TABLE II

ASSOCIATION CONSTANTS OF SOME COMPLEX SULFATES[a]

Ion	K_1, $(MSO_4)/(M)(SO_4)$	K_2/K_1, $M(SO_4)_2/(MSO_4)(SO_4)$	Remarks
U^{+4} [17]	1740	150	25°, $\mu = 3.5$, $(H^+) = 2.0$
Th^{+4} [18,b]	2100	240	25°, $\mu = 2.0$, (H^+) varied
Zr^{+4} [19,c]	6140	708	25°, $\mu = 2.0$, $(H^+) = 2.0$
Fe^{+3}	107	9	28°, $\mu = 1.0$, (H^+) varied
Ce^{+3} [6]	60		25°, $\mu = 0.5–0.9$, $(H^+) \sim 10^{-3}$
Ce^{+3} [20]	34		25°, $\mu = 0.5$, $(H^+) \sim 10^{-2}$
	17.5		$\mu = 1.0$, $(H^+) \sim 10^{-2}$
Cu^{++} [21]	4		25°, $\mu = 1.0$
Cu^{++} [22,d]	9		20°, $\mu = 1.0$
Cd^{++} [23]	7		$\mu = 3.0$
VO_2^{++} [24]	67		25°, $\mu = 3.5$, $(H^+) = 2.0$
Ag^{+} [23]	1.7	1	$\mu = 3.0$

[a] For the sake of intercomparison of results, equilibrium constants for the reaction $M + HSO_4^- \rightarrow MSO_4 + H^+$ have been converted to the form presented here using $K_{HSO_4^-} = 0.075$. [b] The authors use 0.084 for $K_{HSO_4^-}$; for comparative purposes, the results have been recalculated for $K_{HSO_4^-} = 0.075$. There is evidence for the formation of $Th(SO_4)\cdot(HSO_4)^+$ at high acidity. [c] A value for $[Zr(SO_4)_3^=]/[Zr(SO_4)_2](SO_4^=)$ of 1 was also measured. [d] The formation of $Cu(SO_4)_3^{-4}$ was also inferred.

sulfate, not bisulfate (see however footnote (b) of Table II).

The ionic radii of Ce^{+3} and Fe^{+3} are quite different, 1.02 and 0.60 Å., respectively.[25,26] Nevertheless, these two tripositive cations have about the same affinity for $SO_4^=$. They also have about the same affinities for Cl^- and NO_3^-: $K_{CeCl^{++}} = 0.8–1.1$ ($\mu = 0.4–1.5$)[6]; $K_{FeCl^{++}} = 4$, ($\mu = 1.0$)[14]; $K_{CeNO_3^{++}} \sim 1$, ($\mu = 0.89$)[6]; $K_{FeNO_3^{++}} = 6.8–0.6$, ($\mu = 0.066–0.6$, 18°),[5] 0.3, ($\mu = 1$, 25°).[27] On the other hand, the relative affinities of Fe^{+3} and Ce^{+3} for OH^- are quite different, their hydrolysis constants being 2.0×10^{-3} and 5×10^{-8}, respectively, at $\mu = 1$.[28]

It may be noted that, at present, there is no decisive evidence on the question of whether, in some of these complexes, the complexing anion is in the first coördination sphere of the cation, displacing water molecules, or whether the anion and cation are separated by a layer of water molecules, in which case these are pure "ion-pair" complexes.

Acknowledgments.—We are indebted to Professor E. H. Swift for stimulating advice and suggestions. This research has been supported by the Atomic Energy Commission under contract AT-(11-1)-188.

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(17) Data of R. H. Betts and R. Leigh (*Can. J. Research*, **B28**, 514 (1950)) reinterpreted by J. C. Sullivan and J. C. Hindman (THIS JOURNAL, **74**, 6091 (1952)).

(18) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

(19) R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

(20) T. W. Newton and G. M. Arcand, ref. 10.

(21) R. Näsänen, *Acta Chem. Scand.*, **3**, 179 (1949).

(22) S. Fronaeus, *ibid.*, **4**, 72 (1950).

(23) I. Leden, *ibid.*, **6**, 97 (1952).

(24) R. H. Betts and R. K. Michels, *J. Chem. Soc.*, S286 (1949).

(25) W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

(26) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 330.

(27) J. A. Ibers and N. Davidson, THIS JOURNAL, **73**, 476 (1951).

((28) T. Moeller, *J. Phys. Chem.*, **50**, 242 (1946). We have multiplied the value of 1×10^{-9} given by Moeller by 50 to correct for the estimated effect of sulfate on his hydrolysis experiments.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Complex Ions of Chromium. III. Reactions between Hexaquochromium(III) and Oxalate Ions[1]

BY RANDALL E. HAMM AND ROBERT E. DAVIS

RECEIVED NOVEMBER 21, 1952

The formation of dioxalatodiaquochromate(III) ion from hexaquochromium(III) and oxalate ions was shown to be rate limited by two consecutive slow reactions. The slowly reacting species could be reduced at a dropping mercury electrode at half-wave potentials of −0.90 and −1.15 volts *vs.* the saturated calomel electrode. The rates of reaction of the two species were determined by measuring currents at the diffusion plateaus. The reactions were found to be consecutive and first order with respect to the reacting species. The first reaction rate was inversely proportional to hydrogen ion concentration, and the second reaction rate was independent of hydrogen ion concentration. Both rates were independent of oxalate ion concentration. Mechanisms for the reactions were postulated, and some of the intermediates were isolated and identified. Rate constants, heats and entropies of activation for the two slow reactions were reported.

In the study of the oxidation of oxalic acid by potassium dichromate, Werner[2] showed that for potassium dichromate–oxalic acid ratios between 1:1 and 1:9, potassium dioxalatodiaquochromate(III) was always a product. Croft[3] demonstrated that addition of alkali oxalate to a boiling solution of the dioxalatodiaquochromate(III) gave trioxalatochromate(III) ion. These facts suggested that it might be interesting to investigate the formation of the oxalate complexes by direct reaction of oxalate and chromium(III) ions. The existence of a monoxalate complex would also be investigated, even though no mention has been made of it in the literature. Wyrouboff[4] showed that addition of neutral alkali oxalates to chromium(III) salt solutions resulted in the formation of a "practically insoluble" chromium oxalate, indicating that in order to study the direct reaction of hexaquochromium(III) and oxalate ions, dilute solutions would be necessary in order to avoid precipitation. Polarographic measurements were found to be ideal for following the course of such reactions in dilute solutions.

Preliminary polarograms of solutions of approximately 10^{-3} *M* hexaquochromium(III) ion in excess oxalate ion showed the formation of two re-

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(1) The work on this investigation was supported by the National Science Foundation Research Grant, NSF-G62.

(2) E. A. Werner, *J. Chem. Soc.*, **53**, 602 (1888).

(3) H. Croft, *Phil. Mag.*, **21**, 197 (1842).

(4) A. Wyrouboff, *Bull. soc. mineral. Franc.*, **24**, 86 (1901).

ducible substances whose concentrations varied with time.

It was the purpose of this research to investigate the kinetics of the reactions involving the two reducible species, and to attempt to establish the identity of the intermediate ions taking part in the reactions.

Experimental

Apparatus and Materials.—Polarograms were run with a Sargent model XII polarograph. The rate studies were made with a Sargent model XXI polarograph. Both polarographs were equipped with external potentiometric circuits in order that the potentials being applied to the cell could be determined accurately. All polarographic measurements were made with an H-type cell which had a saturated calomel electrode in one side, a saturated potassium chloride–agar bridge in the cross member, and approximately 25 ml. of the solution under investigation in the other side. All measurements were made with the cell suspended in a constant temperature bath which was maintained within 0.05° of the desired temperature. Dissolved oxygen was removed from all solutions by bubbling pure hydrogen through the solutions.

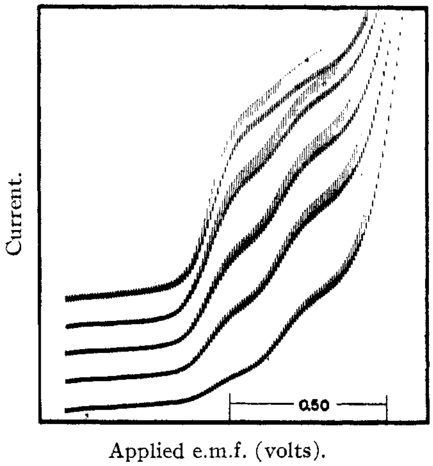

Fig. 1.—Polarograms of 1.00 m*M* chromium(III) nitrate in 0.10 *M* potassium oxalate adjusted to *p*H 5.09 and ionic strength 0.30. Recording of waves started 5, 25, 50, 75 and 125 minutes after mixing the solution. Each recording started at −0.500 volt *vs.* S.C.E.

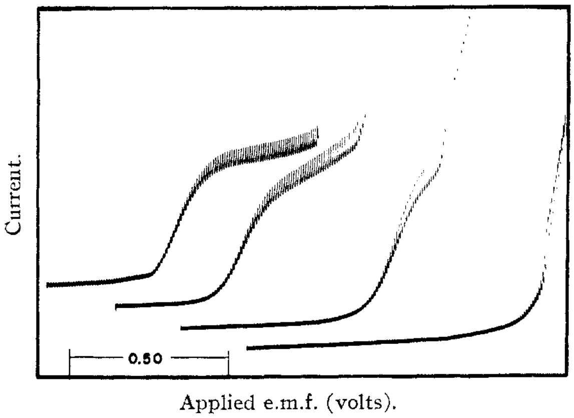

Fig. 2.—Polarograms of 0.001 *M* chromium(III) nitrate, 0.001 *M* chromium(III) nitrate–potassium oxalate (fresh), 0.001 *M* chromium(III) nitrate–potassium oxalate (boiled), and 0.001 *M* *cis*-potassium dioxalatodiaquochromate(III), in a supporting electrolyte of 0.30 *M* potassium nitrate with 0.005% gelatin. Each recording started at −0.500 volt *vs.* S.C.E.

Conductometric titrations were performed, using a 10-ml. buret, and a conductivity bridge which was equipped with an oscilloscope as a null indicator. The titrations were performed in a 400-ml. beaker using platinum disk electrodes. The resistance of the solutions could be determined with a precision of 0.1 to 0.5% under the conditions of the titrations. Complete titration curves were determined in about 15 minutes so that errors due to slow secondary reactions were negligible.

Reagent grade chromium(III) nitrate and potassium oxalate were used as sources of reacting ions. The hydrogen ion concentration was adjusted by adding one-tenth normal, reagent grade, perchloric or nitric acid solution. Reagent grade potassium perchlorate or potassium nitrate was used to adjust ionic strength.

The *p*H of the solutions was determined with a Beckman model G *p*H meter, which was calibrated with a Beckman buffer at *p*H 4.01.

Procedure.—The reaction rate constants were determined by a method similar to that used by Hamm and Shull.[5] The voltage of the diffusion current plateau was applied to the cell, and the current was recorded on the chart which moved at the rate of one-half inch per minute. The voltages on the diffusion current plateaus which were used were −1.08 and −1.31 volts *vs.* S.C.E. for the first and second reactions, respectively.

The solutions for the determination of the rate of the first reaction were prepared by adding 10.0 ml. of 0.0100 *M* chromium(III) nitrate solution to a 100-ml. volumetric flask which contained 0.0100 mole of potassium oxalate solution, enough nitric or perchloric acid to give the desired *p*H, enough potassium nitrate or potassium perchlorate to give the desired ionic strength, 0.50 ml. of 1% gelatin solution, and water to dilute to volume. The solutions used for the determination of the rate of the second reaction were similarly prepared except for using a thoroughly aged solution which was 0.0100 *M* with respect to both chromium(III) nitrate and potassium oxalate instead of the chromium nitrate solution.

The methods of analysis of the salts and solutions containing chromium and oxalate were similar to those reported by Hamm.[6]

Results and Discussion

Figure 1 shows polarograms of solutions of 1.00 m*M* chromium(III) nitrate in 0.100 *M* potassium oxalate and 0.005% gelatin, adjusted to *p*H 5.09 and ionic strength 0.30, taken 5, 25, 50, 75 and 125 minutes after mixing. Figure 2 shows polarograms of solutions of 1.00 m*M* chromium(III) nitrate, 1.00 m*M* chromium(III) nitrate–potassium oxalate (fresh), 1.00 m*M* chromium (III) nitrate–potassium oxalate (boiled), and 1.00 m*M* *cis*-potassium dioxalatodiaquochromate(III), all in 0.30 *M* potassium nitrate supporting electrolyte with 0.005% gelatin.

Comparison of the half-wave potentials of the polarograms of Figs. 1 and 2 shows that the first wave in Fig. 1 is due either to hexaquochromium(III) ion, the ion present in fresh equimolar chromium(III)–oxalate solutions or else both of these ions. The second wave of Fig. 1 is due to the species which is present in boiled equimolar chromium(III)–oxalate solutions. The half-wave potentials of these two waves are −0.90 and −1.15 volts *vs.* S.C.E.

Conductometric titrations of 250 ml. of 0.0100 *M* chromium(III) nitrate with 0.500 *M* oxalic acid and with 0.500 *M* potassium oxalate were performed. In the case of titration with oxalic acid, the slope of the titration curve, when plotting conductance *vs.* volume of added titrant, was slightly less after one mole of oxalate per mole of chromium

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[5] R. E. Hamm and C. M. Shull, Jr., THIS JOURNAL, **73**, 1240 (1951).

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

had been added, while in the case of titration with potassium oxalate the slope was slightly greater after adding one mole of oxalate per mole of chromium. The reactions which were postulated to explain these results were

$$Cr(H_2O)_6{}^{+++} + H_2C_2O_4 \longrightarrow Cr(C_2O_4)(H_2O)_5{}^{+} + 2H^{+} + H_2O \quad (1)$$

$$Cr(H_2O)_6{}^{+++} + C_2O_4{}^{=} \longrightarrow Cr(C_2O_4)(H_2O)_5{}^{+} + H_2O \quad (2)$$

The decrease in slope in the oxalic acid titration was due to the discontinuance of production of free hydrogen ions, and the increase in slope in the potassium oxalate titration was due to the free oxalate ions which were no longer used to complex after one oxalate ion had been added to each chromium ion.

The solutions which resulted from both of the above titrations had a pale green color. A fresh green solution which was equimolar with respect to chromium(III) and oxalate ions gave a precipitate with either ammonium hydroxide or calcium chloride. This evidence along with the conductometric titrations indicated that the green species was a loosely bound complex ion of one oxalate per chromium, and that this complex ion was in equilibrium with hexaquochromium(III) and oxalate ions.

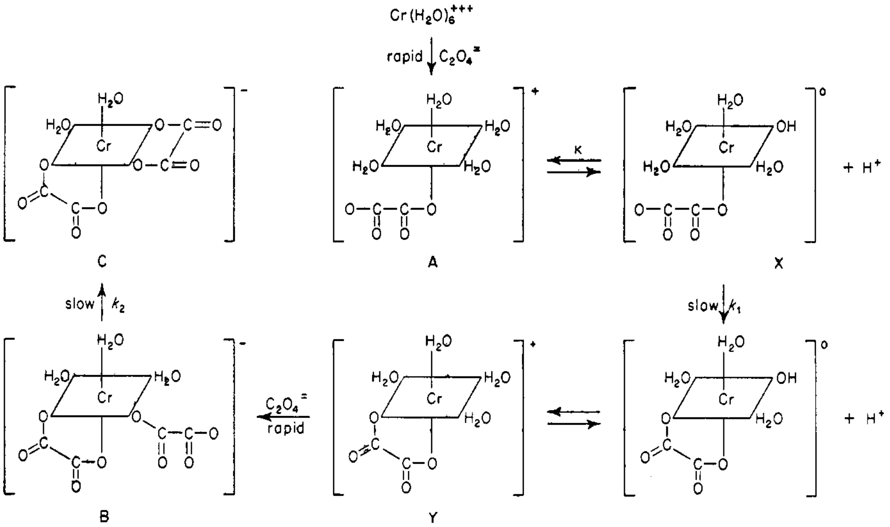
When one of the equimolar green solutions was allowed to stand for several hours at room temperature, or when it was boiled for several minutes, the color changed to a reddish-purple, and the resulting solution no longer gave a precipitate with either ammonium hydroxide or calcium chloride, indicating that a stable complex ion with one oxalate per chromium had been formed. The transition of the green species to the reddish-purple species corresponded to the disappearance of the first polarographic wave of Fig. 1, and the reaction of the reddish-purple species in the presence of excess oxalate corresponded to the disappearance of the second wave of Fig. 1.

At any given pH, plots of the logarithm of the wave height (*i.e.*, concentration) of the first reducible species *vs.* time were straight lines, indicating that the first slow reaction was first order with respect to the first reducible species. When the first reactant was not present, that is, when equimolar boiled chromium(III) nitrate–potassium oxalate solution was used as starting material, the concentration of the second reducible species also decreased exponentially with time.

A plot of the logarithm of the reaction rate constants for the first reactions *vs.* pH was a straight line with a slope of about one. This indicated that either the reaction was second order (depending on hydroxyl ion concentration as well as the concentration of the reducible species) or that a hydrogen ion equilibrium was involved. In the pH range used in the investigation the latter assumption seemed more probable. The rate of the second reaction was found to be independent of hydrogen ion concentration.

Reaction rate constants determined at various oxalate ion concentrations indicated that both of the slow reactions were essentially independent of oxalate concentration. This was further demonstrated by preparing solutions in which the original oxalate ion concentration was equal to the original concentration of the reacting chromium species. Under these conditions a plot of the logarithm of the concentration of the reacting chromium species *vs.* time was a straight line for a period equal to at least twice the half-time of the reaction.

Mechanisms which are consistent with all of the above data are



(3)

The rate expression for the disappearance of the first reducible species may be written

$$d[Cr_t]/dt = -k_1[X] \quad (4)$$

where $[Cr_t]$ represents the total concentration of chromium species that are reducible at the first wave potential. Making an appropriate algebraic substitution for the equilibrium constant, K and the hydrogen ion concentration, the expression may be written

$$d[Cr_t]/dt = -k_1K[Cr_t]/(K + [H^+]) \quad (5)$$

From this equation it is apparent that the measured rate constant, k_1', is related to the real first-order rate constant, k_1, by

$$k_1' = k_1K/(K + [H^+]) \quad (6)$$

Since any free oxalate or chromium(III) ions tended to buffer the solution, and since the final reaction occurred rapidly under alkaline conditions, it was impossible to get a direct measurement of the equilibrium constant, K. A value of 1.0×10^{-6} was used in calculations as this value brought a great degree of uniformity to the rate data. It can be seen from equation 6 and Table I that a value differing greatly from 1.0×10^{-6} would not be in accord with the rate data presented. The value that is selected makes little difference in the heat of activation but is critical for the final value calculated for the entropy of activation.

In the second column of Table I are shown the values of pk_1' determined in solutions of various hydrogen ion concentrations, which were 0.100 *M* with respect to oxalate ion, and which had an ionic strength of 0.30. The final column shows the values of pk_1 calculated by means of equation 6.

TABLE I

Temperature, 25.0°

pH	pk_1'	pk_1
4.42	4.13	2.54
4.52	4.03	2.54
4.73	3.85	2.58
5.10	3.53	2.58
5.15	3.48	2.57
5.18	3.44	2.56
5.30	3.33	2.55
5.49	3.21	2.58
5.71	2.96	2.49

Av. $pk_1 = 2.55$ with std. deviation 0.03

In order that the mechanism of the second slow step in the reaction be consistent with the experimental results, it is necessary to assume that species Y reacts by a very rapid reaction to give species B. If this is true, the rate actually being measured may be represented by

$$d[B]/dt = -k_2[B] \tag{7}$$

The average of 17 values of pk_2 determined over a pH range of 4.25 to 6.19, from rate experiments on thoroughly aged monoxalatochromium(III) and added oxalate, was 3.51 with a standard deviation of 0.12.

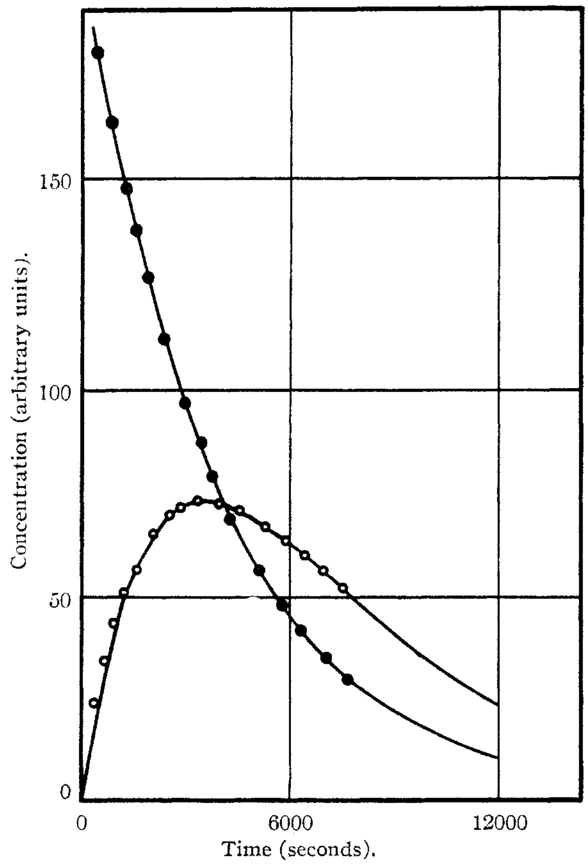


Fig. 3.—Concentration of the first and second reducible species as functions of time. Lines are theoretical curves: ●, first species; O, second species are experimental values.

These facts indicate that the two slow first-order reactions are consecutive, and of the form

$$A \longrightarrow B \longrightarrow C \tag{8}$$

The rate equations are

$$d[A]/dt = -k_1'[A] \tag{9}$$

$$d[B]/dt = k_1'[A] - k_2[B] \tag{10}$$

with the solution

$$[B] = \frac{ak_1'}{(k_2 - k_1')}\left(e^{-k_1't} - e^{-k_2t}\right) \tag{11}$$

Figure 3 shows the relative concentrations of the first and second reacting species plotted as functions of the time after mixing 1.00×10^{-4} mole of hexaquochromium(III) ion with 0.0100 mole of oxalate ion and diluting with nitric acid, potassium nitrate solution, and water to give 100 ml. of solution with ionic strength 0.30 and pH 5.09. A plot of the natural logarithm of the concentration of the first reactant *vs.* time was a straight line of slope -2.48×10^{-4} sec.$^{-1}$. The concentration of the second reactant was found to be represented very closely by the function

$$[B] = 908\left(e^{-2.48\times10^{-4}t} - e^{-3.10\times10^{-4}t}\right) \tag{12}$$

which is plotted as the theoretical curve shown in Fig. 3, while the points were the actual experimental values. It should be noted that the value of k_2 used to fit the curve in Fig. 3 is the value determined under similar conditions from direct experiment on the monoxalatochromium(III).

According to the theory of absolute reaction rates

$$\ln\frac{k_nh}{kT} = \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \tag{13}$$

where k_n is either k_1 or k_2, and k, h and T are the Boltzmann constants, Planck's constant and the absolute temperature, respectively. Plots of log k_nh/kT *vs.* $1/T$ were nearly straight lines, and the slopes and intercepts of the lines were determined by the method of least squares, and the results are summarized in Table II.

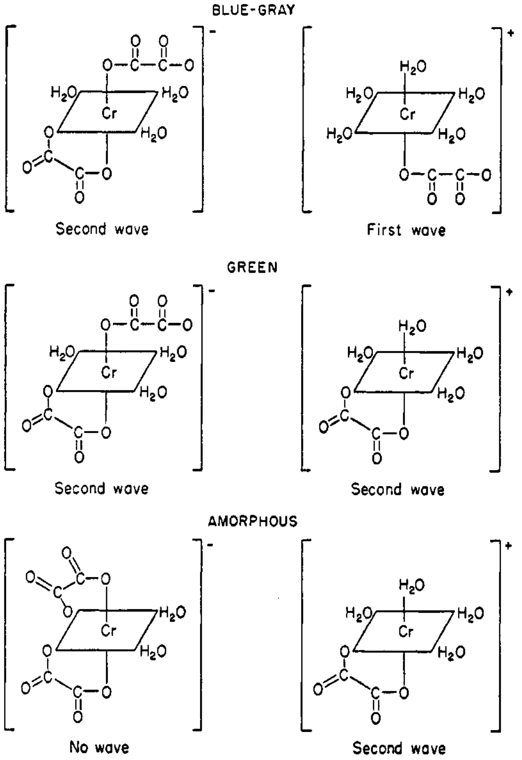
TABLE II

	$\Delta H^{\ddagger}$ kcal./mole	Std. dev.	$\Delta S^{\ddagger}$, cal./deg. mole	Std. dev.
First reacn.	23.2	0.9	7.5[a]	2.9[a]
Second reacn.	23.7	.6	4.4	1.9

[a] Values calculated using $K = 1.0 \times 10^{-6}$ at 25°.

The fact that the activation constants for the two reactions do not differ significantly further substantiates the hypothesis that the two slow steps involve similar mechanisms as illustrated in (3).

Figure 4 shows polarograms of solutions of four forms of a substance which chemical analysis has shown to be $Cr_2(C_2O_4)_3{\cdot}xH_2O$. The silver-gray salt was the form of chromium oxalate which was first prepared by Wyrouboff[4] and later studied by Rosenheim and Cohn.[7] The blue-gray salt was the product formed by allowing the silver-gray salt to stand in air for several months. The green salt was formed by heating either the silver-gray or the blue-gray salt to 110° for one hour. The amorphous form was prepared by enclosing either the silver-gray or blue-gray forms in a container which contained small amounts of water or water vapor.



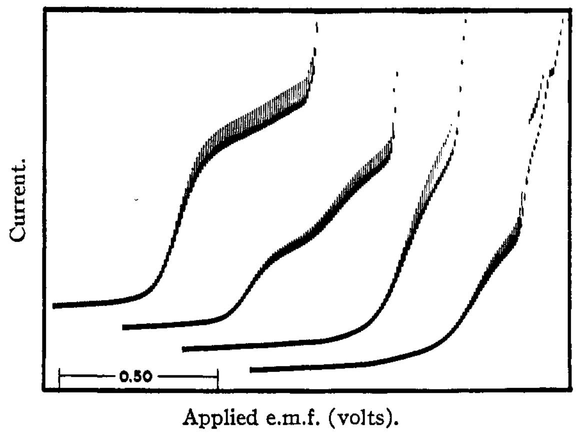


Fig. 4.—Polarograms of solutions of 0.050 g. of silver-gray, blue-gray, green and amorphous chromium(III) oxalate dissolved in 100 ml. of 0.30 *M* potassium nitrate and 0.005% gelatin. Each recording started at −0.500 volt *vs.* S.C.E.

The silver-gray salt was probably composed of hexaquochromium(III) and oxalate ions, but it went into solution as the green equilibrium mixture of species A and X which reacted with the excess oxalate until finally an equimolar mixture of monoxalatotetraquochromium(III) and dioxalatodiaquochromate(III) ions was formed.

The blue-gray salt contained some complexed oxalate as indicated by the presence of the second wave. The green salt contained only the second reducible species in which the oxalate is completely bound (no precipitate was obtained from a solution of the green salt when calcium chloride was added). The amorphous substance contained the second reducible species in about one-half the concentration of a comparable solution of the green salt. From the above observations, the above structures have been proposed for the positive and negative complex ions that exist in these compounds.

SALT LAKE CITY, UTAH

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(7) A. Rosenheim and R. Cohn, *Z. anorg. Chem.*, **28**, 337 (1901).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. III. Kinetics of Aquation of Some Cobalt(III) Complex Ions[1,2]

BY RALPH G. PEARSON, CHARLES R. BOSTON AND FRED BASOLO

RECEIVED FEBRUARY 2, 1953

Rates of aquation have been measured for a series of compounds of the type, *trans*-$[Co(AA)_2Cl_2]^{+1}$, in which the steric properties of the bidentate (AA) group were varied. It was found that in almost every case an increase in size or steric crowding of the bidentate was accompanied by an increase in the rate of aquation. This has been interpreted as evidence for the five coördinated intermediate of the SN1 or dissociation mechanism, and against the seven coördinated activated complex of the SN2 or displacement mechanism.

In the previous papers of this series the problem of determining the mechanism of substitution reactions in complex ions has been approached in two different ways. In the first paper,[3] the group being replaced was varied (with respect to both its size and base strength) and the resulting changes in rates of aquation and hydrolysis were studied. In the second paper,[4] a stereochemical approach to the problem was made by measuring the relative amounts of *cis* and *trans* isomers obtained during substitution reactions involving geometric isomers. The present paper concerns itself with still a third

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(1) Some of this material was presented as a communication, THIS JOURNAL, **74**, 2943 (1952).

(2) This investigation was supported by a grant from the United States Atomic Energy Commission under contract AT(11-1)-89-Project No. 2.

(3) F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

(4) F. Basolo, B. D. Stone and R. G. Pearson, THIS JOURNAL, **75**, 819 (1953).