Inorg. Chem. **1986**, *25*, 266–271

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

The Fate of "Active" Chromium Hydroxide, $Cr(OH)_3 \cdot 3H_2O$, in Aqueous Suspension. Study of the Chemical Changes Involved in Its Aging

Leone Spiccia and Werner Marty*

Received May 30, 1985

"Active" chromium hydroxide, an exclusively hydrogen-bonded, layered array of $Cr(OH)_3(OH_2)_3$ units, dissolves instantaneously in acid to form $Cr(OH_2)_6^{3+}$. One minute after its precipitation in the pH range 8.5–9.7, acidification yields $\geqslant$99.4% of $Cr(OH_2)_6^{3+}$ and $\leqslant$0.6% of hydrolytic oligomers $Cr_n(OH)_rO_p(aq)^{(3n-r-2p)+}$ ($n = 2$–4) are formed. When precipitates of "active" chromium hydroxide are aged in buffered aqueous suspension (25 °C, pH 5–11, $I = 1$ M ($NaClO_4$), $t = 600$–2.592×10^5 s), the amount of $Cr(OH_2)_6^{3+}$ recovered after rapid acid dissolution decreases with time and low ($n = 2$–4) and higher ($n > 4$) soluble oligomers complete the material balance. These oligomers are kinetically stable under the experimental conditions and can be separated chromatographically. Their quantities are a measure of the extent of aging through hydrolytic polymerization, occurring either in the supernatant liquid or in the precipitate itself, or in both. The proportion of oligomers increases nonlinearly with time and is pH dependent. Thus, the rate of polymerization decreases from pH 5 to 6, goes through a minimum (pH ~6–7), and increases above pH 8. This is consistent with the expected decrease in the concentration of deprotonated monomer, in solution [$Cr(OH)_r(OH_2)_{6-r}^{(3-r)+}$] ($r \leqslant 2$) in rapid equilibrium with $Cr(OH)_3 \cdot 3H_2O(s)$ at the low end of the pH range, and with the presence of anionic Cr(III) species, presumably oligomers, at high pH. Aging experiments were carried out in both stirred and unstirred suspensions. The results essentially agreed at pH 8.5 and 10.6. However, aging was much faster in the stirred suspensions at pH 5. Chromatography of the individual oligomers ($\simeq$ 20%) at pH 10.85 and after 2.592×10^5 s aging time showed that dimer, trimer, tetramer, pentamer, hexamer, and higher oligomers are formed. However, the amount of dimer was low ($\simeq$1%). The formation of these oligomers during aging is argued to occur predominantly in homogeneous solution.

Introduction

Freshly precipitated metal hydroxides and metal oxide hydrates have long been known to be *metastable*, i. e. their physical and chemical properties vary as a function of time. The term *aging* refers to the entirety of these changes. The aging of metal hydroxides has important consequences in all applications of these materials, such as in the preparation of metal hydroxide and oxide catalysts. Aging processes include changes in the physical state (recrystallization, with or without changes in crystal habit or surface structure), chemical structure (formation of new crystalline phases accompanied by changes in atom connectivity), and composition (hydrolytic polymerization, with concurrent loss of coordinated water or of protons from coordinated H_2O or OH^-).[1]

Up to the present time, aging processes of metal hydroxides have been studied mainly by morphologically oriented methods, such as X-ray powder diffraction, electron microscopy and surface adsorption studies. This approach is exemplified in a number of seminal papers by Feitknecht et al. on the aging of iron(III) hydroxide.[2–4] However, such morphologically oriented studies remain merely qualitative or semiquantitative at best and suffer from the impossibility of assaying and characterizing any amorphous material present. Also, the changes usually become detectable only if the aging process has progressed considerably.

In this paper, we present a novel approach for the investigation of the *chemical changes* involved in the aging of one particular compound, viz. "active" chromium hydroxide, $Cr(OH)_3 \cdot 3H_2O$. In the aging process of this material, the initially crystalline phase becomes amorphous, and this transformation has apparently not been studied so far by morphological methods.

"Active" chromium hydroxide[5,6] is formed upon addition of base to aqueous solutions of $Cr(OH_2)_6^{3+}$. The structure of this solid is based on an octahedral layer, where one-third of the octahedral sites are occupied.[7] Octahedral $Cr(OH)_3(OH_2)_3$ units are linked through hydrogen bonds between the OH^- and H_2O ligands of adjacent Cr(III) centers. Its structure is complementary to that of bayerite, α-$Al(OH)_3$,[7] in the sense that the occupied octahedral sites in $Cr(OH)_3(OH_2)_3(s)$ match the vacant sites in the two-thirds-occupied octahedral layers of the bayerite structure. "Active" chromium hydroxide does *not* contain any bridging hydroxide ligands, and no exchange with solvent $H_2{}^{18}O$ at kinetically inert Cr(III) is involved in its formation.[8] Samples of "active" chromium hydroxide were claimed to differ in crystallinity when precipitated at different pH.[9] This material is thermally unstable, and thermal dehydration eventually produces α-Cr_2O_3.[10] However, aging at ambient or elevated temperatures, even in aqueous suspension, transforms it into an amorphous phase of unknown composition.[8] This transformation is probably due to the formation of hydroxide or oxide bridging ligands between adjacent metal centers with concurrent release of coordinated water molecules. The relevance of such processes to the treatment of chromium hydroxide to produce the widely used chromia catalysts has been pointed out.[11]

In the course of our work on the hydrolytic polymerization of $Cr(OH_2)_6^{3+}$, we have separated chromatographically the first five members of the homologous series of hydrolytic oligomers of Cr(III).[12] These form readily in homogeneous solution on partial alkalinization of the aqua ion, and they are kinetically quite stable in the pH range 1–3. We have also studied the kinetics of hydrolytic dimer formation

$$2(H_2O)_{6-r}Cr(OH)_r^{(3-r)+} \rightarrow (H_2O)_{8-s}Cr_2(\mu\text{-}OH)_2(OH)_s^{(4-s)+} + mH^+$$

using a pH stat technique.[13] In these pH stat titrations, a transient precipitate of "active" chromium hydroxide was formed in a small volume of the solution, near the tip of the buret where high local concentrations of titrant base prevailed. This precipitate is, however, redissolved within the time of rapid mixing of the solution (<1 s). Thus, it was necessary to check whether dissolution of this fleeting precipitate afforded $Cr(OH_2)_6^{3+}$ quantitatively, or whether some soluble oligomers or even acid-insoluble material formed. The present study has been extended over longer aging times and over the pH range 5.06–10.85 in order to establish the general pattern of the initial stages of the aging of $Cr(OH)_3 \cdot 3H_2O$ at *a molecular level.* This is possible since every act of inter-

---

(1) Jander, G.; Blasius, E. "Lehrbuch der Analytischen und Anorganischen Chemie"; S. Hirzel: Stuttgart, FRG, 1976; p 96.

(2) Feitknecht, W.; Michaelis, W. *Helv. Chim. Acta* **1961**, *45*, 212.

(3) Feitknecht, W.; Giovanoli, R.; Michaelis, W.; Müller, M. *Helv. Chim. Acta* **1973**, *56*, 2847.

(4) Feitknecht, W.; Giovanoli, R.; Michaelis, W.; Müller, M. *Z. Anorg. Allg. Chem.* **1975**, *417*, 114.

(5) Bjerrum, N. *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **1910**, *73*, 724.

(6) von Meyenburg, U.; Široký, O.; Schwarzenbach, G. *Helv. Chim. Acta* **1973**, *56*, 1099.

(7) Giovanoli, R.; Stadelmann. W.; Feitknecht, W. *Helv. Chim. Acta* **1973**, *56*, 839.

(8) Giovanoli, R.; Stadelmann, W.; Gamsjäger, H. *Chimia* **1973**, *27*, 170.

(9) Rossi, P. F.; Lorenzelli, V.; Cotena, N. *Ann. Chim.* (*Rome*) **1980**, *70*, 105.

(10) Giovanoli, R.; Stadelmann, W. *Thermochim. Acta* **1973**, *7*, 41.

(11) Burwell, R. L. Jr.; Haller, G. L.; Taylor, K. C.; Read, J. F., *Adv. Catal.* **1969**, *20*, 1–96.

(12) Stünzi, H.; Marty, W. *Inorg. Chem.* **1983**, *22*, 2145.

(13) Rotzinger, F. P.; Stünzi, H.; Marty, W. *Inorg. Chem.*, in press.

0020-1669/86/1325-0266$01.50/0 © 1986 American Chemical Society

Table I. pH and Time Dependence of the Aging of "Active" $Cr(OH)_3 \cdot 3H_2O$ at 25.0 °C and $I = 1.0$ M ($NaClO_4$)

		% aging products[b]			
pH[a]	time, s × 10^3	monomer	low oligomers	high oligomers	% Cr recovered[b]
5.06[c]	0.6	98.2	1.7	0.3	100.2
	57.6	52.6	19.2	27.3	99.1
	259.2	32.8	12.8	54.0	99.6
5.34[d,e]	0.6	98.2	1.6		99.8
	57.6	78.4	11.3	8.4	98.1
	259.2	62.8	9.5	26.8	99.1
6.08[f]	0.6	98.0	1.1		99.1
	57.6	94.1	4.6	1.3	100.0
	259.2	90.6	5.7	3.5	99.8
		91.9[k]	3.6[k]	3.5[k]	99.1[k]
7.32[g]	0.6	98.6	0.7		99.3
	57.6	97.1	1.5	0.8	99.4
		95.8	2.6	1.2	99.6
	259.2	91.3	4.3	3.9	99.5
		90.1[l]	7.6[l]	2.0[l]	99.7[l]
8.48[h]	0.06	99.2	0.2		99.4
	0.6	98.1	1.6		99.7
	57.6	91.6	5.7	2.3	99.6
		93.0	3.3	2.9	99.2
	259.2	87.8	6.0	4.8	98.6
		86.8[l]	8.5[l]	5.0[l]	100.3[l]
9.72[i]	0.06	98.8	0.6		99.4
	0.6	93.6	4.3	2.1	100.0
	57.6	82.2	12.0	5.8	100.0
	259.2	70.3	15.5	13.9	99.7
		68.8[l]	15.4[l]	13.7[l]	98.9[l]
10.63[j]	0.6	92.3	4.2	2.8	99.3
	57.6	68.2	21.5	9.7	99.4
	259.2	48.0	28.2	21.8	98.0
		46.2	31.4	21.4	99.0

[a] The quoted pH values were measured in the reaction mixture. [b] All percentages are quoted to one decimal place; the uncertainties involved are discussed in the text. [c] Pyridine, 0.2 M. [d] Ethanolamine, 0.1 M. [e] The buffer capacity was exceeded in this case; i.e., pH << pK_a. However, the validity of the results is not affected. [f] Pyridine, 0.4 M. [g] Imidazole, 0.2 M. [h] Triethanolamine, 0.3 M. [i] Ethanolamine, 0.2 M. [j] 3-(Cyclohexylamino)propanesulfonate, 0.2 M and 0.2 M NaOH. [k] Buffer added to Cr^{3+}. [l] No attempt to avoid contact of atmospheric CO_2 with the aging suspension was made.

Table II. Effect of Stirring on the Aging of $Cr(OH)_3 \cdot 3H_2O$ at Different pH Values

			% products			
pH	time, s × 10^3	conditions	monomer	low oligomers	high oligomers	% Cr recovered
5.06	0.6	stirred	96.2	3.8	0.3	100.3
		unstirred	98.2	1.7	0.3	100.2
	3.0	stirred	83.7	11.8	3.7	99.2
	12.0	stirred	53.6	25.0	21.0	99.6
	57.6	stirred	3.3	17.9	77.9	99.1
		unstirred	52.6	19.2	27.3	99.1
8.48	57.6	stirred	91.2	4.1	4.2	99.5
		unstirred	91.6	5.7	2.3	99.6
10.63	57.6	stirred	71.0	18.6	9.6	99.2
		unstirred	68.2	21.5	9.7	99.4

molecular substitution by coordinated OH^- within the lattice and every act of hydrolytic polymerization in the supernatant solution leads to formation of a kinetically inert polynuclear fragment that survives the rapid acid dissolution of the precipitate. These polynuclear fragments may be determined quantitatively following chromatographic separation.

Results

Time and pH Dependence of the Aging Process. Precipitates of "active" chromium hydroxide were prepared by mixing rapidly a continuously stirred, acidic (0.073 M $HClO_4$) solution of $[Cr(OH_2)_6](ClO_4)_3$ (0.0414 M) with appropriate buffers in the range pH 5.06–10.63 (Table I). The suspensions were then thermostated at 25.0 ± 0.1 °C for different times. In the majority of cases the suspensions were allowed to settle during aging (Table I), as in virtually all earlier studies of the aging of metal hydroxides.[2-4] In addition, some experiments were carried out with continuous stirring (Table II). The precipitates were then treated with 5 M $HClO_4$. Homogeneous solutions were obtained in all experiments. These were analyzed by ion-exchange chromatography. A control experiment (see below) indicated that all known hydrolytic oligomers along with higher polymers and $Cr(OH_2)_6^{3+}$ (=monomer) were present. Separation of the individual oligomers was not warranted since in most cases, only small amounts of species other than monomer were formed. Thus, three clearly separated fractions were collected: (i) the *monomer*, obtained by elution with 0.5–1 M $NaClO_4$ ($[H^+] = 0.005–0.01$ M); (ii) the dimer, trimer, and tetramer, obtained as one fraction by elution with 2–4 M $NaClO_4$ ($[H^+] = 0.02–0.04$ M), hereafter referred to as *low oligomers*; (iii) the pentamer, hexamer, and the totality of all other soluble *higher oligomers*, eluted in turn with saturated potassium oxalate, water, and NaOH (0.2 M). The chromium recovery in the eluted bands totalled >99% in the majority of cases, but was always ⩾98%, as determined spectrophotometrically following oxidation to chromate. The lower recoveries were always associated with large amounts of the higher oligomers, which were difficult to remove from the columns. The data are collected in Tables I and II.

The experimental uncertainty in the chromatographic separation and the analytical procedure is ±1% for the monomer. It follows that the usually much smaller, total amount of oligomers is subject to an absolute uncertainty of ±1%, and this propagates proportionally on the individual oligomer fractions since the separation is very good. The complete and rapid solubility of the precipitates in acid and the very good recoveries suggest that neither the known, solid "inactive" chromium hydroxide[8] nor the hydrated oxide phases[14] build up to detectable levels. In addition, no significant amounts of colloidal "$Cr(OH)_3$" particles[15] appear to go undetected. They are retained by the cation exchanger since they are positively charged in acidic solution[15] and become part of the higher oligomer fraction.

These experiments show the following: (i) the proportion of the different oligomers increases nonlinearly with time; (ii) the rate of oligomer formation is pH dependent, with highest values at the lower and upper end of the pH range studied; (iii) in the intermediate range pH 6–7, oligomer formation is slowest and is little dependent on pH (Figure 1); (iv) stirring of the $Cr(OH)_3 \cdot 3H_2O$ suspensions affects the rate of aging markedly at pH ~5. However, at pH 8.48 and 10.63, the aging is not accelerated by stirring. In stirred suspension, at pH ~5, the proportion of monomer decreases nonlinearly with time, as in the unstirred suspensions (Table II, Figure 2).

Composition of the Solid and of the Supernatant Liquid. In another series of experiments, the "active" chromium hydroxide was aged without stirring and was filtered from the supernatant liquid through 0.2-μm median pore size cellulose nitrate membrane filters. This pore size is much too large to retain typical colloidal "$Cr(OH)_3$" particles,[15,16] but is sufficient to retain most of the "active" $Cr(OH)_3 \cdot 3H_2O$ particles.[7,9] Thus, at least some of the higher oligomers found in the solid fraction (Table III) must be adsorbed on, or incorporated into, the "active" chromium hydroxide particles, otherwise they would pass through the membrane filter.

After filtration, the residue and supernatant liquid were separately analyzed as above. The amount of chromium in the supernatant liquid was small under most conditions, and a detailed study was only appropriate for the longest aging period (Table III). The uncertainty in the total amount of chromium in the

---

(14) Christensen, A. N. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 133 and references therein.

(15) Matijevic, E.; Lindsay, A. D.; Kratohvil, S.; Jones, M. E.; Larson, R. I.; Cayey, N. W. *J. Colloid Interface Sci.* **1971**, *36*, 273.

(16) Cornet, D.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 2489.

Table III. pH Dependence of Chromium(III) in Each Polymeric Group for the Liquid and Solid Phases of Hydroxide Suspensions Aged for 2.592×10^5 s (Normalized to 100% Cr Recovery)[a]

pH	phase	monomer	% monomer(s)/% monomer(l)	low oligomers	high oligomers	% Cr
5.06	solid	85.9	11.0	7.7	6.4	32
	liquid	7.8 (5.3)		15.3 (10.4)	76.9 (52.3)	68
	mixture	32.9		12.9	54.2	99.6[b]
5.34	solid	71.0	3.6	9.0	20.0	85
	liquid	20 (3.0)		13 (2.0)	67 (10.0)	15
	mixture	64.0		9.7	27.3	99.1[b]
6.08	solid	93.0	1.9	4.1	2.9	95
	liquid	49 (2.4)		35 (1.8)	16 (0.8)	5
	mixture	90.8		5.7	3.5	99.8[b]
7.32	solid	91.8	1.0	4.2	4.0	95
	liquid	90 (4.5)		8 (0.4)	2 (0.1)	5
	mixture	91.7		4.3	3.9	99.5[b]
8.48	solid	89.7	1.1	5.6	3.7	93
	liquid	81 (5.7)		13 (0.9)	6 (0.4)	7
	mixture	89.1		6.1	4.8	98.6[b]
9.72	solid	70.1	0.9	15.3	14.6	95
	liquid	76 (3.8)		20 (1.0)	4 (0.2)	5
	mixture	70.3		15.5	13.9	99.7[b]
10.63	solid	48.9	0.9	28.8	22.3	99
	liquid	50 (0.6)		20 (0.2)	20 (0.2)	1
	mixture	49.0		28.7	22.3	98.0[b]

[a] Numbers in parentheses refer to the absolute liquid composition. [b] % Cr recovered from analysis.

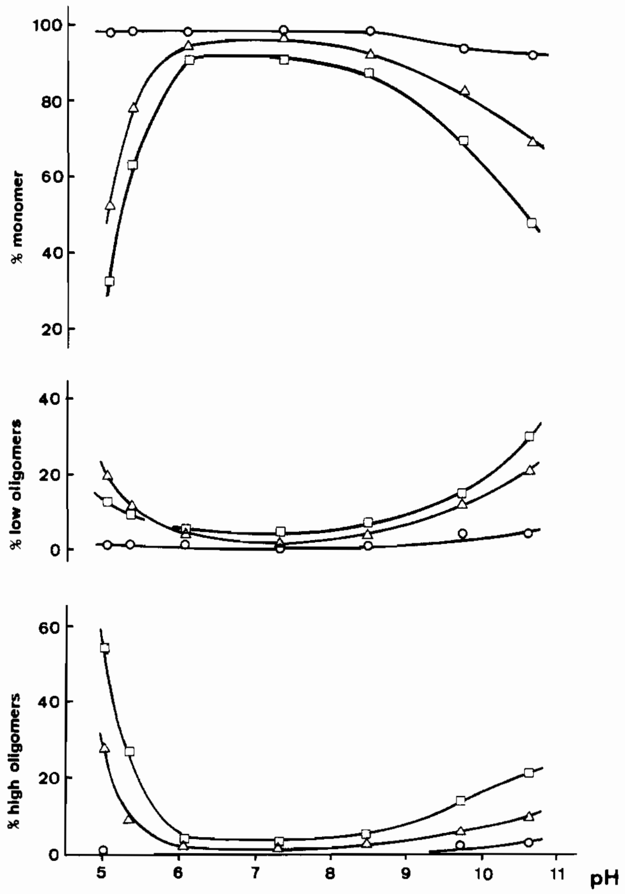


Figure 1. pH and time dependence of the aging of "active" $Cr(OH)_3 \cdot 3H_2O$ at 25 °C: (○) time = 600 s; (△) time = 5.76×10^4 s; (□) time = 2.592×10^5 s (unstirred suspensions).

supernatant liquid is the same as that determined for the solid phase (±1% absolute). However, this error should propagate *proportionally* on the monomer and oligomer fractions in the supernatant liquid.

Within the experimental uncertainty, the following observations are substantiated. (i) The total amount of chromium in the supernatant liquid is found to *decrease* roughly with *increasing pH*. At least at low pH (Table III), the composition of the solid is considerably different from that of the liquid phase. That is, the precipitate yields more monomer than the supernatant liquid. At higher pH, there is little difference in composition between the precipitate and the supernatant liquid. (ii) At pH 5.06 and 5.34, in contrast with all other pH values, there are more higher than lower oligomers in the mother liquor. (iii) At pH 5.06, the solid was composed mainly of monomer (86%), and only small quantities of lower and higher oligomers were present. At the same time, most of the higher polymers were found in the mother liquor.

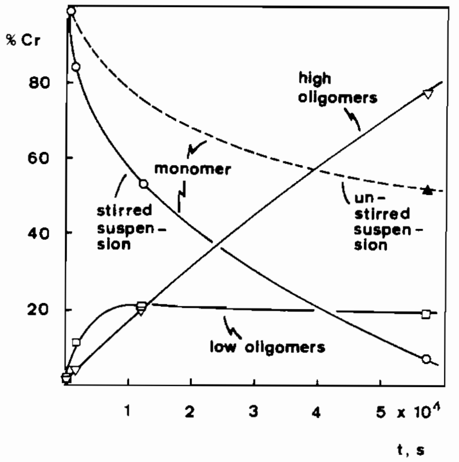
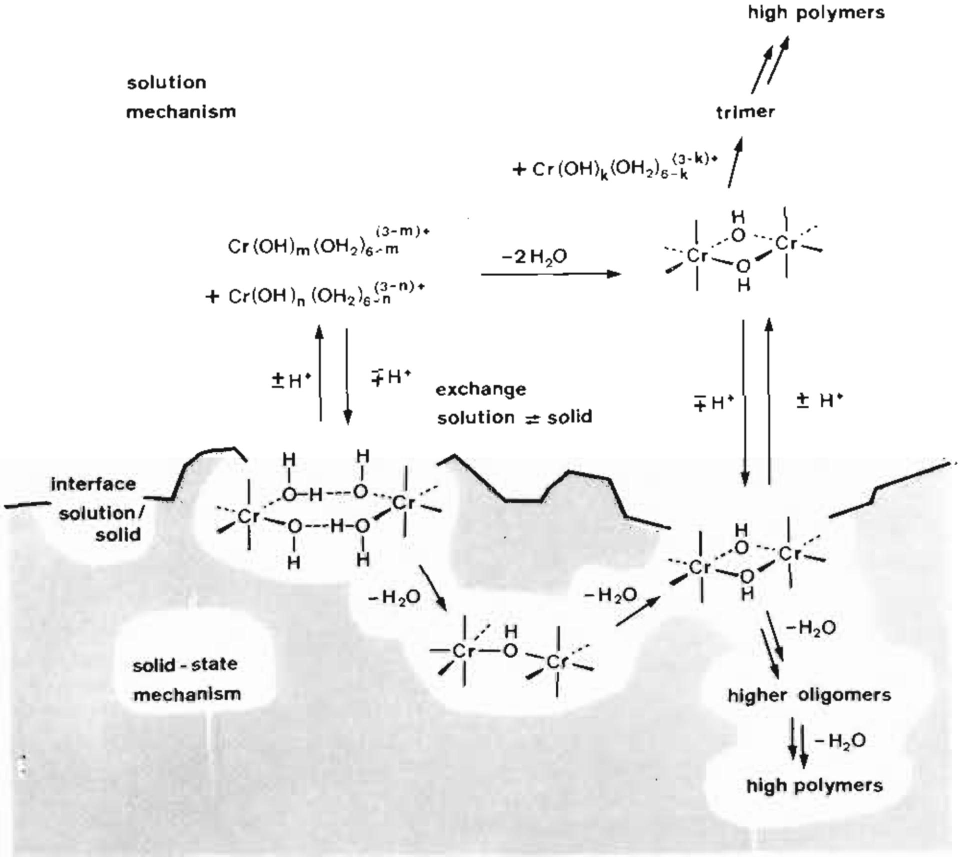


Figure 2. Time dependence of the aging in stirred (full line) and unstirred (broken line) suspensions at pH 5.06 and 25 °C. The data point for the unstirred suspension is from Table I.

Identification of Individual Oligomers. A large-scale experiment was carried out to identify and assay the individual oligomers formed in these aging experiments. Work at pH 10.85 and long aging times were required in order to obtain sufficient amounts of the oligomers for UV–vis spectral characterization. At this pH, 2.5% of the chromium was present as a solid precipitate at the end of the aging and acid dissolution procedure (at pH 10.63, however, a homogeneous solution was obtained; see above). The solution was filtered, and the residue was analyzed for chromium and included as part of the higher polymer fraction. The earlier chromatographic procedure[12] was modified in this large-scale experiment (see Experimental Section) to accommodate the presence of large proportions of the higher oligomers. The product distribution was 48.6% monomer, 1.1% dimer, 8.7% trimer, 2.6%

Scheme I



tetramer, 3.8% pentamer and hexamer (as a combined fraction, since their separation was not complete under these conditions), and 33.6% higher polymers (chromium recovery 98.4%). The oligomers were characterized by their elution behavior and color on the column.[12] In addition, dimer, trimer, and hexamer (tail fraction) were identified by comparison of their UV–vis spectra with those reported in the literature.[12] There was agreement to within the experimental error. No spectral data for comparison are as yet available for the pentamer. The tetramer band overlapped slightly with the trimer band, causing some deviation in the spectral parameters in the expected direction. Thus, the oligomers present are the same as those observed either in the hydrolytic polymerization in homogeneous solution (pH <5)[12,13,17,18] or after dissolution of the monomer in strong base (to form alkali-metal chromites), followed by treatment with 1 M $HClO_4$.[18] However, the amount of dimer found in this experiment is distinctly smaller than that found in the above, alternative syntheses.

Discussion

The present method for studying the aging of "active" chromium hydroxide has enabled us to follow *selectively* the formation of hydroxo bridges between Cr(III) centers; concurrent, purely *physical* changes in the aged hydroxide did *not* interfere. The method is based on the reported observation[12,19–21] that the substitution of H_2O bound to Cr(III) by chromium-bound hydroxide will result in a substitutionally inert fragment. Multiple events of this kind involving more than two metal centers result in the formation of species with greater nuclearity. Since such substitutions may occur independently of each other in parallel and consecutive pathways, there is a necessity to separate the different species that may result. This is now possible for oligomers up to the hexamer, which survive the conditions of chromatographic separation in the pH range 1.5–2.5.[12] This range of pH corresponds to a maximum of kinetic stability, between the acid-induced cleavage (pH <1) and further hydrolytic polymerization of the conjugate bases (pH >3.5).[13,22] However, it has been shown qualitatively that at least some of the higher oligomers (> hexamer) are more labile in this pH range, but their cleavage leads initially to some of the more inert oligomers and not directly to monomer.[18] The possible initial presence of labile, higher oligomers is thus indicated indirectly by equivalent amounts of these more inert oligomers.

Two principal mechanistic pathways appear possible for the transformation of "active" chromium hydroxide into hydrolytic oligomers. (i) In a *solid-state process*, hydrogen-bonded water molecules are eliminated thermally and are substituted by an OH^- ligand of an adjacent Cr(III) center (Scheme I). This results initially in the formation of a mono(μ-hydroxo)dichromium fragment. Upon acid dissolution, $(H_2O)_5CrOHCr(OH_2)_5^{5+}$ should result and would be converted[19] into doubly bridged $(H_2O)_4Cr(OH)_2Cr(OH_2)_4^{4+}$ [19–21] when the solution is diluted for adsorption on the column. If this reaction (or a combination of such steps, leading to the formation of higher polymers) occurs in the interior of the solid, then its rate is expected to be independent of solution pH. (ii) If oligomer formation occurs exclusively in *homogeneous solution*, then monomeric $Cr(OH)_3(OH_2)_3$ is required to leave the surface of the solid before undergoing hydrolytic polymerization. The release of these monomer units may be assisted by protonation or possibly by deprotonation, depending on the solution pH. The kinetics of hydrolytic polymerization processes in homogeneous solution have been studied by us over a pH range of ca. 1.5 units, in the proximity of pK_{a1}.[13,22] All steps are second order in $[\text{monomer}]_{tot}$[13] or in $[\text{starting oligomer}]_{tot}$[22] (these concentrations refer to the sum of the concentrations of the differently deprotonated species). The rate constants increase by ca. 2 orders of magnitude for each deprotonation step of the reactants. The

---

[17] Stünzi, H.; Marty, W., unpublished results.
[18] Toko, A. L. Travail de licence, Université de Neuchâtel, 1985.
[19] Thompson, M.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 2279.
[20] Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197.
[21] Kolaczkowski, R. W.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 322.
[22] Rotzinger, F. P.; Besso, C.; Marty, W., unpublished work.

Table IV. Comparison of the Calculated with the Experimentally Determined (from Filtration) Percentage of Total Monomeric Chromium(III) Species ($[Cr]_{tot}$) Found in Solution at Several pH Values

pH	calcd solubility of $Cr(OH)_3 \cdot 3H_2O$, %	exptl solubility,[a] %
4.95[b]	62[c]	68
5.34	11[c]	15
6.08	0.5[c]	5
7.32	0.009[c]	5
10.63	0.08[d]	1[e]

[a] Determined at 2.592×10^5 s aging time. [b] As a consequence of the continuing hydrolytic polymerization[1,9] the initially measured pH of 5.06 dropped to 4.95 after 2.592×10^5 s aging time, causes a considerable increase in solubility of "active" $Cr(OH)_3 \cdot 3H_2O$. Its solubility at the final pH of 4.95 is therefore a better estimate of the chromium(III) species found in solution. This also applies to the other pH values, but here the change in pH and solubility are much smaller. [c] Reference 6. [d] Reference 25. [e] This drop in the experimentally determined $[Cr]_{tot}$ value is probably due to an increase in the crystallinity of the hydroxide precipitate as previously reported by Rossi et al.[5] As a result filtration is more efficient.

shortest half-lives were in the second to hundred millisecond range.[13,22]

The hydrogen-bonded structure of "active" chromium hydroxide suggests that the $Cr(OH)_3(OH_2)_3$ units might equilibrate between solid and solution faster than the breaking or making of chromium–oxygen bonds. Except for the pH values where the dissolution of "active" chromium hydroxide is strongly accelerated by acid or by base, the concentration of monomer in solution is quite small,[6] and thus, polymerization in homogeneous solution is quite slow.

These possible pathways are summarized in Scheme I, which also accommodates two obvious combinations between the mechanisms: oligomers formed in solution are reversibly incorporated in the "active" chromium hydroxide lattice through hydrogen bonding, and polynuclear fragments formed in a solid-state process pass into solution.

How can these two mechanisms be distinguished? The rate of a proper solid-state process could of course be measured by removing samples of solid $Cr(OH)_3 \cdot 3H_2O$ from solution and following their aging by the method described here. Such a study is indeed planned by us, but is results may not be correlated safely with the present study, since the necessary washing and drying of the precipitate are likely to affect it profoundly. Indeed, striking changes in morphology have been noted as the result of a simple washing of $Cr(OH)_3 \cdot 3H_2O$ with acetone.[9]

The present results are nicely accommodated by the solution mechanism (ii), probably with reversible adsorption or incorporation of solution-formed polynuclear species into the solid. Our arguments are as follows.

(i) At the lower end of the pH range (pH 5–6), there is a close relationship between the rate of transformation of "active" chromium hydroxide and the total soluble chromium concentration, $[Cr]_{tot}$, as estimated from the solubility product[6] of $Cr(OH)_3 \cdot 3H_2O$ (Figure 1, Table IV). On the basis of this solubility product, it is predicted that the concentration of soluble monomer decreases with increasing pH, and this is indeed found. Furthermore, $[Cr]_{tot}$ is close to the calculated value for the total concentration of soluble *monomer* (Table IV) at all reaction times, suggesting that the equilibrium between soluble monomer and "active" chromium hydroxide is established initially. As the aging progresses, increasing amounts of monomer are transformed into oligomers through hydrolytic polymerization in solution. Yet, the supply of soluble monomer from the surface of the solid must be *interrupted* at some stage of the ageing process. This becomes clear from a comparison of the anticipated results for two hypothetical, limiting situations. First, if the reversible release of soluble monomer from the solid phase was always much faster than oligomer formation in solution, then the monomer concentration would be expected to attain a stationary level. This monomer concentration would be maintained until all of the "active" hydroxide is dissolved and the majority transformed into polymers by a solution process, without interaction of the polymers with the solid hydroxide phase. Second, if the release of monomer became sufficiently slow as to be rate-determining, then monomer would not be expected to be an appreciable part of $[Cr]_{tot}$. Furthermore, it would be unlikely to have $[Cr]_{tot}$ near the equilibrium value. Finally, a time-independent rate is anticipated (and observed for similar systems[23]), if the release of monomer from the solid surface is rate-determining. Our observations cannot be described satisfactorily by either of these two models, not even if the rates of release of monomer and of its polymerization become similar to one another. The results are best accommodated by rapid, reversible initial release of monomer from the solid, followed by blocking of the solid surface by solution-formed oligomers.

(ii) From the amphoteric character of Cr(III), an increase in $[Cr]_{tot}$ at equilibrium with $Cr(OH)_3 \cdot 3H_2O$ is anticipated at high pH. Monomeric $Cr(OH)_4^-$ has in fact been reported, but at pH 8–11, $[Cr]_{tot}$ is much greater than calculated from the literature data (Table IV).[24,25] The difference may be made up by additional, still unexplored polynuclear chromite anions. Polymerization is found to be increasingly more rapid as pH and $[Cr]_{tot}$ increase. This is in accord with the generally higher reactivity of multiply deprotonated, soluble species[13,22] and is consistent with a solution mechanism.

(iii) The experiment at pH 5.06 and aging time $t = 2.592 \times 10^5$ s may be related to an experiment on the dimerization of deprotonated monomer in *homogeneous* solution (pH 4.81) where the Cr^{3+} solution does not precipitate any "active" chromium hydroxide.[13] In the homogeneous case, only 1.4% of Cr^{3+} was found after 8.280×10^4 s aging time. Most of the chromium was present as dimer (6.1%), tetramer (10.4%), and higher polymers (82.1%). However, little trimer (<0.1%) was found.[13] From the "active" chromium hydroxide suspension at pH 5.06, 33% monomer was recovered, yet the dimerization of monomer should be faster than at pH 4.81. This discrepancy suggests that the release of monomer from the surface of the solid is indeed retarded at some stage during the aging process. This retardation is probably due to successive covering (by adsorption through hydrogen bonding or otherwise) of the solid surface by oligomers formed in solution. At pH 5.06 and 2.592×10^5 s aging time in unstirred suspension, the pale green precipitate of "active" chromium hydroxide was found to be covered by some dark green material. This latter color is characteristic of hydrolytic oligomers and was particularly intense at the interface between solution and precipitate.

(iv) Under the conditions of continuous stirring, the rate of transformation of "active" chromium hydroxide at pH 5.06 (Table II) was appreciably faster than in the unstirred suspensions and was close to that in *homogeneous* solution. It appears that the stirring of the suspension restricts the oligomers from blocking the surface of the "active" $Cr(OH)_3 \cdot 3H_2O$. The release of monomer is therefore not retarded to the same extent as in unstirred suspensions. This observation, as the one in the preceding paragraph, is also consistent with a solution mechanism. The influence of stirring on the aging of metal hydroxides has, to our knowledge, never been examined before.

(v) As borne out by the analyses of the supernatant liquid (Table III), the amount of higher oligomers is largest at the lowest pH. This is consistent with a general increase of higher polymers where $[Cr]_{tot}$ is highest and thus supports a solution mechanism.

All these observations clearly support a solution mechanism and suggest interactions between the hydrolytic oligomers formed with the surface of the solid starting material. The inferred blocking of the surface should progressively slow down the release of monomer to the point where this becomes the rate-determining step. As a consequence, the true equilibrium between "active"

---

(23) Pulfer, K.; Schindler, P. W.; Westall, J. C.; Grauer, R. *J. Colloid Interface Sci.* **1984**, *101*, 554.

(24) Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; p 214.

(25) Fricke, R.; Windhausen, O. *Z. Anorg. Allg. Chem.* **1924**, *132*, 273.

chromium hydroxide and the polymers is reached extremely slowly. At intermediate pH, less monomer is released since its solubility is smaller. Hydrolytic polymerization is quite slow from the beginning under these conditions, owing to the much smaller monomer concentration prevailing, despite the higher intrinsic reactivity of the multiply deprotonated species. The aging process is therefore slower under these conditions. At higher pH, the higher reactivity is best explained by an increase in solublity of the “active” hydroxide (in the form of anionic species) as well as by a presumably higher reactivity of these soluble species.

The two experiments at 1 min aging time (Table I) gave ≥98.8% of monomer and only ≤0.6% of low oligomers were found. This result confirms that the transient precipitates of $Cr(OH)_3{\cdot}3H_2O$ formed in the polymerization kinetics[13] redissolve instantaneously to form monomer quantitatively and thus do not affect the rate. However, even the minute amounts of oligomers formed in these experiments do not necessarily arise from the transformation of “active” chromium hydroxide, as some hydrolytic polymerization in solution could occur *prior* to formation of the precipitate. This is possible during the mixing of the reactants, since the pH increases sufficiently for partial polymerization to occur before precipitation ensues.[13]

A similar comment applies to the ^{18}O tracer experiment by Giovanoli et al.[8] Here a slightly larger ^{18}O enrichment (0.250 vs. 0.197%) than anticipated for the absence of oxygen exchange at Cr(III) was found in the fresh “active” chromium hydroxide. This was attributed to incomplete washing of the precipitate. While this may be correct, an alternative explanation may be based on the observation that accelerated ^{18}O exchange occurs in the deprotonated aqua ion[26] before $Cr(OH)_3{\cdot}3H_2O(s)$ is formed. Also some aging of the precipitate could take place during the workup, but it is uncertain whether this would occur with or without incorporation of ^{18}O while the label is still present. Regardless of these comments it is worth noting that this tracer experiment does not exclude a priori the formation of hydroxo bridges between Cr(III) centers, since these might form without incorporation of labeled solvent.

The 1.1% of dimer (vs. 8.7% trimer) found among the aging products in the large-scale experiment is remarkably low compared with product distributions from other syntheses,[17,18] and this suggests that the dimer is transformed efficiently into trimer by reaction with monomer. Other studies[13,19] have qualitatively confirmed that this reaction is more rapid than other, parallel polymerization steps.

In conclusion, the present study of the aging of “active” $Cr(OH)_3{\cdot}3H_2O$ has enabled us to trace down either directly or indirectly every act of hydrolytic polymerization occurring in its aqueous suspensions. This is due to the combined effect of the presumed lability of the hydrogen-bonded $Cr(OH)_3(OH_2)_3$ units in the solid and the kinetic inertness of most μ-hydroxobridged oligomers of Cr(III).

This same procedure may be used to chracterize the effects of physical treatments on the solid “active” chromium hydroxide. It might also be extended to study analogous, “active” hydroxides of other inert metal centers.

Experimental Section

Materials. Stock solutions of $[Cr(OH_2)_6](ClO_4)_3$ in perchloric acid were prepared and standardized as described.[12] Buffer solutions were prepared from puriss. grade materials (Fluka), except for imidazole which was recrystallized before use.[13] Sodium perchlorate (Merck, p.a.) was used as received. Water was deionized and distilled before use.

Instruments. A Ross glass electrode (Orion) connected to a Metrohm 605 pH meter was calibrated as described previously[12] and used for all pH measurements at 25.0 ± 0.1 °C. UV–vis spectra were recorded on an Uvikon 810 spectrophotometer with a cell compartment thermostated to 25.0 ± 0.1 °C by using a Haake N3 thermostat.

Buffers. The buffers used in the aging experiments were prepared by mixing the appropriate buffer base (Table I) with the required volume of 0.01 M $HClO_4$. Enough $NaClO_4$ was added to maintain $I = 1.0$ M. The pH was measured directly in the chromium hydroxide suspensions prepared for the aging experiments (see below). The pH values reported may differ slightly from those measured on the filtrates of the suspensions, owing to the presence of a finely dispersed solid.

Aging Experiments. For each buffer, the reaction mixtures were prepared by adding 4 mL of a Cr^{3+} stock solution ($[Cr^{3+}] = 0.0414$ M, $[H^+] = 0.073$ M) to 4 mL of buffer with vigorous stirring. The order of addition of Cr^{3+} to buffer or vice versa (Table I, footnote *k*) or the presence of atmospheric CO_2 (Table I, footnote *l*) had no significant effect on the aging. In general, however, the Cr^{3+} was added to the buffer, and all mixtures were stoppered to exclude CO_2. The suspensions of freshly precipitated $Cr(OH)_3{\cdot}3H_2O$ were then aged for different lengths of time (Table I) in a thermostated water bath, either with or without stirring. The aging process was then quenched by redissolving the precipitate with 1–2 mL of 5 M $HClO_4$. The resulting solutions were then diluted with distilled water (100 mL) and adsorbed onto a Sephadex SP-C25 column (H^+ form, 15 × 1 cm). The Cr(III) species (monomer, low oligomers, and high oligomers) were then eluted as described.[12] The color and elution characteristics of the bands were unaffected by the different buffers used. These buffers seem therefore not to be coordinated to Cr(III) during these experiments. In this work, the solution collected during adsorption on these short columns often contained some Cr^{3+}. This was also converted to CrO_4^{2-}, analyzed spectrophotometrically[12,27] and included in the monomer fraction. Chromium determination in the low and high oligomer fractions was carried out by the same procedure.[12]

The polymer content of the liquid and the solid phase of each suspension was determined separately for the aging period of 2.592×10^5 s. A 5-mL portion of the stirred, homogeneous suspensions was pipetted, centrifuged, and filtered through a Sartorius SM 11307 cellulose nitrate membrane filter (0.2-μm mean pore size). A 4-mL portion of this filtrate and the remaining part (3 mL) of the suspension were then acidified separately with 0.5 or 1 mL of 5 M $HClO_4$, respectively. These solutions were then each adsorbed, eluted, and analyzed for chromium as described above.

The large-scale experiment designed to characterize the individual oligomers was performed as follows. A 150-mL portion of Cr^{3+} stock solution (0.0414 M) was added at once to 150 mL of *tert*-butylamine buffer (0.4 M). The suspension (pH 10.85) was aged for 2.52×10^4 s at 25 °C and then acidified with 50 mL of 5 M $HClO_4$. An amount of 2.5% of the chromium hydroxide did not dissolve instantaneously and was therefore filtered off through a cellulose nitrate membrane filter and analyzed as described above. The filtrate was diluted to give $[H^+] \simeq 0.05$ M and adsorbed onto a Sephadex SP C25 column (H^+ form, 30 × 4 cm). The presence of large amounts of higher polymers caused uneven shrinking and floating of the resin. Thus, following removal of the monomer with 120 mL of 1 M $NaClO_4$, the oligomers up to hexamer were eluted without separation by using 150 mL of 4 M $NaClO_4$ and 100 mL of 4 M $LiClO_4$. The higher polymers were then eluted in turn with saturated potassium oxalate, water, and NaOH and were analyzed for chromium content. In order to separate the oligomers up to hexamer, the eluate containing the totality of the lower oligomers was then diluted ($I \simeq 0.1$ M) and readsorbed onto the same column and eluted in the usual way.[12]

The pH values in these experiments were measured on suspensions made up by mixing 20 mL of the appropriate buffer with 20 mL of the 0.0414 M stock solution of Cr^{3+}, with vigorous stirring (Table I, footnotes *b–j*). The stirred suspensions were equilibrated thermally in a thermostat and bubbled with N_2 continuously. The pH was recorded at constant temperature 25.0 ± 0.1 °C, always 20 min after preparation of the suspensions.

Acknowledgment. We acknowledge support of this work by the Swiss National Foundation (Grant 2.838–0.83). We thank Prof. R. Giovanoli and Drs. H. Stünzi and F. Rotzinger for discussions.

Registry No. $Cr(OH)_3{\cdot}3H_2O$, 41993-26-4; $Cr(OH_2)_6^{3+}$, 14873-01-9; Cr, 7440-47-3.

---

(26) Xu, F.-C.; Krouse, H. R.; Swaddle, T. W. *Inorg. Chem.* **1985**, *24*, 267.

(27) Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.