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

Complex Ions of Chromium. VII. Kinetics of Decomposition of Diol Bonds in Chromium(III) Solutions

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RECEIVED JANUARY 28, 1958

The acid decomposition of the tetraoxalato-μ,μ-dihydroxodichromate(III) ion has been shown to proceed in two slow steps. The second slow step has been shown to be of a different nature when an insufficient amount of acid is added. A mechanism is proposed for the reactions occurring. The results obtained for the enthalpies of activation are shown to be consistent with structures of the molecules undergoing the various steps.

In a preceding paper[2] in this series it was postulated that the kinetics of diol bridge formation in basic oxalato chromium(III) solutions were limited by the rate of a water dissociation step. Therefore, the preceding study did not yield kinetic data which directly involved bonds associated with the diol bridge. The present study, however, concentrates on the kinetics involved in the acid decomposition of the diol bridge structure in which the rate controlling steps are concerned directly with the dissociation of an ol bond.

From absorption-spectral data on reactants and products, the over-all reaction studied during this investigation is proposed to be

$$(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2^{-4} \xrightarrow[2H_2O]{2H^+} 2(C_2O_4)_2Cr(H_2O)_2^{-1} \quad (1)$$

A residual basicity of the dimeric chromium species is explained in terms of the process of oxolation discussed, recently, at length by Rollinson.[3]

Experimental

Instruments.—A conductance bridge was assembled from standard electrical components with a cathode ray oscilloscope serving as the null indicator. A specialized conductance bridge circuit described by Grant and Hamm[4] was also used during part of the investigation.

Chemicals.—Reagent grade potassium dichromate and oxalic acid were source materials for the oxalato chromium(III) complexes. Reagent grade hydroxides of potassium and sodium were used for the preparation of the hydroxy salts in solution and reagent grade 70% perchloric acid to make acid solutions. Potassium dioxalatodiaquochromate(III) was prepared by the method of Werner.[5] The 0.2 *M* stock solution of potassium tetraoxalato-μ,μ-dihydroxodichromate(III) was obtained by mixing in a 1:1 stoichiometric ratio solutions of potassium dioxalatodiaquochromate(III) and potassium hydroxide. The proper dilution and aging of the solution then followed.

Decomposition Rates.—The rate of acid decomposition of tetraoxalato-μ,μ-dihydroxodichromate(III), henceforth referred to as the dimer, was determined by observing the change in conductance of the solution using an a.c. frequency of 1,000 c.p.s. As local excesses of acid resulted in non-reproducible kinetic data, the dimer was added to a diluted perchloric acid solution with vigorous stirring. The newly mixed solution then was placed in a conductivity cell suspended in a constant temperature bath allowing the resistance of the cell to be recorded as a function of time without further handling of the reaction solution. Data obtained in this manner with a standard conductance bridge were satisfactory for calculation of rate constants for the first of two slow steps noted in the decomposition of the dimer. Effective infinite time values for the conductivity of the solution required in calculating rate constants were taken as those values noted when the reaction had proceeded for a period equal to five times the half life of the reaction. The half life was approximated initially by using the Guggenheim method.[6]

Difficulty in obtaining satisfactory infinite-time values for the second slow step was resolved by using a specialized conductance bridge[4] mentioned elsewhere. Data obtained from this bridge can be interpreted directly in accordance with Guggenheim[6] for first-order kinetics.

Residual Basicity of the Dimeric Solutions.—While obtaining kinetic data a residual basicity was noted for the acid–dimer reaction mixture. A normal acid–base titration, however, failed to measure quantitatively this basicity because of the rapidity of the decomposition reaction. The difficulty was resolved by extrapolating to zero time potentiometric data for the hydronium ion obtained on separate solutions having various acid to dimer ratios.

Results and Discussion

Residual Basicity.—For various acid–dimer mixtures it was noted that within experimental error a quantity of acid was consumed which was equivalent to roughly 15% of the chromium present. This phenomenon is explained in terms of a disproportionation of the tetraoxalato-μ,μ-dihydroxodichromate(III) into the oxolated ion, tetraoxalato-μ-hydroxo-μ-oxodichromate(III) and the monomeric species, dioxalatodiaquochromate(III) and dioxalatohydroxoaquochromate(III). The amount of acid consumed would, therefore, be a measure of the amount of the oxolated dimer and the monohydroxo–monomer present in the basic chromium stock. The equations for the rapid acid–base equilibria are proposed to be

$$\underset{\text{A}}{(C_2O_4)_2Cr(H_2O)_2^{-1}} \overset{K_1}{\rightleftarrows} \underset{\text{C}}{(C_2O_4)_2Cr(H_2O)(OH)^{-2}} + H^+ \quad (2)$$

$$\underset{\text{B}}{(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2^{-4}} \overset{K_3}{\rightleftarrows} \underset{\text{O}}{(C_2O_4)_2Cr(OH)OCr(C_2O_4)_2^{-5}} + H^+ \quad (3)$$

The equilibrium between the dimer and the monohydroxy monomer is kinetically slow and will not explain any of the initial basicity.

For a 2×10^{-3} *F* $K_4Cr_2(OH)_2(C_2O_4)_4$ solution having a potentiometric determined free acid concentration of 1.5×10^{-6} *F*, equations 4 and 5 may be written

$$[A] + [C] + 2[B] + 2[O] = 4 \times 10^{-3} \quad (4)$$

$$[C] = (K_1/[H])[A] = 0.27\ [A] \quad (5)$$

$$[O] + [C] = 0.15 \times 4 \times 10^{-3} \quad (6)$$

$$[O] = [A] + [H^+] = [A] \quad (7)$$

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[1] Noyes Laboratory, University of Illinois, Urbana, Illinois.

[2] D. M. Grant and R. E. Hamm, THIS JOURNAL, **78**, 3006 (1956).

[3] "The Chemistry of the Coördination Compounds," Chapter 13, American Chemical Society Monograph Series edited by John C. Bailar, Jr., Reinhold Publ. Corp., New York, N. Y., 1956.

[4] D. M. Grant and R. E. Hamm, *J. Phys. Chem.*, **62**, 118 (1958).

[5] A. Werner, *Ann.*, **406**, 261 (1914).

[6] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

Equations 4 and 7 are conservation of mass expressions. The value of K_1 used in eq. 5 was determined previously[2] to be 4×10^{-7}. Equation 6 expresses quantitatively the 15% residual basicity of the chromium stock. Solution of the above equations allows the estimation of 6×10^{-7} to be made for K_3.

As the first acid dissociation constant for the dimer is approximately equal to that of the diaquo monomer, it is assumed that the second dissociation constants would also be of the same order of magnitude. In which case, the existence of the dioxo bridge compound could be neglected as a result of the high dimer concentration.

Decomposition Rates.—In a preliminary investigation of these rates, four different initial concentrations were observed conductometrically for each of the following dimer to acid ratios: 2:1, 1:1, 1:2 and 1:4. For each of the solutions having an equivalent or an excess of acid, the plot of log $[(1/R)_t - (1/R)_\infty]$ *vs.* t yielded a member of a family of curves which, at a given time, were observed to have slopes that vary only slightly in accordance with the differing ionic atmospheres. A representative set of such curves obtained at 30° is given in Fig. 1 for an eightfold concentration range.

The family of curves obtained for those solutions having a less than equivalent amount of acid was somewhat similar to the first family. The first parts of the curves in the region of high curvature again had slopes which were roughly parallel to those of the former set. The data used in the second half of the plot, however, differed from that of the former family in that a slightly steeper slope was observed, indicating a more rapid reaction rate. Also, instead of the excellent linearity of the sufficient-acid set, a slight curvature was noted in the plots of data taken for extended periods on the deficient-acid solutions. Even so, the slopes for the various curves within the set were essentially parallel at corresponding times.

Postulation of a two step consecutive reaction mechanism for the decomposition of tetraoxalato-μ,μ-dihydroxodichromate(III) explains the initial deviation of the conductivity data from the eventual first-order fit noted in Fig. 1. The plots of log $[(1/R)_t - (1/R)_{3000}]$ *vs.* t, shown in Fig. 2 for the same data as shown above, exhibits an excellent fit with the first-order rate law. The term, $(1/R)_{3000}$, is the conductivity of the reaction mixture for $t = 3000$ sec., a period that is approximately equal to five times the half-life of the first slow step.

Rate constants for the first step calculated from such plots were found to be of the same order of magnitude for all dimer-acid ratios and for dimer concentrations ranging from 2×10^{-3} to 2×10^{-2} *F*. All deviations between rate constants determined at the same temperature are explained by ionic atmosphere effects. The rate constants are proportional to the perchlorate anion concentration in a manner similar to that noted by Plane and Taube[7] for the rate of water exchange in the hexaquochromate(III) ion. As Hunt and Plane[8] pointed out later, this anionic effect can be more properly considered as an ionic strength effect.

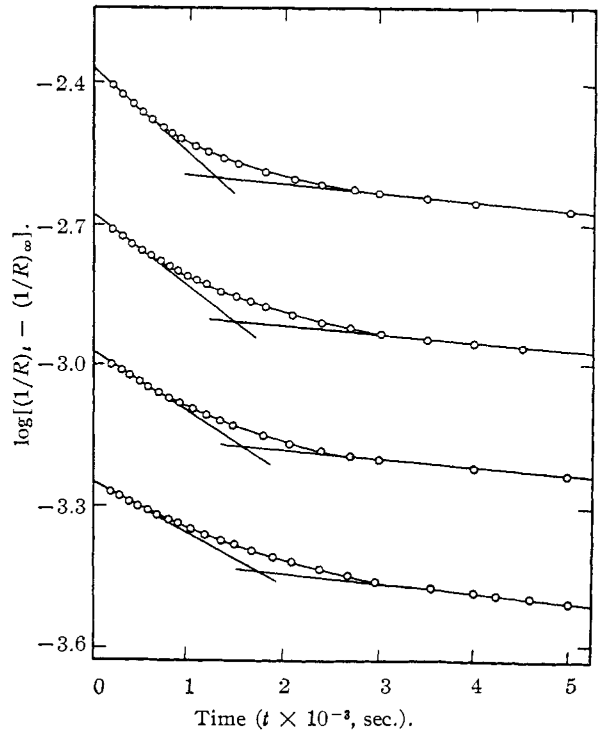

Fig. 1.

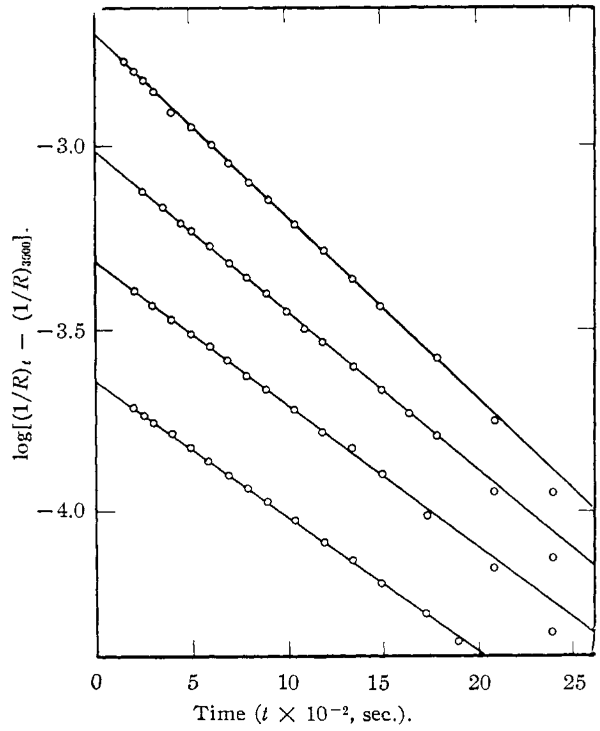

Fig. 2.

Likewise, as the rate constants change at most by 50% for a fivefold increase in the perchlorate concentration, the anionic effect noted in this study is, also, explained as an ionic strength effect.

A thorough investigation of the ionic strength dependency of this reaction was impossible with the methods used in this study. An excess inert electrolyte would obscure the change in conduc-

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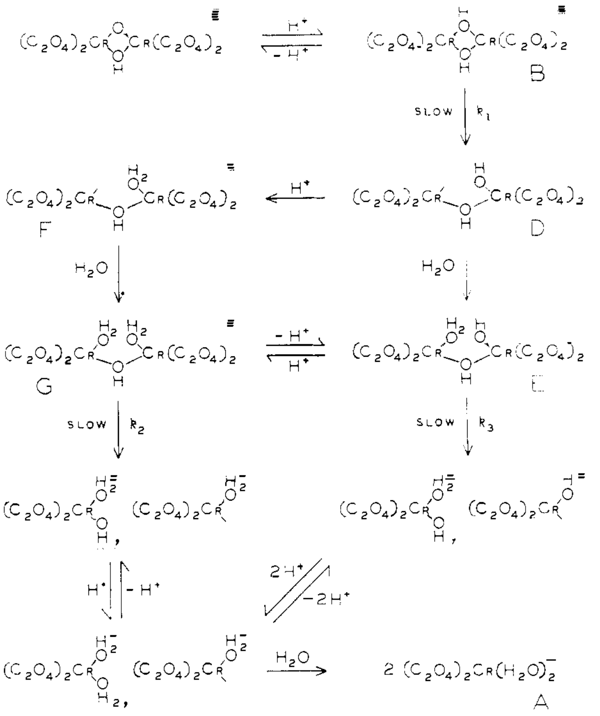
(7) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

(8) J. P. Hunt and R. A. Plane, THIS JOURNAL, **76**, 5960 (1954).

tivity, whereas for solutions in which the ionic strength is not adjusted with an excess inert electrolyte, a meaningful value of the ionic strength is not obtainable. The contribution to the ionic strength is difficult to ascertain for some of the large species such as the quadruply-charged dimer ion in which the charge is extended throughout a large region. In addition, the rates measured in this study as well as in the previous work[7,8] were not affected equally by equivalent amounts of all anions. A better understanding of ionic atmosphere effects is needed.

The second slow step was found to be first order in chromium for solutions containing sufficient acid and pseudo first order for deficient acid solutions. Rate constants were obtained for the sufficient acid rate directly from the conductivity data which fit a linear first-order plot. The apparent rate constants of the second slow step for the deficient-acid case were estimated from the tangent to the log $[(1/R)_t - (1/R)_\infty]$ *vs. t* plot constructed when the degree of reaction completion was the same. This time was determined for each temperature as that time for which linearity was first observed in the corresponding sufficient-acid plot.



The following mechanism, which is in accord with these experimental facts, is postulated.[9] Dissociation mechanisms are proposed for each of the rate determining steps to explain the first-order dependence of the reaction. A mechanism postulating an acid attack of the diol bridge structure will not explain the data.

First Slow Step.—After the dissociation of the first ol bridge in which species D is formed, a rapid proton association will follow in acid solutions to form the compound F which less rapidly hydrates forming species G. Otherwise, the fast rate for the recyclization of D to reform B will rapidly establish equilibrium between B and D before significant acid decomposition can occur. Formation of the species E as a means of shifting the equilibrium between B and D is not favored on the basis of previous work,[2] wherein the rate of hydration was found to be about 10^{-3} times the rate of ol bridge formation. On the basis of these assumptions, an expression for the initial rate controlling step in the decomposition is

$$\text{Rate}_1 = k_1[\text{B}] \tag{8}$$

As the rate of decrease in conductivity can be shown to be proportional to the above rate, it is possible to evaluate the specific first-order rate constant k_1. These values are listed in Table I as a function of temperature and beginning concentrations.

TABLE I

RATE OF DECOMPOSITION OF TETRAOXALATO-μ,μ-DIHYDROXODICHROMATE(III) FOR THE FIRST SLOW STEP AS A FUNCTION OF TEMPERATURE AND CONCENTRATION

Rate constants given in sec.$^{-1}$ × 10^3

Initial perchloric acid concn (moles/l.)	Initial[a] dimer concn. (moles/l.)	Temp., °C. 20.0	25.0	30.0	35.0	40.0	45.0
2.00×10^{-3}	2.00×10^{-3}	0.38	0.52	0.76	1.03	1.49	1.89
2.00×10^{-3}	4.00×10^{-3}	.41	.57	.79	1.10	1.49	2.10
4.00×10^{-3}	8.00×10^{-3}	.45	.63	.92	1.25	1.69	2.23
6.00×10^{-3}	6.00×10^{-3}	.50	.69	1.00	1.41	1.88	2.64
1.00×10^{-2}	1.00×10^{-2}	.57	.83	1.13	1.57	2.25	2.95
1.00×10^{-2}	2.00×10^{-2}	.51	.73	1.08	1.50	2.01	2.69

[a] Initial total chromium concentration expressed as dimer.

Enthalpies and entropies of activation were obtained from the slopes and intercepts, respectively, from plots of log k_1h/kT *vs.* $/T$ using the method of least squares. Values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are shown in Table II.

TABLE II

HEATS AND ENTROPIES OF ACTIVATION FOR THE FIRST STEP OF THE DECOMPOSITION REACTION FOR VARIOUS INITIAL CONCENTRATIONS

Initial perchloric acid concn. (moles/l.)	Initial dimer[a] concn. (moles/l.)	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, cal./mole. deg.
2.00×10^{-3}	2.00×10^{-3}	11.4	−35.3
2.00×10^{-3}	4.00×10^{-3}	11.5	−34.8
4.00×10^{-3}	8.00×10^{-3}	11.6	−34.3
6.00×10^{-3}	6.00×10^{-3}	11.7	−33.7
1.00×10^{-2}	1.00×10^{-2}	11.6	−33.7
1.00×10^{-2}	2.00×10^{-2}	11.7	−33.5

[a] Initial total chromium concentration expressed as dimer.

A plot of the enthalpies and entropies of activation *vs.* the concentration of the perchlorate ion yielded zero extrapolated values of 11.4 kcal./mole and −35 cal./mole deg., respectively, for the activation quantities.

Second Slow Step.—In solutions containing sufficient acid for the complete decomposition of the dimer, the second slow step proceeds in a manner identical to the initial slow step. The

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[9] As in many kinetic investigations it is possible to present other possible mechanisms, which in this case might involve the primary breaking of a chelate bond. The authors, as in the previous paper,[2] have chosen to indicate the direct mechanism, and neglect possible mechanisms involving the opening up on one end of a chelate bond. This is believed to be a reasonable approximation in the absence of any direct experimental evidence. The final word on the exact mechanism will depend upon further experimental work.

dissociation of the remaining ol bridge in species G is followed, as before, by a rapid acid association and by a less rapid hydration step to form A, the dioxalatodiaquochromate(III) end product. The expression for the rate takes the form

$$\text{rate}_2 = k_2[\text{G}] \qquad (9)$$

The rate again can be shown proportional to the rate of conductance decrease, and the specific first-order rate constant k_2 was evaluated. Values are shown in Table III as a function of temperature for initial concentrations of acid = 4.00×10^{-3} *F* and of dimer = 2.00×10^{-3} *F*.

TABLE III

THE RATE CONSTANTS FOR THE SECOND SLOW STEP IN THE DECOMPOSITION OF TETRAOXALATO-μ,μ-DIHYDROXODICHROMATE(III) AS A FUNCTION OF TEMPERATURE

Temp., °C.	$k_2 \times 10^5$, sec.$^{-1}$	$(k_2' + k_3')$ $\times 10^5$, sec.$^{-1}$	$k_3 \times 10^4$, sec.$^{-1}$
34.3	0.70	3.8	3
40.0	1.61	5.4	4
45.4	2.51	7.5	5
50.0	3.25	9.6	6
55.7	4.70	..	..

Mathematical interpretation of the rate data for solutions having insufficient acid for the complete decomposition is greatly complicated. For these solutions the first slow step will proceed normally until a quantity of species F and G has been formed which approximately equals the amount of free acid that was left in solution after mixing. Species B then quickly equilibrates with D and the first rate is terminated. The *p*H of the solution is then at a value where a buffering effect due to the presence of species A, B and G will maintain the hydronium ion concentration somewhat constant during the remainder of the reaction.

If the acid dissociation constant for G is assumed to be equal in magnitude to the corresponding acid dissociation constants for species A and B, consideration must be given to the mechanism proposed by Hamm and Davis[10] and Postmus and King[11] for explaining the *p*H dependence of chromium substitution reactions. According to this mechanism the formation of E by the acid dissociation of G offers a more rapid parallel step for the final dissociation, and the rate must be expressed as

$$\text{rate}_2 = k_2[\text{G}] + k_3[\text{E}] \qquad (10)$$

Substituting the equilibrium constant expression into eq. 10, the rate may be expressed as

$$\text{rate}_2 = (k_2' + k_3')([\text{G}] + [\text{E}]) \qquad (11)$$

where $k_2' = k_2[\text{H}^+]/(K + [\text{H}^+])$ and $k_3' = k_3K/(K + [\text{H}^+])$. *K* is the acid dissociation constant for species G.

As the rate of change in the conductance will be proportional to the rate of decrease in the sum, ([G] + [E]), a first-order plot of the conductance data is possible. Such plots, however, will not be perfectly linear due to slight changes of the [H$^+$] terms in the apparent rate constant $(k_2' + k_3')$. Values for $(k_2' + k_3')$ as determined at the beginning of the second slow step are given in Table III as a function of temperature and initial concentration of acid = 2.00×10^{-3} *F* and dimer = 4.00×10^{-3} *F*.

Values for the specific first-order rate constant, k_3, appearing in Table III are approximated in order of magnitude by making the assumption that the acid dissociation constant, *K*, for species G is about 5×10^{-7}, a value intermediate between the acid dissociation constants noted for species A and B. The value for [H$^+$] is estimated from equilibrium considerations at 5×10^{-6} *F*, and k_2 values are taken from Table III at corresponding temperatures.

Thermodynamic Activation Quantities.—Using the least squares method plots of $\log k_i h/kT$ *vs.* $1/T$ yielded values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both of the second slow steps. These values are listed and compared in Table IV with the corresponding values for the first slow step. The precision is estimated either from the standard deviations calculated according to the least squares method or from the inherent errors within the rate constants.

TABLE IV

HEATS AND ENTROPIES OF ACTIVATION FOR THE SLOW RATES IN THE ACID DECOMPOSITION OF TETRAOXALATO-μ,μ-DIHYDROXODICHROMATE(III)

		$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, cal./mole deg.
First slow step		11.4 ± 0.2	−35 ± 1
Second slow step	Sufficient acid	13.4 ± 0.4	−36 ± 2
	Deficient acid	8 ± 1.5	−49 ± 5

Differences in $\Delta H^{\ddagger}$ are in accord with anticipated inductive effects of adjacent coördinated groups upon the bonds of the ol bridge. The hydroxo group adjacent to the dissociating ol bond for the first rate is not free and therefore cannot be expected to exert the same influence upon the dissociating group as will the free hydroxo group in species E. The coördinated H_2O group adjacent to the breaking bond in species G, as was observed, will enhance the rate even less.

Acknowledgments.—The authors wish to thank the National Science Foundation for a research grant which supported this work and a predoctoral fellowship to D. M. G.

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[11] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).