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Kinetics of the Acid Cleavage of the Di-μ-hydroxo-tetrakis(o-phenanthroline)dichromium(III) Ion[1]

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The kinetics of the cleavage of the di-μ-hydroxo-tetrakis(o-phenanthroline)dichromium(III) ion by aqueous nitric acid have been measured at 60, 65, 70, and 75°. The product of the cleavage reaction is *cis*-$(phen)_2Cr(OH_2)_2{}^{3+}$. The cleavage reaction obeys the rate law: $-d[\text{dimer}]/dt = k[H^+][\text{dimer}]$, where $k = 9.9 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$ at 60° and $\mu = 1.0$; $E_a = 21.3$ kcal/mole. Cleavage is about twice as rapid in D_2O as in H_2O. Oxygen exchange between the dimer and the solvent obeys the rate law: rate $= k_{ex}[\text{dimer}]$, where $k_{ex} = 6 \times 10^{-5}\ \text{sec}^{-1}$ at 35° and $\mu = 0.10$; $E_a = 23.4$ kcal/mole. A mechanism involving a single-bridged intermediate is proposed.

Introduction

Although studies of the kinetics of acid cleavage of several hydroxo-bridged binuclear transition metal complexes have been reported,[2-7] the available data are by no means sufficient to give a clear understanding of the factors which govern the rates of such cleavage reactions. Such binuclear species are encountered frequently in solutions of tripositive ions,[8] and an interest in their chemical properties is also justified by their similarity to the bridged activated complexes by means of which many redox reactions occur.[9] We have therefore undertaken a systematic study of the acid-cleavage reactions of hydroxo-bridged binuclear chromium(III) complexes, and kinetic data are reported here for the cleavage of the di-μ-hydroxo-tetrakis(o-phenanthroline)dichromium(III) ion, hereafter referred to as "the dimer," in nitric acid solutions.

Experimental Section

Materials and Preparations.—The nitrate salt of the dimer $[(phen)_2CrOH]_2(NO_3)_4$ was prepared by a slight modification of the procedure of Inskeep and Benson.[10] An aqueous solution 0.1 *M* in chromic nitrate and 0.4 *M* in both o-phenanthroline and nitric acid was kept at reflux for 8 hr. Solid sodium hydroxide was added to the solution at the end of 1, 3, 5, and 7 hr in sufficient quantity to maintain a pH of 4.0. The solution was allowed to cool slowly to room temperature, upon which violet needles of the nitrate salt precipitated. These violet crystals were separated by suction filtration, washed with cold water, and dried in air and then over concentrated sulfuric acid. It was found that the salt prepared by the procedure of Inskeep and Benson[10] was always contaminated by orange crystals of the monomer, whereas the salt prepared by the above procedure was free of such contamination. The spectrum of a solution of the dimer in 0.1 *M* nitric acid was in excellent agreement with that obtained by Inskeep and Benson[10] (λ_{max} 530 mμ, ϵ_{max} 49.4). *Anal.* Calcd for $(phen)_4Cr_2(OH)_2(NO_3)_4$: Cr, 9.39. Found: Cr, 9.34. Yield, 49%, based on Cr.

To prepare the dimer with the bridging oxygens enriched in oxygen-18, the above procedure was followed except that water sevenfold enriched in oxygen-18 [obtained from YEDA (Research and Development Co. Ltd., Weizmann Institute of Science, Rehovoth, Israel)] was substituted for normal water in the preparation of solutions.

The *cis*-diaquo salt, *cis*-$[(phen)_2Cr(OH_2)_2](NO_3)_3$, was prepared from the filtrate from the dimer preparation. The filtrate was kept at reflux for 3 hr at pH 1. Upon cooling, orange crystals separated. These were separated by suction filtration, washed with cold water, and air dried. The spectrum of a solution of the orange crystals agreed within experimental error with that reported[11] for *cis*-$[(phen)_2Cr(OH_2)_2](NO_3)_3$. *Anal.* Calcd for $[(phen)_2Cr(OH_2)_2](NO_3)_3$: Cr, 8.23. Found: Cr, 8.30.

The above salts were analyzed for chromium spectrophotometrically by measurement of the absorbance at 375 mμ after destruction of the complex by solutions of alkaline peroxide.[12] At this wavelength chromate has an extinction coefficient of 4815. The analyses were corrected for the absorbance of o-phenanthroline (ε 135 at 375 mμ). The chromium content of solutions was determined in the same manner.

A Zeiss PMQ II spectrophotometer was used for all spectrophotometric measurements.

Ordinary Kinetic Runs.—The perchlorate salt of the dimer was found to be too insoluble to allow spectrophotometric measurement of kinetics in perchloric acid solutions. All kinetic runs were therefore done in nitric acid solutions. The limited solubility of the nitrate salt, together with the limitation of absorbancy measurements to path lengths of 1 cm, dictated the method of preparation of solutions for the kinetic runs. Such concentrations of the dimer as were required for kinetic runs could not be attained in 1 *M* nitrate solutions at room temperature. To prepare solutions for kinetic runs solid samples of the dimer nitrate were dissolved in the minimum amount of distilled water at the temperature of the study. To initiate the kinetic run, the water solution was added to a volumetric flask containing the requisite amount of sodium nitrate and nitric acid at the same temperature, and the solution was diluted to the mark. The flask was suspended in a thermostated bath, and aliquots were withdrawn at given time intervals for absorbancy measurements. The ionic strength of solutions was adjusted to 1.00 with sodium nitrate.

The kinetics of the cleavage reaction were followed as the decrease in absorbancy at 530 mμ. At this wavelength the extinction coefficients of the dimer and the *cis*-diaquo complex are 49.4 and 27.1, respectively, per g-atom of chromium. The

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[1] Supported by National Science Foundation Grant GP-2154. Based on the Ph.D. thesis of Sr. Damien Wolcott.

[2] D. M. Grant and R. E. Hamm, *J. Am. Chem. Soc.*, **80**, 4166 (1958).

[3] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

[4] R. E. Connick and M. G. Thompson, 148th National Meeting of the American Chemical Society, Inorganic Division, Chicago, Ill., Sept 1964, Papers 23, 24.

[5] T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965).

[6] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).

[7] J. H. Espenson, *ibid.*, **4**, 1533 (1965).

[8] C. L. Rollinson, "The Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, Chapter 13.

[9] H. Taube, *Can. J. Chem.*, **37**, 127 (1959).

[10] R. G. Inskeep and M. Benson, *J. Inorg. Nucl. Chem.*, **20**, 290 (1961).

[11] R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, **15**, 62 (1961).

[12] G. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

validity of Beer's law was demonstrated for both species at this wavelength.

The procedure for the runs in D_2O solutions was the same as described above except that fuming nitric acid was used in the preparation of solutions to conserve D_2O.

Oxygen-Exchange Experiments.—The rate of the oxygen-exchange reaction between the dimer and solvent water was found to be much more rapid than the rate of the cleavage reaction. It was therefore necessary to carry out the exchange experiments at lower temperatures than had been used for the cleavage kinetics. This in turn necessitated that the exchange studies be carried out at lower nitrate concentrations, hence, lower ionic strength, in order to prevent precipitation of the nitrate salt of the dimer. The ionic strength of all solutions used for the exchange experiments was adjusted to 0.10 M by the addition of sodium nitrate. The dimer concentration was approximately 8×10^{-3} M in all runs.

In a typical run the oxygen-18-enriched dimer was dissolved in a normal water solution of appropriate nitric acid–sodium nitrate concentrations at the desired temperature and placed in a thermostated bath. At suitable intervals 10-ml aliquots were withdrawn and excess solid ammonium thiocyanate was added. The thiocyanate salt of the dimer precipitated immediately and quantitatively. The precipitate was separated on a sintered-glass filter, washed with cold water, acetone, and ether, dried in air for 3 min, and then dried *in vacuo*. *Anal.* Calcd for $[(\mathrm{phen})_4\mathrm{Cr}_2(\mathrm{OH})_2](\mathrm{SCN})_4$: Cr, 9.53. Found: Cr, 9.48.

Oxygen in the precipitate was converted to carbon dioxide according to the method of Anbar and Guttman,[13] except that the thiocyanate ion, rather than mercuric cyanide, served as the source of carbon. The oxygen-18 content of the sample was determined by measuring the mass 44 and 46 peaks for the carbon dioxide with a Consolidated Model 21-620A mass spectrometer.

It should be noted that the product of the cleavage reaction, the *cis*-diaquo monomer, is also precipitated by thiocyanate ion. However, calculations showed that the cleavage reaction would have occurred to only a negligible extent during the exchange runs. Further, appreciable contamination by the *cis*-diaquo complex is ruled out by the analysis of the thiocyanate precipitate.

Treatment of Kinetic Data.—With the exception of two runs at low acidity, all kinetic runs were done under pseudo-first-order conditions; *i.e.*, the hydrogen ion concentration was at least 20 times as great as that of the dimer. Pseudo-first-order rate constants for the cleavage reaction were determined by plotting log $(A_t - A_\infty)$ *vs.* time. Such plots were linear for more than 3 half-lives, and rate constants were calculated from the slopes of these plots using the relationship $k_{\mathrm{obsd}} = (1/t) \ln [(A_0 - A_\infty)/(A_t - A_\infty)]$. In the initial stages of the investigation infinite time absorbancies were measured, but in the later stages infinite time values were calculated from known concentrations and extinction coefficients. Calculated and measured infinite time values were in excellent agreement.

First-order rate constants for the oxygen-exchange reaction were determined from plots of log $(R_t - R_\infty)$ *vs.* time, where R_t and R_∞ are the instantaneous and infinite time ratios of mass 46 to mass 44 for carbon dioxide prepared from dimer thiocyanate. Such plots were linear for at least 3 half-lives. The infinite-time ratio was taken to be 0.0040, the ratio observed for carbon dioxide of normal isotopic composition. Rate constants were calculated using the equation $k = (1/t) \ln [(R_t - R_\infty)/(R_0 - R_\infty)]$. The extrapolated zero-time enrichment of the dimer was that expected for an anhydrous precipitate.

Measurement of pK_1.—Attempts to measure the pK values for the dimer by differential potentiometric titrations against sodium hydroxide solutions gave results which were not reproducible. The method finally adopted for the measurement of pK_1 was based on that of Schwarzenbach and Magyar.[14] To solutions of the dimer nitrate in carbon-dioxide-free distilled water were added sufficient sodium nitrate to give $\mu = 1.00$ and measured quantities of sodium hydroxide solution containing less than 1 mole of base per mole of dimer used. The pH of the resulting solutions was measured with a Metrohm Model E-300 pH meter. Exact dimer concentrations were determined by chromium analyses, and pK values were calculated from the relationship p$K = \log([\mathrm{HB}]/[\mathrm{B}]) + \mathrm{pH}$, where HB and B represent the dimer and its conjugate base, respectively.

Results and Discussion

In two previous studies of the acid cleavage of binuclear chromium(III) complexes having two hydroxo bridges, Grant and Hamm[2] and Connick and Thompson[4] obtained evidence for two slow steps in the reaction sequence. In each case the first slow step was interpreted as involving the cleavage of one bridge, a single-bridged complex being produced thereby, and the second, slower step was interpreted as involving the cleavage of the single-bridged intermediate. In light of these precedents, one concern of the present investigation was to seek evidence for the involvement of a single-bridged intermediate. However, examination of the spectra of solutions in the course of the cleavage reaction revealed no evidence for any colored species other than the dimer and the product *cis*-diaquo ion, and infinite-time spectra were identical with those of freshly prepared solutions of *cis*-diaquobis(*o*-phenanthroline)chromium(III) nitrate. A very good isosbestic point was maintained at 507 mμ throughout the course of the reaction (see Figure 1). Successive spectral scans such as those shown in Figure 1 showed the same fractional change at all wavelengths during the same time interval, and rate plots showed a single slope over more than 3 half-lives. All of these points argue against the formation of a single-bridged intermediate in any substantial concentration. Further, the spectrophotometric data support the conclusion that the stoichiometry of the cleavage reaction is

$$[(\mathrm{phen})_2\mathrm{Cr}(\mathrm{OH})_2\mathrm{Cr}(\mathrm{phen})_2]^{4+} + 2\mathrm{H}^+ + 2\mathrm{H}_2\mathrm{O} \longrightarrow 2[(\mathrm{phen})_2\mathrm{Cr}(\mathrm{OH}_2)_2]^{3+} \quad (1)$$

It is possible that an intermediate such as $[(\mathrm{phen})_2(\mathrm{H}_2\mathrm{O})\mathrm{Cr}(\mathrm{OH})\mathrm{Cr}(\mathrm{OH}_2)(\mathrm{phen})_2]^{5+}$ would have a spectrum similar to either the double-bridged dimer or the *cis*-diaquo ion, so that its presence would not be detected spectrophotometrically. However, the formation of this particular intermediate would involve the consumption of 1 mole of hydrogen ion, and its cleavage to the diaquo ion would involve the consumption of a second mole of hydrogen ion. The uptake of hydrogen ion during the cleavage reaction was followed on a Sargent recording pH-Stat at pH 1.5. No sudden consumption of acid was observed upon the addition of the dimer to the acidic solution at the beginning of the runs, and plots of log $(V_\infty - V_t)$ *vs.* time were linear for *ca.* 3 half-lives, V_∞ and V_t being the volume of acid added at infinite time and at time t, respectively, in order to maintain a constant pH. The cleavage reaction was found to involve the consumption of 1.9 ± 0.1 moles of acid per mole of dimer, whereas the consumption of 2 moles is expected from eq 1. The first-order rate constant calculated from the slope of

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(13) M. Anbar and S. Guttman, *Intern. J. Appl. Radiation Isotopes*, **5**, 233 (1959).

(14) G. Schwarzenbach and B. Magyar, *Helv. Chim. Acta*, **45**, 1425 (1962).

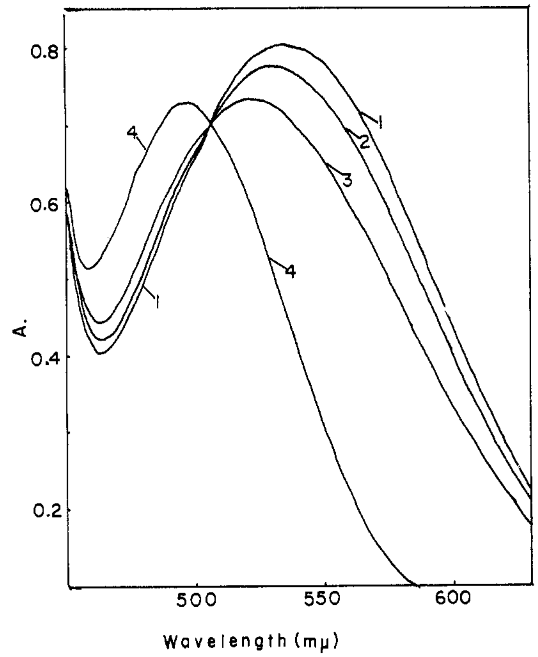

Figure 1.—Successive spectral scans recorded in the order 1, 2, 3, 4 during the cleavage reaction of $[(\mathrm{phen})_2\mathrm{Cr(OH)}_2\mathrm{Cr(phen)}_2]^{4+}$ in 1 *M* HNO_3 at 70°. Spectrum 1 was recorded immediately after mixing, and spectrum 4, after *ca.* 7 half-lives.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR CLEAVAGE OF $[(\mathrm{phen})_4\mathrm{Cr}_2(\mathrm{OH})_2]^{4+}$ IN AQUEOUS NITRIC ACID[a]

Initial $[HNO_3]$, *M*	60.0°	65.0°	70.0°	75.0°
	10^5k_{obsd}, sec^{-1}			
1.000	9.60	15.4	24.2	40.0
0.800	8.25	11.9	19.6	31.3
0.600	5.90	9.10	14.2	25.5
0.400	4.24	5.82	10.9	17.6
0.200	1.92	3.14	5.4	9.7
0.100	0.60	1.87	2.2	4.5
0.050			1.2[b]	
0.010			0.4[b]	

[a] Ionic strength adjusted to 1.00 *M* with $NaNO_3$. Initial [dimer] = 5.0×10^{-3} *M*. [b] From initial linear portion of rate plots.

TABLE II

RATE CONSTANTS CALCULATED BY LEAST-SQUARES TREATMENT OF THE DATA OF TABLE I

Temp, °C	10^5k,[a] $M^{-1}\ \mathrm{sec}^{-1}$	10^5k_1,[b] sec^{-1}	10^5k_2,[b,c] $M^{-1}\ \mathrm{sec}^{-1}$
60	9.9	−0.11	10.0 ± 0.1
65	15.2	0.12	15.0 ± 0.1
70	24.5	0.23	24.1 ± 0.2
75	40.6	1.62	38.3 ± 0.3

[a] See eq 2. [b] See eq 3. [c] Errors are standard deviations.

the log $(V_\infty - V_t)$ *vs.* time plots was $1.3 \times 10^{-5}\ \mathrm{sec}^{-1}$ at pH 1.5 and 70°, which is in fair agreement with the value $k_{\mathrm{obsd}} = 1.2 \times 10^{-5}\ \mathrm{sec}^{-1}$ at $[\mathrm{H}^+] = 0.05\ M$ and 70° from spectrophotometric measurements. Thus the pH-Stat measurements support the notion that the cleavage reaction involves only one slow step.[15]

Pseudo-first-order rate constants for the cleavage of the dimer by nitric acid are presented in Table I. The data of Table I are consistent with the conclusion that the dominant term in the rate law under the experimental conditions is $k[\mathrm{H}^+][\mathrm{dimer}]$. However, it is possible that a second, acid-independent term belongs in the rate law, as is the case for the similar complex $[(\mathrm{en})_2\mathrm{Co(OH)}_2\mathrm{Co(en)}_2]^{4+}$ where en = ethylenediamine.[3] The data of Table I have been evaluated both in terms of a single-term rate law

$$-\mathrm{d}[\mathrm{dimer}]/\mathrm{d}t = k[\mathrm{H}^+][\mathrm{dimer}] \qquad (2)$$

and a two-term rate law

$$-\mathrm{d}[\mathrm{dimer}]/\mathrm{d}t = (k_1 + k_2[\mathrm{H}^+])[\mathrm{dimer}] \qquad (3)$$

The rate constants obtained from linear least-squares fits of the data of Table I to eq 2 and 3 are given in Table II. It is seen from Table II that the data do not justify the inclusion of an acid-independent term in the rate law.[16] Except for the data at 75° the values of k_1 in Table II differ from zero by about the standard deviation of the least-squares fit. Thus the experimental data fit eq 2 better than eq 3.

Allowing that other reaction paths may exist, the remainder of this paper will be concerned with the elucidation of the dominant reaction path, *i.e.*, that path involving a first-order dependence on hydrogen ion concentration.

Proton-transfer reactions in aqueous solutions are far too rapid for the acid dependence of the cleavage rate to be explained in terms of a rate-determining addition of a proton to the dimer. It is suggested therefore that the first-order dependence of the cleavage rate on hydrogen ion concentration is due to a rapid acid–base reaction preceding the rate-determining step and involving the addition of a proton to the dimer. Support for this hypothesis is found in the increased rate of cleavage which accompanies the substitution of D_2O for H_2O in the reaction medium, as shown in Figure 2. The dependence of the rate on the mole fraction of D_2O is in good agreement with that predicted by the Gross–Butler equation (calculated curve in Figure 2).[17]

Germane to the question of what acid–base reactions the dimer might be involved in is the acidity of the dimer as indicated by its p*K* values. According to the data of Table III the $\mathrm{p}K_1$ of the dimer is 6.3 at 25°. Thus the dimer is a weak acid and would exist almost completely in the undissociated form under the conditions of the kinetics measurements. The possibility that added hydrogen ion acts to suppress the dissociation of a proton from the dimer, the undissociated form being the active form, may therefore

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(15) Ion-exchange separations of partially reacted solutions also support this conclusion. Separation of such solutions on columns of Dowex 50 resin yields only two bands with spectra identical with those of the dimer and the *cis*-diaquo ion: M. M. DeMaine and J. B. Hunt, submitted for publication.

(16) It must be admitted that a careful study of the reaction at lower acidities might reveal an acid-independent term. However, it should be noted that the dimer is prepared in solutions of pH 4. It is therefore expected that appreciable amounts of the dimer will be present at equilibrium at pH 3, so that the pH range over which the measurements could profitably be extended is probably quite limited.

(17) W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 330 (1937); E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959).

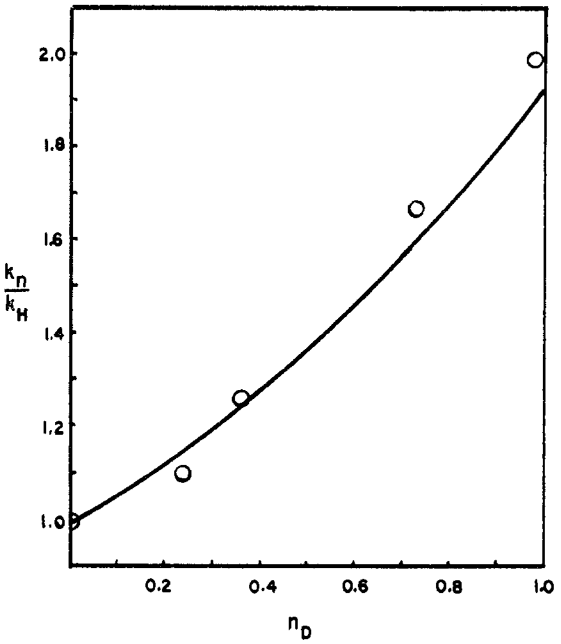


Figure 2.—Effect of substituting D_2O for H_2O on the rate of cleavage of the dimer by 1.00 *M* nitric acid at 70°; k_H and k_n are, respectively, the observed first-order rate constants in H_2O and in D_2O–H_2O mixtures of deuterium mole fraction *n*; n_D = mole fraction of deuterium. The open circles are experimental points. The curve was calculated using the Gross–Butler equation.[17]

Table III

Determination of p*K* of Dimer[a]

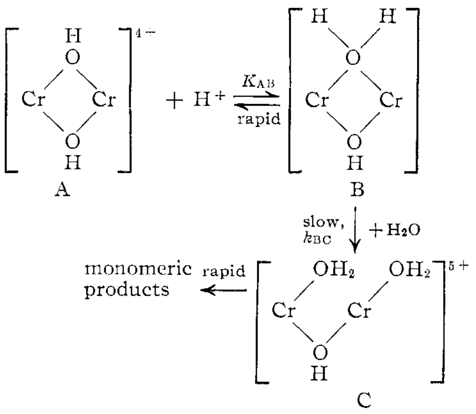
[HB]/[B][b]	pH	p*K*[c]
0.306	6.82	6.31
0.517	6.58	6.29
0.739	6.45	6.32
1.12	6.30	6.35
1.60	6.16	6.36
2.53	5.98	6.38
4.23	5.54	6.17
9.63	5.41	6.39
		Av 6.32 ± 0.07

[a] [Dimer] = 9.0×10^{-3} *M*; [$NaNO_3$] = 0.100 *M*; 25°. [b] [HB] = concentration of undissociated dimer; [B] = concentration of conjugate base of dimer, assuming that each mole of added NaOH forms 1 mole of the conjugate base of the dimer. [c] Calculated using the equation p*K* = log ([HB]/[B]) + pH.

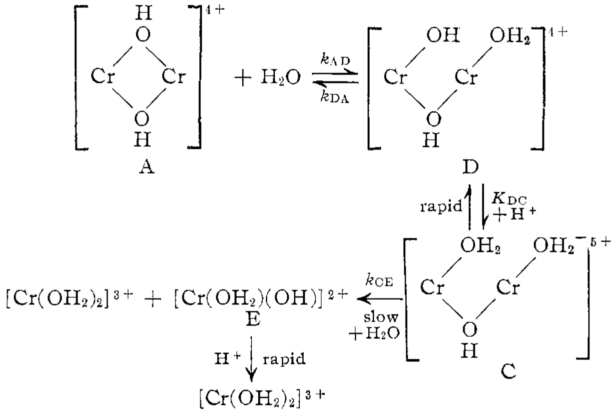
be ruled out immediately. The concentration of the undissociated form of the dimer would change only slightly over the range of acidities studied. Decomposition of the dimer in basic solutions prevented the measurement of pK_2.

It seems likely that the site at which a proton is added to the dimer in the acid–base equilibrium is one of the bridging ligands, and not one of the nitrogen atoms of phenanthroline. Two possible reaction mechanisms, both of which involve protonation of a bridging oxygen and both of which are consistent with the experimental rate law, are outlined below. The Cr–N bonds are assumed to remain intact, and the phenanthroline ligands are omitted for simplicity.

Mechanism I



Mechanism II



The basic distinction between the two mechanisms is that mechanism I assumes the cleavage of the first bridge to be rate-determining, whereas mechanism II assumes the cleavage of the second bridge to be the slow step. According to mechanism I the rate of cleavage of the dimer would be $-d[\text{dimer}]/dt = k_{BC}[B] = k_{BC}K_{AB}[H^+][\text{dimer}]$, which has the same form as the experimental rate law. An unsatisfactory feature of mechanism I is that it involves the formation of a species, B, containing an oxygen atom with coordination number 4. However, an acid–base equilibrium analogous to that of mechanism I has been proposed by Mast and Sykes[18] to explain the first-order dependence on hydrogen ion concentration observed for the reaction of μ-amido-μ-hydroxo-octaamminedicobalt(III) ion with chloride ion. A first-order dependence on hydrogen ion has been observed also in the conversion of the di-μ-hydroxo-octaamminedichromium(III) ion to a single-bridged μ-hydroxo-diaquo species.[19]

The application of the steady-state treatment to mechanism II, assuming D and C to be unstable intermediates, leads to the general rate equation

$$\frac{-d[A]}{dt} = \frac{k_{AD}k_{CE}K_{DC}[H^+][A]}{k_{DA} + k_{CE}K_{DC}[H^+]} \qquad (4)$$

Under conditions such that $k_{DA} \gg k_{CE}K_{DC}[H^+]$, eq 4 reduces to

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[18] R. D. Mast and A. G. Sykes, *Chem. Commun.*, 603 (1965).

[19] J. K. Erbacher and J. B. Hunt, unpublished observations.

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{k_{\mathrm{AD}}k_{\mathrm{CE}}K_{\mathrm{DC}}[\mathrm{H}^+][\mathrm{A}]}{k_{\mathrm{DA}}} \tag{5}$$

which is the same form as the observed rate law. The simplification of eq 4 to eq 5 is equivalent to assuming that species A and D are in rapid equilibrium. Now the reaction A $\rightleftharpoons$ D involves substitution at chromium(III) and is expected therefore not to be instantaneous. However, the present requirements of a "rapid" equilibrium are met if the reaction A $\rightleftharpoons$ D is rapid compared to the rate of the over-all cleavage reaction. The latter point can be subjected to an experimental test: if the reaction A $\rightleftharpoons$ D were rapid compared to the cleavage reaction, then the bridging oxygen atoms would have to exchange with the solvent water at a rate rapid compared to the cleavage rate.

Kinetic data for the exchange of oxygen between the dimer and the solvent are given in Table IV. The exchange rate shows no significant dependence on hydrogen ion concentration over the limited range studied. The half-time for the exchange reaction at 35° is about 3 hr. The half-time for the cleavage reaction in 1 *M* acid is calculated from the data at higher temperatures to be about 30 hr at 35°.[20] Thus the exchange reaction is considerably more rapid than the cleavage reaction, as required by mechanism II. Of course, this does not prove that the cleavage reaction occurs by mechanism II, since the exchange and cleavage reactions may be parallel, and even unrelated, reactions. However, the exchange data establish at least that the Cr–O bonds of the dimer are broken and formed again at a rate considerably faster than the over-all cleavage reaction.

TABLE IV

RATE OF OXYGEN EXCHANGE BETWEEN DIMER AND SOLVENT WATER[a]

$[\mathrm{HNO_3}]$, *M*	Temp, °C	10^5k_{ex}, sec^{-1}
0.100	35.1	6.3
0.050	35.1	6.7
0.010	35.1	6.6
0.100	30.0	3.4
0.100	40.0	12.3

[a] Dimer enriched in ^{18}O; [dimer] = 9×10^{-3} *M;* ionic strength = 0.10 *M* adjusted with $\mathrm{NaNO_3}$.

If it is assumed that the oxygen-exchange reaction occurs *via* the equilibrium between single- and double-bridged dimers as suggested above, then it is possible to assign a value to k_{AD}, the first-order rate constant for the formation of a single-bridged dimer from the double-bridged dimer. Considering the double-bridged dimer, A, to be in equilibrium with the single-bridged intermediates, we have $[\mathrm{D}]/[\mathrm{A}] = k_{\mathrm{AD}}/k_{\mathrm{DA}}$ and $[\mathrm{C}]/[\mathrm{A}] = [\mathrm{H}^+]K_{\mathrm{DC}}k_{\mathrm{AD}}/k_{\mathrm{DA}}$. Intermediate C is expected to be a weak acid, so that $K_{\mathrm{DC}} > 1$. Since the accumulation of single-bridged intermediates was not observed, it then follows that $k_{\mathrm{DA}} > k_{\mathrm{AD}}$. The rate-controlling step for oxygen exchange would then be A → D, *i.e.*, the opening of the first bridge. Under the conditions of the water-exchange experiments, *i.e.*, with low enrichments in oxygen-18, the dominant labeled dimer species would contain oxygen-18 in only one bridge. The probability that the labeled bridge would cleave in the formation of species D from species A would be 0.5, and the probability that the oxygen atom which constituted the cleaved bridge would be eliminated in the formation of species A from species D would likewise be 0.5. The relationship between the observed rate constant for oxygen exchange and k_{AD} would then be $k_{\mathrm{AD}} = 4k_{\mathrm{ex}}$. According to this treatment $k_{\mathrm{AD}} \approx 2.5 \times 10^{-4}$ sec^{-1} at 35°, which is similar in magnitude to the rate constant, 1–1.5 $\times$ 10^{-3} sec^{-1}, reported by Grant and Hamm[2] for the cleavage of the first bridge of the di-μ-hydroxo-tetraoxalatodichromium(III) ion.

If the cleavage mechanism involves an equilibrium between single- and double-bridged dimers, as implied by mechanism II, then the stability of the double-bridged relative to the single-bridged form must be considerably greater when phenanthroline is the nonbridging ligand than when oxalate is the nonbridging ligand.[2] Apparently the equilibrium constants for the single-bridge $\rightleftharpoons$ double-bridge equilibria cover a wide range. In the case of the oxalato complex the single-bridged form is predominant at acidities as low as 10^{-3} *M* H^+. In the case of the related μ-amido-μ-hydroxo-tetrakis(ethylenediamine)dicobalt(III) ion, the double-bridged form is predominant even in 2 *M* $\mathrm{HClO_4}$, although the hydroxo bridge opens at very high acidities.[21]

It may be possible to gain additional insight into the mechanism of the cleavage reaction by making use of the optical activity of the dimer. Three isomers are theoretically possible, a *meso* form and a pair of optical antipodes. The optical isomers of the dimer have been resolved,[22] and the kinetics of the loss of optical activity are currently being investigated.

It is interesting to note that the oxygen-exchange experiments also provided additional evidence for the double-bridged structure of the dimer. The nitrate salt isolated by Inskeep and Benson[10] was formulated as $[(\mathrm{phen})_2\mathrm{Cr(OH)_2Cr(phen)_2}](\mathrm{NO_3})_4\cdot\mathrm{H_2O}$. Formulation of the compound as a single-bridged μ-oxo-diaquo complex would be equally consistent with their analyses, and our own analyses of the "anhydrous" salt were insufficiently precise to preclude the possibility of an additional coordinated water molecule unambiguously. However, rate plots for the exchange reaction were linear for more than 3 half-lives. As noted

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[20] This comparison neglects the effects of ionic strength. Semiquantitative experiments showed the rate of the cleavage reaction to decrease as ionic strength was decreased, so that the contrast in rates is probably more drastic than the given numbers indicate. At 60° the cleavage rate in 0.1 *M* $\mathrm{HNO_3}$ is about 3 times as rapid at $\mu = 1.0$ as at $\mu = 0.1$.

[21] A. G. Sykes and R. D. Mast, *J. Chem. Soc.*, 784 (1967).

[22] M. M. DeMaine and J. B. Hunt, submitted for publication.

in the Experimental Section, these rate plots were based on an assumed R_∞, namely, on the assumption that at infinite time the complex would have essentially the same isotopic composition as the solvent, which was present in vast excess. All oxygen atoms in the dimer must therefore be kinetically equivalent and presumably structurally equivalent as well.[23]

Activation energies and enthalpies, calculated from the data of Tables II and IV, are, for the water-exchange reaction, $E_a = 23.4$ kcal/mole, $\Delta S^{\ddagger} = +0.5$ eu, and for the cleavage reaction, $E_a = 21.3$ kcal/mole, $\Delta S^{\ddagger} = -11$ eu.

[23] Earnshaw and Lewis (*J. Chem. Soc.*, 396 (1961)) assert that the dimer "definitely" falls into the class having two bridging groups, but no reason is given for this assertion. The compound which they prepared, by a method attributed to Dwyer, but never published, was formulated as $[(phen)_2Cr(OH)_2Cr(phen)_2]I_4 \cdot 4H_2O$, so that the distinction between a single oxo and two hydroxo bridges could not be made on the basis of stoichiometry. Probably the most compelling argument against the oxo bridge is that the magnetic susceptibility the compound, measured by Earnshaw and Lewis, is very nearly that expected for three unpaired electrons per chromium atom, whereas considerable interaction between the two chromium atoms would be expected if a single oxo bridge connected them.

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Ferric Complexes with L-Cysteine at Low Temperature[1a]

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Reactions between ferric ion and L-cysteine in ethanolic solution give labile blue, red, and violet ferric complexes, which become inert when chilled to −78°. The violet complex was isolated and characterized for the first time. A green complex was obtained only at low temperatures. The absorption, optical rotatory dispersion, and circular dichroism spectra of these complexes were measured and their structures were assigned as follows. The blue, red, and violet complexes are S,O-coordinated complexes, and the mole ratios of cysteine to iron are 1:1, 1:2, and 1:3, respectively. The new green complex is an S,N-coordinated tris complex. The violet and green complexes are thermally interconvertible in ethanolic solution. The mechanism of the catalytic oxidation of cysteine is discussed briefly.

Introduction

The study of ferric complexes with cysteine is of great interest from biological points of view. One of them is that ferric ion catalyzes the oxidation of cysteine which may occur in living cells. Ferric cysteinate complex is an intermediate compound in this catalytic reaction. The other point is that this complex is a simple model compound for some nonheme iron proteins having iron–sulfur bindings, such as ferredoxin, and this kind of study would give some information about the structures of these proteins. Many studies on this problem have been made, but they leave many questions still unexplored, probably because these complexes are very labile. Harris[2] stated that the violet coloration obtained by adding ammonia to a cysteine solution is due to the presence of ferric ion. Schubert[3] reported that the oxidation of bis(cysteinato)iron(II) gives a violet ferric complex in alkaline media. The blue complex in acidic solution and the red complex in neutral or alkaline solution were also reported,[4,5] and the absorption spectra were determined.[5] Tanaka, Kolthoff, and Stricks[6] studied the catalytic oxidation of cysteine by ferric ion and reported that the violet complex has an absorption maximum at about 580 mμ. Many studies[7,8] on iron thioglycolate complexes have also been made.

In our previous work,[9] we found that these labile complexes become inert in ethanolic solution when chilled to −78°. The present paper deals mainly with an isolated violet complex and a new green complex. In addition, the composition of these colored complexes and the relation among them will be discussed by means of the absorption spectra.

Experimental Section

Materials.—Ferric chloride, ferric ammonium sulfate, L-cysteine, and L-cysteine hydrochloride monohydrate were standard reagent grade chemicals. The purity of amino acids was assayed to be more than 95% by ferricyanide oxidation; they were used without further purification. Ethanol was refluxed over Drierite and twice distilled.

Spectra.—Absorption spectra were recorded on a Hitachi EPS-2 double-beam spectrophotometer. Optical rotatory dispersion (ORD) and circular dichroism (CD) curves were obtained with a Japan Spectroscopic ORD/UV-5 spectropolarimeter with a CD attachment. The cell used for the measurements was a vacuum-jacketed low-temperature cell[10] which was constructed to fit into the cell compartments of the above instruments. The change in temperature of the sample was determined with a copper–constantan thermocouple inserted into the contents of a

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[1] (a) A. Tomita, H. Hirai, and S. Makishima, 10th International Conference on Coordination Chemistry, Nikko, Japan, 1967. (b) To whom correspondence should be directed: Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan.

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