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Complex Ions of Chromium. X. Resolution of *cis*-Dioxalatodiaquochromate(III) and Kinetics of Racemization in Acid Solution

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Received September 6, 1962

A method for the resolution of *cis*-potassium dioxalatodiaquochromate(III) has been devised which permits the recovery of the crystalline *d*- and *l*-isomers. The kinetics of racemization of these compounds in acid solution of ionic strength 1.0 are reported. A two-competing-path mechanism, which fits all the data in the pH range 0 to 7, having one path hydrogen ion independent and the other path first order dependent on hydrogen ion, is proposed.

In earlier work at this Laboratory the diastereoisomer *l*-strychnine-*d*-$Cr(C_2O_4)_2(H_2O)_2$ was recovered.[3] Rates of racemization were determined using the diastereoisomer as the source of the optically active dioxalatodiaquochromate by precipitating the strychnine as the iodide, leaving the *d*-dioxalatodiaquochromate in solution. These rates were found to be first order with respect to the *d*-complex and independent of hydrogen ion concentration in the pH range 2 to 7.

These data were compared to the data obtained for the *trans–cis* isomerization of the dioxalatodiaquochromate(III) ion by Hamm.[4] The *trans–cis*-isomerization rate was parallel to the racemization rate between pH 2 and 7, and the enthalpies of activation were nearly the same, so a single mechanism was proposed for the two reactions.

Experimental

The kinetics of racemization were obtained using a Rudolph Model 85 high precision visual polarimeter equipped with a Rudolph Model 95 spectroscopic monochromator using a tungsten light source. A jacketed, 2-dm. polarimeter cell was used. All kinetic data were taken at 510 mμ because the minimum in the rotary dispersion curves occurs at this wave length[3] for the *d*-isomer, and because the sensitivity of the eye is greatest in the region around 510 mμ.

Stock solutions of different pH over the pH range 0 to 2 were prepared using $HClO_4$. The hydrogen ion concentration of each solution was determined by titrating with standard base. The ionic strength was maintained at 1.0 in each solution by addition of $NaClO_4$. Samples of 25 mg. of *d* or *l*-*cis*-potassium dioxalatodiaquochromate(III) were dissolved in 25.0 ml. of these stock solutions and immediately were transferred to the polarimeter cells. No measurable change in the hydrogen ion concentration was expected from hydrolysis, because in this range the hydrogen ion concentration was very much larger than the total concentration of the metal complex.

The temperature was controlled by keeping the stock solutions in a constant temperature water bath thermostated to ±0.05° and by pumping thermostated water through the jacket of the polarimeter cell during the course of the rate determinations.

Crystalline Compounds.—*cis*-Potassium dioxalatodiaquochromate(III) was prepared by the method of Werner[5] using reagent grade oxalic acid and potassium dichromate and recrystallizing from a water–ethanol mixture.

l-*cis*-**Potassium Dioxalatodiaquochromate**(III).—Sufficient *cis*-dioxalatodiaquochromate was added to a cold supersaturated solution of strychnine sulfate to give a mole ratio of 1.0 mole of the dioxalatodiaquochromate to 0.75 mole of strychnine sulfate. Under these conditions the *d*-dioxalatodiaquochromate-*l*-strychnine diastereoisomer precipitated immediately. The solution was filtered rapidly into cold ethanol, where the crystalline *l*-dioxalatodiaquochromate precipitated. The crystals were washed with ethanol and with ethyl ether before drying under vacuum.

Anal. Calcd. for $K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$: Cr, 15.36; C_2O_4, 52.0. Found: Cr, 15.51; C_2O_4, 52.55. The molecular rotation estimated from the intercept of the rate data was $[M]_{510}^{25} = 2200°$.

d-*cis*-**Potassium Dioxalatodiaquochromate**(III).—The *d*-dioxalatodiaquochromate-*l*-strychnine diastereoisomer was mixed with a stoichiometric amount of potassium iodide in a small amount of water. This solution was rapidly filtered into cold ethanol where the *d*-dioxalatodiaquochromate precipitated. The crystals were washed with ethanol and with ethyl ether before drying under vacuum.

Anal. Calcd. for $K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$: Cr, 15.36; C_2O_4, 52.0. Found: Cr, 15.54; C_2O_4, 52.60. The molecular rotation estimated from the intercept of the rate data was $[M]_{510}^{25} = 2100°$.

The rates of racemization were independent of which isomer was used for the rate determination. The rotary dispersion curve determined for the *l*-isomer was the reflection through the zero-rotation axis of the rotary dispersion curve previously reported for the *d*-isomer.[3] The estimated molecular rotations show that the *l*-isomer was more nearly optically pure than the *d*-isomer. This was thought to be the result of a more direct method of recovery for the *l*-isomer which allowed less time for racemization during the preparation.

Results and Discussion

In Table I the rates of racemization determined on solid samples of pure *l*- and *d*- isomers in the pH range 2.6 to 7 are given.

The rates of racemization of the dioxalatodiaquo-

TABLE I

RATES OF RACEMIZATION OF DIOXALATODIAQUOCHROMATE

(Ionic strength = 1.0, Temp., 25.0°)

pH	$k_r \times 10^4$, sec.$^{-1}$
2.6	4.27
3.3	4.24
4.8	4.28
5.8	4.32
7.0	4.32

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(1) National Defense Graduate Fellow 1959–1962.

(2) This is a portion of a thesis submitted to the Chemistry Department, University of Utah, in partial fulfillment for a Doctor of Philosophy Degree.

(3) R. E. Hamm, R. Kollrack, G. L. Welch, and R. H. Perkins, *J. Am. Chem. Soc.*, **83**, 340 (1961).

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

(5) A. Werner, *Ann.*, **406**, 216 (1914).

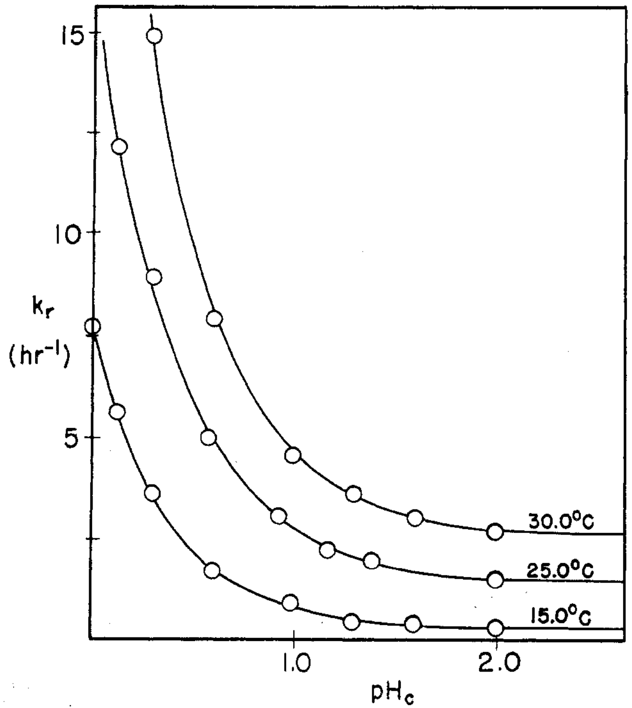

Fig. 1.—Rates of racemization of dioxalatodiaquochromate(III) as a function of pH.

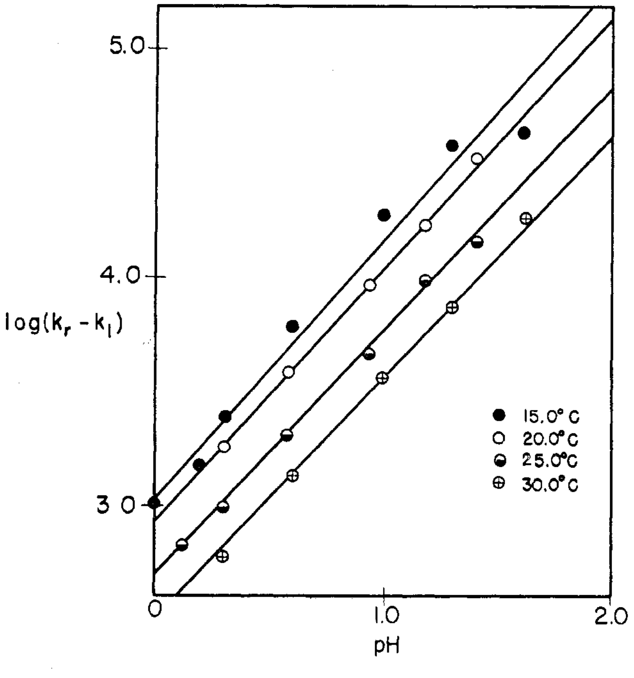

Fig. 2.—Logarithm of difference between acid dependent rate and acid independent rate as a function of pH.

chromate(III) in the pH range 0 to 2 were observed to be first order with respect to complex with a very strong hydrogen ion dependence. These results are shown in Fig. 1. Each of the points is the average of at least four separate rate determinations. The following equation was found to fit these curves: $k_r = k_1 + k_2[H^+]^n$, where k_r is the observed rate of racemization and k_1 is the rate of racemization in the pH range 2.6 to 7. The exponent n was determined by plotting $-\log(k_r - k_1)$ *vs.* pH as shown in Fig. 2. The values of the slopes were not significantly different from 1.0 when least squares fits were made to the data. From this it was concluded that the acid dependent path is first order with respect to hydrogen ion concentration.

In Table II the values of k_1 and k_2 evaluated at various temperatures are given.

Table II

Values of k_1 and k_2 at Various Temperatures

Temp., °C.	$k_1 \times 10^4$ (sec.$^{-1}$)	$k_2 \times 10^3$ (sec.$^{-1}$)(M)$^{-1}$
15.0	2.06	1.40
20.0	3.40	1.84
25.0	4.30	3.72
30.0	7.5	5.4

The values of k_1 and k_2 at various temperatures were used to calculate the enthalpies of activation, ΔH^*, by plotting $-\log k_rh/kt$ *vs.* $1/T$. The values determined were 13.4 kcal./mole for k_1[3] and 19 kcal./mole for k_2.

Preliminary work on the *trans–cis* isomerization of dioxalatodiaquochromate(III) from pH 0 to 2 has shown that the rate constants and enthalpies of activation are essentially the same as those for the racemization reported in this investigation. This lends further support to the assumption that there is a single mechanism for isomerization and racemization.[3]

The mechanism which is proposed for these reactions must satisfy other experimental data than those presented here. Graziano and Harris[6] and Krishnamurty and Harris[7] reported that the exchange of oxalate with trisoxalatochromate was more rapid in acid solutions between pH 0 and 2 than in the pH range above 2. As the first step in the mechanism they proposed, a proton attacks one end of a chelated oxalate group which effects an opening of the oxalate ring. It also was shown[7] that there is no direct oxalate exchange between dioxalatodiaquochromate(III) and free oxalate even at pH 1.0. In a discussion of this paper one of the authors indicated that it is not necessary that a singly-bonded oxalate be very much more rapidly exchangeable than chelated ones.

An additional piece of evidence which indicates the possibility of forming a single-bonded oxalate with one of the oxalates of dioxalatochromate was given by Beck and Seres,[8] who showed that each chromium(III) could protect two oxalates from oxidation by permanganate if the dioxalatochromate complex was formed by boiling at pH 2 to 3, but that if the solution was made more acid than pH 2 and allowed to stand for some time, less than two molecules of oxalate would be protected by each chromium. A further piece of evidence for formation of some single-bonded oxalate species from dioxalatodiaquochromate is the loss of

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(6) F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).
(7) K. V. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960).
(8) M. T. Beck and I. Seres, *Chemist-Analyst*, **50**, 48 (1961).

absorbancy when a solution of the *cis*-compound is made more acid than pH 2.[9]

As a result of these pieces of information a proton attack which causes ring opening of one oxalate group is suggested as the mechanism of the hydrogen ion dependent reaction. At pH 2 and above the reaction could proceed as previously suggested by water dissociation,[3] while at pH values below 2 a two path mechanism is suggested which can be represented by the equations

$$[Cr(C_2O_4)_2(H_2O)_2]^- \xrightarrow{k_1} [Cr(C_2O_4)_2(H_2O)]^- + H_2O \xrightarrow{\text{rapid}} [Cr(C_2O_4)_2(H_2O)_2]^- \quad (1)$$

$$H^+ + [Cr(C_2O_4)_2(H_2O)_2]^- \xrightarrow{k_2} [Cr(C_2O_4)(OC_2O_3H)(H_2O)_2] \xrightarrow{\text{rapid}} [Cr(C_2H_4)_2(H_2O)_2]^- \quad (2)$$

This mechanism is in agreement with the rate data reported. Reaction 1 would explain the hydrogen ion independent rate above pH 2, and reaction 2 would become more and more important as the hydrogen ion concentration increased below pH 2.

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[9] H. L. Schläfer, private communication.

CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION,
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Complexes of 2-Hydroxyethyliminodiacetic Acid

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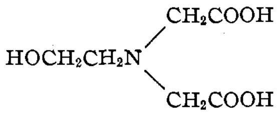
Received August 4, 1962

Several complexes of 2-hydroxyethyliminodiacetic acid were prepared and characterized by means of infrared and visible-ultraviolet spectra, magnetic moments, and molar conductivities. The complexes appear to be of two distinct types; the first type consists of $K_2[Ni(HO\text{-}A)_2]$, $Na[Co(HO\text{-}A)_2]$, $Na_2[Co(HO\text{-}A)_2]$, and $K[Cr(HO\text{-}A)_2]$, which appear to be octahedral complexes with the ligand coördinating through the nitrogen and two carboxyl oxygens. $[Ni(HO\text{-}AH)_2]$ and $[Co(HO\text{-}AH)_2]$ are of a second type and appear to coördinate to the alcohol OH group as well as to one carboxylate.

The solution behavior of 2-hydroxyethyliminodiacetic acid (I) ($HO\text{-}AH_2$) toward metal ions has been studied by several workers[2,3]; however, little attention has been directed toward the isolation of complexes of this compound. Vieles and Seguin[4] appear to have reported the only synthetic work with this ligand in the isolation of a copper(II) salt. It was of interest to us to isolate and characterize complexes of 2-hydroxyethyliminodiacetic acid and, in particular, to determine if the alcohol OH group enters the coördination sphere.



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Experimental

Reagents.—Reagent grade transition metal salts were used as received. A research sample of 2-hydroxyethyliminodiacetic acid was received from the Dow Chemical Company.

Preparation of Complexes.—The complexes were prepared as described below and dried *in vacuo* over P_2O_5. In Table I analytical data for these compounds are summarized.

Dihydrogen Bis-(2-hydroxyethyliminodiacetato)-cobalt(II) and Dihydrogen Bis-(2-hydroxyethyliminodiacetato)-nickel(II), $[M(HO\text{-}AH)_2]$.—Cobalt(II) carbonate (prepared according to Schlesinger[5]) or nickel(II) carbonate was added to a hot aqueous solution containing the theoretical quantity of $HO\text{-}AH_2$. After filtration, the solution was boiled for 1 hr. and the water-insoluble product isolated by filtration and washed with hot water.

Sodium Bis-(2-hydroxyethyliminodiacetato)-cobalt(II), $Na_2[Co^{II}(HO\text{-}A)_2]$.—Solution of $[Co(HO\text{-}AH)_2]$ in aqueous sodium bicarbonate, followed by precipitation with ethanol, conveniently afforded this compound.

Sodium Bis-(2-hydroxyethyliminodiacetato)-cobalt(III), $Na[Co^{III}(HO\text{-}A)_2]$.—$Na_3[Co(CO_3)_3]\cdot 3H_2O$[6] and the theoretical quantity of ligand were mixed in warm water. After effervescence ceased concentrated perchloric acid was added to pH *ca.* 4. The solution was evaporated to low volume and the purple crystals were isolated by filtration and recrystallized from hot water.

Potassium Bis-(2-hydroxyethyliminodiacetato)-chromium(III), $K[Cr(HO\text{-}A)_2]$, and Potassium Bis-(2-hydroxyethyliminodiacetato)-nickel(II), $K_2[Ni(HO\text{-}A)_2]$.—An aqueous solution of $HO\text{-}AH_2$, containing sufficient potassium hydroxide to neutralize one ligand proton, was added to a hot, aqueous solution of the stoichiometric amount of the hydrated metal chloride. The solutions were neutralized with aqueous potassium hydroxide; in the case of the chromium(III) complex neutralization was completed after the color of the solution changed from blue to red. On cooling, $K[Cr(HO\text{-}A)_2]$ crystallized; this complex was recrystallized from hot water. $K_2[Ni(HO\text{-}A)_2]$ was precipitated by the addition of ethanol and recrystallized from ethanol–water.

Infrared Spectra.—Infrared spectra were obtained on a Perkin–Elmer Model 21 spectrophotometer using mineral oil and halocarbon mulls.

Visible-Ultraviolet Spectra.—Visible-ultraviolet absorption spectra of aqueous solutions of the complexes were obtained using a Cary Model 14 recording spectrophotometer. Reflectance spectra were obtained on 1$^1/_8$ in. disks of sample using

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[1] Department of Chemistry, The University of Connecticut, Storrs, Connecticut.

[2] S. Chaberek, R. C. Courtney, and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5057 (1952).

[3] (a) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955); (b) G. Anderegg and G. Schwarzenbach, *ibid.*, **38**, 1940 (1955).

[4] P. Vieles and J. Seguin, *Compt. rend.*, **238**, 1819 (1954).

[5] G. Schlesinger, *Inorg. Syn.*, **6**, 189 (1960).

[6] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).