vestigation of the chemistry and properties of hydrothermal materials.

Acknowledgment. The financial support of a Research Corp. Cottrell Grant is gratefully acknowledged. The assistance of Mr. J. J. Bartell in obtaining tg data and Mr. E. T. Lance with nitrate analysis is greatly appreciated.

Registry No. $La(OH)_2NO_3$, 12507-74-3; $Pr(OH)_2NO_3$, 36306-07-7; $Nd(OH)_2NO_3$, 51364-99-9; $Sm(OH)_2NO_3$, 51365-00-5; $Eu(OH)_2NO_3$, 51365-01-6; $Gd(OH)_2NO_3$, 51365-02-7; $Tb(OH)_2NO_3$, 51365-03-8; $Dy(OH)_2NO_3$, 51381-69-2; $Y(OH)_2NO_3$, 51365-04-9; $Yb(OH)_2NO_3$, 51365-05-0; $Yb(OH)_2NO_3 \cdot 2H_2O$, 51365-06-1; $La(OH)_3$, 14507-19-8; $Pr(OH)_3$, 16469-16-2; $Nd(OH)_3$, 16469-17-3; $Sm(OH)_3$, 20403-06-9; $Eu(OH)_3$, 16469-19-5; $Gd(OH)_3$, 16469-18-4; $Tb(OH)_3$, 12054-65-8; $Dy(OH)_3$, 1308-85-6; $Y(OH)_3$, 16469-22-0; $Yb(OH)_3$, 16469-20-8; $La(NO_3)_3$, 10099-59-9; $Pr(NO_3)_3$, 10361-80-5; $Nd(NO_3)_3$, 10045-95-1; $Sm(NO_3)_3$, 10361-83-8; $Eu(NO_3)_3$, 10138-01-9; $Gd(NO_3)_3$, 10168-81-7; $Tb(NO_3)_3$, 10043-27-3; $Dy(NO_3)_3$, 10143-38-1; $Y(NO_3)_3$, 10361-93-0; $Yb(NO_3)_3$, 13768-67-7; $Y_2(OH)_5NO_3 \cdot 2H_2O$, 51391-32-3; $Yb_2(OH)_5NO_3 \cdot 2H_2O$, 51391-33-4; $GdONO_3$, 14835-96-2; $La_2O_2(OH)NO_3$, 51391-31-2.

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Sulfite-, Acetate-, and Nitrate-Catalyzed Substitution Reactions of Chromium(III)[1a]

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Received February 4, 1974 AIC40077A

Oxygen-bonded sulfite, nitrate, and acetate labilizations of ligands coordinated to chromium(III) in aqueous solution have been investigated. Kinetic and stoichiometric measurements have been made for sulfite labilizations of acetato- and azidoaquochromium(III) species, acetate labilization of acetatopentaaquochromium(III), and nitrate labilizations of acetato- and fluoroaquochromium(III) species. The rate law terms for the catalyses are of the general form $k[\text{oxy anion}]\cdot[\text{Cr complex}][\text{H}^+]$. The results are interpreted in terms of cis effects arising from seven-coordinated intermediates or transition states formed by chelation of the labilizing oxy anion; the positive hydrogen ion dependence is attributed to protonation of the basic leaving group.

Introduction

Oxy anions have recently been shown to catalyze metal ion substitution reactions.[2–10] It appears that the labilizing oxy anion is usually coordinated to the metal in cobalt(III) complexes, where S-bonded[2–4,11] sulfite exerts primarily a trans effect,[2,3] and in chromium(III) complexes, where O-bonded nitrite,[5] nitrate,[6] and carboxylates[7,8] exert primarily cis effects and O-bonded sulfite[9] exerts both cis and trans effects. Most of the chromium(III) studies that have been described previously[5–9] have involved leaving groups not likely to be protonated in the transition state (chloride, bromide, thiocyanate, water, ammonia), although one study[10] indicated that sulfite may be protonated in the bisulfite-catalyzed aquation of sulfitopentaaquoiron(III) and that azide may be protonated in the bisulfite-catalyzed aquation of azidopentaaquochromium(III).

The purpose of the work described in this paper was to learn whether the basicity of the leaving group in chromium(III) aquation reactions generally affects the form of the empirical rate law for oxy anion catalysis and to obtain evidence regarding any associated changes in mechanism.

Experimental Section

Reagents. Acetatopentaaquochromium(III) solutions were obtained by chromium(II) reduction of acetatopentaamminecobalt(III), as described by Deutsch and Taube.[12] Solutions of acetatopentaamminecobalt(III) were prepared in a sequence beginning with carbonatopentaamminecobalt(III) nitrate, made by the method of Lamb and Mysels;[13] solutions of the carbonato complex were treated with perchloric acid and the water ligands in the resulting aquopentaamminecobalt(III) ions were replaced with acetate in the procedure reported by Sebera and Taube.[14] The chromium(II) solutions were obtained by zinc reduction of hexaaquochromium(III) perchlorate[15] which was the product of hydrogen peroxide reduction of potassium dichromate.[16]

Each of three separate attempts to prepare acetatopentaaquochromium(III) by equilibration of hexaaquochromium(III) and acetate led to a species (or a mixture) elutable with 1.0 M electrolyte from Dowex 50W-X8 cation-exchange resin. The spectrum of the elutable species has maxima at 418 and 509 nm, with absorption coefficients of 16.7 and 28.1 (g-ion of Cr)$^{-1}$ cm^{-1}, respectively. A more complete characterization of this species was not attempted; it may be a chelated acetato complex but it is more probably the polynuclear species mentioned earlier.[12]

Azido- and fluoropentaaquochromium(III) perchlorate solutions were prepared by the equilibration methods described in separate papers by Swaddle and King.[17,18] Chloropentaaquochromium(III) perchlorate solutions were prepared by partial aquation of commercial $CrCl_3 \cdot 6H_2O$ followed by ion-exchange separation using the procedure of Gates and King.[19] Solutions of cyanopentaaquochromium(III) perchlorate were made by partial aquation of potassium hexacyano-

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[1] (a) Supported by the Robert A. Welch Foundation. (b) Robert A. Welch Predoctoral Fellow, 1971–1973.

[2] (a) P. H. Tewari, R. W. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, 6, 611 (1967); (b) H. G. Tsiang and W. K. Wilmarth, *ibid.*, 7, 2535 (1968).

[3] (a) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, 88, 2877 (1966); (b) D. R. Stranks and J. K. Yandell, *Inorg. Chem.*, 9, 751 (1970).

[4] (a) G. P. Syrtsova and N. Z. Lyong, *Zh. Neorg. Khim.*, 16, 406 (1971); (b) N. Z. Lyong, and G. P. Syrtsova, *ibid.*, 16, 704 (1971).

[5] (a) T. C. Matts and P. Moore, *Chem. Commun.*, 29 (1969); (b) T. C. Matts and P. Moore, *J. Chem. Soc. A*, 1632 (1971).

[6] G. Guastalla and T. W. Swaddle, *J. Chem. Soc., Chem. Commun.*, 61 (1973); *Can. J. Chem.*, 52, 527 (1974).

[7] M. V. Olson, *Inorg. Chem.*, 12, 1416 (1973).

[8] E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, *Inorg. Chem.*, 11, 1746 (1972).

[9] D. W. Carlyle and E. L. King, *Inorg. Chem.*, 9, 2333 (1970).

[10] D. W. Carlyle, *Inorg. Chem.*, 10, 761 (1971).

[11] (a) S. Baggio and L. N. Becka, *Acta Crystallogr.*, 25, 946 (1969); (b) T. Nomura and M. Nakahara, *Bull. Chem. Soc. Jap.*, 44, 1233 (1971).

[12] E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

[13] A. B. Lamb and K. J. Mysels, *J. Amer. Chem. Soc.*, 67, 468 (1945).

[14] D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, 83, 1785 (1961).

[15] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, 76, 2103 (1954).

[16] J. C. Kenny and D. W. Carlyle, *Inorg. Chem.*, 12, 1952 (1973).

[17] T. W. Swaddle and E. L. King, *Inorg. Chem.*, 3, 234 (1964).

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

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

chromate(III) using the method reported by Wakefield and Schaap.[20] The hexacyanochromate(III) salt was the product of a standard synthesis.[21]

Chloropentaamminechromium(III) perchlorate was precipitated from a solution of the chloride salt in about 10 *M* sodium perchlorate at 0°. The chloride salt was made by the procedure of Palmer.[22] Aquopentaamminechromium(III) perchlorate was made from chloropentaamminechromium(III) chloride, also by a method described by Palmer.[22] Pentaaquoamminechromium(III) solutions were prepared by the reaction of chromium(II) with hydrazoic acid as reported by Ardon and Mayer.[23]

Sulfur dioxide and sodium perchlorate solutions were made and analyzed as described earlier[24] as were those of barium perchlorate,[9] lithium perchlorate,[25] and sodium sulfite.[10] Reagent grade sodium nitrate was recrystallized from water and was analyzed by the ion-exchange displacement procedure used for sodium perchlorate.[10,24]

The water used in all solutions was redistilled from laboratory-distilled water and was stored in a polyethylene tank. Chemicals in addition to those listed above were reagent grade and were not purified further before use.

Rate Measurements. Most rate measurements were performed on solutions contained in spectrophotometer cells in the thermostated cell compartment of a Beckman ACTA V recording spectrophotometer.[24] Cells to contain sulfur dioxide were purged of oxygen by bubbling the contents of the capped cells with nitrogen gas[24] before addition of the sulfur dioxide. Except as specifically noted below, the rate studies were done at 25° and 1.00 *M* ionic strength maintained with sodium perchlorate.

The rates of aquation of chloropentaamminechromium(III) were measured both by spectrophotometry as described above and by analysis of free chloride ion product. Reactions monitored by the chloride analysis method were made to occur in Pyrex bottles stored in a water bath. Aliquots of the reaction mixtures were removed at measured time intervals over the first few per cent of complete aquation. Each aliquot was transferred to a column of Dowex 50W-X8, 50–100 mesh cation-exchange resin. The free chloride was rinsed through the column and was then allowed to displace thiocyanate ion from excess $Hg(SCN)_2$ in the presence of excess ferric ion. The chloride concentration was proportional to the $Fe(H_2O)_5NCS^{2+}$ absorbance at 460 nm, as described by Vogel.[26] The first-order rate constant for appearance of chloride in each experiment was calculated as the initial slope of a concentration–time plot divided by the initial concentration of $Cr(NH_3)_5Cl^{2+}$: $(\Delta[Cl^-]/\Delta(\text{time}))/[Cr(NH_3)_5Cl^{2+}] = k_{Cl}$.

The rate of aquation of fluoropentaaquochromium(III) was measured by determination of unreacted $Cr(H_2O)_5F^{2+}$ as a function of time, using the procedure described earlier.[18] The reaction mixtures were kept in bottles in a water bath thermostated at 67°.

Results

Sulfur(IV)-Catalyzed Aquation of Acetatopentaaquochromium(III). A careful study of net reaction 1 in acidic

$$Cr(H_2O)_5OOCCH_3^{2+} + H_3O^+ = Cr(H_2O)_6^{3+} + HOOCCH_3 \qquad (1)$$

aqueous perchlorate media has been reported.[12] The forward rate for reaction 1 was described[12] as given by eq 2 where k_1 =

$$-\mathrm{d}\ln\,[Cr(H_2O)_5OOCCH_3^{2+}]/\mathrm{d}t = k_{AC} = k_1 + k_2[H^+] \qquad (2)$$

0.4×10^{-5} sec^{-1} and $k_2 = 7.7 \times 10^{-6}$ M^{-1} sec^{-1} at 25° and ionic strength 1.00 *M* maintained with $LiClO_4$.

Sulfur(IV) was found in the present study to catalyze strongly the aquation of $Cr(H_2O)_5OOCCH_3^{2+}$ under conditions that were identical with those of the earlier study[12] except that $NaClO_4$ was used to maintain ionic strength in the sulfur(IV) work. The empirical form of eq 2 was changed in the presence of sulfur(IV), as indicated by eq 3; the k_3·

$$k_{AC} = k_1 + k_2[H^+] + k_3[HSO_3^-] \qquad (3)$$

$[HSO_3^-]$ term was dominant in our experiments. The results of the individual experiments are shown in Table I and Figure 1. Each experiment gave results in accord with a first-order rate law and the observed first-order rate constant k_{AC} was obtained from a log $(A - A_\infty)$ *vs.* time plot, where A and A_∞ represent absorbances at 570 nm, at a particular time and after completion of the reaction, respectively. Each k_{AC} value was converted to an observed $k_3[HSO_3^-]$ value by subtraction of the k_1 and and $k_2[H^+]$ terms using the reported[12] values for k_1 and k_2. The calculated $k_3[HSO_3^-]$ values listed in Table I were obtained from a least-squares fit[27] of $k_{AC} - k_1 - k_2[H^+] = k_3[HSO_3^-]$, with each datum weighted as $(1/k_{AC})^2$. The fit was good, as is illustrated by the upper line in Figure 1; the fitted value of k_3 is $(9.6 \pm 0.2) \times 10^{-4}$ M^{-1} sec^{-1}, where the indicated uncertainty is the calculated[27] standard deviation.

The concentrations of HSO_3^- and H^+ in each reaction mixture were calculated from the amounts of aqueous SO_2 and $HClO_4$ in the stock solutions added initially, together with the value $Q = 0.043$ *m* for eq 4 at 25° in 1.00 *m* $NaClO_4$.[28]

$$SO_2 + H_2O = HSO_3^- + H^+ \quad Q = 0.043 \qquad (4)$$

Sulfur(IV)-Catalyzed Aquation of Azidopentaaquochromium(III). A detailed study of net reaction 5 in acidic aqueous

$$Cr(H_2O)_5N_3^{2+} + H_3O^+ = Cr(H_2O)_6^{3+} + HN_3 \qquad (5)$$

perchlorate solution has been reported.[17,29] The forward rate for reaction 5 in solutions containing 0.024–0.30 *M* H^+ (the range primarily employed in this work) was described[17] according to eq 6. The values of k_4 and k_5, in solutions of

$$-\mathrm{d}\ln\,[Cr(H_2O)_5N_3^{2+}]/\mathrm{d}t = k_{AZ} = k_4 + k_5[H^+] \qquad (6)$$

1.00 *M* ionic strength maintained with $LiClO_4$, were calculated, respectively, as 0.45×10^{-7} sec^{-1} and 7.5×10^{-7} M^{-1} sec^{-1} at 25° from activation data given in ref 17.

Reaction 5 is catalyzed by sulfur(IV); we studied the catalysis at 25° and found the form of k_{AZ} to be as described by eq 7, where the k_4 and k_5 pathways were minor in each of

$$k_{AZ} = k_4 + k_5[H^+] + k_6[HSO_3^-] \qquad (7)$$

our experiments. The results of the individual experiments are shown in Table II and Figure 1. Each experiment yielded a first-order rate constant k_{AZ} from a log $(A - A_\infty)$ *vs.* time plot; the A values were measured at 585 nm. Each k_{AZ} value was converted to an observed $k_6[HSO_3^-]$ value by subtraction of the reported[17] k_4 and $k_5[H^+]$ terms. The calculated k_6 values shown in the table resulted from a least-squares fit[27] of $k_{AZ} - k_4 - k_5[H^+] = k_6[HSO_3^-]$, with each rate constant weighted as $(1/k_{AZ})^2$. The fit was good (see the lower line in Figure 1) and the fitted value of k_6 is $(2.61 \pm 0.07) \times 10^{-4}$ M^{-1} sec^{-1}.

Sulfur(IV)-Catalyzed Aquations of Other Chromium(III) Species. Attempts to describe quantitatively the effect of sulfur(IV) on the aquation rate of cyanopentaaquochromium(III) have not resulted in complete success, owing to extensive scatter in the measured rate constants. However, it was

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(20) D. S. Wakefield and W. B. Schaap, *Inorg. Chem.*, 8, 512 (1969).

(21) J. H. Bigelow, *Inorg. Syn.*, 2, 203 (1946).

(22) W. G. Palmer, "Experimental Inorganic Chemistry," University Press, Cambridge, England, 1954, pp 398–419.

(23) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

(24) D. W. Carlyle, *J. Amer. Chem. Soc.*, 94, 4525 (1972).

(25) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, 5, 586 (1966).

(26) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1961, p 806.

(27) A computer program, based on Report LASL-2367 + Addenda, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1959, was used.

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

(29) J. C. Templeton and E. L. King, *J. Amer. Chem. Soc.*, 93, 7160 (1971).

Table I. Observed and Calculated Rate Constants for Reaction 1, Defined by Eq 2 and 3 (25°, 1.00 *M* Ionic Strength)

$10^3\times$ [Cr-$(H_2O)_5$-OOC-$CH_3^{2+}]_0$[a]	$10^2\times$ $[HSO_3^-]$[b]	$[H^+]$	$10^5\times$ k_{AC}[c]	$10^5k_3[HSO_3^-]$ Obsd	$10^5k_3[HSO_3^-]$ Calcd[d]
1.97	1.08	0.511	1.36	0.93	1.04
2.27	2.85	0.0324	3.13	3.07	2.74
1.97	3.95	0.111	3.74	3.61	3.79
1.97	5.24	0.0700	5.41	5.31	5.03
1.97	7.56	0.111	7.07	6.93	7.26
2.27	9.71	0.101	9.90	9.79	9.32
1.48	10.1	0.114	10.1	10.0	9.70
2.27	13.1	0.135	12.8	12.7	12.6

[a] All concentrations are moles per liter. [b] Calculations of $[H^+]$ and $[HSO_3^-]$ were done using eq 4. [c] Units are sec^{-1}. [d] $k_3[HSO_3^-]$ (calcd) is the least-squares value obtained from a fit to eq 3. See text.

Table II. Observed and Calculated Rate Constants for Reaction 5, Defined by Eq 6 and 7 (25°, 1.00 *M* Ionic Strength)

$10^3\times$ [Cr-$(H_2O)_5$-$N_3^{2+}]_0$[a]	$10^2\times$ $[HSO_3^-]$[b]	$[H^+]$	$10^5\times$ k_{AZ}[c]	$10^5k_6[HSO_3^-]$ Obsd	$10^5k_6[HSO_3^-]$ Calcd[d]
1.48	1.20	0.22	0.385	0.365	0.314
1.48	1.62[e]	0.024	0.475	0.468	0.423
1.48	1.80	0.20	0.446	0.437	0.470
1.48	1.87	0.20	0.495	0.475	0.489
1.90	2.20	0.22	0.617	0.607	0.575
1.48	2.85	0.11	0.660	0.648	0.745
1.48	3.70	0.044	1.05	1.04	0.967
1.68	3.92	0.001	1.04	1.03	1.02
1.31	8.00	0.24	2.23	2.21	2.09
1.48	11.8	0.30	2.94	2.91	3.08
1.48	17.6[e]	0.054	4.47	4.46	4.60

[a] All concentrations are moles per liter. [b] Calculations of $[H^+]$ and $[HSO_3^-]$ were done using eq 4. [c] Units are sec^{-1}. [d] $k_6[HSO_3^-]$(calcd) is the least-squares value obtained from a fit to eq 7. See text. [e] Sodium sulfite was the S(IV) source.

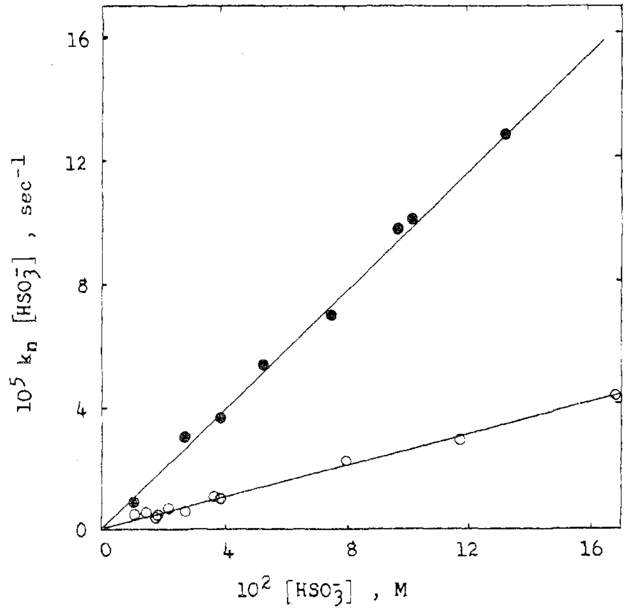

Figure 1. Plots of $k_n[HSO_3^-]$ *vs.* $[HSO_3^-]$: closed circles, $n = 3$ $(Cr(H_2O)_5OOCCH_3^{2+})$; open circles, $n = 6$ $(Cr(H_2O)_5N_3^{2+})$ (at 25° and 1.00 *M* ionic strength).

observed that bisulfite ion (concentrations in the range 0.0044-0.14 *M*, with acidities in the range 0.02-0.43 *M*) does result in an aquation pathway that is dominant over the spontaneous and acid-catalyzed[20,30] pathways. The bisulfite dependence varied between first order at low $[HSO_3^-]$ and approximately zero order at $[HSO_3^-] > 0.1\ M$. Thus, the value of k_{CN} reached a limiting value at high $[HSO_3^-]$, where k_{CN} is approximately described by

$$-d \ln [Cr(H_2O)_5CN^{2+}]/dt = k_{CN} = (1.5 \pm 0.5) \times 10^{-3}[HSO_3^-]/((35 \pm 10) \times 10^{-3} + [HSO_3^-]) \qquad (8)$$

A spectral search was made for significant complex formation between $Cr(H_2O)_5CN^{2+}$ and sulfur(IV), but no spectral evidence for complexation was obtained.

The rate of aquation of chloropentaamminechromium(III) according to reaction 9 was not affected by sulfur(IV). The

$$Cr(NH_3)_5Cl^{2+} + H_2O = Cr(NH_3)_5OH_2^{3+} + Cl^- \qquad (9)$$

aquation rate in the absence of sulfur(IV) was observed by spectrophotometry (515 nm) in one experiment and by analysis of product chloride in one experiment. The aquation rates in the presence of sulfur(IV) were measured by analysis of chloride in two experiments. The results of the experiments are shown in Table III, where the k_{Cl} values are defined by eq 10. The agreement between our results and those of

$$-d \ln [Cr(NH)_5Cl^{2+}]/dt = k_{Cl} \qquad (10)$$

others[31,32] is fair, and no sulfur(IV) effect is found within the precision of our results.

Attempts to use the spectrophotometric technique to measure the rate of reaction 9 in solutions containing sulfur(IV) led only to the conclusion that loss of chloride was followed by subsequent losses of ammonia ligands at appreciable rates. The positions of the maxima in the visible spectrum shifted continuously to higher energy during the aquation, as expected,[31] but isosbestic points were not maintained. Separately prepared $Cr(NH_3)_5OH_2^{3+}$ was observed in the presence of sulfur(IV) to test further the possibility of successive ammonia aquation reactions by the $Cr(NH_3)_5Cl^{2+}$ aquation product. Spectral measurements on the monoaquo complex in sulfur(IV) solutions revealed continuously shifting maxima, this time toward lower energy but again isosbestic points were not maintained. The shift toward lower energy is consistent with loss of coordinated ammonia;[33] the absence of isosbestic points suggests the loss of more than one ammonia (or conceivably isomerization). The loss of ammonia from $Cr(NH_3)_5OH_2^{3+}$ on a time scale similar to that for the loss of chloride from $Cr(NH_3)_5Cl^{2+}$ is a problem not encountered in the absence of sulfur(IV).[31,32] Sulfur(IV) was also shown to have an effect on $Cr(NH_3)(H_2O)_5^{3+}$. The monoammine complex was prepared separately and was followed spectrophotometrically for 55 days at 25° in a solution containing 0.1 *M* H^+ and 0.13 *M* total sulfur(IV); these data led to an estimate of 1300 hr for the half-life, a significantly smaller value than obtained in the absence of sulfur(IV).[25] Thus, sulfur(IV) appears to catalyze the loss of ammonia from at least some aquoamminechromium(III) species.

Nitrate-Catalyzed Aquation of Acetatopentaaquochromium(III). A study of the nitrous acid catalyzed aquation of $Cr(H_2O)_5OOCCH_3^{2+}$ was initiated. Procedures identical with those reported in a study of nitrous acid catalyzed aquations of chloro- and bromochromium(III) complexes[5] were used,

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(30) J. P. Birk and J. H. Espenson, *Inorg. Chem.*, 7, 991 (1968).
(31) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Amer. Chem. Soc.*, 83, 2453 (1961).
(32) S. Hashimoto, *Bull. Chem. Soc. Jap.*, 32, 945 (1959).
(33) M. R. Edelson and R. A. Plane, *Inorg. Chem.*, 3, 231 (1964).

Table III. Observed Rate Constants for Reaction 9, Defined by Eq 10 (25°, 1.00 *M* Ionic Strength)

$10^3\times$ $[Cr(NH_3)_5Cl^{2+}]^a$	$10^2\times$ $[HSO_3^-]^b$	$[H^+]$	$10^6 k_{Cl}{}^c$
1.5	0.0	0.10	10.5^d
15.6	0.0	0.25	8.5
15.6	1.6	0.066	7.9
23.4	6.0	0.10	8.3
	0.0		$9.3,^e$ 8.7^f

[a] All concentrations are moles per liter. [b] Calculations of $[H^+]$ and $[HSO_3^-]$ were done using eq 4. [c] Units are sec^{-1}. [d] Measured spectrophotometrically. [e] From ref 31; at 25° and ionic strength 0.10. [f] From ref 32; at 25° and ionic strength near zero.

including the addition of nitrate ion to suppress the disproportionation of nitrous acid. The nitrous acid work was abandoned, however, when it was recognized that nitrous acid has only a small effect on $Cr(H_2O)_5OOCCH_3^{2+}$, but nitrate ion participates in the unusual sequence indicated by reactions 11 and 12; reaction 11 is sufficiently fast that

$$Cr(H_2O)_5OOCCH_3{}^{2+} + NO_3^- + H^+ = Cr(H_2O)_5ONO_2{}^{2+} + HOOCCH_3 \quad (11)$$

$$Cr(H_2O)_5ONO_2{}^{2+} + H_2O = Cr(H_2O)_6{}^{3+} + NO_3^- \quad (12)$$

replacement of acetate by nitrate is virtually quantitative in solutions containing moderate concentrations of nitrate.

Both kinetic and spectral evidence was obtained to show the importance of reaction 11. Plots of log $(A - A_\infty)$ *vs.* time at 570 nm each show an initial large slope, curving to a much smaller slope after most of the absorbance change is completed. Absorbance *vs.* time curves at 260 nm, a maximum for $Cr(H_2O)_5ONO_2{}^{2+}$,[34] each show an initial rapid absorbance increase, followed by a slower decrease. The rate of one decrease, followed all the way to completion, was identical with the rate reported[34] for aquation of authentic $Cr(H_2O)_5ONO_2{}^{2+}$. One reaction mixture was interrupted after the initial fast portion by absorbing the chromium species on cation-exchange resin. After rinsing the column to remove anions, a chromium species was eluted with 1.00 *M* $HClO_4$. The ultraviolet-visible spectrum of the eluted species perfectly matched that reported for the nitrato complex,[34] the absorbance decrease at 260 nm again occurred at exactly the rate reported for the nitrato complex,[34] and finally, the ultraviolet-visible spectrum of the product mixture was the same as reported for the products of aquation of the nitrato complex, including the absorbance maximum at 300 nm corresponding to free nitrate ion.[34]

The rates of loss of $Cr(H_2O)_5OOCCH_3{}^{2+}$ at high (>0.2 *M*) and intermediate nitrate concentrations, as defined by eq 13, were in accord with the rates of formation of $Cr(H_2O)_5$-

$$-d \ln\ [Cr(H_2O)_5OOCCH_3{}^{2+}]/dt = k_{AC}' = k_7[NO_3^-][H^+] \quad (13)$$

$ONO_2{}^{2+}$ at intermediate and low (<0.1 *M*) concentrations; this observation is consistent with the sequence indicated by eq 11 and 12. The rates of loss of coordinated acetate were measured at 570 nm, where the major (initial fast step) absorbance change is caused by loss of acetate. The rates of nitrate anation were measured at 260 nm. Regrettably, the 260-nm wavelength could not be used with high $[NO_3^-]$ owing to the moderate absorbance of nitrate. Similarly, the 570-nm wavelength did not give precise results at low $[NO_3^-]$ because a small absorption change associated with reaction 12 does occur and reaction 12 is significant at low $[NO_3^-]$.

The rate constants for reaction 11 at low $[NO_3^-]$ were determined from log $(A - A_\infty)$ *vs.* time plots at 260 nm or from the time at which the 260-nm absorption maximum occurred,[35] together with the known[34] rate constant for aquation of the nitrato complex. The rate constants at high $[NO_3^-]$ were determined from log $(A - A_\infty)$ *vs.* time plots at 570 nm.

The rate constants measured for reaction 11, defined by eq 13, are given in Table IV. The calculated values listed in Table IV were obtained by a least-squares fit[27] of the observed k_{AC}' values to eq 13, with each datum weighted as $(1/k_{AC}')^2$. The fitted value of k_7 is $(1.02 \pm 0.02) \times 10^{-2}$ M^{-2} sec^{-1}.

The k_1 and k_2 terms given in eq 3 were negligible in the experiments reported in Table IV. The source of nitrate, recrystallized sodium nitrate or reagent grade nitric acid, did not affect the value of k_{AC}'.

Most of the deviations between the observed and calculated rate constants listed in Table IV are not large, but they appear to indicate a trend; the per cent deviations are largest for the largest rate constants, with *k*(calcd) being larger than *k*(obsd) for the faster reactions.

Nitrate-Catalyzed Aquation of Fluoropentaaquochromium(III). The spontaneous and acid-catalyzed rates of net reaction 14 have been the subjects of a detailed report.[18]

$$Cr(H_2O)_5F^{2+} + H_3O^+ = Cr(H_2O)_6{}^{3+} + HF \quad (14)$$

The forward rate for reaction 14 at acidities in the range 0.2–0.9 *M* (the range observed in this study) is described as eq 15;

$$-d \ln\ [Cr(H_2O)_5F^{2+}]/dt = k_F' = k_8 + k_9[H^+] \quad (15)$$

from the reported activation parameters,[18] k_8 and k_9 are calculated as 3.3×10^{-7} sec^{-1} and 25×10^{-7} M^{-1} sec^{-1}, respectively, at 67° and 1.00 *M* ionic strength.

Nitrate was found to catalyze reaction 14 so that the form of eq 15 is modified as indicated in eq 16. The nitrate-

$$k_F' = k_8 + k_9[H^+] + k_{10}[NO_3^-] + k_{11}[NO_3^-][H^+] \quad (16)$$

dependent terms were dominant under the conditions of this work. The results of our experiments are given in Table V.

Reaction 14 did not go to completion under the conditions of this study and our procedures for evaluating k_F(obsd) were identical with those described earlier.[18] The k_F(cor) values in Table V were obtained as $k_F'(\text{cor}) = k_F{}^1(\text{obsd}) - k_8 - k_9 \cdot [H^+]$ and the calculated values are those obtained by a least-squares fit [27] to eq 16. The fitted[26] values for k_{10} and k_{11} were $(1.6 \pm 0.1) \times 10^{-4}$ M^{-1} sec^{-1} and $(2.4 \pm 0.4) \times 10^{-4}$ M^{-2} sec^{-1}, respectively.

A search was not made for intermediate $Cr(H_2O)_5ONO_2{}^{2+}$ during the nitrate-catalyzed aquation of $Cr(H_2O)_5F^{2+}$ because the reaction temperature was so high and the loss of F^- was so slow that it was assumed aquation of any intermediate nitrato complex would be relatively fast.

Nitrate-Catalyzed Aquation of Other Chromium(III) Species. The catalytic effect of nitrate on other chromium(III) complexes was briefly tested. We found no catalysis for $Cr(H_2O)_5Cl^{2+}$ (0.10 *M* NO_3^-, 0.41 *M* H^+, 50°, *k*(obsd) = 1.7×10^{-5} sec^{-1}), for $Cr(H_2O)_2(C_2O_4)_2^-$ (0.10 *M* NO_3^-, 0.89 *M* H^+, 45°, *k*(obsd) = 2.8×10^{-5} sec^{-1}), or for $Cr(H_2O)_5CN^{2+}$ (0.10 *M* NO_3^-, 0.81 *M* H^+, 25°, *k*(obsd) = 4.2×10^{-4} sec^{-1}; 0.38 *M* NO_3^-, 0.05 *M* H^+, 25°, *k*(obsd) = 3.3×10^{-5} sec^{-1}). We did observe some catalysis of the aquation of $Cr(H_2O)_5$-

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(34) T. W. Swaddle, *J. Amer. Chem. Soc.*, **89**, 4338 (1967).

(35) S. W. Benson, "The Fundamentals of Chemical Kinetics," McGraw-Hill, New York, N. Y., pp 34, 35.

Table IV. Observed and Calculated Rate Constants for Reaction 11, Defined by Eq 13 (25°, 1.00 *M* Ionic Strength)

$10^3\times$ $[Cr(H_2O)_5$-OOC-$CH_3^{2+}]_0$[a]	$[H^+]$	$[NO_3^-]$	$10^4k_{AC}'$[b] Obsd[c]	Calcd[d]
3.03	0.20	0.10	2.23	2.04
3.03	0.20	0.20	4.55	4.08
3.54	0.20	0.40	7.78	8.16
3.54	0.20	0.69	13.7	14.1
3.03	0.40	0.05	2.29	2.04
3.03	0.40	0.10	4.47	4.08
3.03	0.40	0.20	8.59	8.16
3.54	0.40	0.40	15.1	16.3
3.54	0.40	0.80	27.7	32.6
3.54	0.68	0.20	12.6	13.8
3.54	0.69	0.20	12.6	13.9
1.17	0.80	0.02	1.73	1.63
1.38	0.80	0.05	4.00	4.08
2.94	0.80	0.05	3.85	4.08
0.59	0.80	0.10	7.94	8.16
1.77	0.80	0.20	14.7	16.3
3.54	0.80	0.40	30.1	32.6
3.54	0.80	0.80	49.5	65.3

[a] All concentrations are moles per liter. [b] Units are sec^{-1}. [c] Some of the observed values listed are the averages of the values obtained from the $A - A_\infty$ plot at 260 nm and from the time of maximum absorbance at 260 nm. [d] The calculated value is the value obtained from the least-squares fit of k_{AC}'(obsd) to eq 13.

Table V. Observed and Calculated Rate Constants for Reaction 14, Defined by Eq 15 and 16 (67°, 1.00 *M* Ionic Strength)[a]

$[H^+]$	$[NO_3^-]$	$10^5k_F^1$ Obsd[b]	Cor	Calcd
0.20	0.03	0.67 ± 0.02	0.59	0.62
0.20	0.06	1.73 ± 0.02	1.65	1.23
0.20	0.12	2.52 ± 0.14	2.44	2.46
0.20	0.24	4.87 ± 0.25	4.79	4.93
0.20	0.48	11.3 ± 0.3	11.2	9.87
0.20	0.70	14.8 ± 0.9	14.7	14.4
0.41	0.06	1.14 ± 0.05	1.0[c]	1.53
0.41	0.12	2.67 ± 0.07	2.53	3.06
0.41	0.24	6.49 ± 0.18	6.35	6.12
0.41	0.35	8.82 ± 0.19	8.68	8.93
0.70	0.06	2.14 ± 0.12	1.93	1.94
0.70	0.12	4.33 ± 0.05	4.12	3.88
0.70	0.24	8.33 ± 0.20	8.12	7.76
0.90	0.09	3.74 ± 0.06	3.48	3.34

[a] The concentration of $Cr(H_2O)_5F^{2+}$ was 5.9×10^{-3} *M* in each experiment; the units of each concentration and rate constant listed in the table are moles per liter and sec^{-1}, respectively. [b] Each number is the average of three or four determinations (see ref 18) and the indicated uncertainty is the average deviation. [c] Weighted zero in the least-squares calculation.

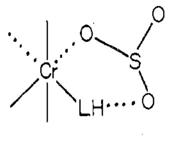
N_3^{2+}. The value of k(obsd) for this aquation in 0.19 *M* NO_3^- and 0.84 *M* H^+, at 25°, was 4.2×10^{-6} sec^{-1}; the uncatalyzed value is calculated from ref 17 to be smaller by a factor of 6.

Discussion

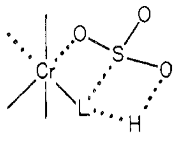
Sulfur(IV) Catalysis. The suggestion[9] that sulfur(IV) labilization of chromium(III) involves inner-sphere complexation of sulfite is supported by the results of this study. The only chromium(III) aquation studied in this or the previous work that was not affected by sulfur(IV) was the $Cr(NH_3)_5Cl^{2+}$ aquation. All the other complexes studied were affected and contained at least one water ligand; O-bonded sulfitochromium(III) complexes are believed to form rapidly from aquo complexes[9] in a mechanism not available to $Cr(NH_3)_5Cl^{2+}$, in accord with the proposed requirement for complexation.

The present work also supports the suggestion,[10] that the acid dependence of the sulfite-catalyzed pathway is affected by the basicity of the leaving group. The rate laws for each of the nonbasic leaving groups studied are of the form[9] $-d \ln [Cr(H_2O)_{6-n}X_n^{(3-n)+}]/dt = k_X[HSO_3^-]/[H^+]$ where X_n = Cl, NCS, and cis and trans $(NCS)_2$. The rate laws for each of the basic leaving groups are of the form $-d \ln [Cr(H_2O)_5L^{2+}]/dt = k_L[HSO_3^-]$ where L = CH_3COO^-, N_3^-, and also CN^- although a more complicated rate law was observed for L = CN^- at high $[CN^-]$.

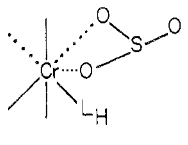
The rate laws imply that an additional proton is present in the transition state if the leaving group is basic, but the locations of the proton and the sulfite group are not established. Some evidence exists regarding these locations, however, as described below. Study of the discussions in ref 5-10 suggests the configurations given in I-III. Structure I is similar to that suggested by Zinato, *et al.*, for carboxylate-catalyzed aquation of ammonia.[8] Structure II, without specifying whether the proton is closer to L or O, is somewhat related to the proposal of Matts and Moore for mechanisms of nitrite labilizations.[5] We consider structure III as most probable, however; it has been called the anchimeric cis effect in conjunction with carboxylate labilization of coordinated water[7] and it has been proposed in conjunction with nitrate labilization of ammonia.[6]



I



II



III

Tests of structure I by construction of models give reasonable distances and angles for L = acetate or ammonia, but if L = cyanide or azide, the proton is too far from the metal for interaction with sulfite unless, improbably, the leaving groups are protonated at the atoms adjacent to the metal. These problems with the models together with the arguments presented by Olson[7] and with the expected weakness of sulfite interaction with nonprotonated leaving groups leads us to reject structure I as a representation of the transition state during sulfur(IV)-catalyzed substitutions on chromium(III).

Models for II indicate satisfactory interactions with acetate and also for cyanide and azide if the sulfur interaction is with the atom bonded to chromium. However, the structure appears poor for ammonia because the indicated interaction would make ammonia five-coordinate. Similarly, the catalytic activity of sulfate[36] is difficult to understand in terms of II, owing to the absence of a vacant coordination site on the sulfur. Thus, II does not appear valid over the complete range of oxy anion catalyses that have been observed.

Acceptable structure III models can be made for all the leaving groups and, indeed, are nearly independent of the identity of the catalytic oxy anion. The possibility that oxy anion catalyzed chromium(III) substitutions have anchimeric assistance as a common feature of the mechanisms is attractive, as has already been suggested.[6,7] We think our work adds strong support to the view that only III can be general. A less probable possibility is that the catalyses occur by a variety of mechanisms.

The approximate constancy of the sulfur(IV) catalytic effect is evidence for a common mechanism for the sulfur(IV) catalyses. Similar arguments for common mechanisms have

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(36) N. V. Duffy and J. E. Earley, *J. Amer. Chem. Soc.*, 89, 272 (1967).

been made, for example, for iron(III)[10,37] and for chromium(III)[38,39] substitution reactions. The constancy of the sulfur(IV) effect is indicated in considering some aquation rate law terms from earlier studies,[9] $k_X[HSO_3^-]/[H^+] + k_X' = -d \ln [CrX]/dt$, where the catalytic ratios k_X/k_X' are 54, 78, 21, and 6.5, respectively, for CrX = $Cr(H_2O)_5Cl^{2+}$, $Cr(H_2O)_5NCS^{2+}$, *trans*-$Cr(H_2O)_4(NCS)_2^+$, and *cis*-$Cr(H_2O)_4(NCS)_2^+$. The constancy is further indicated in considering the corresponding rate law terms pertinent to the present work, $k_L[HSO_3^-] + k_L'[H^+] = -d \ln [CrL]/dt$; the ratios k_L/k_L' [40] are 120, 350, and about 140 for CrL = $Cr(H_2O)_5OOCCH_3^{2+}$, $Cr(H_2O)_5N_3^{2+}$, and $Cr(H_2O)_5CN^{2+}$, respectively. (It must be remembered that we are assuming the rate constants are of the form $k_X = kQ_X$ and $k_L = kQ_L$ where $Q_X = [CrXSO_3{}^m][H^+]/[HSO_3^-][CrX]$ and $Q_L = [CrXHSO_3^+]/[HSO_3^-][CrX]$, so the rate constants are composites.) The entire set of seven ratios falls within a range of less than 2 orders of magnitude, again suggesting common mechanisms for these seven systems.

Nitrate Catalysis. The net reaction given by eq 11 is understandable as a sequence of cis effects. We suggest that reactions 17-19 represent the probable mechanism for the reaction

$$Cr(H_2O)_5OOCCH_3^{2+} + H^+ \overset{\text{fast}}{\rightleftharpoons} \textit{cis}\text{-}Cr(H_2O)_4(H_3O)OOCCH_3^{3+} \quad Q_P \qquad (17)$$

$$\textit{cis}\text{-}Cr(H_2O)_4(H_3O)OOCCH_3^{3+} + NO_3^- \xrightarrow{k_7/Q_P} Cr(H_2O)_4(ONO_2)OOCCH_3^+ + H_3O^+ \qquad (18)$$

$$Cr(H_2O)_4(ONO_2)OOCCH_3^+ + H_3O^+ \xrightarrow{\text{fast}} Cr(H_2O)_5ONO_2^{2+} + HOOCCH_3 \qquad (19)$$

on the basis of the rate law (eq 13) and on the basis of the known cis-labilizing properties of acetate[7,8] and nitrate.[6] According to this mechanism, coordinated acetate labilizes the cis positions and protonation is probably on a labilized water as indicated by III.[41] The labilized cis positions could undergo water exchange without net reaction, but eventual replacement by nitrate is indicated by eq 18 as required by the observation that $Cr(H_2O)_5ONO_2^{2+}$ does form. One modification of the proposal is that the reverse of (18) is not important and reaction 19 is fast. However, an alternate modification which also agrees with the rate law is that reaction 19 is rate determining and reaction 18 is at equilibrium with $Q_{18} << 1$. We suggest that a cis-labilizing effect of nitrate is important regardless of the reversibility of (18). The failure to detect intermediate acetatonitratotetraaquochromium(III) is consistent with either modification. The deviations from the rate law in the fastest reactions (see Results) are likely to be medium effects; the concentrations of three electrolytes were varied over large ranges and such variations have been shown[42] to lead to rate changes of the order of 20%.

Earlier work provides evidence that nitrate exerts a stronger cis-labilizing effect than acetate and so provides some evidence that reaction 18 is rate determining. At 25°, $-d \ln [Cr(NH_3)_5OOCCH_3^{2+}]/dt = 2.3 \times 10^{-4}$ sec^{-1} [8] and $-d \ln [Cr(NH_3)_5ONO_2^{2+}]/dt = 1.6 \times 10^{-3}$ sec^{-1},[6] where both rates pertain to aquation of a cis ammonia. Thus, this one comparison suggests that nitrate is more effective than acetate by a factor of 7.

The empirical rate law for the nitrate-catalyzed aquation of $Cr(H_2O)_5F^{2+}$ (eq 15, 16) has a term analogous to that found in the acetate system, but the rate constant is much smaller. This result is not surprising since coordinated fluoride presumably does not assist nitrate anation. The empirical rate law also shows a term that is independent of $[H^+]$. In accord with the rate law and with the evidence favoring III, we propose that both of these terms arise from coordination of nitrate, with the subsequent losses of fluoride and nitrate occurring rapidly.

The failure of nitrate to catalyze the aquation of $Cr(H_2O)_2(C_2O_4)_2^-$ probably stems from its low charge, making it a poor substrate for nitrate anation. The same reason may apply to the failure to catalyze the aquation of $Cr(H_2O)_5Cl^{2+}$, although eq 16 indicates that unprotonated $Cr(H_2O)_5F^{2+}$ was catalyzed. However, even in 1 *M* nitrate the k_{10} pathway for the fluoro complex would only contribute about the same rate as the spontaneous pathway[18] for the chloro complex, suggesting that nitrate anation may not compete effectively with spontaneous aquation of the chloro complex. The failure of nitrate to catalyze the aquation of $Cr(H_2O)_5CN^{2+}$ is probably also related to the fast spontaneous reaction.[20,30] Catalysis of the aquation of the azido complex is reasonable; the spontaneous reaction is slow[17] and the complex can be protonated[29,41] to probably assist anation by nitrate. An earlier report of the nitrate-catalyzed aquation of $Cr(H_2O)_5NH_3^{3+}$ was attributed to possible redox processes.[25] It now appears, as noted earlier,[6] that the catalysis probably results from a mechanism analogous to that indicated by III.

Registry No. HSO_3^-, 15181-46-1; $[Cr(H_2O)_5OOCCH_3]^{2+}$, 18894-45-6; $[Cr(H_2O)_5N_3]^{2+}$, 18517-09-4; $[Cr(H_2O)_5CN]^{2+}$, 16457-55-9; $[Cr(NH_3)(H_2O)_5]^{3+}$, 42402-03-9; NO_3^-, 14797-55-8; $[Cr(H_2O)_5F]^{2+}$, 19559-07-0.

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[37] D. Seewald and N. Sutin, *Inorg. Chem.*, 2, 643 (1963).

[38] J. H. Espenson, *Inorg. Chem.*, 8, 1554 (1969).

[39] D. Thusius, *Inorg. Chem.*, 10, 1106 (1971).

[40] The k_L' values were taken from ref 12, 17, and 30, respectively; sources of the k_X' values are given in ref 9.

[41] There is evidence for protonation of water in $Cr(H_2O)_6^{3+}$ (T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, 5, 1100 (1966)) and of water in $Cr(H_2O)_5N_3^{2+}$ (R. J. Balahura and R. B. Jordan, *ibid.*, 9, 2639 (1970)). The protonated water is isoelectronic with ammonia making this step analogous to that described in ref 8.

[42] D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, 90, 2272 (1968), and references therein.