Contribution from the Department of Chemistry, Western Illinois University, Macomb, Illinois 61455,
and State University of New York at Buffalo, Buffalo, New York 14214

Kinetics and Mechanisms of the Formation, Acid-Catalyzed Decomposition, and Intramolecular Isomerization of Oxygen-Bonded (Sulfito)pentaaquochromium(III) Perchlorate[1a]

P. A. MORITZEN,[1b] A. A. EL-AWADY,*[1c] and G. M. HARRIS[1d]

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The fast reversible SO_2 uptake by hexaaquochromium(III) perchlorate to form an unstable O-bonded intermediate $[Cr(OH_2)_5(OSO_2)]^+$ was studied by stopped-flow technique. Formation of the O-bonded sulfito species was studied over the range $2.3 \leqslant$ pH $\leqslant 3.8$ and $0.14 \leqslant$ [total sulfite] $\leqslant 0.875$ M at $I = 1.0$ M $(NaClO_4)$ at 25 °C. The second-order rate constant for the formation of the sulfito-O intermediate is $(4.4 \pm 0.2) \times 10^2$ M^{-1} s^{-1}. Retardation by $S_2O_5^{2-}$ is observed and is ascribed to the formation of nonreactive ion pairs $[Cr(OH_2)_6\cdots S_2O_5]^+$ with an association constant of 279 ± 13 M^{-1} at 25 °C and $I = 1.0$ M. The rate of the reverse SO_2 elimination reaction is directly proportional to $[H^+]$ in the range $0.015 \leqslant (H^+) \leqslant 1.0$ M at $I = 1.0$ M $(NaClO_4)$ with a rate constant of 1.58 ± 0.04 M^{-1} s^{-1} at 25 °C. The O-bonded intermediate undergoes intramolecular rearrangement to the S-bonded isomer in the ranges $1.5 \leqslant$ pH $\leqslant 2.5$ and $0.035 \leqslant$ [total sulfite] $\leqslant 0.35$ M and $I = 1.0$ M $(NaClO_4)$ with a rate constant equal to $(1.98 \pm 0.2) \times 10^{-4}$ s^{-1}, at 25 °C. The mechanistic implications of the rate data will be discussed.

Introduction

The chemistry of (sulfito)metal complexes has received considerable attention in recent years.[2-10] The sulfite ligand is ambidentate in the sense that it could coordinate, at least in theory, to a given metal ion through sulfur or one of the oxygens acting as a monodentate ligand or through two oxygens acting as a bidentate ligand. Both S-bonded[7-10] and O-bonded[2-6] sulfito complexes are known and well documented, with the former being the most stable. Although chelated sulfito complexes have been reported,[11,12] the evidence for their existence is not conclusive.

O-bonded sulfito complexes are formed on the stopped-flow time scale by reaction of acidic aqueous sulfite with a number of metal hydroxo complexes and therefore necessitate the postulation of a "direct-addition" mechanism. In this type of mechanism, the reaction takes place without the metal–oxygen bond fission, which is characteristic of conventional hydroxo or aquo ligand replacement. This, of course, will lead to the formation of an O-bonded sulfito complex.

Recently van Eldik[5] studied the SO_2 uptake and elimination reactions of hydroxopentaamminechromium(III) ion with dissolved SO_2. The observed reactions were kinetically fast and form the O-bonded sulfito species $[Cr(NH_3)_5(OSO_2)]^+$ in a similar fashion to the cobalt(III) analogues.[2-4] The resulting sulfito-O complex is unstable and loses SO_2 on acidification, to regenerate the Cr-$(NH_3)_5OH_2{}^{3+}$ species, or undergoes subsequent isomerization and/or substitution reactions. These secondary reactions, which are also observed in the cobalt(III) analogues, make it impossible for the authors to isolate the O-bonded species.

Carlyle and King[13] studied the rate of aquation of chlorochromium(III) ion $[Cr(OH_2)_5Cl]^{2+}$, (isothiocyanato)chromium-(III) ion $[Cr(OH_2)_5NCS]^{2+}$, and isomeric bis(isothiocyanato)-chromium(III) ions $[Cr(OH_2)_4(NCS)_2]^+$ in the presence of sulfite ions. The results demonstrated a noticeable increase in complex lability in the presence of sulfite. In these reactions the sulfite ion is believed to be O-bonded, with the suggested reactive species being $Cr(OH_2)_6{}^{3+}$ and HSO_3^-. The sulfite ligand labilizes the complex, increasing the anation rate, and is easily removed by acidification.

$Cr(OH_2)_6{}^{3+}$ is considered to be one of the few aquo species sufficiently inert so that the exchange rate[14] can be determined by conventional sampling techniques. This inertness also exists for the vast majority of Cr(III) substitution reactions.[15] In these reactions a dissociative or a dissociative interchange mechanism has been invoked.

Formation of Cr(III) complexes of coordinatively unsaturated anions such as the nitrite ion[16,17] was believed to occur by a mechanism termed pseudosubstitution, where substitution takes place without direct metal–ligand bond breakage, and hence will occur on the ligand rather than on the metal.

In this study we report the kinetics and mechanisms of the SO_2 uptake and elimination reaction of hexaaquochromium(III) perchlorate as well as the isomerization of the resulting oxygen-bonded (sulfito)pentaaquochromium(III) ion.

Experimental Section

Materials. Except when indicated, reagent grade chemicals were used without further purification. The laboratory-distilled water was further purified by passage through a mixed-bed anion–cation-exchange resin column. Solid sodium metabisulfite, $Na_2S_2O_5$ (Baker Analyzed), was used as the source of sulfite; this salt is very stable in storage but hydrates very rapidly upon dissolution in water to yield sulfite.[2]

Preparation and Characterization of Compounds. Hexaaquo-chromium(III) perchlorate was prepared by the reduction of reagent grade chromic trioxide (Cr_2O_3) in perchloric acid solutions by hydrogen peroxide according to the reaction

$$2Cr_2O_3 + 6HClO_4 + 3H_2O_2 \rightarrow 2Cr(OH_2)_6(ClO_4)_3 + 3O_2$$
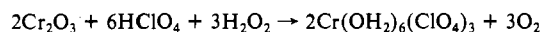
The hydrated salt was then crystallized from the solution.[18] In some cases, purchased samples of chromium(III) perchlorate (Baker Chemical Co.) were also used. Solutions of chromium(III) species were analyzed for total chromium by a spectrophotometric method.[19] The UV–visible spectral parameters of the complex measured by a Cary 118 spectrophotometer were close to those reported earlier.[13] Chromium(III) solutions prepared were stored in the refrigerator and were never kept longer than 3 days at a time.

Isolation of the Solid $Cr(H_2O)_4(OH)(SO_3)$. Our early attempts to isolate the green sulfito product used column chromatography. A solution made of 0.62 g of $Cr(OH_2)_6(ClO_4)_3$ and 3.8 g of $Na_2S_2O_5$ in 100

(1) (a) Taken in part from: Moritzen, P. A. M.S. Thesis, Western Illinois University, 1983. (b) 36 Fellswood Dr., Livingston, NJ 07039. (c) Present address: Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia. (d) State University of New York at Buffalo.
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mL of H_2O was left standing for 6 h. Then, of the above solution 20 mL were placed on a Na^+ form cation-exchange column. The free sulfite was easily removed with H_2O (tested with $Ba(ClO_4)_2$). No movement of the green band was observed with washings of up to 4 M $NaClO_4$. Then, washing with a 1.25 M $Na_2S_2O_5$ solution (2.5 M S(IV)) moved the green band with the phase line. The visible spectrum of the solution collected was the same as that observed in the kinetic runs. Thus, it appears there is a sulfite-dependent equilibrium where removal of sulfite from the reaction mixture forms a product that cannot be eluted except by addition of sulfite.

We next tried to isolate the product by precipitation. The reactant solution was made by dissolving 4 g of $Cr(OH_2)_6(ClO_4)_3$ and 15 g of $Na_2S_2O_5$ in 100 mL of H_2O and adjusting the pH to 2.9 with NaOH. Bubbling SO_2 through the solution for 1 h lowered the pH to 1.9. Letting the solution stand overnight yielded a green precipitate. It had been noted[20] that (sulfito)metal complexes dissolve readily in water containing sulfur dioxide, owing to the formation of the bisulfite. Also, the green band, which could not be eluted from the cation-exchange resin until aqueous sulfite was used, may be a precipitate formed when free sulfite was initially eluted off. On the premise that the loss of sulfite caused both precipitations, a reactant solution of 4 g of $Cr(OH_2)_6(ClO_4)_3$ and 2 g of $Na_2S_2O_5$ dissolved in 100 mL of H_2O was adjusted to pH 2.9. After the mixture was allowed to stand for 30 min, the green solid began to precipitate. Repeating the experiment in 25 mL of H_2O yielded a precipitate in 15 min. Mixing the reagents dry and then adding enough water to make a slurry, filtering, and washing with water yielded the product almost immediately. The solid obtained was redissolved in 1 M $HClO_4$ and the resultant mixture heated nearly to boiling. The visible spectrum of the solution was similar to those observed experimentally. The spectrum had λ_{max} at 430 and 594 nm at pH 1.

Results of an analysis of the solid product:[21] Cr, 22.86; S, 15.19; Cl, <0.05. These results coupled with the chromatographic behavior of its aqueous solution are consistent with the formula $Cr(H_2O)_4(OH)[(SO_3)]$: Anal. Calcd: Cr, 23.51; S, 14.5.

General Rate Measurements. All kinetic data were obtained by following absorbance change vs. time at 423 nm and 25 °C, except the sulfite dependence of the S-bonded sulfito formation, which was studied at 580 nm. All other spectra were recorded at room temperature. The ionic strength of the reaction mixtures was adjusted to 1 M with 4 M $NaClO_4$.

Rate measurements for the SO_2 uptake were made by using the "equilibrium method", previously designed to study CO_2-uptake reactions[22] under pseudo-first-order conditions with an excess of sulfite. In this procedure, appropriate amounts of hexaaquochromium(III) perchlorate were dissolved in water, the pH was adjusted to a predetermined value with perchloric acid or sodium hydroxide as needed, and the ionic strength was adjusted to 1 M. The same was done for solutions of sodium metabisulfite except acid was not added. These solutions were introduced separately into the reservoirs of an automated Durrum Model 110 stopped-flow assembly, and the runs were made in the usual manner. Final pH determination is discussed later. After mixing, the Cr(III) concentration was 0.0175 M in all uptake measurements. The S(IV) concentration was kept at 0.525 M during the pH dependence study and was varied in the range of 0.14–0.875 M (0.14 M ≤ [S(IV)] ≤ 0.875 M) for the study of rate dependence on S(IV). We have thus utilized the sulfite buffering capacity in these experiments.

Rate measurements for SO_2 elimination were followed by acidifying the O-bonded (sulfito)pentaaquochromium(III) species with perchloric acid. This complex was prepared in situ by dissolving appropriate amounts of $Cr(OH_2)_6(ClO_4)_3$ (0.035 M) and $Na_2S_2O_5$ to give $S_T = 0.525$ M (S_T = total sulfur(IV) concentration) and the ionic strength adjusted to 1 M. The perchloric acid concentration varied in the range 0.1 M ≤ $[HClO_4]$ ≤ 2.0 M. In the SO_2-elimination experiment, each solution was placed in one of the two reservoir syringes of the automated Durrum Model 110 stopped-flow assembly. The time from mixing Cr(III) and S(IV) to the first stopped-flow measurement was always less than 15 min

to avoid O- to S-bonded isomerization. The initial pH of the Cr–S mixture and final pH of the reaction mixtures were recorded (see pH measurements).
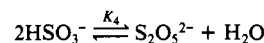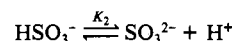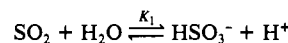
The observed pseudo-first-order rate constants were calculated in the usual way using a linear least-squares program and are reported as the mean of at least six measurements for the S(IV) dependence study of SO_2 uptake and at least 10 measurments for the elimination reactions.

Kinetic studies of the slow secondary step were performed in a thermostated cell holder of a Cary UV–visible spectrophotometer (Cary 118 Cary 15, or Cary 14) in self-buffered sulfite media. The reagent solutions were thermostated at the reaction temperature and then rapidly mixed in a thermostated 1-cm curvette. The reaction mixture was allowed to stand 2 min before recording the absorbance. This time was to allow the uptake and elimination reactions to reach equilibrium. The chromium-(III) was always 0.011 M after mixing, and the sulfur(IV) concentration was varied in the range 0.035 M ≤ [S(IV)] ≤ 0.29 M, as specified in the Results and Discussion. The observed pseudo-first-order rate constants were calculated from plots of $\ln (A_\infty - A_0)/(A_\infty - A_t)$ vs. time, where A_0, A_t, and A_∞ are the absorbances at time zero, t, and infinity, respectively. Most of the experiments were done at $\lambda = 423$ nm where the transformation of the O-bonded to S-bonded sulfito product is associated with a substantial absorbance difference. In a number of experiments, complete spectral curves were run at a series of time intervals over the wavelength range 350–600 nm with the rate of isomerization followed at $\lambda = 423$ nm. The data proved that there is no wavelength dependence of the observed rate constant.

pH Measurement. The pH measurements were made with a Beckman Research Model pH meter and a calomel reference electrode or a Fisher Accumet Model 420 pH/ion meter equipped with a Markson combination electrode. The meters were standardized against commercially available standard buffers.
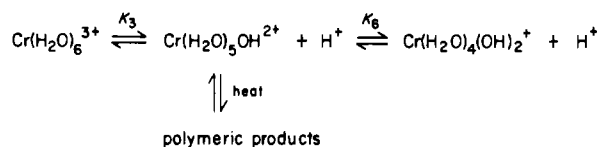
In the uptake reaction, equal volumes of the two reactant solutions were rapidly mixed in a water-jacketed sample holder and the pH was measured. For the elimination reaction, equal volumes of the reactant solutions were rapidly mixed, the pH was immediately measured, and the pH was measured again when the kinetic measurements were completed. The kinetic measurements took a total of between 15 and 20 min. No noticeable pH change was observed. In the slow O- to S-bonded isomerization, equal volumes of Cr(III) and S(IV) solutions were mixed at 25 °C. The initial pH was recorded after 2 min, and the solution was returned to the water bath. At t_∞, the final pH of the thermostated solution was also measured.

Acid Dissociation Constants. The dissociation equilibria for SO_2 in aqueous solution may be represented by

$$SO_2 + H_2O \xrightleftharpoons{K_1} HSO_3^- + H^+$$

$$HSO_3^- \xrightleftharpoons{K_2} SO_3^{2-} + H^+$$

$$2HSO_3^- \xrightleftharpoons{K_4} S_2O_5^{2-} + H_2O$$

Analysis of our data was done on the basis of $K_1 = 1.26 \times 10^{-2}$ M, $K_2 = 5.01 \times 10^{-7}$ M, and $K_4 = 7.0 \times 10^{-2}$ M^{-1} at 25 °C and $I = 1.0$M as reported in the literature.[2]

Solutions of hexaaquochromium(III) are an equilibrium mixture of $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_5OH^{2+}$, and $Cr(OH_2)_4(OH)_2^+$ as well as a number of polymeric products. The equilibria can be presented by

$$Cr(H_2O)_6{}^{3+} \xrightleftharpoons{K_3} Cr(H_2O)_5OH^{2+} + H^+ \xrightleftharpoons{K_6} Cr(H_2O)_4(OH)_2{}^+ + H^+$$
$$\Big\downarrow\text{heat}$$
$$\text{polymeric products}$$

The values[13,15] of K_3 and K_6 used in this work, are $K_3 = 1.32 \times 10^{-4}$ M and $K_6 = 2.5 \times 10^{-6}$ M.

Results and Discussion

Qualitative Observations. When SO_2 gas is bubbled through a $Cr(H_2O)_6{}^{3+}$ solution, the color changes from blue to green. When SO_2 is removed, by acidification or bubbling N_2 through the solution, the characteristic blue of $Cr(H_2O)_6{}^{3+}$ is obtained. The blue to green color change was rapid when sodium metabisulfite was used as the sulfur(IV) source. This reaction is completely reversible if the solution is immediately acidified. The degree of $Cr(H_2O)_6{}^{3+}$ regeneration was shown spectrophotometrically to decrease with an increase in time before acidification. The slow secondary reaction is complete in several hours and was determined to be irreversible.

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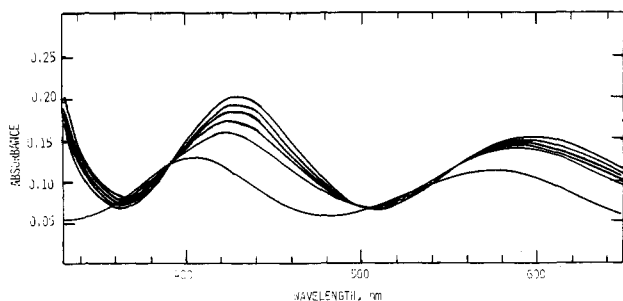
Figure 1. Successive scans of the spectral changes during the SO₂ uptake by $Cr(OH_2)_5OH^{2+}$ and isomerization of $Cr(OH_2)_5(OSO_2)^+$ to its S-bonded form: [complex] = 0.10 M, $[S_t]$ = 0.35 M, pH 2.60, temp 25 °C, I = 1.0 M ($NaClO_4$). Time in minutes reading upward at 440 nm: 0, 1, 10, 45, 80, and ∞ respectively.

The complete reaction sequence was followed spectrophotometrically (Figure 1) in the UV–visible spectrum. The observed reaction rates of the initial and secondary steps are sufficiently different to study them separately. Carlyle and King[13] used formate buffer for their investigation of chromium complex reactivity in the presence of sulfite, but our investigation showed a reaction between the buffer and $Cr(H_2O)_6^{3+}$ solutions. Several other buffer systems were tested but proved too reactive in the Cr(III)–S(IV) system. For these reasons we decided to study the reactions using the sulfite buffering capacity. The experimental values obtained for the pseudo-first-order rate constants were found to be unaffected when the experiments were done in the presence or absence of dissolved oxygen.

O-Bonded Sulfito Formation. The kinetics of the formation of the O-bonded sulfito species was studied over the range 2.3 < pH < 3.8 and 0.14 < S_T < 0.875 M at 25 °C and I = 1.0 M (NaClO₄). The experimental results obtained are summarized in Table I. All the tabulated pseudo-first-order rate constants, k_{obsd}, were calculated by means of a linear least-squares analysis of log (A_t − A_∞) vs. t data obtained directly from the automated stopped-flow system, where A_t and A_∞ are functions of the absorbances at time t and ∞, respectively. These plots were linear at least up to 3 half-lives.

The observed rate constants of Table I may be treated as done in similar previous studies[2–4] as the sum of the overall rate constants for SO₂ uptake by $Cr(OH_2)_5OH^{2+}$ (k_f) and SO₂ elimination (k_b) from $[Cr(OH_2)_5(OSO_2H)]^{2+}$ (eq 1). As a first approxi-

$$k_{obsd} = k_f + k_b \qquad (1)$$

mation, we neglected the back-reaction rate constant, k_b, in our attempt to fit the data of the SO₂-uptake experiments to the concentrations of hydrogen ions and the various sulfur(IV)-containing species in solution. This approximation is quite valid for the present system since the observed rate constants for the SO₂ elimination were found to be much less than for the uptake reaction, even at hydrogen ion concentrations 10–1000 times greater than those used for the uptake experiments.

An investigation of the aqueous $S_2O_5^{2-}/SO_2/HSO_3^-/SO_3^-$ equilibria reveals that, unlike our previous studies, the $S_2O_5^{2-}$ species cannot be neglected in the calculations. The concentration of the metabisulfite ion ranges from 0.001 to 0.04 M. The concentration of the various sulfur(IV)-containing species are given by the series of equations (2)–(5), where K_1, K_2, and K_4 are the

$$[S_2O_5^{2-}]^{1/2} = \frac{K_1 K_4^{1/2}[H^+]}{[H^+]^2 + K_1[H^+] + K_1 K_2} \{S_T - 2[S_2O_5^{2-}]\} \qquad (2)$$

$$[SO_2] = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1 K_2} S_c = f_1 S_c \qquad (3)$$

$$[HSO_3^-] = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1 K_2} S_c = f_2 S_c \qquad (4)$$

$$[SO_3^{2-}] = \frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2} S_c = f_3 S_c \qquad (5)$$

Table I. Dependence of k_{obsd} on pH and [Total Sulfite] for SO₂ Uptake by $Cr(OH_2)_6^{3+}$ in Sulfite Buffer at 25 °C

pH	$[S]_T$	$10^2 k_{obsd}$, s⁻¹	k_1, M⁻¹ s⁻¹			
			a	b	c	d
2.34	0.525	42 ± 2	155	1.16	401.7	4.21
2.50	0.525	42 ± 2	104	1.09	418.5	4.38
2.70	0.525	41 ± 1	97	1.01	427.7	4.48
2.90	0.525	40 ± 1	94	0.98	430.4	4.51
2.92	0.525	39 ± 1	91	0.96	420.7	4.41
3.03	0.525	38 ± 1	90	0.94	416.7	4.36
3.12	0.525	36 ± 2	87	0.91	399.1	4.18
3.24	0.525	37 ± 2	92	0.96	418.2	4.37
3.34	0.525	38 ± 1	98	1.03	434.1	4.56
3.39	0.525	37 ± 1	98	1.03	427.6	4.48
3.50	0.525	36 ± 1	102	1.06	425.0	4.44
3.51	0.525	34 ± 1	96	1.01	400.2	4.20
3.59	0.525	36 ± 1	108	1.13	431.2	4.52
3.69	0.525	34 ± 0.3	111	1.16	417.2	4.37
3.78	0.525	36 ± 2	127	1.33	452.5	4.74
3.86	0.525	34 ± 2	131	1.57	438.6	4.59
3.06	0.14	41 ± 0.4	350	3.67	448.5	4.70
3.07	0.28	42 ± 0.4	183	1.91	381.3	3.99
3.04	0.35	40 ± 0.3	194	1.46	373.2	3.91
3.06	0.525	44 ± 0.3	105	1.10	403.9	4.23
3.00	0.700	51 ± 0.4	92	0.96	663.4	6.95
3.05	0.875	49 ± 0.4	72	0.76	752	7.08

[a] Calculated rate constants by using eq 6. [b] Calculated rate constants by use of a scheme in which the reacting species are $Cr(OH_2)_6^{3+}$ and HSO_3^-. [c] Calculated rate constants by use of Scheme I and eq 10 with Q_2 = 279 M⁻¹. [d] Calculated rate constants by use of a scheme in which the reacting species are $Cr(OH_2)_6^{3+}$ and HSO_3^- in the presence of metabisulfite ion pairs.

equilibrium constants for the SO_2/HSO_3^-, HSO_3^-/SO_3^{2-}, and $HSO_3^-/S_2O_5^{2-}$ pairs, respectively, S_T is the total concentration of all the sulfur(IV)-containing species, and $S_c = (S_T - 2[S_2O_5^{2-}])$. The data were then fitted with a mechanism for the SO₂-uptake/elimination process as outlined in previous studies.[2–4] With the assumption that $Cr(OH_2)_5OH^{2+}$ and SO₂ are the reacting species, the expression for the observed rate constant k_{obsd} takes the form (6), where K_3 and K_5 are acid dissociation constants for $Cr(OH_2)_6^{3+}$ and $Cr(OH_2)_5OSO_2H^{2+}$, respectively, k_1 is the second-order rate constant for SO₂ uptake by $Cr(OH_2)_5OH^{2+}$, and k_2 is the second-order rate constant for SO₂ elimination.

$$k_{obsd} = k_1 \frac{K_3}{K_3 + [H^+]}[SO_2] + k_2 \frac{[H^+]}{[H^+] + K_5} \qquad (6)$$

Values of k_1 calculated from the known values of k_{obsd}, K_3, [SO₂], and [H⁺] and utilizing eq 6 are given in Table I. (Note that the values of k_b were neglected in these and subsequent calculations). One notes that k_1 calculated in this way is not constant and decreases with pH to a minimum value and then increases when S_T is kept constant. For data at varied S_T and constant pH, the calculated k_1 values decrease also with increasing S_T. This type of behavior is inconsistent with simultaneous addition of SO₂ to $Cr(OH_2)_6^{3+}$ and $Cr(OH_2)_5OH^{2+}$ as proposed in the SO₂-uptake study of $Co(tren)(OH_2)_2^{3+}$.[3] An attempt to fit the data to a reaction scheme in which the reacting species are $Cr(OH_2)_6^{3+}$ and HSO_3^- resulted in similar behavior for k_1 (Table I). It should be noted, however, that, kinetically, SO₂ addition to $Cr(OH_2)_5OH^{2+}$ is indistinguishable from HSO_3^- addition to $Cr(OH_2)_6^{3+}$. The apparent anomalous behavior of k_1 with pH and its continuous fall off with increase in total S(IV) concentration led us to investigate other possible mechanisms.

Careful consideration of the data, particularly those at essentially constant pH and varied S_T over a 6-fold order of magnitude, reveals that one of the sulfur(IV)-containing species has a retarding influence on the rate of the reaction. A similar rate-retarding influence was observed in the study of the SO₂-uptake/elimination processes of $Co(tetren)OH_2^{3+}$.[4] This influence was ascribed to the SO_3^{2-} ion due to the formation of a nonreactive ion pair $Co(tetren)OH_2^{2+}\cdots SO_3^{2-}$. We have attempted to test this possibility and assume the formation of the nonreactive ion pair

Scheme I. Mechanism for the O-Bonded Sulfito Formation and Elimination via Addition of SO_2 to $Cr(OH_2)_5OH^{2+}$ in the Presence of Metabisulfite Ion Pairs
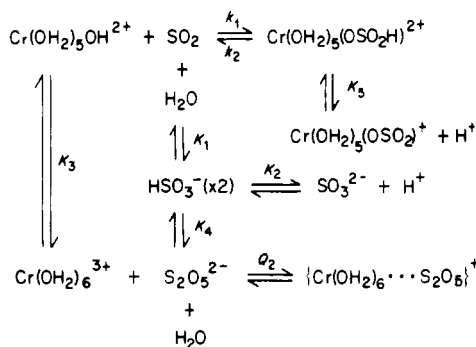
$Cr(OH_2)_6^{3+}\cdots SO_3^{2-}$. In this scheme, the observed rate constant is given by the equation (7), which upon rearrangement takes the

$$k_{obsd} = k_1 \frac{K_3}{K_3 + [H^+] + Q_1[H^+]f_3S_c} f_1S_c + k_2\frac{[H^+]}{[H^+] + K_5} \quad (7)$$

form (8) or (9). In these equations Q_1 is the ion-pair formation

$$\frac{[H^+]}{k_{obsd} - k_b} = \left(\frac{1}{k_1}\right)\left\{\frac{K_3 + [H^+]}{K_3}\right\}\left\{\frac{[H^+]}{f_1S_c}\right\} + \frac{Q_1K_1K_2}{k_1K_3} \quad (8)$$

$$\frac{[H^+]}{k_{obsd} - k_b} = \left(\frac{1}{k_1}\right)\left\{\frac{K_3 + [H^+]}{K_3}\right\}\left\{\frac{[H^+]}{[SO_2]}\right\} + \frac{Q_1K_1K_2}{k_1K_3} \quad (9)$$

constant, $f_1S_c = [SO_2]$ given by eq 3, and f_3S_c is the SO_3^{2-} concentration given by eq 5. If this mechanism is applicable, then a plot of

$$\frac{[H^+]}{k_{obsd} - k_b} \quad \text{vs.} \quad \left\{\frac{K_3 + [H^+]}{K_3}\right\}\left\{\frac{[H^+]}{[SO_2]}\right\}$$

should be linear for all the data. This, however, was not the case, and it was obvious that such a scheme does not interpret the data, particularly when one considers the data at constant pH and varied S(IV) concentrations. Careful investigation of the $S_2O_5^{2-}/SO_2/HSO_3^-/SO_3^{2-}$ equilibrium shows, however, that in the range of pHs used in this study the predominant species are $S_2O_5^{2-}$, SO_2, and HSO_3^-. The behavior of SO_2 and HSO_3^- are identical as we have shown previously. However, the presence of $S_2O_5^{2-}$ in the concentration ranges given could explain the observed rate-retarding effects. This fact, however, does not eliminate the possible formation of sulfite ion pairs with the hexaaquochromium(III) ion since such an ion pair might very well be important at higher pH values, a region in which the SO_3^{2-} ion concentration becomes meaningful.

Scheme I gives a mechanistic interpretation of the data in which a metabisulfite ion pair is formed between $S_2O_5^{2-}$ and $Cr(OH_2)_6^{3+}$, leading to rate retardation. This scheme leads to an observed rate constant given by (10) in which Q_2 is the metabisulfite ion-pair
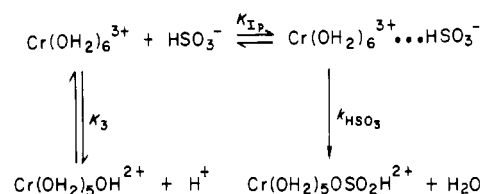
$$k_{obsd} = \frac{k_1K_3[SO_2]}{K_3 + [H^+] + Q_2[H^+][S_2O_5^{2-}]} + \frac{k_2[H^+]}{[H^+] + K_5} \quad (10)$$

formation constant and all the other quantities and constants are as defined earlier. Rearrangement of eq 10 gives (11). A plot

$$\left(\frac{1}{k_{obsd} - k_b}\right)\left\{\frac{[SO_2]}{[H^+][S_2O_5^{2-}]}\right\} =$$
$$\left(\frac{1}{k_1}\right)\left\{\frac{K_3 + [H^+]}{K_3}\right\}\left\{\frac{1}{[H^+][S_2O_5^{2-}]}\right\} + \frac{Q_2}{k_1K_3} \quad (11)$$

of $[1/(k_{obsd} - k_b)]\{[SO_2]/[H^+[S_2O_5^{2-}]\}$ vs. $\{(K_3 + [H^+])/K_3\}\{1/$

Scheme II. Mechanism for O-Bonded Sulfito Formation via an Interchange Mechanism with Bisulfite Ion Pairs

$[H^+][S_2O_5^{2-}]\}$ for all data gave a good straight line, and a least-squares fit of the data gave the values $k_1 = (4.36 \pm 0.23) \times 10^2$ s^{-1} M^{-1} and $Q_2 = 279 \pm 13$ M^{-1}. The value of 436 s^{-1} M^{-1} for the second-order rate constant for the SO_2-uptake process is some 10^6 smaller than the corresponding constant for the Cr-$(NH_3)_5OH_2^{3+}$ system[5] or the cobalt(III) systems studied.[2-4]

The slow water-exchange rate of hexaaquochromium(III) and the relative inertness of aquochromium(III) compounds toward anation[15] rule out the possibility of formation of the O-bonded sulfito complex via conventional HSO_3^- substitution for ligand water. Rate-limiting addition of HSO_3^- to $Cr(OH_2)_6^{3+}$ without Cr-O bond fission (cleavage) remains a possibility. As indicated previously, this process is kinetically indistinguishable from SO_2 addition to $Cr(OH_2)_5OH^{2+}$.

Application of this mechanism gives $k_1' = 4.58 \pm 0.25$ s^{-1} M^{-1} and $Q_2 = 282 \pm 13$ M^{-1}. One notes, however, that the second-order rate constant for SO_2 addition "k_1" and for HSO_3^- addition "k_1'" are related by the equation (12).

$$k_1 = k_1'K_1/K_3 \quad (12)$$

The values of 436 and 4.58 s^{-1} M^{-1} for the second-order rate constants k_1 and k_1', respectively, are some 10^6 smaller than the corresponding constants for the $Cr(NH_3)_5OH_2^{3+}$ systems[5] or the cobalt(III) systems studied.[2-4] These are, however, of comparable order of magnitude to those observed for the reactions of $HSeO_3^-$ with a number of Co(III) aquo and hydroxo species.[31] In these systems, an interchange mechanism was suggested, involving the rapid formation of a precursor outer-sphere species in a preequilibrium followed by rate-determining interchange between outer and inner spheres of the complex. Application of this mechanism to the present system (Scheme II) gives (13) or (14). A plot of

$$k_{obsd} = \frac{k_{HSO_3}K_{Ip}[H^+][HSO_3^-]}{K_3 + [H^+] + K_{Ip}[H^+][HSO_3^-]} \quad (13)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_{HSO_3}} + \left\{\frac{K_3 + [H^+]}{[H^+][HSO_3^-]}\right\}\left(\frac{1}{k_{HSO_3}K_{Ip}}\right) \quad (14)$$

$1/k_{obsd}$ vs. $(K_3 + [H^+])/[H^+][HSO_3]$ should yield a straight line with an intercept of $1/k_{HSO_3}$ and a slope of $1/(k_{HSO_3}K_{Ip})$. Least-squares fit of the data to this form with the exclusion of the point at $S_T = 0.14$ M gave acceptable straight line fit and yielded values of $k_{HSO_3} = 0.50 \pm 0.06$ s^{-1} and $K_{Ip} = 10 \pm 4$ M^{-1}.

Of interest is the comparison of the product $k_{HSO_3}K_{Ip} = 5.0$ s^{-1} M^{-1} to the second-order rate constant $k_1' = 4.58$ s^{-1} M^{-1}, which are essentially the same, leading one to conclude that on the basis of kinetic data alone one cannot distinguish between the two pathways. Nevertheless the fact that these second-order rate constants are of comparable orders of magnitude to those obtained for $HSeO_3^-$ addition reaction to a number of aquo- and hydroxocobalt(III) species and to the HSO_3^- pathway in $Pt(NH_3)_5OH^{2+}$ interaction with aqueous sulfite (Table IV) suggests that the reacting species in the present system might very well be the bisulfite ion instead of molecular SO_2 and that the chromium(III) species reacting might be the hexaaquo cation $Cr(OH_2)_6^{3+}$.

SO_2-Elimination Process. The rate data for the SO_2-elimination reaction are given in Table II. In a manner similar to the uptake

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Table II. Dependence of k_{obsd} on [H⁺] for the SO₂-Elimination Reaction of $Cr(OH_2)_5(OSO_2)^+$ at 25 °C

[H⁺], M	k_{obsd}, s⁻¹	k_f,[a] s⁻¹	k_b,[b] s⁻¹
0.015	0.498	0.426	0.072
0.031	0.407	0.310	0.097
0.110	0.365	0.121	0.244
0.340	0.571	0.143	0.527
0.750	1.213	0.020	1.193
1.000	1.677	0.015	1.662

[a] Calculated by using eq 10. [b] $[S]_T = 0.2625$ M.

Table III. Dependence of k_{obsd} on pH and [Total Sulfite] for the Isomerization of $Cr(OH_2)_5(OSO_2)^+$ at 25 °C

pH	$[S]_T$, M	$10^5 k_{obsd}$, s⁻¹	pH	$[S]_T$, M	$10^5 k_{obsd}$, s⁻¹
2.2	0.035	1.14	1.65	0.350	15.09
2.2	0.058	1.88	1.81	0.350	19.10
2.2	0.093	3.29	2.04	0.350	16.04
2.2	0.140	5.65	2.15	0.350	19.51
2.2	0.187	8.14	2.24	0.350	21.67
2.2	0.233	8.50	2.35	0.350	21.60
2.2	0.292	10.13	2.60	0.350	20.92
1.53	0.350	17.74	2.83	0.350	19.82

experiments, the observed pseudo-first-order rate constant is expressed as the sum of the forward reaction and back-reaction rate constants, as given by eq 1. The forward rate constant contribution to the overall observed rate constant is calculated from the known values of k_1, Q_2, [H⁺], and the various sulfur(IV)-containing species by the use of eq 10 or 12. A plot of k_b vs. hydrogen ion concentration gave a good straight line with an intercept of 0.04 ± 0.02 and a slope of 1.58 ± 0.04 (obtained from a least-squares fit). These values indicate that the elimination process involves direct reaction of hydrogen ions with $Cr(OH_2)_5(OSO_2)^+$ followed by rate-determining loss of SO₂ from the protonated species as illustrated in the various schemes given. However, for the latter case to be valid, it is necessary that the equilibrium constant K_5 be very large and that $Cr(OH_2)_5(OSO_2H)^+$ acts as a strong acid in the Brønsted sense. In either case, the value of k_2 or k_2/K_5 is 1.58 ± 0.04 M⁻¹ s⁻¹. The intercept of 0.04 ± 0.02 is essentially

zero and does not warrant additional consideration.

Isomerization of $Cr(OH_2)_5(OSO_2)^+$. The slow secondary step, following the SO₂/HSO₃⁻ addition reaction, is assumed to be associated with O-bonded to S-bonded isomerization. As we indicated in the Experimental Section, the results of elemental analysis as well as chromatographic behavior of solutions of the final product are consistent with the formula $Cr(OH_2)_4OH(SO_3)$. The isolated product, however, could very well be a polymer. It is very resistant to solubility in aqueous as well as acid solutions. The only other possibility is the formation of a dinuclear complex—a common occurence with Cr(III) species. The present reaction is associated with isosbestic points at 559, 498, and 393 nm (Figure 1). The reaction was studied in the ranges 1.5 ≤ pH ≤ 2.8 and 0.035 ≤ S(IV) ≤ 0.35 M. The data obtained are summarized in Table III. One notes that the pseudo-first-order rate constant sharply increases with total S(IV) and attains a limiting value that is independent of pH used. Under these conditions, the rate law for isomerization of $Cr(OH_2)_5(OSO_2)^+$ to its S-bonded sulfito analogue is best described by (15). Lack

$$\frac{-\partial[Cr(OH_2)_5(OSO_2)^+]}{\partial t} = k_{obsd}[Cr(OH_2)_5(OSO_2)^+] \quad (15)$$

of dependence on pH or the various S(IV)-containing species suggests that the process is totally intramolecular. The low values of k_{obsd} at low S(IV) concentration is best explained as due to the incomplete conversion of the aquo complex to the O-bonded sulfito complex. Similar behavior to this was observed in the study of the $Co(tetren)(OSO_2)^+$ isomerization reaction (4). The average first-order rate constant obtained in the present system is (1.98 ± 0.2) × 10⁻⁴ s⁻¹ compared to 2.8 × 10⁻⁴ s⁻¹ for the cobalt system.

A summary of data concerning the various isomerization and sulfite addition reactions of a number of sulfito complexes is presented in Table IV. It is clearly noticeable that the isomerization reactions have very similar rate constants at 25 °C with only but a slight dependence on the nature of the central metal atom and/or other ligands. This result lends support to the intramolecular mechanism suggested for the isomerization process. Similar argument was used in the interpretation of isomerization rates of the nitrito complexes of the type $M(NH_3)_5ONO^{n+}$.[16] This was shown to be the case for the Co(III) complex using ¹⁸O tracer studies.[26]

Table IV. Rate Parameters for the Isomerization of (Sulfito-O)metal Complexes and the Reactions of Various Aquo- and Hydroxometal Complexes with SO₂/HSO₃⁻/HSeO₃⁻ and the Acid Dissociation Constants of the Corresponding Aquo Complexes

I. Isomerization Reactions

complex ion	k_1, s⁻¹	ref	complex ion	k_1, s⁻¹	ref
$Co(tetren)(OSO_2)^+$	2.7×10^{-4}	4	$Cr(OH_2)_5(OSO_2)^+$	1.98×10^{-4}	this work
$Pt(NH_3)_5(OSO_2)^+$	5.6×10^{-4}	25			

II. SO₂/HSO₃⁻/HSeO₃⁻ Addition Reactions

complex ion	reactant	k_1, M⁻¹ s⁻¹	pK_a	ref
$Co(NH_3)_5OH^{2+}$	SO₂	4.7×10^8	6.30	2
$Co(tetren)OH^{2+}$	SO₂	3.3×10^8	6.30	4
$Co(tren)(OH_2)_2^{3+}$	SO₂	9×10^8	5.80	3
$Co(tren)(OH_2)OH^{2+}$	SO₂	5.3×10^7	5.80	3
$Co(tren)(OH)_2^+$	SO₂	2.4×10^9	8.23	3
cis-$Co(en)_2(OH_2)OH^{2+}$	SO₂	1.0×10^8	6.06	23
cis-$Co(en)_2(OH)_2^{2+}$	SO₂	10^{10}	8.20	23
$trans$-$Co(en)_2(OH_2)OH^{2+}$	SO₂	1.4×10^8	4.40	24
$trans$-$Co(en)_2(OH)_2^+$	SO₂	1.9×10^{10}	7.90	24
$Rh(NH_3)_5OH^{2+}$	SO₂	1.8×10^8	6.80	5
$Pt(NH_3)_5OH^{3+}$	SO₂	6.8×10^6	4.23	25
$Cr(NH_3)_5OH^{2+}$	SO₂	2.9×10^8	5.20	5
$Cr(OH_2)_5OH^{2+}$	SO₂	4.4×10^2	3.88	this work
$Pt(NH_3)_5OH^{3+}$	HSO₃⁻	590	4.23	25
$Cr(OH_2)_6^{3+}$	HSO₃⁻	5	3.88	this work[a]
$Cr(OH_2)_6^{3+}$	HSO₃⁻	4.58	3.88	this work[b]
$Co(NH_3)_5(OH_2)^{3+}$	HSeO₃⁻	147	6.3	31
$Co(NH_3)_5(OH)^{2+}$	HSeO₃⁻	8	6.3	31
cis-$Co(en)_2(OH_2)_2^{3+}$	HSeO₃⁻	281	6.06	31
cis-$Co(en)_2(OH_2)OH^{2+}$	HSeO₃⁻	4	6.06	31

[a] Using an I_a mechanism. [b] Using the direct-addition mechanism in the presence of metabisulfite ion pairs.

Another comparison of interest concerns the SO_2-addition reactions to a number of metal hydroxo complexes (Table IV). It is noted that in all cases, with the exception of $Cr(OH_2)_5OH^{2+}$, studied in this work the direct SO_2 addition to the mono and dihydroxo forms of the various species are very rapid, ranging from a low of 6.8×10^6 s^{-1} for the monohydroxoplatinum(IV) to a high of 2.2×10^{10} s^{-1} for the *cis*-dihydrobis(ethylenediamine)cobalt(III) complex, a value within only 1 or less order of magnitude of the diffusion-controlled limit. The value of 4.4×10^2 s^{-1} M^{-1} for $Cr(OH_2)_5OH^{2+}$ obtained in this work is clearly an exception especially when compared to the pentaammine analogue, 2.9×10^8 s^{-1} M^{-1}. The value, however, of 4.38 s^{-1} M^{-1} obtained by using a mechanism in which the reacting species are $Cr(OH_2)_6^{3+}$ and HSO_3^- is of comparable magnitude to that observed for the reactions of $Co(NH_3)_5OH^{2+}$ and $HSeO_3$ (8 s^{-1} M^{-1}) and *cis*-Co(en)$_2$(OH$_2$)OH^{2+} and $HSeO_3^-$ (4 s^{-1} M^{-1}) (see Table IV), suggesting very strongly that this is the preferred route in the present

system.

It has previously been shown[27,30] that log k for the CO_2 uptake by various metal hydroxo complexes depends linearly with the pK value of the corresponding aquo form. Analysis of the data given in Table IV suggests the possibility of such a trend over the limited range of available data. The observed variations, however, suggest that the nature of the central metal atom and/or other ligands must play an important role in determining the value of the rate-limiting step for the SO_2-addition reactions.

Contribution from the Department of Chemistry,
University of Victoria, British Columbia, Canada V8W 2Y2

(Phosphinoalkyl)silyl Complexes. 5.[1] Synthesis and Reactivity of Congeneric Chelate-Stabilized Disilyl Complexes of Rhodium(III) and Iridium(III): Chlorobis[[(diphenylphosphino)ethyl]dimethylsilyl]rhodium and -iridium

MARY J. AUBURN and STEPHEN R. STOBART*

Reaction of [M(COD)Cl]$_2$ (M = Rh, Ir; COD = cycloocta-1,5-diene) with excess PPh$_2$CH$_2$CH$_2$SiMe$_2$H in THF solution affords the 5-coordinate M(III) complexes M(PPh$_2$CH$_2$CH$_2$SiMe$_2$)$_2$Cl (1, M = Rh; 2, M = Ir), which are enantiomeric with the two P atoms trans; the common geometry for 1 and 2 deduced from spectroscopic data has been substantiated with X-ray diffraction that shows crystals of the two compounds to be isomorphous. Halide ion exchange reactions yield the analogues 3–6 M-(PPh$_2$CH$_2$CH$_2$SiMe$_2$)$_2$X in which X = Br or I. Treatment of [Ir(COD)Cl]$_2$ with 2 mol equiv of PPh$_2$CH$_2$CH$_2$SiMe$_2$H allows the 6-coordinate intermediate Ir(PPh$_2$CH$_2$CH$_2$SiMe$_2$)(COD)(H)(Cl) (7) to be recovered, in which the chelating ligands occupy a plane with H and Cl mutually trans and from which chel (diphos, dpm, PPh$_2$CH$_2$CH$_2$SiMe$_2$H) displaces COD, yielding respectively Ir(PPh$_2$CH$_2$CH$_2$SiMe$_2$)(chel)(H)(Cl) (8, diphos; 9, dpm) or compound 2, although under similar reaction conditions a Rh analogue of 7 could not be obtained. The coordinatively unsaturated Ir complex 2 reacts rapidly with a variety of neutral molecules (CO, PF$_3$, P[OR]$_3$, RNC), generating 6-coordinate adducts as single isomers possessing a common structure with L entering cis to Cl, trans to Si; with L = *t*-BuNC, Me$_3$CCH$_2$CMe$_2$NC, or Me$_2$CHNC, Rh analogues 10–12 are also formed from 1. Compounds 1 and 10–12 offer the first fully characterized examples respectively of bis(silyl)rhodium, octahedral silylrhodium species, the stability of which contrasts remarkably with the sensitivity toward dissociative cleavage of unsupported Si–Rh bonds.

Conversion of 1 or 2 to the corresponding hydrido complexes M(PPh$_2$CH$_2$CH$_2$SiMe$_2$)$_2$H (23, M = Rh; 24, M = Ir) has been demonstrated in solution with NMR spectroscopy, and although the structures of these species remain uncertain since attempted isolation leads to decomposition, compound 24 has been intercepted to form 6-coordinate CO or *t*-BuNC adducts.

Introduction

Silyl complexes of rhodium and iridium have been studied in considerable detail,[2] principally because of putative intermediacy in metal-catalyzed hydrosilylation of olefins.[3] To date, all examples of such species, regardless of whether M = Rh or Ir, are M(III) derivatives,[2,4] accessed virtually without exception via

oxidative addition of silanes to d^8 precursors including [M(PPh$_3$)$_3$Cl] or *trans*-[M(PPh$_3$)$_2$(CO)X] (M = Rh, Ir; X = Cl, Br), [IrH(PPh$_3$)$_3$CO], or [Ir(diphos)$_2$]$^+$ (diphos = PPh$_2$CH$_2$CH$_2$PPh$_2$). In other respects, however, it has become clear that silyl compounds formed by the two elements are conspicuously dissimilar, rather than resembling one another; in particular, most representative rhodium species are 5-coordinate at the metal center and are very sensitive to reductive cleavage of the Rh–Si bond,[2,5] while iridium analogues, which are ac-

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