

Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 3. Kinetics of Dimerization of the Deprotonated Aqua Ion¹

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The initial step of hydrolytic polymerization of Cr(III) is the dimerization of the monomer: $\text{Cr}(\text{OH})_r^{(3-r)+} \rightarrow \frac{1}{2}\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_s^{(4-s)+} + m\text{H}^+$ ($m = 1 + s/2 - r$). At constant pH, maintained with a pH stat, this reaction leads to a net consumption of base. The kinetics may, thus, be followed by measuring on a pH stat the volume of base added as a function of time. Only the initial rates in this system are relevant to dimer formation, for as soon as dimer is formed, it reacts with monomer to form trimer, or with dimer to form tetramer, etc. Weakly alkaline titrants, e.g. ethanolamine, were required and necessitated work under variable-volume conditions. The appropriate rate expressions have been derived. Chromatographic product analysis as a function of time established formation of dimer as the main product for the first 5% of the reaction. Small amounts of trimer and higher oligomers result from polymerization steps subsequent to dimer formation. Nevertheless, the measured rates correspond quite precisely to the true initial rates in the system. The initial rate kinetics of dimerization have been measured in the pH range 3.5–5.0 (25 °C, $I = 1.0$, NaClO_4) and were consistent with the following rate law: $-\frac{1}{2}d[\text{monomer}]/dt = [\text{monomer}]^2(b_2[\text{H}^+]^{-2} + b_3[\text{H}^+]^{-3} + b_4[\text{H}^+]^{-4})/(1 + K_{M1}[\text{H}^+]^{-1} + K_{M1}K_{M2}[\text{H}^+]^{-2})^2$, where b_2 , b_3 , and b_4 are observed, gross rate constants and K_{M1} and K_{M2} are the first and second acid dissociation constants of Cr^{3+} , respectively. From the observed pH dependence of the rate, the following rate constants were deduced: $b_2 = (5.3 \pm 1.2) \times 10^{-13} \text{ M}^{-3} \text{ s}^{-1}$; $b_3 = (8.0 \pm 2.0) \times 10^{-17} \text{ M}^{-4} \text{ s}^{-1}$; $b_4 = (2.9 \pm 0.3) \times 10^{-21} \text{ M}^{-5} \text{ s}^{-1}$. Numerator terms independent of $[\text{H}^+]$ ($=b_0$) or dependent on $[\text{H}^+]^{-1}$ ($=b_1$) were not observed. These rate constants are subject to ambiguity as to how many protons are removed from each individual monomer species. However, assuming that proton transfer between differently deprotonated monomer species is much faster than any substitution at Cr(III), then the observed rate constants b_2 , b_3 , and b_4 may be interpreted as follows: $\text{CrOH}^{2+} + \text{CrOH}^{2+} \rightarrow \text{dimer}$, rate constant $k_{11} = (2.0 \pm 0.4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$; $\text{CrOH}^{2+} + \text{Cr}(\text{OH})_2^+ \rightarrow \text{dimer}$, $k_{21} = (3.8 \pm 1.0) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$; $\text{Cr}(\text{OH})_2^+ + \text{Cr}(\text{OH})_2^+ \rightarrow \text{dimer}$, $k_{22} = 1.8 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$. These rate constants represent significant accelerations relative to the water-exchange rate in Cr^{3+} ($k_{\text{H}_2\text{O}} = 2.4 \times 10^{-6} \text{ s}^{-1}$).

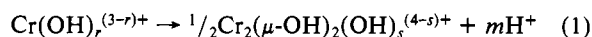
Introduction

The relevance of the hydrolytic polymerization of metal ions is widely recognized,⁴ yet the present knowledge of this topic is in no way commensurate with its importance. In most cases, hydrolytic polymerization eventually leads to formation of precipitates that are usually poorly crystalline and equilibrate with solution species extremely slowly. A closer look at the possibilities of how these might form readily reveals the immense complexity of the phenomenon. Nevertheless, a great deal of structural and thermodynamic information is available on intermediate stages of hydrolytic polymerization. However, these data are unsystematically scattered over many different elements and oxidation states and refer to very different stages of hydrolytic polymerization. Although considerable knowledge on the stability and connectivity of hydrolytic polymers of different degrees of condensation has accumulated, there exists a remarkable, almost complete lack of kinetic and mechanistic data on hydrolytic polymerization reactions.

Our previous work on the hydrolytic polymerization of Cr(III)^{1,5} has led us to recognize that the formation and interconversion of hydrolytic Cr(III) oligomers occurs sufficiently slowly to permit separation and isolation of individual species in solution. Thus, a complete series of hydrolytic oligomers up to and including a hexamer was obtained.⁵ Significantly, only one oligomer has been found so far for each nuclearity, despite numerous possibilities of isomeric configurations for species higher than the dimer. This suggests that intermolecular polymerization steps might be governed by clearly defined, kinetically controlled, inter- and intramolecular pathways and that the structural patterns for the buildup of infinite polymers might eventually be derived from a systematic knowledge of these pathways.

No kinetic data appear to be available on intermolecular polymerization of Cr^{3+} (or of any of its hydrolytic oligomers). This paper reports on the kinetics of dimerization of the Cr(III) mo-

nomer, in the range of pH 3.5–5.0. Under these conditions, Cr^{3+} , CrOH^{2+} , and $\text{Cr}(\text{OH})_2^+$ are initially present in significant amounts and may be reactive species in dimer formation:



Reaction 1 most likely occurs in two steps, via formation of a singly bridged intermediate, $\text{Cr}_2(\mu\text{-OH})(\text{OH})_t^{(5-t)+}$. In this paper, only the gross rate constants for reaction 1 are discussed. The reactivity of the singly bridged intermediate is being investigated under the conditions of the present study.⁶

Definitions

Total concentrations of monomer and dimer are given by

$$[\text{monomer}] = [\text{Cr}^{3+}] + [\text{CrOH}^{2+}] + [\text{Cr}(\text{OH})_2^+] + \dots$$

$$[\text{dimer}] = [\text{Cr}(\text{OH})_2\text{Cr}^{4+}] + [\text{Cr}(\text{OH})_2\text{CrOH}^{3+}] + [\text{HO}(\text{Cr}(\text{OH})_2\text{CrOH}^{2+})] + [\text{HO}(\text{Cr}(\text{OH})_2\text{Cr}(\text{OH})_2^+)] + \dots \\ = [\text{Cr}_2(\text{OH})_2^{4+}] + [\text{Cr}_2(\text{OH})_3^{3+}] + [\text{Cr}_2(\text{OH})_4^{2+}] + [\text{Cr}_2(\text{OH})_5^+] + \dots$$

The relevant acid dissociation constants are⁵

$$K_{M1} = [\text{CrOH}^{2+}][\text{H}^+]/[\text{Cr}^{3+}] = 10^{-4.29} \text{ M}$$

$$K_{M2} = [\text{Cr}(\text{OH})_2^+][\text{H}^+]/[\text{CrOH}^{2+}] = 10^{-6.1} \text{ M}$$

$$K_{D1} = [\text{Cr}_2(\text{OH})_3^{3+}][\text{H}^+]/[\text{Cr}_2(\text{OH})_2^{4+}] = 10^{-3.68} \text{ M}$$

$$K_{D2} = [\text{Cr}_2(\text{OH})_4^{2+}][\text{H}^+]/[\text{Cr}_2(\text{OH})_3^{3+}] = 10^{-6.04} \text{ M, etc.}$$

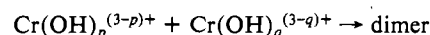
and for the singly bridged dimer

$$K_{S1} = [\text{OHC}(\text{OH})\text{Cr}^{4+}][\text{H}^+]/[\text{Cr}(\text{OH})_2\text{Cr}^{4+}] = 10^{-1.6} \text{ M}^7$$

The stability constant of the doubly bridged dimer is⁵

$$\beta_{22} = [\text{Cr}_2(\text{OH})_2^{4+}][\text{H}^+]^2/[\text{Cr}^{3+}]^2 \approx 10^{-5.26} \text{ M}$$

The rate constants for the reactions



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are designated k_{pq} with $p, q = 0, 1, 2, 3$.

Results and Experimental Considerations

Preliminary Experiments. In the first series of experiments, acidic solutions of Cr^{3+} (1–5 mM) were titrated at 25 °C and $I = 1.0 \text{ M}$ (NaClO_4) to a predetermined pH value between 4.2 and 4.8. Hydrolytic polymerization then liberated H^+ according to reaction 1 and similar, subsequent processes. These protons were then continuously neutralized by adding NaOH (0.01 M) from a pH stat; i.e., the pH was kept constant. The consumption of base as a function of time was followed for up to 1 week in order to estimate the base consumption at $t \rightarrow \infty$. The measured curves, milliliters of titrant as a function of time, were almost linear at early stages of the reaction and leveled off at later stages. Although a constant base volume was not reached, it became apparent that the final base consumption depended on the pH of the solution. No attempt was made to establish the stoichiometry of the end product.

In these experiments, the Cr(III) solutions remained homogeneous throughout. Chromatographic separations established that higher oligomers (more than six Cr atoms per unit) were the predominant species at the end of the reactions. In addition, hard, dark green granules of a water-insoluble material were deposited at the tip of the buret during the titrations. This material accounted for less than 2–3% of total chromium at the end of the titration. From its method of formation, it is presumably a chromium hydroxide or oxide-hydroxide phase.

These experiments also revealed that the observed rates ($=d(\text{milliliters of titrant})/dt$) were accelerated by diffuse daylight. Thus, the definitive titrations were carried out under exclusion of light.

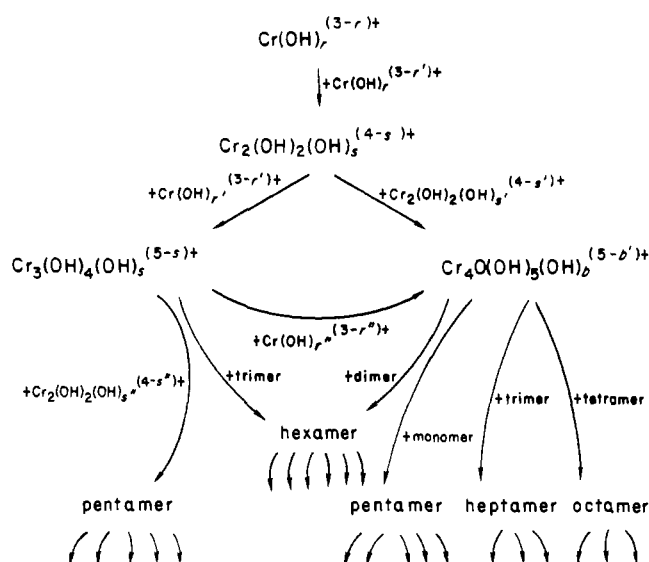
A Complication: Formation of "Active" Chromium Hydroxide and Its Dissolution in Alkaline Solution. Alkalinization of Cr^{3+} leads to dark green solutions containing CrOH^{2+} and $\text{Cr}(\text{OH})_2^+$ in the range 4.0–5.0.⁸ As will be shown below, these species are reactive in hydrolytic polymerization. Above $\text{pH} \approx 5.0$ insoluble, pale green, "active" hydrated chromium hydroxide precipitates immediately.^{9,10} This material has a layer structure consisting of hydrogen-bonded $\text{Cr}(\text{OH})_3(\text{OH})_2$ units.¹¹ This precipitate readily dissolves in acid, regenerating the monomer quantitatively.¹² Thus, hydrolytic polymerization is not involved in the formation of "active" chromium hydroxide.

Chromium(III) in aqueous solution is amphoteric; i.e., "active" chromium hydroxide also dissolves rapidly in alkali hydroxide above $\text{pH} 12$. The nature and reactivity of the alkaline chromite solutions are not well established.¹³ However, when alkaline chromite solutions were acidified, $\text{Cr}_3(\text{OH})_4^{5+}$ was the predominant species,^{13,14} at least after some reaction time.

The pH state titrations inevitably lead to a local excess of OH^- on addition of the titrant. Depending on the pH chosen, this will lead to precipitation of "active" chromium hydroxide or even to its dissolution to form anionic chromites. The fate of chromites before and during reacidification is not yet established. Thus, the pH stat kinetics were run with use of different buffers as the titrants, and $\text{pH} 10.5$ was never exceeded, not even locally. Under these conditions, the deposition of insoluble material at the tip of the buret never exceeded 0.2% of the total chromium.

Determination of Initial Rates in the System $\text{Cr}^{3+} + \text{OH}^-$. The only rate process to be considered here is the dimerization of the monomer (eq 1). However, as soon as the dimer is formed, further

Scheme I



polymerization occurs concurrently (Scheme I) and the reaction system branches out progressively as the reaction proceeds. If the steps subsequent to the initial dimer formation are sufficiently rapid, then they interfere with the initial rate, even if the dimer concentration is low. However, in the present system, such interference can be checked by chromatographic product analysis as a function of time (see below).

Proton Balance in the Dimerization Reaction. At $\text{pH} \leq 5$, the concentration of more than doubly deprotonated species is negligible. Thus, the coefficients r and s in eq 1 are related to the pH of the solution by the equations

$$r = \frac{K_{M1}[\text{H}^+]^{-1} + 2K_{M1}K_{M2}[\text{H}^+]^{-2}}{1 + K_{M1}[\text{H}^+]^{-1} + K_{M1}K_{M2}[\text{H}^+]^{-2}} = \frac{[\text{CrOH}^{2+}] + 2[\text{Cr}(\text{OH})_2^+]}{[\text{monomer}]}$$

$$s = \frac{K_{D1}[\text{H}^+]^{-1} + 2K_{D1}K_{D2}[\text{H}^+]^{-2}}{1 + K_{D1}[\text{H}^+]^{-1} + K_{D1}K_{D2}[\text{H}^+]^{-2}} = \frac{[\text{Cr}_2(\text{OH})_3^{3+}] + 2[\text{Cr}_2(\text{OH})_4^{2+}]}{[\text{dimer}]}$$

Here, terms involving the small (see below) third acid dissociation constants, K_{M3} and K_{D3} , have been neglected. The number of equivalents of protons released, m (eq 1), is a simple function of r and s and thus of pH :

$$m = 1 + s/2 - r \quad (2)$$

The total base consumption therefore depends on [monomer] as well as on the pH . The dimerization was found to be essentially irreversible in the pH range studied (see below).

Product Analysis as a Function of Time for Different Titrant Bases. For the purpose of product analysis the pH stat kinetics were followed with use of 0.02 M ethanolamine solutions ($\text{pH} \approx 10.5$) as well as an imidazole buffer (0.2 M imidazole (im), 0.3 M $\text{im}\cdot\text{HClO}_4$, $\text{pH} 7.2$) as the titrants (Table I). These two uncharged buffer bases differ by a factor of 10 in concentration and by ca. 3.3 units in pH . Samples of the reacting mixtures were quenched with acid, separated by cation exchange, and analyzed for chromium.⁵ The data (Table I, Figure 1) are subject to $\pm 10\%$ relative error in the oligomers for $<10\%$ conversion and are thus less precise than those in previous work,⁵ since small quantities of dimer and other oligomers had to be separated from large amounts of unreacted monomer.

In the imidazole buffer runs, no detectable amounts of trimer are formed for $<5\%$ conversion of the monomer (Table Ia,b). This degree of conversion matches the 2–5% of the reaction followed in the kinetics (see below). Trimer and tetramer are formed only

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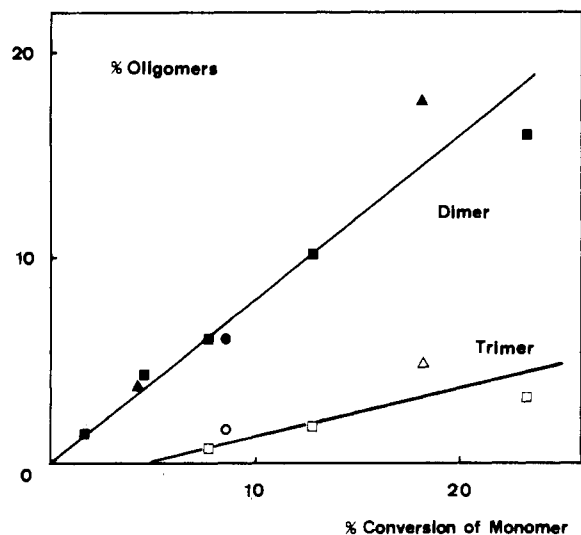


Figure 1. Product analysis in the early stages of hydrolytic polymerization of Cr^{3+} . The amounts of dimer and trimer formed increase nearly linearly with increasing extent of reaction. The different symbols for the data points refer to different pH and titrant bases: (squares) see part a of Table I; (triangles) see part b of Table I; (circles) see part c of Table I.

at later stages of the reaction, but $<0.4\%$ of higher polymers appear already for $<5\%$ conversion. The delayed appearance of trimer and tetramer is consistent with their formation from dimer in *consecutive* steps. However, the dimer concentration is still very small at the time of the first appearance of trimer, and this suggests that the reaction $\text{dimer} + \text{monomer} \rightarrow \text{trimer}$ is distinctly faster than $\text{monomer} + \text{monomer} \rightarrow \text{dimer}$.

The presence of higher oligomers, along with the absence of detectable quantities of trimer, as observed for $<5\%$ of monomer conversion, is analogous to the product distribution after long reaction times (Table Ib, last entry), except that little monomer and dimer are left under these last conditions. It is likely that these minute (but clearly detectable) amounts of higher oligomers result from the reaction of monomer with the titrant base in local excess, near the tip of the buret, within the time of mixing. In this transient excess of titrant base, hydrolytic polymerization is expected to be very fast and to lead to a product distribution similar to that at long reaction times at lower pH.

In the imidazole buffer runs, a nearly constant ratio (% dimer)/(% trimer) ≈ 4 is found for 5–25% conversion of the monomer. This is consistent with trimer formation first order in [monomer] and in [dimer], since [dimer] increases nearly linearly with time (Figure 1) while [monomer] remains constant within ca. $\pm 10\%$ and $<3\%$ of tetramer and higher polymers are formed. The titrant bases appear not to be incorporated into the product species, for their elution behavior and color on the columns matched those of authentic samples.¹⁵

The product analyses for ethanolamine and imidazole buffers agreed (Figure 1). In these experiments the pH of the titrant bases does not exceed 10.5. In contrast, product formation followed a distinctly different pattern, when Cr^{3+} was treated at once with NaOH (0.2 M) to make up $\bar{n} = 0.3$ (Table Id). As expected from eq 1, the pH of the solution decreased with time as a consequence of hydrolytic polymerization. In these experiments, dimer, tetramer, and higher oligomers were clearly detectable from the beginning of the reaction. This is possibly related in some way to a high local excess of base during the initial mixing of Cr^{3+} with OH^- .

In conclusion, the product distribution is independent of the nature, total concentration, and pH of titrant bases, provided a local pH of ca. 10.5 is not exceeded. Detectable amounts of trimer and tetramer appear only at $>5\%$ conversion of monomer.

Table I. Product Analysis for Hydrolytic Polymerization of Cr^{3+} at Constant (a–c) or Variable (d) pH ($I = 1.0$ (NaClO_4), 25°C)

(a) Conditions: $[\text{Cr}^{3+}]_0 = 0.04$ M; pH 4.51;
Base Added for pH Control 0.2 M im/0.3 M im· HClO_4

time, min	% Cr				
	monomer	dimer	trimer	tetramer	higher polymers
5	98.4	1.4			0.2
10	95.5	4.3			0.2
20	92.3	6.1	0.7		≈ 0.9
40	87.2	10.2	1.8	0.8	0.8
80	76.7	16.0	3.2	1.6	≈ 2.6
160	59.5	20.6	6.3	6.7	6.9

(b) Conditions: $[\text{Cr}^{3+}]_0 = 0.02$ M; pH 4.81;
Base Added for pH Control as in (a)

time, min	% Cr				
	monomer	dimer	trimer	tetramer	higher polymers
5	95.8	3.8			0.4
60	71.8	17.7	4.9	3.5	2.1
120	52.8	20.8	7.6	9.3	9.5
1380	1.4	6.1		10.4	82.1

(c) Conditions: $[\text{Cr}^{3+}]_0 = 0.08$ M; pH 3.63;
Base Added for pH Control 0.2 M Ethanolamine

time, min	% Cr				
	monomer	dimer	trimer	tetramer	higher polymers
22.5	91.4	6.1		1.7	<0.8

(d) Conditions: $[\text{Cr}^{3+}]_0 = 0.04$ M; $\bar{n} = 0.3$ (Constant);^a
Initial Solution pH Made up with 0.2 M NaOH

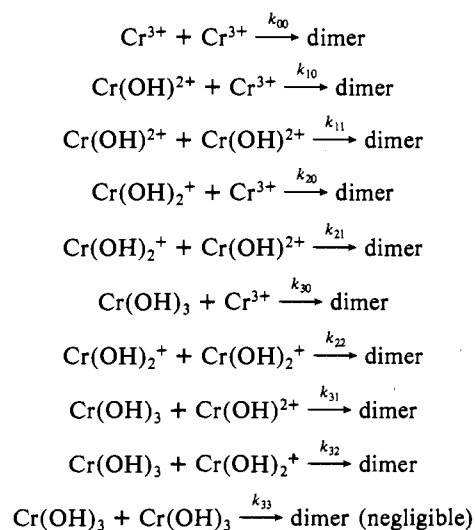
time, h	pH	% Cr				
		monomer	dimer	trimer	tetramer	higher polymers
0.5	3.94	98.7	0.5	0.1	0.05	0.5
1	3.91	97.2	1.4	0.3	0.1	1.0
2	3.86	95.8	2.3	0.7	0.2	1.0
4	3.77	94.5	3.1	0.6	0.2	1.7
6	3.68	91.6	3.9	0.6	0.5	3.3
8	3.58	89.8	4.3	1.1	0.6	4.4

^a \bar{n} = mol of OH^- added/mol of Cr^{3+} .

Kinetics. General Considerations. The product analyses confirm that the first 5% of Cr^{3+} is essentially all converted into dimer; hence, the initial rates as obtained from pH stat runs afford the rate of dimerization.

In the pH range studied, Cr^{3+} and CrOH^{2+} are the predominant species. Toward the upper limit of the pH range, $<10\%$ of $\text{Cr}(\text{OH})_2^+$ is also present. Monomeric $\text{Cr}(\text{OH})_3$ will only be present in very small concentrations,¹⁰ but it could be more reactive than the other species. When all the above species are taken into account, 10 pathways may be considered (Scheme II):

Scheme II



(15) The total amounts of chromium in the oligomer bands were too small for recording UV/vis spectra.

The corresponding differential rate law is

$$-\frac{1}{2} \frac{d[\text{monomer}]}{dt} = k_{00}[\text{Cr}^{3+}]^2 + k_{10}[\text{CrOH}^{2+}][\text{Cr}^{3+}] + k_{11}[\text{CrOH}_2^{+}]^2 + k_{20}[\text{Cr}(\text{OH})_2^{+}][\text{Cr}^{3+}] + k_{21}[\text{Cr}(\text{OH})_2^{+}][\text{CrOH}^{2+}] + k_{30}[\text{Cr}(\text{OH})_3][\text{Cr}^{3+}] + k_{22}[\text{Cr}(\text{OH})_2^{+}]^2 + k_{31}[\text{Cr}(\text{OH})_3][\text{CrOH}^{2+}] + k_{32}[\text{Cr}(\text{OH})_3][\text{Cr}(\text{OH})_2^{+}] = k_{\text{obsd}}[\text{monomer}]^2 \quad (3)$$

The pH dependence of k_{obsd} may be expressed with use of the first three acid dissociation constants of Cr^{3+} , viz. K_{M1} , K_{M2} , K_{M3} :

$$k_{\text{obsd}} = (b_0 + b_1[\text{H}^+]^{-1} + b_2[\text{H}^+]^{-2} + b_3[\text{H}^+]^{-3} + b_4[\text{H}^+]^{-4} + b_5[\text{H}^+]^{-5}) / \{(1 + K_{M1}[\text{H}^+]^{-1} + K_{M1}K_{M2}[\text{H}^+]^{-2} + K_{M1}K_{M2}K_{M3}[\text{H}^+]^{-3})^2\} \quad (4)$$

where $b_0 = k_{00}$, $b_1 = k_{10}K_{M1}$, $b_2 = k_{11}K_{M1}^2 + k_{20}K_{M1}K_{M2}$, $b_3 = k_{21}K_{M1}^2K_{M2} + k_{30}K_{M1}K_{M2}K_{M3}$, $b_4 = k_{22}K_{M1}^2K_{M2}^2 + k_{31}K_{M1}^2K_{M2}K_{M3}$, and $b_5 = k_{32}K_{M1}^2K_{M2}^2K_{M3}$.

From the necessity to avoid high local concentrations of OH^- , the required volume of the titrant buffers was too large to be neglected. Thus, the kinetic analysis has to take into consideration the total change of [monomer] by dimerization and dilution

$$-d[\text{monomer}] = 2k_{\text{obsd}}[\text{monomer}]^2 dt + [\text{monomer}] \frac{dV}{V_0 + V} \quad (5)$$

where V_0 is the volume at $t = 0$ and V the volume of base added at time t . At constant pH, the degree of conversion into dimer and V are related and this relationship defines the boundary condition for integrating eq 5 (Appendix, part A):

$$k_{\text{obsd}} = \frac{1}{2t} \left\{ \frac{V}{[\text{Cr}^{3+}]_0 V_0 - \frac{V}{m}([\text{B}] + [\text{H}^+])} \left(\frac{[\text{B}] + [\text{H}^+]}{m[\text{Cr}^{3+}]_0} + 1 \right) + \frac{m}{[\text{B}] + [\text{H}^+]} \ln \left[1 - \frac{V([\text{B}] + [\text{H}^+])}{m[\text{Cr}^{3+}]_0 V_0} \right] \right\} \quad (6)$$

where $[\text{Cr}^{3+}]_0$ is [monomer] at $t = 0$, [B] the concentration of the titrant base, and m the number of moles of base consumed per mole of reacted monomer (eq 2). Parameter m is defined by eq 1 and 2. For small volumes, eq 6 reduces¹⁶ to

$$k_{\text{obsd}} \approx \frac{V}{t} \frac{m[\text{Cr}^{3+}]_0 + [\text{B}] + [\text{H}^+]}{2m[\text{Cr}^{3+}]_0^2 V_0}$$

i.e., the volume becomes a linear function of time.

Kinetic Data Collection. The kinetics of reaction 1 were studied at 25.0 ± 0.1 °C and $I = 1.0$ (NaClO₄). In these pH stat runs at constant pH in the range 3.5–5.0, released protons were neutralized with use of either "Tris" or ethanolamine solutions (0.02 M). For the degree of conversion of monomer considered (ca. 5%), the added volume of base (V) was found to be a practically linear function of time. The experimental rate constants, k_{obsd} , were determined at 5–15 points (V , t) with use of eq 6, for known values of $[\text{H}^+]$, [B], $[\text{Cr}^{3+}]_0$, V_0 , and m . Runs at different $[\text{Cr}^{3+}]_0$ were consistent with the supposed second-order dependence (eq 3 and 5) at all pH values studied (Table II).

The standard deviation in k_{obsd} was ca. 7% of the values, and the rate constants may be subject to some systematic error: acidic stock solutions of Cr^{3+} (pH < 2.5) were brought close to the reaction pH with 0.2 M "Tris" or ethanolamine. The final setting of the pH was then reached by pH stat titration, and $t = 0$ was set at the moment that the pH stat was activated. However, there

Table II. Experimental Parameters, Observed Rate Constants, and Degrees of Reversibility for the Dimerization of Cr^{3+} at 25.0 ± 0.1 °C and $I = 1.0$ (NaClO₄)

pH ^a	m^b	$10^3[\text{Cr}^{3+}]_0$, M	V_0 , mL	k_{obsd} , M ⁻¹ s ⁻¹ c	$p(\geq)^d$
3.506	1.060	33.9	58.34	5.85×10^{-6}	85
3.506	1.060	58.5	33.80	5.42×10^{-6}	150
3.506	1.060	92.0	32.84	5.41×10^{-6}	230
3.627 ^e	1.057	58.4	33.82	1.10×10^{-5}	260
3.627 ^e	1.057	59.8	33.02	1.03×10^{-5}	270
3.627 ^e	1.057	92.8	32.53	1.18×10^{-5}	420
3.755	1.046	18.1	54.44	2.32×10^{-5}	150
3.755	1.046	33.2	59.49	2.06×10^{-5}	280
3.755	1.046	58.0	34.08	2.15×10^{-5}	490
3.882	1.026	18.0	43.90	4.45×10^{-5}	280
3.881	1.026	32.5	24.35	4.27×10^{-5}	500
3.880	1.027	55.6	35.53	3.99×10^{-5}	850
4.009	0.996	9.39	105.23	9.11×10^{-5}	260
4.009	0.996	17.8	55.45	8.01×10^{-5}	500
4.009	0.996	32.7	60.41	7.63×10^{-5}	910
4.127	0.960	9.38	105.32	1.50×10^{-4}	450
4.127	0.960	17.6	56.00	1.43×10^{-4}	840
4.127	0.960	31.7	62.25	1.35×10^{-4}	1500
4.259	0.911	9.18	107.62	2.69×10^{-4}	770
4.259	0.911	17.4	56.74	2.68×10^{-4}	1500
4.259	0.911	31.4	62.96	2.32×10^{-4}	2600
4.377	0.862	4.80	102.98	4.95×10^{-4}	650
4.377	0.862	17.6	56.27	4.57×10^{-4}	2400
4.377	0.862	31.6	62.49	4.27×10^{-4}	4300
4.506	0.806	4.73	104.38	8.13×10^{-4}	1100
4.505	0.806	9.07	108.95	7.46×10^{-4}	2000
4.506	0.806	17.5	56.60	8.21×10^{-4}	3900
4.627	0.753	4.77	103.54	1.67×10^{-3}	1600
4.627	0.753	17.3	57.00	1.38×10^{-3}	6000
4.627	0.753	30.8	64.23	1.22×10^{-3}	11000
4.756	0.700	4.77	103.63	2.28×10^{-3}	2500
4.756	0.700	9.13	108.25	2.38×10^{-3}	4800
4.755	0.700	9.20	107.38	2.16×10^{-3}	4900
4.756	0.700	17.2	57.41	2.33×10^{-3}	9100
4.881	0.652	4.76	103.81	5.21×10^{-3}	3700
4.882	0.651	4.76	103.70	5.30×10^{-3}	3700
4.882	0.651	9.18	91.46	5.27×10^{-3}	7200
5.006	0.608	4.75	103.93	7.44×10^{-3}	5300
5.005	0.608	4.76	103.82	8.78×10^{-3}	5300
5.005	0.608	9.16	107.91	8.02×10^{-3}	10000

^apH kept constant with 0.02 M Tris titrant; $\text{p}K_w = 13.80$. ^bEq 2. ^cEq 6. ^dSee part B of the appendix and the text. ^eTitant base was 0.02 M ethanolamine.

is some dimerization during the time required for reaching the initial pH. This error is negligible at low pH, where the reaction is slow, but appreciable ($\approx 3\%$) toward the upper limit of the pH range.

The possible reversibility of the dimerization could introduce another systematic error, and this needs to be examined. Using the stability constant of the dimer β_{22} , we obtain the conditional (pH-dependent) equilibrium constant for the dimer:

$$\beta_{22}' = \frac{[\text{dimer}]}{[\text{monomer}]^2} = \frac{[\text{Cr}_2(\text{OH})_2^{4+}] + [\text{Cr}_2(\text{OH})_3^{3+}] + [\text{Cr}_2(\text{OH})_4^{2+}]}{([\text{Cr}^{3+}] + [\text{CrOH}^{2+}] + [\text{Cr}(\text{OH})_2^{+}])^2} = \frac{\beta_{22}(1 + K_{D1}[\text{H}^+]^{-1} + K_{D1}K_{D2}[\text{H}^+]^{-2})}{[\text{H}^+]^2(1 + K_{M1}[\text{H}^+]^{-1} + K_{M1}K_{M2}[\text{H}^+]^{-2})^2} \quad (7)$$

It is shown in part B of the appendix that the effect of reversibility is negligible, if the quantity $p = 2\beta_{22}'(0.95)^2[\text{Cr}^{3+}]_{\text{tot}}/0.05$ is much greater than 1. In these experiments p varies between 85 and 10^4 (Table II), and the reaction may thus be considered irreversible

(16) Since for small x , $\ln(1-x) \approx -x$.

Table III. pK_a Values of Mononuclear Tri- and Tetraaquachromium(III) Complexes: Basis for an Estimate of pK_{a3} of Cr^{3+}

complex	pK_{au}	pK_{ai}	pK_{ao}	conditions	ref
<i>trans</i> (?)- $Cr(NH_3)_2(OH_2)_4^{3+}$	4.20			25 °C, 1 M $NaNO_3$	<i>a</i>
	4.11	6.59	9.18	20 °C, 0.5 M $NaNO_3$	<i>b</i>
$Cr(en)(H_2O)_4^{3+}$	4.15	6.75	8.6	20 °C, 0.1 M $NaClO_4$	<i>c</i>
$Cr(py)_2(H_2O)_4^{3+}$	3.2	5.8	8.5	20 °C, 0.1 M $NaClO_4$	<i>c</i>
$Cr(NH_3)_3(OH_2)_3^{3+}$	4.25	7.0	9.15	20 °C, 0.1 M $NaClO_4$	<i>c</i>

^aSchäffer, C. E. *Spec. Publ.—Chem. Soc.* **1964**, 55. ^bJørgensen, E.; Bjerrum, J. *Acta Chem. Scand.* **1952**, 12, 1047. ^cReference 9.

Table IV. pH Dependence of the Second-Order Rate Constants, k_{obsd} , and of the Conditional Equilibrium Constants, β_{22}'

pH ^a	$k_{obsd}, M^{-1} s^{-1} b$	$k_{calcd}, M^{-1} s^{-1} c$	$-\log k^* d$	$(-\log k^*)_{calcd} e$	$10^3 \beta_{22}', M^{-1} f$
3.506	$(5.6 \pm 0.3) \times 10^{-6}$	6.2×10^{-6}	5.12	5.10	0.070
3.627 ^g	$(1.10 \pm 0.08) \times 10^{-5}$	1.1×10^{-5}	4.80	4.79	0.13
3.755	$(2.2 \pm 0.1) \times 10^{-5}$	2.1×10^{-5}	4.44	4.46	0.23
3.881	$(4.2 \pm 0.2) \times 10^{-5}$	3.9×10^{-5}	4.09	4.11	0.43
4.009	$(8.3 \pm 0.8) \times 10^{-5}$	7.4×10^{-5}	3.72	3.75	0.77
4.127	$(1.43 \pm 0.08) \times 10^{-4}$	1.3×10^{-4}	3.39	3.40	1.3
4.259	$(2.6 \pm 0.2) \times 10^{-4}$	2.6×10^{-4}	3.01	3.00	2.3
4.377	$(4.6 \pm 0.3) \times 10^{-4}$	4.6×10^{-4}	2.64	2.63	3.8
4.506	$(7.9 \pm 0.4) \times 10^{-4}$	8.7×10^{-4}	2.24	2.21	6.2
4.627	$(1.4 \pm 0.2) \times 10^{-3}$	1.6×10^{-3}	1.82	1.81	9.5
4.756	$(2.3 \pm 0.1) \times 10^{-3}$	2.9×10^{-3}	1.42	1.36	15
4.882	$(5.26 \pm 0.05) \times 10^{-3}$	5.2×10^{-3}	0.86	0.92	22
5.006	$(8.1 \pm 0.7) \times 10^{-3}$	9.1×10^{-3}	0.46	0.46	31

^apH kept constant with 0.02 M Tris titrant unless stated otherwise. ^bErrors are $\sigma_{k_{obsd,i}}$; for number of determinations, see Table II. ^cEq 4, assuming $b_0, b_1,$ and $K_{M3} = 0$. ^dEq 8. ^eEq 9. ^fEq 7. ^gTitrant base was 0.02 M ethanolamine.

Table V. Results of Least-Squares Calculations for Different Sets of Parameters^a

no. of params, ^b <i>f</i>	std dev ^b	$10^9 b_1, M^{-2} s^{-1}$	$10^{13} b_2, M^{-3} s^{-1}$	$10^{17} b_3, M^{-4} s^{-1}$	$10^{21} b_4, M^{-5} s^{-1}$	$10^{26} b_5, M^{-6} s^{-1}$
3	2.311		5.3 ± 1.2	8.0 ± 2.0	2.9 ± 0.3	
4	1.757		2.6 ± 1.3	15 ± 3	(-0.9 ± 1.3)	3.8 ± 1.3
4	1.984	(-2.4 ± 1.1)	13 ± 4	(2.4 ± 3.2)	3.5 ± 0.4	
5	1.838	(-0.7 ± 1.5)	(5.5 ± 6.3)	13 ± 7	(-0.01 ± 2.3)	3.1 ± 2.0

^aNegative or insignificant values are given in parentheses. ^b $\{[\sum_{i=1}^N w_i (k_{obsd,i} - k_{calcd,i})^2] / (N - f)\}^{1/2}$; $w_i = 1/\sigma_i^2$, $N = 13$.

in the range of pH, $[Cr^{3+}]_{tot}$, and time studied.

At pH > 5, the rates became fast beyond control, whereas they were very slow at pH < 3.5, and this limited the accessible pH range. In order to assess the reactivity of mononuclear $Cr(OH)_3$, the pH range would have to be extended to >>5.

We note the good agreement in k_{obsd} for the different amine titrant bases. The rate constant measured with use of ethanolamine fits well into the curve obtained for the "Tris" buffers (Figure 2).

Rate Law and Rate Parameters. The third dissociation constant of the monomer, K_{M3} , is unknown. However, an estimate based on known values for aqua amine complexes of Cr(III) (Table III) is $K_{M3} < 10^{-8.5}$ M, and the concentration of monomeric $Cr(OH)_3$ is thus negligible in the pH range 3.5–5.0. The last denominator term in eq 4 can therefore be neglected, and the equation becomes

$$k^* = k_{obsd}(1 + K_{M1}[H^+]^{-1} + K_{M1}K_{M2}[H^+]^{-2})^2$$

$$= b_0 + b_1[H^+]^{-1} + b_2[H^+]^{-2} + b_3[H^+]^{-3} + b_4[H^+]^{-4} + b_5[H^+]^{-5} \quad (8)$$

A plot of $\log k^*$ vs. $\log [H^+]$ (Figure 2, Table IV) may serve to determine the significant terms in $[H^+]^n$. The limiting reaction orders at pH 3.5 and 5.0 were determined from the slopes of this graph by using a parabolic expression, with empirical parameters a_n ($n = 0, 1, 2, \dots$):

$$\log k^* = a_0 + a_1 \log [H^+] + a_2 (\log [H^+])^2 \quad (9)$$

The corresponding slope is

$$\frac{d \log k^*}{d \log [H^+]} = a_1 + a_2 \log [H^+]$$

At pH 3.5, 4.0, 4.5, and 5.0, the slopes were calculated as -2.5 , -2.9 , -3.3 , and -3.7 , respectively. Obviously, at each pH, several terms contribute to the slope. From the limiting slopes, the powers in $[H^+]$ are -2 , -3 , and -4 . Thus, only the terms containing the

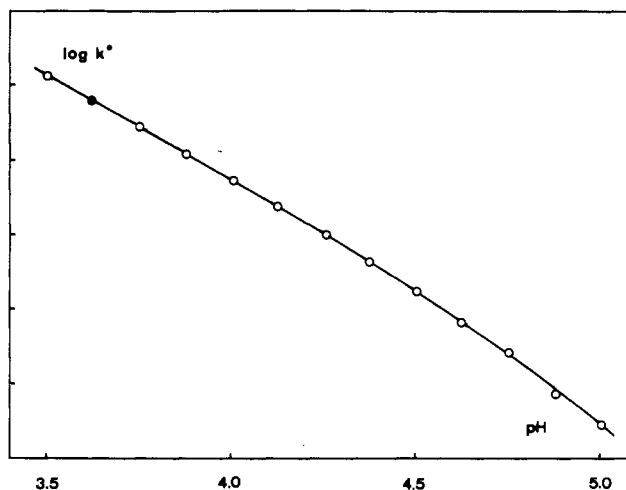


Figure 2. Plot of $\log k^*$ (see text for definition) as a function of pH: (full circle) ethanolamine buffer; (open circles) "Tris" buffer. This defines the reaction order in $[H^+]$ as a function of pH. Ordinate scale: -6 (top) to 0 (bottom) (Table IV).

parameters $b_2, b_3,$ and b_4 are important. The parameters b_i were calculated by a least-squares procedure, minimizing

$$\sum_i w_i (k_{obsd,i} - k_{calcd,i})^2; w_i = 1/\sigma_{k_{obsd,i}}$$

Further parameter calculations also included the terms $b_0, b_1,$ and b_5 (Table V), but these additional parameters were insignificant or negative in all cases. Curve fits, based on one or two parameters only, could be rejected with >90% probability, with use of the *F* test.

In conclusion, dimerization of the monomer in the pH range 3.5–5.0 occurs through three parallel pathways second order in [monomer], with reaction orders in $[H^+]$ of -2 , -3 , and -4 .

Table VI. Numerical Values of Rate Constants k_{pq} (25.0 ± 0.1 °C, $I = 1.0$ (NaClO₄))

reacn	rate constant
$\text{CrOH}^{2+} + \text{Cr}^{3+} \rightarrow \text{dimer}$	$k_{10} \approx 6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ ^a
$\text{CrOH}^{2+} + \text{CrOH}^{2+} \rightarrow \text{dimer}$	$k_{11} = (2.0 \pm 0.4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$
$\text{CrOH}^{2+} + \text{Cr}(\text{OH})_2^+ \rightarrow \text{dimer}$	$k_{12} = (3.8 \pm 1.0) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
$\text{Cr}(\text{OH})_2^+ + \text{Cr}(\text{OH})_2^+ \rightarrow \text{dimer}$	$k_{22} = 1.8 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$

^a Estimated.¹⁹

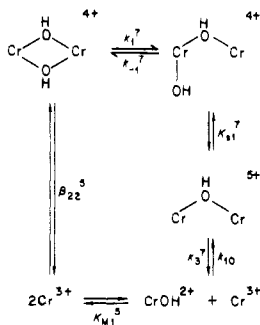
Discussion

The present pH stat initial rate study of a hydrolytic polymerization step is, to our knowledge, the first of its kind. The only other kinetic studies of individual, intermolecular polymerization steps of deprotonated metal aqua ions that we are aware of, involve the dimerization of FeOH^{2+} ¹⁷ and VOOH^+ .¹⁸ These studies were carried out on solutions of dimeric product at equilibrium with large amounts of monomer. The reactivity of $\text{Fe}(\text{OH})_2^+$ or of $\text{VO}(\text{OH})_2$ could thus not be assessed from these experiments.

In contrast, the present pH stat study has established the rate parameters of three pathways (b_1 , b_2 , and b_3), which differ in the number n of protons abstracted from the reacting monomer species. However, n cannot be determined a priori for each individual reacting species, since the terms in the rate law indicate only the *sum* of the protons removed from the two reacting species. Only the rate parameters b_0 and b_1 may be interpreted unambiguously, but they are negligible; i.e., k_{00} and k_{10} are too small to be observed.¹⁹ Thus, the aqua ion, Cr^{3+} is much less reactive with its like or with CrOH^{2+} in dimerization.

The absence of general base catalysis, as inferred from the identical rates with different titrant buffers, is consistent with preequilibrium proton transfer. Thus, any encounter between differently deprotonated monomer species should first result in rapid proton transfer, until the two species have the same value of n if the total number of protons is even or differ by only one proton if the total number of protons is odd. On this account, the parameters b_2 , b_3 , and b_4 correspond respectively to the k_{11} , k_{21} , and k_{22} pathways alone (Table VI).

A rather regular increase by a factor of ca. 50–200 is found for each deprotonation step in the series k_{11} , k_{21} , and k_{22} .²⁰ These

(17) Wendt, H. *Z. Elektrochem.* **1962**, *66*, 235.(18) Wendt, H. *Inorg. Chem.* **1969**, *8*, 1527.(19) An estimate for k_{10} can be obtained from the data in ref 5 and 7, neglecting some disparities in ionic strengths and extrapolating to 25 °C where necessary. In the scheme

all quantities but k_{10} are known. At equilibrium, we have

$$\beta_{22} = \frac{k_{-1}}{k_1} K_{S1} \frac{k_{10}}{k_3} K_{M1}$$

Rearrangement gives

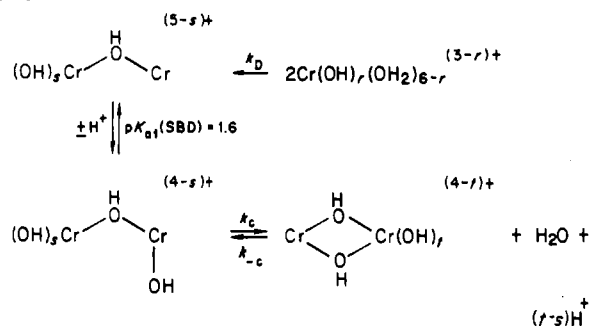
$$k_{10} = \beta_{22} \frac{k_1}{k_{-1}} \frac{1}{K_{S1}} \frac{1}{K_{M1}} k_3$$

$$\approx 10^{-5.26} (1.2) (10^{pK_{S1}}) (10^{pK_{M1}}) (1.2 \times 10^{-6})$$

$$\approx 6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$$

(20) The water-exchange rate ($k = 2.4 \times 10^{-6} \text{ s}^{-1}$)²¹ may be converted into the bimolecular rate constant $k_{\text{H}_2\text{O}} = k/[\text{H}_2\text{O}] = 2.4 \times 10^{-6}/55.5 = 4.2 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$. This last value is 140 times smaller than the estimate for k_{10} .¹⁹

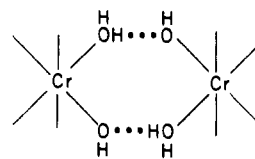
Scheme III^a

^a Water ligands have been omitted.

increments may be compared with the 75-fold increase in reactivity found for water exchange in CrOH^{2+} ($k = 1.8 \times 10^{-4} \text{ s}^{-1}$), relative to Cr^{3+} .²¹ The rate constants of anation of CrOH^{2+} by Cl^- , Br^- , I^- , NO_3^- , and NCS^- are some 60–5500 times higher than the corresponding anations of Cr^{3+} .²² Thus, a distinct conjugate base effect of a similar magnitude operates both in unidentate ligand substitution and in dimer formation.

Formation of dimer involves two consecutive substitution steps: intermolecular substitution to form a singly bridged dimer (=SBD), followed by ring closure (Scheme III). These steps have been observed in a study of the acid-induced cleavage of the dimer.⁷ Ring closure of the SBD (Scheme III) was found to be reversible at $\text{pH} > 2$; from the kinetics, k_c was determined as $8.12 \times 10^{-4} \text{ s}^{-1}$. However, from the general trends in pK_a for $\text{Cr}(\text{III})$ oligomers,⁵ SBD is expected to be deprotonated more than once in the pH range 3.5–5.0, and k_c and k_{-c} for these multiply deprotonated species are still unknown. Nevertheless, it appears very likely that the rate constants k_{pq} of this study represent k_D to a reasonable approximation.

Formation of the singly bridged dimer is likely to be preceded by aggregation of pairs of reactive monomer species through hydrogen bonds:



Evidence for such aggregates has recently been found in crystal structures^{23–26} as well as in solution.²⁷ In $\text{Cr}(\text{III})$ aqua ion chemistry, aggregation through hydrogen bonds has precedent in the structure of “active” $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, where all chromium-bound water and hydroxide ligands are involved in hydrogen bonding (see above).¹¹ The formation of *soluble*, hydrogen-bonded pairs of deprotonated aqua ions is expected to be rapid and reversible and should therefore give rise to a preequilibrium. No estimate of the corresponding preequilibrium constant can be made from the present data. Also, it is not possible to determine whether these preequilibrium aggregates are reactive or unreactive species. However, the rate of hydrolytic dimer formation (involving substitution at $\text{Cr}(\text{III})$) is quite fast under conditions where the concentration of deprotonated dimer is high. Thus, hydrolytic polymerization is likely to interfere with determinations of the supposed preequilibrium constants by methods based on the measurement of equilibrium concentrations on a minutes to hours time scale.

The present pH stat technique can be applied to study the reactions of other $\text{Cr}(\text{III})$ oligomers, e.g. dimer + dimer \rightarrow tet-

(21) Xu, Fan-Chou; Krouse, R.; Swaddle, T. W. *Inorg. Chem.* **1985**, *24*, 267.(22) Espenson, J. H. *Inorg. Chem.* **1969**, *8*, 1554.(23) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1981**, *103*, 6741.(24) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1982**, *104*, 4383.(25) Ardon, M.; Bino, A. *J. Am. Chem. Soc.* **1983**, *105*, 7747.(26) Bino, A.; Gibson, D. *Inorg. Chem.* **1984**, *23*, 109.(27) Ardon, M.; Magyar, B. *J. Am. Chem. Soc.* **1984**, *106*, 3359.

ramer,²⁸ or trimer + trimer → hexamer, etc. With these results in hand, reactions between unlike oligomers may possibly also be studied, e.g. monomer + dimer → trimer, etc. Thus, a complete kinetic description of the earlier stages of Cr(III) hydrolytic polymerization may eventually result from such studies. The validity of the initial rates may presently be checked by chromatographic product analysis up to the hexamer.

Experimental Section

Instruments. pH values of solutions and the pH stat kinetics were measured on a Metrohm instrument (pH meter 605, Impulsomat 614, Dosimat automatic buret with recorder) using a Ross Glass electrode (Orion). The pH scale was calibrated as in ref 5. All measurements were performed in a thermostated (25.0 ± 0.1 °C, Haake Model N3 thermostat) double-wall vessel covered with black tape to exclude light. UV-visible spectra were recorded on a Kontron Uvikon 810 spectrophotometer.

Materials. Stock solutions of Cr(OH)₂(ClO₄)₃ were prepared and checked as before.⁵ Sodium perchlorate (Merck, p.A.) solutions were filtered through Millipore membrane filters before use. Water was deionized and distilled. The buffer bases were prepared from purissimum commercial products (Fluka), except for imidazole, which was recrystallized twice from benzene before use. Imidazole-hydroperchlorate for buffer preparation was precipitated from aqueous solution with tetrahydrofuran and recrystallized from H₂O/THF. *Caution!* Preparation and handling of this material presents a hazard of explosion.

Kinetics. In typical pH stat runs, 25–100 mL of Cr³⁺ stock solution of known excess acid concentration (determined by ion exchange)²⁹ was thermostated in a light-protected 100-mL reaction vessel. The pH of the stirred solutions was brought to near the desired value by adding from an automatic buret the calculated amount of prethermostated titrant base at $t = 1.0$ (usually 10 times more concentrated than the one used in the pH stat titration). The exact pH value was then attained by base addition using the pH stat. The moment of reaching the desired value was set as $t = 0$. The reactions were followed for 5% or more conversion of the monomer.

Product Analysis. Aliquots of solutions from pH stat titrations in progress were taken at accurately determined times and quenched with acid to give $[H^+] \approx 0.04$ M. These solutions were then diluted and adsorbed on Sephadex SP-C25 ion-exchange resin. The products were eluted as described previously.⁵ However, since the amount of dimer was very small under initial rate conditions, its separation from the monomer was not always quite complete. However, the dimer-trimer separation was always satisfactory. No evidence for the presence of singly bridged dimer, (H₂O)₂CrOHCr(OH)₂⁵⁺, was found. The fractions were analyzed for total chromium as described.⁵

Acknowledgment. This work was supported by the Swiss National Science Foundation (Grant 2.838-0.83).

Appendix

A. Derivation of Eq 6. In eq 5

$$-d[\text{monomer}] = 2k_{\text{obsd}}[\text{monomer}]^2 dt + [\text{monomer}] \frac{dV}{V_0 + V}$$

the last term expresses the decrease in [monomer] due to volume change. This term must be additive, as in principle, volume change must be allowed for, even if there is no transformation of monomer into oligomers. However, in the present study, volume change is linked to the progress of the reaction, since any volume change involves the addition of one of the reactant species, viz. OH⁻. The number of moles of monomer converted is given by

$$[\text{Cr}^{3+}]_0 V_0 - [\text{monomer}](V + V_0)$$

As m moles (eq 2) of H⁺ per mole of converted monomer is produced, the number of moles of base added is

$$m([\text{Cr}^{3+}]_0 V_0 - [\text{monomer}](V + V_0))$$

Also, the added water has to be brought to the reaction pH (3.5–5.0). Note that pH would rise due to dilution even if only pure water was added. Thus, the total number of moles of base added at any time t is $V([\text{B}] + [\text{H}^+]) = m([\text{Cr}^{3+}]_0 V_0 - [\text{monomer}](V + V_0))$, or

$$[\text{monomer}] = \frac{[\text{Cr}^{3+}]_0 V_0 - \frac{V}{m}([\text{B}] + [\text{H}^+])}{V + V_0}$$

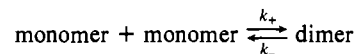
$$-d[\text{monomer}] = \frac{[\text{Cr}^{3+}]_0 V_0 + \frac{V_0}{m}([\text{B}] + [\text{H}^+])}{(V + V_0)^2} dV$$

Substitution of [monomer] in eq 5 and rearrangement leads to

$$k_{\text{obsd}} = \frac{[\text{B}] + [\text{H}^+]}{2m} \frac{\int_0^V \frac{(V_0 + V) dV}{\left\{ [\text{Cr}^{3+}]_0 V_0 - \frac{V}{m}([\text{B}] + [\text{H}^+]) \right\}^2}}{\int_0^t dt}$$

After integration with respect to variable V , eq 6 is readily obtained for $V < m[\text{Cr}^{3+}]_0 V_0 / ([\text{B}] + [\text{H}^+])$.

B. Reversibility of Reaction 1 at Constant Volume. Dimer formation from monomer in their different deprotonated forms may be represented by



Its rate law can be expressed as

$$d[\text{dimer}]/dt = -1/2 d[\text{monomer}]/dt = k_+[\text{monomer}]^2 - k_-[\text{dimer}]$$

At equilibrium, $k_+[\text{monomer}]^2 = k_-[\text{dimer}]$ at a given pH:

$$\beta_{22}' = \frac{k_+}{k_-} = \frac{[\text{dimer}]}{[\text{monomer}]^2} = \frac{[\text{Cr}_2(\text{OH})_2^{4+}](1 + K_{D1}[\text{H}^+]^{-1} + K_{D2}K_{D1}[\text{H}^+]^{-2})}{[\text{Cr}^{3+}]^2(1 + K_{M1}[\text{H}^+]^{-1} + K_{M1}K_{M2}[\text{H}^+]^{-2})^2}$$

The initial conditions are $[\text{monomer}]_{t=0} = [\text{Cr}^{3+}]_0$ and $[\text{dimer}]_{t=0} = 0$. At constant volume, conservation of mass obtains: $[\text{Cr}^{3+}]_0 = [\text{monomer}] + 2[\text{dimer}]$. The above equations are combined to give $-1/2 d[\text{monomer}]/dt = k_+[\text{monomer}]^2 - k_-([\text{Cr}^{3+}]_0 - [\text{monomer}])/2 = k_+[\text{monomer}]^2 - ([\text{Cr}^{3+}]_0 - [\text{monomer}])/2\beta_{22}'$. The dimerization reaction may be considered irreversible, if $[\text{monomer}]^2 \gg ([\text{Cr}^{3+}]_0 - [\text{monomer}])/2\beta_{22}'$ or $2\beta_{22}'[\text{monomer}]^2/([\text{Cr}^{3+}]_0 - [\text{monomer}]) \gg 1$. Under initial rate conditions (i.e. for <5% conversion of monomer), $[\text{monomer}] > 0.95[\text{Cr}^{3+}]_0$ and $[\text{Cr}^{3+}]_0 - [\text{monomer}] < 0.05[\text{Cr}^{3+}]_0$, the reaction may be considered irreversible, if the quantity p , defined as $p = \{2\beta_{22}' - (0.95)^2[\text{Cr}^{3+}]_0\}/0.05$, is $\gg 1$.

Registry No. Cr(H₂O)₆³⁺, 14873-01-9; Cr(H₂O)₅(OH)²⁺, 27454-20-2; Cr(H₂O)₄(OH)₂⁺, 76792-04-6.

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