

various Zn(en)Cl_2 phases, one of which contains nearly C_{2h} en ligands, is consistent with the nearly identical values of $r_{\text{Zn}^{2+}}$ and r_{cav} . Similarly, the lack of C_{2h} en ligands in Zn(en)Br_2 and Zn(en)I_2 is consistent with the values of r_{cav} for bromide and iodide, $r_{\text{cav}} = 0.81$ and 0.89 \AA , respectively, which are larger than $r_{\text{Zn}^{2+}}$.

The r_{cav} values for chloride, bromide, and iodide are satisfactory for cadmium(II) and mercury(II). On this basis, C_{2h} en ligands would be expected for all of these systems. However, one must also consider whether or not en is capable of spanning two metal ions in the lattice. The structure illustrated in Figure 3 may be simplified to a close-packed array of halide ions. For this idealized structure two metal atoms bridged by an en molecule will be separated by 4 times the ionic radius of the halide. A distance of 3.8 \AA between two terminal nitrogen atoms of an en molecule in the trans form is calculated assuming a C-C bond length of 1.52 \AA , a C-N bond length of 1.47 \AA , and bond angles in the NCCN chain of 109.5° . Therefore the minimum possible metal-nitrogen bond length is

$$r_{\text{M-N}} = \frac{1}{2}(4r_{\text{X}^-} - 3.8)$$

In the real crystal, repulsion between the halide layers leads to a distortion of the crystal away from the close-packed halide configuration and this in turn yields a larger value for $r_{\text{M-N}}$ than that calculated by eq 1. For Cd(en)I_2 the calculated minimum value of $r_{\text{M-N}}$ is 2.4 \AA . This is larger than the sum of the Cd(II) and N covalent radii, 2.2 \AA .¹⁵ Thus, it appears that en bridging should be energetically unfavorable for the cadmium iodide system. For the other cadmium ha-

lides and the mercuric halides the metal ions may approach sufficiently close to give reasonable metal-nitrogen bond lengths. Consistent with these estimates is the observation of effective C_{2h} symmetry for en in the cadmium and mercuric halide systems with the exception of Cd(en)I_2 .

Octahedral coordination around a mercury(II) atom is occasionally compressed with two shorter and four longer mercury-ligand atom distances.¹⁶ For the present mercury compounds, the compression along the N-Hg-N axis is suggested from the high frequency of the NH_2 rocking bands, which are observed at 687 and 662 cm^{-1} for Hg(en)Cl_2 and Hg(en)Br_2 , higher by *ca.* 120 – 154 cm^{-1} than those observed for Cd(en)Cl_2 and Cd(en)Br_2 , respectively. The hypothetical model proposed by Brodersen⁸ for Hg(en)Cl_2 with the Hg-N bond length 2.18 \AA and the Hg-Cl bond length 2.9 \AA is reasonable in this sense.

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(15) The Cd-N(en) bond length $2.26 \pm 0.05 \text{ \AA}$ has been reported for $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$ in which the en bridges between two cadmium atoms, and a Cd-N(NH_2) bond length of 2.31 \AA has been reported for $\text{Cd}(\text{NH}_2)_2\text{Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$. In each of these compounds, the cadmium atom occupies an octahedral site with trans $\text{CdN}_2\text{N}_4(\text{NC})$ coordination. Cf. ref 5 and Y. Sasaki, *Bull. Chem. Soc. Jap.*, **42**, 2412 (1969).

(16) D. Grdenic, *Quart. Rev., Chem. Soc.*, **19**, 303 (1965).

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Kinetic Study of the Chromium(II) Reductions of Oxalatotetraammine- and Maleatopentaamminechromium(III)

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The reduction of oxalatotetraamminechromium(III) by chromium(II) obeys the rate law $-d \ln [(\text{NH}_3)_4\text{CrC}_2\text{O}_4^+]/dt = 6.37 \times 10^{-3}[\text{Cr}^{2+}]$ at 25° and $1.0 M$ ionic strength, with $\Delta H^\ddagger = 12.6 \pm 0.9 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -26.7 \pm 3 \text{ cal mol}^{-1} \text{ deg}^{-1}$. The analogous reduction of maleatopentaamminechromium(III) obeys the rate law $-d \ln [(\text{NH}_3)_5\text{Cr}(\text{mal})]_{\text{total}}/dt = (k_1 + k_2'[\text{H}^+]^{-1})[\text{Cr}^{2+}]$. At 25° in $1 M \text{ LiClO}_4$ $k_1 = 1.79 \times 10^{-2} M^{-1} \text{ sec}^{-1}$ and $k_2' = 1.50 \times 10^{-3} \text{ sec}^{-1}$. The acid dissociation constant, K_a , of $(\text{NH}_3)_5\text{CrO}_2\text{CCH}=\text{CHCO}_2\text{H}^{2+}$ has been determined between 0 and 30° in $1 M \text{ LiClO}_4$. At 25° , $K_a = 1.89 \times 10^{-3} M$ with $\Delta H^\circ = 5.3 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = 5.3 \pm 1 \text{ cal mol}^{-1} \text{ deg}^{-1}$. The specific rate constant for reduction of the unprotonated form of the complex, k_2 , is calculated as $0.795 M^{-1} \text{ sec}^{-1}$ with $\Delta H_2^\ddagger = 3.4 \pm 2 \text{ kcal mol}^{-1}$ and $\Delta S_2^\ddagger = -48 \pm 6 \text{ cal mol}^{-1} \text{ deg}^{-1}$. The activation parameters for k_1 are $\Delta H_1^\ddagger = 10.4 \pm 0.7 \text{ kcal mol}^{-1}$ and $\Delta S_1^\ddagger = -32 \text{ cal mol}^{-1} \text{ deg}^{-1}$. These results are compared to previous work on the analogous amminecobalt(III) and aquochromium(III) systems. It is concluded that rate comparisons for the latter two systems are not necessarily reliable in differentiating radical ion and resonance-exchange mechanisms. Differences in the activation parameters indicate that different rate-controlling steps are involved when the oxidizing center is chromium(III) or cobalt(III).

Introduction

Oxidation-reduction reactions in which the electron transfer occurs through a bridging group have been widely studied and the field has been reviewed recently by Gould and Taube.¹ Two limiting cases have been

proposed for this type of electron transfer. In the superexchange or resonance-transfer mechanism an electron is transferred from the reducing agent to the bridging ligand while an electron is simultaneously transferred from the bridging ligand to the oxidizing agent. In the chemical or radical ion mechanism the bridging

(1) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

ligand is reduced to form a radical intermediate, which is oxidized subsequently by the oxidizing agent.

Taube and coworkers²⁻⁴ have proposed that the rate for the radical ion mechanism should be rather insensitive to the nature of the oxidizing species, since ligand reduction is assumed to be the rate-controlling factor. In studies with the bridging ligands isonicotinamide,² fumarate,³ and maleate,⁴ the ratios for reduction of the analogous amminecobalt(III) and aquochromium(III) complexes by chromium(II) were found to be in the range of 10–80. For the simple halide and pseudohalide anion bridging ligands this ratio is much higher (10^4 – 10^7) indicating that the greater reducibility of the cobalt(III) is influencing the rate of reduction. For the systems in which a relatively low ratio has been found, it has been argued that the radical ion mechanism is operative. It has been pointed out by Hwang and Haim⁵ that this criterion indicates a resonance-transfer mechanism for the reduction of $(\text{NH}_3)_4\text{CoC}_2\text{O}_4^+$ by chromium(II).

All of the comparisons made thus far have involved the amminecobalt(III) and aquochromium(III) complexes. In order to make the systems strictly analogous, a study of the amminechromium(III) systems is required. It might be expected that, if changing from amminecobalt(III) to aquochromium(III) changes the rate by less than 10^2 , then changing from aquo- to amminechromium(III) should have an even lesser effect, if a radical ion mechanism is operative.

The kinetics of the chromium(II) reductions of maleatopentaamminechromium(III) and oxalatotetraamminechromium(III) are reported here. The results will be compared to those of Olson and Taube⁴ and Hwang and Haim⁵ on the analogous cobalt(III) complexes.

Experimental Section

Materials.—Water redistilled from alkaline permanganate in an all-glass apparatus was used to prepare solutions for the kinetic studies. Lithium perchlorate solutions were prepared by dissolving weighed samples of reagent grade lithium carbonate in standardized solutions of perchloric acid. Stock solutions of chromous perchlorate were prepared by dissolving electrolytic grade chromium (99.999% purity, United Mineral and Chemical Corp.) in dilute perchloric acid–lithium perchlorate solutions. These solutions were periodically analyzed for chromium(II) by treating a known volume of the chromium(II) solution with an excess of standard ferric ammonium sulfate solution and determining the excess ferric ion present iodometrically.

Oxygen was removed from all solutions by purging with nitrogen which was deoxygenated by passing through two solutions of chromous perchlorate over zinc amalgam. The solutions were handled using standard syringe techniques.

Preparation of Complexes.—Maleatopentaamminechromium(III) perchlorate was prepared by a method similar to that described previously for the trifluoroacetatopentaamminechromium(III) complex.⁶ A slight excess of maleic anhydride (0.7 g) was added to a solution of aquopentaamminechromium(III) perchlorate (3.0 g) dissolved in *N,N*-dimethylformamide in the presence of excess *N,N*-dimethylbenzylamine (3.0 ml). The product was precipitated 1 min after mixing by the addition of *sec*-butyl alcohol to the reaction mixture. The crude product was recrystallized by dissolving in the minimum amount of water at room temperature followed by the addition of sufficient 70% perchloric acid to make the final solution 1 *M* in perchloric acid. The mixture was cooled for 30 min in a refrigerator and the

product was collected and washed with ethanol and ether and dried under vacuum.

The visible absorption spectrum of this salt shows maxima at 490 nm (ϵ 55.0 $M^{-1} \text{ cm}^{-1}$) and at 365 nm (ϵ 36.0 $M^{-1} \text{ cm}^{-1}$) in 1 *M* LiClO_4 and at 490 nm (ϵ 56.6 $M^{-1} \text{ cm}^{-1}$) and 364 nm (ϵ 38.1 $M^{-1} \text{ cm}^{-1}$) in 1 *M* HClO_4 . The infrared spectrum of the complex shows the expected features and is very similar to that of the analogous cobalt(III) complex. The most characteristic feature is the carbonyl absorption at 1700 cm^{-1} for the cobalt complex and at 1704 cm^{-1} for the chromium complex, both measured in KBr disks. *Anal.* Calcd for $(\text{NH}_3)_5\text{CrO}_4\text{C}_4\text{H}_2(\text{ClO}_4)_2$: C, 10.60; H, 3.98; N, 15.50. Found: C, 10.67; H, 3.98; N, 15.0.

Oxalatotetraamminechromium(III) nitrate was prepared and recrystallized as described by Schlessinger.⁷ Treatment of a saturated solution of the nitrate salt at 50° with an equal volume of a saturated solution of sodium perchlorate gave the perchlorate salt of the chromium complex on cooling in the refrigerator.

The visible absorption spectrum shows maxima at 501 nm (ϵ 59.5 $M^{-1} \text{ cm}^{-1}$) and 373 nm (ϵ 74.8 $M^{-1} \text{ cm}^{-1}$). *Anal.* Calcd for $(\text{NH}_3)_4\text{CrC}_2\text{O}_4(\text{ClO}_4)\cdot\text{H}_2\text{O}$: C, 7.37; H, 4.30; N, 17.20. Found: C, 7.74; H, 4.30; N, 17.26.

Stoichiometry Measurements.—Kinetic studies revealed that two reactions were occurring in the maleatopentaamminechromium(III) system. It appeared reasonable that the first reaction was reduction of $(\text{NH}_3)_5\text{Cr}^{\text{III}}$ which should involve no consumption of chromium(II), and the second reaction is reduction of the maleate double bond which should consume 2 mol of chromium(II). The stoichiometry experiments were designed to test this hypothesis. A sample of maleatopentaamminechromium(III) perchlorate was dissolved in *ca.* 40 ml of dilute HClO_4 and a known excess of chromium(II) perchlorate was added. In some experiments LiClO_4 was added to adjust the ionic strength to 1.0 *M*. Some solutions were allowed to stand for a long time (24 hr) before analysis, while others were followed spectrophotometrically and the reaction was stopped 60–120 min after commencement. The reaction was quenched by the addition of a known excess of ferric chloride solution. The excess ferric ion was determined iodometrically. Blank experiments containing only chromium(II) were also carried out.

Kinetic Measurements.—The spectrophotometer cell and reagent solution containers were all sealed with rubber serum caps and flushed with deoxygenated nitrogen. Reagents were all handled and mixed using standard syringe techniques.

The rate of reduction of maleatopentaamminechromium(III) by chromium(II) was determined by following the decrease in absorbance at 490 nm on a Bausch and Lomb Precision spectrophotometer. To start the reaction a solution of the chromium(III) complex in water (usually 1 ml) was added to a solution of HClO_4 – LiClO_4 – $\text{Cr}(\text{II})$ in the concentrations necessary to give a final ionic strength of 1.0 *M* in a 5-cm path length cell.

The chromium(II) reduction of oxalatotetraamminechromium(III) was followed by observing the decrease in absorbance at 501 nm. A solution of chromium(II) (usually 1 or 2 ml) was added to a solution of HClO_4 – LiClO_4 –complex in the concentrations necessary to give a final ionic strength of 1.0 *M* in a 5-cm path length cell.

All solutions were thermostated prior to mixing and during the reaction using a Colora constant-temperature bath and a Thermistemp temperature controller (Model 71) with a thermistor probe in the cell holder.

It should be noted that pentaamminechromium(III) complexes have a much greater tendency to hydrolyze with loss of NH_3 than do cobalt(III) complexes. Hydrolysis of maleatopentaamminechromium(III) has been observed during our studies. Spectral changes are just detectable after 1 hr, and the next reaction appears to have a half-time of 40–50 hr in 0.12 *M* HClO_4 at 25° and therefore does not interfere significantly with the chromium(II) reaction. However hydrolysis has proven to be a severe limitation in our attempts to study the reductions of more slowly reacting complexes such as acetatopentaamminechromium(III).

Determination of Ionization Constant.—The equilibrium constant for the proton dissociation from $(\text{NH}_3)_5\text{CrO}_2\text{CCH}=\text{CHCO}_2\text{H}^{2+}$ to give $(\text{NH}_3)_5\text{CrO}_2\text{CCH}=\text{CHCO}_2^+$ was determined potentiometrically at 0, 10, 15, 24, and 30°. A solution of the complex in 5 ml of water, to give a final concentration of *ca.*

(2) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

(3) H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970).

(4) M. V. Olson and H. Taube, *ibid.*, **9**, 2072 (1970).

(5) C. Hwang and A. Haim, *ibid.*, **9**, 500 (1970).

(6) R. Davies, G. B. Evans, and R. B. Jordan, *ibid.*, **8**, 2025 (1969).

(7) G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., Inc., New York, N. Y., 1962, p 225.

$10^{-2} M$, was added to 45 ml of a solution containing the required amount of LiClO_4 to give a final ionic strength of $1.0 M$. The solution was thermostated at the required temperature and titrated against $0.25 M \text{ NaOH}$ using a Beckman Expandomatic pH meter to follow the change in pH. The method and treatment of data follow that outlined by Albert and Sergeant.⁸

Ion-Exchange Separations.—All ion-exchange experiments were carried out at 5° using Dowex 50W-X12 cation-exchange resin. The resin was pretreated with 30% HClO_4 , distilled water, 50% acetone, ethanol, and distilled water in order to remove all traces of organic material. Several reaction mixtures with the concentrations of $\sim 5 \times 10^{-3} M$ maleatopentaamminechromium(III), $\sim 1.5 \times 10^{-2} M$ chromium(II), and $0.06 M \text{ H}^+$ were quenched either by bubbling oxygen through the solution or by the addition of excess of a solution of $\text{Fe}(\text{ClO}_4)_3$ or AgClO_4 over that required to oxidize all the chromium(II) present. Spectrophotometric observations on identical reaction mixtures enabled the extent of reduction of the chromium(III) complex to be calculated. The quenched solutions were passed onto an ion-exchange column. A green eluent passed directly through the column, while the reacted solution was being added. This eluent was completely removed by a small volume of a solution of $0.05 M \text{ HClO}_4$ and $0.25 M \text{ NaClO}_4$. A second green eluent was removed down the column with the above solution and was removed from the column with a solution of $0.1 M \text{ HClO}_4$ and $0.5 M \text{ NaClO}_4$. The eluents were characterized spectrophotometrically on a Cary Model 14 spectrophotometer. The extinction coefficients were calculated on the basis of the chromium concentration which was determined spectrophotometrically as chromate.

Results

The change in the visible absorption spectrum during the reaction of maleatopentaamminechromium(III) with chromium(II) is shown in Figure 1. There is an

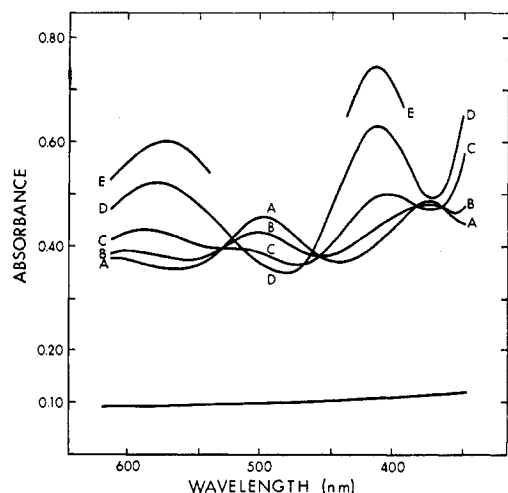


Figure 1.—Changes in visible absorption spectrum during the reduction of $(\text{NH}_3)_5\text{CrO}_2\text{CCH}=\text{CHCO}_2\text{H}^{2+}$ ($1.3 \times 10^{-3} M$) by chromium(II) ($10^{-2} M$), with $[\text{HClO}_4] = 0.20 M$ and $\mu = 1.00 M$ at 25° in a 5-cm cell. The curves represent spectral scans started at zero (A), 14.3 (B), 42.3 (C), 203 (D), and 384 min (E).

initial decrease in absorbance in the 490-nm region due to the consumption of the pentaamminechromium(III) complex and a slight increase at about 580 nm due to production of the initial chromium(III) product. Isosbestic points occur at *ca.* 360, 375, 455, and 521 nm. The initial change is followed by a slow general increase in absorbance over the whole range of wavelength scanned, this increase being more pronounced at *ca.* 413 and *ca.* 575 nm.

(8) A. Albert and E. P. Sergeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962.

Results of stoichiometry experiments carried out on the overall reaction and on runs stopped during the initial decrease in absorbance at 490 nm are shown in Table I. The results on those runs which were stopped

TABLE I
STOICHIOMETRY OF THE REDUCTION OF
MALEATOPENTAAMMINECHROMIUM(III) BY CHROMIUM(II)

10^3 [complex], M	10^2 [Cr(II)], M	$[\text{H}^+]$, M	[Cr(II) consumed]/ [complex]	
			Calcd ^a	Obsd
5.20	1.90	0.062	2.00	1.91 ^b
5.20	1.90	0.062	2.00	1.90
3.30	0.90	0.062	0.19	0.23
3.20	0.90	0.062	0.19	0.17
2.88	1.13	0.063	0.34	0.35
2.85	1.13	0.063	0.34	0.23
2.50	2.40	0.13	2.00	2.20
2.50	1.20	0.13	2.00	1.82
2.00	2.40	0.20	2.00	1.97
2.00	1.20	0.20	2.00	1.87
2.20	1.20	0.20	0.48	0.32

^a Stoichiometry calculated on the basis of two consecutive reactions, the first reaction consuming no chromium(II) and the second reaction consuming 2 mol of chromium(II) per mole of reactant. Reaction times of 15–24 hr were used when a value of 2.00 is predicted, otherwise the run was stopped after 1–2 hr and the extent of the reaction determined spectrophotometrically at 490 nm. ^b Ionic strength adjusted to $1.0 M$ using LiClO_4 .

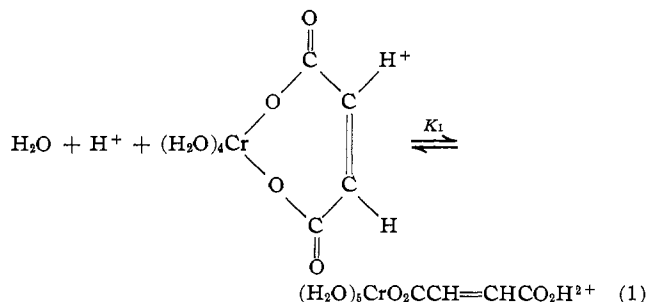
after the initial reaction are in agreement with a reaction involving no consumption of chromium(II) during the initial decrease of absorbance at 490 nm, as expected for reduction of the pentaamminechromium(III) complex by chromium(II).

The second reaction, which increases the absorbance at 413 and 575 nm and consumes 2 mol of chromium(II) per mole of chromium(III) complex, is probably due to reduction of the organic ligand. A similar slow reaction was also observed following the chromium(II) reduction of maleatopentaamminecobalt(III).⁹ Attempts to follow the kinetics of the second reaction gave irreproducible results, possibly because of air oxidation over the long times necessary to follow the reaction. The rate law appears to have a first-order and possibly a second-order term in chromium(II). The reaction is about a factor of 10 slower than the reduction of maleic acid in $0.2 M \text{ HClO}_4$. It is not clear from these results whether the chromium(II) dependence results from direct reduction of the coordinated ligand or possibly from electron-transfer-catalyzed hydrolysis of the product of the first reaction followed by rapid reduction of free maleic acid. In any case this reaction was sufficiently slow so that it did not interfere significantly with kinetic studies of the first reaction.

Ion-exchange experiments carried out on runs which were stopped after the first reaction yielded two aquochromium(III) products in 85–95% yield of that expected from the disappearance of the peak at 490 nm. At $[\text{H}^+] = 0.06 M$ the two products were found in nearly equivalent concentrations. The first green product passes straight through the column and was found to have absorption maxima at 582 and 415 nm with extinction coefficients of 25.1 and $23.3 M^{-1} \text{ cm}^{-1}$, respectively, by chromate analysis. The second product was eluted in a solution of $0.05 M \text{ HClO}_4$ and $0.25 M \text{ NaClO}_4$ and had absorption maxima at 576 and 415 nm with extinction coefficients of 23.8 and $23.2 M^{-1} \text{ cm}^{-1}$, respectively.

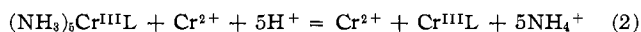
(9) E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2893 (1966).

The extinction coefficients of the chromium(III) products obtained here are in good agreement with those obtained by Olson and Taube⁴ for the products of the chromium(II) reduction of maleatopentaamminecobalt(III). The rate data in ref 4 predict that the ion-exchanged reaction product obtained here is an equilibrium mixture of maleatopentaquo chromium(III) and maleatotetraquo chromium(III)



The values of K_1 given by Olson and Taube⁴ at 25 and 40° predict a value of $21.0 M^{-1}$ at 5°. This is in excellent agreement with the values of $22.1 M^{-1}$ ($[\text{H}^+] = 0.06 M$) and $20.1 M^{-1}$ ($[\text{H}^+] = 0.7 M$), obtained in this work at 5°.

The stoichiometry and product analysis both indicate that the initial decrease in absorbance at 490 nm is due to a reaction of the type



Rate plots obtained from a plot of $\log(A_t - A_\infty)$ with time were generally linear to >80% reaction. The results (Table II) may be adequately described by a

TABLE II

RATE CONSTANTS FOR THE REDUCTION OF MALEATOPENTAAMMINECHROMIUM(III) BY CHROMIUM(II)							
[H ⁺], M	10 ³ [oxi-dant], M	10 ³ [reduc-tant], M	10 ² <i>k</i> _{obsd} , M ⁻¹ sec ⁻¹	[H ⁺], M	10 ³ [oxi-dant], M	10 ³ [reduc-tant], M	10 ² <i>k</i> _{obsd} , M ⁻¹ sec ⁻¹
0.05	1.141	8.73	4.56	0.077	1.914	10.54	5.14
0.077	2.013	10.54	3.93	0.100	1.796	10.01	4.34
0.10	1.088	8.75	3.55	0.100	1.830	10.01	4.24
0.134	1.907	10.54	2.98	0.134	2.024	10.54	3.72
0.20	1.095	5.00	2.47	0.200	1.801	10.01	3.22
0.20	1.136	5.00	2.40	0.500	1.755	10.03	2.71
0.20	1.100	8.75	2.36	0.941	1.757	10.03	2.60
0.20	1.083	11.00	2.45	35.0°			
0.20	1.070	11.00	2.59	0.077	1.914	10.54	6.60
0.20	1.101	11.00	2.49	0.100	2.040	10.34	5.60
0.20	1.925	11.00	2.57	0.134	1.706	10.54	5.19
0.20	1.030	15.00	2.73	0.200	2.009	10.34	4.47
0.20	1.084	16.50	2.64	0.500	1.882	10.34	3.71
0.50	1.083	8.73	2.24	0.941	1.799	10.34	3.60
0.50	1.219	8.75	2.05				
0.874	1.109	8.73	1.89				
0.874	1.107	8.75	1.78				

rate law of the form

$$-\frac{d \ln [(\text{NH}_3)_5\text{Cr}(\text{mal})]_{\text{total}}}{dt} = k_{\text{obsd}}[\text{Cr}^{2+}] = \frac{k_1 + k_2'[\text{H}^+]^{-1}}{k_1 + k_2'[\text{H}^+]^{-1} + [\text{Cr}^{2+}]} [\text{Cr}^{2+}] \quad (3)$$

A plot of k_{obsd} against $[\text{H}^+]^{-1}$ is linear, with slope k_2' and intercept k_1 . This rate law is consistent with reduction of $(\text{NH}_3)_5\text{CrO}_2\text{CCH}=\text{CHCO}_2^+$ and $(\text{NH}_3)_5\text{CrO}_2\text{CCH}=\text{CHCO}_2\text{H}^{2+}$ with specific rate constants of k_1 and k_2 , respectively. The value of k_2 can be determined from the acid dissociation constant of the acidic form, K_a , and k_2' , since $k_2' = k_2K_a$ when $[\text{H}^+] \gg K_a$ as is the case here.

TABLE III
ACID DISSOCIATION CONSTANT OF MALEATOPENTAAMMINECHROMIUM(III) (IONIC STRENGTH = 1.0 M (LiClO₄))

Temp, °C	p <i>K</i> _a	10 ³ <i>K</i> _a , ^a M	Temp, °C	p <i>K</i> _a	10 ³ <i>K</i> _a , ^a M
0	3.08 ± 0.05	0.83 ± 0.05	24	2.71 ± 0.04	1.95 ± 0.17
10	2.94 ± 0.06	1.15 ± 0.15		2.73 ± 0.04	1.86 ± 0.16
	2.95 ± 0.04	1.22 ± 0.12		2.75 ± 0.08	1.78 ± 0.30
15	2.85 ± 0.06	1.41 ± 0.18	30	2.69 ± 0.04	2.04 ± 0.18
				2.61 ± 0.10	2.46 ± 0.41
				2.59 ± 0.03 ^b	2.57 ± 0.17 ^b

^a From plots of $\log K_a$ vs. $T(^{\circ}\text{K})^{-1}$, $\Delta H^{\circ} = 5.3 \pm 0.3$ kcal mol⁻¹, and $\Delta S^{\circ} = 5.3 \pm 1$ cal mol⁻¹ deg⁻¹. ^b Determined in water with no ionic strength control, $[\text{complex}] = 10^{-2} M$.

TABLE IV
SUMMARY OF RATE CONSTANTS^{a, b} OBTAINED FOR THE CHROMIUM(II) REDUCTION OF MALEATOPENTAAMMINECHROMIUM(III)

Temp, °C	10 ² <i>k</i> ₁ , M ⁻¹ sec ⁻¹	10 ³ <i>k</i> ₂ ' (= <i>k</i> ₂ <i>K</i> _a)	<i>k</i> ₂ , M ⁻¹ sec ⁻¹
25.0	1.79 ± 0.06	1.50 ± 0.10	0.795 ± 0.043
30.0	2.35 ± 0.08	1.90 ± 0.11	0.868 ± 0.053
35.0	3.26 ± 0.06	2.50 ± 0.10	0.995 ± 0.049

^a Errors given on the rate constants are 95% confidence limits as calculated from a least-squares analysis. ^b For k_1 ΔH^{\ddagger} and ΔS^{\ddagger} are 10.4 ± 7 kcal mol⁻¹ and -32 ± 3 cal mol⁻¹ deg⁻¹, respectively. These values for k_2 are 3.4 ± 2 kcal mol⁻¹ and -48 ± 6 cal mol⁻¹ deg⁻¹.

Values of k_1 , k_2 , and K_a are given in Tables III and IV, along with the appropriate enthalpy and entropy parameters. The K_a value of $1.86 \times 10^{-3} M$ at 24° is quite similar to the value of $1.82 \times 10^{-3} M$ at 25° quoted by Olson and Taube⁴ for the analogous cobalt(III) complex.

The chromium(II) reduction of oxalatotetraamminechromium(III) was followed spectrophotometrically at 501 nm. The usual plots of $\log(A_t - A_\infty)$ vs. time were generally linear to greater than 90% reaction. The results are given in Table V and may be described by

TABLE V

RATE CONSTANTS OBTAINED FOR THE CHROMIUM(II) REDUCTION OF OXALATOTETRAAMMINECHROMIUM(III)

Temp, °C	[H ⁺], M	10 ² [Cr ^{II}], M	10 ³ [oxidant], M	10 ⁴ <i>k</i> _{obsd} , sec ⁻¹
27.0	0.1	3.46	1.82	2.58
27.0	0.1	4.98	2.42	3.87
27.0	0.1	6.00	1.91	4.52
35.0	0.1	1.72	1.95	2.98
35.0	0.1	3.46	1.19	5.33
35.0	0.1	3.46	1.94	5.27
35.0	0.1	6.64	2.05	9.20
35.0	0.5	1.66	2.19	4.33
35.0	0.5	3.46	1.59	6.71
45.0	0.1	1.72	1.91	5.95
45.0	0.1	2.58	1.92	8.20
45.0	0.1	3.46	2.02	10.50

the rate law

$$-\frac{d \ln [(\text{NH}_3)_4\text{CrC}_2\text{O}_4]}{dt} = k_1'' + k_2''[\text{Cr}^{2+}] = k_{\text{obsd}} \quad (4)$$

The rate constant k_1'' results from the aquation of the complex and increases with increasing $[\text{H}^+]$, as indicated by the results in 0.1 and 0.5 M H^+ at 35° (Table V). However, the same results indicate that k_2'' is independent of $[\text{H}^+]$. Therefore k_2 was determined from the slope of plots of k_{obsd} vs. $[\text{Cr}^{2+}]$ at constant

acidity. The activation enthalpy and entropy for k_2'' are given in Table VI.

TABLE VI

SUMMARY OF RATE CONSTANTS OBTAINED FOR THE CHROMIUM(II) REDUCTION OF OXALATOTETRAAMMINECHROMIUM(III)

Temp, °C	[H ⁺], M	10 ³ k_1'' , sec ⁻¹	10 ³ k_2'' , ^a M ⁻¹ sec ⁻¹
27.0	0.1	2.0 ± 1.5	0.73 ± 0.017
35.0	0.1	7.5 ± 1.0	1.30 ± 0.05
35.0	0.5	20.9	1.33
45.0	0.1	15.0 ± 3.5	2.59 ± 0.15

^a $\Delta H^\ddagger = 12.6 \pm 0.9$ kcal mol⁻¹; $\Delta S^\ddagger = -26.7 \pm 3.0$ cal mol⁻¹ deg⁻¹.

Ion-exchange experiments on the chromium(III) product give a 93% recovery of a species with ion-exchange properties typical of a 1+ charged species. The visible spectrum of the product shows maxima at 417 and 556 nm, with extinction coefficients of 39.4 and 34.3 M⁻¹ cm⁻¹, respectively. These results are in good agreement with wavelength maxima of 418 and 556 nm and extinction coefficients of 40.1 and 34.8 M⁻¹ cm⁻¹, given by Price and Taube¹⁰ for (H₂O)₄CrC₂O₄⁺.

Discussion

The results of the ion-exchange studies on the chromium(III) products show that both the reactions studied here proceed by a bridging mechanism with ligand transfer. However, the results are not informative as to whether chelation occurs in the transition state because the initial electron transfer is too slow with respect to chelate ring opening and closing reactions in the products.

The results of this and previous studies for comparison of analogous cobalt(III) and chromium(III) systems are collected in Table VII. The rate ratios (at

TABLE VII

KINETIC DATA FOR THE CHROMIUM(II) REDUCTION OF OXALATO AND MALEATO COMPLEXES

Complex	Rate constant at 25°, M ⁻¹ sec ⁻¹	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹
(NH ₃) ₅ CoC ₂ O ₄ H ⁺ ^a	1 × 10 ²
(NH ₃) ₅ CoC ₂ O ₄ ⁺ ^a	4.6 × 10 ²	2.3	-20
(NH ₃) ₄ CoC ₂ O ₄ ^b	~2 × 10 ⁵
(NH ₃) ₄ CrC ₂ O ₄ ^c	6.4 × 10 ⁻³	12.6	-26.7
(H ₂ O) ₄ CrC ₂ O ₄ ^d	1.3 × 10 ⁻¹	10.8	-26.4
(NH ₃) ₅ CoC ₄ H ₂ O ₄ H ²⁺ ^e	2 × 10 ²	2.9	-38
(NH ₃) ₅ CrC ₄ H ₂ O ₄ H ²⁺ ^c	1.8 × 10 ⁻²	10.4	-32
(NH ₃) ₅ CrC ₄ H ₂ O ₄ ^c	8 × 10 ⁻¹	3.4	-48
(H ₂ O) ₅ CrC ₄ H ₂ O ₄ H ²⁺ ^g	4.0	~9	...
	1.7 × 10 ⁻¹ ^f

^a Reference 10. ^b Reference 5. ^c This work. ^d T. Spinner and G. M. Harris, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J. Sept 1968, No. INOR 36. ^e Reference 4; the reaction gives 80% chelated product. ^f Rate constant for the [H⁺]⁻¹ term in the rate law, in sec⁻¹. ^g Reference 4; these values are for formation of chelated product only.

25°) with O₂CCH=CHCO₂H⁻ as a bridging ligand for (NH₃)₅Co³⁺: (H₂O)₅Cr³⁺: (NH₃)₅Cr³⁺ are 50:1:4.5 × 10⁻³.¹¹ The two chromium(III) systems are more different from each other than is (H₂O)₅Cr³⁺ from

(NH₃)₅Co³⁺. These observations do not substantiate the conclusion of Olson and Taube⁴ that the rate is relatively independent of the oxidizing center. In fact the rate constant similarity for (NH₃)₅Co³⁺ and (H₂O)₅Cr³⁺ maleate systems is largely fortuitous since the activation parameters are quite different. The activation parameters for the two chromium(III) systems do show a "normal" relationship, as noted below. Therefore on the basis of the ΔH^\ddagger and ΔS^\ddagger values it seems logical to conclude that the rate-controlling step is the same for these two chromium(III) maleate systems but different for cobalt(III).

The mechanism of the electron transfer remains undetermined however. If a general chemical mechanism is operative, then the rate-controlling step with cobalt(III) could be reduction of the maleate bridging group, while for the chromium(III) complexes, the reduction of chromium(III) by the maleate radical could be rate controlling.

A comparison of the analogous aquo- and amminechromium(III) oxalato and maleato systems in Table VII shows that the aquo systems have a more favorable ΔH^\ddagger by several kilocalories per mole. This result is also found when the corresponding chloro and azido complexes are compared.^{12,13} The latter seem unlikely to proceed by a chemical mechanism; therefore the results indicate that electron transfer in the oxalato- and maleatochromium(III) systems proceed by a resonance-exchange mechanism. It will be necessary to study more of these chromium(III) systems to determine if this difference in ΔH^\ddagger is a general and mechanistically useful feature.

The reduction of (NH₃)₅CrO₂CCH=CHCO₂⁺ has an unusually low ΔH^\ddagger and negative ΔS^\ddagger when compared to other chromium(III) complexes. In fact the activation parameters are similar to those for the hydrogen ion independent path for maleatopentaamminecobalt(III). This observation would suggest that these reactions are proceeding by a radical ion mechanism. A difficulty arises in the chromium(III) system however in explaining why the dianion form of the bridge reacts by the radical mechanism with ligand reduction, whereas the monohydrogen form reacts by the resonance-exchange mechanism. Ligand reducibility would be expected to give the opposite result, since the dianion should be less easily reduced. It is possible that the monohydrogen maleate radical is not a sufficiently strong reducing agent to reduce (NH₃)₅Cr³⁺. An analogous argument has been advanced by Diaz and Taube³ to explain the absence of a term in the rate law first order in hydrogen concentration for the electron-exchange reaction between chromium(II) and pentaquo chromium(III) fumarate.

The above considerations give rise to a difficulty with the monohydrogen maleate system, however, since the radical intermediate [(NH₃)₅Cr^{III}O₂CCH=CHCO₂-HC^{III}]⁵⁺ would be expected to lose a proton easily to give the same radical intermediate as that formed with the maleate dianion bridging ligand. The monohydro-

(12) R. Davies and R. B. Jordan, *ibid.*, **10**, 1102 (1971), and references therein.

(13) By analogy to the oxalate, azide, and chloride complexes the values of ΔH^\ddagger and ΔS^\ddagger for (H₂O)₅CrOCC=CHCO₂H reduction are estimated as 7.5 kcal mol⁻¹ and -30 cal mol⁻¹ deg⁻¹. The predicted rate constant at 25° is 5.5 M⁻¹ sec⁻¹, quite consistent with the observed value of 4.0 M⁻¹ sec⁻¹.

(10) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(11) The rate constant used for (H₂O)₅CrO₂CCH=CHCO₂H²⁺ is that for the path forming chelated product only. The value for the total rate may actually be higher making this complex appear even more similar to (NH₃)₅Co³⁺.

gen maleate should be reduced by a radical intermediate mechanism. This mechanistic problem may be explained by assuming either that the ΔH^\ddagger correlation noted previously is fortuitous and the maleate reactions

all proceed by a radical mechanism or that the low ΔH^\ddagger and negative ΔS^\ddagger for the maleate dianion bridge are the results of better chelation to the reducing agent with a general resonance-exchange mechanism.

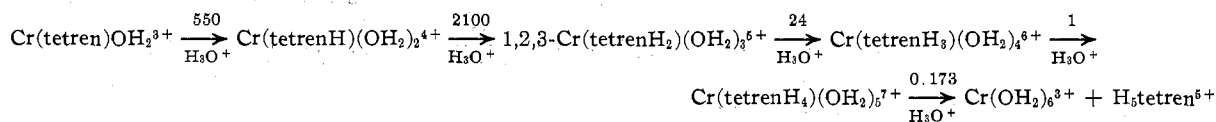
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Kinetics of the Stepwise Aquation of Aquotetraethylenepentaminechromium(III) Cation to Hexaaquochromium(III) Cation¹

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The stepwise "unwrapping" of the tetraethylenepentamine (tetren) ligand from Cr(tetren)OH₂³⁺ to give Cr(OH₂)₆³⁺ has been investigated spectrophotometrically and chromatographically in 0.1–4 *F* HClO₄ ($\mu = 2\text{--}4$ *M*, NaClO₄) from 10° (first stages) to 80° (last stages). The reaction scheme



with first-order rate constants ($10^6 k$, sec⁻¹) accounts for the observations in 4 *F* HClO₄ at 60°; the tetraaquo complex gave kinetic evidence of being a mixture, probably of geometric isomers, inasmuch as the k value obtained from a consecutive first-order treatment decreased with increasing reaction extent (the value given above is based on initial slopes of the rate plots). Acid dependences of the rates are negligible in the range studied, except for the pentaquo aquation, for which the apparent first-order rate constant k_5 obeys the relation $k_5 = k_{5a} + (k_5'/[\text{H}^+])$. The activation energies increase progressively from 20.7 to 27.7 kcal mol⁻¹ with the successive stages of aquation, but the entropies of activation exhibit no regularity. Comparisons are made with amine ligand "unwrapping" for related chromium(III) complexes. The d–d absorption spectra of the tetren complexes are given.

Introduction

Recently this laboratory has been engaged in studies of the kinetics of amine ligand "unwrapping"² in the stepwise aquation of tetraaquoethylenediaminechromium(III), Cr(en)(OH₂)₄³⁺,³ of 1,2,3- and 1,2,6-triaquodiethylenetriaminechromium(III), 1,2,3- and 1,2,6-Cr(djen)(OH₂)₃³⁺,⁴ and of 1,2,3- and 1,2,6-triaquo(1-azonia-4,7,10-triazadecane)chromium(III) cations, 1,2,3- and 1,2,6-Cr(trienH)(OH₂)₃³⁺,⁵ to hexaaquochromium(III) cation, Cr(OH₂)₆³⁺.

With the recent synthesis and characterization⁶ of aquotetraethylenepentaminechromium(III) cation, Cr(tetren)OH₂³⁺ (hereafter referred to as "monoquo"), in which the tetraethylenepentamine ligand (hereafter

referred to as "tetren") has its normal denticity of five, and of the isolable aquation intermediates Cr(tetrenH)-(OH₂)₂⁴⁺ ("diaquo"), 1,2,3-Cr(tetrenH₂)(OH₂)₃⁵⁺ ("triaquo"), Cr(tetrenH₃)(OH₂)₄⁶⁺ ("tetraquo"), and Cr(tetrenH₄)(OH₂)₅⁷⁺ ("pentaquo"), in which the tetren ligand is partially "unwrapped" and protonated and has respective denticities of four, three, two, and one, it has become possible to investigate the kinetics of these successive aquations. We report here the results of that study, which allow a more complete examination of the factors affecting the rates of amine ligand "unwrapping" from Cr(III) centers. We also present the complete d–d absorption spectra of these tetren complexes, for which only band maxima and minima were reported earlier.⁶

Experimental Section

Aquo-tetren Complexes.—The above aquo-tetren complexes were individually chromatographically isolated in aqueous HClO₄ solutions, free of other chromium species (except possibly for tetraquo—see below), as described previously.⁶ Purity was established by agreement of the d–d electronic band maxima and minima with those reported earlier.⁶

Other Materials and Procedures.—The source or preparation of all other chemicals, the analytical methods, kinetic run procedures, spectrophotometry, and calculation of rate constants from optical absorbance data were essentially as described earlier.⁴ Chromatographic procedures were essentially those used in the isolation⁶ of the complexes, with tetraquo and pentaquo solutions prepared in the more concentrated form described previously.⁶ First-order aquation rate constants k_n are defined by $-dC_n/dt = k_n C_n$ where C_n is the molar concentration of the given substrate complex ($n = 1$ for monoquo aquation, $n = 2$ for diaquo aquation, etc.). Kinetic overlap between succes-

(1) (a) Work partly supported under Contract AT(04-3)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-18 to the AEC. (b) Abbreviations used: en, ethylenediamine, H₂N(CH₂)₂NH₂; dien, diethylenetriamine, H₂N(CH₂)₂NH(CH₂)₂NH₂; trien, triethylenetetramine, H₂N(CH₂)₂NH(CH₂)₂NH(CH₂)₂NH₂; tetren, tetraethylenepentamine, H₂N(CH₂)₂NH(CH₂)₂NH(CH₂)₂NH(CH₂)₂NH₂. (c) Based upon the Ph.D. dissertation of S. J. Ranney, UCLA, March, 1971.

(2) The term "unwrapping" is used here to refer to the successive rupture of M–N bonds between a multidentate amine ligand and a metal center M, without regard to which M–N bonds are broken. Examination of Fisher-Hirschfelder models indicates that rupture of a Cr–N bond between two amino N atoms which are still bound to the Cr atom is very improbable; especially when steric requirements are considered for the proton taken up by the freed amino N atom, and which stabilizes each isolable intermediate.

(3) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749, 2678 (1968).

(4) D. K. Lin and C. S. Garner, *J. Amer. Chem. Soc.*, **91**, 6637 (1969).

(5) D. A. Kamp, R. L. Wilder, S. C. Tang, and C. S. Garner, *Inorg. Chem.*, **10**, 1396 (1971).

(6) S. J. Ranney and C. S. Garner, *Syn. Inorg. Metal-Org. Chem.*, **1**, 179 (1971).