[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

Complex Ions of Chromium. IV. The Ethylenediaminetetraacetic Acid Complex with Chromium(III)[1]

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The absorption spectra of both the violet and the blue forms of the ethylenediaminetetraacetic acid complex with chromium(III) ion and the dependence of these forms on the hydrogen ion concentration are reported. It was found that the formation of the complex involves several slow steps. The rate of the first slow step in the formation of the violet compound was followed spectrophotometrically and is first order with respect to chromium and inversely proportional to the hydrogen ion concentration. The entropy and heat of activation for this first step are calculated from the data on temperature dependence.

Brintzinger, Thiele and Müller[2] first prepared the violet complex compound $H[Cr(C_{10}H_{12}N_2O_8)(H_2O)]$ by reaction of chromium(III) chloride and ethylenediaminetetraacetic acid. In solution the violet colored ion was shown to transform into a blue compound upon the addition of base. The formula of the blue ion is very likely $[Cr(C_{10}H_{12}N_2O_8)(OH)]^-$.

Direct observation of mixtures of chromium(III) nitrate and the disodium salt of ethylenediaminetetraacetic acid showed that the reaction was slow at the usual hydrogen ion concentrations of such mixtures. In a previous paper[3] it has been shown that the reaction between oxalate and chromium(III) ions is first order in chromium ion concentration and independent of oxalate ion concentration. This was explained by a mechanism in which the oxalate ion reacted rapidly to occupy one coördinate position, followed by a slow step involving the occupation of the second coördinate position to form the chelate structure. A mixture of chromium(III) nitrate and the disodium salt of ethylenediaminetetraacetic acid shows a pale green color almost identical to the color developed when oxalate and chromium(III) ions are mixed. This may indicate a reaction which is similar in the first step. The final compound formed has five coördinate positions occupied by ethylenediaminetetraacetic acid; therefore, the reaction may take place in a series of slow steps. It was the purpose of this investigation to study the kinetics of the reaction. Since the products formed in this reaction absorb light much more strongly than the original chromium solution it was possible to follow the reaction by means of the light absorption at the wave length of maximum absorption of the complex formed.

Experimental

Apparatus and Methods.—The apparatus and methods of chemical analysis were similar to those reported in a previous paper.[4]

To determine the rate of the first step in the reaction a pipetted sample (from 2 to 5 ml.) of 0.05 molar solution of chromium(III) nitrate was placed in a 100-ml. volumetric flask, 2 g. of disodium salt of ethylenediaminetetraacetic acid was added, enough sodium hydroxide or nitric acid was added to give the desired *p*H, and the solution was diluted and placed in a constant temperature bath. Samples were taken from time to time in a 1-cm. cell, for absorbancy[5] measurements at 545 mμ. The *p*H was determined on the same sample that was used for absorbancy measurement. Early experiments having indicated that the rate was independent of the concentration of disodium salt of ethylenediaminetetraacetic acid, a relatively large quantity of this reagent was added to act as a buffer. It is always advisable in such methods to avoid addition of other buffers, since other materials added to buffer the solution may interact with the species being studied.

The method of determining the rate constant of the first step in the reaction was to plot the absorbancy as a function of time, as is shown in the left hand curve of Fig. 3, and from that plot to determine the molar absorbancy index at the asymptote which the curve is approaching as shown by the dashed line. This molar absorbancy index was used to calculate the absorbancy at infinite time, $(A_s)_\infty$, for the first step on any future runs. The apparent rate constant was then calculated from the slope of a plot of log $[(A_s)_\infty - (As)_t]$ *vs.* time, where $(A_s)_t$ is the absorbancy at time *t*.

The spectrophotometric titration was performed in a 400-ml. beaker which was equipped with glass and calomel electrodes, and an electric stirrer. A 4.85 millimolar solution of $HCrYH_2O$ (where Y^{4-} is the ethylenediaminetetraacetate ion) with sufficient potassium nitrate added to give an ionic strength of 0.05 was placed in the beaker. Samples of this solution were taken in a 1-cm. cell to determine the absorbancy after the addition of each increment of base, the sample being returned to the beaker before adding the next increment of base. The cell was rinsed with the solution upon taking each sample.

The violet chromium(III) complex with ethylenediaminetetraacetic acid, used for absorption spectra measurement and spectrophotometric titration was prepared by a method which differed from that previously reported.[2] One-tenth of a mole of chromium(III) nitrate was dissolved in 50 ml. of hot water and slightly more than one-tenth of a mole of the disodium salt of ethylenediaminetetraacetic acid was added. The solution was maintained just below the boiling point for 30 minutes. The solution was cooled and treated with 10 ml. of concentrated nitric acid and 20 ml. of dioxane. The violet crystals that were recovered were recrystallized twice from a water–dioxane mixture containing about 10% by volume dioxane.

Attempts to prepare the potassium salt of either the violet or the blue form in the solid state were failures and always led to extremely viscous oily appearing materials.

Results and Discussion

The absorption spectra of the violet and the blue forms of the ethylenediaminetetraacetic acid complex of chromium(III) are shown in Fig. 1. It may be seen that the absorption peaks are much higher for the violet form than for the blue form. Using this fact as the basis of a spectrophotometric titration, which was performed while making both *p*H and absorbancy measurements after each addition of base, Fig. 2 resulted. The upper curve shows absorbancy plotted *vs.* *p*H for the titration, and the lower curve shows the absorbancy plotted *vs.* moles of base per mole of chromium.

The breaks in the lower curve of Fig. 2 indicate that the violet solid compound may be considered

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[2] H. Brintzinger, H. Thiele and U. Müller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

[3] R. E. Hamm and R. E. Davis, THIS JOURNAL, **75**, 3085 (1953).

[4] R. E. Hamm, *ibid.*, **75**, 609 (1953).

[5] For definition of spectrophotometric terms used see National Bureau of Standards, Letter Circular, LC-857 (1947).

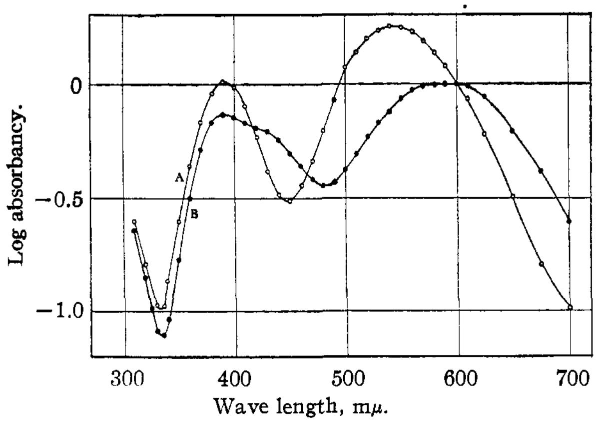

Fig. 1.—Absorption spectra of: O(A), 9.59 millimolar solution of H[CrYH$_2$O], and ●(B), 8.91 millimolar solution of Na$_2$[CrYOH], in 1.002-cm. cell. Minimum slit width used at each wave length.

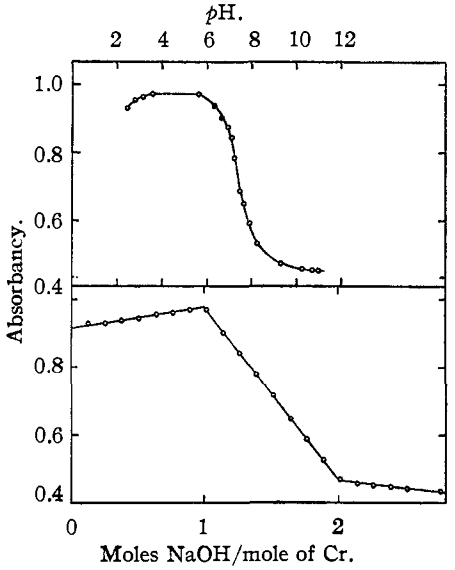

Fig. 2.—Spectrophotometric titration of 4.85 millimolar H[CrYH$_2$O] with NaOH: upper curve absorbancy *vs.* pH; lower curve moles NaOH/mole of Cr.

as having the following acid ionizations in water solution.

$$HCrYH_2O \rightleftarrows CrYH_2O^- + H^+ \quad (1)$$

$$CrYH_2O^- \rightleftarrows CrYOH^= + H^+ \quad (2)$$

The first break in the lower curve indicates the quantitative formation of $CrYH_2O^-$ and the second break indicates the quantitative formation of $CrYOH^=$. The solution is violet until the first break is reached and is blue past the second break. The fact that the curve slopes downward past the the second break is due to dilution The upward slope before the first break indicates that the ion is a stronger absorber than the free acid. From the points on the titration curve the acid ionization constants, at ionic strength 0.05, have been calculated as $K_1 = 8 \times 10^{-4}$ and $K_2 = 3 \times 10^{-8}$. The second of these ionization constants comes directly from the point of inflection on the right side of the upper curve in Fig. 2. The first ionization constant was calculated from the pH at the first end-point and checked at other points along the titration curve.

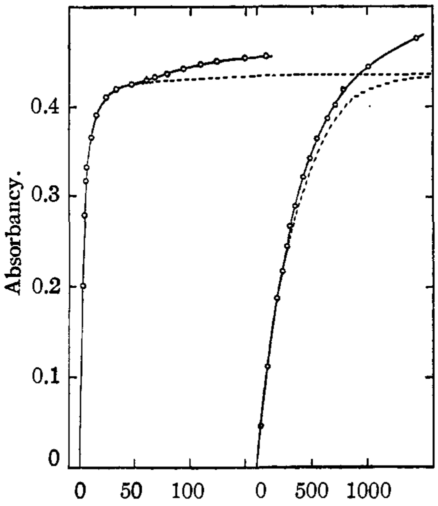

Fig. 3.—Absorbancy of mixtures of ethylenediaminetetraacetic acid and chromium(III) nitrate: left-hand curve at pH 5.86; right-hand curve at pH 3.40; temperature 31.0°.

Figure 3 shows plots of absorbancy of mixtures of chromium(III) nitrate and disodium salt of ethylenediaminetetraacetic acid *vs.* time after mixing, at pH 5.86 for the left-hand curve and pH 3.40 for the right-hand curve. The absorbancy increased exponentially with time until a point well past one half-life in all cases and toward 90% completion in most cases. Rate data when logarithmically plotted as previously indicated gave straight lines up to this point. The dashed curve is a continuation of the exponentially increasing absorbancy which fitted the first points. The fact that the experimental points deviated from the dashed line indicated that a further slow step was involved. Continued observation of the absorbancy with time showed additional stepwise change in absorbancy indicating that other slow steps were likely as the absorbancy very slowly approached the value for $HCrYH_2O$. Further verification that the product of the first order reaction was an intermediate in the formation of $CrYH_2O^-$ comes from the molar absorbancy index. At 545 mμ, the molar absorbancy index of $HCrYH_2O$ in solution at pH 5.0 was 200, while the molar absorbancy index of the product of the first slow step, evaluated from the dashed line in Fig. 3, was 176. Since the difference in molar absorbancy index was small it was not possible to determine rate constants for any slow step past the first by direct spectrophotometric means, although the steps resulting were considerably larger than experimental error.

When the rate of the first slow step was determined it was evident from the logarithmic plot that the reaction was first order in chromium ion concentration. Investigation of the rate as a function of pH showed that the rate was inversely proportional to the hydrogen ion concentration over the range pH 1.65 to 4.0 and deviated from this above 4.0, as shown by Fig. 4, which is a plot of *pk'* *vs.* pH, where *k'* is the apparent rate constant.

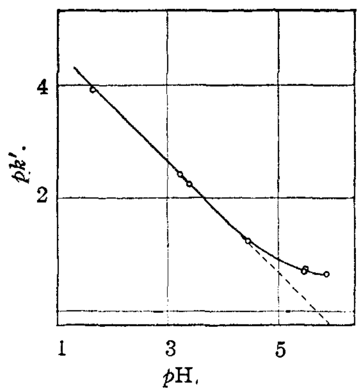

Fig. 4.—Negative log of apparent rate constant *vs.* pH.

A mechanism which is consistent with all the data obtained for the reaction between chromium(III) ion and ethylenediaminetetraacetic acid is the following. Relatively rapid reaction takes place in which one of the carboxyl groups occupies one coordinate position of the chromium by displacing a water molecule,[3] forming an intermediate B.

$$Cr(H_2O)_6^{+++} + H_2Y^{=} \xrightarrow{\text{rapid}} B \qquad (3)$$

This is followed by an equilibrium step involving hydrogen ion

$$B \rightleftarrows B' + H^+ \qquad (4)$$

and a slow step which involves the formation of the first chelate ring structure, C.

$$B' \xrightarrow{k} C \qquad (5)$$

Since the absorbancy was negligible for all materials present except the material being formed

$$d[C]/dt = k[B'] \qquad (6)$$

$$(A_s)_t = a_C b[C]_t \qquad (7)$$

where a_C is the molar absorbancy index of C and b is the cell thickness. The expression for the equilibrium of equation 4 is

$$[H^+][B']/[B] = K \qquad (8)$$

Combining equations 6–8 with the fact that the concentration of C is zero at the start, the following expression results

$$2.303 \log \frac{(A_s)_\infty - (A_s)_t}{(A_s)_\infty} = - \frac{kKt}{([H^+] + K)} \qquad (9)$$

where k is the actual rate constant. The apparent rate constant evaluated by plotting $\log [(A_s)_\infty - (A_s)_t]$ *vs.* time is $kK/([H^+] + K)$.

Making use of the value of the apparent rate constant at the highest pH shown in Fig. 4 and the inverse first order dependence on the hydrogen ion concentration found for pH values below 4, the equilibrium constant, K, of equation 8 was calculated to be 1.2×10^{-5} at 31.0°. This value was then used to calculate the actual first order rate constant for all the runs made at various hydrogen ion concentrations. The results are shown in Table I.

TABLE I

RATE CONSTANTS FOR THE FIRST SLOW STEP OF THE REACTION BETWEEN CHROMIUM(III) ION AND ETHYLENEDIAMINETETRAACETIC ACID AT 31.0°

Units of k' and k are sec.$^{-1}$; av. $k = 2.19 \times 10^{-3}$; std. dev. 0.16

pH	pk'	pk	pH	pK'	pK
1.65	5.93	2.63	5.45	2.73	2.65
3.22	4.44	2.68	5.52	2.78	2.67
3.40	4.28	2.72	5.86	2.70	2.63
4.45	3.28	2.66			

The temperature dependence of the rate was evaluated by determinations at various temperatures. The rates determined are given in Table II.

TABLE II

RATE CONSTANTS FOR THE FIRST SLOW STEP OF THE REACTION BETWEEN CHROMIUM(III) ION AND ETHYLENEDIAMINETETRAACETIC ACID AT VARIOUS TEMPERATURES

Cr, millimoles per liter	Temp., °C.	No. of runs	$k \times 10^3$, sec.$^{-1}$
2.52	25.2	2	1.02
1.01	25.2	1	0.98
2.52	31.0	7	2.19
1.01	31.0	1	2.30
2.52	37.3	2	4.56
2.52	42.5	2	7.6

A plot was made of $k_r h/kT$ *vs.* $1/T$, where k_r is the rate constant, h is Planck's constant, k is Boltzmann's constant and T is the absolute temperature. The plot was a straight line which enabled the calculation of the heat of activation and entropy of activation. The values obtained were $\Delta H^{\ddagger} = 21.3$ kcal. per mole with a standard deviation of the slope 0.6 kcal., and $\Delta S^{\ddagger} = -8.7$ cal. per mole degree with a standard deviation of the intercept 2.2 cal. per mole degree.

The value for the heat of activation is completely in accordance with the heat of activation for other slow-step processes for chromium(III) ion which have been determined,[3,4] the comparable value for the chromium(III) reaction with oxalate being 23.2 and 23.7 for the first and second oxalate ions reacting. A negative entropy of activation is reasonable since the ethylenediaminetetraacetate molecule will be somewhat more restricted in the activated state than it is when just bonded at one carboxyl.

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