Acknowledgments.—The authors wish to acknowledge the coöperation of their associates at Shell Development Company laboratories, particularly that of Francis Powell and G. A. Harlow, who determined the equilibrium partition coefficients.

EMERYVILLE, CALIFORNIA

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

Complex Ions of Chromium. VI. Kinetics of Formation of Diol Bonds in Chromium(III) Solutions[1-3]

BY DAVID M. GRANT[4] AND RANDALL E. HAMM

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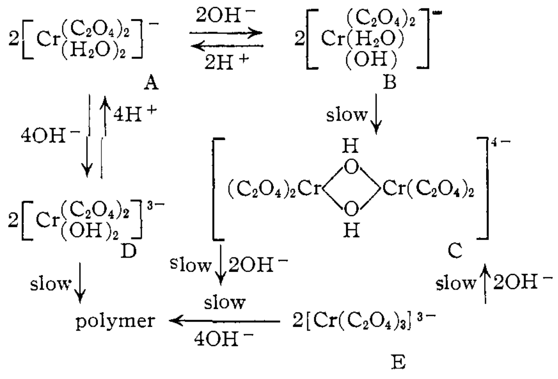
By a spectrophotometric method, the rates of dimerization of *cis*-hydroxydioxalatoaquochromate(III) were determined over a range of temperatures and ionic strengths. After a short induction period, the dimerization reaction was found to be first order in chromium concentration, when at concentrations above 0.01 molar. A mechanism is proposed for the dimerization reaction which accounts for the induction period of the reaction and the deviation from first-order kinetics at low concentrations. The activation energies and entropies were determined at the various ionic strengths and extrapolated values at zero ionic strength have been estimated.

Werner[5] characterized the *cis*-hydroxydioxalatoaquochromate(III) and *cis*-dihydroxydioxalatochromate(III) and recognized that the monohydroxy compound would dimerize to form a relatively stable ion, which he claimed would not revert to the original dioxalatodiaquochromate(III) ion upon the addition of acid, although he recognized that the freshly prepared hydroxy compounds would immediately revert to the aquo ions upon the addition of acid.

A number of investigators[6-8] have studied the process of aging in chromium(III) solutions. Although there is still some question of the exact extent to which it takes place there is now general agreement that it involves the formation of ol or diol linkages. Mattock[9] has shown that polymerization through formation of ol bonds is normal for several metal ions, including chromium(III).

The absorption spectra of solutions of either *cis*-hydroxydioxalatoaquochromate(III) of *cis*-dihydroxydioxalatochromate(III) showed changing spectral absorption indicating the occurrence of a slow reaction. The first of these reactions has been identified as a dimerization, while the second involves some replacement of oxalato groups by hydroxy groups followed by polymerization to some degree through diol bond formation. The monohydroxy dimer was found to split slowly and give back the original dioxalatodiaquochromate(III) ion upon the addition of acid. The dihydroxy aged product gave an immediate precipitate upon the addition of acid. This precipitate then slowly went into solution, as the oxalate slowly recombined to form dioxalatochromate(III).

The authors believe that by studying the formation of the diol linkage in the case of dioxalatochromate(III) where the process will stop at the formation of the dimer, one may get information to better understand the process where polymer formation is likely. The following are the interrelations which have been developed in the course of the present investigation.



The tris-(oxalato)-chromate(III) ion is included in this reaction scheme because spectrophotometric investigation showed that the products formed using it as starting material gave the same absorption curves as were obtained by using dioxalatodiaquochromate(III) as starting material.

This investigation has attempted to quantitatively study the slow step in the dimerization reaction and to suggest a reasonable mechanism for the process.

Experimental

Reagents.—The potassium dioxalatodiaquochromate(III) was prepared by the method of Werner.[5] Carbonate-free sodium hydroxide was used for preparation of the hydroxy salts in solution.

Procedure.—The equipment and methods were those reported in previous papers from this Laboratory.[10]

Potassium Bis-(dioxalato)-chromate(III)-μ-diol (C).—A (0.1 mole in 100 ml. H_2O) was treated with 0.1 mole of KOH and maintained at a temperature just below the boiling point for two hours, after which the solution was cooled to room temperature and slowly poured into 200 ml. of cool rapidly stirred dioxane. The precipitate was filtered off and washed with alcohol and ether. The solid obtained was dried at 100° and analyzed for chromium and oxalate.

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[2] Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society meeting, September 16, 1955, in Minneapolis, Minn.

[3] Paper V in this series, THIS JOURNAL, **77**, 2083 (1955).

[4] National Science Foundation Research Fellow, 1954–1956.

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

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[10] R. E. Hamm, THIS JOURNAL, **75**, 609, 5670 (1953).

Anal. Calcd. for $Cr_2(C_2O_4)_4(OH)_2K_4$: Cr, 16.09; C_2O_4, 54.56. Found: Cr, 16.15; C_2O_4, 54.30. A sample of this compound in solution gave an absorption spectrum which was within experimental error of the aged product formed in solution when dioxalatodiaquochromate(III) ion and potassium hydroxide were mixed in 1:1 ratio.

Dimerization Rates.—The rates of dimerization were determined by observation of changes in spectrophotometric absorption at 480 mμ. Since experiment showed that excess base would split out oxalate and lead to polymerization, a solution of dioxalatochromate(III) which had slightly less than a stoichiometric quantity of base added to form the monohydroxy compound was used (*i.e.*, exactly 1% deficiency in base). The change of absorbancy was observed using 1-, 2- or 10-cm. cells depending upon the concentration of chromium salt used.

The rate of reaction was determined from the experimentally determinable data, by plotting log $[(A_s)_t - (A_s)_\infty]$ against time. The slope of the plot was determined and the specific rate constant was calculated, $k = 2.303$ slope/2. The reproducibility of determination of rates on identical solution was found to be within 2%.

Polymerization of Dihydroxydioxalatochromate(III).—Attempts to prepare the end product of aging of dihydroxydioxalatochromate(III) always led to compounds which indicated some degree of polymerization. The analysis of products recovered from completely aged solutions of dihydroxydioxalatochromate (III) indicated a polymer averaging between 3 and 4 chromium atoms per molecule.

Results and Discussion

The absorption curves obtained on freshly prepared hydroxydioxalatoaquochromate(III) and completely aged dimer are shown in Fig. 1 in the lower curves, where the logarithm of the absorbancy is plotted against the wave length. The upper curve is a plot of the absorbancy difference between the freshly prepared and the completely aged solutions. From these curves it may be seen that the rate of dimerization could be determined by observation of the change of absorbancy at 480 mμ.

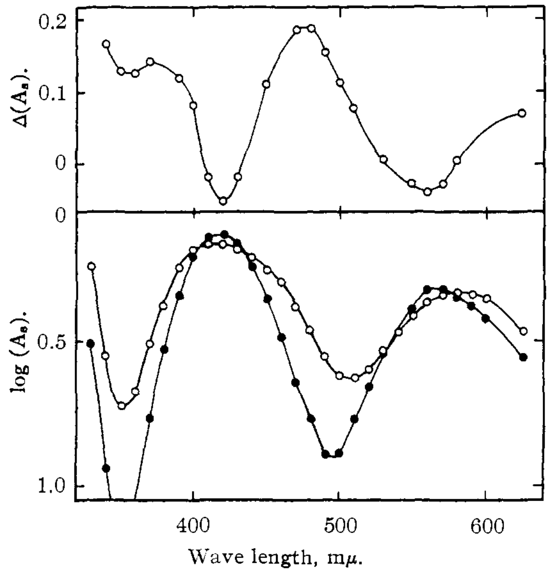


Fig. 1.—Visible absorption spectra of *cis*-hydroxyoxalatoaquochromate(III) solution, 0.020 *M* in 1-cm. cell. Upper curve is the absorbancy of a fresh solution taken with an aged solution as reference. The lower curves are: ○, fresh; ●, aged.

The results of a spectrophotometric titration of dioxalatodiaquochromate(III) with potassium hydroxide in which the absorbancy was measured at 420 and 480 mμ is shown in Fig. 2. The upper part of this figure shows the absorbancy plotted against *p*H and enables an estimation of the acid ionization constants of dioxalatodiaquochromate(III). The values estimated for *pK* are 6.4 and 8.8. The lower part of this figure indicates that there are formed two different hydroxy compounds.

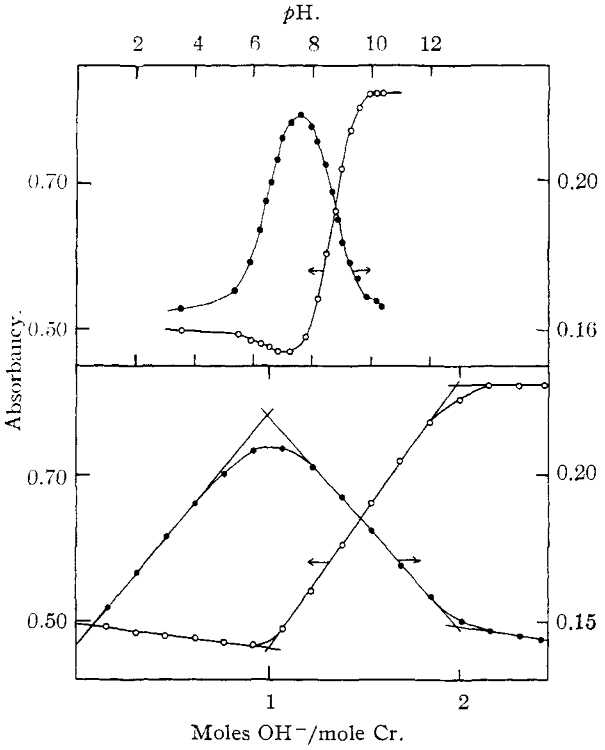
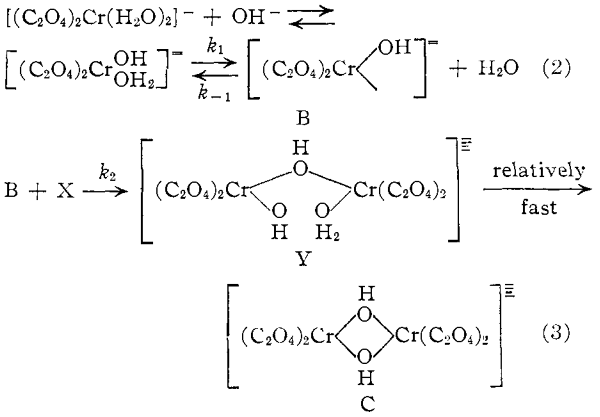


Fig. 2.—Spectrophotometric titration of dioxalatochromate (III) with sodium hydroxide: ○, 420 mμ; ●, 380 mμ.

Dimerization of *cis*-Hydroxydioxalatoaquochromate(III).—Preliminary investigations of this rate using 1-cm. cells and starting concentrations of total chromium of about 0.05 mole per liter indicated that the slow step in the reaction was first order in chromium. However, when this was checked over a wide concentration range using 2- and 10-cm. cells, it became apparent that there was an induction period preceding the slow first-order step, and that for solutions more dilute than 0.01 molar only a short section or none of the total reaction appeared to be first order. In all cases the points deviated from the first-order plot as the reaction approached completion. Points taken on very dilute solutions fitted a second-order plot fairly well. Since the reaction was not fitted by first-order kinetics in very dilute solution it was reasonable that the reactions should deviate from first-order kinetics as the concentration of the reacting species diminishes.

The following mechanism, which is in accord with these experimental facts, is proposed.

The mechanism of the reaction has been postulated to be a dissociation mechanism in order to explain the first-order dependence of the reaction. At high concentrations a mechanism through a hepta-coördinate intermediate is excluded because this would necessarily be second order in chro-



mium.[11] The final step of reaction (3) can be relatively rapid with respect to the slow step, or it can be that the difference in absorption spectra between Y and C is not experimentally significant. In either case the final formation of the diol bond would not be measurable by the method used in this investigation. We can express the rate of formation of the product

$$\text{rate} = k_2[\text{B}][\text{X}] \qquad (4)$$

and assuming a steady-state condition for the result of the dissociation product X.

$$\text{d}[\text{X}]/\text{d}t = k_1[\text{B}] - k_{-1}[\text{X}] - k_2[\text{B}][\text{X}] = 0 \qquad (5)$$

$$[\text{X}] = k_1[\text{B}]/(k_{-1} + k_2[\text{B}]) \qquad (6)$$

$$\text{rate} = k_1k_2[\text{B}]^2/(k_{-1} + k_2[\text{B}]) \qquad (7)$$

Under the conditions where $k_{-1} \gg k_2[\text{B}]$ we will have a second-order rate expression

$$\text{rate} = k_1k_2[\text{B}]^2/k_{-1} \qquad (8)$$

if, however, $k_2[\text{B}] \gg k_1$ the rate expression will be first order

$$\text{rate} = k_1[\text{B}] \qquad (9)$$

Experimentally this is the condition which has been found at concentrations above 0.01 mole per liter.

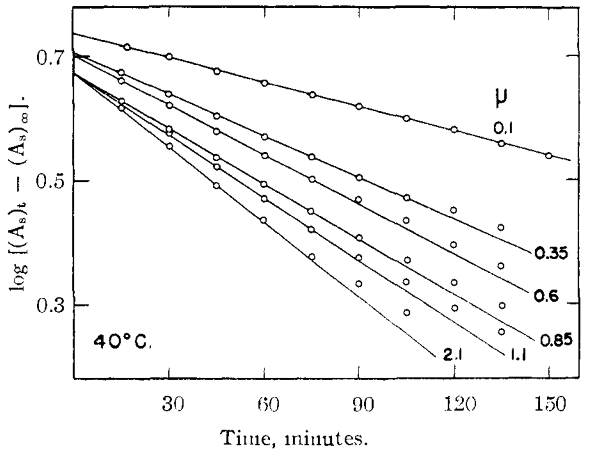


Fig. 3.—Dimerization rate determination at 40° and varying ionic strength.

Figure 3 shows a series of runs which have been made at 40° at different ionic strengths. It can be seen that the points begin to deviate from the straight lines at a point which is almost the same vertical position for each of the curves. This is in agreement with the expectation from the mechanism proposed above, that deviation from first order will occur when the concentration of the reacting species goes below a certain value. A similar set of runs was made at temperatures separated by 5° over the range 25 to 50°.

At 25° the induction period was very apparent. This induction period can be explained by the fact that the steady-state condition cannot be assumed during the initial period of the reaction. Integration of equation 5 at the boundary conditions $[\text{X}]_0 = 0$, $[\text{X}]_t = \text{X}$ and $[\text{B}] = \text{Const.}$, gave

$$[\text{X}] = \frac{k_1[\text{B}]}{(k_{-1} - k_2[\text{B}])}\{1 - e^{-(k_{-1} + k_2[\text{B}])t}\} \qquad (10)$$

This equation reduces to (6) when $(k_{-1} + k_2[\text{B}])t$ is large, which will depend upon both t and [B]. Thus at low values of [B] more time is required to reach the steady-state condition than at high values of [B]. Experimental values were taken of the time to reach the steady-state condition at 25° for various starting concentrations, $[\text{B}]_0$. These are plotted in Fig. 4, with time to reach steady state plotted against $[\text{B}]_0t$. From the slope of this plot a value of $k_{-1} = 10^{-3}k_2$ is obtained. This relationship between k_1 and k_2 is in accord with concentration limit at which the reaction appears to be first order.

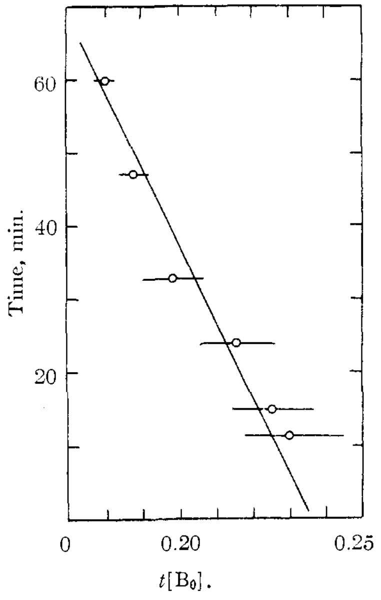


Fig. 4.—Plot of the time to reach the steady state against the product of the time and original concentration.

The values of the specific first-order rate constants determined are given in Table I.

For each of the ionic strengths given in k_rh/kT was plotted against $1/T$, where k_r is the rate constant, h is Planck's constant, k is the Boltzmann constant, and T is the Kelvin temperature. From these plots the heat of activation and entropy of

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[11] As far as the authors know this is the first direct evidence which enables one to exclude the hepta-coördinate intermediate in any reaction involving chromium(III); (a) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952); (b) C. Postmus and E. L. King, *ibid.*, **59**, 1216 (1955); (c) R. E. Hamm and R. H. Perkins, THIS JOURNAL, **77**, 2083 (1955).

TABLE I

RATE OF DIMERIZATION OF HYDROXYDIOXALATOAQUOCHROMATE(III) AS A FUNCTION OF TEMPERATURE AND IONIC STRENGTH

Rate constants given in sec.$^{-1}$ × 10^5.

Ionic strength	Temperature, °C. 25	30	35	40	45	50
0.10	0.277	0.87	1.66	2.52	3.78	6.5
0.35	0.75	1.30	2.40	4.28	6.9	10.6
0.60	0.85	1.83	3.25	5.1	8.9	12.6
0.85	1.08	2.12	3.68	5.6	10.3	14.4
1.10	1.21	2.27	4.08	6.5	11.0	17.1
2.10	1.80	2.80	4.84	8.0	12.6	20.4

activation were determined for each ionic strength by using the method of least squares. The heats and entropies of activation obtained are given in Table II. The plot of these values against the square root of the ionic strength was such that the method of least squares was used to evaluate the extrapolated values at zero ionic strength of $\Delta H^{\ddagger}$ = 22.5 kcal./mole and $\Delta S^{\ddagger}$ = −8 cal./mole degree.

TABLE II

HEATS OF ACTIVATION AND ENTROPIES OF ACTIVATION

Ionic strength	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, cal./mole degree
0.10	22.1	− 9.3
0.35	20.1	−14.7
0.60	19.9	−14.8
0.85	19.3	−16.4
1.10	19.6	−15.1
2.10	18.2	−19.4

The considerably lower values of the heat of activation at higher values of ionic strength are in accord with the idea that it should be much easier for a polar water molecule to leave the ion in the dissociation process.

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[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY]

Metal Fluorides as Acids in the Hydrogen Fluoride System

BY D. A. MCCAULAY, W. S. HIGLEY AND A. P. LIEN

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Various metal fluorides and other metal salts were evaluated as acids in the hydrogen fluoride system. In each test, a mixture of *m*- and *p*-xylene was treated with hydrogen fluoride plus the metal salt. In this medium, a fluoride may act as a Lewis acid and coördinate with a fluoride ion. The proton released then adds preferentially to *m*-xylene. Three fluorides proved to be strong acids: titanium tetrafluoride, columbium pentafluoride and tantalum pentafluoride. Phosphorus pentafluoride acted as a weak acid. The acidity of the fluorides was attributed to the high positive valence of the metal and its ability to form covalent bonds with fluorine. All acidic fluorides show about the same preference for *m*-xylene *vs.* *p*-xylene as does BF_3. The acid HF–TiF_4 also extracts, isomerizes and disproportionates arenes in the same manner as HF–BF_3. The arene cation is therefore the same regardless of the metal fluoride present.

Hydrogen fluoride, when promoted by boron trifluoride, is a strong acid. It is capable of donating a proton to even as weak a base as an alkylbenzene molecule.[1] The hydrogen fluoride, present in excess, acts as an ionizing solvent and furnishes the proton. The boron trifluoride participates by coördinating with the fluoride ion to form the fluoroborate ion

$$\text{Arene} + \text{HF} \rightleftarrows [\text{Arene}\cdot\text{H}]^+ + \text{F}^-$$

$$\text{BF}_3 + \text{F}^- \rightleftarrows \text{BF}_4^-$$

There is no reason why this property should be limited to boron trifluoride, and, therefore, other prospective fluoride ion acceptors were examined.

As many fluorides as could be readily purchased or easily prepared were tested. The fluorides rather than other salts were chosen to avoid reaction of the salt anion with hydrogen fluoride. If the fluoride could not be prepared, the chloride, oxide or carbonate was used with the hope that enough metal ion would go into solution for a test. The test procedure consisted of attempting to extract the weak bases, *m*- and *p*-xylene, from a solution in *n*-heptane by means of a mixture of hydrogen fluoride and the metal salt. The resulting composition of the hydrocarbon furnished a measure of the effectiveness of the fluoride. One of the acidic fluorides, titanium tetrafluoride, was examined in more detail for comparison with boron trifluoride in conversion reactions.

Experimental

Preparations of the fluorides, extraction experiments and conversion reactions were carried out in a 1570-ml. carbon-steel autoclave.[2] The hydrogen fluoride used, a commercial grade of 99.6% purity supplied by the Matheson Company, was distilled before each experiment. No effort was made to remove the last traces of water.

Lead fluoride (PbF_2), zirconium tetrafluoride, zinc fluoride, bismuth trifluoride, silicon tetrafluoride and antimony trifluoride were purchased as such and were used without purification.

Titanium tetrafluoride, tantalum pentafluoride and columbium pentafluoride were prepared from the corresponding chlorides by stirring with two equivalents of hydrogen fluoride for 1 hr. at room temperature. Conversion was rapid, as shown by a rapid rise in pressure due to liberation of hydrogen chloride. After the pressure had leveled off, the liberated hydrogen chloride and the excess hydrogen fluoride were removed by pumping. The metal fluorides were left in the reactor for use in the extraction experiments. Tungsten hexafluoride was prepared from tungsten hexachloride in a similar manner, except that the liberated hydrogen chloride was not pumped off because of the high volatility of tungsten hexafluoride, which boils at 17.5°.

Cadmium fluoride was prepared from the carbonate by stirring with two equivalents of hydrogen fluoride for 1 hr. at room temperature. Pumping for 1 hr. at 100° removed the carbon dioxide, water of reaction and excess hydrogen fluoride.

Phosphorus pentafluoride was prepared from benzene dia-

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(1) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

(2) D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).