Inorg. Chem. 1994, 33, 465–470

# Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 9. Kinetics of Water Exchange on the Hydrolytic Dimer

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*Received May 20, 1993*®

Oxygen-18-labeling techniques have been used to study the kinetics of water exchange on the Cr(III) hydrolytic dimer at $I = 1.0$ M, $[H^+]$ in the range 0.003–0.1 M, and temperatures between 287.2 and 305.2 K. Three distinct pathways for exchange of oxygen-18 from the labeled dimer into the bulk solvent were observed. Two of these rate constants ($k_{fast}$ and $k_{slow}$) correspond to the exchange of coordinated water molecules occupying positions *trans* and *cis* to the bridging OH groups. They were found to show a linear dependence on $1/[H^+]$, $k_i = k_i^O + k_i^{OH}/[H^+]$, consistent with the involvement of both fully protonated and monodeprotonated dimer. The following parameters were found: for exchange on $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ at 298 K, $k_{fast}^O = 3.6 \times 10^{-4}$ s$^{-1}$ ($\Delta H^* = 81 \pm 8$ kJ mol$^{-1}$ and $\Delta S^* = -40 \pm 26$ J K$^{-1}$ mol$^{-1}$) and $k_{slow}^O = 6.6 \times 10^{-5}$ s$^{-1}$ ($\Delta H^* = 97 \pm 10$ kJ mol$^{-1}$ and $\Delta S^* = 0 \pm 32$ J K$^{-1}$ mol$^{-1}$); for exchange on $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH)(H_2O)_3]^{3+}$, $k_{fast}^{OH} = 2.6 \times 10^{-6}$ s$^{-1}$ ($\Delta H^* = 157 \pm 2$ kJ mol$^{-1}$ and $\Delta S^* = 174 \pm 8$ J K$^{-1}$ mol$^{-1}$) and $k_{slow}^{OH} = 1 \times 10^{-6}$ s$^{-1}$ ($\Delta H^* = 114 \pm 4$ kJ mol$^{-1}$ and $\Delta S^* = 23 \pm 14$ J K$^{-1}$ mol$^{-1}$). Comparison of these data with those of previous studies suggests that there is a correlation between exchange rates and OH/Cr which holds for both bridging and terminal hydroxide groups. Deprotonation has been found to cause significant labilization of all the aquo groups on the dimer regardless of whether they are *cis* or *trans* to the hydroxide bridges. Mechanistic implications of the activation parameters are discussed. A third exchange process was identified and, from the correspondence of rate and activation parameters with data on the interconversion between singly and doubly bridged dimers, attributed to the release of label from the bridging groups through bridge cleavage and re-formation reactions.

## Introduction

The hydrolytic polymerization of Cr(III) has been the subject of detailed kinetic investigations[3–7] aimed at providing an understanding of the basic hydrolytic processes involved in the formation,[3,4] cleavage,[7] and rearrangement[5,6] of small oligomers formed in the very early stages of polymerization. These studies have been made possible by the availability of a complete series of oligomers (dimer–hexamer) and include measurements of the rates of the formation of dimer from $Cr^{3+}$ [3] and tetramer from dimer,[4] the cleavage of dimer to monomer,[7] and the intramolecular rearrangement of dimer[6] and tetramer.[5] Deprotonation of the metal ions (or oligomers) has emerged as an extremely important factor having considerable influence on the rate and mechanisms of both intermolecular (oligomer formation) and intramolecular condensation reactions (e.g. conversion of singly bridged into doubly bridged dimer). Deprotonation promotes these processes in several ways: (i) it generates a coordinated hydroxide, which is a better nucleophile than coordinated water for attacking another Cr(III) center; (ii) it significantly increases the lability of the primary coordination sphere of Cr(III), leading to faster condensation rates; (iii) it reduces the charge on the reactants, thus increasing ion-pair association constants; (iv) it can bring the reactants (or reacting components) into close proximity through hydrogen-bond formation. For the condensation reactions studied so far,[3–6] all of these factors come into play on deprotonation of the reactants and there have been difficulties in attempting to determine whether, for example, the greater nucleophilicity of coordinated OH groups has more of an effect on rates than labilization of the coordination sphere. For these same reasons, changes in the mechanism of substitution at Cr(III) have proved quite difficult to ascertain. In principle, the relative importance of the various factors can be better disentangled by studying reactions which involve a common nucleophile or, alternatively, reactions between different nucleophiles and Cr(III) centers with constant lability. The former approach is exemplified by water-exchange reactions where $H_2O$ from the bulk solvent is used as a nucleophile to probe the effect of deprotonation on the lability of the Cr(III) coordination sphere.

Previous investigations of the acid dependence of the rates of water exchange on $[Cr(H_2O)_6]^{3+}$,[8] $[Rh(H_2O)_6]^{3+}$,[9] and $[Fe(H_2O)_6]^{3+}$ [10,11] have found a two-term rate equation of the form

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

where the $k^O$ pathway corresponds to exchange on the $[M(H_2O)_6]^{3+}$ ions and $k^{OH}$ to exchange on the monodeprotonated species, $[M(H_2O)_5OH]^{2+}$. In the case of Cr(III), deprotonation results in an acceleration of ca. 75-fold, which is a measure of the increase in lability of the Cr(III) primary coordination sphere. A variable-pressure study[8] has shown that this reactivity increase is coupled with an increase in the dissociative character of the substitution process from $[Cr(H_2O)_6]^{3+}$ to $[Cr(H_2O)_5OH]^{2+}$. Compared with studies on mononuclear metal ions, relatively little work has been carried out on the rates of $H_2O$ exchange on hydrolytic oligomers. Rogers *et al.*[12] were first to measure the rates of $H_2O$-exchange studies on a Mo(IV) trimer, $[Mo_3O_4(H_2O)_9]^{4+}$, using $^{18}O$-labeling techniques. Subsequently, Richens

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* Abstract published in *Advance ACS Abstracts,* December 15, 1993.

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0020-1669/94/1333-0465$04.50/0

*et al.*[13] applied $^{17}O$ NMR spectroscopy in the study of $H_2O$ exchange on the same oligomer. The six water ligands trans to the $\mu_2$-O were found to exchange about $10^5$ times faster than those trans to the $\mu_3$-O. In both cases, the effect of deprotonation on rates of exchange could not be determined because only the conjugate pathway was observed and rates of exchange on the fully protonated oligomer could not be estimated. $^{17}O$ NMR spectroscopy[13] has also been used to show that both types of bridging oxygens exchange extremely slowly (half-life > 10 yr), contrary to previous reports[12] based on $^{18}O$ studies.

We report here the application of $^{18}O$-labeling techniques in the measurement of $H_2O$ exchange rates on the Cr(III) hydrolytic dimer $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$. Rate constants and thermal activation parameters have been obtained for $H_2O$ exchange on the fully protonated and the monodeprotonated dimer and for exchange of the bridging hydroxide groups.

**Table 1.** Acid Concentration and Temperature Dependence of the Rate Constants for the Water Exchange on the Cr(III) Hydrolytic Dimer $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ [a]

| $T$ (K) | $[H^+]_{tot}$ (mol dm$^{-3}$) | $10^5k_{fast}$ (s$^{-1}$) | $10^5k_{slow}$ (s$^{-1}$) | $10^5k_{bridge}$ (s$^{-1}$) |
|---|---|---|---|---|
| 287.2 | 0.0983 | 10.38 ± 0.83 | 1.70 ± 0.18 | 0.256 ± 0.031 |
| | 0.0590 | 10.18 ± 0.83 | 1.84 ± 0.17 | 0.367 ± 0.038 |
| | 0.0394 | 13.0 ± 1.4[b] | 2.45 ± 0.31 | 0.247 ± 0.052 |
| | 0.0198 | 10.6 ± 2.8 | 2.68 ± 0.44 | 0.248 ± 0.050 |
| | 0.0073 | 11.89 ± 0.80 | 3.09 ± 0.28 | 0.523 ± 0.064 |
| | 0.0058[c] | 12.8 ± 1.5 | 4.64 ± 0.41 | 0.748 ± 0.085 |
| | 0.0038 | 16.1 ± 1.5 | 7.84 ± 0.73 | 0.849 ± 0.091 |
| | 0.0031 | 17.4 ± 1.1 | 7.44 ± 0.51 | 1.19 ± 0.11 |
| 299.0 | 0.0984 | 53.4 ± 3.2 | 6.64 ± 0.46 | 1.76 ± 0.34 |
| | 0.0787 | 49.9 ± 3.7 | 7.35 ± 0.68 | 1.85 ± 0.45 |
| | 0.0297 | 58.5 ± 8.9 | 16.0 ± 2.2 | 2.72 ± 0.69 |
| | 0.0076 | 75.9 ± 9.9 | 14.2 ± 2.2 | 5.1 ± 1.5 |
| | 0.0042 | 129 ± 12 | 35.5 ± 3.7 | 11.0 ± 1.7 |
| 305.2 | 0.0984 | 84.2 ± 8.2 | 19.7 ± 1.9 | 3.52 ± 0.59 |
| | 0.0493 | 98.1 ± 8.7 | 23.4 ± 1.8 | 5.48 ± 0.65 |
| | 0.0297 | 118 ± 21 | 34.8 ± 5.6[b] | 6.94 ± 0.14 |
| | 0.0202[c] | 127 ± 19 | 31.7 ± 4.6 | 8.80 ± 0.16 |

[a] [dimer] ~ 0.026 M except where indicated; $I$ = 1.0 M ($NaClO_4$). [b] These values were obviously outliers and were not included in the analysis of the data. [c] [dimer] ~ 0.04 M.

**Table 2.** Temperature Dependence of the Rate Constants for Water-Exchange and Bridge-Cleavage Processes on Fully Protonated and Monodeprotonated Cr(III) Dimer

| | $T$ = 287.2 K | $T$ = 299.0 K | $T$ = 305.2 K |
|---|---|---|---|
| $10^5k_{fast}{}^{O}$ (s$^{-1}$) | 9.67 ± 0.37 | 48.2 ± 2.5 | 73.5 ± 2.9 |
| $10^7k_{fast}{}^{OH}$ (M$^{-1}$ s$^{-1}$) | 2.24 ± 0.23 | 30.2 ± 4.5 | 116 ± 13 |
| $10^5k_{slow}{}^{O}$ (s$^{-1}$) | 1.54 ± 0.20 | 5.8 ± 1.0 | 16.72 ± 0.62 |
| $10^7k_{slow}{}^{OH}$ (M$^{-1}$ s$^{-1}$) | 1.75 ± 0.21 | 10.0 ± 3.0 | 31.3 ± 3.0 |
| $10^5k_{bridge}{}^{O}$ (s$^{-1}$) | 0.231 ± 0.035 | 1.37 ± 0.15 | 2.77 ± 0.31 |
| $10^7k_{bridge}{}^{OH}$ (M$^{-1}$ s$^{-1}$) | 0.258 ± 0.038 | 3.77 ± 0.35 | 12.26 ± 0.77 |
| $10^4K_{a_1}$ (M) | 1.312 ± 0.033 | 2.089 ± 0.028 | 2.818 ± 0.025 |

## Experimental Section

**Materials.** Analytical grade reagents were used throughout. Water was deionized and distilled prior to use. $^{18}O$-labeled water (98%) was obtained from Novachem and used without further purification. Crystals of the dimer, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4](dmtos)_4\cdot 4H_2O$ (dmtos = mesitylene-2-sulfonate), were prepared using a previously described procedure.[14] Enrichment of the dimer was achieved by dissolving this dimer salt in 10% $H_2{}^{18}O$, adjusting the pH to 2 with mesitylene-2-sulfonic acid, and heating the solution at 50 °C for 24 h. At this pH, minimal amounts of the dimer convert to Cr(III) tetramer via dimerization or undergo cleavage to $Cr^{3+}$. The solution was then cooled to room temperature and reduced in volume on a vacuum line. Crystals of the enriched dimer formed within 2 h. They were collected by filtration and stored in a sealed sample jar until required. Spectrophotometric and chromatographic analyses were used to show that the enriched dimer samples were analytically pure. The Cr content of the crystals, determined spectrophotometrically following conversion to $CrO_4{}^{2-}$,[15] was found to correspond to that expected for the formula $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4](dmtos)_4\cdot 4H_2O$. Anal. Calc for $Cr_2C_{26}H_{70}O_{36}S_4$: Cr, 9.03. Found: Cr, 9.03.) These analyses indicate that excess mesitylene-2-sulfonic acid was not present in the crystals.

**pH and p$K_a$ Determinations.** Solution pH and p$K_a$ values were measured on a Metrohm 605 pH meter connected to a Metrohm 665 Dosimat autoburet using a Ross combination glass electrode (ORION). During these measurements, solutions were kept at constant temperature (±0.1 K) by circulating water through a double-walled reaction vessel from a water bath fitted with a Haake D8 thermostat and Haake D12 compressor. The pH meter and Dosimat were interfaced to a Pericom AT computer through an IEEE interface (IO tech). This system allowed the direct acquisition of titration data, from which the hydrolysis constants of the dimer ($K_{a1}$ and $K_{a2}$) could be determined at the temperatures used in the kinetic study (287.2, 299, and 305.2 K) and $I$ = 1.0 M ($NaClO_4$).

**Kinetic Experiments.** Solutions of known acid concentration for use in kinetic experiments were prepared by adding $NaClO_4$ to a solution of $HClO_4$ (of known concentration) so as to give a 1-mL solution with ionic strength, $I$, just below 1.0 M. This solution was allowed to equilibrate at the desired temperature and a sample taken to measure the isotopic composition of the solvent. An accurately known mass of the enriched dimer (ca. 10% enrichment in $^{18}O$) was then added to the solution to give $I$ = 1.0 M and [dimer] = 0.026 M. As soon as the dimer had totally dissolved, a sample was taken (zero-time sample). The solutions were kept in closed, darkened flasks to avoid photochemical exchange[16] and maintained at constant temperature (±0.1 K) in a water bath. Samples (0.004 mL) were collected at regular intervals with a microsyringe such that 25–30 samples were taken over at least 3 half-lives of the slowest reaction. The final sample was taken after more than 10 half-lives.

The microsyringe was used to transfer the samples to glass tubes (6-mm o.d.) which had been filled with dry argon. The solution was frozen by immersion in an acetone/dry ice bath, and the tubes were individually connected to the vacuum line and evacuated. The frozen solvent water was volatilized by rapid warming to 0 °C and condensed into another evacuated tube which contained guanidine hydrochloride. This tube was then heated at 300 °C for 20 h to allow complete conversion of the water to $CO_2$.[17] The tubes were cooled and then reconnected to the vacuum line, where the mixture of $CO_2$ and $NH_3$ was allowed to pass over concentrated $H_2SO_4$ to scrub out the ammonia. They were then warmed gently to decompose any ammonium carbamate to $NH_3$ and $CO_2$. The $CO_2$ was collected in a fresh tube which was immersed in liquid nitrogen and the tube sealed. The $^{18}O$ enrichment in carbon dioxide was determined with an isotope ratio mass spectrometer constructed around VG Micromass 903 components. These measurements gave the abundance of $^{12}C^{16}O^{18}O$ relative to $^{12}C^{16}O_2$. Triple collection of ion currents of singly charged masses 44, 45, and 46 permitted corrections for any minor variations in $^{13}C$ and $^{17}O$ abundances.

## Results

The kinetics of water exchange on the Cr(III) hydrolytic dimer were followed by measuring the release of oxygen-18 label from the complex into the bulk solvent. Kinetic data (Table 1) were obtained at several $[H^+]$ (0.003–0.1 M) and temperatures (287.2, 299, and 305.2 K) while [dimer] (~0.026 M but for two of the runs at ~0.04 M) and ionic strength (1.0 M) were maintained constant. The final acid concentrations are the sum of the acid added to the reaction mixtures and that liberated through the hydrolysis of the dimer (eq 1). In order to determine the latter, acid dissociation constants for the dimer were measured at each of the temperatures of this study (Table 2). Substitution of eq 2 into eq 1 gives a quadratic equation which can be solved to give $[H^+]_{tot}$. Initial attempts to fit the stable isotope composition data were made under the assumption that only water ligands exchanged during the reaction and that the four water molecules *trans* to bridging hydroxide groups exchanged at a rate different

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$$[H^+]_{tot} = [H^+]_{added} + [H^+]_{hyd} \qquad (1)$$

$$[H^+]_{hyd} = K_a[\mathrm{Cr(III)\ dimer}]/[H^+]_{tot} \qquad (2)$$

from that of the *cis* water molecules (see diagram of dimer, Scheme 1a). However, plots of the residuals versus time for each of the runs showed systematic deviations. This led to the conclusion that the bridging hydroxide groups were also exchanging. Scheme 1 describes the three pathways proposed to be responsible for the exchange of oxygen-18 label from the Cr(III) primary coordination sphere into the bulk solvent. Least-squares analysis was used to fit the stable isotope composition versus time data to eq 3, where $F$ is the fraction of exchange at time $t$ and the coefficients

$$1 - F = 0.4\exp(-k_{fast}{}^{*}t) + 0.4\exp(-k_{slow}{}^{*}t) + 0.2\exp(-k_{bridge}{}^{*}t) \qquad (3)$$

represent the proportion of each type of coordinated $H_2O$ or bridging $OH^-$ groups that undergo exchange. Each rate constant was found to be significantly different from the others, $k_{fast} > k_{slow} > k_{bridge}$, and convergence problems were not encountered during the data-fitting procedures. The distribution of residuals with time was random in all cases, indicating good fits to the data. A typical plot of the experimental data and fitted curve is shown in Figure 1.

The rate constants for the three reaction pathways ($k_{fast}$, $k_{slow}$, and $k_{bridge}$) are summarized in Table 2. At all the temperatures of this study, these rate constants were found to vary linearly with $1/[H^+]$ with a nonzero intercept and were independent of [dimer]; i.e., rate constants for runs carried out with [dimer] ~ 0.04 and 0.026 M were found to satisfy the same linear relationship. Figure 2 shows this dependence at 299 K. It can be concluded that the exchange reactions are first order in [dimer] and that the overall rate for each reaction pathway contains contributions from exchange on both protonated and monodeprotonated forms of dimer (see Scheme 1). Rate constants for each of these contributions were determined by linear least-squares analysis (eq 4) and are listed in Table 2.

$$k_i = k_i^{\,O} + k_i^{\,OH}/[H^+] \qquad (4)$$

Activation parameters were determined from the the temperature dependence of each rate constant and are listed in Table 3 together with recalculated values of the rate constant at 298 K. Given the complex nature of this water-exchange process, the uncertainties in each rate constant and activation parameter are quite acceptable.

## Discussion

The kinetics of water exchange on a Cr(III) hydrolytic oligomer, specifically the dimer, have been studied for the first time using established isotope-labeling techniques[8] in combination with mass spectrometric analyses. In development of a rate expression for fitting the isotope data, account was taken of the three oxygen environments that are present in the dimer: four *trans* and four *cis* to the bridging groups and two as bridging hydroxides. Thus, the data have been fitted to a rate expression which assumes that each of the types of oxygens exchange at different rates and that the pathways contribute 0.4, 0.4, and 0.2 to the overall process (Scheme 1).

The faster rate constant, $k_{fast}$, can be assigned to the exchange of water molecules *trans* to the bridging hydroxide (since this group has a greater *trans*-labilizing effect than water), and the slower rate constant, $k_{slow}$, to the exchange of water molecules *trans* to each other. These assignments are supported by previous studies on tetraamine complexes of the type *trans*-$[A_4MX(OH_2)]^{2+/3+}$, where X = $H_2O$, $Cl^-$, $OH^-$, etc., which have shown that the rate of water exchange is dramatically affected by the nature of the ligand *trans* to the bridging group.[18,19] For example, exchange was much faster for X = $Cl^-$ and $OH^-$ than for X = $H_2O$. Smaller but significant effects have also been observed for the corresponding *cis*-$[A_4MX(OH_2)]^{2+/3+}$ complexes.[18]

The third, and slowest, exchange process can be attributed to the loss of oxygen-18 label through the replacement of the bridging hydroxide groups. This occurs through a ring-opening, ring-closure mechanism (Scheme 1a) similar to that invoked in the interconversion between singly and doubly bridged forms of dimer (Scheme 2).[6] As in the case of the two faster exchange processes, fully protonated and monodeprotonated forms of doubly bridged dimer are expected to be involved in the process, in the pH range of this study. The ring-opening processes are likely to determine the rate of exchange of oxygen-18 label from the bridging groups, since it has been previously shown that these ring-opening processes are substantially slower than the corresponding ring-closure reactions.[6] Conversion of monodeprotonated singly bridged dimer (SBD) into doubly bridged dimer (DBD) is about 10 times faster than the reverse ring-opening process. A similar calculation shows that the conversion of doubly deprotonated SBD into monodeprotonated DBD is ca. 40 times faster than the reverse. The activation parameters for both bridge-exchange pathways are in good agreement with those obtained in studies of the dimer interconversion. For the pathway involving DBD, $\Delta H^* = 100 \pm 6$ kJ mol$^{-1}$ and $\Delta S^* = -10 \pm 18$ J K$^{-1}$ mol$^{-1}$ obtained here compare well with $\Delta H^* = 103$–$110$ kJ mol$^{-1}$ and $\Delta S^* = 15$–$36$ J K$^{-1}$ mol$^{-1}$ reported previously.[6] Given the slight differences in these activation parameters, a 2-fold difference in the rate constant at 298 K may be considered small ($k_{bridge}{}^{O} = 1.1 \times 10^{-5}$ s$^{-1}$ found here is in good agreement with $k_{-1} = 2.2 \times 10^{-5}$ s$^{-1}$ from interconversion studies[6]).

The rate of exchange of oxygen-18 label in monodeprotonated DBD ($k_{bridge}{}^{OH}/K_{a1}(\mathrm{DBD}) = 1.5 \times 10^{-3}$ s$^{-1}$) is a measure of the rate of ring opening within monodeprotonated DBD, which can be compared with estimates from interconversion data ($k_{-2} = 2.1 \times 10^{-4}$ s$^{-1}$ was calculated using eq 5, where $k_1$ and $k_2$ are the rates

$$k_{-2} = k_2K_{a2}(\mathrm{SBD})\,k_{-1}/K_{a1}(\mathrm{DBD})\,k_1 \qquad (5)$$

of ring closure within singly and doubly deprotonated SBD, respectively, $K_{a1}$(DBD) and $K_{a2}$(SBD) are the first acid dissociation constant of DBD and second acid dissociation constant of SBD, respectively, and $k_{-1}$ is the rate of conversion of DBD into monodeprotonated SBD). Although the indirect method of estimating $k_{-2}$ results in relatively poor agreement with the oxygen-18-labeling data, the values of the activation parameters obtained by either method are remarkably high. The parameter for $k_{bridge}{}^{OH}/K_{a1}(\mathrm{DBD})$ determined from labeling studies are $\Delta H^* = 127 \pm 4$ kJ mol$^{-1}$ and $\Delta S^* = 125 \pm 12$ J K$^{-1}$ mol$^{-1}$, while those for $k_{-2}$ estimated from interconversion data are $\Delta H^* = 143 \pm 5$ kJ mol$^{-1}$ and $\Delta S^* = 166 \pm 15$ J K$^{-1}$ mol$^{-1}$ (see Table 3). These values, and in particular $\Delta S^*$, are much higher than those reported for ring opening within fully protonated DBD (see parameters for $k_{-1}$ and $k_{bridge}$ in Table 3). They indicate that deprotonation of the dimer leads to a substitution mechanism with more dissociative character.

The rates of water exchange on fully protonated dimer (OH/Cr = 1) are 28 and 150 times faster than exchange on $Cr^{3+}$ (OH/Cr = 0) for waters *cis* and *trans* to the hydroxide bridges, respectively. Similarly, the two corresponding rates of exchange are 27 and 70 times faster on monodeprotonated dimer (OH/Cr = 1.5) than on $CrOH^{2+}$. These data suggest that the degree of condensation of the oligomer is one important factor which will determine the rates of water exchange on that oligomer. Apart from bridging hydroxide groups that may be present in the

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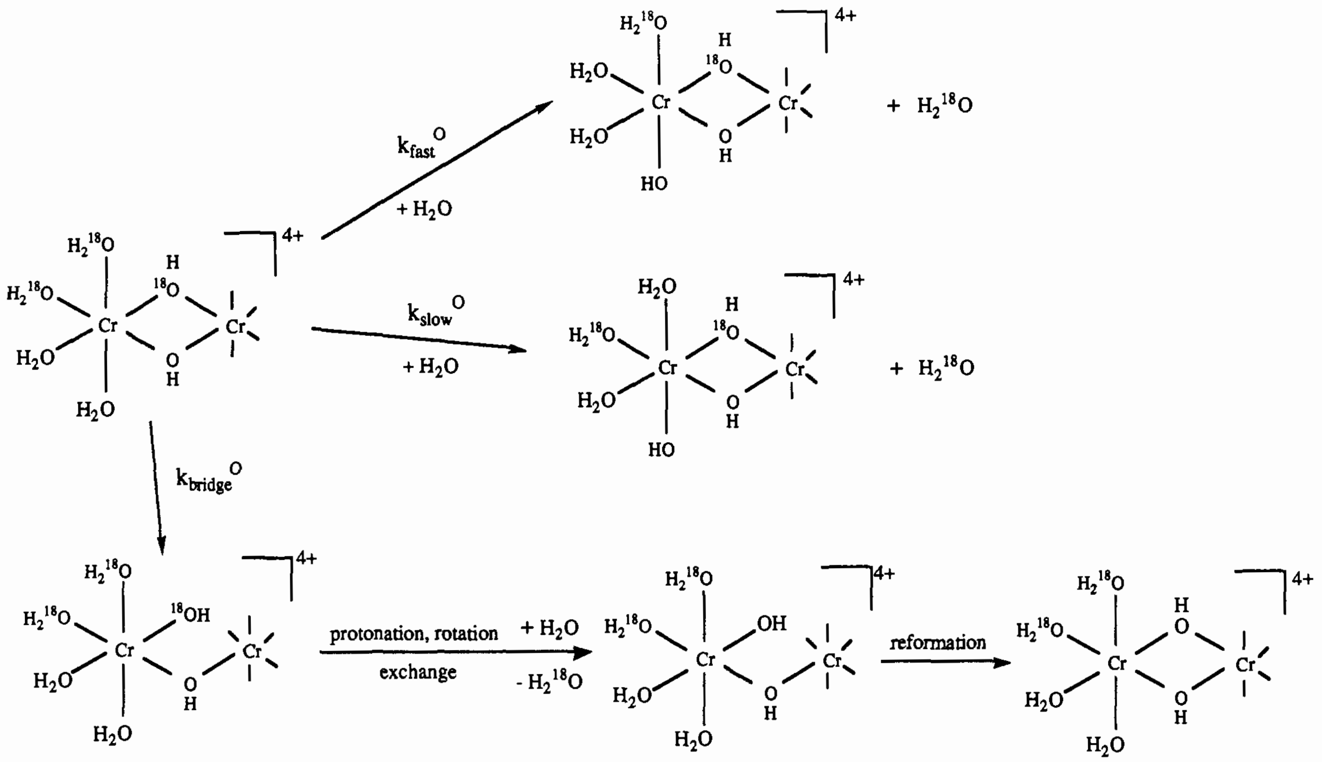
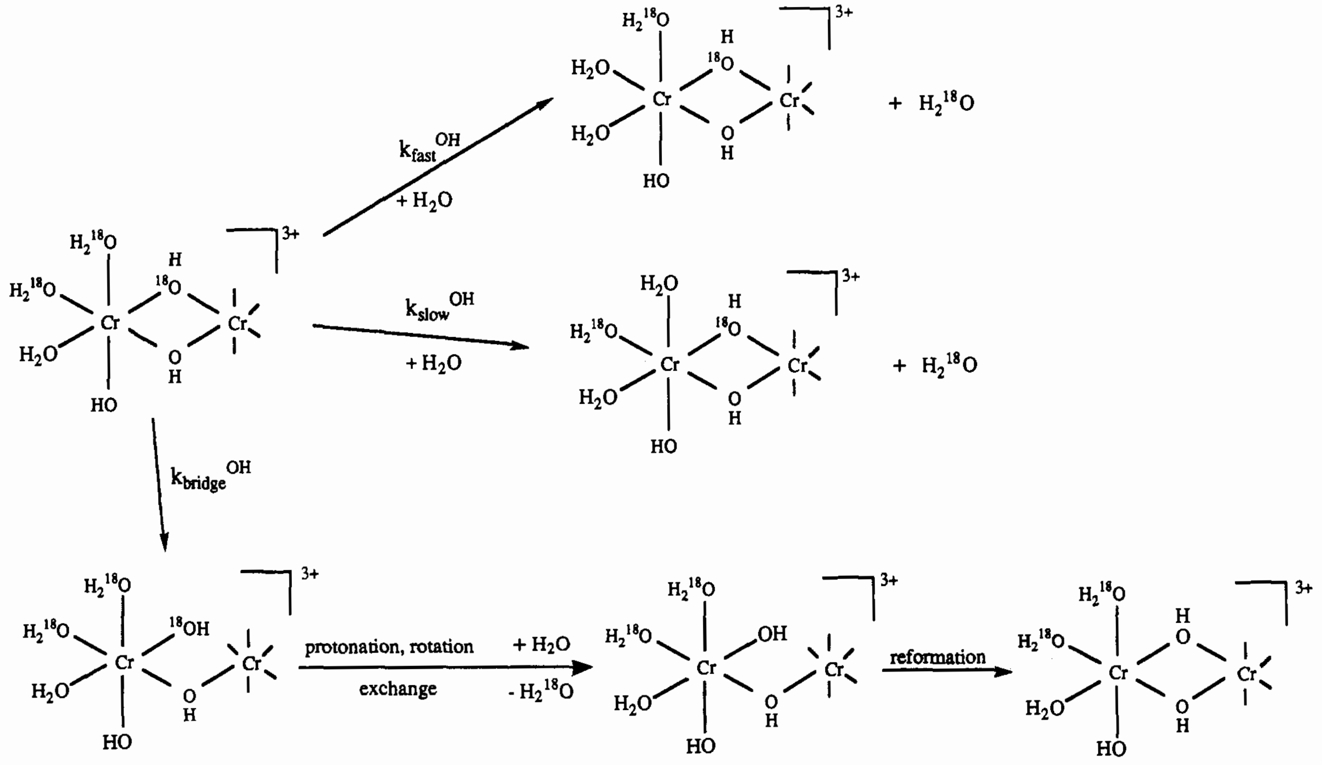
**Scheme 1.** Water-Exchange Pathway[a]

(a) On the Fully Protonated Cr(III) Dimer



(b) On the Monodeprotonated Cr(III) Dimer



[a] *Water molecules occupy the unlabeled coordination sites around the Cr(III).*

oligomer, deprotonation of the oligomer or ion has a considerable influence on the rates of water exchange. In the case of dimer, deprotonation has been found to enhance the rate of water substitution at both positions *cis* and positions *trans* to the bridging groups. It is worthwhile noting that the rates of water exchange on the Cr(III) dimer are in fact very similar to that reported for $CrOH^{2+}$ (OH/Cr = 1 for both these ions) and much faster than the rate of exchange on $Cr^{3+}$ (see Table 4). This observation indicates that the bridging OH groups are comparable to terminal OH groups in terms of their effect on the rate of substitution at Cr(III).

A broad correlation exists between exchange rate and OH/Cr ratios of the oligomers or ions undergoing exchange (Figure 3) which is relatively little affected by whether the OH groups occupy bridging or terminal positions. Thus, the increases in lability that result from successive deprotonations (and in the case of

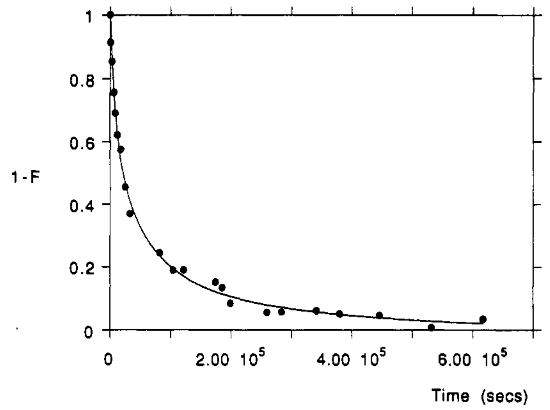


**Figure 1.** Typical plot of the decrease in the fraction of oxygen-18 label on the Cr(III) dimer, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O_4)]^{4+}$, with time ([dimer] ~0.026 M, $[H^+] = 0.059$ M, $T = 287.2$ K): solid circles, experimental values; solid line, fitted curve based on eq 3. The rate constants are given in Table 2.

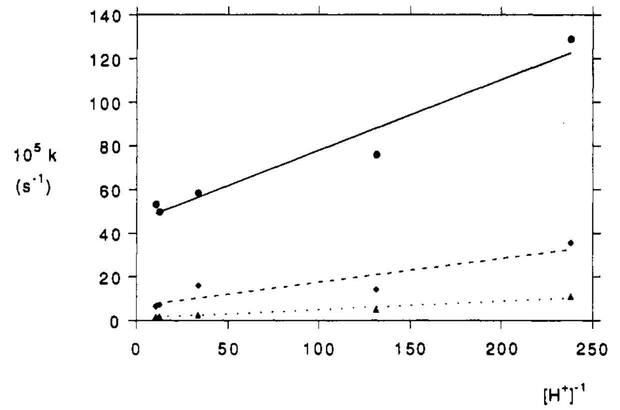


**Figure 2.** Inverse acid dependence of the rate constants for each of the three pathways involved in the release of oxygen-18 label from Cr(III) dimer at 299 K: ●, $k_{fast}$; ◆, $k_{slow}$; ▲, $k_{bridge}$.

**Table 3.** Activation Parameters and Rate Constants at 298 K for the Water-Exchange and Bridge-Cleavage Processes on Fully Protonated and Monodeprotonated Cr(III) Dimer

| parameter | $10^5$ × rate const | $\Delta H^*$ (kJ $mol^{-1}$) | $\Delta S^*$ (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|
| $k_{fast}$ ($s^{-1}$) | 35.8 ± 3.3 | 80.8 ± 8.0 | –40 ± 26 |
| $k_{fast}{}^{OH}$ ($M^{-1}$ $s^{-1}$) | 0.2601 ± 0.0066 | 156.7 ± 2.3 | 173.8 ± 7.5 |
| $k_{fast}{}^{OH}/K_{a_1}$ ($s^{-1}$) | 1240 ± 55 | 125.3 ± 3.9 | 139 ± 13 |
| $k_{slow}$ ($s^{-1}$) | 6.60 ± 0.61 | 97 ± 10 | 0 ± 32 |
| $k_{slow}{}^{OH}$ ($M^{-1}$ $s^{-1}$) | 0.1048 ± 0.0050 | 114.2 ± 4.2 | 23 ± 14 |
| $k_{slow}{}^{OH}/K_{a1}$ ($s^{-1}$) | 475 ± 33 | 82.8 ± 5.8 | –12 ± 19 |
| $k_{bridge}$ ($s^{-1}$) | 1.14 ± 0.059 | 99.5 ± 5.6 | –10 ± 18 |
| $k_{bridge}{}^{OH}$ ($M^{-1}$ $s^{-1}$) | 0.030 94 ± 0.000 50 | 158.1 ± 1.9 | 160.8 ± 6.5 |
| $k_{bridge}{}^{OH}/K_{a1}$ ($s^{-1}$) | 146.8 ± 5.2 | 126.7 ± 3.5 | 125 ± 12 |
| $K_{a1}$ (M) | 21.07 ± 0.41 | 31.4 ± 1.6 | 35.1 ± 5.3 |
| $k_{-1}{}^{a}$ ($s^{-1}$) | 2.2 ± 0.1 | 110 ± 5 | 35 ± 16 |
| $k_2{}^{a}$ ($s^{-1}$) | 1140 ± 20 | 67 ± 2 | –57 ± 6 |
| $k_{-2}{}^{a}$ ($s^{-1}$) | 21 ± 2 | 143 ± 5 | 166 ± 15 |

[a] Data taken from ref 6.

**Scheme 2**

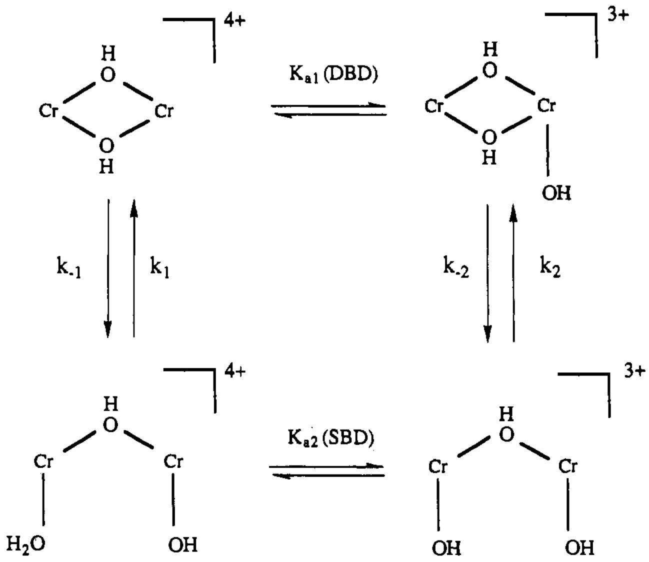


**Table 4.** Variation in the Rates of Hydrolytic Processes with OH/Cr ratios of Oligomers and Ions at 298 K and $I = 1.0$ M

| reactant(s) | OH/Cr | $10^5$ × rate ($s^{-1}$) | ref |
|---|---|---|---|
| 1. Water-Exchange Processes | | | |
| $Cr^{3+}$ | 0 | 0.24 | 8 |
| $CrOH^{2+}$ | 1 | 18 | 8 |
| $[Cr(\mu\text{-}OH)_2Cr]^{4+}$ | | | |
| trans μ-OH | 1 | 36 | this work |
| cis μ-OH | 1 | 6.6 | this work |
| $[Cr(\mu\text{-}OH)_2CrOH]^{3+}$ | | | |
| trans μ-OH | 1.5 | 1260 | this work |
| cis μ-OH | 1.5 | 490 | this work |
| 2. Intramolecular Bridge Formation Processes | | | |
| $[Cr(\mu\text{-}OH)Cr]^{5+}$ (→DBD + $H^+$) | 0.5 | 10 | 6 |
| $[Cr(\mu\text{-}OH)CrOH]^{4+}$ (→DBD) | 1.0 | 40 | 6 |
| $[HOCr(\mu\text{-}OH)CrOH]^{3+}$ (→DBD-H) | 1.5 | 1140 | 6 |
| $[Cr_4(OH)_6]^{6+}$ (→closed tetramer) | 1.5 | 8700 | 5 |
| $[Cr_4(OH)_7]^{5+}$ (→closed tetramer) | 1.75 | 24000 | 5 |
| 3. Sulfate Anation | | | |
| $Cr^{3+}$ | 0 | 1.1 | 23 |
| $CrOH^{2+}$ | 1 | 61 | 23 |
| $[Cr(\mu\text{-}OH)_2Cr]^{4+}$ | 1 | 35 | 24 |
| $[Cr(\mu\text{-}OH)_2CrOH]^{3+}$ | 1.5 | 1700 | 24 |

oligomers, also from increases in the degree of condensation of oligomers) can convert the normally quite inert $Cr^{3+}$ and Cr(III) oligomers into relatively labile ions. For example, exchange rates of about 0.1, 100, and $10^4$ $s^{-1}$ can be interpolated for ions with OH/Cr ratios of 2, 3, and 4, respectively. Although direct measurements on species with high OH/Cr ratios are extremely difficult because of fast, competing polymerization rections, the proposed rate enhancements are supported by qualitative observations. For example, in excess base, where species such as $[Cr(OH)_4(OH_2)_2]^-$ (OH/Cr = 4) are likely to exist, $Cr^{3+}$ is rapidly converted into large polynuclear species with little or no mononuclear Cr(III) species being present immediately after mixing.[20] In the pH range 5–6, the aging of Cr(III) "active " hydroxides has been shown to occur via a solution mechanism involving cationic species of varying degree of deprotonation. The observed increase in aging rate with oligomer nuclearity (i.e. monomer < dimer < trimer)[20-22] can be attributed to an increase in lability of species present in solution which, in turn, can be related to an increase in the average OH/Cr ratio of species present in solution with oligomer nuclearity.

A correlation also exists between the rates of intramolecular bridge formation processes and anation reactions of Cr(III) oligomers and OH/Cr ratios (Figure 3).[5,6] Moreover, both the absolute rates and the variations in rates for these two types of processes with OH/Cr ratio match closely those found for water-exchange rates, even though there are subtle variations in

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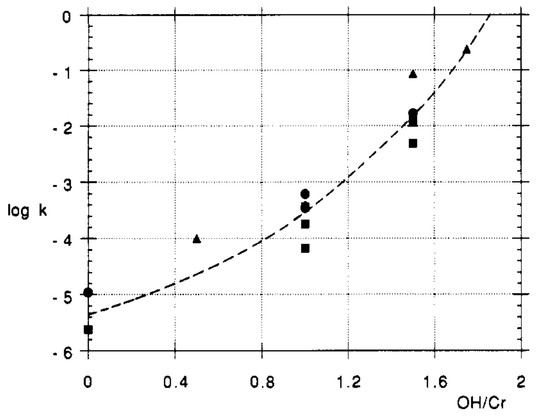

**Figure 3.** Correlation between rate constants for various hydrolytic processes and OH/Cr ratios of the oligomers or ions undergoing reaction at 298 K: ■, water exchange; ▲, intramolecular bridge formation; ●, sulfate anation. The curve is included to highlight the increase in reactivity with OH/Cr ratio.

nucleophile, H-bond stabilization, and ion pairing. This further strenghtens the view that, at least for the nucleophiles studied to present time, labilization of the primary coordination sphere of Cr(III) overrides changes in the nucleophilic character of the entering ligand.

The activation parameters (Table 3) for the exchange processes involving fully protonated dimer are similar and seem to indicate a common reaction mechanism with more associative than dissociative character but with significant bond breaking in the transition state. For water exchange on monodeprotonated dimer, the activation parameters (particularly $\Delta S^*$) support a similar mechanism for substitution at positions *cis* to the bridging hydroxides. On the other hand, for water exchange on monodeprotonated dimer at positions *trans* to the bridging hydroxides, an increase in the dissociative nature of substitution is indicated by the much more positive values of $\Delta H^*$ and $\Delta S^*$ (see Table 3).

In summary, the water-exchange data indicate that bridging and terminal OH groups have similar effects on substitution rates and that deprotonation of the Cr(III) dimer causes considerable labilization of aquo groups regardless of whether they are *cis* or *trans* to the bridging hydroxides. The observed rate enhancements parallel closely those observed in substitution processes associated with the intramolecular rearrangement and sulfate anation of Cr(III) oligomers, and there is a good correlation between substitution rates and the degree of deprotonation of the Cr(III) species undergoing substitution. For these systems, it can be concluded that labilization of the primary coordination sphere of Cr(III) by both bridging and terminal hydroxide groups has a greater effect on substitution rates than changes in the entering nucleophile.

**Acknowledgment.** Financial support in the form of an Australian Postgraduate Research Award to S.J.C. and equipment and research grants from the Natural Sciences and Engineering Research Council of Canada to H.R.K. and T.W.S. is gratefully acknowledged.