Kinetics of Water Exchange on the Dihydroxo-Bridged Rhodium(III) Hydrolytic Dimer

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Conventional ^{18}O isotopic labeling techniques have been used to measure the water exchange rates on the Rh(III) hydrolytic dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ at $I = 1.0$ M for $0.08 < [H^+] < 0.8$ M and temperatures between 308.1 and 323.1 K. Two distinct pathways of water exchange into the bulk solvent were observed (k_{fast} and k_{slow}) which are proposed to correspond to exchange of coordinated water at positions *cis* and *trans* to bridging hydroxide groups. This proposal is supported by ^{17}O NMR measurements which clearly showed that the two types of water ligands exchange at different rates and that the rates of exchange matched those from the ^{18}O labeling data. No evidence was found for the exchange of label in the bridging OH groups in either experiment. This contrasts with findings for the Cr(III) dimer. The dependence of both k_{fast} and k_{slow} on $[H^+]$ satisfied the expression $k_{obs} = (k^O[H^+]_{tot} + k^{OH}K_{a1})/([H^+]_{tot} + K_{a1})$ which allows for the involvement of fully protonated and monodeprotonated Rh(III) dimer. The following rates and activation parameters were determined at 298 K. (i) For fully protonated dimer: $k_{fast} = 1.26 \times 10^{-6}\ s^{-1}$ ($\Delta H^* = 119 \pm 4$ kJ mol^{-1} and $\Delta S^* = 41 \pm 12$ J K^{-1} mol^{-1}) and $k_{slow} = 4.86 \times 10^{-7}\ s^{-1}$ ($\Delta H^* = 64 \pm 9$ kJ mol^{-1} and $\Delta S^* = -150 \pm 30$ J K^{-1} mol^{-1}). (ii) For monodeprotonated dimer: $k_{fast} = 3.44 \times 10^{-6}\ s^{-1}$ ($\Delta H^* = 146 \pm 4$ kJ mol^{-1} and $\Delta S^* = 140 \pm 11$ J K^{-1} mol^{-1}) and $k_{slow} = 2.68 \times 10^{-6}\ s^{-1}$ ($\Delta H^* = 102 \pm 3$ kJ mol^{-1} and $\Delta S^* = -9 \pm 11$ J K^{-1} mol^{-1}). Deprotonation of the Rh(III) dimer was found to labilize the primary coordination sphere of the metal ions and thus increase the rate of water exchange at positions *cis* and *trans* to bridging hydroxides but not to the same extent as for the Cr(III) dimer. Activation parameters and mechanisms for ligand substitution processes on the Rh(III) dimer are discussed and compared to those for other trivalent metal ions and in particular the Cr(III) dimer.

Introduction

The kinetic inertness of metal ions such as Cr(III) and Rh(III) has allowed the study of their hydrolytic polymerization processes. For Cr(III), a series of hydrolytic oligomers has been isolated and characterized[3] and detailed kinetic investigations[4−8] have revealed that deprotonation of the oligomers has a considerable effect on the rates and mechanisms of both intermolecular and intramolecular condensation reactions. However, the complexity of these processes can lead to difficulty in the interpretation of kinetic data. Additional important information can be obtained from the rates and mechanisms of water exchange reactions on these oligomers.

Kinetic data for the acid dependence of the rates of water exchange on the monomer[9] $[Cr(H_2O)_6]^{3+}$ and the dimer[10] $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ was recently obtained using ^{18}O labeling techniques. For the Cr(III) dimer,[10] three independent pathways for exchange of the ^{18}O label were observed and were proposed to be due to exchange of (i) waters positioned *trans* to bridging hydroxides (k_{fast}), (ii) waters positioned *cis* to bridging hydroxides (k_{slow}), and (iii) the ^{18}O label present in the bridging hydroxide groups (k_{bridge}); where $k_{fast} > k_{slow} > k_{bridge}$. For the two water exchange processes (k_{fast} and k_{slow}) and water exchange on $[Cr(H_2O)_6]^{3+}$, the acid dependence of the rate constant could be accounted for by the expression

$$k_{obs} = k^O + k^{OH}/[H^+] \tag{1}$$

where k^O and k^{OH} refer to pathways of exchange on the fully protonated and monodeprotonated aqua ions, respectively. This dependence was consistent with water exchange data for $[Fe(H_2O)_6]^{3+}$ [11,12] and $[Rh(H_2O)_6]^{3+}$.[13,14] In all systems studied, deprotonation caused considerable labilization of the H_2O groups, and in the case of the Cr(III) dimer, this effect was observed for H_2O groups that are both *cis* and *trans* to the bridging OH groups. Furthermore, the rates of water exchange on the Cr(III) dimer were ca. 20−200 times faster than those on the Cr(III) monomer, which indicated that the introduction of bridging OH groups causes significant increases in water substitution rates. For substitution reactions of Cr(III) oligomers in general, labilization of the primary coordination sphere of Cr(III) by both bridging and terminal hydroxide groups was concluded to have a greater effect on substitution rates than changes in the entering nucleophile.

Recent studies[15] on the hydrolytic polymerization of Rh(III) allowed the separation and characterization of a doubly bridged

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dimer, $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$. However, kinetic and mechanistic information on Rh(III) hydrolytic chemistry is generally lacking. Reported here are measurements of the rates of water exchange on the Rh(III) dimer made using ^{18}O and ^{17}O labeling techniques. Activation parameters have been determined from a variable temperature study and the results compared to those obtained for other metal ions, in particular, the Cr(III) dimer.

Experimental Section

Materials. Analytical grade reagents were used throughout, and water was deionized and distilled prior to use. Crystals of the dimer salt $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4](dmtos)_4\cdot 8H_2O$ (dmtos = mesitylene-2-sulfonate) were prepared as described previously.[15] ^{18}O enriched samples were prepared by dissolving samples of dimer in 10% $H_2{}^{18}O$ (obtained by diluting 98% $H_2{}^{18}O$ from Novachem) and heating this solution ($1.5 < pH < 2$) at 60 °C for 50 h. The solution was then cooled to room temperature and reduced in volume on a vacuum line to initiate crystallization. The mixture was stored at 4 °C for 24 h, and the crystals were collected by filtration and stored in a sealed sample jar until required. Chromatographic and spectrophotometric analyses[15] were used to show that the enriched dimer crystals were pure and had not undergone cleavage or polymerization during enrichment. The Rh content of the crystals was determined spectrophotometrically[16] and corresponded to that expected for the formula $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4](dmtos)_4\cdot 8H_2O$. This indicated that mesitylene-2-sulfonic acid had not coprecipitated with the product. Crystals of ^{17}O enriched dimer were obtained by the same procedure, except that the dimer was dissolved in 10% $H_2{}^{17}O$ (Novachem) and the solution was heated at 75 °C for 6 h.

pK_a Measurements. Solution pH measurements were made as previously described.[10] Changes in the UV spectrum of dimer with $[H^+]$ were used to determine values of pK_{a1} at 298 K and the temperatures used in the kinetic study and at ionic strength $I = 1.0$ M ($NaClO_4$).

Absorbance changes were measured at the peak maximum of 242 nm on a Cary 3E UV−vis spectrophotometer for 11 acid standards, $0.0020 < [H^+] < 1.0$ M ($HClO_4$), with $[Rh]_{total} = 9.45 \times 10^{-4}$ M. The data were successfully fitted to the expression

$$\epsilon_{242}{}^{obs} = (\epsilon_{242}{}^{O}[H^+] + \epsilon_{242}{}^{OH}K_{a1})/([H^+] + K_{a1}) \qquad (2)$$

where $\epsilon_{242}{}^{O}$, $\epsilon_{242}{}^{OH}$, and K_{a1} are adjustable parameters for the extinction coefficients of fully protonated and monodeprotonated dimer and the first acid dissociation constant of the dimer, respectively. A typical plot of the experimental data and fitted curve is shown in Figure 1. Values of pK_{a1} are listed in Table 2. The value of pK_{a1} at 298 K was also determined from a pH titration, using the method described in the literature,[10] and is also given in Table 2. There is good agreement between the two methods of determination.

Kinetic Studies. Kinetic experiments were conducted as previously described[10] with the exception that 0.5 mL sampling solutions were prepared with Rh(III) dimer concentrations of 0.025 or 0.044 M. The resulting CO_2 was analyzed on a high-precision isotope ratio mass spectrometer built around Micromass 903 components for measurement of the $^{12}C^{16}O^{18}O$:$^{12}C^{16}O^{16}O$ abundance ratio of the sample relative to a "normal" CO_2 standard (seawater). The spectrometer readout expressed this conventionally as $\delta_{^{18}O}$ in parts per thousand:

$$\delta_{^{18}O} = \{[(I_{46}/I_{44})_{sample}/(I_{46}/I_{44})_{std}] - 1\} \times 1000$$

where I_m is the ion current for singly ionized molecules of mass m. Triple collection of ion currents for $m = 44$, 45, and 46 permitted corrections for any minor variations in ^{13}C and ^{18}O abundances.

Chromatographic and spectrophotometric analyses[15] were used to show that the dimer remains unchanged over the sampling period ($t >$ 10 half-lives of the slowest reaction).

Complete exchange of ^{18}O label was made possible by transferring a 0.004 mL sample, taken after over 10 half-lives, to a dry argon-filled glass tube (6 mm o.d.). The solution was frozen in an acetone/dry ice bath and evacuated on a vacuum line. The tube was then flame-sealed and immersed in an oil bath for 1 week at 93 °C. Analysis of ^{18}O label in the bulk solvent was then performed as previously described.[10]

Table 1. Acid Concentration and Temperature Dependence of the Rate Constants[a] for the Water Exchange on $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ [b] at $I = 1.0$ M ($NaClO_4$)

temp (±0.1) (K)	$[H^+]_{tot}$ (M)	10^5k_{fast} (s^{-1})	10^6k_{slow} (s^{-1})
308.1	0.1107	1.080 ± 0.044	3.55 ± 0.12
	0.1107[c]	1.123 ± 0.066	3.72 ± 0.35
	0.1599	1.024 ± 0.040	2.740 ± 0.092
	0.2083[d]	0.968 ± 0.027	2.533 ± 0.062
	0.3109	0.782 ± 0.037	2.180 ± 0.089
	0.3109[c]	0.812 ± 0.054	2.05 ± 0.21
	0.4523	0.787 ± 0.030	1.811 ± 0.070
	0.6019	0.759 ± 0.032	1.859 ± 0.079
	0.7517	0.776 ± 0.023	1.570 ± 0.042
	0.7517[c]	0.737 ± 0.034	1.58 ± 0.16
313.1	0.1176[d]	2.786 ± 0.059	7.64 ± 0.12
	0.1612	2.409 ± 0.062	5.82 ± 0.13
	0.2058	2.155 ± 0.060	4.97 ± 0.11
	0.3116	1.869 ± 0.046	4.061 ± 0.075
	0.4528	1.797 ± 0.051	3.609 ± 0.083
	0.6022	1.674 ± 0.036	3.385 ± 0.058
	0.6022[e]	1.72 ± 0.13	3.43 ± 0.19
		$C_1 = 0.493 \pm 0.032$	$C_2 = 0.510 \pm 0.034$
	0.7520	1.632 ± 0.038	3.292 ± 0.064
	0.7520[e]	1.66 ± 0.14	3.32 ± 0.21
		$C_1 = 0.496 \pm 0.035$	$C_2 = 0.506 \pm 0.037$
318.5	0.0845	8.12 ± 0.41	20.54 ± 0.92
	0.1146	8.18 ± 0.48	17.86 ± 0.86
	0.1628	5.52 ± 0.24	13.50 ± 0.52
	0.3124	3.94 ± 0.26	7.78 ± 0.38
	0.7523	3.38 ± 0.27	4.95 ± 0.34
323.1	0.1645	15.00 ± 0.43	22.05 ± 0.57
	0.17[f]	12 ± 1	47 ± 9
	0.2085	13.07 ± 0.28	19.90 ± 0.37
	0.2085[e]	13.10 ± 0.87	19.89 ± 0.98
		$C_1 = 0.500 \pm 0.022$	$C_2 = 0.500 \pm 0.024$
	0.3134	11.67 ± 0.33	14.33 ± 0.32
	0.4540	9.90 ± 0.15	12.06 ± 0.13
	0.4540[e]	9.95 ± 0.39	12.13 ± 0.34
		$C_1 = 0.497 \pm 0.011$	$C_2 = 0.503 \pm 0.011$
	0.6032	8.77 ± 0.27	10.92 ± 0.24
	0.7527	8.53 ± 0.14	10.05 ± 0.12

[a] Rate constants obtained by fitting eq 8 except where indicated. [b] [dimer] = 0.025 M except where indicated. [c] Rate constants obtained by fitting eq 10. [d] [dimer] = 0.044 M. [e] Rate constants and pre-exponential factors (C_1 and C_2) determined by fitting eq 9. [f] Rate constants determined from ^{17}O NMR measurements.

^{17}O NMR Studies. ^{17}O NMR spectra of the Rh(III) dimer were recorded in 5 mm NMR tubes on a Bruker DRX 400 spectrometer operating at 54.2 MHz and fitted with a variable temperature facility (90° pulses of 18 μs were used with 0.1 s between pulses). Chemical shifts are referenced against the bulk water signal at $\delta = 0$ ppm. A polynomial fitting procedure was used to correct the spectra for baseline roll. To obtain a spectrum, 10 000 scans were made over a spectral width of 16 400 Hz and a line broadening correction of 10 Hz was applied. Samples for NMR measurements were prepared by dissolving the ^{17}O enriched dimer in $HClO_4/NaClO_4$ acid standards such that I = 1.0 M and [dimer] = 0.05 M. The measured spectrum matched that reported by Glaser *et al.*[17] with two overlapping signals due to the coordinated waters observed at −122.7 and −130.9 ppm and a bridging hydroxo group at −320 ppm. Dimer spectra were also recorded at three acid concentrations, 0.02, 0.15, and 0.45 M, to check the effect of deprotonation on the ^{17}O signal.

Kinetic data were obtained at 323.1 K by recording the spectrum of a solution of enriched dimer every hour until equilibrium was reached.

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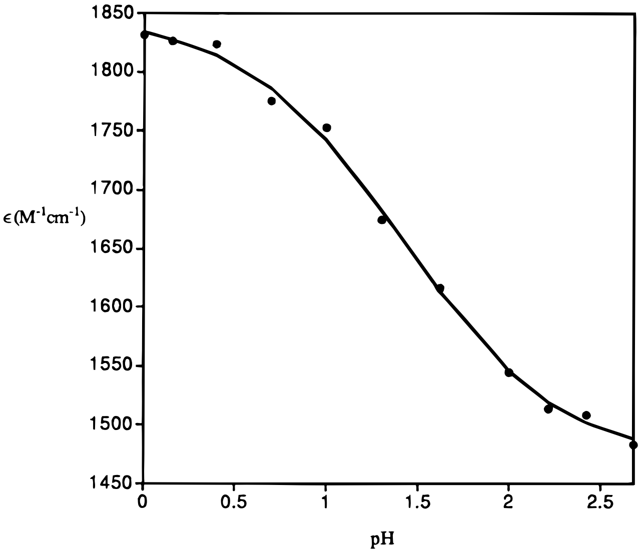

Figure 1. $[H^+]$ dependence of the extinction coefficients for solutions of the Rh(III) dimer recorded at 242 nm and 308.1 K. The solid line represents a fit of eq 2 to data points.

At this time, the signals from the coordinated waters could no longer be observed. For each spectrum, analysis of the overlapping water signals was carried out, and the data were used to determine first-order rate constants by literature methods.[14,18]

Results

The kinetics of water exchange on the Rh(III) hydrolytic dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ were followed by measuring the release of ^{18}O label from the complex into the bulk solvent with an isotope ratio mass spectrometer, following conversion of water into carbon dioxide with guanidine hydrochloride. The final acid concentration ($[H^+]_{tot}$) is the sum of the added acid ($[H^+]_{add}$) and that liberated from the hydrolysis of the dimer ($[H^+]_{hyd}$) and can be determined by combining eqs 3 and 4 and substituting values for K_{a1} at the temperatures

$$[H^+]_{tot} = [H^+]_{add} + [H^+]_{hyd} \qquad (3)$$

$$[H^+]_{hyd} = K_{a1}[\text{Rh(III) dimer}]/[H^+]_{tot} \qquad (4)$$

used in this study. The values of K_{a1} for the Rh(III) dimer required here and required in the analysis of kinetic data were determined spectrophotometrically and are listed in Table 2.

Least-squares analysis was used to fit $\delta_{^{18}O}$ (stable isotope composition) versus time data where F is the fraction of exchange at time t defined by eq 5. Fitting the data to a single-exponential function (eq 6) was unsuccessful, giving fits with systematic deviations in plots of residuals versus time. Attempts to fit the data to eq 7, which rationalized the $\delta_{^{18}O}$ versus time data for water exchange on Cr(III) dimer,[10] also gave systematic deviations. Equation 7 allows for two pathways for exchange of the eight terminal water ligands (*cis* and *trans* to the bridging groups) and one for exchange of the two bridging OH^- groups, and the coefficients represent the proportion of that particular type of oxygen undergoing exchange. The data at all temperatures and acid concentrations were fitted successfully using eq 8, as indicated by the random distribution of residuals with time observed in each case.

$$F = [\delta_{^{18}O}(t) - \delta_{^{18}O}(t{=}0)]/\{\delta_{^{18}O}(t{=}\infty) - \delta_{^{18}O}(t{=}0)\} \qquad (5)$$

$$1 - F = \exp(-kt) \qquad (6)$$

$$1 - F = 0.4\exp(-k_{fast}t) + 0.4\exp(-k_{slow}t) + 0.2\exp(-k_{bridge}t) \qquad (7)$$

$$1 - F = 0.5\exp(-k_{fast}t) + 0.5\exp(-k_{slow}t) \qquad (8)$$

This equation assumed that only coordinated water ligands exchanged during the reaction and that the four water molecules at positions *trans* to bridging hydroxide groups exchanged at a rate different from the rate of exchange for those at the *cis* positions (Scheme 1). A typical plot of the experimental data and fitted curve (from eq 8) is shown in Figure 2, and the results of the analysis are summarized in Table 1. The rate constants were found to be independent of the concentration of Rh(III) dimer used.

The validity of eq 8 was checked by fitting some data sets to eq 9, which allows the pre-exponential terms to be refined as part of the analysis.

$$1 - F = C_1\exp(-k_{fast}t) + C_2\exp(-k_{slow}t) \qquad (9)$$

In all the cases examined, the values of C_1 and C_2 were within error of 0.5 (see Table 1) and support the model chosen to describe the water exchange on the Rh(III) dimer. Substitution of eq 5 into eq 8 yields eq 10, which was

$$\delta_{^{18}O}(t) = \{[(\delta_{^{18}O}(t{=}\infty) - \delta_{^{18}O}(t{=}0)][1 - 0.5\exp(-k_{fast}t) - 0.5\exp(-k_{slow}t)]\} + \delta_{^{18}O}(t{=}0) \qquad (10)$$

also used to successfully fit $\delta_{^{18}O}$ versus time data for each kinetic run and provided another way of checking the results obtained in Table 1. This gave values of $\delta_{^{18}O}(t{=}0)$ and $\delta_{^{18}O}(t{=}\infty)$ which were in agreement with the experimental values and rates of water exchange which were concordant with those obtained by fitting eq 8 (Table 1). Figure 3 shows a fit of eq 10 to the $\delta_{^{18}O}$ versus time data used to produce Figure 2.

The proportion of ^{18}O label exchanged from the dimer at the completion of each run remained constant at ca. 10% for all the experiments. Treatment of reaction mixtures at elevated temperature for prolonged periods to ensure complete exchange of label (see Experimental Section) followed by mass spectrometric analysis revealed that 10% of the ^{18}O label remains unexchanged after 10 half-lives of the slowest reaction, confirming the observation made in the kinetic analysis. This means that, unlike the case of the Cr(III) dimer, only partial enrichment of the bridging OH groups was achieved for the Rh(III) dimer. More importantly, it indicates that the label present in the bridging OH groups is not released under the conditions used in this study.

Oxygen-17 NMR studies were carried out to confirm the interpretation of the ^{18}O labeling data. The ^{17}O NMR spectrum of the enriched Rh(III) dimer (enrichment ca. 10%) was in agreement with that reported by Glaser *et al.*,[17] with two overlapping signals observed for the two types of coordinated water molecules and a signal due to the bridging OH groups. A kinetic experiment conducted with ^{17}O labeled dimer ($[H^+] = 0.17$ M and [dimer] = 0.05 M at 323.1 K) over a period of 72 h showed that both water signals diminish with time, consistent with the exchange of ^{17}O labeled water with unlabeled water from the bulk solvent, and that there was no change in the intensity of the signal due to the bridging OH groups. The two water signals were found to diminish at different rates. Under the experimental conditions used here, the signal at −131 ppm could no longer be seen after 12 h while that at −123 ppm was still clearly present after the same time. Analysis[14,18] of the time-dependent spectra gave rate constants for the two processes. The values obtained were $12\ (\pm 1) \times 10^{-5}\ s^{-1}$ and

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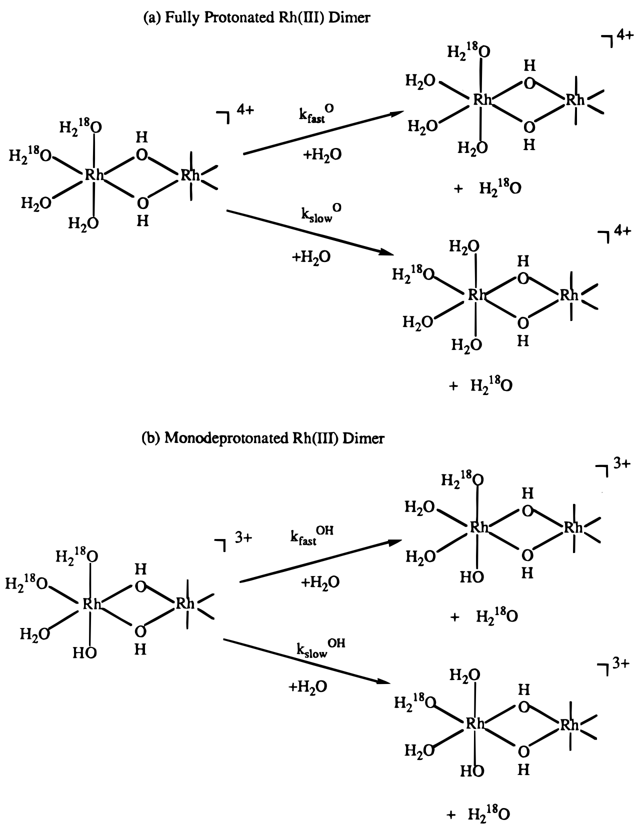
Table 2. Temperature Dependence of the Rate Constants for Water Exchange on Fully Protonated and Monodeprotonated Rh(III) Dimers

	temp (±0.1) (K)			
	308.1	313.1	318.2	323.1
$10^5k_{fast}^{O}$ (s^{-1})	0.662 ± 0.033	1.296 ± 0.050	1.85 ± 0.74	5.87 ± 0.28
$10^5k_{fast}^{OH}$ (s^{-1})	2.36 ± 0.19	6.28 ± 0.25	18.0 ±2.0	36.0 ± 1.2
$10^5k_{slow}^{O}$ (s^{-1})	0.1189 ± 0.0087	0.191 ± 0.028	0.095 ± 0.067	0.464 ± 0.065
$10^5k_{slow}^{OH}$ (s^{-1})	0.992 ± 0.051	2.04 ± 0.14	4.95 ± 0.19	6.30 ± 0.28
pK_{a1}[a]	1.41 ± 0.04	1.33 ± 0.06	1.24 ± 0.04	1.16 ± 0.06

[a] pK_{a1} values determined at 298 K using spectrophotometric and pH titration methods gave values of 1.59 ± 0.07 and 1.67 ± 0.01, respectively.

Scheme 1. Pathways for Water Exchange on the Rh(III) Dimer[a,b]



[a] Water molecules occupy the unlabeled coordination sites around Rh(III). [b] Site of deprotonation could not be clearly established.

47 (± 9) × 10^{-6} s^{-1} at −131 and −123 ppm, respectively. Given that these constants were obtained by analysis of overlapping, broad signals, there is acceptable agreement with those obtained by the ^{18}O experiments (see Table 1). Although the errors in these rate constants are larger than those for the ^{18}O experiments, the NMR data do provide strong support for the proposed interpretation of the ^{18}O labeling data.

The rate constants k_{fast} and k_{slow} show a systematic increase with decreasing acid concentration at each temperature of the kinetic study (Table 1), indicating that both protonated and monodeprotonated Rh(III) dimers are involved in the exchange process. Least-squares analysis using eq 11, an extended version

$$k_{obs} = (k^{O}[H^+]_{tot} + k^{OH}K_{a1})/([H^+]_{tot} + K_{a1}) \qquad (11)$$

of eq 1 which allows for the partial deprotonation of Rh(III) dimer over the experimental range of $[H^+]_{tot}$, gave the final rate constants for the fast and slow pathways of exchange on both fully protonated and monodeprotonated Rh(III) dimers. A typical example of the experimental and fitted data is shown in Figure 4. The results are summarized in Table 2. Activation parameters were determined from the temperature dependence of each rate constant and are listed in Table 3 together with calculated values of the rate constants at 298 K.

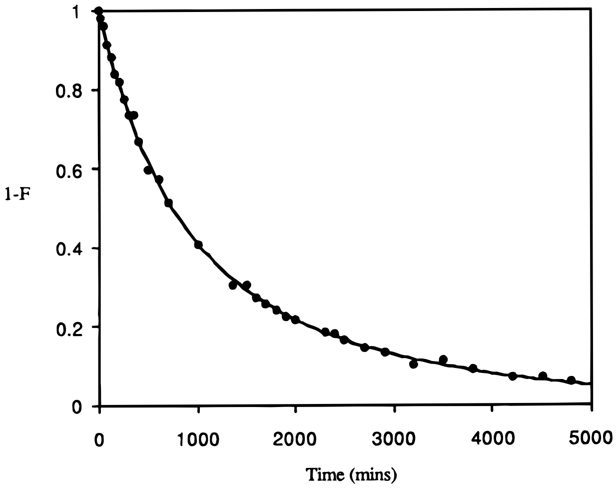


Figure 2. Typical plot showing the fractional decrease of ^{18}O label from the Rh(III) dimer with time at [dimer] = 0.044 M, $[H^+]_{tot}$ = 0.1176 M, and T = 313.1 K. Rate constants are given in Table 1, and the solid curve represents a fit of eq 8 to the experimental data.

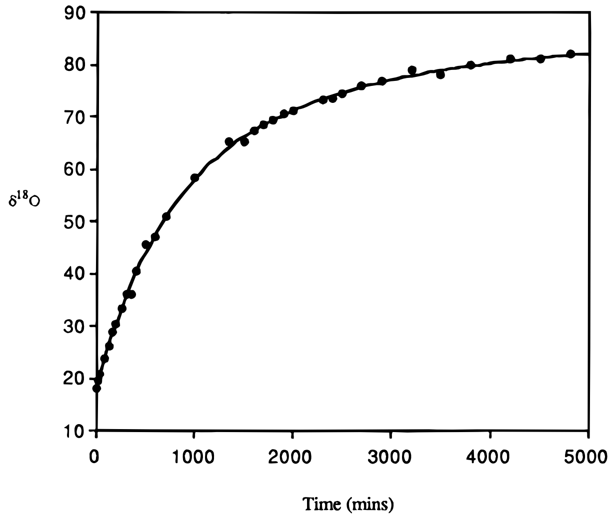


Figure 3. Plot showing the variation of $\delta_{^{18}O}$ with time for the same data used for Figure 2. The solid curve represents a fit of eq 10 to the experimental data.

^{17}O NMR spectra of $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ were recorded at three acid concentrations (0.02, 0.15, and 0.45 M) in order to establish the site of deprotonation. These conditions were such that the variation in the proportion of the monodeprotonated form with $[H^+]$ was substantial. However, the spectra showed no systematic change with $[H^+]$.

Discussion

The Rh(III) dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ is the first Rh(III) oligomer for which water exchange rates have been

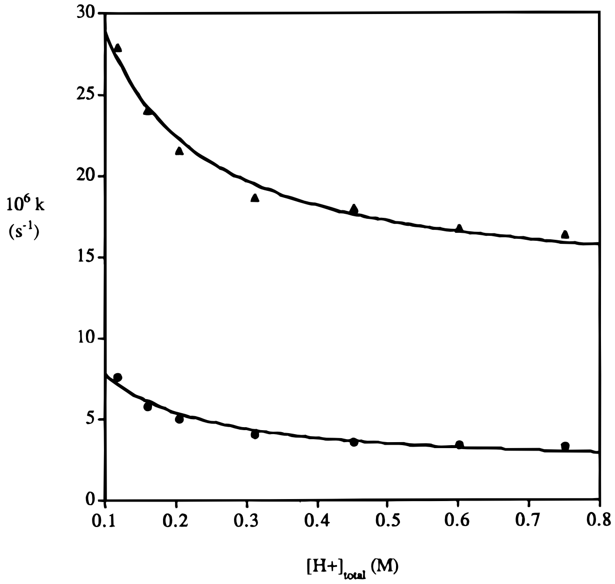


Figure 4. Acid dependence of the rate constants for water exchange on the Rh(III) dimer at positions *cis* and *trans* to bridging hydroxides at 313.1 K; ▲, k_{fast} ; ●, k_{slow}. The solid curves were obtained by fitting the experimental data to eq 11.

measured using isotopic labeling techniques. This investigation provides the opportunity for comparison with water exchange data obtained for the Cr(III) dimer.[10] The rate expression which fitted the isotope labeling data for the Rh(III) dimer (see eq 8 and Figure 2) better than any other reasonable alternative (for example, eqs 6 and 7) was one which assumed the presence of only two types of water exchange processes occurring at significantly different rates. The coefficients used in the rate expression indicate that the two processes involve the release of the same amount of label, and assuming that uniform enrichment has been achieved, this would suggest that the numbers of molecules being exchanged by each process are equal. This proposal is supported by the fact that floating the pre-exponential terms (eq 9) gave the same rate constants as those obtained by fitting eq 8 and pre-exponential factors that were within error of 0.5. The presence of two reaction pathways is confirmed by the ^{17}O NMR data which clearly show that the two water sites present on the Rh(III) dimer exchange at different rates. The NMR data further show that no measurable exchange of the bridging OH groups takes place on the time scale of the water exchange processes. This is in agreement with mass spectrometric data which showed that there was no exchange of label in the bridging groups, even though both the kinetic traces and high-temperature measurements indicated 50% enrichment of the bridging OH groups.

The existence of two pathways for water exchange coupled with the absence of exchange of the bridging OH groups is strong evidence in support of the view that the reaction occurs with retention of stereochemistry. If this were not the case, both water ligands should exchange at the one rate and only one reaction pathway should be observed. The possibility that exchange occurs through a ring opening process can be discounted because this would also result in only one exchange rate which would be equal to the rate of exchange of the bridging groups. The results for the Rh(III) dimer system are consistent with those for the Cr(III) dimer[10] where it has been demonstrated that three pathways contribute to the exchange of label, two attributed to water ligands and a third to the bridging OH groups. The rate of exchange of label from the bridging groups[10] was found to match the rate of interconversion between singly and doubly bridged Cr(III) dimers.[7] The absence of a bridge cleavage pathway for the Rh(III) dimer is in keeping with the extremely slow cleavage of Rh(III) oligomers[19] and the fact that the singly bridged form of this dimer has, so far, proved difficult to prepare.

In the assignment of the two pathways for water substitution, the interpretation which is consistent with all the data is one which proposes that water ligands *trans* to the bridging hydroxide groups are exchanged at a faster rate (k_{fast}) than those in the *cis* positions (k_{slow}), as described in Scheme 1. This is in keeping with the now well established greater *trans* labilizing effect of OH^- over H_2O.[10,20,21] The ^{17}O NMR data indicate that the water ligands with a signal at −131 ppm, assigned by Glaser *et al.*[17] as those *trans* to the bridging groups, exchange faster than those with a signal at −123 ppm, assigned as *cis* to the bridging group. The low-temperature X-ray crystal structure of the Rh(III) dimer[22] provides evidence for the presence of a weak *trans* influence in the complex; viz., the Rh−O distances *trans* to the bridging group are 2.042(2) and 2.038(2) Å while those *cis* are 2.020(2) and 2.026(2) Å. While the effect is small, it could be the origin of the small but measurable differences in water exchange rates.

The pH dependence of both k_{fast} and k_{slow} is typical of hydrolytic processes which are accelerated by deprotonation of at least one reactant. Measurements of the first acid dissociation constant of the Rh(III) dimer, made by both pH and spectrophotometric titration, indicate that this oligomer is quite acidic (pK_{a1} 1.6). Since $[Rh(H_2O)_6]^{3+}$ (pK_{a1} 3.2)[13] is much more acidic than $[Cr(H_2O)_6]^{3+}$ (pK_{a1} 4.3),[3] the Rh(III) dimer was expected to be more acidic than the Cr(III) dimer (pK_{a1} 3.7). However, the difference in acidity for the Rh(III) pair is greater than might have been anticipated from the data for the Cr(III) pair. The kinetic parameters obtained by fitting eq 11 to the pH dependence of k_{fast} and k_{slow} (Table 3) reveal that water exchange on fully protonated Rh(III) dimer is 200−600-fold faster than that on $[Rh(H_2O)_6]^{3+}$.[14] This enhancement is similar to that found for the Cr(III) dimer and $[Cr(H_2O)_6]^{3+}$, but it must be stressed that the two Rh(III) studies were carried out at very different ionic strengths. Nevertheless, it appears that, as in the case of Cr(III) dimer, the introduction of OH bridges does have a labilizing effect on the Rh(III) coordination sphere. Attempts to establish the site of deprotonation were foiled by the absence of a hydrogen ion effect in the ^{17}O NMR spectrum of the Rh(III) dimer.

A comparison of the water exchange data for Rh(III) and Cr(III) dimers (Table 3) shows that the equivalent processes are 100−4000-fold slower on Rh(III) than on Cr(III) and clearly emphasizes greater inertness of the Rh(III) center. There is only a 3-fold difference in rate for the two water exchange pathways on the fully protonated dimer, but this compares reasonably well with the 5-fold difference observed for the Cr(III) dimer. As outlined above, this small rate change suggests that the *trans* labilizing effect of bridging OH groups is marginally greater than the effect of *cis* labilization. The rate of water exchange at positions *cis* and *trans* to the bridging hydroxides is enhanced by deprotonation. However, the increases in rate of 3- and 6-fold, respectively, are much smaller than found for the corresponding processes on the Cr(III) dimer and those previ-

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(22) Crimp, S. J. Honours Thesis, Monash University, 1990.The structure of $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4](dmtos)_4\cdot 8H_2O$ was redetermined at low temperature (173 K) as outlined in ref 15. Since the room temperature structure has been reported previously,[15] only data that are relevant to the discussion of water exchange rates are presented.

Table 3. Comparison of the Activation Parameters and Rate Constants at 298 K for the Water Exchange Processes on Fully Protonated and Monodeprotonated Rh(III) and Cr(III) Dimers

	Rh(III) dimer[a]			Cr(III) dimer[b]		
	10^6k (s^{-1})	$\Delta H^{*/\circ}$ (kJ mol^{-1})	$\Delta S^{*/\circ}$ (J K^{-1} mol^{-1})	10^6k (s^{-1})	$\Delta H^{*/\circ}$ (kJ mol^{-1})	$\Delta S^{*/\circ}$ (J K^{-1} mol^{-1})
k_{fast}^{O}	1.26	118.8 ± 3.9	41 ± 12	358	80.8 ± 8.0	−40 ± 26
k_{fast}^{OH}	3.44	145.9 ± 3.7	140 ± 11	12 400	125.3 ± 3.9	139 ± 13
k_{slow}^{O}	0.486	64.2 ± 9.4	−150 ± 30	66.0	97 ± 10	0 ± 32
k_{slow}^{OH}	2.68	102.0 ± 3.4	−9 ± 11	4750	82.8 ± 5.8	−12 ± 19
k_{bridge}^{O}	not obs	not obs	not obs	11.4	99.5 ± 5.6	−10 ± 18
k_{bridge}^{OH}	not obs	not obs	not obs	1468	126.7 ± 3.5	125 ± 12
pK_a	1.59	31.74 ± 0.48	76.1 ± 1.5	3.68	31.4 ± 1.6	35.1 ± 5.3

[a] This work. [b] Data taken from ref 10.

ously observed for the mononuclear aqua ions $[Fe(H_2O)_6]^{3+}$ [11,12] and $[Cr(H_2O)_6]^{3+}$.[9] The Rh(III) dimer data appear to contrast those reported by Plumb and Harris[13] and Laurenczy *et al.*[14] for exchange on $[Rh(H_2O)_6]^{3+}$, where respective enhancements of 100- and 20000-fold were observed on deprotonation albeit under different conditions.

The enthalpies of activation for the Rh(III) dimer (Table 3) are generally higher than those for the Cr(III) dimer, reflecting the greater inertness of Rh(III). For both reaction pathways, deprotonation of the Rh(III) dimer causes an increase in ΔS^* consistent with a more dissociative mechanism of substitution. This observation is consistent with water exchange studies on Cr^{3+},[9] Fe^{3+},[11,12] Rh^{3+},[14] and the Cr(III) dimer.[10] The ΔS^* values for water exchange at positions *trans* to bridging hydroxides are more positive than those for exchange at the *cis* positions for both fully protonated and mondeprotonated Rh(III) dimers and are indicative of a more dissociative mechanism of substitution.

In summary, deprotonation of the Rh(III) dimer enhances the rate of water exchange at positions *cis* and *trans* to bridging hydroxide groups but not to the same extent as for the Cr(III) dimer. Further evidence has been provided that condensation of the oligomers results in increases in the lability of the primary coordination sphere of the metal ions in solution and that deprotonation leads to more dissociative activation mechanisms for ligand substitution. Information on water exchange reactions of the recently characterized heterobinuclear aqua ion $[(H_2O)_4Cr(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ [23] would provide a valuable comparison to exchange data for both the Rh(III) and Cr(III) dimers.

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