

Equilibrium Studies of Chromium(III) Complexes.

III. The Complex Formation between Chromium(III) and Ethylenediaminetetraacetic Acid

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It has previously been shown that under the combined catalytic effect of Cr(II) and charcoal equilibrium between the mononuclear Cr(III) amines or Cr(III) ethylenediamine complexes is established within a few days. In the present work it has been shown that the Cr(III) complexes $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Cr}(\text{NH}_3)_5\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$ and $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ react with EDTA in aqueous solution within a few hours using this catalyst to give the Cr(III) EDTA complex quantitatively.

From emf measurements with a mercury electrode in such solutions with $C_{\text{KCl}} = 0.60 \text{ M}$, $C_{\text{EDTA}} = 65 \text{ mM}$, $C_{\text{Cr}} = 5.0 \text{ mM}$ and $4.5 < \text{pH} < 9.5$ (22°C) the stability constant for the formation of the Cr(III) EDTA complex was found to be $10^{23.1} \text{ M}^{-1}$.

In recent papers we described a method by which it is possible to establish equilibrium between the mononuclear chromium(III) complexes with ethylenediamine¹ or ammonia² as ligands in aqueous solution within a few days at room temperature. The method is based on the combined catalytic effect of chromium(II) (1–2 % of the total chromium content) and charcoal, which must both be present. During the equilibration chromium(II) is continuously generated by electrolytic reduction so as to compensate for the amount of chromium(II) which is oxidized to chromium(III) by the medium, this oxidation being catalyzed by the charcoal. The emf was measured continuously during the equilibration using a mercury electrode, and from these emf measurements it was possible to determine the chromium(II) content of the solutions¹ as well as the gross stability constants.

We describe here a similar investigation of the chromium(III)-EDTA system (EDTA \equiv ethylenediaminetetraacetic acid $\equiv \text{H}_4\text{Y}$). Our intention was to find out whether it was possible, using this catalytic procedure, to establish equilibrium over a large pH range (4.5–9.5), and to see whether the mercury electrode worked satisfactorily under these conditions. EDTA is suitable for this purpose because of its high stability and because of the simplicity of the system involving only a few species (*vide infra*).

EXPERIMENTAL

Procedure. The experimental arrangement has been described by us previously.¹ Table 1 gives the experimental conditions and results of a single typical experiment (exp. 1 of Table 2): After the first *ca.* 6 h with an electrolysis current of *ca.* 20 mA the emf had dropped to between –1.1 and –1.2 V and this could subsequently be maintained by using 1–5 mA, giving $[\text{Cr}(\text{II})]/[\text{Cr}(\text{III})] \simeq 0.01–0.1$. From time to time the current was switched off in order to measure E and $[\text{Cr}(\text{II})]$ simultaneously as described previously.¹ At the same time a small sample was removed for analysis.

Table 2 gives the experimental conditions employed in a series of experiments involving various pH, initial Cr(III) compounds, times of equilibration, *etc.*

All experiments were performed at $22 \pm 1^\circ\text{C}$.

Chemicals and apparatus. All chemicals used were reagent grade or were analyzed by us. *cis*- $[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$,³ $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$,⁴ $[\text{Cr}(\text{urea})_6]\text{Cl}_3 \cdot \text{H}_2\text{O}$,⁵ and $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$ ⁶ were prepared according to the literature methods and were analyzed for Cr, N, chloride, Cr(II)

Table 1. Experimental details for exp. 1 (Table 2). $C_{Cr} = 5.0$ mM (from $CrCl_3 \cdot 6H_2O$ heated at $90^\circ C$ for 5 min with the $Na_2H_2Y \cdot 2H_2O$ -solution), $C_{EDTA} = 65$ mM, $pH_{start} = 6.0$ (adjusted to this pH with 0.1 M $NaOH$), 50 mg charcoal, 0.60 M KCl , $22^\circ C$, 50 ml solution.

Meas- ure- ment	Total time h	Electrolysis mA	Current mA	Voltage V	Total amount of electricity C	pH	emf, E Hg, sat. calomel mV	$(\partial E/\partial t)_0$ mV min ⁻¹	Hydrogen vol. V_{H_2}	$[Cr(II)]_0$ from $(\partial E/\partial t)_0$ mM	$[Cr(II)]_0$ from V_{H_2} mM	$\log(K_{III}/K_{II})$ from $(\partial E/\partial t)_0$ V_{H_2}	$\log(K_{III}/K_{II})$ from V_{H_2}
	1	2.0	20	25	144	6.1	-611						
	2	6.0	16	28	360	6.2	-1171						
	3	6.5	4.0	8.5	367	6.2	-1158						
	4	7.5	3.3	7.7	379	6.2	-1143	2.1	0.34	0.50	0.56	9.32	9.26
	5	27.5	0.5	3.0	415	6.2	-1110	1.8	0.14	0.089	0.23	9.54	9.42
	6	29.0	1.0	3.9	420	6.3	-1128	1.7	0.28	0.48	0.46	9.19	9.21
	7	30.0	1.5	4.4	425	6.3	-1135	1.0					

Table 2. $\log K_{III}/K_{II}$ determined under different conditions. $C_{Cr} = 5.0$ mM, $C_{EDTA} = 65$ mM, 0.6 M KCl (except for exp. 14), $22^\circ C$, 50 ml solution.

Exp. No.	pH	Initial Cr(III) compound	$\log K_{III}/K_{II}$	Other experimental details different from those in exp. 1 (Table 1)
1	6.2	$CrCl_3 \cdot 6H_2O$ heated at $90^\circ C$ with EDTA	9.35	
2	6.2	as exp. 1	9.38	
3	6.3	as exp. 1	9.45	100 mg charcoal (100 mg was also used in exp. 3-10 and 14) 0.1 mM $< [Cr(II)] < 0.6$ mM in 5 E -measurements 0.08 mM $< [Cr(II)] < 0.3$ mM in 3 E -measurements electrolyzed for 4 days with 1117 C 0.01 mM $< [Cr(II)] < 0.7$ mM in 3 E -meas. with 1 day's interval
4	6.2	as exp. 1	9.38	pH variation
5	4.6	as exp. 1	9.42	
6	7.6	as exp. 1	9.39	
7	9.7	as exp. 1	9.34	0.03 mM $< [Cr(II)] < 0.5$ mM in 3 E -meas. per exp.
8	6.1	cis - $[Cr(NH_3)_3Cl_3(H_2O)_2]Cl$	9.47	Variation of initial Cr-compound, which was not heated with the EDTA-solution.
9	5.6	$[Cr(NH_3)_4Cl_3]$	9.58	0.04 mM $< [Cr(II)] < 0.7$ mM in 2 E -meas. per exp.
10	5.6	$[Cr(NH_3)_4Cl_3]$	9.42	After the second E -meas. of exp. 11 5.13 mg $CrSO_4 \cdot 5H_2O$ was added to the solution at $E = -1000$ mV: $[Cr(II)] = 0.43$ mM (calc.), 0.41 mM (from V_{H_2}), $E = -1145$ mV leading to $\log(K_{III}/K_{II}) = 9.47$
11	5.7	$[Cr(urea)_4Cl_3 \cdot H_2O]$	9.52	
12	6.2	The equilibrated sol. from exp. 4	9.35	The solution had been left for 12 months, charcoal was removed, 2.41 mg $CrSO_4 \cdot 5H_2O$ was added giving $[Cr(II)] = 0.20$ mM (from V_{H_2}), $E = -1120$ mV
13	6.1	as exp. 1	9.60	6.83 mg $CrSO_4 \cdot 5H_2O$ was added giving $[Cr(II)] = 0.54$ mM (from V_{H_2}), $E = -1161$ mV (no charcoal)
14	5.6	as exp. 1	9.41	$C_{Cr} = 1.0$ mM, $C_{EDTA} = 5.0$ mM, 0.1 M KCl , $[Cr(II)] = 0.03$ mM
	6.2	Average exp. 1-13	9.41	in 2 E -meas.
			9.44	

and sulfate. All analyses agreed within 1–2 % (relative) with the formulae given. The charcoal used was a Norit W product, and purified redistilled mercury was used for the electrodes.

The emf and pH measurements were made with a Radiometer PHM 52, the G 202 C glass electrodes being tested in the relevant media according to Bjerrum.⁷ Visible spectra were recorded on a Cary 14 or a Bausch and Lomb Spectronic 505 spectrophotometer.

RESULTS

In the pH range investigated only two Cr(III)-EDTA complexes need to be taken into consideration, namely $\text{CrY}(\text{H}_2\text{O})^-$ and $\text{CrY}(\text{OH})^{2-}$ since the acid dissociation constants of Cr(HY) (H_2O) are $\text{p}K_{\text{S}_1}^{\text{III}}=1.95$ and $\text{p}K_{\text{S}_2}^{\text{III}}=7.39$ (0.1 M KCl, 20 °C)⁸ and $\text{CrY}(\text{OH})^{2-}$ takes up a second OH^- with “ $\text{p}K_{\text{S}_3}^{\text{III}}=12.25$.” Cr(II) exists as CrY^{2-} under our conditions, Cr(HY) (H_2O)⁻ having $\text{p}K_{\text{S}_1}^{\text{II}}=3.00$ and $\text{p}K_{\text{S}_2}^{\text{II}}>11$.¹⁰

In order to minimize pH changes during the electrolysis C_{EDTA} was chosen to be as high as 6.5×10^{-3} M, giving a reasonably high buffer capacity which was almost independent of pH between pH 5.5 and 8. A 0.6 M KCl medium was chosen as a compromise so as to ensure a medium of constant ionic strength and at the same time facilitate comparison of our results with stability constants from the literature, most of which have been determined for 0.1 M KCl. Table 1 shows that during the first 5–6 h with high electrolysis current the pH increased by 0.2 after which it was nearly constant and in no case increased more than 0.1 pH unit except in exp. 14 with $C_{\text{EDTA}}=5 \times 10^{-3}$ M (0.1 M KCl), where the pH increase was *ca.* 5 times as great. E does not, however, depend very much on pH in this pH range (see the following equation).

The ratio of the EDTA stability constants K^{III} and K^{II} for Cr(III) and Cr(II), respectively, is calculated from

$$\log \frac{K^{\text{III}}}{K^{\text{II}}} = \log \frac{[\text{CrY}(\text{H}_2\text{O})^-][\text{Cr}^{2+}]}{[\text{CrY}^{2-}][\text{Cr}^{3+}]}$$

$$= -\frac{E+652}{58.5} + \log \frac{\{C_{\text{Cr}} - [\text{Cr}(\text{II})]\}[\text{H}^+]}{[\text{Cr}(\text{II})]\{[\text{H}^+] + K_{\text{S}_2}^{\text{III}}\}}$$

“652” is the difference between the standard potentials of the $\text{Cr}^{2+} - \text{Cr}^{3+}$ couple and of the saturated calomel electrode (–410 mV¹¹ and 242 mV, respectively).

The calculated values of $\log(K^{\text{III}}/K^{\text{II}})$ are given in Tables 1 and 2. $\text{p}K_{\text{S}_4}^{\text{III}}$ was determined from spectral data for Cr(III)-EDTA solutions in 1 M KCl at various pH as 7.34 ± 0.06 to be compared with a value of 7.39 ± 0.02 (0.1 M KCl, 20 °C) determined by other workers.⁸

The rate of formation of $\text{CrY}(\text{H}_2\text{O})^-$ from $\text{Cr}(\text{NH}_3)_6^{3+}$ under a variety of conditions was followed spectrophotometrically. The reaction time for the formation of 90 % $\text{CrY}(\text{H}_2\text{O})^-$ is given in Table 3.

DISCUSSION

The average value of $\log K^{\text{III}}/K^{\text{II}}=9.4$ from Table 2 corresponds to a standard potential (*versus* the saturated calomel electrode) $E^{\circ}_{\text{SCE}} = -1204$ mV. Pecsok *et al.* determined $\log K^{\text{II}}=13.61$ in 0.1 M KCl at 20 °C and from polarographic measurements found $\log K^{\text{III}}/K^{\text{II}}=9.79$.¹⁰ The experiment 14 in 0.1 M KCl medium (Table 2) shows that $\log K^{\text{III}}/K^{\text{II}}$ in this medium is the same within experimental error as in 0.6 M KCl. Using $\log K^{\text{II}}=13.61$ this equilibrium determination of $\log K^{\text{III}}/K^{\text{II}}$ gives $\log K^{\text{II}}=23.1$ in good agreement with the previous determination¹⁰ (see Table 4). A comparison of the stability constant data for chromium(III), cobalt(III), and nickel(II) with

Table 3. Rate of formation of $\text{CrY}(\text{H}_2\text{O})^-$ (90 mol-%) under various catalytic conditions. $C_{\text{Cr}}=5.0$ mM, $C_{\text{EDTA}}=65$ mM, pH=5.5 (0.6 M KCl, 22 °C, 50 ml). $[\text{CrY}(\text{H}_2\text{O})^-]/C_{\text{Cr}}$ was measured spectrophotometrically.

Exp.	90 % $\text{CrY}(\text{H}_2\text{O})^-$ after	Catalytic conditions
a	< 4 h	100 mg charcoal, Cr(II) produced electrolytically (15–20 mA), daylight, exp. 10 (Table 2)
b	30 d	no charcoal, no Cr(II)
c	65 d	100 mg charcoal, no Cr(II)
d	83 d	as c but in the dark
e	163 d	as b but in the dark
f		addition of 1.2 mg $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$ (2 mol-%).
	After 1 day:	No detectable Cr(II) and 70 mol-% $\text{CrY}(\text{H}_2\text{O})^-$.

Table 4. Comparison of stability constants at room temperature for Cr(III), Co(III), and Ni(II) with ammonia (extrapolated values), en (= ethylenediamine) and EDTA.

	NH ₃ log K _s	log K _s	log β _s	en log K _s	log β _s	EDTA log K
Cr(III) ^{1,2,10}	1.6	1.5	13	6.4	19.5	23.1 ^a 23.4 ^b
Co(III) ^{7,12-15}	5.5	4.9	38	13.3	48.7	40.7
Ni(II) ^{7,14,17}	0.9	0.2	10	4.4	18.3	18.6 ^b
Medium	4.5 M NH ₄ Cl			1 M 1:1 salt		^a 0.6 M KCl ^b 0.1 M KCl

the ligands ammonia, ethylenediamine, and EDTA is given in Table 4.

The mercury electrode worked reproducibly within 1–2 mV under these conditions with varying [Cr(II)] and pH, and equilibrium was attained within 4–5 h irrespective of the initial Cr(III) compound. We also performed some experiments with charcoal-free solutions by adding known amounts of CrSO₄·5H₂O to a solution which had been equilibrated with charcoal and Cr(II) and then aged for 12 months (exp. 12), and also by adding Cr(II) to a thermally treated solution (exp. 13), both experiments giving results in agreement with the others in Table 2.

Table 3 shows that the rate of formation of CrY(H₂O)⁻ from the very robust Cr(NH₃)₆³⁺ in the presence of Cr(II) and charcoal is increased at least 400 times relative to the rate in solutions without Cr(II). Charcoal alone has only a small effect. Exposure to daylight has some effect and the lower rate of exp. c compared to exp. b (Table 3) is probably due to the light shielding effect of the charcoal. It was difficult to measure the effect of the few per cent Cr(II) alone because of the rapid oxidation to Cr(III) especially with charcoal present. Thus no Cr(II) could be detected after one day in charcoal-free solution starting with 2 % Cr(II) (as CrSO₄·5H₂O, exp. f). As exp. f shows, Cr(II) alone definitely shows a large catalytic effect in this system, in contrast to our observations in the ethylenediamine and ammonia systems.^{1,2}

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