general one for the *cis*-$W(CO)_4L_2$ series; as ϕ_{cr} is reduced, ϕ_e is increased.

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Registry No. phen, 66-71-7; *cis*-$Cr(CO)_4(py)_2$, 43118-74-7; *cis*-$Cr(CO)_4$(4-Ph-py)$_2$, 90245-53-7; *cis*-$Cr(CO)_4$(3,5-Cl_2-py)$_2$, 90245-54-8; *cis*-$Cr(CO)_4$(4-Bz-py)$_2$, 90245-55-9; *cis*-$Cr(CO)_4$(4-CN-py)$_2$, 90245-56-0; *cis*-$Mo(CO)_4$(4-Et-py)$_2$, 90245-57-1; *cis*-$Mo(CO)_4$(4-Me-py)$_2$, 16244-56-7; *cis*-$Mo(CO)_4(py)_2$, 16742-99-7; *cis*-$Mo(CO)_4$(4-Ph-py)$_2$, 90245-58-2; *cis*-$Mo(CO)_4$(3,5-Cl_2-py)$_2$, 90245-59-3; *cis*-$Mo(CO)_4$(4-Bz-py)$_2$, 90245-60-6; *cis*-$Mo(CO)_4$(4-CN-py)$_2$, 90245-61-7; *cis*-$W(CO)_4$(4-Et-py)$_2$, 67951-65-9; *cis*-$W(CO)_4$(4-Me-py)$_2$, 84076-49-3; *cis*-$W(CO)_4(py)_2$, 16743-01-4; *cis*-$W(CO)_4$(4-Ph-py)$_2$, 67921-71-5; *cis*-$W(CO)_4$(3,5-Cl_2-py)$_2$, 67921-72-6; *cis*-$W(CO)_4$(4-Bz-py)$_2$, 67921-74-8; *cis*-$W(CO)_4$(4-CN-py)$_2$, 67921-75-9; $W(CO)_4$phen, 14729-20-5; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

Contribution from the Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 2. Kinetics and Mechanism of the Interconversion between Two Tetrameric Species

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The hydrolytic chromium(III) tetramer in acidic solution is predominantly $Cr_4(OH)_6^{6+}$ (HTO). On deprotonation (pK_a = 3.53 ± 0.08), the resulting complex, $Cr_4(OH)_7^{5+}$ (TO), slowly isomerizes to $Cr_4O(OH)_5^{5+}$ (TC), which contains a tetracoordinate oxo bridge. Protonation of TC gives HTC (pK_a = 0.89 ± 0.01) as an unstable intermediate. HTO is then formed by cleavage of the oxo bridge. The isomerization constants are K_i = [TC]/[TO] = 8.8 ± 2.3 and $K_{i,H}$ = [HTC]/[HTO] = 0.020 ± 0.003, respectively. The following rate constants were determined: k_o = 0.027 ± 0.004 s^{-1} for TC + H_2O → TO; $k_{o,H}$ = 4.35 ± 0.05 s^{-1} for HTC + H_2O → HTO; k_c = 0.24 ± 0.07 s^{-1} for TO → TC + H_2O; $k_{c,H}$ = 0.087 ± 0.014 s^{-1} for HTO → HTC + H_2O. These data were determined from spectrophotometric kinetics at 25.0 ± 0.1 °C and I = 1.0 ($NaClO_4$) in the pH range 0.3–4.0. The pK_{a1} of the tetramer deduced from these parameters is consistent with that previously determined by potentiometric determination (2.55 ± 0.06). The proposed reaction sequence is consistent with the slow equilibration observed in these titrations and confirms the structural assignments made earlier. Both formation and cleavage of the oxo bridge in the tetramer are much faster than known cases of hydroxo bridge formation and cleavage in other Cr(III) species. Contrary to substitution in monomeric Cr(III), deprotonation of coordinated water does not appreciably accelerate substitution in the reaction TO → TC + H_2O.

Introduction

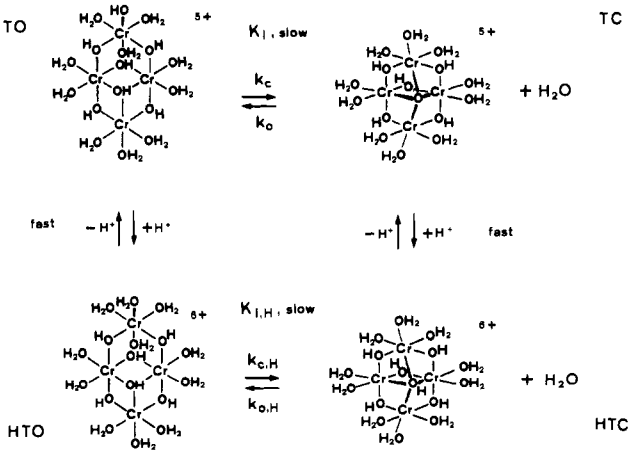
In previous work,[2] a complete series of hydrolytic oligomers of Cr(III) up to, and including, the hexamer has been obtained in solution by ion-exchange chromatography. The configuration of the tetramer, $Cr_4O(OH)_5^{5+}$, has been deduced from a series of buildup and cleavage reactions involving other, known oligomers and from the general trends in pK_a values.

In the course of potentiometric pK_a determinations of the tetramer, the electrode potentials reached equilibrium unusually sluggishly compared with the lower oligomers. This was explained by a reversible, intramolecular condensation reaction accompanying deprotonation of the tetramer. As this presumed process provided an important argument in deducing the configuration of the tetramer, we have now studied its kinetics in more detail. This has enabled us to explore, for the first time, the reactivity pattern of an oxo bridge in a hydrolytic species of Cr(III).

Results

Description of the Reaction System and Data Collection. The hydrolytic tetramer, $Cr_4(OH)_6^{6+}$, was synthesized by dimerization of $Cr_2(OH)_2^{4+}$ with base and isolated in solution by ion-exchange chromatography as described.[2] The purity of these fractions was checked by UV/vis spectroscopy, using the distinctive, high intensity ratio of the maxima, $\epsilon_{426}/\epsilon_{580}$ = 1.95 ± 0.04 at [H^+] = 0.04 M of the tetramer. The band positions for this species and for the essentially monodeprotonated tetramer are nearly the same, but there are small changes in intensity.[2]

Scheme I. Interconversion of Forms of the Tetramer, $Cr_4O(OH)_5^{5+}$



The potentiometric pK_a determinations (pK_{a1} = 2.55, pK_{a2} = 5.08, 25 °C, I = 1.0 ($NaClO_4$))[2] also established the stoichiometry of the deprotonation reaction. Thus, one proton per tetramer is lost in the buffer region up to pH 3.8. These titrations showed that this reversible protonation–deprotonation

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(2) Part 1: Stünzi, H.; Marty, W. *Inorg. Chem.* **1983**, *22*, 2145.

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Table I. Rate Constants for the Equilibration of the Tetramer (I = 1.0 ($NaClO_4$); 25 °C)

pH[a]	k_{obsd},[b] s^{-1}	k_{calcd},[c] s^{-1}	$\epsilon_0 - \epsilon_\infty$[d] 425 nm	$\epsilon_0 - \epsilon_\infty$[d] 579 nm	acid or buffer	10^3[T], M
			Acidification of Monodeprotonated Tetramer			
0.30	3.55 ± 0.10 (12)	3.55	−6.6	2.7	$HClO_4$	3.05
0.30	3.60 ± 0.06 (11)	3.55	−6.4	2.6	$HClO_4$	3.17
0.52	3.15 ± 0.06 (11)	3.14			$HClO_4$	~1.4
0.82	2.44 ± 0.03 (9)	2.45	−5.3	3.7	$HClO_4$	3.05
1.00	2.01 ± 0.03 (12)	2.00	−4.7	3.7	$HClO_4$	2.85
1.29	1.33 ± 0.01 (9)	1.34	−3.9	4.2	$HClO_4$	3.05
1.45	1.06 ± 0.02 (13)	1.05	−3.4	4.1	$HClO_4$	2.85
1.79	0.62 ± 0.01 (8)	0.60	−3.0	4.1	$HClO_4$	3.05
1.90	0.51 ± 0.01 (13)	0.50	−2.3	3.6	0.2 M triazole/$HClO_4$	1.94
2.10	0.37 ± 0.01 (15)	0.37	−2.1	3.3	0.2 M triazole/$HClO_4$	1.94
2.41	0.247 ± 0.017 (15)	0.251	−1.1	2.7	0.2 M triazole/$HClO_4$	1.94
2.60	0.210 ± 0.008 (15)	0.212	−1.3	2.1	0.2 M triazole/$HClO_4$	1.94
2.90	0.177 ± 0.008 (13)	0.184	−0.9	1.3	0.2 M triazole/$HClO_4$	1.94
			Alkalinization of Protonated Tetramer			
3.23	0.188 ± 0.009 (13)	0.183	2.5	≲−4	0.1 M sulfanilic acid/NaOH	3.14
3.58	0.197 ± 0.010 (11)	0.201	3.0	−4.3	0.15 M sulfanilic acid/NaOH	2.63
3.79	0.219 ± 0.009 (13)	0.215	3.2	−4.0	0.2 M sulfanilic acid/NaOH	3.14
4.01	0.228 ± 0.008 (13)	0.229	3.6	−4.0	0.2 M sulfanilic acid/NaOH	2.63
			Runs with Alanine Buffers–Acidification			
1.63	0.84 ± 0.02 (11)	0.79[e]	−3.2	4.1	0.2 M alanine/$HClO_4$	3.17
2.00	0.495 ± 0.013 (10)	0.43[e]	−2.5	3.9	0.2 M alanine/$HClO_4$	3.17
2.31	0.329 ± 0.009 (11)	0.282[e]	−2.1	3.2	0.2 M alanine/$HClO_4$	3.17
2.52	0.285 ± 0.012 (10)	0.226[e]	−1.8	2.5	0.2 M alanine/$HClO_4$	3.17
			Runs with Alanine Buffers–Alkalinization			
2.56	0.250 ± 0.017 (11)	0.218[e]	1.5	−2.5	0.1 M alanine/$HClO_4$	3.14
2.86	0.222 ± 0.013 (12)	0.186[e]	1.6	−2.9	0.15 M alanine/$HClO_4$	2.63
3.02	0.210 ± 0.009 (14)	0.181[e]	1.7	−3.1	0.2 M alanine/$HClO_4$	2.63

[a] Accurate to ±0.02 unit. [b] Number of runs considered in parentheses. [c] Calculations using eq 3. Equation 2 gave almost identical values. Results for alanine buffers were not considered in the calculation. [d] Accurate to ca. ±10%. [e] Calculated by using rate law 3, *exclusive* of all values of k_{obsd} for alanine buffers.

sequence is too slow for a simple proton transfer. Scheme I presents our interpretation of these phenomena. Upon neutralization of acidic solutions, the protonated, open tetramer (HTO) is deprotonated (TO) and turns slowly and reversibly into the unprotonated closed species (TC). On acidification, this last species is protonated (HTC) and reacts rapidly to HTO. The more reactive complexes, TO and HTC, are present in minor concentrations.

The kinetics of interconversion of the open and closed forms of the tetramer were studied by stopped-flow spectrophotometry at 25.0 ± 0.1 °C and I = 1.0 ($NaClO_4$). The monitoring wavelengths 425 and 579 nm are near the two absorption maxima and give the largest accessible optical density changes. The reaction sequence was studied in both directions: either deprotonated tetramer (at pH 3.8) was reacted with perchloric acid, triazole, and alanine buffers or protonated tetramer (at pH ≈1) was mixed with alanine or sulfanilate buffers. In all cases, except for the alanine buffer runs,[3] uniphasic pseudo-first-order kinetics were observed for 3–4 half-lives. Table I shows the experimental conditions and results. Despite the weak optical density changes observed (Table I, fourth column), the reproducibility was good.

The possibility of contributions from general-acid or general-base catalysis deserves attention. No systematic variation of the buffer-acid or buffer-base concentration at constant pH was attempted,[4] but the rate data show no discontinuity upon change of the buffer system (except for alanine; see below).

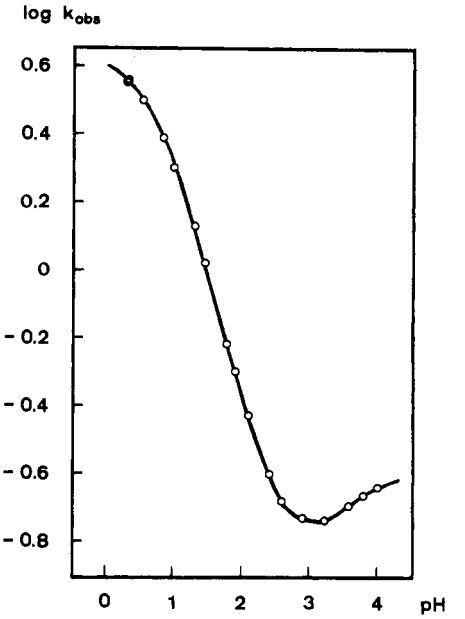


Figure 1. Rate–pH profile for the interconversion of forms of the tetramer.

Possible buffer catalysis is therefore considered negligible.

Characterization of Products. The identity of the reaction products was checked as follows: The spent solutions from the stopped-flow instrument were ejected into an ice bath and adsorbed on Sephadex SP C-25. In the runs with perchloric acid, triazole, and sulfanilic acid buffers, more than 80% of the tetramer was recovered unchanged and no other species became apparent on the column. Thus, the tetramer does not react with these buffer species on the time scale of these experiments (<20 s).

(3) A much slower second reaction phase became apparent in these runs ($t_{1/2}$ > 10 s). The corresponding optical density change was ca. 4% of that of the fast reaction phase, during the measuring time of 20 s.

(4) To achieve efficient buffering at the equired, high concentration of tetramer, the buffer concentration could not be made <0.1 M, but buffer concentrations >0.2 M risk giving rise to medium effects. However, experiments at variable $[alanine]_{tot}$ (0.1–0.2 M) gave no evidence for buffer catalysis.

In contrast, no unchanged tetramer was recovered at the end of the alanine buffer runs.[5] In addition, the observed rate constants for these runs were 10–20% larger than the calculated values deduced from all other experiments. On these two accounts, and from the observation of a slow, second reaction phase,[3,6] the alanine buffer data will not be considered further in this context.

Equilibria and Rate Law. As illustrated by the rate–pH profile (Figure 1), the observed rate constants decrease from pH 0.3 to 3 but increase again above pH 3. If the study is to be restricted to the reactions of the fully protonated and to the monodeprotonated tetramer, then the ascending branch of the rate profile is limited to pH $\lesssim$4 as $pK_{a2} = 5.08$.[2]

In terms of the reactions in Scheme I, the prevailing form of the protonated tetramer (pH <1) is taken to be the open form HTO ($=Cr_4(OH)_6^{6+}$), and at pH $\approx$3.8 most of the tetramer is thought to be the closed, unprotonated tetramer, TC ($=Cr_4O(OH)_5^{5+}$). The acidic branch of the rate profile is therefore interpreted by the H^+-catalyzed opening of the closed form

$$TC + H^+ \overset{\text{fast}}{\rightleftharpoons} HTC \qquad HTC + H_2O \underset{k_{c,H}}{\overset{k_{o,H}}{\rightleftharpoons}} HTO$$

as the predominant reaction. Above pH 3, the main reaction is the conjugate base pathway of forming the closed species:

$$HTO \overset{\text{fast}}{\rightleftharpoons} TO + H^+ \qquad TO \underset{k_o}{\overset{k_c}{\rightleftharpoons}} TC + H_2O$$

As the reaction can be run in both directions (kinetics and titrations), the closing and opening reaction steps must be reversible. We define the following equilibrium constants, omitting charges throughout (brackets indicate molar concentrations): $K_c = [HTC]/[H][TC]$, protonation of TC, log $K_c = pK_a$ of HTC; $K_o = [HTO]/[H][TO]$, protonation of TO, log $K_o = pK_a$ of HTO; $K_i = [TC]/[TO]$, isomerization constant of the unprotonated forms; $K_{i,H} = [HTC]/[HTO] = K_iK_c/K_o$, isomerization constant of the protonated forms. The total concentrations (subscript tot) are expressed as $[TO]_{tot} = [TO] + [HTO] = [TO](1 + K_o[H])$, $[TC]_{tot} = [TC] + [HTC] = [TC](1 + K_c[H])$, and $[T]_{tot} = [TO]_{tot} + [TC]_{tot}$.

The potentiometrically determined pK_{a1} (=2.55)[2] of the tetramer then turns out not to represent the protonation equilibrium of a single species but to represent that of a mixture of all four species present (Scheme I). Thus, K_1 ($=10^{pK_{a1}}$) may be expressed in terms of, e.g. K_c, K_o, and K_i:

$$K_1 = ([HTC] + [HTO])/\{[H]([TC] + [TO])\} = (K_cK_i + K_o)/(K_i + 1) \quad (1)$$

On the basis of Scheme I, the derived rate law is

$$d[TC]_{tot}/dt = -[TO]_{tot}/dt = k_c[TO] + k_{c,H}[HTO] - k_o[TC] - k_{o,H}[HTC] = (k_c + k_{c,H}K_o[H])[TO] - (k_o + k_{o,H}K_c[H])[TC]$$

For this reversible system at equilibrium, $d[TC]_{tot}/dt = -d[TO]_{tot}/dt = 0$ and $[TC]_{eq}/[TO]_{eq} = K_i = (k_c + k_{c,H}K_o[H])/(k_o + k_{o,H}K_c[H])$ must hold for all [H]. This leads to the relations $k_c = k_oK_i$ and $k_{c,H} = k_{o,H}K_{i,H} = k_{o,H}K_cK_i/K_o$. With the use of the equilibrium constants as defined initially and the expressions for the total concentrations, substitution of k_c, $k_{c,H}$, [TO], and [TC] yields

$$\frac{d[TC]_{tot}}{dt} = -\frac{d[TO]_{tot}}{dt} = \frac{k_o + k_{o,H}K_c[H]}{1 + K_o[H]}K_i[T]_{tot} - \left(\frac{k_o + k_{o,H}K_c[H]}{1 + K_o[H]}K_i + \frac{k_o + k_{o,H}K_c[H]}{1 + K_c[H]}\right)[TC]_{tot}$$

The first term is time independent. Thus, in the present case of pseudo-first-order kinetics, this differential equation has the general form, $d[TC]_{tot}/dt = \text{constant} - k_{obsd}[TC]_{tot}$, where

$$k_{obsd} = \frac{k_o + k_{o,H}K_c[H]}{1 + K_c[H]} + \frac{k_o + k_{o,H}K_c[H]}{1 + K_o[H]}K_i \quad (2)$$

Equation 2 contains the five unknown parameters k_o, $k_{o,H}$, K_c, K_o and K_i. An equation with only four unknown parameters is derived by using $K_1 = 10^{pK_{a1}}$ as a known parameter (eq 3).

$$k_{obsd} = \frac{k_o + k_{o,H}K_c[H]}{1 + K_c[H]} + \frac{K_o - K_1}{K_1 - K_c}\frac{k_o + k_{o,H}K_c[H]}{1 + K_o[H]} \quad (3)$$

In eq 2 and 3, the first term represents the acid-catalyzed and spontaneous intramolecular Cr–O bond breaking of the closed tetramer. The second term arises from the intramolecular condensation from the open to the closed form by way of spontaneous and conjugate base pathways, respectively.

When monodeprotonated tetramer (at pH 3.8) is acidified to a final pH of 0.3–1.5 ($\ll pK_{a1}$), the acid-catalyzed pathway predominates over the spontaneous cleavage and, in this pH range, a plot of $1/k_{obsd}$ vs. $1/[H]$ is linear. The corresponding, approximate rate law (eq 4) gave $k_{o,H} \approx 4.3\ s^{-1}$ and $K_c \approx 9.2\ M^{-1}$.

$$k_{obsd} \approx k_{o,H}K_c[H]/(1 + K_c[H]) \quad (4)$$

Alkalinization of $Cr_4(OH)_6^{6+}$ to pH >3.5 leads to predominant formation of TC from the deprotonated, open tetramer, TO. However, the range of observation is limited to pH $\lesssim$4 as the second deprotonation step would interfere at higher pH. Analogous linearization of the rate law for the conjugate base pathway (TO $\rightarrow$ TC) is not possible in the small pH range 3.5–4.

Hence, the unknown parameters in rate laws 2 and 3 were determined by nonlinear least-squares regression. The minimized function was $\sum_j w_j(k_{obsd,j} - k_{calcd,j})^2$, by using the standard deviation of $k_{obsd,j}$ (σ_j) to determine the weight $w_j = 1/\sigma_j^2$. The data (Table I) were fitted to eq 3, by using $K_1 = 10^{pK_{a1}} = 10^{2.55}$. From the resulting parameters were derived k_c, $k_{c,H}$, K_i, and $K_{i,H}$ (Table II). The value of pK_{a1} was checked independently by fitting the data to eq 2 and was found to agree well with the potentiometric data.[2] Both

Table II. Kinetic and Thermodynamic Parameters from Least-Squares Calculations

parameter	fit: 5 parameters (eq 2)	fit: 4 parameters + pK_{a1} (exptl) (eq 3)
k_o, s^{-1}	0.018 ± 0.008	0.027 ± 0.004
$k_{o,H}$, s^{-1}	4.36 ± 0.05	4.35 ± 0.05
k_c, s^{-1}	0.26 ± 0.20[a]	0.24 ± 0.07[b]
$k_{c,H}$, s^{-1}	0.10 ± 0.08[c]	0.087 ± 0.014[d]
log K_c (pK_a of HTC)	0.88 ± 0.01	0.89 ± 0.01
log K_o (pK_a of HTO)	3.7 ± 0.2	3.53 ± 0.08
pK_{a1} (=log K_1)	2.5 ± 0.3[e]	2.55 ± 0.06[f]
K_i	15 ± 9	8.8 ± 2.3[g]
$K_{i,H}$	0.024 ± 0.017[h]	0.020 ± 0.003[i]

[a] $k_c = k_oK_i$. [b] $k_c = k_o(K_o - K_1)/(K_1 - K_c)$. [c] $k_{c,H} = k_{o,H}(K_cK_i/K_o)$. [d] $k_{c,H} = k_{o,H}(1 - K_1/K_o)/[(K_1/K_c) - 1]$. [e] $pK_{a1} = \log[(K_cK_i + K_o)/(K_i + 1)]$. [f] Reference 2. [g] $K_i = (K_o - K_1)/(K_1 - K_c)$. [h] $K_{i,H} = K_iK_c/K_o$. [i] $K_{i,H} = (1 - K_1/K_o)/(K_1/K_c - 1)$.

(5) A green (λ_{max} = 574, 416 nm) and a blue-gray (λ_{max} = 581, 422 nm) species were seen on the column. When L-alanine was used, both species exhibited CD effects of the same magnitude after removal of excess amino acid and elution from Sephadex SP C-25. The green species is converted to the blue complex in the presence of alanine. These species are being investigated further: Favre, A., unpublished work.

(6) The slightly larger values of k_{obsd}(alanine) relative to k_{obsd}(triazole) are consistent with a reaction scheme where e.g. both TO and TC react concurrently with alanine in addition to the reactions given in Scheme I. It can be shown that the larger of the two eigenvalues of the corresponding system of differential equations turns out to be higher than the rate constant of equilibration alone.

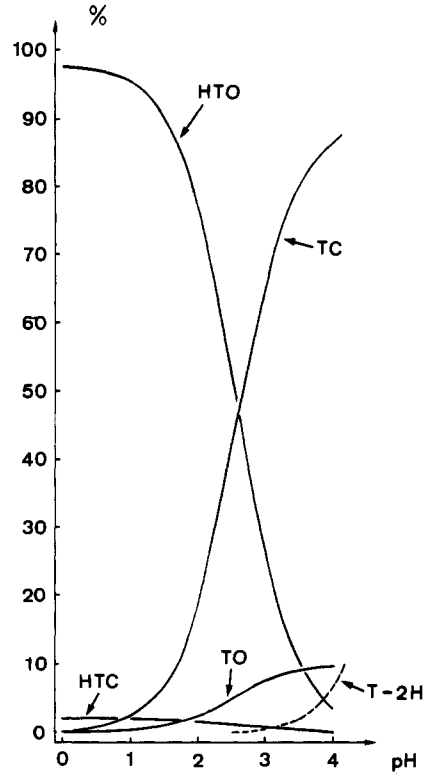


Figure 2. Relative concentrations of the species TO, HTO, TC, and HTC and of the doubly deprotonated tetramer, T-2H.

procedures gave almost identical results for $k_{o,H}$ and K_c, and these values are close to the estimates from eq 4. The good agreement between the parameter sets from rate laws 2 and 3 also extends to all other parameters that are not amenable to independent checks.

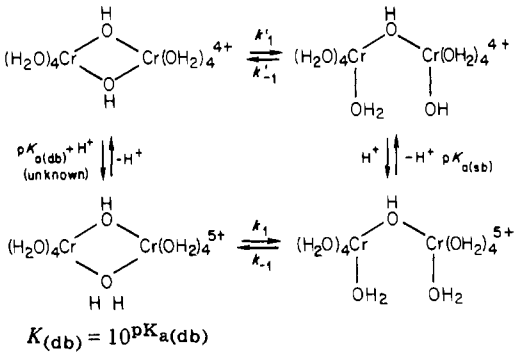
The set of derived equilibrium constants (Table II) was used to calculate the species distribution diagram in Figure 2. As mentioned above, HTO and TC are the major species and the equilibrium concentrations of HTC and TO never exceed 4 and 9.5%, respectively, in the pH range studied. In addition, the doubly deprotonated tetramer appears above pH 3, but it never makes up for more than 7.5%.

Discussion

The pK_a of HTO (log K_o = 3.5) is essentially the same as pK_{a1} of $Cr_2(OH)_2^{4+}$ (=3.68).[2] This last value has been considered typical of a Cr(III) center with a *trans*-H_2O–Cr–OH_2 unit.[2] This is consistent with the structural proposal made for HTO (Scheme I), where the semidetached, single chromium center closely resembles the two centers present in $Cr_2(OH)_2^{4+}$. The site of deprotonation of HTO accordingly would be the water molecule trans to the unique water presumed to leave in the condensation to TC, or this leaving water molecule itself. Thus, TO contains a nonbridging OH group that is protonated with relative ease. In contrast, such a group is not present in the proposed structure for TC, and the pK_a of HTC is in fact much lower (0.89). The protonated species, HTC, is more reactive than TC by a factor of ~290 (=$k_{o,H}/k_o$), and this is consistent with protonation at the tetracoordinate O^{2-} ligand in TC.

On the other hand, for the intramolecular condensation step, the conjugate base of HTO gives rise to a rate enhancement by a factor of only 2. In comparison, the conjugate base pathway (k'_{-1}) in the ring closure of singly bridged dimer (Scheme II) is 7 times faster than spontaneous ring closure.[7]

Scheme II



The deprotonated monomer, $(H_2O)_5CrOH^{2+}$, is about 60 times more reactive than $Cr(OH_2)_6^{3+}$.[8] This acceleration factor, though modest, is larger than in the intramolecular condensation processes of the tetramer.

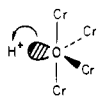
The suggested, intramolecular cleavage and condensation processes involving a tetracoordinate, bridging O^{2-} are remarkably fast in both directions. The closest basis for comparison is the dimer, $Cr_2(OH)_2^{4+}$. Some rate and equilibrium constants for the following transformations are known: At 25 °C and I = 2.0 ($LiClO_4$), $k_1K_{(db)} = 9.40 \times 10^{-5}$ s^{-1}, $k_{-1} = 1.17 \times 10^{-4}$ s^{-1}, $k'_{-1} = 8.12 \times 10^{-4}$ s^{-1}, and pK_a(sb) = 1.6. The spontaneous ring opening to give the deprotonated, singly bridged dimer was not observed.[7] The acceleration factors for analogous pathways in the tetramer relative to the dimer are $(k_{o,H}K_c)/(k_1K_{(db)}) = 3.6 \times 10^5$, $k_{c,H}/k_{-1} = 850$, and $k_c/k'_{-1} = 320$. In the tetramer, the acid-catalyzed opening is the most efficient pathway relative to the dimer. This supports our assertion that protonation of TC takes place at an oxygen that is structurally different from a μ-OH bridge in a diol. We propose as the site of protonation a tetracoordinate O^{2-} ligand with a "wedge-shaped" (nontetrahedral) geometry.[9] This configuration appears to be unprecedented in hydrolytic oligomers, but it is found in solids such as lepidocrocite, γ-FeO(OH),[11] and γ-CrO(OH).[12,13]

Further evidence in favor of our structural assignments is obtained from the quantities $\epsilon_0 - \epsilon_\infty$ in the stopped-flow runs. Thus, at pH 4.0, of the total amount of TC formed, 30% arises from HTO and 70% from TO, as follows from the pK_a of HTO (=3.5). From the known spectral difference[2] between HTO and TC and the $\epsilon_0 - \epsilon_\infty$ for the isomerization, one obtains the following spectral data for TO: $\epsilon_{425} \approx 31.9$; $\epsilon_{579} \approx 18.7$ (per Cr). Compared with HTO,[2] both absorbancies are somewhat larger and the differences (+1.6 and 3.1, respectively) are comparable to the differences at λ_{max} upon deprotonation of the dimer.[2] In both cases, a *trans*-H_2O–Cr–OH_2 unit of a –(OH)[$Cr(OH_2)_4$](OH)– fragment is deprotonated. Similarly, the reactions occurring at pH 0.3 are TC → HTO (20%) and HTC → HTO (80%), and the spectral data for HTC are $\epsilon_{425} \approx 22.8$ and $\epsilon_{579} \approx 17.4$. Upon deprotonation, the absorbancies

(7) (a) Thompson, G. Ph.D. Thesis, University of California, Berkeley, 1964; Lawrence Radiation Laboratory Report UCRL-11410. (b) Thompson, M. E.; Connick, R. E., unpublished work.

(8) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

(9) In this nontetrahedral oxygen, some electron density is available for binding a proton on the side that is not occupied by Cr(III):



Five-[10] and six-coordinate oxygens are known in polynuclear molybdate, vanadate, and other polyoxymetalate structures. The suggested protonated $HOCr_4$ species is unstable (pK_a = 0.9) and labile ($t_{1/2}$ ~ 7 s).

(10) Kroenke, W. J.; Fackler, J. P.; Mazany, A. M. *Inorg. Chem.* **1983**, *22*, 2412.

(11) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975; pp 527–529.

(12) Nørlund Christensen, A. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 133.

(13) Hund, F. *Naturwissenschaften* **1959**, *46*, 320.

increase by 5.0 and 4.4, which is considerably more than in the dimer.[2] Also the trimer gives smaller increases (−0.9, +3.9) than the tetramer. Again, these data are consistent with a structurally different site of protonation/deprotonation in the pair TC–HTC for which we postulate a tetracoordinated O^{2-} ligand.

Finally, the intramolecular lability of the tetramer is potentially useful in synthesis, as external nucleophiles may compete effetively in opening and closing reactions. This is confirmed by the rapid incorporation of alanine into the tetramer (k_{obsd} = 0.2–0.9 s^{-1}).[4]

Conclusion

The data presented here are consistent with the proposed structures and interconversions of $Cr_4O(OH)_5^{5+}$ (Scheme I), and insofar, they add considerable strength to the structural proposals made in ref 2. The mechanistic information gained in this study is complete to the extent that significant values could be determined for all parameters. Their accuracy is as good as possible in view of the limited range of accessible pH values. The proposed structures are quite consistent with the stabilities and reactivities attributed to them. The rates of these intramolecular reactions are remarkably higher than those of other known oligomers of Cr(III). Furthermore, the overall consistency of the data suggests that the tetramer is not a mixture of species other than those considered in Scheme I.

The isomerization constants, $K_{i,H}$ = 0.020 and K_i = 8.8, are in keeping with the earlier assertion[2] that the protonated tetramer is more stable in the open form and the unprotonated in the closed form. In both protonated and unprotonated forms, the stability differences between closed and open forms are modest, suggesting a rather high thermodynamic stability of the oxo ligand in this particular environment.

Experimental Section

Materials. The tetramer, $Cr_4(OH)_6^{6+}$, in sodium perchlorate solution was prepared as described.[2] Triazole and alanine (Fluka, puriss.) were used as such; solutions of commercial 4-sulfanilic acid (Fluka, puriss.) were filtered before use.

Instrumentation. Visible spectra and pH values were measured as described.[2] Stopped-flow kinetics were run on a HI-Tech instrument where the transmission (T) vs. time (t) trace was recorded on a Nicolet 2090 digital oscilloscope. In most experiments, half of a track of a mini floppy disk (2048 points) was used. The data were then transmitted to a SORD laboratory computer. From the transmission data (voltage scale, V) the change in optical density was obtained as $\Delta D_t = D_t - D_\infty = \log (V_t/V_\infty)$ by using an estimate of V_∞. The computer program searched for an approximate value of the half-life and performed a linear regression, ln ($|\Delta D_t|$) vs. t to give k_{obsd} and $|D_0 - D_\infty|$. Some 500–1300 readings were taken from a chosen first point (T_0) up to 4 approximate half-lives. Intermediate results for k_{obsd}, $|D_0 - D_\infty|$, and the standard deviations were displayed after 1–4 half-lives. When systematic drifting occurred, V_∞ or T_0 were varied and the computation was repeated until a constant value for k_{obsd} resulted within the successive ranges T_0–$nT_{1/2}$ (n = 1–4). In many runs, the differences between the values of k_{obsd} thus obtained differed by less than 1%. For a visual check of the fitting procedure, the plot of ln ($|\Delta D|$) vs. t was transferred from the computer to the oscilloscope.

The reactions were followed at 425 and 579 nm, taking 6–8 runs at each wavelength and pH. Of these 12–16 runs, usually more than 8 gave an acceptable fit. The values of k_{obsd} at 425 and 579 nm agreed within the experimental error.

Stopped-Flow Experiments. (i) Acidification. A solution of the tetramer with I = 1.0 ($NaClO_4$) was titrated to ca. pH 3.85 to yield the monodeprotonated form. At this pH, the tendency of the tetramer to polymerize by intermolecular reactions is negligible. In the stopped-flow instrument, the tetramer solution was mixed with $HClO_4$, triazole, or alanine buffers of the same ionic strength.

For pH determination in the buffers, equal amounts of buffer (0.4 M, I = 1.0 ($NaClO_4$)) and 1 M $NaClO_4$ containing alanine at the same concentration as the tetramer in the stopped-flow experiments were mixed. (Alanine has pK_{a1} = 2.5, which is very close to that of the tetramer.) The pH values measured on these mixtures correspond closely to the final pH values in the stopped-flow runs. On the other hand, the pH of mixtures of buffer solutions with $NaClO_4$ alone corresponds to the initial pH just after mixing, but before interconversion of the different forms sets in.

(ii) Alkalinization. In a preliminary experiment, an acidic solution of tetramer was reacted with an appropriate solution of NaOH to achieve nearly complete removal of one proton per tetramer. However, owing to high local concentrations of OH^-, a precipitate formed and buffers were therefore needed. Hence, a solution of tetramer was brought to $[H]_{tot} = [Cr_4(OH)_6] + [H]$ = 0.1 M and was mixed in the stopped-flow instrument with the corresponding buffer bases (sulfanilate, triazole, alanine). The pH was determined by mixing equal volumes of buffer with 0.1 M $HClO_4$ (both solutions at I = 1.0 ($NaClO_4$)). The measured pH was corrected for the presence of tetramer by using the pK_a of HTO (=3.5) (initial pH) and with pK_{a1} (=2.55) at equilibrium (final pH). The observed reaction amplitudes were near the practical limits of detection with typical values of $|\Delta D|$ = 0.007–0.08.

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