodium(III) ions as chain carriers. Once the reaction was initiated photolytically, the growth of $(NH_3)_4(H_2O)RhOOH^{2+}$ continued even in the dark as long as sufficient amounts of oxygen were available.

We carried out an independent kinetic and mechanistic study of the thermal reaction between $L'(H_2O)MOO^{2+}$ (L' = $(NH_3)_4$, *trans*-L^1, *cis*-L^1, $(H_2O)_5$; M = Rh^{III}, Cr^{III}) and $L''(H_2O)RhH^{2+}$ (L'' = $(NH_3)_4$, *trans*-L^1, or *meso*-Me_6-cyclam).[12] In that work, hydrogen atom transfer from rhodium hydrides to the superoxo complexes has been unambiguously established on the basis of reaction products and large kinetic isotope effects, $k_{RhH}/k_{RhD} = 7.6$. The activation parameters, especially the large negative entropies of activation, are also consistent with the bimolecular process shown in eq 1, followed by rapid capture of $L''(H_2O)Rh^{2+}$ with O_2, eq 2. For the $L^1(H_2O)RhH^{2+}/(H_2O)_5CrOO^{2+}$ reaction, the values are $\Delta H^‡ = 20.3$ kJ mol^{-1} and $\Delta S^‡ = -136$ J K^{-1} mol^{-1}. The chemistry in eqs 1 and 2 becomes catalytic when $L' = L''$.

$$L'(H_2O)MOO^{2+} + L''(H_2O)RhH^{2+} \rightarrow L'(H_2O)MOOH^{2+} + L''(H_2O)Rh^{2+} \qquad (1)$$

$$L''(H_2O)Rh^{2+} + O_2 \rightarrow L''(H_2O)MOO^{2+} \qquad (2)$$

In an earlier NMR study of the dynamics of the Rh−H bond[26] in $L^1(H_2O)RhH^{2+}$, we have established a first order kinetic dependence on hydroxide concentration for the exchange of hydrogen between rhodium hydride and solvent water. That work was carried out in D_2O at pD 8−9. The attack by OD^- was proposed to take place at the hydride and to lead to a Rh(I) species, followed by fast reaction with D_2O, as in eqs 3 and 4.

$$L^1(OD)Rh^{III}H^+ + OD^- \xrightarrow{k_3} L^1(OD)Rh^I + HOD \qquad (3)$$

$$L^1(OD)Rh^I + D_2O \xrightarrow{\text{fast}} L^1(OD)RhD^+ + OD^- \qquad (4)$$

OH^- catalysis in both H-exchange and oxygen insertion into Rh−H bond suggested to us that similar intermediates might be involved in the two reactions. To address this possibility and to resolve the mechanism of oxygen insertion, we have now undertaken a detailed kinetic and mechanistic study of the reaction of O_2 with several rhodium hydrides. Our findings are presented herein.

Experimental Section

Perchlorate or trifluoromethanesulfonate salts of the hydrides $(NH_3)_4(H_2O)RhH^{2+}$, *trans*-(cyclam)$(H_2O)RhH^{2+}$ (hereafter *trans*-$L^1(H_2O)RhH^{2+}$), and *cis*-$L^1(H_2O)RhH^{2+}$, as well as the deuterated analogues *trans*-$L^1(D_2O)RhD^{2+}$ and *cis*-$L^1(D_2O)RhD^{2+}$ were prepared according to published procedures.[12,27,28] $NaClO_4$, NaOH (both from Fisher), D_2O (99.9%, Aldrich), piperazine-*N*,*N'*-bis(4-butanesulfonic acid) (PIPBS), and 2-(*N*-morpholino)-butanesulfonic acid (MOBS) (both from GFS Chemicals) were used as received. The pH was adjusted with buffers (MOBS, PIPBS, pH 8−9) and NaOH (pH 11−13) and was measured with Accumet AP71 pH meter after completion of each experiment. The ionic strength was maintained with $NaClO_4$ at 0.10 M. In-house distilled water was further purified with a Barnstead EASY pure II system. UV−vis spectral and some kinetic measurements utilized a Shimadzu 3101 PC spectrophotometer at 25.0 ± 0.2 °C. Reactions with half-lives shorter than 10 s were studied with an Applied Photophysics stopped-flow instrument.

Kinetics of oxygen insertion were studied with $[O_2]$ in large excess over the concentration of rhodium hydrides (0.020 to 0.10 mM). Typically, an aqueous solution containing 0.020 M buffer was placed in a UV−vis cell and saturated with oxygen or air at the reaction temperature. The appropriate amount (usually 20 μL) of $L(H_2O)RhH^{2+}$ stock solution was added to initiate the reaction. The kinetics were monitored at 241 nm, the maximum absorbance of all three hydroperoxides.

For the stopped-flow experiments, two solutions were prepared. One contained 0.040 mM $L(H_2O)RhH^{2+}$ and the other appropriate concentrations of NaOH and $NaClO_4$. The desired concentration of O_2 in both solutions was achieved by mixing stock solutions that were saturated with air, O_2, or Ar at the temperature of the kinetic experiment (between 278 and 308 K). The kinetic solutions were loaded into the stopped-flow syringes and thermostatted for an additional 10 min at the desired temperature before the reaction was initiated. Kinetic analyses were performed with KaleidaGraph 4.0 PC software.

Results

The complexes $L(OH)RhH^+$ (L = $(NH_3)_4$, *cis*-L^1, and *trans*-L^1) in alkaline solutions react rapidly with dioxygen to give $L(OH)RhOOH^+$, as shown in eq 5. Figure 1 presents UV−vis spectra of the reactants and products of the $(NH_3)_4(OH)RhH^+/O_2$ reaction. At the 241-nm maximum, the molar absorptivity of $(NH_3)_4(H_2O)RhOOH^{2+}/(NH_3)_4(HO)RhOOH^+$ varies from 4000 M^{-1}cm^{-1} to 4600 M^{-1}cm^{-1}, depending on pH.[29]

$$L(OH)RhH^+ + O_2 \xrightarrow{OH^-} L(OH)RhOOH^+ \qquad (5)$$

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(26) Lemma, K.; Ellern, A.; Bakac, A. *Inorg. Chem.* **2003**, *42*, 3662–3669.

(27) Thomas, K.; Osborn, J. A.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc., A* **1968**, 1801–1806.

(28) Bakac, A.; Thomas, L. M. *Inorg. Chem.* **1996**, *35*, 5880–5884.

(29) Szajna-Fuller, E.; Bakac, A. *Inorg. Chem.* **2007**, *46*, 10907–10912.

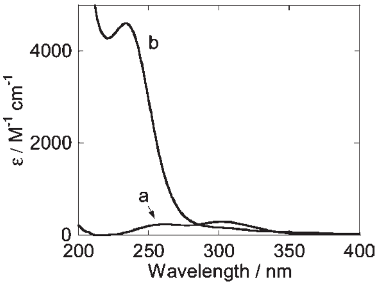

Figure 1. UV−vis spectra of $(NH_3)_4(OH)RhH^+$ (a) and $(NH_3)_4(OH)RhOOH^+$ (b) obtained by oxidation of $(NH_3)_4(OH)RhH^+$ with O_2 at pH 11.

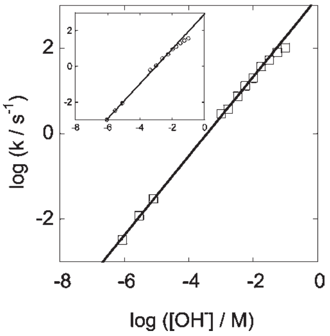

Figure 2. Plot of the logarithm of the pseudofirst order rate constant vs log $[OH^-]$ for the reaction between $(NH_3)_4(OH)RhH^+$ and O_2 in solutions saturated with O_2 (main figure) or air (inset) at 25 °C.

In strongly basic solution, the coordinated water molecule in the hydroperoxorhodium complexes is deprotonated (pK_a = 7.8 for $(NH_3)_4(\mathbf{H_2}O)RhOOH^{2+}$).[29] The corresponding pK_a for the hydrido complexes is not known, but most likely the hydroxo form predominates at pH ≥ 8. The expected similarity in the pK_a of the coordinated water in hydrido and hydroperoxo complexes comes from the general similarity in their chemical structures and identical overall charge (2+). It has been established before that the pK_a of coordinated waters for superoxo and hydroperoxo complexes in similar chemical environments are also almost identical, that is, pK_a = 6.6 for $L^2(H_2O)RhOOH^{2+}$ and 6.9 for $L^2(H_2O)RhOO^{2+}$ (L^2 = *meso*-hexamethylcyclam).[29]

With $[O_2]$ present in large excess over the hydride, the kinetic traces were exponential and yielded the observed pseudo-first order rate constants k_{obs}. These were independent of $(NH_3)_4(OH)RhH^+$ concentration in the range 0.020−0.10 mM, which confirms the first order dependence on $[(NH_3)_4(OH)RhH^+]$.

The rate increased with an increase in pH. The plot of log k_{obs} against log $[OH^-]$ is linear over a wide range of pH values, as shown in Figure 2 at two concentrations of O_2. The slope of the line drawn through the linear portion of the curve (pH range 8−12) is 0.93 in O_2-saturated solutions, and 0.97 in air, confirming the first-order dependence on $[OH^-]$. Slight curvature is noticed at the highest OH^- concentrations (pH > 12) at both O_2 concentrations. We have not been able to establish the source of this deviation. A possibility of partial deprotonation of either an N−H or O−H site in $L(OH)RhH^+$ ($L = L^1$ or $(NH_3)_4$), which would make the Rh−H less acidic and less reactive toward OH^-, is considered unlikely in view of the low acidity of the more highly charged rhodium complexes $(NH_3)_4Rh(OH)(O_2)Rh(NH_3)_4^{4+}$ (pK_a = 14) and $(NH_3)_4Rh(OH)(O_2)Rh(NH_3)_4^{3+}$ (pK_a>14).[30] Another possibility is that the final step in the proposed mechanism of eqs 6−8, see below, is not much faster than the rest of the chemistry at the highest pH and becomes a kinetic step under those conditions.

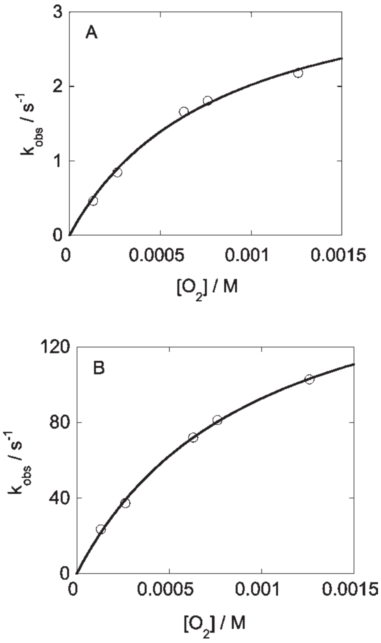

Figure 3. Plot of k_{obs} vs $[O_2]$ for the reaction with $(NH_3)_4(OH)RhH^+$ (0.02 mM) at pH 11 (a) and pH 13 (b) at 25 °C. Data were fitted to eq 9.

The dependence on $[O_2]$ for the reaction with $(NH_3)_4(OH)RhH^+$ at a constant pH is nonlinear as shown for pH 11 and pH 13 in Figure 3. The rate increases with $[O_2]$ at low concentrations but levels off at the high end of $[O_2]$.

The kinetic behavior of two other complexes, *trans*- and *cis*-$L^1(OH)RhH^+$, closely parallels that of $(NH_3)_4(OH)RhH^+$. As shown in Figures S1−S4 (Supporting Information), these reactions are also first order in [rhodium hydride] and $[OH^-]$ and exhibit saturation in $[O_2]$.

A mechanism consistent with all the data is presented in eqs 6−8. The OH^--assisted removal of H^+ from the hydride generates a Rh(I) intermediate that can react with either H_2O to return to the starting complex or O_2 to generate a peroxorhodium(III) species that rapidly acquires a proton from H_2O and generates the observed hydroperoxo product. The competition between steps −1 and 2 is the source of kinetic saturation at high $[O_2]$, as is obvious from the rate law in eq 9, which was derived by applying the steady state approximation to the concentration of Rh(I). At high $[O_2]$, the term $k_2[O_2]$ becomes much greater than k_{-1}, and the rate law reduces to $k_{obs} = k_1[OH^-]$.

$$L(OH)Rh^{III}H^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LRh^I + H_2O \tag{6}$$

$$LRh^I + O_2 \xrightarrow{k_2} L(OH)Rh^{III}OO \tag{7}$$

$$L(OH)Rh^{III}OO + H_2O \xrightarrow{\text{fast}} L(OH)Rh^{III}OOH^+ + OH^- \tag{8}$$

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(30) Springborg, J.; Zehnder, M. *Acta Chem. Scand., Ser. A* **1987**, *A41*, 484–495.

Table 1. Summary of Kinetic Data for the Reactions of Rhodium Hydrides with O_2[a]

complex	temp, K	k_1, 10^3 M^{-1} s^{-1}	k_{-1}/k_2, 10^{-3} M^{-1}	
$(NH_3)_4(OH)RhH^+$	278	0.608 ± 0.009	1.03 ± 0.03	
$(NH_3)_4(OH)RhH^+$	288	1.52 ± 0.09	0.92 ± 0.10	
$(NH_3)_4(OH)RhH^+$	298	3.68 ± 0.30	0.82 ± 0.13	
		1.83 ± 0.06[b]	0.962 ± 0.08[b]	
$(NH_3)_4(OH)RhH^+$	308	9.06 ± 0.52	0.93 ± 0.09	
trans-$L^1(OH)RhH^+$	298	1.45 ± 0.25	1.18 ± 0.35	$k_{1H}/k_{1D} = 1.7$
trans-$L^1(OD)RhD^+$	298	0.857 ± 0.034	0.401 ± 0.044	$k_{-1H}/k_{-1D} = 3.0$
cis-$L^1(OH)RhH^+$	298	2.68 ± 0.33	4.08 ± 0.63	$k_{1H}/k_{1D} = 1.7$
cis-$L^1(OD)RhD^+$	298	1.56 ± 0.07	1.23 ± 0.10	$k_{-1H}/k_{-1D} = 3.3$

[a] Solvent is H_2O for hydrides and D_2O for deuterides. Rate constants k_1 and k_{-1}/k_2 were obtained from the dependence of k_{obs} on $[O_2]$ at pH 11. [b] Obtained at pH 13, see text.

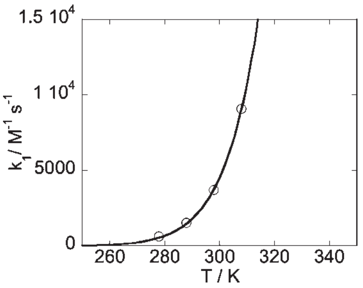

Figure 4. Plot of k_1 vs temperature for $(NH_3)_4(OH)RhH^+$ reacting with O_2 at pH 11. The line is a fit to Eyring equation.

$$\text{Rate} = k_{obs}[L(OH)RhH^+] = \frac{k_1k_2[OH^-][O_2]}{k_{-1}+k_2[O_2]}[L(OH)RhH^+] \qquad (9)$$

The kinetics were studied as a function of temperature in the range 278−308 K at pH 11. The fit to eq 9 yielded the values of k_1 and k_{-1}/k_2 at four different temperatures, as shown in Table 1. The activation parameters were obtained by fitting the data to the Eyring equation. The fit, shown in Figure 4, yielded $\Delta H_1^{\ddagger} = 64.6 \pm 1.3$ kJ mol^{-1} and $\Delta S_1^{\ddagger} = 40 \pm 4$ J $mol^{-1}K^{-1}$. The ratio k_{-1}/k_2 is temperature independent within the error of determination.

Kinetic data were also obtained for the deuterated complexes *trans*-$L^1(OD)RhD^+$ and *cis*- $L^1(OD)RhD^+$ in D_2O at 25 °C. These results are also shown in Table 1 and yielded the kinetic isotope effects $k_{1H}/k_{1D} = 1.7$ for both *trans*-$L^1(OH)$-RhH^+ and *cis*-$L^1(OH)RhH^+$. The corresponding isotope effects for the ratios k_{-1}/k_2 are 3.0 and 3.3.

Discussion

The mechanism in eqs 6−8 features a bimolecular reaction between rhodium hydrides and OH^- as the rate determining step. The same step has been observed earlier in hydrogen exchange between *trans*-$L^1(OH)RhH^+$ and solvent water.[26] The rate constant obtained in that earlier work from experiments at pD 8−9 in D_2O, eq 3, was $k_3 = 1.42 \times 10^3$ M^{-1} s^{-1}.[26] The reverse reaction was prevented by working in D_2O, which made the concentrations of HOD negligible in comparison.

The value of k_1 obtained in this work from $[O_2]$ dependence at pH 11, $k_1 = (1.45 \pm 0.25) \times 10^3$ M^{-1} s^{-1}, is identical to k_3, strongly supporting the idea of common rate determining step in the two reactions. Even though the attacking species is OH^- in eq 6 and OD^- in eq 3, the same Rh−H bond is cleaved in the two reactions and replaced with an O−H bond in water. One would thus expect the rate constants to be very close, the only difference being a small secondary isotope effect.

The k_1 values for the three rhodium complexes in Table 1 fall within a narrow range, $(1.45-3.68) \times 10^3$ M^{-1} s^{-1}. This result, and especially the similarity of the values for *cis*- and *trans*-cyclam complexes, also supports the proposed acid−base chemistry in the rate determining step which should not favor either isomer.

A variation of the mechanism in eqs 6−8, shown in eqs 10 and 11, features an unassisted deprotonation of the hydride followed by the reaction of Rh(I) with O_2 in competition with the reverse reaction with H^+. This mechanism yields a rate law in eq 12 (where $K_w = 10^{-14}$ M^2), which in the limiting cases reduces to $k_{obs} = k_1'$ (when $k_2[O_2] \gg k_{-1}'[H^+]$) and $k_{obs} = k_1'k_2[O_2]/k_{-1}'[H^+]$ (when $k_2[O_2] \ll k_{-1}'[H^+]$). These limits have the same general form as those indicated by eq 9. In the intermediate regime, the two rate laws are different in that both $[O_2]$ and $[OH^-]$ contribute to the denominator in eq 12, unlike the straight first-order dependence on $[OH^-]$ in eq 9.

$$L(OH)Rh^{III}H^+ \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} LRh^I + H^+ \qquad (10)$$

$$LRh^I + O_2 \xrightarrow{k_2} L(OH)Rh^{III}OO \underset{H_2O}{\overset{\text{fast}}{\rightarrow}} L(OH)Rh^{III}OOH^+ + OH^- \qquad (11)$$

$$k_{obs} = \frac{k_1'k_2[O_2]}{k_{-1}'[H^+]+k_2[O_2]} = \frac{k_1'k_2[O_2][OH^-]}{k_{-1}'K_w + k_2[O_2][OH^-]} \qquad (12)$$

The mechanism in eqs 10 and 11 can be discarded on several grounds. Most importantly, it requires a pH-independent limiting first-order rate constant at high $[O_2]$. This contradicts the experimental data which yielded a saturation rate constant that is clearly $[OH^-]$-dependent, as shown in Figure 3. The limiting value at pH 13 is 50 times greater than that at pH 11. A factor less than 10^2 simply confirms the less than first order dependence on $[OH^-]$ at pH > 12, as shown in Figure 2. In addition, the mechanism in eq 10-11 would require an unreasonably acidic hydride ($pK_a \leq 8$) for all three complexes studied. There is no experimental evidence for a pK_a in this range, except for that attributed to coordinated water.[29] A literature estimate for the hydride acidity in

$Rh(NH_3)_4(H_2O)H^{2+}$ is $pK_a > 14$.[31] Our data and the fit to the mechanism in eqs 6−8 place that pK_a in the range $14 < pK_a < 17$.

The kinetic isotope effect, KIE = k_{RhH}/k_{RhD}, was measured for the *trans*- and *cis*-$L^1(OH)RhH^+$ complexes at pH 11. Because of the similar kinetics for O_2 insertion and hydrogen exchange, the hydrogen in the rhodium complex and solvent were always matched, that is, $L(OH)RhH^+$ was studied in H_2O, and $L(OD)RhD^+$ in D_2O. The change in solvent is not expected to have a significant effect, based on our earlier studies of $L(H_2O)RhH^{2+}/L(H_2O)RhOO^{2+}$ reactions, which did not exhibit a solvent isotope effect, $k_{H2O}/k_{D2O} = 1.0$.

Kinetic isotope effects in Table 1 further support the proposed mechanism. The value of 1.7 for k_1 is significant and consistent with the breaking of the Rh−H bond. The maximum calculated KIE for this bond is 4.2, although values close to 8 have been obtained earlier for hydrogen abstraction from the hydrides by a superoxochromium complex.[12] According to the mechanism in eqs 6−8, step k_2 should not be affected by isotopic substitution in either the hydride or solvent. Consequently, the KIEs of 3.0 and 3.3 for the two $L^1(OH)RhH^+$ complexes applies to k_{-1} alone, that is, to the breaking of H−OH and D−OD bonds in the reaction with LRh^I.

The activation parameters, particularly the activation entropy for the $(NH_3)_4(OH)RhH^+/OH^-$ reaction, 40 ± 4 J mol^{-1} K^{-1}, are consistent with the proposed reaction between oppositely charged reactants. The decrease in entropy expected for a bimolecular reaction is counteracted by entropy increase that accompanies charge neutralization and the reduction of rhodium from 3+ to 1+. Both of these effects cause the solvation in the transition state to relax, and the entropy to increase.

The exact nature of the peroxorhodium product of eq 7 is not known. It may be the side-on species, as is commonly assumed in this type of reactions, but it might be difficult to accommodate such geometry around Rh(III), especially in the *trans*-L^1 complex. As shown recently, the side-on arrangement is not a requirement for hydroperoxo formation.[14] A peroxide bound end-on to palladium and hydrogen-bonded to the coordinated carboxylic acid has been proposed as a low-energy intermediate in the reaction between $(py)(AcOH)Pd^0$ and O_2 to generate (py)(κ^2-OAc)Pd^{II}(OOH), where AcOH is acetic acid. Similarly stabilized end-on peroxide by hydrogen bonding to the amine hydrogens could be envisaged in the present work, although the five-membered ring implied in such an intermediate presents a geometry that is far from ideal for hydrogen bonding.

This work provides strong evidence for a previously proposed,[8] but unconfirmed bimolecular, OH^--induced O_2 insertion into a metal hydrogen bond, and extends the already impressive array[4] of mechanisms established for this type of reactions. Interestingly, the opposite end of the spectrum, that is, an acid-catalyzed O_2 insertion into a metal−hydrogen bond, has also been observed.[32] The source of the beneficial effect of benzoic acid on the kinetics of the reaction between Pd(II) hydride and O_2 in benzene appears, however, to be the stabilization of the transition state for reductive elimination,[4] and not the direct acid-Pd(H) interaction.

Finally, the $L(OH)RhH^+$ reaction in eq 6 is a convenient source or Rh(I) for reactivity studies with substrates other than oxygen. We are currently exploring several such reactions.

Acknowledgment. This manuscript has been authored under Contract No. DE-AC02-07CH11358 with the U.S. Department of Energy.

Supporting Information Available: Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Pearson, R. G. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; pp 251−262.

(32) Konnick, M. M.; Gandhi, B. A.; Guzei, I. A.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2904–2907.