

EARLY STAGES OF THE HYDROLYSIS OF CHROMIUM(III) IN AQUEOUS SOLUTION—X. KINETICS OF FORMATION OF TRIMER FROM MONOMER AND DIMER

ALEXANDER DRLJACA and LEONE SPICCIA*

Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia

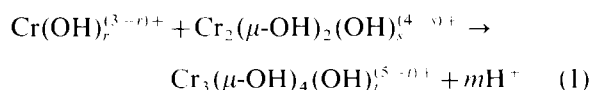
(Received 21 September 1994; accepted 3 October 1994)

Abstract—Conversion of chromium(III) monomer and dimer to trimer have been studied in the pH range 3.2–5.1 using a pH-stat facility which monitored the volume of base consumed during reaction at constant pH. The reaction, found to be irreversible, was followed for up to 5% conversion of reactants to ensure that trimer was a major product. The pH dependence of k_{obs} , after correction for dimerization of monomer and dimer to dimer and tetramer, respectively, has been fitted to an expression which accommodates the three reaction pathways: $\text{Cr}(\text{OH})^{2+} + \text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{3+} \rightarrow \text{trimer}$ [$k_{11} = (3.13 \pm 0.30) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$]; either $\text{Cr}(\text{OH})^{2+} + \text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{2+} \rightarrow$ ($k_{12} \leq 1.16 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$) or $\text{Cr}(\text{OH})_2^+ + \text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{3+} \rightarrow \text{trimer}$ ($k_{21} \leq 2.09 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$); and $\text{Cr}(\text{OH})_2^+ + \text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{2+} \rightarrow \text{trimer}$ [$k_{22} = (3.12 \pm 0.67) \text{ M}^{-1} \text{ s}^{-1}$]. Reaction between one monodeprotonated and one doubly deprotonated reactant is 400 times faster than reaction between the two monodeprotonated reactants (k_{11}). Double deprotonation of both reactants (k_{22}) gave a 10,000-fold increase in rate compared with the monodeprotonated reactants (k_{11}). These increases in reactivity on deprotonation are consistent with a common trend observed in other hydrolytic processes of chromium(III).

The occurrence and importance of hydrolytic reactions of metal ions in natural waters, biological systems and industry has been well established.¹ Chromium(III), an inert metal centre with almost exclusive octahedral coordination and whose hydrolytic polymerization processes are not complicated by redox processes, has been successfully applied in the study of processes taking place in the early stages of polymerization. These wide-ranging investigations have included the isolation and characterization of a series of chromium(III) oligomers (dimer–hexamer)² and detailed kinetic investigations have attempted to define the conditions and mechanisms of oligomer formation,^{3,4} interconversion^{5,6} and cleavage⁷ in aqueous solution. Investigations of the dimerization of Cr^{3+} and $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8]^{4+}$ to give dimer³ and tetramer,⁴ respectively, have indicated that reaction takes

place between mono- and doubly-deprotonated forms of the reactants and that deprotonation affords systematic increases in rate. The data are consistent with increases in the rates of H_2O exchange on Cr^{3+8} and dimer⁹ with deprotonation.

In this paper, we describe the application of pH-stat techniques in the study of kinetics of polymerization between deprotonated forms of Cr^{3+} and dimer, $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8]^{4+}$ (1),¹⁰ to give deprotonated forms of trimer, $[\text{Cr}_3(\mu\text{-OH})_4(\text{OH}_2)_9]^{5+}$ (2),^{2,11} [eq. (1)]. It is the first attempt to measure polymerization rates between ions of different nuclearity.



EXPERIMENTAL

Materials

$[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8]((\text{CH}_3)_3\text{C}_6\text{H}_5\text{SO}_3)_4 \cdot 4\text{H}_2\text{O}$ and $[\text{Cr}(\text{OH}_2)_6](\text{ClO}_4)_3$ were prepared as described

* Author to whom correspondence should be addressed.

Table 1. Product analysis for hydrolytic polymerization of chromium(III) monomer and dimer at $I = 1.0$ (NaClO_4) and $298.2 (\pm 0.1)$ K [base added for initial pH control (0.2 M imidazole); constant pH was maintained by addition of 0.02 M imidazole]

Time (min)	% Cr				
	Monomer	Dimer	Trimer	Tetramer	Higher polymers
(a) Conditions: $[\text{Cr}^{3+}] = 6.73 \times 10^{-3}$ M; $[\text{Cr}_2(\text{OH})_2^{4+}] = 3.29 \times 10^{-3}$ M; pH 3.83					
2	50.3	49.3			0.3
360	48.1	47.3	2.7	1.1	0.7
(b) Conditions: $[\text{Cr}^{3+}] = 1.33 \times 10^{-2}$ M; $[\text{Cr}_2(\text{OH})_2^{4+}] = 7.81 \times 10^{-3}$ M; pH 4.03					
2	46.0	53.8			0.2
40	45.4	52.6	0.8	0.5	0.6
80	44.8	52.1	1.7	0.9	0.5
100	43.6	51.9	2.8	1.2	0.4
140	42.1	51.4	4.0	1.9	0.6
180	41.7	49.3	5.1	2.6	1.2
(c) Conditions: $[\text{Cr}^{3+}] = 1.89 \times 10^{-3}$ M; $[\text{Cr}_2(\text{OH})_2^{4+}] = 9.26 \times 10^{-4}$ M; pH 4.51					
2	50.4	49.2			0.4
120	48.4	47.5	2.5	0.9	0.6
(d) Conditions: $[\text{Cr}^{3+}] = 4.60 \times 10^{-3}$ M; $[\text{Cr}_2(\text{OH})_2^{4+}] = 2.79 \times 10^{-3}$ M; pH 4.95					
2	45.1	54.6			0.3
10	43.3	52.2	2.8	1.1	0.5
15	41.7	51.5	4.0	1.9	0.8
20	39.7	51.1	5.7	2.8	0.8
30	37.1	50.2	7.2	4.0	1.5
40	36.5	49.5	7.5	4.3	2.2
70	34.9	48.7	8.1	4.5	3.7
100	34.1	46.5	9.4	5.0	5.1

in the literature.^{2,12} All other reagents were of A.R. grade and were used as received. Aqueous solutions for use in pH measurements and kinetic studies were prepared with distilled water which had been degassed to remove dissolved CO_2 and their ionic strength adjusted to 1.0 M (NaClO_4). Solutions of dimer and Cr^{3+} in perchlorate media were prepared by loading $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8](\text{CH}_3)_3\text{C}_6\text{H}_5\text{SO}_3)_4 \cdot 4\text{H}_2\text{O}$ and $[\text{Cr}(\text{OH}_2)_6](\text{ClO}_4)_3$ solutions onto Sephadex SP C25 cation exchange resin and eluting with 1.0 M $\text{NaClO}_4/0.01$ M HClO_4 solution. The ionic strength (I) and $[\text{Cr}^{\text{III}}]$ of solutions were determined by established methods.^{2,4} The ionic strength was adjusted to 1.00 (± 0.02) M (NaClO_4) prior to use in kinetic studies.

Instruments

The instrumentation for measuring pH values and for following polymerization reactions has been described previously.⁴ All measurements were carried out under nitrogen at $298.2 (\pm 0.1)$ K and with the exclusion of light. The pH-stat data were

analysed using the Kaleidagraph v2.1.1 curve fitting program on a Macintosh Centris 650 computer.

Kinetic measurements

Aliquots of monomer and dimer solution at $I = 1.0$ M were introduced into the reaction vessel such that the final conditions were: $[\text{Cr}^{3+}]$ in the range 1–50 mM and $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8]^{4+}$ in the range 0.8–30 mM. After the solution had reached thermal equilibrium and the electrode had stabilized (10 min), the solution pH was adjusted to close to the desired value with imidazole solution (0.2 M, $I = 1.0$ M). This was added dropwise and with vigorous stirring to avoid localized areas of high pH, which could result in artificially high polymerization rates. The computer-controlled titration system was then used to set the starting pH by the initial addition of imidazole solution (0.02 M, $I = 1.0$ M). This system followed the reaction of monomer with dimer by measuring the volume of base required to maintain constant pH as a function of time over *ca* 5% conversion of reactants.

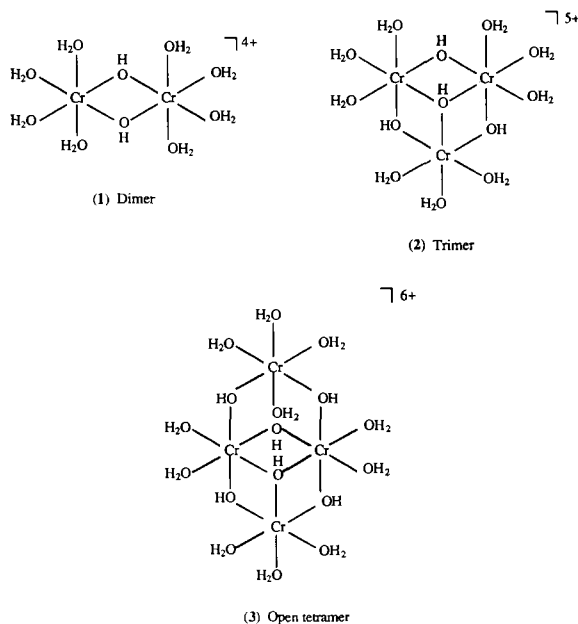
Product analysis

Product analyses were conducted under the same conditions as the kinetic experiments over a range of [reactants] and pH (Table 1). Aliquots of solutions were taken from the reaction vessel at various times, acidified to pH ~ 2, diluted to $I < 0.1$ M and analysed by ion-exchange chromatography. The products were identified from their UV-vis spectra and the amount of each determined by literature methods.² The data are summarized in Table 1.

RESULTS AND DISCUSSION

Product analyses

Homogeneous solutions of Cr^{3+} and dimer, $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8]^{4+}$ (1), have been found to polymerize slowly in the pH range 3.2–5.1. Product distributions (Table 1), determined under various conditions of pH, [reactant] and reaction time, indicate that increasing amounts of trimer (2) and tetramer (3) are the dominant products formed during

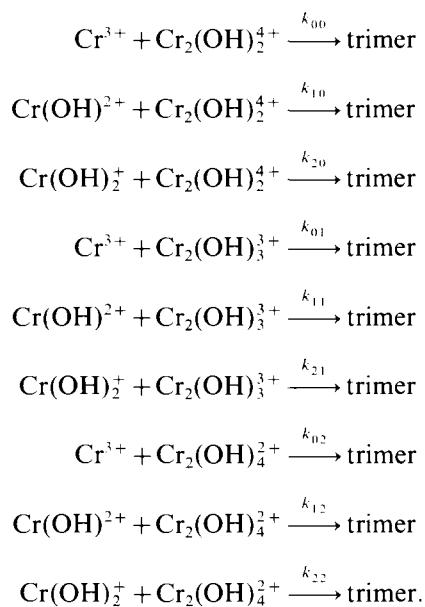


initial stages of reaction (<5% conversion of reactants). The rate of formation of tetramer from dimer³ is only slightly different from the rate of dimer from monomer,⁴ which suggests that dimer should also form. However, the amount of dimer produced cannot be determined by chromatography, as it is a small fraction of [dimer]_T. Only small amounts of higher oligomers (<1.0%) formed in the early stages of polymerization, but these increased substantially for >5% conversion of reactants. The initial, relatively constant amounts

of these higher oligomers have been shown previously to form during pH adjustment.^{3,4} Rates of formation of trimer have been determined from changes in volume of added base with time after corrections were made for volume changes due to formation of dimer and tetramer (see later).

Determination of observed rate constants

In the pH range 3–5, formation of trimer could involve several deprotonated forms of Cr^{3+} [in particular, $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_2^+$] and dimer [in particular, $\text{Cr}_2(\text{OH})_3^{3+}$ and $\text{Cr}_2(\text{OH})_4^{2+}$]. In addition, $\text{Cr}(\text{OH})_3^0$, $\text{Cr}_2(\text{OH})_5^+$ and $\text{Cr}_2(\text{OH})_6^0$ could be present, but their concentrations are probably too low to affect the overall reaction rate. Thus, any of the following processes could generate trimer:



In subsequent discussion the kinetically significant pathways will be established.

The rate law which allows for contributions from each of these pathways is:

$$\begin{aligned} \frac{-d([\text{monomer}])}{dt} &= \frac{-d([\text{dimer}])}{dt} \\ &= k_{00}[\text{Cr}^{3+}][\text{Cr}_2(\text{OH})_2^{4+}] \\ &\quad + k_{10}[\text{Cr}(\text{OH})^{2+}][\text{Cr}_2(\text{OH})_2^{4+}] \\ &\quad + k_{20}[\text{Cr}(\text{OH})_2^+][\text{Cr}_2(\text{OH})_2^{4+}] + \dots \\ &= k_{\text{obs}}[\text{monomer}][\text{dimer}]. \end{aligned} \quad (2)$$

The concentration of all deprotonated monomer and dimer species in solution are related by their appropriate dissociation constants. In this work, the K_a values for dimer and trimer were taken from the literature,^{2,4} while for Cr^{3+} $K_{M1} = 5.11$

$(\pm 0.11) \times 10^{-5}$ M and $k_{M2} = 8.21 (\pm 0.31) \times 10^{-7}$ M were determined as part of this work. Applying these constants to eq. (2) gives the following expression:

$$k_{\text{obs}} = \{k_{00} + (k_{10}K_{M1} + k_{01}K_{D1})[H^+]^{-1} + k_{11}K_{M1}K_{D1}[H^+]^{-2} + (k_{12}K_{M1}K_{D1}K_{D2} + k_{21}K_{M1}K_{M2}K_{D1})[H^+]^{-3} + k_{22}K_{M1}K_{M2}K_{D1}K_{D2}[H^+]^{-4}\} / \{(1 + K_{M1}[H^+]^{-1} + K_{M1}K_{M2}[H^+]^{-2}) \times (1 + K_{D1}[H^+]^{-1} + K_{D1}K_{D2}[H^+]^{-2})\}. \quad (3)$$

As the reaction proceeds, the solution volume increases as dilute base is added to maintain constant pH. Therefore, the kinetic analysis has to take into consideration both the change in [reactant] due to polymerization and dilution. Changes in [monomer] and [dimer] due to dilution are accounted for by the following equation:

$$-(d[\text{monomer}] + d[\text{dimer}]) = 2k_{\text{obs}}[\text{monomer}][\text{dimer}]dt + ([\text{monomer}] + [\text{dimer}])dV/(V + V_0), \quad (4)$$

where V_0 is the volume at reaction time $t = 0$ and V is the volume of base added at time t .

At constant pH, the degree of conversion into trimer and V are related and this relationship defines the boundary condition for integrating eq. (4). Integration gives eq. (5), which holds for small volumes (see Appendix):

$$k_{\text{obs}} = \frac{V}{t} \frac{([\text{B}] + [\text{H}^+])}{m[\text{monomer}]_0[\text{dimer}]_0V_0}. \quad (5)$$

In eq. (5), V is the volume of base consumed by trimer formation alone, V_0 is the initial volume of the reaction mixture, t is the time, $[\text{B}]$ is the concentration of titrant base, $[\text{H}^+]$ is the acid concentration of a particular experiment, $[\text{monomer}]_0$ is the [monomer] at $t = 0$, $[\text{dimer}]_0$ is [dimer] at $t = 0$ and m is the number of moles of base consumed per mole of reactant. From eq. (1), the value of m is defined as follows:

$$m = 2 + t - (r + s), \quad (6)$$

where

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

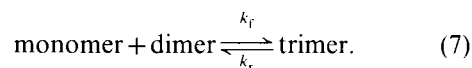
$$s = \frac{\{K_{D1}[H^+]^{-1} + 2K_{D1}K_{D2}[H^+]^{-2}\}}{\{1 + K_{D1}[H^+]^{-1} + K_{D1}K_{D2}[H^+]^{-2}\}} = \frac{[\text{Cr}_2(\text{OH})_3^{3+}] + 2[\text{Cr}_2(\text{OH})_4^{2+}]}{[\text{dimer}]_T}$$

$$t = \frac{\{K_{T1}[H^+]^{-1} + 2K_{T1}K_{T2}[H^+]^{-2}\}}{\{1 + K_{T1}[H^+]^{-1} + K_{T1}K_{T2}[H^+]^{-2}\}} = \frac{[\text{Cr}_3(\text{OH})_5^{4+}] + 2[\text{Cr}_3(\text{OH})_6^{3+}]}{[\text{trimer}]_T}.$$

Plots of corrected V against time were found to be linear for at least 5% conversion of reactants over the whole range of experimental conditions, as predicted by eq. (5). In order to obtain corrected volumes, rate constants for formation of dimer³ and tetramer⁴ were used to calculate the volumes of base consumed by each of these processes, which were then subtracted from the overall volume. Values of k_{obs} were determined by linear least-squares fitting of the data to eq. (5) and are summarized in Table 2.

Reaction reversibility

It is important to consider whether the formation of trimer is a reversible reaction [eq. (7)], since this would complicate the interpretation of k_{obs} :



Reaction reversibility may be determined from the stability constants of monomer, dimer and trimer. Using eq. (7) the rate law becomes:

$$\frac{-d([\text{monomer}])}{dt} = \frac{-d([\text{dimer}])}{dt} = k_f[\text{monomer}][\text{dimer}] - k_r[\text{trimer}]. \quad (8)$$

The equilibrium constant (K) for the reaction given by eq. (9):

$$K = \frac{k_f}{k_r} = \frac{[\text{trimer}]}{[\text{monomer}][\text{dimer}]} = \frac{\{[\text{Cr}_3(\text{OH})_5^{4+}] + [\text{Cr}_3(\text{OH})_6^{3+}] + [\text{Cr}_3(\text{OH})_3^{3+}]\}}{\{[\text{Cr}^{3+}] + [\text{Cr}(\text{OH})_2^{2+}] + [\text{Cr}(\text{OH})_2^+]\} \{[\text{Cr}_2(\text{OH})_2^{2+}] + [\text{Cr}_2(\text{OH})_3^{3+}] + [\text{Cr}_2(\text{OH})_4^{2+}]\}}. \quad (9)$$

Table 2. Experimental parameters and observed rate constants for the polymerization of monomer and dimer to trimer at 298.2 ± 0.1 K and $I = 1.0$ M (NaClO_4)

pH	[monomer] ₀ ($\times 10^3$ M)	[dimer] ₀ ($\times 10^3$ M)	V_0 (cm^3)	m	$10^{-5}k_{\text{obs}}$ ($\text{M}^{-1} \text{s}^{-1}$)	$10^{15}k^{\#}$ ($\text{M}^{-1} \text{s}^{-1}$)
3.253	26.96	13.22	19.40	1.7123	1.48 ± 0.07	3.89 ± 0.22
3.271	50.54	25.95	22.00	1.7036	1.60 ± 0.06	3.78 ± 0.17
3.299	26.63	13.05	19.64	1.6896	1.79 ± 0.08	3.57 ± 0.20
3.352	26.82	13.15	19.50	1.6621	2.43 ± 0.13	3.53 ± 0.23
3.353	50.32	25.84	22.10	1.6616	2.43 ± 0.10	3.51 ± 0.18
3.413	26.68	13.08	19.60	1.6289	3.28 ± 0.13	3.33 ± 0.17
3.472	49.64	25.49	22.40	1.5955	4.42 ± 0.18	3.20 ± 0.17
3.554	26.41	12.95	19.80	1.5472	6.56 ± 0.30	2.99 ± 0.18
3.604	24.60	12.63	20.34	1.5170	8.38 ± 0.40	2.91 ± 0.18
3.677	26.15	12.82	20.00	1.4724	11.9 ± 0.7	2.79 ± 0.21
3.766	24.40	12.53	20.51	1.4181	18.2 ± 1.0	2.70 ± 0.20
3.833	13.08	6.410	20.00	1.3779	24.5 ± 1.5	2.59 ± 0.21
3.906	13.05	6.397	20.04	1.3354	35.9 ± 2.6	2.67 ± 0.25
4.035	6.570	3.221	19.90	1.2653	62.6 ± 5.1	2.57 ± 0.28
4.155	6.544	3.208	19.98	1.2076	107 ± 10	2.64 ± 0.33
4.228	6.538	3.205	20.00	1.1766	151 ± 17	2.77 ± 0.39
4.326	6.505	3.189	20.10	1.1401	228 ± 28	2.86 ± 0.45
4.416	1.712	0.8397	19.10	1.0993	414 ± 60	3.20 ± 0.58
4.498	24.89	12.78	22.34	1.0899	453 ± 74	3.10 ± 0.62
4.508	3.509	1.721	18.64	1.0875	548 ± 86	3.63 ± 0.62
4.610	1.718	0.8429	19.03	1.0656	873 ± 150	4.17 ± 0.89
4.681	1.721	0.8433	19.00	1.0530	1130 ± 220	4.37 ± 1.0
4.746	1.719	0.8416	19.02	1.0430	1890 ± 390	6.04 ± 1.5
4.852	1.716	0.8416	19.06	1.0289	2310 ± 530	5.54 ± 1.5
4.961	1.714	0.8407	19.08	1.0160	2870 ± 740	5.25 ± 1.6
5.071	1.713	0.8403	19.09	1.0028	3500 ± 1000	5.04 ± 1.7

Simplification using the stability constants¹³ of dimer ($\beta_{22} = [\text{Cr}_2(\text{OH})_2^{4+}][\text{H}^+]^2/[\text{Cr}^{3+}]^2 = 10^{-5.25}$) and trimer ($\beta_{34} = [\text{Cr}_3(\text{OH})_4^{5+}][\text{H}^+]^4/[\text{Cr}^{3+}]^3 = 10^{-8.72}$) gives eq. (10):

$$K = \frac{\beta_{34}(1 + K_{T1}[\text{H}^+]^{-1} + K_{T1}K_{T2}[\text{H}^+]^{-2})}{\beta_{22}[\text{H}^+]^2(1 + K_{M1}[\text{H}^+]^{-1} + K_{M1}K_{M2}[\text{H}^+]^{-2})(1 + K_{D1}[\text{H}^+]^{-1} + K_{D1}K_{D2}[\text{H}^+]^{-2})} \quad (10)$$

Over the range of experimental conditions for the reaction, the smallest value of K was 780 M^{-1} obtained at pH 3.25, while the value at pH 5.00 was 1.55

$\times 10^5 \text{ M}^{-1}$. A reversibility factor (t) can be defined as in previous work,^{3,4} $t \sim K(0.95)^2 [\text{monomer}]_0/0.05$ ($\gg 1$ for irreversible process). For the concentrations used in this study, the value of t was large, 380

at pH 3.25 and 4700 at pH 5.00. This suggests that the reaction is essentially irreversible, with back reactions making little contribution to the reaction rate.

Rate constants for trimer formation

For the purpose of determining the processes contributing to trimer formation, the expression for k_{obs} can be modified to:

$$\begin{aligned}
 k^* &= k_{\text{obs}}(1 + K_{M1}[\text{H}^+]^{-1} \\
 &\quad + K_{M1}K_{M2}[\text{H}^+]^{-2})(1 + K_{D1}[\text{H}^+]^{-1} \\
 &\quad + K_{D1}K_{D2}[\text{H}^+]^{-2}) \\
 &= a_0 + a_1[\text{H}^+]^{-1} + a_2[\text{H}^+]^{-2} \\
 &\quad + a_3[\text{H}^+]^{-3} + a_4[\text{H}^+]^{-4}, \quad (11)
 \end{aligned}$$

where a_n are composite values, i.e. $a_0 = k_{00}$, $a_1 = k_{10}K_{M1} + k_{01}K_{D1}$, $a_2 = k_{11}K_{M1}K_{D1}$, $a_3 = k_{12}K_{M1}K_{D1}K_{D2} + k_{21}K_{M1}K_{M2}K_{D1}$ and $a_4 = k_{22}K_{M1}K_{M2}K_{D1}K_{D2}$.

In previous work concerning the dimerization of monomer³ and dimer,⁴ the significant terms in $[\text{H}^+]^n$ were identified from a plot of $\log k^*$ vs $\log [\text{H}^+]$. For the data in Table 2, the plot gives slopes of -2.6 , -3.0 and -3.3 at pH 3.4, 4.0 and 4.8, respectively. These limiting slopes indicate that the important terms in the expression for k^* are $[\text{H}^+]^n$, where $n = -2, -3, -4$, or a_2, a_3 and a_4 . Integer values are not obtained in this analysis because, at a particular pH, more than one process contributes to the overall rate. Based on these considerations, eq. (11) simplifies to:

$$k^\# = k^*[\text{H}^+]^3 = a_2[\text{H}^+] + a_3 + a_4[\text{H}^+]^{-1}. \quad (12)$$

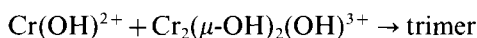
Values of $k^\#$ (see Table 2) were plotted against $[\text{H}^+]$ and analysed using a weighted least squares fitting procedure [$w(i) = 1/\sigma_{k(i)}^2$]. The experimental and fitted data are shown in Fig. 1. Attempts to fit

alternative expressions with other terms in $[\text{H}^+]^n$ [see eq. (3)] gave much poorer fits than eq. (12).

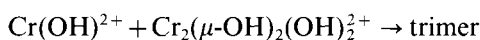
From $a_2 = 3.43 (\pm 0.17) \times 10^{-12} \text{ M s}^{-1}$ the rate constant k_{11} can be calculated as $3.13 (\pm 0.30) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, while $a_4 = 4.14 (\pm 0.35) \times 10^{-20} \text{ M}^3 \text{ s}^{-1}$ gives $k_{22} = 3.12 (\pm 0.67) \text{ M}^{-1} \text{ s}^{-1}$. On the other hand, two processes could be contributing to a_3 [$= 1.88 (\pm 0.07) \times 10^{-15} \text{ M}^2 \text{ s}^{-1}$], reaction between $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}_2(\text{OH})_2^{4+}$ (k_{12}) and/or reaction between $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}_2(\text{OH})_3^+$ (k_{21}). Upper limits for k_{12} and k_{21} can be obtained by assuming only one of the two processes contributes to the total rate. This gives $k_{12} = (1.16 \pm 0.15) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ or $k_{21} = (2.09 \pm 0.25) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$.

Interpretation of rate constants

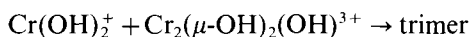
The kinetics of trimer formation from dimer and monomer can be rationalized in terms of the existence of three or four reaction pathways:



$$k_{11} = 3.13 (\pm 0.30) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$



$$k_{12} \leq 1.16 (\pm 0.15) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$$



$$k_{21} \leq 2.09 (\pm 0.25) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$$



$$k_{22} = 3.12 (\pm 0.67) \text{ M}^{-1} \text{ s}^{-1}$$

In principle, it is possible that the first pathway

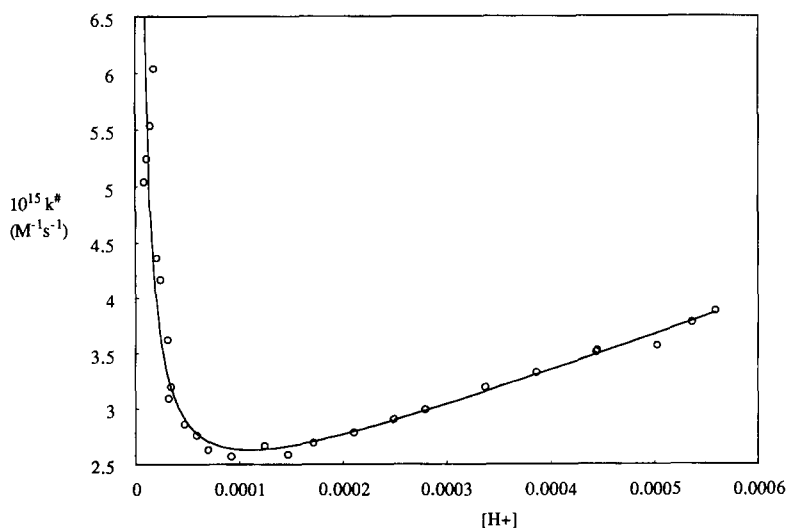


Fig. 1. Weighted least-squares fitting of the $k^\#$ vs $[\text{H}^+]$ data to eq. (12).

involves reaction of doubly deprotonated monomer, $\text{Cr}(\text{OH})_2^+$, with fully protonated dimer, $\text{Cr}_2(\mu\text{-OH})_2^{4+}$, or alternatively reaction of Cr^{3+} with doubly deprotonated dimer, $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{2+}$, rather than reaction between the mono-deprotonated reactants. However, it has been clearly demonstrated in previous investigations of the rates of dimerization^{3,4} and water exchange^{8,9} on both monomer and dimer that pathways involving fully protonated oligomers are considerably slower than those involving the deprotonated reactants. It is difficult to establish whether one or both of the k_{12} and k_{21} pathways are important. In this case the available kinetic data do not allow distinctions to be made about which pathway will result in the faster rate of trimer formation.^{3,4,8,9} The same considerations apply to the pathway involving the doubly deprotonated reactants. In this case, however, the alternative pathways would involve the triply deprotonated reactants. These forms of the reactants are unlikely to be present in sufficiently high concentrations to contribute to the reaction rate, since $\text{p}K_{a2}$ for both Cr^{3+} and $\text{Cr}_2(\mu\text{-OH})_2^{4+}$ is about 6, suggesting that $\text{p}K_{a3}$ would be about 8, and that at $\text{pH} < 5$ hydroxides precipitate. Moreover, even if very low concentrations of these oligomers were present, the magnitude of the rate enhancements that would be required to make these pathways significant would be much larger than those observed in many other hydrolytic reactions involving chromium(III) oligomers.³⁻⁹

Investigations of the rate of dimerization of Cr^{3+} and dimer have shown that these rates depend on the degree of deprotonation of the reactants, i.e. $\text{Cr}(\text{OH})_2^{2+}$ and $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{3+}$ dimerize at the same rate and so do $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{2+}$. Similarly, $\text{Cr}(\text{OH})_2^{2+}$ reacts with $\text{Cr}(\text{OH})_2^+$ at a rate comparable with $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{3+}$ with $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{2+}$. This indicates that both k_{12} and k_{21} could contribute to the rate of trimer formation. Regardless of this, substantial increases in trimer formation rates occur on deprotonation of the reactants; a rate increase of ca 500-fold is observed on going from reaction between $\text{Cr}(\text{OH})_2^{2+}$ and $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{3+}$ to reaction between $\text{Cr}(\text{OH})_2^{2+}$ and $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{2+}$. Double deprotonation of both reactants (k_{22}) results in a further increase of up to 30-fold. This is consistent with a number of studies which have concluded that substitution rates at chromium(III) increase dramatically as the number of hydroxides coordinated to chromium(III) increases. For example, increases in the lability of the chromium(III) coordination sphere with the degree of deprotonation are evident from studies of the kinetics of water exchange,^{8,9} i.e. rates increase

in the order $\text{Cr}^{3+} < \text{Cr}(\text{OH})_2^{2+} \approx \text{Cr}_2(\mu\text{-OH})_2^{4+} < \text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{3+}$. Such data provide an indication of the rate of other substitution reactions (including polymerization reactions), but for trimer formation, data on H_2O exchange rates on $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_2^{2+}$ are needed in order to assess the relative importance of k_{12} and k_{21} fully.

Combining the data reported here with dimerization rates,^{3,4} preferred pathways for the very early stages of polymerization of Cr^{3+} can be identified. What happens when base is added to a 1 M solution of Cr^{3+} ? Initially, dimer will form until it reaches a critical concentration, at which time trimer or tetramer can begin to form. About 5% conversion to dimer is possible before other oligomers are evident. The data indicate that formation of trimer would be preferred over tetramer because of concentration effects, particularly the higher [monomeric species], rather than intrinsic differences in reactivity of the species present. This is being further explored through the study of the reactions: trimer + monomer, trimer + trimer and trimer + dimer.

Acknowledgement—A. D. acknowledges support in the form of an Australian Postgraduate Research Award.

REFERENCES

1. C. B. Baes Jr. and R. E. Mesmer, *The Hydrolysis of Cations*. Wiley, New York (1976).
2. H. Stünzi and W. Marty, *Inorg. Chem.* 1983, **22**, 2145.
3. F. P. Rotzinger, H. Stünzi and W. Marty, *Inorg. Chem.* 1986, **25**, 489.
4. M. R. Grace and L. Spiccia, *Polyhedron* 1991, **10**, 2389.
5. L. Spiccia and W. Marty, *Polyhedron* 1991, **10**, 619.
6. H. Stünzi, F. P. Rotzinger and W. Marty, *Inorg. Chem.* 1984, **23**, 2160.
7. L. Spiccia, *Polyhedron* 1991, **10**, 1865.
8. F.-C. Xu, H. R. Krouse and T. W. Swaddle, *Inorg. Chem.* 1985, **24**, 267.
9. S. J. Crimp, L. Spiccia, H. R. Krouse and T. W. Swaddle, *Inorg. Chem.* 1994, **33**, 465.
10. L. Spiccia, H. Stoeckli-Evans, W. Marty and R. Giovanoli, *Inorg. Chem.* 1987, **26**, 474.
11. L. Spiccia, W. Marty and R. Giovanoli, *Inorg. Chem.* 1988, **27**, 2660.
12. T. Merakis, A. Murphy, L. Spiccia, A. Beguin and W. Marty, *Helv. Chim. Acta* 1989, **72**, 993.
13. H. Stünzi, L. Spiccia, F. P. Rotzinger and W. Marty, *Inorg. Chem.* 1989, **28**, 66.

APPENDIX: DERIVATION OF VOLUME-TIME RELATIONSHIP FOR THE DETERMINATION OF k_{obs}

The number of moles of trimer formed is equivalent to both the number of moles of monomer and dimer converted, respectively, which is shown in eq. (A1):

$$\begin{aligned} & \{[\text{monomer}]_0 V_0 - [\text{monomer}]_0 (V + V_0)\} \\ & = \{[\text{dimer}]_0 V_0 - [\text{dimer}]_0 (V + V_0)\}. \quad (\text{A1}) \end{aligned}$$

As m moles [eq. (6)] of H^+ per mole of converted monomer or dimer is produced, the number of moles of base added is

$$\frac{-d[\text{dimer}]}{dV} = \frac{[\text{dimer}]_0 V_0 + V_0([\text{B}] + [\text{H}^+])/m}{(V + V_0)^2}. \quad (\text{A7})$$

Substituting eqs. (A4), (A5), (A6) and (A7) into eq. (4) and rearranging gives:

$$\begin{aligned} & \{(V + V_0)([\text{B}] + [\text{H}^+])/m\} dV = \\ & k_{\text{obs}} \{[\text{monomer}]_0 V_0 - V([\text{B}] + [\text{H}^+])/m\} \{[\text{dimer}]_0 V_0 \\ & - V([\text{B}] + [\text{H}^+])/m\} dt. \quad (\text{A8}) \end{aligned}$$

Rearrangement of eq. (A8) for integration with boundary limits gives:

$$k_{\text{obs}} = \frac{([\text{B}] + [\text{H}^+])}{m} \frac{\int_0^V \frac{(V + V_0) dV}{([\text{monomer}]_0 V_0 - V([\text{B}] + [\text{H}^+])/m) \{[\text{dimer}]_0 V_0 - V([\text{B}] + [\text{H}^+])/m\}}{\int_0^t dt}. \quad (\text{A9})$$

$$\begin{aligned} & m\{[\text{monomer}]_0 V_0 - [\text{monomer}]_0 (V + V_0)\} \\ & = m\{[\text{dimer}]_0 V_0 - [\text{dimer}]_0 (V + V_0)\}. \quad (\text{A2}) \end{aligned}$$

The total number of moles of base added to the reaction mixture at any time t to maintain constant desired pH is

$$\begin{aligned} V([\text{B}] + [\text{H}^+]) & = m\{[\text{monomer}]_0 V_0 \\ & - [\text{monomer}]_0 (V + V_0)\} \\ & = m\{[\text{dimer}]_0 V_0 - [\text{dimer}]_0 (V + V_0)\}. \quad (\text{A3}) \end{aligned}$$

Rearrangement of eq. (A3) yields:

$$[\text{monomer}] = \frac{[\text{monomer}]_0 V_0 + V([\text{B}] + [\text{H}^+])/m}{(V + V_0)} \quad (\text{A4})$$

$$[\text{dimer}] = \frac{[\text{dimer}]_0 V_0 + V([\text{B}] + [\text{H}^+])/m}{(V + V_0)}. \quad (\text{A5})$$

Differentiation of eqs (A4) and (A5) yields:

$$\begin{aligned} & \frac{-d[\text{monomer}]}{dV} \\ & = \frac{[\text{monomer}]_0 V_0 + V_0([\text{B}] + [\text{H}^+])/m}{(V + V_0)^2} \quad (\text{A6}) \end{aligned}$$

Let $A = [\text{dimer}]_0 V_0$, $B = [\text{monomer}]_0 V_0$ and $C = ([\text{B}] + [\text{H}^+])/m$, substitute into eq. (A9) and integrate the numerator:

$$\begin{aligned} & \Rightarrow \int_0^V \frac{(V + V_0) dV}{(A - CV)(B - CV)} \\ & \Rightarrow \int_0^V \frac{V_0 dV}{(A - CV)(B - CV)} + \int_0^V \frac{V dV}{(A - CV)(B - CV)} \\ & \Rightarrow (AC - BC)^{-1} \{ [V_0 \ln(B - CV) - V_0 \ln(A - CV)]_0^V \\ & + [(B/C) \ln(B - CV) - (A/C) \ln(A - CV)]_0^V \} \\ & \Rightarrow (AC - BC)^{-1} \{ V_0 \ln((B - CV)/B) - V_0 \ln((A - CV)/A) \\ & + (B/C) \ln((B - CV)/B) - (A/C) \ln((A - CV)/A) \}. \quad (\text{A10}) \end{aligned}$$

For values of $V < B/C$ $\{ = [\text{monomer}]_0 V_0 m([\text{B}] + [\text{H}^+])^{-1}$ and $V < A/C$ $\{ = [\text{dimer}]_0 V_0 m([\text{B}] + [\text{H}^+])^{-1}$, $\ln(1 - (CV/B))$ and $\ln(1 - (CV/A))$ approximate to CV/B and CV/A , respectively. Using this, eq. (A10) simplifies to $V_0 V/AB$. Thus, putting real values of A and B and substituting $V_0 V/AB$ into eq. (A9) yields the required expression for k_{obs} [eq. (5)].