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Chromium(III) Sulfate in Acid Sulfate Solutions[1]

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The complexes present in dilute sulfuric acid solutions of chromium(III) sulfate were studied spectrophotometrically and were separated by using ion exchange resins. The complexes found had, respectively, one and two sulfate ions per chromium. The complex with one sulfate is present as an inert inner sphere complex $Cr(H_2O)_xSO_4^+$ and a labile outer-sphere (ion pair) complex, $(Cr(H_2O)_6{}^{+3}SO_4^-)^+$. Association constants were determined for five temperatures (48.2 to 82°) at an ionic strength of one and at two temperatures (56° and 65°) at an ionic strength of two. For $Cr(H_2O)_xSO_4^+$, ΔH is 7.2 kcal./mole for both ionic strengths and ΔS is 29.3 and 25.3 e.u. The outer-sphere complex association constant is 12 ± 3 at an ionic strength of one and is not temperature dependent. $Cr(SO_4)_2^-$ appears when the sulfate ion concentration is increased and has been identified and separated into two isomers (*cis* and *trans*) by use of an anion exchange column. The rate of formation of inner sphere $CrSO_4^+$ was studied and found to be first order in chromium(III) and partial order in sulfate. Two possible mechanisms are discussed, with the process of dissociation of the complex the same in both mechanisms. The dissociation has an activation energy of 20.8 kcal. and an entropy of −17.7 e.u.

Introduction

It is known that chromium(III) ion is complexed by many ligands, including anions. The formation of sulfate complexes has been widely studied.[3] The qualitative results indicate that uncomplexed $Cr(H_2O)_6^{+3}$ is violet while the sulfate complexes are green.

It has also been shown[3] that in basic solutions of chromium(III) sulfate, various hydroxy complexes and polymeric species are present. It is clear from studies of the chromium(III) complexes[4–7] that in acid solutions the presence of these more complicated ions is reduced to a minimum and the complex ions present could be determined quantitatively. King and his co-workers[6,7] have shown, by using a cation exchange column, that in chloride solutions $Cr(H_2O)_5Cl^{++}$ and $Cr(H_2O)_4Cl_2^+$ are present. Only $Cr(H_2O)_5Br^{++}$ is definitely known to be present in bromide solutions.

The best conditions to study the chromium(III) sulfate system should be in strongly acid solutions where negligible amounts of more complicated chromium complexes would be present. This would make it possible to separate the simpler sulfatochromium(III) complexes on cation and anion exchange columns and to study the equilibria spectrophotometrically without interference from other species. When this work was almost completed, confirmatory evidence was discovered in two theses[8,9] which reported on studies of chromium(III) sulfate carried out by different methods and under different conditions.

Most of the experiments were performed using solutions of ionic strength 1.0 and 2.0 since high acid concentrations were used to prevent polymerization. It was assumed that a relatively inert $Cr(H_2O)_xSO_4^+$ [10] was present in equilibrium with the $Cr(H_2O)_6^{+3}$ ion. The experimental evidence indicated the presence of a labile outer-sphere association complex($Cr(H_2O)_6{}^{+3}SO_4^-)^+$, similar to that found when solutions of $Co(NH_3)_5H_2O^{+3}$ or $Co(NH_3)_6^{+3}$ are mixed with sulfate solutions.[11] It was postulated that the data could be explained by two reactions

$$Cr^{+3} + SO_4^= = CrSO_4^+ \tag{a}$$

and

$$Cr^{+3} + SO_4^= = (Cr^{+3}SO_4^=)^+ \tag{b}$$

where reaction a is the formation of an inner sphere complex and b is the formation of an outer-sphere (ion pair) association complex.

Experimental

Materials.—Chromium(III) perchlorate was prepared by dissolving chromium(III) nitrate in approximately 2 *N* perchloric acid and heating 0.5 hr. to help break up any hydroxy complexes or polymeric species. The solution was then diluted and passed through a cation exchange column (Dowex 50W × 8, 50–100 mesh). The column was washed and eluted with 2.0 *N* perchloric acid. Those fractions whose spectra agreed with the spectra of chromium perchlorate were combined and the other fractions were discarded. The spectrum that was used for the uncomplexed hexaquochromium(III) perchlorate was that of the carefully eluted ion. The method was to take the first elution, dilute this material and reabsorb it on the column. This technique was repeated until there was no further change in the molar absorption. The final elution was used to determine the spectrum of the hexaquochromium(III) ion. These data agree, within experimental error, with the results of Tong[9] and Plane and Hunt.[12] The purity of each stock solution was established by the spectrum.

Sulfuric acid stock solutions prepared from reagent grade sulfuric acid were standardized against standard sodium hydroxide. Sodium sulfate stock solutions were prepared by dissolving recrystallized sodium sulfate in distilled water. The resulting stock solution was standardized by weighing precipitated barium sulfate.

Sodium perchlorate stock solutions were prepared by neutralizing weighed amounts of sodium carbonate with standard perchloric acid and boiling out the carbon dioxide. Perchloric acid stock solutions, prepared from reagent grade perchloric acid, were also standardized with standard sodium hydroxide.

Distilled water was used in all experiments.

All chemicals used were reagent grade.

Method. Determination of Chromium and Sulfate Concentrations.—The sulfatochromium(III) complex ion in the equilibrium solution was isolated on a cation exchange column and eluted with 0.15 *N* perchloric acid. An aliquot of the eluent was decomposed by adding sodium hydroxide and oxidizing the chromium(III) to chromate with an excess of 30% hydrogen peroxide. The excess hydrogen peroxide

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[1] Presented in part at the September 1959 A. C. S. meeting in Atlantic City, New Jersey.

[2] Taken in part from a thesis for the degree of M.S. in Chemistry.

[3] M. J. Udy, "Chromium," Vol. I, Reinhold Publishing Corp., New York, N. Y., pp. 213 ff.

[4] N. Bjerrum, *Z. Physik. Chem.*, **59**, 581 (1907).

[5] J. Olie, *Z. anorg. Chem.*, **51**, 29 (1907).

[6] H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5011 (1958).

[7] J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

[8] Maak-sang Tsao, Ph.D. Thesis, University of California, Berkeley, Calif., 1952.

[9] J. Y. P. Tong, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1953.

[10] For the sake of simplicity, hydration will usually be omitted.

[11] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **78**, 15 (1956).

[12] R. A. Plane and J. P. Hunt, *ibid.*, **79**, 3343 (1957).

was allowed to decompose, the solution was acidified and an acetate buffer solution was added to keep the *p*H at 4.2. Enough ethyl alcohol was added to make a 30% alcoholic solution, and the sample was titrated amperometrically with a standardized lead nitrate solution. Both lead chromate and sulfate precipitated, but under different conditions, so both end-points could be determined separately for the same sample.[13] This method gave both chromium and sulfate concentrations. The ratio of sulfate to chromium was 0.98 ± 0.04 for the complex eluted from the cation exchange column, indicating one sulfate to one chromium. The ratio of sulfate to chromium was 1.96 ± 0.04 for the complex eluted from the anion exchange column, indicating two sulfates per chromium. Both values are average of at least three different samples.

Separation of Species and Spectral Measurements.—The spectral measurements were made with a Beckman D. U. quartz spectrophotometer equipped with a photomultiplier unit and thermostated cell compartment kept constant at 19.2 ± 0.3°. The sensitivity values allowed slit widths in the range of 0.01 to 0.02 for both the visible and the ultraviolet. Matched silica cells 1.000 ± 0.003 cm. and 5.000 ± 0.004 cm. were used. The one centimeter cells were used in all of the equilibrium and kinetic experiments. The five centimeter cells were used in the study of the disulfatochromate(III) ion.

Beer's law, $A = acl$, where A is the absorbance, a is the molar absorptivity, c is the concentration in moles per liter and l is the length in centimeters, was used to calculate the molar absorptivities reported here.

To determine the spectra, it was necessary to separate the desired species from the other species present. Hexaquochromium(III) and monosulfatochromium(III) ions were separated by use of a cation exchange column (Dowex 50W × 8, 50–100 mesh). The column was loaded with an equilibrium mixture and eluted with approximately 0.15 *N* perchloric acid. This concentration readily eluted the compound in the green band which had previously been analyzed and found to have the formula $CrSO_4^+$. Hexaquochromium(III) ion was left behind as a violet band which did not elute until the concentration of the acid was increased to 1.6 to 2.0 *N*. Elutions were performed at 10 to 15° in water jacketed columns, the low temperatures prevented any decomposition or reaction during the elution. Absorbancies of aliquots of the eluent were measured in the spectrophotometer and the molar absorptivity calculated from Beer's law.

The outer-sphere association complex could not be isolated by ordinary chemical methods. Molar absorptivities at several different wave lengths were determined by preparing cold mixtures of hexaquochromium(III) perchlorate in increasing concentration of sulfate ion. The absorbancies of these solutions were measured rapidly at 19.2°, so that none of the inner monosulfatochromium(III) ion was formed before or during the measurements. The absorbancy was plotted against increasing sulfate concentration until no further change in absorbance was observed when the sulfate concentration was increased. Molar absorptivities were calculated from the constant absorbance by using Beer's Law. This was checked by using the molar absorptivities and the concentration of the species to predict an absorbance for the solutions. Agreement with observed values was within experimental error (approximately 3%).[14]

Molar absorptivities for the wave lengths used in calculations are in Table I. The spectra of hexaquochromium(III) and inner-sphere monosulfatochromium(III) are compared in Fig. 2. The formation, separation and spectra of the disulfatochromate(III) ion are discussed in a later section.

TABLE I

MOLAR ABSORPTIVITIES

Ion	240 mμ	600 mμ
Cr^{+3}[a]	2.61	10.0
$(Cr^{+3}SO_4^{=})^+$	9.40[b]	10.0
$CrSO_4^+$	68.6	15.8

[a] The molar absorptivities are in good agreement with those reported by Tong[9] and Plane and Hunt (P and H).[12] Maxima and minima are observed at the same wave lengths. Some values are 260 mμ P and H 5.0 this work 4.99, 570 mμ P and H 12.8, this work 12.0. [b] Tong[9] reports a value of 10.0 at the same wave length.

Preparation of Equilibrium Solutions.—Equilibrium solutions were prepared from standard solutions of hexaquochromium(III) perchlorate, perchloric acid, sulfuric acid and sodium sulfate (if necessary). Solutions at the chosen ionic strength (1 or 2) were prepared and equilibrated in a constant temperature bath. Equilibration time varied from approximately two weeks (at 84°) to over a month (at 48°). Aliquots were removed and rapidly chilled (to 0°) to quench the reaction. The absorbance of the quenched aliquots was measured. When the spectrum remained constant for one week, the absorbance at 240 mμ was measured for use in the calculations. The absorbancies of the series at 84° were determined at both 240 and 600 mμ so that calculations could be carried out at both wave lengths.

Results and Data

In strongly acid sulfate solutions where the chromium(III) concentration (0.02 *M*) was larger than or equal to the sulfate ion concentrations, the data could be explained by reactions (a) and (b). The total chromium concentration is the sum of all chromium(III) species present

$$Cr_t = (Cr^{+3}) + (CrSO_4^+) + ((Cr^{+3}SO_4^{=})^+) \quad (1)$$

where Cr_t is total chromium(III), (Cr^{+3}) is the concentration of the hexaquochromium(III) ion, $(CrSO_4^+)$ is the concentration of inner sphere complex and $((Cr^{+3}SO_4^{=})^+)$ is the concentration of the outer-sphere association complex. Since the inner sphere complex was inert and its concentration was the most easily determined, the concentrations of Cr^{+3} and $(Cr^{+3}SO_4^{=})^+$ were solved as functions of the $CrSO_4^+$ concentration using the appropriate association constants. These functions were substituted for the concentration of the respective species in equation 1, which was rearranged to

$$(CrSO_4^+)/(SO_4^{=}) = -(Q_i + Q_o)(CrSO_4^+) + Q_iCr_t \quad (2)$$

where Q_i is the association constant for the formation of inner sphere complex (reaction a) and Qo is the association constant for the formation of outer-sphere complex (reaction b), both at the chosen ionic strength.

Plots of $(CrSO_4^+)/(SO_4^{=})$ *vs.* $(CrSO_4^+)$ will be linear if one sulfate is involved in the complexes. The slope is the sum of association constants and the intercept is Q_iCr_t. Since the total chromium concentration is known, only the concentrations of the inner sphere complex and free sulfate ion are necessary. The inner sphere complex is inert, and quenched solutions preserved at low

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[13] H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," 3rd Ed., D. Van Nostrand Co., Inc., Princeton, N. J., 1958, pp. 555–565.

[14] An independent check for the association constant (Q_o) and the molar absorptivity (a_o) of the outer-sphere (ion pair) complex could be made because of the slow equilibration of the inner sphere complex. The immediate formation of the outer sphere complex could be measured at unit ionic strength and 19.2° by using varying sulfate concentrations (0.05, 0.10, 0.15, 0.20 and 0.30 *M*) with a constant hexaquochromium(III) concentration (0.0056 *M*). The absorbance was measured immediately after mixing at the desired temperature. The equation $A = -(A - A_1)/Q_o(SO_4^{=}) + A_o$ was used, where A is the absorbance, A_1 is the absorbance of the hexaquochromium(III) ion, A_o is the absorbance of the outer-sphere complex and $(SO_4^{=})$ is the concentration of the free sulfate. A straight line was observed when A was plotted against $-(A - A_1)/(SO_4^{=})$ and from the slope of the line, the association constant (Q_o) was found to be 15 and 16 for the two parallel experiments. The molar absorptivity was found to be 9.6 and 10.2, averaging out at 9.9, in good agreement with the value derived from the other method. The value of 9.40 was used in the paper because the average error was better.

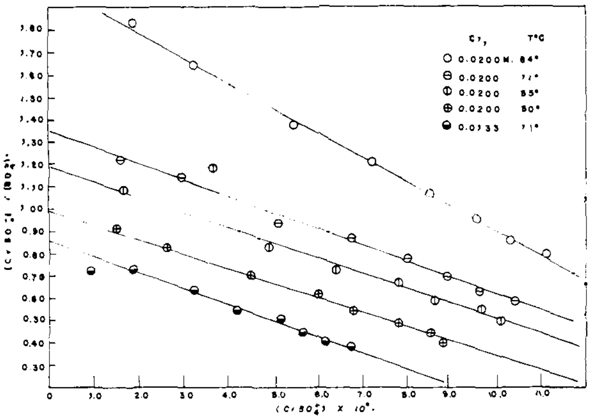

Fig. 1.—Plot for calculating the association constants ($\Gamma/2$ = 1.0) from equation 2; final plots for several representative temperatures.

temperatures (10 to 20°) show no change after standing several days.

The concentration of the inner sphere monosulfatochromium(III) was calculated from the absorbance by assuming that no outer-sphere complex was present. This was possible at 240 mμ because the molar absorptivities of both hexaaquochromium(III) and outer-sphere complex are small compared to that of the inner sphere complex. (For the series at 600 mμ, the chromium(III) and outer-sphere complex have the same molar absorptivities (see Table I).) A preliminary plot of $(CrSO_4^+)/(SO_4^=)$ *vs.* $(CrSO_4^+)$ was prepared and values of Q_i and Q_o were estimated. The concentration of $CrSO_4^+$ was then recalculated more accurately using the estimated values of Q_i, Q_o, the molar absorptivities, the free sulfate ion concentration and the measured absorbance. The new values for $(CrSO_4^+)/(SO_4^=)$ *vs.* $(CrSO_4^+)$ were plotted to re-evaluate Q_i and Q_o. The process was iterated until changes were within experimental error.

The free sulfate ion concentration was calculated from the total stoichiometric sulfate, the sulfate ion complexed and the literature values for the dissociation of the bisulfate ion.[15] The dissociation constants were corrected for ionic strength effects.[16]

The straight lines observed in Fig. 1 support the assumption that only complexes with one sulfate are important in these solutions. The total chromium concentration was varied by 60–70%, but this had no effect on the association constants, indicating that chromium polymers were unimportant or absent.

During the course of the calculations it became apparent that the temperature coefficient for Q_o was smaller than the errors inherent in calculation. The average value of Q_o over the temperature range (48 to 82°) was 12 ± 3. Fairly large deviations in the value of Q_o (16 to 8) or the molar absorptivity of the outer-sphere complex (7.1 to 12) had little effect on the association constant for the inner sphere complex (2 to 3%). The results of the calculations are in Table II, and some typical plots are shown in Fig 1.

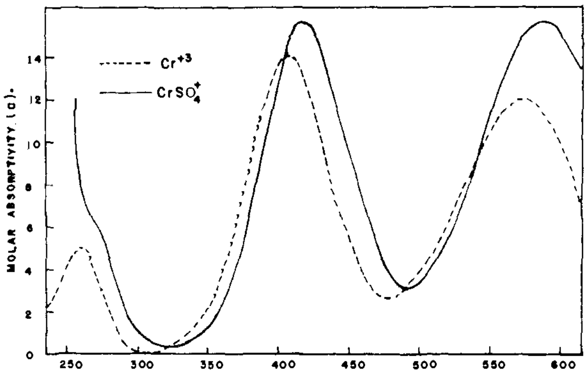

Fig. 2.—Spectra of the Cr(III) species Cr^{+3} and $CrSO_4^+$ in $HClO_4$ at 19.2°: $a = A/cl$ where $A = \log I_0/I$, l = 1.00 cm. and c is approximately 0.02 *M*.

TABLE II

ASSOCIATION CONSTANTS FOR THE FORMATION OF $CrSO_4^+$

Temp., °C.	Total chromium[a]	$\Gamma/2$ = 1.0[b]		$\Gamma/2$ = 2.0	
		$Q_i + Q_o$	Q_i	$Q_i + Q_o$	Q_i
48.2	0.0200	44	33		
56	.0200			47	41
60	.0200	67	50		
	.0133	65	49		
65	.0200	68	58	60	53
71	.0200	74	67		
	.0133	75	65		
84	.0200	112	101		
	.0200[c]	110	101		

[a] The stoichiometric sulfuric acid concentrations used were, $\Gamma/2$ = 1.0, 0.6976 *M*, 0.6016 *M*, 0.4992 *M*, 0.4000 *M*, 0.3008 *M*, 0.1984 *M*, 0.0992 *M*, 0.0512 *M*. For $\Gamma/2$ = 2.0 only the four most concentrated solutions were used to evaluate association constants. Solutions were all made up to the chosen ionic strengths with perchloric acid and sodium perchlorate. In most cases (H^+) = 1.0, but at the higher ionic strength this was varied, never getting below 0.200 *N*. [b] $\Gamma = \Sigma c_i Z_i^2$. [c] These data were measured at 600 mμ.

Observations on Disulfatochromate(III) Ion.—Solutions in which the total sulfate concentration was increased (1 to 2 *M*) had different properties than the more dilute solutions. Plots of equation 2 were no longer linear, and when equilibrium solutions were passed through an anion exchange resin (Dowex 2 × 8, 50–100 mesh, acetate form), a new green band appeared. This indicated a negatively charged ion different in its properties from the species in the green band on the cation exchange column ($CrSO_4^+$). The amount absorbed on the anion exchange column was too small for accurate work, so ordinary green chromic sulfate *n*-hydrate (reagent grade) was dissolved in water and passed through both cation and anion exchange columns. A large green band was observed on the cation exchange column, and the eluted material from this band had all the characteristics

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(15) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1959, p. 568.

(16) T. F. Young and L. A. Blatz, *Chem. Revs.*, **44**, 104 (1949). T. F. Young, L. F. Maranville and H. M. Smith in W. J. Hamer, Ed., "The Structure of Electrolytic Solutions," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 56.

The correction factor for the ionic strength effect was equal to $\gamma_{H^+}\gamma_{SO_4^=}/\gamma_{HSO_4^-}$ and for ionic strength 1.0 and 2.0 was, respectively, 0.11 and 0.050. Young and Blatz indicate that the factor is independent of temperature.

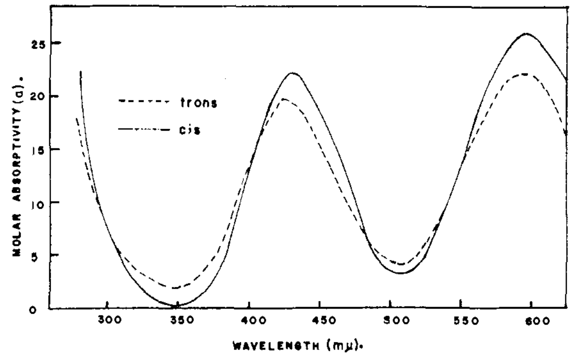

Fig. 3.—Absorption spectra of *trans* and *cis* $Cr(SO_4)_2^-$ at 19.2° in 0.15 *M* $HClO_4$: $a = A/cl$ where $A = \log I_0/I$, $l = 5.00$ cm. and *c* is approximately 0.0043 *M*.

of the $CrSO_4^+$ ion. There was also a smaller violet band which was shown to be hexaquochromium(III) ion. The anion column showed a large green band with the same elution behavior and spectra as the green band absorbed from the equilibrium solutions. This band on the anion exchange column was eluted by 0.15 *N* perchloric acid, indicating that the absorbed species had a low negative charge. The material from this band had a sulfate to chromium ratio of 1.96 ± 0.04 for three different samples, and the spectrum was different than the spectrum of the monosulfatochromium(III) ion. The ease of elution and the sulfate to chromium ratio indicate the correct formula is $Cr(SO_4)_2^-$.

It is possible by controlling the perchloric acid concentration and eluting slowly, to separate the green band on the anion exchange column into two components, both having the same sulfate to chromium ratio (2 to 1), but with slightly different spectra. These two species probably correspond to *cis* and *trans* configurations expected from octahedral complexes of the types Ma_4b_2 or $M(bidentate)_2b_2$.[17] Since chromium complexes have been shown to be octahedral, this is a confirmation of the assigned formula with waters occupying the other positions in the inner coordination sphere (*i.e.* $Cr(H_2O)_x(SO_4)_2^-$). *cis* and *trans* structures were assigned on the basis of behavior on the ion exchange column. On cation exchange columns, *trans* isomers of octahedral complexes always elute more easily than *cis* isomers,[18] though the rate of elution is similar. This has been attributed to the polarity of the complexes. On this basis the less polar *trans* isomer should be eluted first on the anion exchange column.

A theoretical treatment of spectra using crystal field theory[19] predicted that for the types of complex discussed above, the area under the absorption bands of an unsymmetrical *cis* form would be greater than the area under the absorption bands of a more symmetrical *trans* form. In agreement with this, the area under the absorption bands of the species on the anion exchange column that was more strongly absorbed (*i.e. cis*) was 8% greater than the area under the absorption bands of the other species (*trans*). This was additional confirmation for the assignment of configuration. These spectra are in Fig. 3.

Kinetics and Formation of $CrSO_4^+$ from Hexaquo Chromium(III) and Sulfate Ion.—It was considered that some information might be obtained from a study of the rates of formation of the inner sphere monosulfatochromium(III) complex ion. From equilibrium studies it is known that there are three species present, hexaquochromium(III), inner sphere monosulfatochromium(III) and an outer-sphere monosulfatochromium(III) which could be involved in the kinetics.

Experimental

The samples containing unreacted chromium perchlorate and sulfuric acid were placed in a constant temperature bath and allowed to equilibrate. Aliquots were removed at convenient times, and the reaction was quenched by rapid cooling to 0°. The absorbance of each aliquot was determined in the thermostated cell compartment (19°) of the spectrophotometer.

The absorbance (*A*) was measured at 240 mμ where the difference between the spectra of the complexed and uncomplexed chromium was largest. The reaction was followed until no further change occurred in absorbancy, even after several days.

Theory and Results

A plot of $\ln (A_\infty - A_t)$ against time is linear where A_∞ is the absorbance at equilibrium and A_t is the absorbance at time *t*. The observed rate constants calculated from the slope of these plots are reported in Table III. The linearity of this type of plot indicates that the approach to equilibrium is first order in chromium(III). The stoichiometric sulfate concentration is large compared to the chromium concentration, and calculations indicate that in most experiments the free sulfate ion concentration, changes by only 4–5% during a reaction and by not more than 10%, even under unfavorable conditions. Experiments where the sulfate concentration was varied while the temperature was held constant showed a

TABLE III

OBSERVED FIRST ORDER RATE CONSTANTS FOR $Cr^{+3} + SO_4^{=} = CrSO_4^+$

$(H^+) = 1.0$ $\Gamma/2 = 1.0$

Temp., °C.	Total chromium	Total sulfate	$k \times 10^5$ (in sec.$^{-1}$)[a]	$k_{-1} \times 10^5$ (in sec.$^{-1}$)[b]
71	0.0200	0.400	25.3	16.0
65.5	.0200	.400	17.1	10.8
60	.0200	.400	10.4	6.46
55	.0200	.400	6.19	4.05
50	.0200	.557	3.58	2.16
	.0200	.372	3.34	2.27
	.0300	.372	3.36	2.27
48.2	.0200	.400	2.42	1.63
45	.0200	.557	2.84	1.76
	.0200	.352	2.44	1.73
	.0300	.352	2.47	1.73

[a] $k = d \ln (A_\infty - A_t)/dt$. [b] Calculated from equation 9 or rearranged equation 10.

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[17] Equilibrium solutions were too dilute in the concentration of the disulfatochromate(III) to get reliable values for the ratio of *cis* to *trans*. In the reagent grade chromic sulfate the situation is complicated by the presence of a polymer which formed a second green band on the anion exchange column and did not elute except with very concentrated perchloric acid. We hope to report more fully on the disulfato complex in a later paper.

[18] E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952). M. Mori, M. Shibata and M. Nanasawa, *Bull. Chem. Soc. Japan*, **24**, 9476 (1956). E. L. King, M. Woods and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5615 (1958).

[19] F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

slight dependence of the observed first order rate constant on the sulfate concentration (Table III).

In these solutions unreacted chromium is present as hexaquochromium(III) and an outer-sphere association complex ion. The outer-sphere complex is in rapid equilibrium with hexaquochromium(III) and sulfate ion. Therefore the approximately zero order dependence of the reaction with respect to sulfate ion suggests that there may be only one sulfate in the transition state.

Two obvious possibilities exist for the rate determining step

$$(Cr^{+3}SO_4^{=})^+ \underset{k_{-1}'}{\overset{k_1}{\rightleftarrows}} CrSO_4^+ \qquad (c)$$

or the kinetically indistinguishable

$$Cr^{+3} + SO_4^{=} \underset{k_{-1}''}{\overset{k_1'}{\rightleftarrows}} CrSO_4^+ \qquad (a)$$

The spectrophotometric method measures reacted chromium (Cr_r), but from stoichiometry $d(Cr_r)/dt = -d(Cr_u)/dt$ where (Cr_u) is unreacted chromium. If c is the most plausible rate determining step, then

$$-d(Cr_u)/dt = k_1((Cr^{+3}SO_4^{=})^+) - k_{-1}'(CrSO_4^+) \qquad (3)$$

where Cr_u = unreacted chromium =

$$(Cr^{+3}) + ((Cr^{+3}SO_4^{=})^+) \qquad (4)$$

From a mass balance

$$(CrSO_4^+) = Cr_t - Cr_u \qquad (5)$$

where Cr_t is the total chromium concentration.

Equation 4 can be solved for the concentration of $(Cr^{+3}SO_4^{=})^+$ as a function of Cr_u by using the association constant (Q_o) for the outer-sphere complex. If this result is substituted into equation 3 and if equation 5 is substituted for ($CrSO_4^+$) in equation 3, then by rearranging

$$-\frac{d\,(Cr_u)}{dt} = \left[\frac{(k_1 + k_{-1}')Q_o(SO_4^{=}) + k_{-1}'}{1 + Q_o(SO_4^{=})}\right]Cr_u - k_{-1}'Cr_t \qquad (6)$$

which can be integrated by standard means.[20] By proper substitution and expansion

$$\ln(A_\infty - A_t) = \left[\frac{(k_1 + k_{-1}')Q_o(SO_4^{=}) + k_{-1}'}{1 + Q_o(SO_4^{=})}\right] t + c \qquad (7)$$

If reaction a is rate determining, by the same type of operations

$$\ln(A_\infty - A_t) = \left[\frac{(k_1' + k_{-1}''Q_o)(SO_4^{=}) + k_{-1}''}{1 + Q_o(SO_4^{=})}\right] t + c \qquad (8)$$

The observed rate constant is a function of the two rate constants, the association constant for the outer-sphere complex and the sulfate ion concentration. The interpretation of the forward step depends upon the mechanism chosen, but the reverse step, the dissociation of the inner sphere complex, has the same form for the activated complex in both mechanisms, and the interpretation of k_{-1}' or k_{-1}'' is straightforward. The result of solving either mechanism for k_{-1} ($= k_{-1}'$ or k_{-1}'') is

$$k_{-1} = k_{\text{obsd.}}[1 + Q_o(SO_4^{=})]/[1 + Q_i + Q_o)(SO_4^{=})] \qquad (9)$$

The association constants can be evaluated from equilibrium data, while the values for the other quantities are either measured experimentally or can be found in the literature. Calculated values of k_{-1} are recorded in Table III. When ln k_{-1} *vs.* $1/T$ is plotted, the result is a straight line which leads to an activation energy (E_a) of 20.8 ± 0.6 kcal./mole and an entropy of reaction ($\Delta S^{\pm}$) of -17.7 ± 2.0 e.u.

The observed sulfate dependency is small, being much less than 1 and close to zero. This observed dependency can be explained by rearranging equation 9 to give

$$k_{\text{obsd.}} = k_{-1}\,[1 + (Q_i + Q_o)(SO_4^{=})]/[1 + Q_0(SO_4^{=})] \qquad (9a)$$

or for a more complete description, substituting for the free sulfate ion concentration, the stoichiometric sulfate$[H_2SO_4]_T$ and the dissociation constant K of the bisulfate ion at the given temperature and ionic strength.[15,16] This gives

$$k_{\text{obsd.}} = k_{-1}[(H^+) + K(1 + (Q_i + Q_o)[H_2SO_4]_T)]/[(H^+) + K(1 + Q_o[H_2SO_4]_T)] \qquad (10)$$

These equations developed from either of the two proposed mechanisms predict the sulfate ion dependency correctly within the limits of the experimental error expected which is demonstrated by the constancy of the values for k_{-1} at 50 and 45° where the sulfate concentration was varied (Table III). It is to be regretted that a more stringent test was not performed, but this does demonstrate that the proposed mechanisms are compatible with the experimental data.

Discussion

In dilute solutions of sulfate and chromium(III) ion, the important chromium species is the monosulfatochromium(III) complex, present as an inner sphere inert complex and an outer-sphere association (ion-pair) complex ion. The association constants have been determined at ionic strengths 1.0 and 2.0 for a series of different temperatures. Since the values at the higher ionic strength are fewer and not as accurate, most of the discussion and comparison will be restricted to the values at unit ionic strength.

The enthalpy for the inner sphere complex was calculated from the linear plot of log Q_i against $1/T$ and the entropy was calculated at each of the measured temperatures from the free energy at that temperature. The enthalpy and entropy are in Table IV. The error in evaluating the association constant for the outer-sphere complex is greater, and there is more error in the enthalpy and entropy. Within the limit of error of our data, there is little or no change in the association constant when the temperature is varied. This leads to a ΔH of approximately 0 kcal./mole and a ΔS of $+4.9 \pm 1$ e.u. A linear relationship has been observed if the entropy is plotted against the enthalpy for those ion pair complexes which have been investigated.[21] The values for the ion pair complex investigated here fit into this linear plot.

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[20] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Son, Inc., New York, N. Y., 1953, p. 172.

[21] J. F. Duncan and D. L. Kepert in W. J. Hamer, Ed., "The Structure of Electrolytic Solutions," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 384.

Association constants for sulfate complexes can be compared with the values found in this work. In an earlier study of chromium(III) sulfate, Maak-Sang Tsao[10] reports that at 25° and unit ionic strength the inner and outer-sphere association constants were respectively 21.5 and 13.2, compared to extrapolated values of 13.2 and 12 in this work. This is good agreement considering the methods used in both researches.

TABLE IV

HEAT AND ENTROPY OF FORMATION OF THE INNER SPHERE COMPLEX

$Cr^{+3} + SO_4^{=} = CrSO_4^{+}$

$\Gamma/2$	ΔH, kcal./mole	ΔS, e.u.
1.0	7.2 ± 0.3	29.3 ± 0.8
2.0	7.2 ± 0.6	25.3 ± 1.2

When the association constants for several +3 ions such as $Co(NH_3)_6^{+3}$, $Co(NH_3)_5H_2O^{+3}$, [11] Fe^{+3}, [22] Ce^{+3}, [23] La^{+3} [24] interacting with a sulfate ion are compared under the same conditions, it is observed that the order of magnitude of the constants are the same, though the ionic size of the central atom varies considerably. This suggests that these systems are similar in their behavior. In all the systems mentioned here, monosulfato complexes have been observed and in most cases the disulfato complex also.[25] The outer-sphere complex has been reported in the case of Cr^{+3}, $Co(NH_3)_6^{+3}$ and $Co(NH_3)_5H_2O^{+3}$, but for the other ions, the methods either would not differentiate between the two types of complexes or else the outer-sphere association complex was not suspected. Further experiments on these systems might yield more information.

Where the outer-sphere association complex was studied, many similarities were observed. In all three cases, at unit ionic strength, ΔH was either very small or zero, and the entropy values were all close (between 3.3 and 6 e.u.) and relatively small on the positive side. The small positive value of the entropy fits the picture that water molecules are being displaced or rearranged in the outer hydration sphere. It was also observed that in the case of Cr^{+3} and $Co(NH_3)_5H_2O^{+3}$ where both inner and outer-sphere complexes are formed the association constant for the outer-sphere complex (Q_o) was approximately equal to that of the inner sphere (Q_i') at 25° and unit ionic strength. Taube and Posey[11] first observed this with $Co(NH_3)_5H_2O^{+3}$ and it holds true for Cr^{+3}.

In most cases sulfate ions in complexes are present as $SO_4^{=}$ ions, not bisulfate ions. In this work the experiments where the acidity was varied did not affect the association constants, which indicated the same form for the sulfate in this complex. That the sulfate is in the form of the bare ion does not indicate whether the ion is acting as a monodentate or bidentate group. There are cases such as $Co(NH_3)_5SO_4^{+}$ where the sulfate can only occupy one position in the inner coordination sphere and therefore acts as a monodentate group. At unit ionic strength and 25°, the entropy of formation of this ion is 16.6 e.u.[11] For the same conditions the entropy of formation of $CeSO_4^{+}$ is 17.8 e.u. and for $LaSO_4^{+}$ it is 15 e.u.[23] Even with no corrections in the entropy for any outer-sphere complex for the last two ions, these values are low compared to the 29.3 e.u. we find for the formation of $CrSO_4^{+}$. The positive value of the entropy indicates an extensive rearrangement in the inner coördination sphere, most probably the ejection of water molecules. If the sulfate acts as a bidentate group in the chromium complex and as a monodentate group in the other cases, the value for the entropy would be expected to be higher as is observed in the case of the chromium complex.

There is some support for the idea that the sulfate ion acts as a bidentate group from the behavior of the chromium(III) sulfate hydrates.[26] Three types of hydrate are reported, (1) a violet salt containing the $Cr(H_2O)_6^{+3}$ ion, (2) a green crystalline salt, which will be discussed further and (3) an amorphous green salt with no definite structure, that is thought to be a polymer. When the green crystalline chromium(III) sulfate is formed from solution, it contains six molecules of water which are strongly bonded. The ion exchange studies in our work indicate that this hydrate is composed of $Cr(H_2O)_xSO_4^{+}$ cations and $Cr(H_2O)_y(SO_4)_2^{-}$ anions. The fact that $x + y$ equals six is best explained by the sulfate ion acting as a bidentate group, which leaves four positions for water molecules in the cation and two in the anion to reproduce the observed formula $Cr_2(SO_4)_3 \cdot 6H_2O$ for the stable green salt. If the sulfate ion were acting as a monodentate group, the hydration number would be expected to be nine, rather than six, for the stable salt.

It has proved impossible, so far, to form a trisulfato complex, which is understandable in terms of the difficulty of fitting a doubly negative group into a negative ion, but the $Cr(SO_4)_2^{-}$ is present at high sulfate ion concentrations in acid solutions (1 to 2 molar in sulfate). This ion has been separated into two isomers as expected for octahedral complexes, and tentative configurations have been assigned. A simple crystal field argument[27] indicates that the shift in the maxima in these spectra are in the direction expected for the formation of a disulfato complex, but no calculations have been attempted and the data are not complete enough to warrant a more thorough discussion.

The kinetics can be explained by the species necessary to explain the equilibrium. It is impossible from these experiments to specify a rate determining step for the formation of the inner sphere complex ion. A plausible rate determining step would be the formation of an inner sphere species from an outer-sphere ion pair complex ion, but this is speculation, and the formation of the product from a direct reaction of Cr^{+3} with $SO_4^{=}$ cannot be excluded from consideration. The re-

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[22] R. A. Whitaker and N. Davidson, *J. Am. Chem. Soc.*, **75**, 3081 (1953).

[23] T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).

[24] K. L. Mattern, in ref. 23.

[25] The exceptions are $Co(NH_3)_6^{+3}$, where it would be difficult to put two sulfate ions and La^{+3} where the information is incomplete.

[26] F. Krauss, N. Quesngasser and P. Weyer. *Z. anorg. Chem.*, **179**, 413 (1929).

[27] C. C. Lin, private communication.

verse step, the dissociation of the inner sphere complex is a simple first order involving the same form of the activated complex for both mechanisms. The entropy of activation for the dissociation step (−17.7 e.u.) is in agreement with the idea that the activated complex has a greater charge separation than the reactant, and such would be the case if waters entered the inner sphere and displaced the sulfate ion. The value would seem to indicate that the sulfate ion is just displaced and not completely eliminated from the coördination sphere.

It appears that at high acidity, low chromium(III) and sulfate ion concentrations, only three chromium species, Cr^{+3} ion, outer-sphere association (ion pair) complex ion $(Cr^{+3}SO_4^{=})^+$ and inner sphere complex ion $CrSO_4^+$, are necessary to explain the behavior of chromium(III) sulfate solutions.

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The Activation Energies of Proton Transfer Reactions in Water[1]

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The rate constants of the acid and base catalyzed proton transfer reactions in water were measured in the temperature range of 20–80°, by the n.m.r. technique. The pH was controlled through the use of buffers. The Arrhenius activation energies obtained are: 2.6 ± 0.3 kcal./mole in the acidic range and 4.8 ± 0.5 kcal./mole in the basic range. In addition transverse and longitudinal relaxation times (T_2 and T_1) were measured at very low and high pH values.

Introduction

The study of proton transfer reactions in water is of importance to the understanding of the anomalous conductivities of hydronium and hydroxyl ions. Furthermore, in aqueous solutions of acids and bases, fast proton transfer in the water may be involved as part of the reaction scheme.

Three mechanisms are supposed to contribute to proton transfer in water

$$H_2O + H_3O^+ \overset{k_1}{\rightleftarrows} H_3O^+ + H_2O \tag{1}$$

$$H_2O + OH^- \overset{k_2}{\rightleftarrows} OH^- + H_2O \tag{2}$$

$$H_3O^+ + OH^- \overset{k_R}{\rightleftarrows} H_2O + H_2O \tag{3}$$

The recombination rate of hydronium and hydroxyl ions (reaction 3) was measured by Eigen and de Maeyer[2] using chemical relaxation methods. It was found that $k_R = (1.4 \pm 0.2) \times 10^{11}$ sec.$^{-1}$ M^{-1} at 25°, and its temperature dependence is described by an activation energy of 2–3 kcal./mole. Preliminary measurements on water, using the nuclear magnetic resonance (n.m.r.) technique, were reported by Meiboom, Luz and Gill.[3] Recently these measurements were extended and reinterpreted by Meiboom.[4] The rate constants thus obtained for reactions 1 and 2 were: $k_1 = (10.6 \pm 4) \times 10^9$ sec.$^{-1}$ M^{-1} and $k_2 = (3.8 \pm 1.5) \times 10^9$ sec.$^{-1}$ M^{-1} at 25 ± 1°. A measurement, performed with water containing the natural abundance of O^{17}, of the activation energy of reaction 1 was reported by Weiss,[5] who obtained a value of $0.7 < \Delta E < 8$ kcal/mole.

In the present work, measurements of these rate constants by the n.m.r. technique are reported over the temperature range of 20–80°. The results at room temperature reproduce those given by Meiboom,[4] under better controlled chemical conditions. From the dependence of the rates on temperature, the Arrhenius activation energies were evaluated.

Another problem studied was the apparent decrease[3] in T_2 (the transverse relaxation time) at pH values below 3 or above 10. It is shown that this decrease is accompanied by a similar decrease in T_1 (the longitudinal relaxation time) and thus has no significant connection with the exchange reactions.

Experimental Procedure

All n.m.r. measurements were performed at a proton frequency of 31.65 Mc./sec. Transverse relaxation times (denoted henceforth by T_2 in H_2O^{17} enriched water and T_2' in ordinary water) were measured by the modified Carr-Purcell method.[6] The accuracy of T_2 measurements was estimated to be ± 0.1 sec. T_1 was measured by the 180°–90° pulses method.[7] The values of T_1 were close to those obtained (in degassed samples) by Simpson and Carr[8] and were measured with an accuracy of ± 0.1 sec.

Temperature control was accomplished by passing a heated air current of constant flow around the sample. The temperature was measured with the aid of a Copper-Constantan thermocouple inserted in the air gap near the coils. The accuracy of the temperature data is estimated to be ± 1°.

Solutions were prepared in H_2O^{17} enriched water containing between 0.6 and 1.2 atom per cent of O^{17}. The concentration of O^{17} was determined by a mass-spectrometer.[9]

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(1) A preliminary report of this work was presented at the 29th meeting of the Israeli Chemical Society and was published in the *Bull. Res. Counc. of Israel*, **10A**, No. 3, 28 (1961).

(2) M. Eigen and L. de Maeyer, *Naturwissenschaften*, **42**, 413 (1955).

(3) (a) S. Meiboom, Z. Luz and D. Gill, *J. Chem. Phys.*, **28**, 1611 (1957); (b) D. Gill, Thesis, The Hebrew University, Jerusalem, 1959.

(4) S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

(5) K.-H. Weiss, private communication.

(6) S. Meiboom and D. Gill, *Revs. of Scient. Instr.*, **29**, 688 (1958).

(7) H. Y. Carr and F. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

(8) J. H. Simpson and H. Y. Carr, *ibid.*, **111**, 1201 (1958).

(9) The authors are indebted to the Isotope Department of the Weizmann Institute for kindly supplying the H_2O^{17} enriched water and for the mass spectrometer determinations of the O^{17} concentration.