

taken for granted. The ratio of cross-reaction rate constants, $R = k(\text{Ru}(\text{NH}_3)_6^{2+})/k(\text{Cr}^{2+})$, offers one criterion for distinguishing between oxidants attacked by $\text{Cr}^{2+}(\text{aq})$ through inner- and outer-sphere pathways. If electrostatic work terms are neglected, the relationship of eq 8³⁵ (for 25 °C) is predicted for outer-sphere

$$R = \left[\frac{k_{22}(\text{Ru}(\text{NH}_3)_6^{3+/2+})}{k_{22}(\text{Cr}(\text{H}_2\text{O})_6^{3+/2+})} \exp(38.94(\Delta E')) \right]^{1/2} \quad (8)$$

reactions, where the k_{22} 's are self-exchange electron-transfer rate constants and $\Delta E'$ is the difference between $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ standard reduction potentials (-0.46 V). Since direct measurements of the $\text{Cr}(\text{H}_2\text{O})_6^{3+/2+}$ ($\leq 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$)³⁶ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ ($8.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$)¹⁵ k_{22} values are available, an outer-sphere R on the order of ≥ 1 , independent of oxidant, may be predicted. It should be noted that $R \ll 1$ may be anticipated in cases where the reactivity of Cr^{2+} is promoted by an effective bridging ligand.³⁷ The experimental R (aquo dimer) (16) is in reasonable agreement with this estimation and analogous ratios from unambiguously outer-sphere oxidants such as $\text{Co}(\text{NH}_3)_6^{3+}$ (11)³⁷ and $\text{Ru}(\text{NH}_3)_6^{3+}$ (4),³⁷ supporting the assignment of the Cr^{2+} -aquo dimer reaction to the outer-sphere class. Indeed, the absence of an $[\text{H}^+]^{-1}$ -dependent term in the rate law rules out a hydroxo-bridged inner-sphere intermediate in this reaction. Outer-sphere reactivity appears likely in the ascorbic acid-aquo dimer reaction as well, considering that $(\text{Cr}(\text{H}_2\text{O})_5)_2\text{O}^{4+}$ water

exchange is not known to occur on the fast time scale of the catalyzed cleavage reaction.¹⁷

From the rate constant and standard cell potential of an outer-sphere cross-reaction, the Marcus relationship may be used to calculate an apparent self-exchange electron-transfer rate constant for one redox partner (k_{11}) given that of the other (k_{22}).³⁸ This calculation yields $(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+/3+}$ k_{11} estimates of ≥ 1.3 and $15 \text{ M}^{-1} \text{ s}^{-1}$ from aquo dimer reductions by Cr^{2+} ^{13,36} and $\text{Ru}(\text{NH}_3)_6^{2+}$,^{15,20} respectively, including the f term but neglecting small electrostatic work corrections. Although this k_{11} calculation is only approximate at best, an impressive 10^6 -fold increase in intrinsic electron-transfer reactivity (8 kcal/mol decrease in ΔG^\ddagger) is apparent upon comparison with the parent $\text{Cr}(\text{H}_2\text{O})_6^{3+/2+}$ couple ($k_{11} \leq 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 21 \text{ kcal/mol}$, $\Delta S^\ddagger = -8 \text{ eu}$).³⁶ This increase confirms the π^n character of the aquo dimer redox orbital, which should be reflected in a much smaller Franck-Condon inner-sphere reorganization barrier than is required for electron transfer involving the e_g (σ^*) orbital of $\text{Cr}(\text{H}_2\text{O})_6^{3+/2+}$.³⁸ Such benefit of electron acceptance into an essentially nonbonding orbital is also seen in ΔH^\ddagger of the $\text{Cr}^{2+}-(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}$ reaction, smaller by 15 kcal/mol than that of the analogous $\text{Cr}(\text{H}_2\text{O})_6^{3+/2+}$ self-exchange electron-transfer process.

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Registry No. $(\text{H}_2\text{O})_5\text{CrOCr}(\text{H}_2\text{O})_5^{4+}$, 73347-70-3; $(\text{H}_2\text{O})_4\text{Cr}(\text{OH})(\text{OC}_6\text{H}_4\text{OH})\text{Cr}(\text{H}_2\text{O})_4^{4+}$, 73360-43-7; $(\text{H}_2\text{O})_5\text{CrOCr}(\text{H}_2\text{O})_5^{3+}$, 97644-50-3; $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, 14873-01-9; $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, 20574-26-9; $\text{Ru}(\text{NH}_3)_6^{2+}$, 19052-44-9; H_2A , 50-81-7; HA^- , 299-36-5; Ce , 7440-45-1; carbon, 7440-44-0.

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Anion and Cation Effects on the Acid Hydrolysis Rate of the (μ -Oxo)bis(pentaaquochromium(III)) Ion

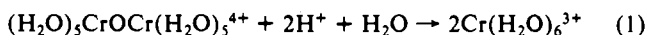
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Anion (ClO_4^- , Cl^- , Br^-) and cation ($\text{Cr}(\text{H}_2\text{O})_6^{3+}$) catalysis of oxo-bridge cleavage in the (μ -oxo)bis(pentaaquochromium(III)) ion (aquo dimer) has been examined. Increases in pseudo-first-order acid hydrolysis rate constants (k_{obsd}) caused by LiClO_4 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Al}(\text{ClO}_4)_3$, and $\text{Fe}(\text{ClO}_4)_3$ in HClO_4 media at 25 °C are entirely attributable to perchlorate ion, according to $k_{\text{obsd}} = k_0 + k'_1[\text{H}^+] + ab[\text{H}^+][\text{ClO}_4^-]/(1 + b[\text{H}^+])$, where $k_0 = 5 \times 10^{-5} \text{ s}^{-1}$, $k'_1 = 1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, $a = 2.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and $b = 1.6 \text{ M}^{-1}$. The rate expressions pertaining to Cl^- (parameters c and d analogous to a and b , respectively) and Br^- (parameters e and f) exactly parallel that of ClO_4^- ; $c = 2.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $d = 1.2 \text{ M}^{-1}$, $e = 3.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and $f = 2.0 \text{ M}^{-1}$. Anation of $\text{Cr}(\text{III})$ is not responsible for oxo-bridge cleavage, as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ was the sole hydrolysis product under conditions where the chloride-assisted pathway contributed 83% of the overall reaction. Since catalytic activity appears to be governed by anion charge, the proposed mechanism involves bending of the initially linear $\text{Cr}-\text{O}-\text{Cr}$ unit within an ion pair, providing electrostatic anion-incipient dipole stabilization to compensate for the loss of π bonding. Further lowering of the transition-state energy would then be achieved by protonation of an emergent lone pair on oxygen. This improved understanding of anion-assisted aquo dimer hydrolysis now permits the incorporation of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ into the rate law: $k_{\text{obsd}} = k_0 + k'_1[\text{H}^+] + ab[\text{H}^+][\text{ClO}_4^-]/(1 + b[\text{H}^+]) + [\text{Cr}(\text{H}_2\text{O})_6^{3+}]^2(k_2 + k_3[\text{H}^+])$, where $k_2 = 1 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ and $k_3 = 9.0 \times 10^{-2} \text{ M}^{-4} \text{ s}^{-1}$ (25 °C, $\text{HClO}_4/\text{Cr}(\text{ClO}_4)_3$ medium). A bonding interaction between the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ t_{2g} (π^n) and approximately nonbonding e_g ($(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}$) orbitals, accompanied by protonation of the oxo bridge, is proposed to account for the distinctive catalytic activity of the chromic ion. Unexpectedly greater resistance of the oxo bridge to acid hydrolysis in the presence of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and especially $\text{Ce}(\text{H}_2\text{O})_6^{3+}$ also is reported.

Introduction

The acid hydrolysis reaction (eq 1) of the (μ -oxo)bis(pentaaquochromium(III)) ion (aquo dimer) is accelerated by H^+ and many salts, including alkali-metal, alkaline-earth-metal, and transition-metal perchlorates.^{1,2} The rate law of eq 2 was es-



established for this reaction in our initial study¹ at constant ionic strength of 1.0 M ($\text{HClO}_4/\text{LiClO}_4$); $k_0 = 5 \times 10^{-5} \text{ s}^{-1}$ and $k_1 = 1.61 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. Protonation of the weakly basic bridging oxygen atom before or during the rate-limiting step was

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$$-d[(\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}]/dt = (k_0 + k_1[\text{H}^+])[(\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}] \quad (2)$$

proposed to account for the predominant k_1 hydrolysis pathway. More recently, we have shown that both weak and strong reducing agents, including ascorbic acid, $\text{Ru}(\text{NH}_3)_6^{2+}$, and $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, strongly catalyze aquo dimer hydrolysis through electron transfer to the essentially nonbonding e_g molecular orbital of the linear ($\text{Cr}-\text{O}-\text{Cr}$), binuclear complex.³

Salt effects on the aquo dimer hydrolysis rate are the primary focus of this paper. Our initial motivation in this area was the unexpected discovery that $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ exerts a substantial autocatalytic effect on $(\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}$ hydrolysis in spite of the very slow rate of water displacement from the first coordination sphere of the monomer chromic ion.^{1,2} Considering the difficulty of separately evaluating kinetic ionic strength and specific cation effects,¹ we report here the influence of many diverse metal salts on the aquo dimer hydrolysis rate. Having realized that ClO_4^- does not fulfill its usual, noncoordinating role⁴ in the present context, we have now incorporated this species into the rate law and characterized other anion-catalyzed (Cl^- , Br^- , HSO_4^- , SO_4^{2-}) aquo dimer hydrolysis pathways. Considering the potential roles of anions as nucleophiles and, in the extreme, reducing agents, mechanistic parallels between reductant- and anion-assisted hydrolysis pathways may be anticipated. Finally, a deeper insight into $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ autocatalysis is presented in view of these anion effects. Comparative studies of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, and $\text{Ce}^{3+}(\text{aq})$ influences on $(\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}$ reactivity were also useful in this regard.

Experimental Section

Materials and Solution Preparation. Reagent grade ammonium or perchlorate salts, including $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, NaClO_4 , and LiClO_4 (G. F. Smith), NH_4Cl , NH_4Br , NH_4I , NH_4SCN , and NH_4NO_3 (Fisher), NH_4HSO_4 (Baker), and NH_4ClO_4 (Fluka) were used as received. Triply distilled water was used throughout. Ammonium salt solutions could be prepared by weight, and $[\text{ClO}_4^-]$ in metal perchlorate stock solutions was assayed with an Orion perchlorate-sensitive electrode, as previously described.¹ SP-Sephadex C-25 resin (Na^+ form) was used in cation-exchange experiments. For kinetic measurements, $(\text{H}_2\text{O})_5\text{CrOCr}(\text{H}_2\text{O})_5^{4+}$ was generated in situ from the oxidation of chromatographically pure $(\text{H}_2\text{O})_4\text{Cr}(\text{OH})(\text{OC}_6\text{H}_4\text{OH})\text{Cr}(\text{H}_2\text{O})_4^{4+}$ by stoichiometric Br_2 .¹ Direct conversion of this precursor into the aquo dimer was accomplished rapidly by simply mixing with $\text{Ce}(\text{ClO}_4)_3$.²

Hydrogen ion concentrations were calculated in most cases from the dilution of a HClO_4 stock solution, but the ionization of HSO_4^- must also be taken into account in $\text{NH}_4\text{HSO}_4/\text{HClO}_4$ mixtures. This HSO_4^- contribution to $[\text{H}^+]$ at a particular ionic strength and perchloric acid concentration was computed by using a $K_a(\text{HSO}_4^-)$ value extrapolated from a linear ionization constant-ionic strength correlation.^{5,6}

Kinetic Measurements. Kinetic measurements were initiated on aerobic solutions in capped 1-cm cells immediately following the Br_2 addition, which generates the reactant. Decay of $(\text{H}_2\text{O})_5\text{CrOCr}(\text{H}_2\text{O})_5^{4+}$ (initial concentration 0.50 mM) was followed at 443 nm on Perkin-Elmer Lambda 5 or Spectronic 100 spectrophotometers, with cell compartments thermostated at 25.0 °C.¹ Rate data (256 absorbance-time points per run) were transmitted to an Apple II Plus computer, stored on floppy disks, and quantitatively interpreted through an A/D interface, as previously described.³ Observed first-order rate constants (k_{obsd}), reported as the mean of at least three trials, were calculated as the linear least-squares slopes of $\ln(A_t - A_\infty)$ vs. time fits with correlation coefficients of ≥ 0.99 in the post-induction interval, where the reactant is fully generated from $(\text{H}_2\text{O})_4\text{Cr}(\text{OH})(\text{OC}_6\text{H}_4\text{OH})\text{Cr}(\text{H}_2\text{O})_4^{4+}$ and Br_2 .¹

Results

Perchlorate-Catalyzed Aquo Dimer Hydrolysis. Anticipating specific cation catalysis analogous to that of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, we studied the effects of variable LiClO_4 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, and $\text{Al}(\text{ClO}_4)_3$ concentrations on the aquo dimer

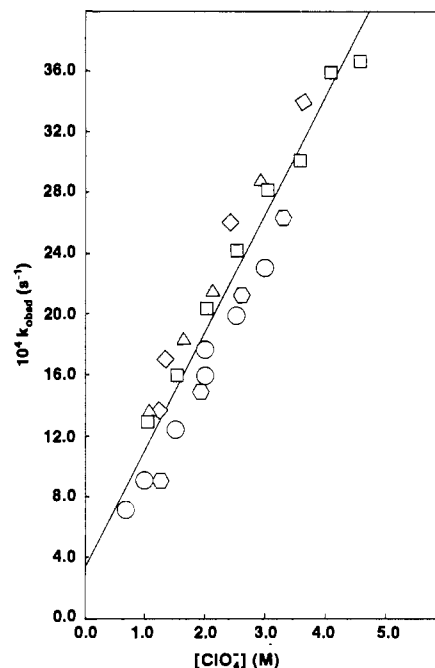


Figure 1. Effect of metal perchlorates on the aquo dimer acid hydrolysis rate at 25.0 °C and $[\text{HClO}_4] = 0.550 \text{ M}$: LiClO_4 (○); NaClO_4 (□); $\text{Mg}(\text{ClO}_4)_2$ (○); $\text{Zn}(\text{ClO}_4)_2$ (Δ); $\text{Al}(\text{ClO}_4)_3$ (◇).

hydrolysis rate (25 °C), while holding $[\text{HClO}_4]$ constant at 0.550 M. Upon examining the data, however, it was seen that k_{obsd} correlates most simply with perchlorate concentration, independent of the cation, in the $0.690 \leq [\text{ClO}_4^-] \leq 4.59 \text{ M}$ range. Figure 1 shows, in fact, that eq 3 quantitatively describes all of these

$$k_{\text{obsd}} = k + k'[\text{ClO}_4^-] \quad (3)$$

salt-effect results remarkably well, considering that constant ionic strength was not maintained. This relationship certainly is not as expected for a simple ionic strength effect on a bimolecular activation process involving only H^+ and $(\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}$. Although rigorously applicable in a quantitative sense only at low ionic strengths, eq 4 correctly predicts that the rate constant of

$$\log k = \log k_0 + 0.509Z_A Z_B I^{1/2} / (1 + I^{1/2}) \quad (4)$$

a second-order ionic reaction in water at 25 °C should approach independence on I at the large limiting ionic strengths in excess of 5 M employed in these studies; k_0 = rate constant extrapolated to zero ionic strength and Z_A and Z_B are ionic charges of reactants A and B.⁷

We conclude, therefore, that the rate law of eq 2, which pertains at constant $I = [\text{ClO}_4^-] = 1.0 \text{ M}$, must be expanded to explicitly account for the influence of perchlorate ion on the aquo dimer hydrolysis rate. Since ClO_4^- will now be included in the rate law, the maintenance of constant ionic strength with salts of other potentially catalytic anions clearly would be self-defeating. The intrinsic effect of ionic strength alone on the aquo dimer hydrolysis rate remains, therefore, a necessarily elusive quantity. Fortunately, this intrinsic ionic strength effect, although not entirely negligible, can now be invoked to quantitatively understand anion-promoted aquo dimer hydrolysis.

The kinetic perchlorate effect was further explored in $\text{Al}(\text{ClO}_4)_3/\text{HClO}_4$ solutions with $0.428 \leq [\text{ClO}_4^-] \leq 3.63 \text{ M}$ and $0.50 \leq [\text{H}^+] \leq 1.02 \text{ M}$ (Table I). At constant $[\text{H}^+] = 0.100, 0.300, 0.550, \text{ and } 1.00 \text{ M}$, the $[\text{ClO}_4^-]$ dependence of k_{obsd} is as described by eq 3. The full rate law (eq 5) was then determined

$$k_{\text{obsd}} = k_0 + k'_1[\text{H}^+] + \frac{ab[\text{H}^+][\text{ClO}_4^-]}{1 + b[\text{H}^+]} \quad (5)$$

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Table I. Perchlorate Effect on the Aquo Dimer Hydrolysis Rate^a

[H ⁺], M	[ClO ₄ ⁻], M	10 ³ k _{obsd} , s ⁻¹	10 ³ k _{calcd} , ^b s ⁻¹
0.100	0.428	0.22 (0.01)	0.18
0.100	0.818	0.33 (0.01)	0.29
0.100	1.21	0.45 (0.02)	0.40
0.100	1.60	0.63 (0.03)	0.51
0.300	0.980	0.82 (0.02)	0.73
0.300	1.58	1.2 (0.1)	1.1
0.300	2.18	1.6 (0.1)	1.5
0.300	3.38	2.5 (0.1)	2.3
0.550	1.23	1.4 (0.1)	1.4
0.550	1.83	1.7 (0.1)	1.9
0.550	2.43	2.7 (0.1)	2.4
0.550	3.63	3.4 (0.1)	3.6
1.00	1.47	2.1 (0.3)	2.0
1.00	1.86	2.4 (0.1)	2.5
1.00	2.25	3.0 (0.1)	3.0
1.00	2.64	3.3 (0.1)	3.5
1.02	1.12	1.6 (0.1)	1.6
0.857	1.00	1.5 (0.1)	1.4
0.780	1.00	1.3 (0.1)	1.3
0.643	1.00	1.1 (0.1)	1.1
0.549	1.00	0.91 (0.05)	1.0
0.429	1.00	0.74 (0.03)	0.92
0.326	1.00	0.55 (0.01)	0.78
0.214	1.00	0.45 (0.01)	0.59
0.102	1.00	0.23 (0.02)	0.35
0.050	1.00	0.10 (0.01)	0.20

^aAt 25.0 °C. HClO₄/Al(ClO₄)₃ medium except for constant [ClO₄⁻] = 1.00 M runs (HClO₄/LiClO₄) from ref 1. Average deviations from the mean shown in parentheses. ^bRate constant calculated from eq 5 by using nonlinear least-squares rate parameters (see text).

from variations in k and k' with $[H^+]$. Thus, k vs. $[H^+]$ and k^{-1} vs. $[H^+]^{-1}$ correlations were found to be linear, yielding initial estimates of the parameters k_0 , k'_1 , a , and b for subsequent nonlinear least-squares refinement.⁸ Nonlinear least-squares rate parameters derived from the fit of data in Table I to eq 5, including previously reported $I = 1.0$ M (HClO₄/LiClO₄) results, are $k_0 = (5 \pm 2) \times 10^{-5} \text{ s}^{-1}$, $k'_1 = (1 \pm 1) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, $a = (2.0 \pm 0.3) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and $b = 1.6 \pm 0.4 \text{ M}^{-1}$. The quality of this fit is quite good, as judged by a comparison of k_{obsd} values with rate constants calculated on the basis of the least-squares parameters (k_{calcd} , Table I). It is now clear that the k_1 term (eq 2) discovered in our original work at constant ionic strength of 1.0 M actually corresponds to the sum of the second and third terms of the expanded rate law (eq 5), such that $k_1 = k'_1 + ab[\text{ClO}_4^-]/(1 + b[H^+])$. The major pathway dependent upon both $[H^+]$ and $[\text{ClO}_4^-]$ carries 89% of the hydrolysis reaction at $[H^+] = [\text{ClO}_4^-] = 1.0$ M.

Catalysis of Aquo Dimer Hydrolysis by Chloride, Bromide, and Sulfate Ions. The effects of chloride and bromide ions on the aquo dimer hydrolysis rate were also studied without maintaining constant ionic strength in NH₄Cl/HClO₄ or NH₄Br/HClO₄ media (Tables II and III). The reactivity influences of Cl⁻ and Br⁻ directly parallel and are additive to that of ClO₄⁻. Specifically, at constant $[H^+] = [\text{ClO}_4^-]$, the relationship $k_{\text{obsd}} = k + k[X^-]$ describes the modest influence of $X^- = \text{Cl}^-$, Br⁻ on the hydrolysis rate. Considering H⁺, ClO₄⁻, Cl⁻, and Br⁻ effects simultaneously, eq 6 satisfactorily fits all of the rate constants in Tables I-III.

$$k_{\text{obsd}} = k_0 + k'_1[H^+] + \frac{ab[H^+][\text{ClO}_4^-]}{1 + b[H^+]} + \frac{cd[H^+][\text{Cl}^-]}{1 + d[H^+]} + \frac{ef[H^+][\text{Br}^-]}{1 + f[H^+]} \quad (6)$$

The small k_0 term was fixed at $5 \times 10^{-5} \text{ s}^{-1}$ in the nonlinear least-squares fit of these data to eq 6, treating only k'_1 , a , b , c , d , e , and f as variables in the optimization routine. Initial estimates

Table II. Chloride Effect on the Aquo Dimer Hydrolysis Rate^a

[H ⁺], M	[ClO ₄ ⁻], M	[Cl ⁻], M	10 ³ k _{obsd} , s ⁻¹	10 ³ k _{calcd} , ^b s ⁻¹
0.100	0.174	4.00	1.1 (0.1)	1.2
0.100	0.174	2.50	0.80 (0.04)	0.76
0.100	0.174	2.00	0.60 (0.10)	0.63
0.100	0.174	1.00	0.35 (0.03)	0.37
0.100	0.174	0.500	0.24 (0.01)	0.24
0.300	0.374	4.00	2.9 (0.1)	2.9
0.300	0.374	3.00	2.4 (0.1)	2.3
0.300	0.374	2.50	1.8 (0.1)	1.9
0.300	0.374	2.00	1.6 (0.1)	1.6
0.300	0.374	1.00	1.1 (0.1)	0.97
0.300	0.374	0.500	0.84 (0.06)	0.65
0.550	0.624	4.00	4.8 (0.1)	4.5
0.550	0.624	3.00	3.7 (0.1)	3.6
0.550	0.624	2.50	2.8 (0.1)	3.1
0.550	0.624	2.00	2.3 (0.1)	2.6
0.550	0.624	1.00	1.6 (0.1)	1.7
0.550	0.624	0.500	1.3 (0.1)	1.2
0.800	0.874	2.50	3.9 (0.1)	4.1
0.800	0.874	2.00	3.3 (0.1)	3.5
0.800	0.874	1.00	2.3 (0.1)	2.3
0.800	0.874	0.500	1.6 (0.2)	1.7
1.00	1.07	1.50	3.6 (0.1)	3.5
1.00	1.07	1.00	3.0 (0.1)	2.8
1.00	1.07	0.500	2.3 (0.1)	2.1

^aAt 25.0 °C. NH₄Cl/HClO₄ medium with 0.074 M LiClO₄ present throughout. Average deviations from the mean shown in parentheses.

^bRate constant calculated from eq 6 by using nonlinear least-squares rate parameters (see text).

Table III. Bromide Effect on the Aquo Dimer Hydrolysis Rate^a

[H ⁺], M	[ClO ₄ ⁻], M	[Br ⁻], M	10 ³ k _{obsd} , s ⁻¹	10 ³ k _{calcd} , ^b s ⁻¹
0.300	0.374	0.500	1.0 (0.1)	0.88
0.300	0.374	1.00	1.2 (0.1)	1.4
0.300	0.374	1.50	2.3 (0.1)	2.0
0.300	0.374	2.00	2.6 (0.1)	2.6
0.550	0.624	0.500	1.0 (0.1)	1.5
0.550	0.624	1.00	1.9 (0.3)	2.2
0.550	0.624	2.00	3.7 (0.3)	3.8
0.550	0.624	2.50	4.5 (0.2)	4.6
0.550	0.624	3.00	5.6 (0.1)	5.4
0.800	0.874	0.500	1.9 (0.1)	2.0
0.800	0.874	1.00	3.1 (0.1)	3.0
0.800	0.874	1.50	3.9 (0.1)	3.9
1.00	1.07	0.500	2.4 (0.2)	2.5
1.00	1.07	1.00	4.0 (0.1)	3.5
1.00	1.07	1.50	4.3 (0.1)	4.5

^aAt 25.0 °C. NH₄Br/HClO₄ medium with 0.074 M LiClO₄ present throughout. Average deviations from the mean shown in parentheses.

^bRate constant calculated from eq 6 by using nonlinear least-squares rate parameters (see text).

of c , d , e , and f were obtained from linear k^{-1} (Cl⁻ or Br⁻) vs. $[H^+]^{-1}$ plots. Optimized parameters are $c = (2.4 \pm 0.3) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $d = 1.2 \pm 0.3 \text{ M}^{-1}$, $e = (3.0 \pm 0.4) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and $f = 2.0 \pm 0.5 \text{ M}^{-1}$. Once again, the good agreement between k_{obsd} and k_{calcd} values in Tables II and III supports the validity of this analysis, in which the contribution of each anion is limited to a single term in the rate law.

Complications were encountered in the study of sulfate, nitrate, iodide, and thiocyanate effects on the aquo dimer hydrolysis rate. A detailed investigation of ((H₂O)₅Cr)₂O⁴⁺ decay in NH₄HSO₄/HClO₄ media (Table IV) showed that HSO₄⁻/SO₄²⁻ exhibits a moderate catalytic influence on the same order as the ClO₄⁻, Cl⁻, and Br⁻ results. Nevertheless, attempts to quantitatively fit these HSO₄⁻/SO₄²⁻ kinetic results to a variety of rate laws were uniformly unsuccessful. Very slow 443-nm absorbance increases were observed upon the addition of NH₄I and NH₄SCN (0.50, 1.0, and 2.0 M) to 0.5 mM aquo dimer in 0.550 M HClO₄ (25 °C). The oxidations of I⁻ ($E^\circ(\text{I}_3^-/\text{I}^-) = +0.536 \text{ V}$)⁹ and SCN⁻

(8) Program NLLSQ (CET Research Group Ltd., Norman, OK). This Apple II+ program uses an optimum-seeking routine based on the Levenberg-Marquardt algorithm. See: Christian, S. D.; Tucker, E. E. *Am. Lab. (Fairfield, Conn.)* 1982, 14 (9), 31.

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Table IV. Sulfate/Bisulfate Effect on the Aquo Dimer Hydrolysis Rate^a

[HClO ₄], M	[H ⁺], ^b M	[ClO ₄ ⁻], M	[sulfate] _{tot} , ^c M	10 ³ k _{obsd} , s ⁻¹
0.100	0.246	0.174	0.500	2.2 (0.1)
0.100	0.410	0.174	1.00	2.7 (0.2)
0.100	0.720	0.174	2.00	3.3 (0.3)
0.100	0.867	0.174	2.50	3.8 (0.1)
0.100	1.03	0.174	3.00	6.2 (0.9)
0.100	1.34	0.174	4.00	12.2 (0.5)
0.300	0.429	0.374	0.500	1.9 (0.1)
0.300	0.576	0.374	1.00	2.3 (0.1)
0.300	0.880	0.374	2.00	3.9 (0.1)
0.300	1.03	0.374	2.50	4.2 (0.1)
0.300	1.19	0.374	3.00	5.9 (0.1)
0.550	0.661	0.624	0.500	1.8 (0.1)
0.550	0.796	0.624	1.00	2.4 (0.1)
0.550	1.09	0.624	2.00	3.3 (0.3)
0.550	1.24	0.624	2.50	4.1 (0.4)
0.800	0.900	0.874	0.500	2.5 (0.2)
0.800	1.02	0.874	1.00	3.2 (0.1)
0.800	1.16	0.874	1.50	3.9 (0.1)
1.00	1.04	1.07	0.250	2.9 (0.1)
1.00	1.09	1.07	0.500	3.2 (0.3)
1.00	1.15	1.07	0.750	3.7 (0.2)
1.00	1.21	1.07	1.00	4.4 (0.1)

^aAt 25.0 °C. NH₄HSO₄/HClO₄ medium with 0.07 M LiClO₄ present throughout. Average deviations from the mean shown in parentheses. ^bCalculated from [HClO₄] and the ionization of HSO₄⁻, as described in the experimental section. ^c[sulfate]_{tot} = [NH₄HSO₄]₀ = [HSO₄⁻] + [SO₄²⁻].

$E^{\circ}((\text{SCN})_2/\text{SCN}^-) = +0.77 \text{ V})^9$ by the aquo dimer and/or residual Br₂ in the reaction mixture evidently obscure ((H₂O)₅Cr)₂O⁴⁺ decay in the presence of these anions. Since a maximum in A₄₄₃ was still not attained after 24 h, no kinetic interpretation of increasing absorbance-time traces was attempted. Finally, we note that reproducibly *linear* rather than exponentially decreasing absorbance-time traces pertain through 90% of ΔA₄₄₃ when ((H₂O)₅Cr)₂O⁴⁺ decays in the presence of 0.550 M HClO₄ and 4.0 M NH₄NO₃; the half-life was ca. 3 min, as compared with 27 min estimated for 4.0 M NH₄ClO₄ at the same acidity. This interesting behavior, which suggests that aquo dimer decay is zeroth order with respect to the reactant in nitrate media, is still under investigation.

Chromatographic product analysis has already shown that Cr(H₂O)₆³⁺ is formed quantitatively from aquo dimer hydrolysis in HClO₄/LiClO₄ media.¹ In order to determine whether anation of Cr(III) accompanies chloride-catalyzed aquo dimer hydrolysis, a 25.0 °C reaction mixture in which the Cl⁻-assisted pathway carried 83% of the overall decay ([NH₄Cl] = 2.0 M, [HClO₄] = 0.10 M, [LiClO₄] = 0.07 M) was diluted 20-fold with water after 1 h and subjected immediately to cation-exchange chromatography at 5 °C. Upon elution with 0.5 M LiClO₄/0.1 M HClO₄, chromium was again quantitatively recovered in a single blue-violet band as Cr(H₂O)₆³⁺; not even a trace of green (H₂O)₅CrCl²⁺ was seen in front of the Cr(H₂O)₆³⁺ fraction. Given the known small aquation rate of (H₂O)₅CrCl²⁺ under our conditions,¹⁰ we estimate that only 5% of any (H₂O)₅CrCl²⁺ formed during aquo dimer hydrolysis would decay in the time interval required to complete the chromatography experiment.

Cation Effects on the Aquo Dimer Hydrolysis Rate. Kinetic results on Cr(H₂O)₆³⁺ autocatalysis of the aquo dimer hydrolysis reaction were reported previously at [H⁺] = 0.10, 0.30, 0.55, 0.84, and 1.00 M with [Cr(H₂O)₆³⁺] = 0.10–0.50 M.¹ Although the rate enhancement owing to Cr(ClO₄)₃/HClO₄ (k'_{obsd}) fit the relationship $k'_{\text{obsd}} = [\text{Cr}(\text{H}_2\text{O})_6^{3+}]^2 (k_2 + k_3[\text{H}^+]^2)$, this chromic ion effect was not formally incorporated into the rate law in view of the variable ionic strength and unknown influence of other electrolytes on k_{obsd} . Now that the catalytic influences of many

Table VI. Cation Effects on the Aquo Dimer Hydrolysis Rate^a

salt	[salt], M	[ClO ₄ ⁻], M	10 ³ k _{obsd} , s ⁻¹
Fe(ClO ₄) ₃ ^b	0.100	1.14	0.09 (0.01)
	0.200	1.44	0.15 (0.01)
	0.300	1.74	0.29 (0.02)
	0.400	2.04	0.60 (0.03)
	0.500	2.34	1.10 (0.03)
	0.640	2.76	1.6 (0.1)
Fe(ClO ₄) ₂ ^c	0.050	0.674	0.55 (0.05)
	0.125	0.874	0.8 (0.1)
	0.280	1.17	1.0 (0.1)
	0.480	1.57	1.2 (0.1)
	0.720	2.07	1.6 (0.2)
	Ce(ClO ₄) ₃ ^c	0.050	0.774
0.150		1.07	7.8 (0.1)
0.250		1.37	5.5 (0.2)
0.450		1.97	0.35 (0.02)

^aSalt/HClO₄ medium with [H⁺] = 0.550 M. Average deviations from the mean shown in parentheses. Fe(ClO₄)₃ and Fe(ClO₄)₂ studies at 25.0 °C; Ce(ClO₄)₃ runs at 50.0 °C. ^b0.29 M LiClO₄ present. ^c0.074 M LiClO₄ present.

metal perchlorates have been attributed to ClO₄⁻ rather than the cation, we consider here the appropriateness of a quantitative treatment in which chromic ion is included in the rate law. A useful criterion for identifying an authentic cation effect in perchlorate media is implicit in Figure 1, where k_{obsd} vs. [ClO₄⁻] is displayed at constant [H⁺]. Thus, such a cation effect would be reflected in significant deviations of k_{obsd} from the correlation line based on metal perchlorates whose catalytic activity is solely attributable to ClO₄⁻.

The Cr(ClO₄)₃ k_{obsd} values measured at 25 °C, [H⁺] = 0.550 M consistently fall well above the correlation line in Figure 1, supporting the genuineness of Cr(H₂O)₆³⁺ autocatalysis. We conclude, therefore, that the ((H₂O)₅Cr)₂O⁴⁺ hydrolysis product, unlike Li⁺, Na⁺, Mg²⁺, Zn²⁺, and Al³⁺, may legitimately be included in the rate law of this reaction. Considering both past¹ and present results, eq 7 is thought to be the rate expression that

$$k_{\text{obsd}} = k_0 + k'_1[\text{H}^+] + \frac{ab[\text{H}^+][\text{ClO}_4^-]}{1 + b[\text{H}^+]} + \frac{[\text{Cr}(\text{H}_2\text{O})_6^{3+}]^2(k_2 + k_3[\text{H}^+]^2)}{7} \quad (7)$$

pertains to aquo dimer hydrolysis in Cr(ClO₄)₃/HClO₄ media. In order to avoid bias and unnecessary propagation of errors in the quantitative treatment, we performed a nonlinear least-squares fit of the k_{obsd} vs. [Cr(H₂O)₆³⁺], [H⁺], and [ClO₄⁻] data (Table V)¹¹ to eq 7 by regarding k'_1 , a , and b in addition to k_2 and k_3 as variables; once again, the minor k_0 term was fixed at $5 \times 10^{-5} \text{ s}^{-1}$.¹ This fit was highly successful, as judged by the close correspondence between k_{obsd} and k_{calcd} values (Table V)¹¹ and the similarity (to within experimental error) of k'_1 , a , and b values to those determined on the basis of Table I. It is also clear, therefore, that the two Cr(H₂O)₆³⁺-dependent pathways compete with, but do not replace, the alternative hydrolysis mechanisms available in perchlorate media. The importance of Cr(H₂O)₆³⁺-assisted aquo dimer hydrolysis is readily apparent from the least-squares $k_2 = (1 \pm 1) \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ and $k_3 = (9.0 \pm 0.2) \times 10^{-2} \text{ M}^{-4} \text{ s}^{-1}$ values. Thus, the contribution of the third term in eq 7 to k_{obsd} falls from 89% to 60% and 12% in 1.00 M HClO₄ containing 0, 0.1, and 0.5 M Cr(ClO₄)₃, respectively. Correspondingly, the predominant k_3 chromic-dependent pathway accounts for 34% and 87% of the overall hydrolysis reactivity in the latter two solutions.

The effects of Fe(ClO₄)₃ and Ce(ClO₄)₃ on the aquo dimer hydrolysis rate are markedly different from that of Cr(ClO₄)₃ and those of the metal perchlorates, whose influence is entirely attributable to ClO₄⁻. A comparison of k_{obsd} values at constant [H⁺] = 0.550 M but variable Fe(ClO₄)₃, Fe(ClO₄)₂, and Ce(ClO₄)₃

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(11) Supplementary material.

concentrations is given in Table VI. In contrast to $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ evidently perturbs the dimeric reactant in such a way that the three hydrolysis pathways normally available in acidic perchlorate media (eq 5) are no longer accessible. While k_{obsd} increases with ferric ion concentration according to eq 8 ($k_4 = (4.0 \pm 0.2) \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$, 25 °C, $[\text{H}^+]$

$$k_{\text{obsd}} = k_4[\text{Fe}(\text{H}_2\text{O})_6^{3+}]^2 \quad (8)$$

= 0.550 M), observed rate constants at each $[\text{Fe}(\text{H}_2\text{O})_6^{3+}]$ are smaller than those expected (eq 5) from the perchlorate and hydrogen ion concentrations. Looked at in another way, $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{ClO}_4)_2$ data points fall well below and right on the Figure 1 correlation line, respectively. The intercept of a k_{obsd} vs. $[\text{Fe}(\text{H}_2\text{O})_6^{3+}]^2$ plot is indistinguishable from zero, indicating that iron-independent hydrolysis pathways contribute negligibly in the presence of $\text{Fe}(\text{ClO}_4)_3$.

Surprisingly, $\text{Ce}(\text{ClO}_4)_3$ strongly stabilizes $((\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}$ toward acid hydrolysis, without notably perturbing its spectroscopic² or electrochemical³ properties. While the 25 °C half-lives for aquo dimer hydrolysis in 1 M HClO_4 and 1 M $\text{HClO}_4/0.5$ M $\text{Cr}(\text{ClO}_4)_3$ are 7.0 and 0.4 min, respectively, this reaction requires several days to be complete in 1 M $\text{HClO}_4/0.5$ M $\text{Ce}(\text{ClO}_4)_3$. In order to quantitatively document this effect, we report a brief 50.0 °C study (Table VI), which shows that k_{obsd} does in fact decrease sharply with increasing $[\text{Ce}^{3+}(\text{aq})]$. No rate law may be deduced from this limited data set.

Discussion

Our results show that anions exert a modest catalytic influence on oxo-bridge cleavage within the (μ -oxo)bis(pentaaquo-chromium(III)) ion. In contrast, reductant-catalyzed hydrolysis rates are 3–4 orders of magnitude larger in acidic solution at 25.0 °C and $I = 1.0$ M ($\text{HClO}_4/\text{LiClO}_4$).³ The anion findings are remarkable, however, in that the activity of ClO_4^- is comparable to those of Cl^- and Br^- . While the tendency of perchlorate ion to ligate metal ions is negligible in dilute solution, its capacity to form ion pairs approaches those of other uninegative ions.¹² Competition between ClO_4^- and DMF for an outer-sphere coordination position would account for decreases in the DMF/ $\text{Cr}(\text{DMF})_6^{3+}$ solvent-exchange rate with increasing perchlorate concentration.¹² Conversely, ion pairing may accelerate an aquation reaction through electrostatic assistance of anion departure from the first coordination sphere.¹²

Considering first the hydrolysis results in HClO_4 /metal perchlorate media, the legitimacy of including ClO_4^- in the rate law must be addressed. From a purely statistical point of view, the previously reported¹ kinetic $[\text{H}^+]$ -dependence results at constant $I = [\text{ClO}_4^-] = 1.0$ M may be fit equally well to either eq 2 or eq 5 (see Table I). The importance of the third term in eq 5 became apparent only through the use of a wide variety of metal perchlorate salts at ionic strengths considerably larger than 1 M. The linearity of k_{obsd} vs. $[\text{ClO}_4^-]$ plots at fixed $[\text{H}^+]$ is not readily explicable as an ionic strength effect, and perchlorate is clearly implicated as the kinetically relevant species by relationship 3, which accounts for the influences of six different metal perchlorates remarkably well, considering the variable ionic strength. Finally, the functional similarity of ClO_4^- , Cl^- , and Br^- terms in eq 6 implies that many anions, including perchlorate, may catalyze aquo dimer hydrolysis through a common mechanism.

Coupled anation and protonation of the aquo dimer to give "aquo erythro" ions ($[(\text{H}_2\text{O})_5\text{Cr}(\text{OH})\text{Cr}(\text{H}_2\text{O})_4\text{X}]^{4+}$) similar to the well-known rhodo erythro series^{13,14} (NH_3 replaces H_2O) might be anticipated. This supposition is not supported by our product distribution studies, however, as there is no evidence for a long-lived binuclear product. More importantly, the absence of $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ as a product of chloride-assisted aquo dimer hydrolysis indicates that Cl^- never enters the first coordination sphere

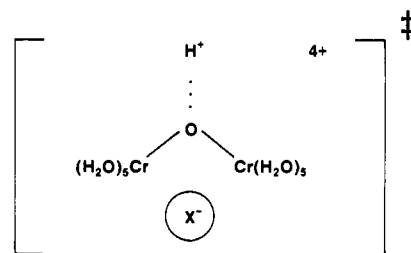
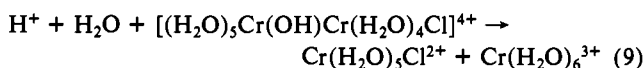
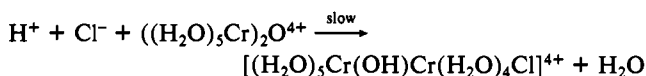


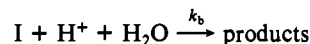
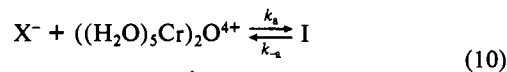
Figure 2. Proposed activated complex in the anion-catalyzed aquo dimer acid hydrolysis pathway.

of $\text{Cr}(\text{III})$. If anation of $\text{Cr}(\text{III})$ was responsible for oxo-bridge cleavage, as in eq 9, then the relatively inert $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ ion

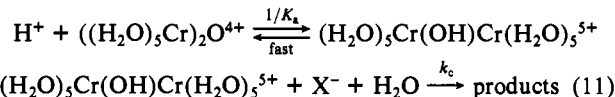


should account for about 41% of the $\text{Cr}(\text{III})$ product when the Cl^- -assisted pathway carries 83% of the overall reaction. A noncoordinative interaction must therefore be sought as the basis for anion-catalyzed $((\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}$ breakdown.

At least two kinetically indistinguishable mechanisms must be considered for anion catalysis. The first (eq 10) involves the initial



formation of a steady-state intermediate (I) from $((\text{H}_2\text{O})_5\text{Cr})_2\text{O}^{4+}$ and X^- . In the second alternative (eq 11) a rapid protonation



preequilibrium is followed by slow attack of X^- on the intermediate. On this basis, the theoretical rate expressions agree with the anion-dependent terms in eq 6, where a , c , and $e = k_a$ or k_c and b , d , and $f = k_b/k_{-a}$ or $1/K_a$. Thus, the order of addition of H^+ and X^- to the activated complex is not easily specified.

Although the protonation preequilibrium option accounts for our previous constant ionic strength results in straightforward fashion, we now favor mechanism 10. The $(b, d, \text{ or } f)[\text{H}^+]$ denominator terms in eq 6 are comparable in value to one, consistent with eq 11 only if aquo dimer protonation is appreciable in the $[\text{H}^+] = 0.05\text{--}1.00$ M interval. Indeed, the apparent K_a value of 0.63 M (b^{-1}) calculated from the ClO_4^- catalysis data implies that 60% of the reactant is protonated at $[\text{H}^+] = 1.0$ M. The aquo dimer UV-visible spectrum is independent of $[\text{H}^+]$ in the 0.05–1.00 M range,² however, meaning that very little complex actually is protonated or that the UV-visible spectrum is essentially invariant with uptake of H^+ . The latter contingency is highly unlikely, however, considering the loss of intense near-UV features that accompanies the protonation of $((\text{NH}_3)_5\text{Cr})_2\text{O}^{4+}$.¹⁵

The mechanism of eq 10 provides an excellent framework for understanding ClO_4^- , Cl^- , and Br^- catalysis of oxo-bridge cleavage. The similarity of k_a ($=a, c, \text{ and } e$) and k_b/k_{-a} ($=b, d, \text{ and } f$) values among the three anions reinforces the conclusion that anation of chromium does not occur in the catalytic pathway. The opposite extreme of simple ion pairing in the k_a aquo dimer- X^- reactions must also be ruled out, however, as being much faster than the maximum observed rates. We propose that the k_a step involves bending of the initially linear $\text{Cr}\text{--}\text{O}\text{--}\text{Cr}$ unit within an ion pair, providing electrostatic anion-incipient dipole stabilization to compensate for the loss of π bonding. Further stabilization of the activated complex would then be achieved by protonation of

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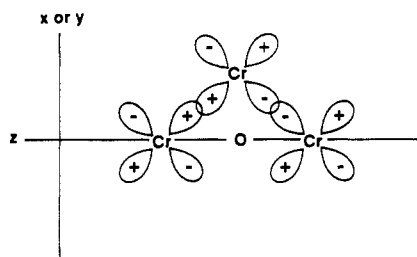


Figure 3. Overlap of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ t_{2g} and aquo dimer e_g π orbitals proposed to account for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ autocatalysis.

an emergent lone pair on oxygen (Figure 2), as proposed previously.¹ On this basis, k_a and k_b/k_{-a} should be governed by the charge rather than the chemical composition or Lewis basicity of the anion; a slight dependence of the hydrolysis rate on anion charge/radius ratio might be anticipated.

The k'_1 term most likely corresponds to solvent-induced aquo dimer hydrolysis, where the H_2O molecular dipole provides less satisfactory electrostatic stabilization of the bent activated complex than does X^- . While this term contributes little to the rate of oxo-bridge cleavage, the existence of a pathway with simple first-order H^+ dependence supports the preference of mechanism 10 over 11. Such a term cannot be rationalized through the preequilibrium protonation option under conditions where the anion-dependent contributions to k_{obsd} are *not* likewise first order in H^+ . A significant decrease in the k_b/k_{-a} ratio from X^- to H_2O would account well for the distinctive k'_1 term, however.

Improved quantitative understanding of anion-assisted aquo dimer hydrolysis now allows us to distinguish genuine kinetic cation effects from those related to the counterion. Although we were originally reluctant to include $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ in the rate law,¹ the overall $\text{Cr}(\text{ClO}_4)_3$ influence on the reaction of interest actually is best understood as the sum of separate ClO_4^- and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ contributions. The distinctively greater catalytic potency of $\text{Cr}(\text{ClO}_4)_3$, as compared with other metal perchlorates, requires that an exceptional role be assigned to $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. The fact that $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ also is the product of aquo dimer hydrolysis cannot be regarded as circumstantial. Taken literally, the dominant k_3 term in eq 7 specifies an activated complex with composition $[(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}, 2\text{Cr}(\text{H}_2\text{O})_6^{3+}, 2\text{H}^+] \pm (\text{integer}) \text{H}_2\text{O}$ and charge of $12+$.

Preequilibrium generation of an intermediate with the composition of this activated complex, succeeded by rate-limiting oxo-bridge rupture, formally rationalizes the $k_3[\text{Cr}(\text{H}_2\text{O})_6^{3+}]^2 \cdot [\text{H}^+]^2$ term (eq 7), provided that the concentration of this intermediate is always negligible as compared with that of the binuclear reactant. Strong, coupled interactions of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and H^+ with the aquo dimer apparently offset the destabilizing influence of positive charge aggregation in this pathway. As previously described for reductant-catalyzed aquo dimer hydrolysis,³ the molecular orbital analysis of Dunitz and Orgel¹⁶ offers an attractive potential link between the electronic structure

and reactivity of $(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}$. The reactant electronic configuration would be $(e_u^b)^4[(e_g)(b_{2g})(b_{1u})]^6(e_u^*)^0$ according to this model, where e_u^b and e_u^* are the strongly bonding and antibonding π orbitals based on $d_{xz,yz}(\text{Cr})-p_{x,y}(\text{O})-d_{xz,yz}(\text{Cr})$ overlap ($\text{Cr}-\text{O}-\text{Cr}$ is the z axis). Although displacement of H_2O from $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is far too slow to be involved in the present chromic catalysis,¹ overlap between t_{2g} (π^n) $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and approximately non-bonding e_g ($d_{xz,yz}(1) + d_{xz,yz}(2)$) ($(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}$ orbitals is symmetry allowed (Figure 3) and favored by the energetic proximity of catalyst and reactant $\text{Cr}(\text{III})$ d_{xz} and d_{yz} atomic orbitals. Consistent with the second-order chromic dependence, two such interactions of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with the doubly degenerate e_g level are conceivable.

Although the electronic population of the e_g level is uncertain,³ electron exchange certainly would stabilize a tetranuclear $\text{Cr}(\text{III})$ intermediate constructed in this way. Enhancements in the three-centered overlaps depicted in Figure 3, coupled with protonation of the two oxygen lone pairs emergent from the former e_u^b level, could partially offset the destruction of $\text{Cr}-\text{O}-\text{Cr}$ π overlap when this unit is bent to achieve hydrolysis. This mechanistic hypothesis is similar to that advanced in support of unexpectedly rapid nucleophilic attack of CrO_4^{2-} on $\text{Cr}_2\text{O}_7^{2-}$, where π bonding within a trinuclear intermediate is thought to lower the energy of the transition state leading to CrO_4^{2-} exchange.¹⁷ The k_2 term (eq 7) presumably reflects $\text{Cr}-\text{O}-\text{Cr}$ bending unassisted by protonation of the bridging oxygen atom.

The unexpected stabilizing effects of $\text{Fe}(\text{ClO}_4)_3$ and especially $\text{Ce}(\text{ClO}_4)_3$ on the aquo dimer merit more detailed examination. At this point it is clear, however, that both $\text{Fe}^{3+}(\text{aq})$ and $\text{Ce}^{3+}(\text{aq})$ interact with the binuclear reactant in such a way that the free-reactant hydrolysis pathways no longer are available. Considering the substitutional labilities and large hydrolytic tendencies of both cations,¹⁸ bidentate bridging of the $\text{Cr}-\text{O}-\text{Cr}$ unit could inhibit its rupture. The failure of $\text{Fe}(\text{ClO}_4)_2$ to exhibit a reactivity influence other than that of ClO_4^- is consistent with this model and the expected inability of $\text{Fe}(\text{II})$ to function as a reducing agent ($E^\circ(\text{Fe}(\text{H}_2\text{O})_6^{3+/2+}) = 0.77 \text{ V}$)⁹ toward $(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}$. The second-order $\text{Fe}(\text{III})$ dependence causes aquo dimer hydrolysis rates in the presence of large $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$ concentrations to become comparable. The possibility that $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and other mild oxidants may facilitate aquo dimer hydrolysis through the oxidation of $\text{Cr}(\text{III})$ to $\text{Cr}(\text{IV})$ is currently being explored.

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Registry No. ClO_4^- , 14797-73-0; Cl^- , 16887-00-6; Br^- , 24959-67-9; $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, 14873-01-9; $(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}$, 73347-70-3; $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, 15377-81-8; $\text{Ce}(\text{H}_2\text{O})_6^{3+}$, 19578-59-7.

Supplementary Material Available: Table V, showing a comparison of k_{obsd} with k_{calcd} in $\text{Cr}(\text{ClO}_4)_3$ -assisted aquo dimer hydrolysis (1 page). Ordering information is given on any current masthead page.

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