Table II, reactions 15–19, considers the possibilities of the dihydroxy intermediates formed with OH groups occupying positions (2) and (3) and water in the (6) position. In all these reaction pathways, the major criticisms are as follows: (I) the attack of the initial OH, whether it be in position (2) or (3), is not consistent with the above-proposed mechanisms; (II) the hydroxy groups are eliminated too soon in the reaction sequence to account properly for the observed increase in the rate; (III) the entering ligand experiences great steric hindrances between its cyclohexane ring and the acetato groups of the leaving ligand.

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The Influence of Sulfite Ion upon the Rate of Aquation of Various Complexes of Chromium(III) Ion. The Stability of Sulfitochromium(III) Ion[1]

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Chromium(III) forms a sulfite complex $CrOSO_2^+$ rapidly and reversibly, suggesting strongly that it forms without breaking the chromium(III)–oxygen bond in hexaaquochromium(III) ion. The equilibrium quotient for formation of this species at 25°, $I = 0.25\ M$, is $Q_1 = [CrOSO_2^+][H^+]/[Cr^{3+}][HOSO_2^-] = 0.061$. Dimeric hydroxychromium(III) ion, $Cr_2(OH)_2^{4+}$, also forms a relatively stable sulfite complex. Coordinated sulfite labilizes chromium(III), and the rates of several ligand-substitution reactions of chromium(III) in the presence of sulfite have been studied; these are the aquation of chlorochromium(III) ion, the aquation of isothiocyanatochromium(III) ion, the aquation of isomeric bis(isothiocyanato)chromium(III) ions, and the decomposition of dimeric hydroxychromium(III) ion. These reactions of chromium(III) complexes of charge $\leq 2+$ are first order in sulfite ion, with no evidence for measurable association of sulfite ion at the highest concentrations studied.

Introduction

Sulfite ion as a ligand has been shown to labilize other ligands bonded to the same metal ion.[2] In these earlier investigations, the complexes studied were $Co(NH_3)_5SO_3^+$ and $Co(CN)_5SO_3^{4-}$, in each of which the sulfite ligand is assumed to be sulfur bonded. The present study deals with the stability of aquosulfitochromium(III) ion, which is oxygen bonded, and the influence of sulfite ion on the rates of aquation of chloro- and isothiocyanatochromium(III) species and upon the rate of decomposition of dimeric hydroxychromium(III) ion.[3] The labilizing effect of sulfite ion upon chromium(III) appears to be qualitatively similar to that reported recently for nitrite ion.[4]

Experimental Procedures

Reagents.—Except where noted, reagent grade chemicals were used without further purification. Solutions were prepared with doubly distilled water; between distillations, the water was passed through an ion-exchange deionizer.

Chromium(III) perchlorate was prepared by reduction of reagent grade chromium trioxide with reagent grade hydrogen peroxide in perchloric acid solution. The hydrated salt was then crystallized from the solution. Previously described methods were used to prepare aqueous perchloric acid solutions of chromium(III) complexes with thiocyanate ion[5,6] and chloride ion.[7] Solutions of the individual chromium(III) complexes were stored at 0° in the dark for periods up to several weeks.

A solution containing dimeric hydroxychromium(III) ion ($Cr_2(OH)_2^{4+}$), calcium ion, and perchlorate ion was prepared by the method of Thompson.[3b] Oxygen gas was passed through a chromium(II) perchlorate solution (containing zinc(II) ion) for 20 min; the chromium(III) dimer formed was separated from other cationic species by ion exchange using a 15 in. × 0.5 in. column of Dowex 50W-X8, 200–400 mesh resin and using 1.2 *M* calcium perchlorate solution as the eluting agent.

Solutions of chromium(III) species were analyzed for total chromium by a spectrophotometric method.[8] Before determination of total chromium in solutions of dimeric hydroxychromium(III), the calcium(II) ion (used as eluting agent) was removed by ion exchange.

The concentration of calcium(II) ion in the stock solution of dimeric hydroxychromium(III) ion was measured by an ion-exchange method. The aliquot was loaded on a column of Dowex 50W resin in the hydrogen ion form, and the amount of acid liberated was determined by titration with standard base;

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(1) Supported under National Science Foundation Grant GP-7185X.

(2) (a) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, **88**, 2877 (1966); (b) H. H. Chen, M.-S. Tsao, R. W. Gaver, P. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).

(3) (a) J. A. Laswick and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3564 (1959); (b) G. Thompson, Thesis, University of California, Berkeley, Calif., June 1964 (University of California Radiation Laboratory Report 11410).

(4) T. C. Matts and P. Moore, *Chem. Commun.*, 29 (1969); T. C. Matts and P. Moore, *J. Chem. Soc. A*, 1997 (1969).

(5) E. L. King and E. B. Dismukes, *J. Amer. Chem. Soc.*, **74**, 1674 (1952).

(6) J. T. Hougen, K. Schug, and E. L. King, *ibid.*, **79**, 519 (1957); in the present study, Dowex 50W-X4, 200–400 mesh resin was used to separate the isomers, and separation was complete.

(7) E. L. King, M. J. M. Woods, and H. S. Gates, *ibid.*, **80**, 5015 (1958).

(8) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

it was assumed that 2 protons per chromium atom and 2 protons per calcium ion were produced. The concentrations in the stock solution were 0.048 M $Cr_2(OH)_2^{4+}$ and 0.27 M Ca^{2+}.

The spectrum of dimeric hydroxychromium(III) ion prepared for this study had the following features (given as λ (nm) and a (with dimensions 1 (g-atom of Cr)$^{-1}$ cm^{-1})): 580, 18.0 (a_{max}); 487, 5.4 (a_{min}); 414, 21.3 (a_{max}); 340, 1.7 (a_{min}). The corresponding values reported by Thompson[3b] are 580, 17.3; 490, 5.0; 416, 20.3; and 340, 1.5.

Sulfur(IV) solutions were prepared by dissolving reagent grade sodium sulfite in oxygen-free water or dilute aqueous perchloric acid solutions. These solutions were stored under nitrogen in glass bottles fitted with rubber self-sealing caps; withdrawals were made by syringe, using steel needles. Sulfur(IV) solutions were not stored for more than a few days. An iodometric method,[9] using potassium iodate as the primary standard, was employed to determine total sulfur(IV) in experimental solutions.

The perchlorate salts of sodium, barium, and calcium were crystallized from the solutions prepared by mixing perchloric acid with the respective carbonates; this was followed by recrystallization from water. The perchlorate ion concentration in stock solutions of each of these salts was measured by titration of the acid displaced from Dowex 50W resin columns in the hydrogen ion form.

Solutions of sodium thiocyanate were analyzed by the ion-exchange technique described for perchlorate salts. The concentration of free thiocyanate ion in solutions also containing isothiocyanatochromium(III) species was measured spectrophotometrically at 460 nm, in the presence of a large excess of iron(III).[10] Sulfur(IV) ion interferes with the spectrophotometric analysis for thiocyanate, and it was removed before analysis by bubbling the acidified sample with air under partial vacuum.

Calibration of pH Meter.—A Beckman Zeromatic pH meter, with a glass electrode and a silver–silver chloride reference electrode using saturated KCl as the electrolyte solution, was used to determine the concentration of hydrogen ion. No difficulty was caused by precipitation of potassium perchlorate at the liquid junction in the reference electrode. Perchloric acid–sodium perchlorate solutions of 0.25 M ionic strength were used to calibrate the meter. As had been observed previously,[11] a linear relation between measured pH and $-\log [H^+]$ was observed.

Equilibrium between $Cr(OH_2)_6^{3+}$ and $HOSO_2^-$.—A spectrophotometric study of the rapidly established equilibrium between chromium(III) and hydrogen sulfite ion was made in solutions of ionic strength 0.25 M. Solutions containing chromium(III) perchlorate, sodium perchlorate, and perchloric acid were prepared in volumetric flasks. After temperature equilibration (25°), each nearly filled flask was removed from the thermostated bath and the following operations, requiring about 15 min, were performed. Sodium sulfite solution was added, and the flask was filled to the mark; the solution then was transferred to a beaker for pH measurement. After pH measurement, the solution was transferred to a thermostated spectrophotometer cell, and the absorbance was measured at 340, 430, 440, 590, and 620 nm. Finally, the solution was analyzed for total sulfur(IV). No effort was made to exclude air from these solutions, but preliminary experiments indicated that appreciable sulfur(IV) was not lost from acidic solutions of chromium(III) and sulfur(IV) during times in excess of 30 min.

Interactions between $Cr_2(OH)_2^{4+}$ and $HOSO_2^-$.—Perchloric acid–sodium perchlorate solution (ionic strength 1 M), in a thermostated (25°) spectrophotometer cell fitted with a rubber serum cap, was bubbled with nitrogen to remove oxygen. Then, an oxygen-free solution of dimeric hydroxychromium(III) ion was added, and the addition of sodium sulfite solution was started using a microliter syringe. The absorbance of each solution was measured at 450, 430, or 420 nm before addition of any sulfite and, again, after each addition. Each of the steps after addition of chromium(III) was done quickly.

The rate of dissociation of dimeric hydroxychromium(III) ion to give monomeric species in the presence of sulfur(IV) was measured. Oxygen-free solutions of the dimeric species were prepared in sealed spectrophotometer cells, as described above. The reactions were initiated by adding sodium sulfite solution using a syringe. The rate of decrease in absorbance was measured at one or more of the wavelengths 600, 550, 460, 450, 430, or 420 nm for each solution. The cells were immersed to the filling neck in a 25° water bath between absorbance measurements. The water in the bath was opaque to visible and ultraviolet light, but no precautions were taken to shield the cells from light during handling.

Aquation of $Cr(OH_2)_5X^{2+}$.—The effect of sulfur(IV) on the rate of aquation of chlorochromium(III) ion and isothiocyanatochromium(III) ion was investigated in solutions of ionic strength 0.25 M at 25°. Each experimental solution was bubbled with nitrogen through a steel syringe needle before addition of sulfite. Sulfur(IV) solution was then added by syringe; the pH of an aliquot was measured and was adjusted by addition of more sodium sulfite or perchloric acid solution if necessary. The adjusted pH of at least one aliquot of each solution was measured carefully using the calibration procedure described earlier. The total sulfur(IV) concentration was measured at least once during each experiment.

The initial concentration of chromium(III) complex was always low in these experiments, causing the aquation reactions to go essentially to completion. The change in concentration of chromium complex was observed by taking samples at measured times, separating the complex of charge 2+ from other chromium(III) species by ion exchange,[5,7] followed by analysis of chromium in this fraction. Some samples were quenched before performing this separation by delivering them into an acidic solution and storing at 0° up to 18 hr for chlorochromium(III) ion and 48 hr for isothiocyanatochromium(III) ion.

Formation of $Cr(OH_2)_5NCS^{2+}$.—The formation of isothiocyanatochromium(III) ion was studied in experiments which were done like the aquation experiments, except that some free thiocyanate ion was present initially. The procedure for separation of isothiocyanatochromium(III) ion included rinsing the loaded ion-exchange column with 0.12 M perchloric acid to remove any bis species of charge 1+ that may have formed.

Aquation of Isomeric $Cr(OH_2)_4(NCS)_2^+$.—The rate of aquation of each of the isomeric bis(isothiocyanato)chromium(III) ions was studied in the dark at 25° as a function of the concentration of hydrogen ion in solutions of 0.25 M ionic strength. The hydrogen ion concentration of each reactant solution was measured with a pH meter, as already described. The aquation was followed, to only a few per cent of completion, using the spectrophotometric analysis for thiocyanate ion.

The effect of sulfur(IV) on the aquation of each isomeric bis(isothiocyanato)chromium(III) species was studied as described above, except the solutions were oxygen-free and the pH was measured of an aliquot rather than of the entire solution.

Determination of the Relative Concentration of Isomeric $Cr(OH_2)_4(NCS)_2^+$ Species.—A spectrophotometric method was devised for determining the relative concentrations of isomeric bis(isothiocyanato)chromium(III) ions. Values of the ratios of absorbance at 310 and 280 nm (A_{310}/A_{280}) and at 300 and 270 nm (A_{300}/A_{270}) provide two independent calculations of the concentration ratio[12] [*trans*-$Cr(NCS)_2^+$]/[*cis*-$Cr(NCS)_2^+$]. The molar absorbancy indices used in this calculation were as follows (given as λ (nm), a_{trans}, a_{cis} (in 1 mol^{-1} cm^{-1})): 270, 5904, 5433; 280, 6455, 5685; 300, 7709, 5160; 310, 6600, 4574.

Equilibrium in Solutions of Isothiocyanate Complexes of Chromium(III).—Acidic aqueous mixtures of thiocyanate ion and chromium(III) with an ionic strength of 0.25 M were pre-

(9) A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1961, p 370.

(10) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(11) W. P. Schaefer and M. E. Mathisen, *Inorg. Chem.*, **4**, 431 (1965).

(12) Coordinated water molecules will not, in general, be shown in formulas for species of chromium(III).

pared and equilibrated in the dark at 25°. Sulfur(IV) was included in the reaction mixtures to hasten the attainment of equilibrium. Concentrations of each of the isothiocyanatochromium(III) species were measured occasionally until the concentrations of each of these species was approximately constant with time or until the same results were obtained from pairs of solutions prepared with identical composition but with different chromium(III) complexes present initially. The concentration of each species was determined by the following procedure. A diluted aliquot of the reaction mixture was taken up on a 5 in. × 0.25 in. column of freshly cleaned Dowex 50W-X2, 100–200 mesh cation-exchange resin. After being loaded, the resin was rinsed with 50 ml of 0.008 *M* perchloric acid to remove sulfur(IV). The isomeric bis(isothiocyanato)chromium(III) species were eluted as a mixture from the rinsed column with 50 ml of 0.25 *M* perchloric acid. An additional 20–50-ml portion of 0.25 *M* acid was passed through the column and collected as a blank; the monoisothiocyanato species then was eluted with 50 ml of 1.2 *M* perchloric acid. By the spectrophotometric analysis described above and using the 0.25 *M* perchloric acid blank eluent solution to correct for the small absorbance added by contamination from the column, the distribution of isomers in the mixture of bis species was determined. The total chromium concentration was measured[8] also for both eluate fractions. In one experiment, the isomeric species were separated from one another. The equilibrium concentration of free thiocyanate ion was measured spectrophotometrically.

Isomerization of $Cr(OH_2)_4(NCS)_2^+$.—Acidic aqueous solutions, initially containing only isomeric bis-isothiocyanato species and no free thiocyanate ion, were stored at 25° in black or amber bottles. Some of the solutions contained sulfur(IV) and some did not. Aliquots were taken at intervals, the bis species were separated from other cationic species in the way described for the equilibrium experiments, and the isomer distribution was determined spectrophotometrically. The total chromium concentration was determined in the eluted solutions containing only bis species either by the alkaline chromate method[8] or using the known extinction coefficients.

Results

Qualitative Observations.—A number of observations indicate that sulfitochromium(III) species rapidly come to equilibrium with their environment and that inert species are not formed. A violet to green color change occurs upon mixing solutions of aquochromium(III) ion and sulfur(IV); the reverse color change occurs rapidly if a solution containing sulfitochromium(III) species is acidified to pH ≤ 2. (Although these qualitative observations are consistent with the green color being due to hydroxychromium(III) species, the results of quantitative studies (to be described) show that the spectral changes are not due primarily to hydroxy species.) Attempts to separate sulfitochromium(III) species from aquochromium(III) ion by ion-exchange procedures failed, and the observations are consistent with the above-suggested lability of such species. In charging a column containing cation-exchange resin with a freshly prepared solution of sulfitochromium(III) ion, the green species moves down the column[13] as if it had a charge of 1+. When, however, the charging process was completed and elution with ~0.1 *M* perchloric acid begun, the chromium(III) species changed color (to pale purple) and the elution rate was negligible. The observations were essentially unchanged if the reaction mixture was heated at 60° for times up to 8 days before being subjected to the ion-exchange procedure. (Under these circumstances, however, some polymeric chromium(III) species formed.)

Equilibrium in the Reaction Forming $Cr(OH_2)_5OSO_2^+$.—The labile equilibrium between hexaaquochromium(III) ion and hydrogen sulfite ion, demonstrated to be

$$Cr(OH_2)_6^{3+} + HOSO_2^- \rightleftharpoons (H_2O)_5CrOSO_2^+ + H_3O^+$$

with an equilibrium quotient $Q_1 = [CrOSO_2^+][H^+]/[Cr^{3+}][HOSO_2^-]$, has been studied spectrophotometrically at 25° in solutions of 0.25 *M* ionic strength. The reaction mixtures contain an appreciable amount of hydroxychromium(III) ion; its spectrum is different from that of aquochromium(III) ion and a correction for this was made. A value of $Q_2 = [H^+][CrOH^{2+}]/[Cr^{3+}] = 1.25 \times 10^{-4}$ *M* for 25° and $I = 0.25$ *M* was obtained from the work of Postmus and King[10] by extrapolation of data as a function of ionic strength and interpolation of data as a function of temperature. This value was used in calculation of the molar absorbancy index of hydroxychromium(III) ion from spectral observations on formate buffer solutions containing chromium(III). The measurements on formate buffer solutions were made at varying concentrations of formate ion (0.046–0.116 *M*) to show that formate complexing was not interfering. Molar absorbancy index values for aquochromium(III) ion (a_0) and hydroxychromium(III) ion (a_2) used in the treatment of data were as follows (given as λ (nm), a_0, and a_2 in l. mol^{-1} cm^{-1}): 340, 1.5, 1.8; 430, 12.0, 23.1; 440, 9.1, 21.4; 590, 12.7, 14.6; 620, 8.1, 11.5. Sixteen solutions with ranges of concentrations $[H^+] = 6.4 \times 10^{-4}$–$2.1 \times 10^{-3}$ *M*, [total sulfur(IV)] = 0.018–0.081 *M*, and [total chromium(III)] = 2×10^{-3}–8.8×10^{-3} *M* were studied. The data[15] were plotted as $\tilde{a}$ *vs.* $\{[H^+](\tilde{a} - a_0) + Q_2(\tilde{a} - a_2)\}/[HOSO_2^-]$; $\tilde{a} = (\log I_0/I)/(C_{Cr}b)$ where C_{Cr} is the total concentration of chromium(III) and b is the cell length. In calculation of the concentration of hydrogen sulfite ion, account was taken of the formation of sulfur dioxide ($Q = [H^+][HOSO_2^-]/[SO_2] = 0.043$);[16] in a second approximation account also was taken of the sulfite bound by chromium(III). The light absorption at 340 nm was subject to mild correction for that due to sulfur(IV). The plots involving $\tilde{a}$ as ordinate, one of which is given in Figure 1, were linear, and a straightforward derivation[17] identifies the slope of the line as $-Q_1^{-1}$ and the intercept as a_1, the molar absorbancy index of sulfitochromium(III) ion. The derived results are as follows

(13) Some observations similar to these have been reported.[14]

(14) G. P. Haight, Jr., E. Perchonock, J. Emmenegger, and G. Gordon, *J. Amer. Chem. Soc.*, **87**, 3835 (1965).

(15) These data are available as Document No. NAPS-01036 from ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. The price is $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to: CCMIC-NAPS.

(16) M. Frydman, G. Nilsson, T. Rengemo, and L. G. Sillén, *Acta Chem. Scand.*, **12**, 878 (1958).

(17) T. W. Newton and G. M. Arcand, *J. Amer. Chem. Soc.*, **75**, 2449 (1953).

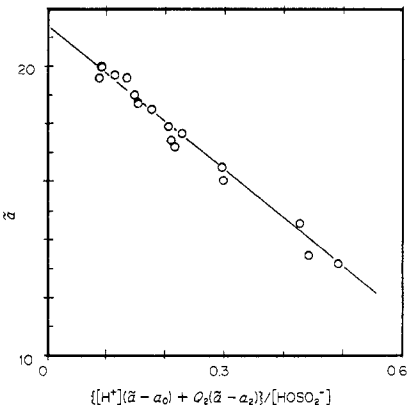

Figure 1.—Spectrophotometric data at 440 nm for evaluation of Q_1. The line gives a_1 = 21.4 l. mol^{-1} cm^{-1} and Q_1 = 0.060.

(presented as λ (nm), a_1 (in l. mol^{-1} cm^{-1}), Q_1): 340, 17.7, 0.064; 430, 22.2, 0.059; 440, 21.4, 0.060; 590, 20.5, 0.060; 620, 17.6, 0.0635. The consistency of the data at the several wavelengths supports the assumption that no complications are present due to species containing two (or more) bound sulfite ions.[18] Since the concentration of hydrogen ion varied by a factor of 3, the sulfite-containing species is identified as $CrOSO_2^+$, not $CrOSO_2H^{2+}$. (The concentration ratio $[HSO_3^-]/[H^+]$ varied by a factor of ~15, from 7.3 to 115.) Of course, a species $Cr(OH)(OSO_2H)^+$ is indistinguishable from $CrOSO_2^+$.

Use of the derived value of Q_1 (Q_1 = 0.061 ± 0.002) and the values of a_1 at each of the wavelengths studied as well as the other relevant equilibrium quotients and molar absorbancy indices allows calculation of the expected values of $\tilde{a}$. The average of all measured values of $|\tilde{a}(\text{obsd}) - \tilde{a}(\text{calcd})|/\tilde{a}(\text{obsd})$ is ~0.012.

The Interaction of $Cr_2(OH)_2^{4+}$ and SO_2.—Solutions with the ranges of concentrations 1.6 × 10^{-3}–3.2 × 10^{-3} *M* $Cr_2(OH)_2^{4+}$, 0.03–0.50 *M* H^+, and 0.003–0.011 *M* SO_2 showed spectra with constant values of molar absorbancy indices from λ 360 to 650 nm. This indicates the formation of a single relatively stable complex between a sulfur(IV) species and dimeric hydroxychromium(III) ion. The molar absorbancy indices obtained from eight different solutions are as follows (given as λ (nm), a (l. (mol of dimer)$^{-1}$ cm^{-1})): 650, 22.0; 600, 39.0; 588, 41 (a_{max}); 570, 38.8; 540, 25.2; 520, 15.8; 501, 11.8 (a_{min}); 480, 17.6; 460, 31.8; 450, 39.8; 430, 51.2; 424, 52.2 (a_{max}); 420, 51.0; 400, 37.8; 380, 18.2; 360, 7.8. With these spectral data establishing the molar absorbancy indices of the complex involving sulfur(IV) and dimeric hydroxychromium(III) ion, the relative concentrations of complexed and uncomplexed dimer can be calculated from spectrophotometric measurements on solutions containing less sulfur(IV). Eleven measurements on three solutions into which sulfite was added in successive small amounts established the form of the equilibrium quotient and its value

$$Q = \frac{[Cr_2(OH)(OSO_2)^{3+}][H^+]}{[Cr_2(OH)_2^{4+}][SO_2]} = 158 \pm 12$$

(18) R. F. Kruh, *J. Amer. Chem. Soc.*, **76**, 4865 (1954); C. F. Baes, *J. Phys. Chem.*, **60**, 878 (1956).

The range of concentrations of sulfur dioxide and hydrogen ion over which the spectral data are correlated were 8 × 10^{-5}–1.5 × 10^{-3} and 0.04–0.5 *M*, respectively. In the measurements upon which these calculations are based the ratio $[Cr_2(OH)(OSO_2)^{3+}]/[Cr_2(OH)_2^{4+}]$ ranged from 0.3 to 8. Formation of the sulfite complex of dimeric hydroxychromium(III) ion occurred at a measurable rate (over a period of several minutes).

The Aquation of Chlorochromium(III) Ion in the Presence of Sulfite Ion.—The aquation of chlorochromium(III) ion in acidic oxygen-free solutions containing sulfite ion was determined at 25° in solutions of ionic strength equal to 0.25 *M*. The concentration of chlorochromium(III) ion (initially 1.7 × 10^{-4}–1.9 × 10^{-3} *M*) was followed as a function of time by an analysis which involved ion-exchange separation of the unreacted chlorochromium(III) ion from the products, hexaaquochromium(III) ion and sulfitochromium(III) ion. In each experiment, the aquation followed first-order kinetics, $-\text{d ln } [CrCl^{2+}]/dt = k_{obsd}$. The dependence of the apparent first-order rate coefficient upon sulfite ion was derived from the data after first correcting for pathways involving transition states of composition $\{CrCl^{2+}\}^{\ddagger}$ and $\{Cr(OH)Cl^+\}^{\ddagger}$ already studied[19]

$$k_{Cl} = \frac{[H^+]}{[HOSO_2^-]}\left\{k_{obsd} - 2.77 \times 10^{-7} - \frac{2.84 \times 10^{-8}}{[H^+]}\right\}$$

in which the rate constants are based upon the second as the unit of time and the numerical values are taken from ref 19. Since the correction to k_{obsd} was small, the fact that the ionic strength employed in the earlier study was 1.0 *M* was considered unimportant. Values of k_{Cl} derived from solutions with various values of the concentration ratio $[HOSO_2^-]/[H^+]$ are given in Table I. Over a tenfold range of $[HOSO_2^-]/[H^+]$, the

TABLE I
THE RATE OF AQUATION OF CHLOROCHROMIUM(III) ION IN THE PRESENCE OF SULFITE ION[a]

$10^2[HOSO_2^-]$, *M*	$[HOSO_2^-]/[H^+]$	$10^5 k_{obsd}$,[b] sec^{-1}	$10^6 k_{Cl}$, sec^{-1}
0.46	0.96	2.60	2.07
1.7	2.7	4.71	1.57
1.4	3.4	5.95	1.54
4.1	9.4	15.3	1.55
8.1	10.9	16.9	1.52
8.6	18.0	28.4	1.54
8.0	22.0	29.5	1.30
8.0	22.0	34.9	1.55
8.0	34	52.5	1.51

[a] 25°; I = 0.25 *M*. [b] $k_{obsd} = -\text{d ln } [CrCl^{2+}]/dt$.

derived values of k_{Cl} are essentially constant; the average value is 1.51 × 10^{-5} sec^{-1}. Although most of these experiments were done in light, one (that with $[HOSO_2^-]/[H^+]$ = 18) was done in the dark. The reaction went essentially to completion in all cases, and addition of 0.01 *M* chloride ion in two experiments or 0.001 *M* hexaaquochromium(III) ion in one experiment had no appreciable effect upon the derived value of k_{Cl}.

(19) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

The Aquation and Formation of Isothiocyanatochromium(III) Ion in the Presence of Sulfur(IV).—The aquation of isothiocyanatochromium(III) ion in acidic oxygen-free solutions (I = 0.25 M) containing sulfur(IV) was studied at 25° in the same manner as that employed in study of the chlorochromium(III) ion system. The initial concentration of complex was kept low (1×10^{-4}–3×10^{-4} M) to eliminate the reverse reaction. Correction for aquation occurring by pathways involving the transition states of composition[20] $\{CrNCS^{2+}\}^{\ddagger}$, $\{Cr(OH)(NCS)^{+}\}^{\ddagger}$, and $\{Cr(OH)_2(NCS)\}^{\ddagger}$ was negligible. The value of k_{NCS} was obtained from the observed first-order rate coefficient (k_{obsd})

$$k_{NCS} = \frac{[H^+]}{[HOSO_2^-]} k_{obsd}$$

Values obtained as a function of solution composition are given in Table II. The average value of k_{NCS} is

TABLE II

THE RATE OF AQUATION OF ISOTHIOCYANATOCHROMIUM(III) ION IN THE PRESENCE OF SULFITE ION[a]

$10^2 \times$ $[HOSO_2^-]$, M	$[HOSO_2^-]/[H^+]$	$10^7 \times$ k_{NCS^-},[b] sec^{-1}	$10^2 \times$ $[HOSO_2^-]$, M	$[HOSO_2^-]/[H^+]$	$10^7 \times$ k_{NCS^-},[b] sec^{-1}
1.79	1.4	6.6	6.35	11.8	6.4
3.47	3.0	6.6	7.23	15.8	7.0
1.56	3.8	7.6	7.46	18.4	6.5
6.03	6.3	6.5	8.06	20.2	6.9
2.19	6.5	7.0	3.36	27.3	8.1
8.31	8.7	5.6	7.76	30.2	7.3
2.32	9.5	7.4	8.06	33.6	7.1
1.79	11.5	9.5	9.71	39.5	6.8

[a] 25°, I = 0.25 M. [b] $k_{NCS^-} = [H^+]k_{obsd}/[HOSO_3^-]$.

7.1×10^{-7} sec^{-1} (with the average difference between the individual values and this average being 0.6×10^{-7} sec^{-1}). Some of these experiments were done in the dark; the derived rate constants were essentially the same as those obtained in experiments done in the light.[21]

Experiments on the rate of formation of monoisothiocyanatochromium(III) ion from hexaaquochromium(III) ion and thiocyanate ion in the presence of sulfur(IV) were less precise than the aquation experiments just described. From the rate coefficient for the first-order approach to equilibrium, one can calculate $k \cong 2.8 \times 10^{-3}$ l. mol^{-1} sec^{-1} for the rate constant associated with the term $k[CrOSO_2^+][SCN^-]$ at 25° (I = 0.25 M).

Equilibria Involving Bis(isothiocyanato)chromium(III) Species.—The procedures already outlined allowed evaluation of the equilibrium quotients

$$Q_{2c} = \frac{[cis\text{-}Cr(NCS)_2^+]}{[CrNCS^{2+}][SCN^-]}$$

$$Q_{2t} = \frac{[trans\text{-}Cr(NCS)_2^+]}{[CrNCS^{2+}][SCN^-]}$$

Six solutions (I = 0.25 M) were studied at 25°; the species present at zero time were *trans*-$Cr(NCS)_2^+$ (1 experiment), *cis*-$Cr(NCS)_2^+$ (1 experiment), a mixture of the two isomers (1 experiment), and $CrNCS^{2+}$ (3 experiments). Some hexaaquochromium(III) was present also in two of the experiments. The presence of sulfur(IV) to catalyze establishment of equilibrium does not influence the equilibrium concentrations of species containing one and two bound thiocyanate ions since there is inappreciable net binding of sulfite ion by these species (at $[HOSO_2^-]/[H^+] \leq 17$, the maximum value employed). Equilibrium values for the ratio [cis]/[trans] did not depend upon $[HOSO_2^-]/[H^+]$ over the range 7.2–17. The values of Q_{2c} and Q_{2t} obtained are 15.9 ± 0.5 and 8.5 ± 0.5, respectively. These values correspond to an equilibrium distribution of isomers [cis]/[trans] = 1.9 ± 0.13. This agrees reasonably well with the value[6] ~2 for 95°.

The Aquation of Bis(isothiocyanato)chromium(III) Species.—The rate of aquation of each isomeric bis(isothiocyanato)chromium(III) species was studied at 25° (I = 0.25 M) in both the absence and presence of sulfur(IV). The analytical procedure (spectrophotometric determination of free thiocyanate ion), capable of determining a concentration of $\geq 7 \times 10^{-6}$ M, allowed evaluation of the rate over only a few per cent reaction. It was observed that light increased the rate of aquation of the bis species, and the results reported here were obtained with the samples kept in the dark. In the absence of sulfur(IV), the dependence of the apparent rate coefficient upon the concentration of hydrogen ion is

$$k_{app} = \frac{\Delta[SCN^-]/\Delta t}{[Cr(NCS)_2^+]} = a + b\frac{1}{[H^+]}$$

For five experiments with the trans isomer ($[Cr(NCS)_2^+] = 1.4 \times 10^{-3}$–$2.2 \times 10^{-3}$ M) over the acidity range $[H^+] = 8.9 \times 10^{-4}$–$3.0 \times 10^{-2}$ M, the values of k_{app} are correlated (with an average deviation of ~10%) with rate constants $a = 2.8 \times 10^{-8}$ sec^{-1} and $b = 3.8 \times 10^{-11}$ mol l.$^{-1}$ sec^{-1}. For nine experiments with the cis isomer ($[Cr(NCS)_2^+] = 1.4 \times 10^{-3}$–$2.8 \times 11^{-3}$ M) over the acidity range $[H^+] = 9.8 \times 10^{-4}$–0.18 M, the values of k_{app} are correlated (with an average deviation of ~6%) with rate constants $a = 2.3 \times 10^{-8}$ sec^{-1} and $b = 2.0 \times 10^{-10}$ mol l.$^{-1}$ sec^{-1}.

The rate of aquation of each of these isomers was determined also in the presence of sulfur(IV); the pathways not involving sulfur(IV) contributed less than 10% to the observed rate in these experiments. Five experiments with the trans isomer ($[Cr(NCS)_2^+] = 1.1 \times 10^{-3}$–$2.2 \times 10^{-3}$ M) gave, after correction for the contribution of these other pathways, values for the rate constant for the term $k[Cr(NCS)_2^+][HOSO_2^-]/[H^+]$ of 5.8×10^{-8}, 5.8×10^{-8}, 5.5×10^{-8}, 5.5×10^{-8}, and 6.3×10^{-8} sec^{-1} at $[HOSO_2^-]/[H^+]$ = 7.2–25.1. Five experiments with the cis isomer ($[Cr(NCS)_2^+] = 1.2 \times 10^{-3}$–$2.6 \times 10^{-3}$ M) gave, after appropriate correction, values of the rate constant defined above of 1.3×10^{-7}, 1.3×10^{-7}, 1.6×10^{-7}, 1.5×10^{-7}, and 1.5×10^{-7} sec^{-1} at $[HOSO_2^-]/[H^+]$ = 5.3–24.6.

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

(21) Pentaammineisothiocyanatochromium(III) is known to photoaquate: E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, **91**, 1076 (1969).

The Isomerization of Isomeric Bis(isothiocyanato)-chromium(III) Species.—Since direct isomerization of bis(chloro)chromium(III) species occurs,[22] some experiments to investigate the analogous reactions for bis(isothiocyanato)chromium(III) species were attempted. These were done both in the presence and absence of sulfur(IV). The data, obtained as already described, could not be correlated quantitatively in terms of a reaction scheme analogous to that which correlated data for the chloride system. The rate constants obtained for aquation of each of the isomers are considered reliable; these experiments lasted only 1–10 hr. The isomerization experiments, on the other hand, lasted up to 600 hr. It seems probable that slight decomposition of thiocyanate ion during this period produces species which catalyze the ligand displacement reactions of chromium(III).[23] Although direct isomerization of *cis*- and *trans*-bis(isothiocyanato)chromium(III) species occurs, reliable values of the rate constants are not available.

The Rate of Conversion of $Cr_2(OH)_2^{4+}$ to $Cr(OH_2)_6^{3+}$ in the Presence of Sulfur(IV).—Sulfur(IV) increases the rate at which dimeric hydroxychromium(III) ion dissociates to yield hexaaquochromium(III) ion. Under conditions of the experiments, 81–99% of the dimer was present as sulfite complex and 1.5% or less of the monomer was present as sulfite complex. The net reaction is, therefore, $Cr_2(OH)(OSO_2)^{3+} + 3H^+ = 2Cr^{3+} + 2H_2O + SO_2$. Although the reaction is nicely first order in each experiment,[24] the dependence of the first-order rate coefficient upon sulfur dioxide concentration is not simple. Values of the empirical first-order rate coefficient ($k = -\mathrm{d} \ln [\mathrm{dimer}]/\mathrm{d}t$) are consistent with the equation

$$k = \left(\frac{158[SO_2]}{158[SO_2] + [H^+]}\right)\frac{a[H^+] + b\dfrac{[SO_2]}{[H^+]}}{1 + c\dfrac{[SO_2]}{[H^+]^2}}$$

with $a = 2.4 \times 10^{-5}$ l. mol^{-1} sec^{-1}, $b = 7.5 \times 10^{-4}$ sec^{-1}, and $c = 2.2_4$ mol l.$^{-1}$ Table III summarizes the experimental observations and presents a comparison of the observed first-order rate coefficient with that calculated using these three parameters.

TABLE III

RATE OF CONVERSION OF THE SULFITE COMPLEX OF DIMERIC HYDROXYCHROMIUM(III) TO HEXAAQUOCHROMIUM(III) ION[a]

$-\mathrm{d} \ln [\mathrm{dimer}]/\mathrm{d}t = k$

		10^5k, sec^{-1}	
$[H^+]$, M	$10^2[SO_2]$, M	Obsd	Calcd
0.033	0.64	1.1	1.0
0.037	0.68	1.0	1.1
0.054	0.275	1.1	1.1
0.054	1.11	2.1	1.6
0.154	1.06	2.6	2.5
0.303	2.10	3.4	3.6
0.310	3.90	4.7	5.1
0.417	3.10	4.3	4.3
0.500	5.81	5.8	6.2
0.506	1.38	2.4	2.4
0.506	3.49	4.2	4.5
0.512	8.87	8.2	7.8
0.800	3.76	4.1	4.2
0.800	4.26	4.6	4.6

[a] 25.0°, $I = 1.00 \pm 0.02$ M, initial concentration of dimer 1.1×10^{-3}–4.3×10^{-3} M.

Discussion

The lability of sulfitochromium(III) ion suggests strongly that it contains the linkage $CrOSO_2$ (not $CrSO_3$), formation of the species occurring without breaking the chromium(III)–oxygen bond. This behavior resembles that in the chromium(III)–chromium(VI)[25] and the chromium(III)–nitrite[4] systems, and it is consistent with the relatively high rate of the sulfur dioxide–sulfite transformation.[26] Combination of the equilibrium quotient $Q_1 = [CrOSO_2^+][H^+]/[Cr^{3+}][HOSO_2^-] = 0.061$ (for 25° and $I = 0.25$ M) with the equilibrium quotient for the acid dissociation of hydrogen sulfite ion ($K_2 \cong 6 \times 10^{-8}$)[27] gives $Q = [CrOSO_2^+]/[Cr^{3+}][SO_3O_3^{2-}] \cong 1 \times 10^6$. This is $\sim 10^5$-fold larger than the corresponding equilibrium quotient for the formation of sulfatochromium(III) ion (inner-sphere species).[28] Chromium(III) discriminates in favor of sulfite ion (compared to sulfate ion) to approximately the same extent as does hydrogen ion

$$CrOSO_3^+ + SO_3^{2-} = CrOSO_2^+ + SO_4^{2-} \qquad Q \cong 10^5$$
$$HOSO_3^- + SO_3^{2-} = HOSO_2^- + SO_4^{2-} \qquad Q \cong 10^5$$

The approximate constancy of the rate constants defined as

$$k_X = \frac{[H^+]}{[HOSO_2^-]}\frac{\Delta \ln [CrX^{2+}]}{\Delta t}$$

with X = SCN or Cl, to the highest values of the concentration of sulfite ion studied indicates in each case that the chromium(III) species containing both sulfite ion and anionic ligand ion does not form to an appreciable extent at this limiting concentration condition. An appreciable trend in values of this quotient would be observable if $[Cr(X)(OSO_2)]/[CrX^{2+}] \geq 0.3$; therefore, upper limits to the equilibrium quotients

$$Q_X = \frac{[Cr(X)(OSO_2)][H^+]}{[CrX^{2+}][HOSO_2^-]}$$

are $Q_{Cl} \leq 0.01$ (maximum value of $[HOSO_2^-]/[H^+] \cong 34$) and $Q_{NCS} \leq 0.008$ (maximum value of $[HOSO_2^-]/[H^+] \cong 40$).

The remarkable catalytic effect of sulfite ion on displacement reactions of chromium(III) is shown most clearly in a comparison of second-order rate constants for the formation of isothiocyanatochromium(III) ion and chlorochromium(III) ion from the incoming ligand and hexaaquochromium(III) ion, hy-

(22) J. D. Salzman and E. L. King, *Inorg. Chem.*, **6**, 426 (1967).

(23) Postmus and King[20] reported that abnormally high rates of aquation of $(H_2O)_5CrNCS^{2+}$ are observed in solutions containing decomposition products of thiocyanate ion.

(24) In some experiments a higher rate was observed in the initial portion of the experiment.

(25) E. L. King and J. A. Neptune, *J. Amer. Chem. Soc.*, **77**, 3186 (1955).

(26) M. Eigen, K. Kustin, and G. Maass, *Z. Phys. Chem. (Frankfurt am Main)*, **30**, 130 (1961).

(27) H. V. Tartar and H. H. Garretson, *J. Amer. Chem. Soc.*, **63**, 808 (1941).

(28) N. Fogel, J. M. J. Tai, and J. Yarborough, *ibid.*, **84**, 1145 (1962).

droxypentaaquochromium(III) ion, and sulfitopentaaquochromium(III) ion; these derived rate constants are given in Table IV. The relative reactivities of

TABLE IV
SECOND-ORDER RATE CONSTANTS DEFINED BY THE RATE LAW[a]

$$d[CrX^{2+}]/dt = k[Cr^{III}][X^-] \quad (t = 25°)$$

Cr^{III} species	$X^- = NCS^-$	$X^- = Cl^-$
$Cr(OH_2)_6^{3+}$	2×10^{-6} [b]	3×10^{-6} [d]
$Cr(OH_2)_5OH^{2+}$	6×10^{-6} [b]	2×10^{-5} [d]
$Cr(OH_2)_5OSO_2^+$	3×10^{-3} [c]	3×10^{-5} [e]

[a] Dimensions of k are l. mol^{-1} sec^{-1}. [b] From ref 20. [c] Calculated from the equilibrium quotient[10] and the rate constant for aquation measured in this work. Value measured directly in this work (see text) agrees with this value. [d] From combining data of ref 19 ($I = 1.0$ M) and equilibrium data in R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, **86**, 795 (1964). [e] Calculated from equilibrium data in the reference cited in *d* and rate of aquation obtained in the present study.

aquochromium(III) ion, hydroxychromium(III) ion, and sulfitochromium(III) ion toward thiocyanate ion are approximately 1:30:1500 and toward chloride ion are approximately 1:700:1000.

The question of whether the labilizing effect of sulfite is a trans effect, as it is in the sulfur-bonded amminesulfitocobalt(III) species,[2a] was explored in the aquation reactions of isomeric bis(isothiocyanato)-chromium(III) species. There is, at most, slight evidence for the labilizing effect of sulfite ion or hydroxide ion being attributable to a trans effect. Comparing aquation rate constants for the two isomers, the ratio for the uncatalyzed pathways (k_{cis}/k_{trans}) is 2.3/2.8 = 0.82, and for the sulfite-catalyzed pathway the value is 15/5.9 = 2.5. The corresponding ratio for the pathways involving transition states of the composition $\{Cr(OH)(NCS)_2\}^+$ is $2.0 \times 10^{-10}/3.8 \times 10^{-11} = 5.3$. Before a completely rational comparison of these ratios can be made, one would have to know the equilibrium constants for association of sulfite with the two isomeric bis species and also the acid dissociation constant for the isomeric bis species. These values are not known. The problem is complicated further by the possibility of cis bis species forming isomeric species upon associating with sulfite ion or hydroxide ion. Of course, the simple presence of the inverse hydrogen ion concentration term and the sulfite ion concentration term in the rate law for aquation of the trans isomer shows that the effect of neither ion can be solely a trans effect. It would appear, therefore, that oxygen-donating sulfite and hydroxide as ligands exert less of a trans effect than sulfur-donating sulfite as a ligand; this conclusion is consistent with trends in trans-activating ability of ligands discussed by Basolo and Pearson.[29]

The rate law for conversion of $Cr_2(OH)(OSO_2)^{3+}$ to $Cr(OH_2)_6^{3+}$ is consistent with the mechanism

$$Cr_2(OH)(OSO_2)^{3+} + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr_2OSO_2^{4+} + H_2O$$

$$Cr_2OSO_2^{4+} \xrightarrow{k_3} 2Cr^{3+} + SO_3^{2-}$$

$$Cr_2OSO_2^{4+} + SO_3^{2-} \xrightarrow{k_4} 2Cr^{3+} + 2SO_3^{2-}$$

with a, b, and c of the empirical rate law identified as $a = k_1k_3/(k_2 + k_3)$, $b = k_1k_4Q/(k_2 + k_3)$, and $c = k_4Q/(k_2 + k_3)$, where $Q = [H^+]^2[SO_3^{2-}]/[SO_2]$. The value of k_1 is obtainable from the empirical parameters: $k_1 = b/c = 3.3 \times 10^{-4}$ l. mol^{-1} sec^{-1}. This value of k_1 is only slightly larger than the analogous rate constant for ring opening of $Cr_2(OH)_2^{4+}$, found by Thompson[3b] to be 9×10^{-5} l. mol^{-1} sec^{-1}.

(29) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, pp 369–375.

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π-Bonded Complexes of the Tetraphenylborate Ion with Rhodium(I) and Iridium(I)

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Several complexes of tetraphenylborate ion with Rh(I) and Ir(I) have been isolated in which tetraphenylborate coordinates to the metal *via* a $\pi(h^6)$-bonded interaction. The protonation of a π-cyclopentadienyl complex to yield cyclopentadiene-tetraphenylboratorhodium(I) was found by deuteration studies to give exclusively endo product. The nmr and infrared spectra of these complexes are discussed.

Introduction

Tetraphenylborate ion has been widely used as a counterion for the isolation of cationic species from solution. During our investigation[1,2] of the catalytic properties of the weakly solvated cationic species of the type $Rh(P(C_6H_5)_3)_2H_2S_2^+$ (S = solvent), totally different behavior was found using tetraphenylborate as anion in place of perchlorate or hexafluorophosphate. Further investigation of this anomalous behavior shows that tetraphenylborate can readily coordinate to transition metals *via* a π-bonded interaction of one of

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(1) J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969).

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