The Rate of Aquation of Sulfatopentaaquochromium(III) Ion in Acidic, Aqueous Solution

BY JAMES E. FINHOLT AND STANLEY N. DEMING

The rate of aquation of sulfatopentaaquochromium(III) ion has been studied in acidic, aqueous solution of unit ionic strength as a function of temperature and hydrogen ion concentration. Three reaction pathways were observed: all were first order with respect to sulfatochromium(III), but the pathways were +1, 0, and −1 order with respect to hydrogen ion. The activation parameters, ΔH^* and ΔS^*, were evaluated for each pathway.

Introduction

This paper presents a study of the rate of aquation of the sulfatopentaaquochromium(III) ion (hereafter called the sulfatochromium(III) ion). The net equation for the reaction at all but the lowest hydrogen ion concentrations is shown

$$Cr(H_2O)_5SO_4^+ + H^+ + H_2O \longrightarrow Cr(H_2O)_6^{3+} + HSO_4^- \quad (1)$$
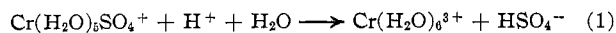
At the lowest hydrogen ion concentrations studied SO_4^{2-} is probably a more important species than HSO_4^-. In recent years a number of studies have been made of the aquation kinetics of species having the general formula CrX^{2+}, where X is a singly charged negative ion.[1-5] Equation 2 represents the general reaction.

$$Cr(H_2O)_5X^{2+} + H_2O \longrightarrow Cr(H_2O)_6^{3+} + X^- \quad (2)$$
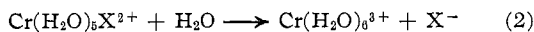
The sulfate ligand has been shown to be a monodentate ligand,[6] and it carries a charge of −2. Thus, this study allows the effect of ligand charge on the rate of aquation to be examined by comparing the aquation kinetics of the sulfatochromium(III) ion with the aquation kinetics of chromium species containing singly charged negative ligands.

Experimental Section

Reagents.—Distilled water was used in preparing all solutions. Lithium perchlorate was recrystallized twice from distilled water. Reagent grade perchloric acid was used without further purification. Monosulfatopentaaquochromium(III) perchlorate was prepared as described elsewhere.[6] Dowex AG 50W X8 200–400 mesh cation-exchange resin was used in all experiments.

Kinetics Experiments.—The reaction was carried out in a 1-l. glass bottle immersed in a constant-temperature bath. About 0.5 l. of solution was used in each run. All runs were made in the dark. The reaction was initiated by pipetting 3 ml of sulfatochromium(III) solution into an appropriate mixture of perchloric acid and lithium perchlorate. The solution was stirred during the addition of the chromium(III) solution and for 5 min thereafter.

The reaction flask contained a glass sampling tube running from the bottom of the bottle up and out over the edge of the water bath. This tube was connected to a U-shaped collecting tube which was immersed in an ice bath. Samples were removed by using a low pressure of about 200 mm to suck solution into the U-shaped receiver. This arrangement allowed a sample to be quenched from 80 to 20° in 30 sec. Samples were stored from 1 to 3 days at 0° before being analyzed. In most runs 10 samples were taken. The reaction was followed from 12 to 72 hr, during which time the concentration of the sulfatochromium(III) usually fell to about 10% of its initial value.

The ratio of $CrSO_4^+/Cr^{3+}$ in each sample was determined by an ion-exchange procedure. An ion-exchange column with a resin bed 20 cm in length and having a volume of 10 ml was prepared. A 20-ml volume of sample was pipetted onto the column and then eluted with 20 ml of 1 M perchloric acid. All of the hexaaquochromium(III) was held on the column while all of the sulfatochromium(III) was displaced and collected in a volumetric flask. The sulfatochromium(III) solution was then subjected to alkaline peroxide oxidation and diluted to volume; then the absorption was measured at the chromate maximum, 372 mμ. A total-chromium analysis was done on the first, eighth, and last sample of each experiment. Tests showed that more than 99% of the sulfatochromium(III) was recovered by this method with no contamination by hexaaquochromium(III).

All solutions were prepared at room temperature and made up so that the ionic strength was 1.00 at 25°. Hydrogen ion concentrations were corrected for the expansion of the solution at higher temperatures by assuming that the solutions would have the same coefficient of expansion as water. A correction factor, $V_T/V_{25°}$, of 1.0091 was used at 50°, 1.0168 at 65°, and 1.0260 at 80°.[7]

Throughout the first part of the study the sampling tube was immersed in the solution before the sulfatochromium(III) solution was added to initiate the reaction. This caused an error in the sulfatochromium(III) concentration in the first sample. The total chromium(III) concentration in the first sample was 1–3% lower than the total chromium(III) concentration in later samples. It was assumed that the sulfatochromium(III) concentration in the first sample was in error by the same factor, so a corrected sulfatochromium(III) concentration for the first sample was used in calculating the rate constants. The corrections were made using eq 3. The subscripts refer to the sample num-

$$[CrSO_4^+]_{cor} = [CrSO_4^+]_1 \frac{[Cr_{tot}]_8}{[Cr_{tot}]_1} \quad (3)$$

ber. In later runs the sampling tube was not inserted into the reaction solution until after the reaction had been initiated. Several of the earlier runs were repeated using this improved technique and essentially the same results were obtained as were obtained from the earlier runs using a corrected first point.

Experiments were made at three temperatures: 50, 65, and 80°. At each temperature, runs were made at hydrogen ion concentrations of 1, 0.5, 0.2, 0.1, and 0.05 M. The initial sulfatochromium(III) concentration was 3×10^{-3} M in most runs, but in a few cases it was 1.5×10^{-3} M. Under these conditions

(1) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).
(2) F. A. Guthrie and E. L. King, *ibid.*, **3**, 916 (1964).
(3) J. H. Espenson and D. E. Binau, *ibid.*, **5**, 1365 (1966).
(4) T. W. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964).
(5) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).
(6) J. E. Finholt, R. W. Anderson, J. A. Fyfe, and K. G. Caulton, *Inorg. Chem.*, **4**, 43 (1965).

(7) R. C. West and S. E. Selby, Ed., "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, pp F4, F5.

the reaction is pseudo-first order. At the lowest hydrogen ion concentration a maximum of 4% of the hydrogen ions would be consumed if the reaction went to completion.

Results

The rate of aquation of sulfatochromium(III) under conditions of constant hydrogen ion concentration is given by

$$-\frac{d[CrSO_4^+]}{dt} = k[CrSO_4^+] - k'[Cr^{3+}][HSO_4^-] \quad (4)$$

When eq 4 is integrated and k' is eliminated, one obtains

$$k = \frac{2.30([Cr_{tot}] - [CrSO_4^+]_\infty)}{t([Cr_{tot}] + [CrSO_4^+]_\infty)} \log$$
$$\left\{ \frac{([Cr_{tot}]^2 - [CrSO_4^+][CrSO_4^-]_\infty)([CrSO_4^+]_0 - [CrSO_4^+]_\infty)}{([Cr_{tot}]^2 - [CrSO_4^+]_0[CrSO_4^+]_\infty)([CrSO_4^+] - [CrSO_4^+]_\infty)} \right\} \quad (5)$$

In deriving eq 5, it was assumed that the initial concentration of hexaaquochromium(III) ion was not zero. It was not necessary to make any allowance for the fact that some, or most, of the sulfate present might be SO_4^{2-} rather than HSO_4^-. The hydrogen ion concentration was essentially constant in each experiment; therefore, the ratio $[SO_4^{2-}]/[HSO_4^-]$ was also constant throughout each experiment. Thus, the constant, k', may actually not be a true rate constant, but since it does not appear in eq 5, it does not matter. The zero time of the reaction was taken to be the time at which the first sample was taken rather than the time at which sulfatochromium(III) was added to the reaction vessel. This procedure has the advantage that the presence of a small amount of hexaaquochromium(III) in the stock sulfatochromium(III) solution will not affect the results. A second advantage is that one need not be concerned with the amount of time required for mixing. The major disadvantage of this procedure is that eq 5 is made more complex than it would be if the initial concentration of hexaaquochromium(III) were zero. Since all of our calculations were carried out on a computer, this was not very important.

A nonlinear least-squares technique based on methods developed by Wentworth was used to determine the pseudo-first-order rate constant in each experiment.[8] In order to use eq 5, it is necessary to know the equilibrium, or infinite time, value of the sulfatochromium(III) concentration. A least-squares analysis was used to calculate the equilibrium sulfatochromium(III) concentration at the same time as the rate constant was determined. With this procedure it was not necessary to follow each experiment until it reached equilibrium. A FORTRAN computer program was written to carry out these calculations on the Carleton IBM 1620 computer. The procedure was checked by running test calculations with artificially prepared data. If the data are good, both the rate constant and the equilibrium concentration can be determined, even if the reaction proceeds only 15% of the way to equilibrium. These tests also revealed that an error of 1% in the

(8) W. E. Wentworth, *J. Chem. Educ.*, **42**, 162 (1965).

initial sulfatochromium(III) concentration would produce an error of about 1% in the rate constant and an error of about 2% in the equilibrium concentration of the sulfatochromium(III). Thus, the method is not a good one for determining equilibrium constants, but it works well for kinetic investigations. In a few cases the reactions were allowed to proceed to equilibrium and the actual equilibrium concentrations were found to be in good agreement with the concentrations calculated using only data from the first part of the experiment.

Table I presents a summary of the results of all experiments. The least-squares k values reported in Table I agree very well with an average of k values obtained directly through the use of eq 5. In no case did the difference exceed 1%.

TABLE I

VALUES OF THE PSEUDO-FIRST-ORDER RATE CONSTANT[a]

$$-d[CrSO_4^+]/dt = k[CrSO_4^+]$$

50.0°		65.1°		80.3°	
$[H^+]$, M[b]	$10^5 k$, sec^{-1}	$[H^+]$, M[b]	$10^5 k$, sec^{-1}	$[H^+]$, M[b]	$10^5 k$, sec^{-1}
0.991	1.84[c]	0.983	9.76[c]	0.969	44.5[c]
0.496	1.68[c]	0.983	9.62[c]	0.975	45.2[d]
0.1982	1.58[c]	0.492	8.10[c]	0.487	39.2[c]
0.1982	1.60	0.1967	7.96[c]	0.487	39.5[d]
0.0991	1.61	0.1967	7.78	0.1950	35.5[c]
0.0496	1.73	0.0983	7.94[c]	0.1950	35.5[d]
		0.0492	9.12[c]	0.1005	36.7[c]
		0.0492	9.01	0.0484	43.7[c]

[a] $[CrSO_4^+]_0 = 3 \times 10^{-3}$ M and $I = 1.00$ M; ionic strength was maintained with lithium perchlorate to be 1.00 M at 25°. [b] The hydrogen ion concentration was corrected for the expansion of the solution with increasing temperature. [c] The $[CrSO_4^+]$ of the first point in these experiments was corrected using eq 3. [d] In these experiments $[CrSO_4^+]_0 = 1.5 \times 10^{-3}$ M.

A second least-squares analysis was applied to the results at each temperature to analyze the hydrogen ion concentration dependence. A satisfactory fit was obtained by using

$$-\frac{d[CrSO_4^+]}{dt} = \{k_0 + k_1[H^+] + k_{-1}[H^+]^{-1}\}[CrSO_4^+] \quad (6)$$

The constants k_0, k_1, and k_{-1} were evaluated using the computer. The results are given in Table II.

TABLE II

VALUES OF THE RATE CONSTANTS k_0, k_1, AND k_{-1}

$$-d[CrSO_4^+]/dt = \{k_0 + k_1[H^+] + k_{-1}[H^+]^{-1}\}[CrSO_4^+]$$

T, °C	$10^5 k_0$, sec^{-1}	$10^5 k_1$, sec^{-1} M^{-1}	$10^5 k_{-1}$, sec^{-1} M
50.0	1.45	0.388	0.0129
65.1	6.59	2.99	0.114
80.3	29.6	15.5	0.621

The variation with temperature of the rate constants for each pathway was used to calculate the activation parameters, ΔH^* and ΔS^*. These parameters are defined in eq 7. This calculation was also done

$$k = (k_B T/h) \exp[(\Delta S^*/R) - (\Delta H^*/RT)] \quad (7)$$

by computer using a least-squares analysis. The results are presented in Table III. Table III also contains activation parameters for a number of other chromium(III) species.

TABLE III
ACTIVATION PARAMETERS

	[H+]$^{-1}$ pathway		[H+]^0 pathway		[H+]^1 pathway	
Species	ΔH^*, kcal mole^{-1}	ΔS^*, cal mole^{-1} deg^{-1}	ΔH^*, kcal mole^{-1}	ΔS^*, cal mole^{-1} deg^{-1}	ΔH^*, kcal mole^{-1}	ΔS^*, cal mole^{-1} deg^{-1}
CrSO$_4$$^+$	27.7 ± 0.8	-4.4 ± 2.3	21.9 ± 0.2	-13.0 ± 0.5	26.5 ± 0.6	-1.3 ± 1.7
CrF^{2+} [a]	Not observed		28.7 ± 0.6	-3.9 ± 1.8	24.5 ± 0.3	-12.4 ± 0.8
CrCl^{2+} [a]	29.4 ± 0.1	5.5 ± 0.3	24.3 ± 0.2	-7.1 ± 0.5	Not observed	
CrBr^{2+} [b]	27.1 ± 0.2	4.7 ± 0.7	23.8 ± 0.3	-3.5 ± 0.9	Not observed	
CrI^{2+} [a]	28.9 ± 0.2	17.9 ± 0.8	23.0 ± 0.3	-0.2 ± 0.9	Not observed	
CrH$_2$PO$_2$$^{2+}$ [c]	Not observed		Not observed		18.1 ± 0.2	-24.1 ± 0.5
CrN$_3$$^{2+}$ [d]	37–44	17–36	32.4	16.2	23.2	-8.3
CrNCS^{2+} [e]	Not observed		27.5	-3.1	Not observed	

[a] Reference 1. [b] Reference 2. [c] Reference 3. [d] Reference 4. [e] Reference 5.

The procedures for calculating k_0, k_1, and k_{-1} and the activation parameters were tested by using them to calculate ΔH^* and ΔS^* for the aquation of chlorochromium(III) using the data published by Swaddle and King.[1] The results agreed exactly with those obtained by Swaddle and King. A two-stage procedure was used in making the calculations for this study because of the limited storage capacity of the IBM 1620 computer. Swaddle and King were able to use a one-step procedure and treat all of the data simultaneously. The excellent agreement obtained between the two methods indicates that the two-step procedure is reliable. The activation parameters were used to calculate pseudo-rate constants for the conditions of each of our experiments. The average deviation between the calculated and observed pseudo-rate constants for all experiments was 1.2%.

Fogel and his associates studied the equilibrium among sulfate, hexaaquochromium(III), and sulfatochromium(III).[9] They also studied the rate of formation of sulfatochromium(III) from hexaaquochromium(III). From the rate of formation and the equilibrium constants they calculated pseudo-first-order rate constants for the aquation reaction at a number of different temperatures. For comparison purposes pseudo-first-order rate constants were calculated using the activation parameters found in this study at the temperatures used by Fogel, *et al.* Some examples are as follows: at 71°, $k_{\text{Fogel}} = 16.0 \times 10^{-5}$ sec^{-1}, $k_{\text{this study}} = 18.0 \times 10^{-5}$ sec^{-1}; at 60°, $k_{\text{Fogel}} = 6.46 \times 10^{-5}$ sec^{-1}, $k_{\text{this study}} = 5.90 \times 10^{-5}$ sec^{-1}; at 50°, $k_{\text{Fogel}} = 2.23 \times 10^{-5}$ sec^{-1}, $k_{\text{this study}} = 1.84 \times 10^{-5}$ sec^{-1}. The agreement is satisfactory considering the difference in approach between the two studies.

Discussion

The major purpose of this study was to compare the aquation kinetics of sulfatochromium(III) with the aquation kinetics of other CrX^{n+} species. To facilitate such comparisons Table III contains activation parameters for a number of CrX^{n+} species whose aquation kinetics have been studied.

The data in Table III show that sulfatochromium(III) behaves very much like monobromo- or monochlorochromium(III). The most striking difference is that sulfatochromium(III) aquates *via* a first-order

(9) N. Fogel, J. M. J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84**, 1145 (1962).

hydrogen ion pathway and the chloro and bromo species do not. This difference is probably due to the fact that sulfate is a much stronger base than chloride or bromide. Apparently the effect of increased charge on sulfate is offset by its increased size when compared to a halide ligand.

In comparing the activation parameters for the [H+]$^{-1}$ pathway to those obtained for the [H+]^0 and the [H+]^1 pathways, a definite trend can be discerned. Both ΔH^* and ΔS^* become less positive as the order with respect to hydrogen ion becomes more positive. The only exception to this trend is for the sulfatochromium(III) [H+]^0 and [H+]^1 activation parameters. The generalization can be made that the [H+]^1 pathway is only important for species containing ligands which are somewhat basic. For both azide and fluoride ΔS^* is more negative for the [H+]^1 pathway than for the [H+]^0 pathway while for sulfate ΔS^* is less negative for the [H+]^1 pathway than for the [H+]^0 pathway. This difference is explained by noting that for sulfate the leaving group is probably SO$_4$$^{2-}$ in the [H+]^0 pathway while it is probably HSO$_4$$^-$ in the [H+]^1 pathway. Since $\bar{S}^0$ is much more positive for HSO$_4$$^-$ than for SO$_4$$^{2-}$ it is not surprising that ΔS^* for the [H+]^1 pathway is more positive than ΔS^* for the [H+]^0 pathway. For azide and fluoride the leaving group is probably the protonated ligand in both pathways and so a similar trend is not expected. The general trend in ΔS^* values might be due to the fact that the total charge on the transition state is increasing as the order with respect to hydrogen ion becomes more positive. We are unable to offer any explanation for the trend in ΔH^*.

Hypophosphite and sulfate are similar in several respects. K_a for HSO$_4$$^-$ is about the same as K_a for H$_3$PO$_2$ and both species are roughly the same size. The only apparent difference is that sulfate is a doubly charged negative ligand while hypophosphite is only a singly charged negative ligand. For the [H+]^1 aquation pathway the activation parameters are very different for hypophosphitochromium(III) and sulfatochromium(III). It would seem that it is the hypophosphitochromium(III) values which are anomalous since both ΔH^* and ΔS^* are far more negative than corresponding values for any other species in Table III. This difference might be explicable if the hypophosphite ligand were assumed to be a bidentate ligand when

coordinated to chromium(III). The failure of sulfate to act as a bidentate ligand with chromium(III) has been attributed to the fact that the O–O distance in sulfate is too small.[6,10] Finholt, *et al.*, have estimated that for bidentate attachment the O–O distance in a ligand should be about 2.78 A. The sulfate O–O distance is 2.34 A,[11] while for hypophosphite the O–O distance is 2.56 A.[12] One can speculate that hypophos-

phite is more likely than sulfate to act as a bidentate ligand because of its greater O–O distance. Infrared studies of hypophosphitochromium(III) might indicate whether the ligand is bidentate or monodentate.

(10) The correct values for the O–O distances calculated for a typical chromium(III) complex and for the sulfate ion are exactly twice the values cited in ref 6.

(11) F. Mazzi, *Acta Cryst.*, **8**, 137 (1955).

(12) B. O. Loopstra, *JENER Rept. Publ.*, No. 15 (1958).

A Kinetic Study of the Hexaaquoiron(III)–Hexacyanoferrate(III) Complex

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The mechanism for the complexation reaction between hexaaquoiron(III), $Fe(H_2O)_6^{3-}$, and hexacyanoferrate(III), $Fe(CN)_6^{3-}$, is

$$Fe(H_2O)_6^{3+} + Fe(CN)_6^{3-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Fe(H_2O)_6Fe(CN)_6$$

$$Fe(H_2O)_6Fe(CN)_6 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} Fe(H_2O)_5Fe(CN)_6 + H_2O$$
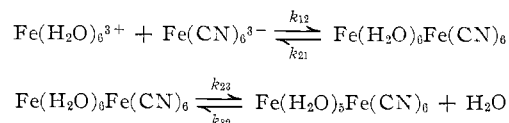
where $Fe(H_2O)_6Fe(CN)_6$ is an ion pair and $Fe(H_2O)_5Fe(CN)_6$ is the complex. The equilibrium concentration quotient for the first reaction above is K. At 298°K $k_{32} = 15.0 \pm 1.0$ sec^{-1} and $k_{23}K = 1750 \pm 250$ M^{-1} sec^{-1}. Values of $\Delta H^{\pm}$ and $\Delta S^{\pm}$ for k_{32} are 8.8 $\pm$ 0.6 kcal/mole and 5.5 $\pm$ 2.0 eu, and $\Delta H^{\pm}$ for $k_{23}K$ is 24.6 $\pm$ 1.6 kcal/mole. The rate constant k_{23} and K are estimated to be 50 sec^{-1} and 35 M^{-1} at 298°K. Comparisons of k_{23} are made with the water-exchange rate constant for hexaaquoiron(III) and rate constants for the formation of other iron(III) complexes.

Introduction

The equilibrium properties of the aqueous hexaaquoiron(III)–hexacyanoferrate(III) [$Fe(H_2O)_6^{2+}$–$Fe(CN)_6^{3-}$] system have been studied in some detail by Ibers and Davidson.[1] The concentration quotient for the reaction

$$Fe(H_2O)_6^{3+} + Fe(CN)_6^{3-} = Fe(H_2O)_5Fe(CN)_6 + H_2O \quad (1)$$
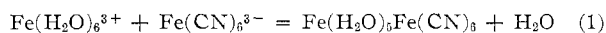
has been determined under a variety of conditions. This work reports a kinetic study of reaction 1 by temperature-jump relaxation techniques. The kinetic results are correlated with the rate constant for water exchange of hexaaquoiron(III) and rate constants for the formation of other iron(III) complexes.

Experimental Section

Chemicals.—Hydrated iron(III) perchlorate was prepared by evaporation of a solution of hydrated iron(III) chloride (Mallinckrodt, analytical reagent) in 70% perchloric acid. Sodium perchlorate was prepared by boiling sodium carbonate (Baker, reagent) in a perchloric acid solution to dryness. Potassium hexacyanoferrate(III) (Mallinckrodt, reagent) was used without additional purification. The potassium ion concentration was

sufficiently small so that potassium perchlorate did not precipitate. Sodium hexacyanoferrate(III) which had been recrystallized from water–ethanol mixtures was used in experiments where excess hexacyanoferrate(III) was required.

Solutions.—Deionized water was used in the preparation of all solutions. The concentration of iron(III) in stock iron(III) perchlorate solutions was determined by first reducing iron(III) to iron(II) with a Jones reductor followed by titration with dichromate using diphenylamine as an indicator.[2] The iron(III) perchlorate solutions were made up in 1.0 or 0.5 M perchloric acid to prevent hydrolysis. Hexacyanoferrate(III) solutions were analyzed by measurement of the absorbance at 420 mμ where ϵ is 1.1×10^3 M^{-1}.[1] The pH values of the solutions were measured with a Leeds and Northrup 7401 pH meter. The saturated KCl solution in the calomel electrode was replaced with a 4.0 M lithium chloride solution to prevent precipitation of potassium perchlorate. The pH meter was calibrated in the pH 0–1.0 range with standardized perchloric acid solutions at the same ionic strength as the solutions used in the experiments. The hydrogen ion concentration was accurate to ± 0.02 M.

Apparatus.—The temperature-jump relaxation instrumentation was manufactured by the Messanlagen Studiengeschellschaft, G.m.b.H., Göttingen, Germany. The instrument was thermostated to $\pm 0.5°$ and the change in visible spectrum was

(1) J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **73**, 476 (1951).

(2) K. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 579.