

Labilization of Chromium(III) by Coordinated Oxoanions. Solvolysis of (Nitrate)chromium(III) Ion in Acidic Dimethyl Sulfoxide-Water Mixtures¹

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Pentaaqua(nitrate)chromium(III) ion rapidly ($t_{1/2} \approx 10$ s at 25 °C) reacts in acidic aqueous solution to form species in which one to five molecules of dimethyl sulfoxide have become coordinated to chromium(III). Nitrate ion is lost by such species at a moderate rate ($t_{1/2} \approx 3$ h at 25 °C) to form aqua(dimethyl sulfoxide)chromium(III) species in which the number of coordinated molecules of dimethyl sulfoxide does not exceed 5. One interpretation of these data is that solvolysis of (nitrate)chromium(III) ion occurs with nitrogen-oxygen bond breaking. Complexes of chromium(III) with hydrogen sulfite ion or with hydrogen carbonate ion form rapidly without chromium(III)-oxygen bond breaking, and these species also react with dimethyl sulfoxide much more rapidly than does hexaaquachromium(III) ion.

The rates of reactions of most ligands with hexaaquachromium(III) ion are very low. For instance, the displacement of water by dimethyl sulfoxide has a half-time of ~ 380 h at 25 °C in an acidic solution with Z, the mole fraction of dimethyl sulfoxide, equal to 0.705.² The reaction of pentaaqua(nitrate)chromium(III) ion with dimethyl sulfoxide, in sharp contrast, has a half-time of ~ 10 s at Z = 0.004-0.04.³ Labilization of chromium(III) ion by nitrate ion has been observed before,^{4,5} and there are other oxoanion ligands that labilize chromium(III) ion toward substitution: sulfite ion,^{5,6} carbonate ion,⁷ nitrite ion,⁸ acetate ion,⁹ and ethylenediaminetetraacetate ion.¹⁰

The present study deals with the labilization of aquachromium(III) ion toward reaction with dimethyl sulfoxide by coordinated sulfite and carbonate species. The nonmetal-oxygen bond breaking in these oxoanions is rapid compared to chromium(III)-oxygen bond breaking in hexaaquachromium(III) ion, and the inner-sphere interaction of chromium(III) ion with these ligands occurs rapidly, presumably by a mechanism which involves nonmetal-oxygen bond breaking. In contrast, the rate of nitrogen-oxygen bond breaking in nitrate ion, as elucidated by its rate of oxygen exchange with water,¹¹ is low. (Nitrate)chromium(III) ion undergoes solvolysis slowly, and the slow loss of nitrate ion by the mixed-ligand species $\text{Cr}(\text{ONO}_2)(\text{OH}_2)_{5-d}(\text{OS}(\text{CH}_3)_2)_d^{2+}$ in aqueous dimethyl sulfoxide is another subject of the present study. In particular, the composition of the solvolysis product $\text{Cr}(\text{OH}_2)_{6-d}(\text{OS}(\text{CH}_3)_2)_d^{3+}$ has been studied as a function of solvent composition, and it has been found that the maximum value of d in the product species is 5.

Experimental Section

Reagents. Commercially available reagent grade chemicals were used without additional purification unless otherwise noted. Reagent

grade Dowex 50W-X8 cation-exchange resin was used in the hydrogen ion form after being treated alternately with alkaline hydrogen peroxide and hydrochloric acid followed by thorough rinsing. Pentaaqua(nitrate)chromium(III) ion was prepared and purified as described by Swaddle.¹²

Analyses. Chromium was analyzed by conversion with alkaline hydrogen peroxide to chromate ion, in which form it was determined by light absorption ($\epsilon[\text{CrO}_4^{2-}] = 4820 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 372 nm).¹³ Dimethyl sulfoxide was analyzed by oxidation with permanganate ion in acidic solution, a procedure used in an earlier study.² In the study of labilization by sulfite and carbonate, the acidity was adjusted by addition of perchloric acid to solutions of the sodium salts of these anions. Measurement of the pH was used to monitor the acidity of a solution, even though the measured values of pH do not have the conventional meaning in solvents containing appreciable dimethyl sulfoxide since the pH meter was calibrated by using standard aqueous buffers. For solutions with $[\text{H}^+] = 0.0100 \text{ mol L}^{-1}$, the measured values of the pH for solutions with Z = 0-0.38 are an approximately linear function of Z, $\text{pH}(\text{meas}) = 1.937 + 2.138Z$. This equation generates calculated values of pH which agree with the measured values with an average deviation of 0.022 unit. For solutions with Z = 0.283, the quantity $[\text{pH}(\text{meas}) + \log([\text{H}^+]/\text{mol L}^{-1})]$ is approximately constant over the tenfold range of concentration of hydrogen ion, $[\text{H}^+] = 9.6 \times 10^{-4}$ to $9.6 \times 10^{-3} \text{ mol L}^{-1}$.

Evaluation of \bar{d} . A direct method of evaluation of \bar{d} , the average number of molecules of dimethyl sulfoxide coordinated to chromium(III) ion, was employed in the study of solvation equilibrium in aqueous dimethyl sulfoxide.² This method involves analysis for both dimethyl sulfoxide and chromium on samples from which free-solvent dimethyl sulfoxide has been separated by an ion-exchange procedure. This direct method cannot be used, however, for analysis of chromium(III) species containing a labilizing ligand (e.g., nitrate ion). Coordinated dimethyl sulfoxide in such species does not survive in the coordination shell in the ion-exchange procedure. It is rinsed away by the aqueous acid used to remove free dimethyl sulfoxide. A rapid estimation of the value of \bar{d} can be made by measurement of the positions of the two absorption peaks in the visible spectra of chromium(III) species. This procedure was used in the study³ of species in the system $\text{Cr}(\text{ONO}_2)(\text{OH}_2)_{5-d}(\text{OS}(\text{CH}_3)_2)_d^{2+}$.

Peak positions reported earlier² for each species in the system $\text{Cr}(\text{OH}_2)_{6-d}(\text{OS}(\text{CH}_3)_2)_d^{3+}$ ($d = 0-6$, with two isomers for $d = 2, 3$, and 4) are correlated by this average environment approximation.¹⁴ Using these observed spectra to evaluate the two parameters $\nu(\text{Cr}(\text{OH}_2)_6^{3+})$ and $\nu(\text{Cr}(\text{OS}(\text{CH}_3)_2)_6^{3+})$ for each of the two peaks gives the equations for the peak positions as a function of d : $10^{-3}\lambda/\text{nm} = (1.736 - 0.0260d)^{-1}$ and $10^{-3}\lambda/\text{nm} = (2.443 - 0.0327d)^{-1}$. The calculated peak positions agree with the observed values with an average deviation of 1.5 nm for the long-wavelength peak and 0.9 nm for short-wavelength peak. These equations can be rearranged to provide an equation for $d(\lambda)$ and in this form used to estimate values of \bar{d} : $\bar{d} = (1.736 - 1000 \text{ nm}/\lambda)/0.0260$ and $\bar{d} = (2.443 - 1000$

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nm/λ)/0.0327. These equations have been used throughout this study. An uncertainty of 1 nm in the peak position results in an uncertainty of ~0.1 unit in \bar{d} for the long-wavelength peak and ~0.16 unit in \bar{d} for the short-wavelength peak. In general the positions of both peaks will be used, with an average value of \bar{d} being obtained by doubly weighting the position of the long-wavelength peak. Five different solutions also were analyzed directly, and the values of \bar{d} so determined were compared with the estimated values. The estimated and analyzed values differed by an average of 0.13 unit. The spectrally estimated value of \bar{d} was lower than the directly analyzed value in all cases except one. Values of \bar{d} estimated from the peak positions are judged to be uncertain to between 0.1 and 0.2 unit, and these averaged values will be given to the nearest 0.1 unit.

The spectral estimation of \bar{d} is employed on mixed-solvent systems, but the basis for the equations for $\bar{d}(\lambda)$ is a correlation of positions of spectral peaks in aqueous solution. A solution equilibrated with $Z = 0.283$ displayed peak positions at an average of 0.7 nm longer wavelength than the same solution immediately after dilution to $Z = 0.016$. This limited study of a possible medium effect on spectral peak positions indicates the effect is small but would result in estimates of \bar{d} for species in dimethyl sulfoxide rich solutions that are too large. If this medium effect is real, it is in the opposite direction of the error of the spectrally estimated values compared to the values obtained by direct analysis. This point is relevant in our later argument that in the solvolysis product the estimated values of \bar{d} , which do not exceed 5, truly indicate that species formed from (nitrate)chromium(III) ion do not contain more than five-coordinated molecules of dimethyl sulfoxide.

Ion-Exchange Separation Procedures. Column ion-exchange procedures were used in several aspects of this work. In one type of experiment, portions of solution in which (nitrate)chromium(III) ion was allowed to undergo solvolysis for varying periods of time were analyzed by an ion-exchange procedure. The separation consisted of rinsing free dimethyl sulfoxide from the column with cold (0 °C) 0.10 M HClO₄, elution of (nitrate)chromium(III) ion (of charge 2+) with 0.50 M H₂SO₄, and finally elution of the variously solvated species of charge 3+, Cr(OH₂)_{6-d}(OS(CH₃)₂)_d³⁺, with 7 M H₂SO₄. In experiments on (sulfito)chromium(III) species, the sulfur(IV) was removed from both the solution acidified to [H⁺] ≈ 0.5 mol L⁻¹ and the coordination shell of chromium(III) ion by aeration with nitrogen. All of the chromium(III) then is in the form of species of charge 3+, and an ion-exchange procedure yields, upon elution with 7 M H₂SO₄, solutions which can be analyzed for chromium and for dimethyl sulfoxide. In some experiments on chromium(III) in a mixed solvent ($Z = 0.283$) containing carbon dioxide, the unreacted hexaaquachromium(III) ion was separated from the less easily eluted species² containing coordinated dimethyl sulfoxide by elution with 1.5 M HClO₄.

Studies of (Nitrate)chromium(III) Ion in Aqueous Dimethyl Sulfoxide. As reported earlier,³ a rapid ($t_{1/2} \approx 10$ s) spectral change occurs when dimethyl sulfoxide is added to an acidic aqueous solution of (nitrate)chromium(III) ion. The earlier measurements have been repeated extending the solvent composition range to $Z \approx 0.80$ with the same results. The spectral peak positions at the highest values of Z are, for $Z = 0.705$, $\lambda_{\max} = 440$ and 624.5 nm and, for $Z = 0.804$, $\lambda_{\max} = 440.5$ and 626 nm. These peak positions and the average environment approximation³ indicate $\bar{d} \approx 4.9$ and 5.0 for the species Cr(ONO₂)(OH₂)_{5-d}(OS(CH₃)₂)_d²⁺ at these solvent compositions. (Quantitative estimation of \bar{d} from spectral peak positions for mixtures of species containing three different ligands is probably less accurate than for the mixtures of species containing two different ligands. Thus for the nitrate-containing species, the values of \bar{d} estimated in the previous study³ should not have been given to 0.01 unit.) The species Cr(ONO₂)(OH₂)_{5-d}(OS(CH₃)₂)_d²⁺ ($d = 0-5$), formed rapidly in the reaction Cr(ONO₂)(OH₂)₅²⁺ + d(CH₃)₂SO = dH₂O + Cr(ONO₂)(OH₂)_{5-d}(OS(CH₃)₂)_d²⁺, slowly lose nitrate ion to give species Cr(OH₂)_{6-d}(OS(CH₃)₂)_d³⁺. Solutions of ten compositions ($Z = 0.028-0.804$) were allowed to stand 5 days at 22 °C, at which time the value of \bar{d} for the chromium(III) species in each solution was estimated by use of the positions of the spectra peaks, as already described. The estimated values of \bar{d} (given as Z, \bar{d}) are as follows: 0.028, 0.5; 0.062, 1.5; 0.101, 2.2; 0.147, 2.7; 0.208, 3.3; 0.283, 3.8; 0.377, 4.1; 0.511, 4.7; 0.705, 4.9; 0.804, 5.0. These estimated values of \bar{d} are displayed in Figure 1; the plot suggests that the value of \bar{d} in the solvolysis product does not exceed 5.0 at any value of Z . Estimated values of \bar{d} for (nitrate)chromium(III) ion³ and five-sixths

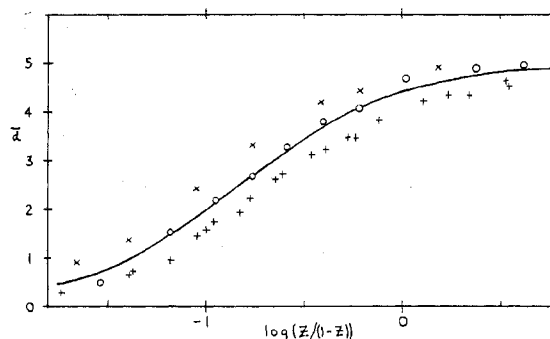


Figure 1. Values of \bar{d} , estimated from positions of spectral peaks, for species Cr(OH₂)_{6-d}(OS(CH₃)₂)_d³⁺ formed in solvolysis of (nitrate)chromium(III) ion in mixed solvent: O, \bar{d} for Cr(OH₂)_{6-d}(OS(CH₃)₂)_d³⁺ formed in solvolysis; x, \bar{d} for Cr(ONO₂)(OH₂)_{5-d}(OS(CH₃)₂)_d²⁺; +, $5/6 \bar{d}$ for equilibrated solutions at 35 °C.² Solid line, $\bar{d}/(5-\bar{d}) = 7.7(Z/(1-Z))^{1.07}$, correlates the solvolysis data. The calculated values of \bar{d} agree with estimated values with an average difference of 0.1 unit.

of the equilibrium values of \bar{d} , reported earlier,² also are given in this figure.

For solutions with $Z = 0.511, 0.705$, and 0.804, portions of solution taken at 10–140 h were treated by a column ion-exchange procedure to separate the species at charge 2+, Cr(ONO₂)(OH₂)_{5-d}(OS(CH₃)₂)_d²⁺, and charge 3+, Cr(OH₂)_{6-d}(OS(CH₃)₂)_d³⁺. The mixtures of species of charge 3+, the solvolysis products, were analyzed for dimethyl sulfoxide and chromium. The values of \bar{d} , so determined, did not vary appreciably with the time of reaction at $Z = 0.511$ ($\bar{d} = 4.36 \pm 0.04$), at $Z = 0.705$ ($\bar{d} = 5.0 \pm 0.1$; values obtained only at 10.7–41.5 h), or at $Z = 0.804$ ($\bar{d} = 5.0 \pm 0.1$). Since these values of \bar{d} for the mixtures of solvolysis products are smaller than equilibrium values ($\bar{d} \approx 4.8$ at $Z = 0.51$, $\bar{d} \approx 5.4$ at $Z = 0.71$, and $\bar{d} \approx 5.7$ at $Z = 0.80$),² the data indicate that reequilibration of the species formed in solvolysis does not occur appreciably during the time interval in question (up to 6 days).

Rate of Aquation of (Nitrate)chromium(III) Ion in Acidic Solutions.

The rate of aquation of (nitrate)chromium(III) ion was determined by measurement of the light absorption at 260 nm, where the molar absorptivity index of the complex is larger than that of the hydrated ion, $a((\text{H}_2\text{O})_5\text{CrONO}_2^{2+}) \gg a(\text{Cr}(\text{OH}_2)_6^{3+})$. Nicely linear plots of $\ln(A - A_\infty)$ vs. time were obtained over >90% reaction ($A = \log(I_0/I)$). The values of the first-order rate constant ($k_1 = (d \ln(A - A_\infty))/dt$) for 25.0 °C as a function of the concentration of perchloric acid (given as C(HClO₄)/mol L⁻¹, 10³k/s⁻¹) are as follows: 1.03, 7.28; 2.07, 7.38; 2.97, 7.22; 3.99, 6.89; 5.07, 6.36; 6.22, 5.83; 6.98, 5.26; 7.82, 4.73.

Experiments also were performed on solutions of constant ionic strength and varying concentration of perchloric acid. With the ionic strength maintained at 5.0 mol L⁻¹ with lithium perchlorate, k increases by ~2% as the concentration of perchloric acid is decreased from 5.0 to 3.5 mol L⁻¹. With the ionic strength maintained at 7.0 mol L⁻¹ with sodium perchlorate, k increases significantly as the concentration of perchloric acid decreases; the data (given as C(HClO₄)/mol L⁻¹, 10³k/s⁻¹) are as follows: 6.00, 5.82; 5.00, 6.44; 4.00, 7.11; 3.00, 7.65.

Measurements on Solutions Containing Sulfur Dioxide. The rate of spectral change in a solution of aquachromium(III) ion in the mixed-solvent system under study is increased in the presence of sulfur dioxide. Since appreciable coordination of sulfite by chromium(III) may occur in the solutions being studied,⁶ measurements of spectra to use in estimation of the value of \bar{d} were deferred until sulfur(IV) was removed from each portion (15 cm³) of solution being analyzed. This was done by aeration with nitrogen gas after the acidity was increased. The species Cr(OH₂)_{6-d}(OS(CH₃)₂)_d³⁺ were present in the aerated solution, and the value of \bar{d} was estimated as already described. Values for \bar{d} as a function of time in three such experiments at $Z = 0.283$ are given in Figure 2. In one of these experiments, the source of chromium(III) was a mixed-solvent mixture with $Z = 0.68$ which had been maintained in the presence of sulfur(IV) for 12 h at 25 °C. At the time of dilution to $Z = 0.283$, the estimated value of \bar{d} was 4.5, a value greater than the equilibrium value ($\bar{d} = 4.0$); in this experiment, the value of \bar{d} decreased with time. At $Z = 0.208$

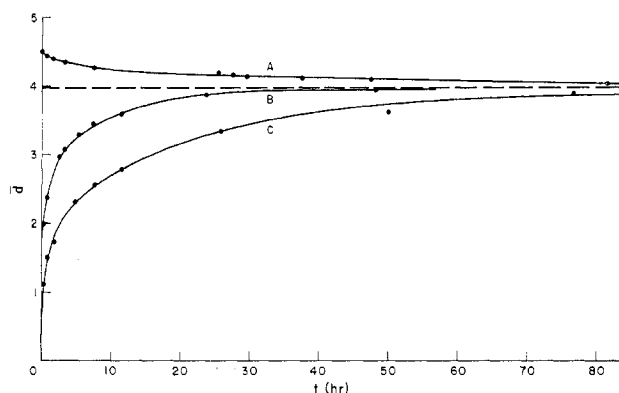


Figure 2. Dependence of \bar{d} upon time in solutions containing sulfur(IV) ($Z = 0.283$, $t = 25^\circ\text{C}$, $[\text{S}^{\text{IV}}] = 0.10 \text{ mol L}^{-1}$): curve A, $\bar{d}_0 = 4.5$ (starting mixture of species formed in medium with $Z = 0.680$ predominantly by sulfur(IV)-catalyzed pathway; therefore $d(\text{max}) = 5.0$), pH 2.37; curve B, $\bar{d}_0 = 0$, pH 2.37; curve C, $\bar{d}_0 = 0$, pH 1.98.

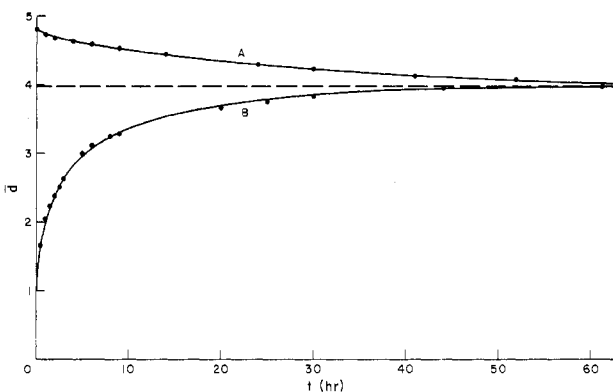


Figure 3. Dependence of \bar{d} upon time in solutions containing carbon dioxide, ($Z = 0.283$, $t = 25^\circ\text{C}$, $P(\text{CO}_2) = 630 \text{ torr}$): (A) $\bar{d}_0 = 4.8$ (starting mixture of species formed in medium with $Z = 0.705$ predominantly by carbon dioxide catalyzed pathway; therefore $d(\text{max}) = 5.0$), pH 2.80; (B) $\bar{d}_0 = 0$, pH 2.80.

and 0.705 experiments were done also in which portions of solution equilibrated in the presence of sulfur(IV) were acidified to $[\text{H}^+] = 0.5 \text{ mol L}^{-1}$, aerated, and then processed by the column ion-exchange procedure to allow direct analysis of \bar{d} . The values so obtained were, for $Z = 0.208$, $\bar{d} = 3.7$ and, for $Z = 0.705$, $\bar{d} = 4.7$. The values of \bar{d} obtained in these experiments at three different values of Z are close to the values observed in the samples of solvolyzed (nitrate)chromium(III) at the same solvent compositions.

Measurements on Solutions Containing Carbon Dioxide. Treatment of an acidic solution of chromium(III) ion in aqueous dimethyl sulfoxide with carbon dioxide causes a color change which indicates that the inner-sphere solvation of chromium(III) by dimethyl sulfoxide has occurred more rapidly than in the absence of this reagent. An inappreciable fraction of chromium(III) ion is complexed by carbonate ion (or hydrogen carbonate ion) in these solutions, and estimation of the value of \bar{d} from the spectral peak positions can be carried out without aeration of the solution to rid it of carbon dioxide. Figure 3 presents the results of experiments at $Z = 0.283$ in which the CO_2 -catalyzed solvation of chromium(III) ion is approached from initial states in which \bar{d} was on either side of the final value.

Several types of kinetic studies have been performed on this system. The rate of disappearance of hexaaquachromium(III) ion in a solution with $Z = 0.283$, pH 2.535, and $P(\text{CO}_2) = 630 \text{ torr}$ at 25°C has been determined by an ion-exchange procedure for analysis of aliquots of reaction mixture for hexaaquachromium(III) ion. The first-order disappearance of hexaaquachromium(III) ion in this solvent is governed by a rate constant $k = 2.6 \times 10^{-4} \text{ s}^{-1}$ ($t_{1/2} = 44 \text{ min}$).

Experiments were performed to measure the rate of aquation of $(\text{H}_2\text{O})_4\text{Cr}(\text{OS}(\text{CH}_3)_2)_2^{3+}$ in solutions with $Z = 0.010$ having different values of acidity and partial pressure of carbon dioxide. (At this low concentration of dimethyl sulfoxide, aquation proceeds $\sim 81\%$ to completion at equilibrium.¹⁵ The relative concentration of

$(\text{H}_2\text{O})_4\text{Cr}(\text{OS}(\text{CH}_3)_2)_2^{3+}$ at this value of Z is $\sim 5\%$;¹⁵ the possible formation of this species will be ignored.) The approach to equilibrium was followed spectrophotometrically at 630 or 640 nm; plots of $\ln(A_t - A_\infty)$ vs. time or $\ln(A_t - A_{t+\tau})$ vs. time were approximately linear for $\sim 70\%$ reaction. (The data were treated both by the conventional method and by the Guggenheim method¹⁶ involving the constant time interval τ .) The total change in absorbance in these experiments was not large (0.20–0.30 unit), and, therefore, the rate constants are judged to be uncertain to $\pm 10\%$. (The experiments at pH 2.04 and 2.24 were less precise; the uncertainty in k for these experiments may be as large as $\pm 20\%$.) The measured values of the first-order rate constant for the approach to equilibrium are (given as $P(\text{CO}_2)/\text{torr}$, pH, $10^5 k/\text{s}^{-1}$) as follows: 0, 2.44, 1.45; 630, 2.04, 2.9; 630, 2.24, 4.1; 630, 2.39, 6.3; 630, 2.44, 6.6; 630, 2.54, 9.8; 630, 2.74, 16.5; 780, 2.44, 7.4, 930, 2.44, 8.9.

Derived Results and Discussion

The solvolysis of (nitrate)chromium(III) ion in aqueous dimethyl sulfoxide mixed solvents gives species with approximately the same average number of coordinated molecules of dimethyl sulfoxide as are present in the reactant species, and hexakis(dimethyl sulfoxide)chromium(III) ion does not form, even in the mixed solvents in which the equilibrium value of \bar{d} exceeds 5.0 ($Z > \sim 0.5^2$). These observations lead to one of two possible conclusions: that (nitrate)chromium(III) ion loses nitrate ion by nitrogen-oxygen bond breaking, not chromium(III)-oxygen bond breaking, or that water exclusively replaces departing intact nitrate ion in the solvolysis even at high values of Z . In the absence of an appropriate oxygen-18 tracer experiment to settle which of these conclusions is correct, relevant information from other systems can be mentioned.

Among other data suggesting that the aquation of (nitrate)chromium(III) ion occurs via nitrogen-oxygen bond breaking is the failure of the rate of this process in pentaqua(nitrate)chromium(III) ion to be correlated with the linear free-energy relationship $\log(k/\text{s}^{-1}) = -6.89 + 0.56 \log(Q/\text{mol L}^{-1})$ to which the data for halo- and (isothiocyanato)chromium(III) ion fit nicely.¹⁷ (The first-order rate constant k pertains to the hydrogen ion independent pathway for aquation, and Q is the equilibrium constant for dissociation of the complex.) The rate constant for aquation of the (nitrate)chromium(III) ion is ~ 21 -fold larger than given by this correlation. (In this correlation the value of Q to be used is the experimental value multiplied by 3 to correct for the statistical factor to take into account the three equivalent sites for coordination of nitrate ion.) As Swaddle points out,¹⁷ the enthalpy change upon activation for the aquation of (nitrate)chromium(III) ion, $\Delta H^\ddagger = 21.6 \text{ kcal mol}^{-1}$,^{12,18} is very close to the value for oxygen exchange between nitrate ion and water via a transition state of charge 1+, $[(\text{H}_2\text{O})_n\text{NO}_2^+]^\ddagger$, $\Delta H^\ddagger \approx 22 \text{ kcal mol}^{-1}$.¹¹ Among data which hint that the aquation of an inert trivalent transition metal ion complex with nitrate ion occurs by metal(III)-oxygen bond breaking is the oxygen-18 tracer experiment which shows that pentaammine(nitrate)cobalt(III) ion aquates in alkaline solution by cobalt(III)-oxygen bond breaking.¹⁹ Values of the activation enthalpy for the aquation of the cobalt(III) complex in acid (24.3 kcal mol⁻¹) and in base (28.8 kcal mol⁻¹) are greater than that for oxygen exchange between nitrate ion and water in acidic solution.

(15) This percentage of $\text{Cr}(\text{OH}_2)_6^{3+}$ ion is taken from ref 2. Both \bar{d} data at 35°C and direct analysis for $\text{Cr}(\text{OH}_2)_6^{3+}$ in equilibrated solutions at 60°C give $81 \pm 1\%$ for this quantity. The relative concentration of $\text{Cr}(\text{OH}_2)_4(\text{OS}(\text{CH}_3)_2)_2^{3+}$ was calculated by using the equilibrium constant derived in ref 2.

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In addition, the rate constant for aquation of pentaammine(nitrato)cobalt(III) ion is ~ 0.3 times the value expected on the basis of a linear free-energy relationship ($\log(k/s^{-1}) = -5.71 + 1.00 \log(Q/\text{mol L}^{-1})$) which correlates the data for pentaamminehalocobalt(III) ions ($X^- = F^-, Cl^-, Br^-$).²⁰ Thus, pentaqua(nitrato)chromium(III) ion and pentaammine(nitrato)cobalt(III) ion deviate in different ways from linear free-energy relationships which correlate data for aquation of halide complexes. Neither this contrast nor the contrasting correlations of activation energies prove that there are different modes of bond breaking in the two systems, but they do make more attractive the interpretation of data presented here in terms nitrogen-oxygen bond breaking.

For aquation of (nitrato)chromium(III) ion to occur by nitrogen-oxygen bond breaking, participation of a water molecule is needed to obviate the production initially of the unstable species NO_2^+ and $Cr(OH_2)_5O^+$. However, involvement in the transition state of an appropriately oriented water molecule or its constituent proton and hydroxide ion allows the production of the stable products NO_3^- and $Cr(OH_2)_6^{3+}$. The coordination of four oxygen atoms to nitrogen in the transition state would resemble that in hypothetical ortho-nitrates. The observed value of ΔV^\ddagger for aquation of (nitrato)chromium(III) ion ($-13 \text{ cm}^3 \text{ mol}^{-1}$)²¹ is qualitatively consistent with this type of transition state. Failure to detect a transition state of charge 3+ (i.e., failure to detect a dependence of reaction rate upon the concentration of hydrogen ion) indicates the absence of pathways producing initially either of the unstable combinations $(H_2O)_5CrOH^{2+} + NO_2^+$ or $Cr(OH_2)_6^{3+} + HONO_2$.

If, however, this solvolysis reaction occurs by chromium-oxygen bond breaking, the predominant outer-sphere coordination at sites adjacent to nitrate ion in $Cr(ONO_2)(OH_2)_{5-d}(OS(CH_3)_2)_d^{3+}$ is by water, not dimethyl sulfoxide, and the seven-coordinate transition state for loss of nitrate must form from such species.

Choi and Carlyle⁵ have observed that nitrate ion catalyzes the aquation of (acetato)chromium(III) ion, with no detectable formation of (acetato)(nitrato)chromium(III) ion as an intermediate but with virtually quantitative formation of (nitrato)chromium(III) ion as an intermediate. The reaction step corresponding to the rate law $-d \ln [(H_2O)_5CrOOCCH_3^{2+}] = k[H^+][NO_3^-]$ may involve the displacement of acetic acid without chromium(III)-oxygen bond breaking, the coordinated nitrate ion in the intermediate being formed with nitrogen-oxygen bond breaking. Deutsch and Taube²² have proposed that the hydrogen ion promoted aquation of (acetato)chromium(III) ion occurs without chromium(III)-oxygen bond breaking.

The alkaline hydrolysis of organic nitrate esters has been shown to involve both C-O bond breaking and N-O bond breaking; e.g., *tert*-butyl nitrate hydrolyzes with 100% C-O bond breaking,²³ 1-octyl nitrate hydrolyzes with 85% N-O bond breaking,²³ and 2-octyl nitrate in aqueous ethanol hydrolyzes with 67% N-O bond breaking.²⁴

In solutions containing sulfur(IV), the rate of approach to solvation equilibrium does not follow simple first-order kinetics.

The data presented in Figure 2 do not give straight lines when plotted as $\log(\bar{d}_\infty - \bar{d})$ vs. time. This indicates that the various rate constants for the several reactions are not simply related to one another by the appropriate statistical factors.²⁵⁻²⁷ If the initial slopes in first-order plots for the runs at two different pH values are compared, an approximately inverse dependence upon the concentration of hydrogen ion is observed. (Although the measured pH values in the mixed solvent with $Z = 0.283$ cannot be interpreted in the usual way, it is assumed that the difference of 0.39 unit between the experiments depicted in curves B and C corresponds to a change of hydrogen ion concentration by a factor of ~ 2.5 .) This inverse dependence is the hydrogen ion concentration dependence that has been observed in the sulfur(IV) labilization of other displacement reactions of chromium(III),⁶ and it indicates that hydrogen sulfite ion is the sulfur(IV) species coordinated to chromium(III) in the transition state.^{5,6}

The first-order approach to equilibrium in the aquation of pentaqua(dimethyl sulfoxide)chromium(III) ion in acidic media with $Z = 0.010$ is increased by increasing the concentration of carbon dioxide and by decreasing the concentration of hydrogen ion. Under the assumption that the measured pH values can be converted to concentrations of hydrogen ion, $[H^+]/\text{mol L}^{-1} = 10^{-\text{pH}}$, and that Henry's law constant for carbon dioxide is the same for this medium as it is for water ($k = 2.24 \times 10^4 \text{ torr L mol}^{-1}$), values of the first-order rate constant for 25 °C have been correlated with eq 1 in which

$$k = k_0 + k_1[CO_2]/[H^+] + k_2[CO_2]/[H^+]^2 \quad (1)$$

$k = -(d \ln(A_t - A_\infty))/dt$ or $k = -(d \ln(A_t - A_{t+\tau}))/dt$. The values of $k_0 = 1.45 \times 10^{-5} \text{ s}^{-1}$, $k_1 = 3.7 \times 10^{-6} \text{ s}^{-1}$, and $k_2 = 1.2 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$ yield calculated values of k which agree with the experimental values with an average deviation of 5%. The concentration of hydrogen ion is large enough to suppress appreciable acid dissociation of aquachromium(III) species [$Cr(OH_2)_6^{3+}$ and $Cr(OH_2)_5(OS(CH_3)_2)^{3+}$] and also to suppress carbonate or hydrogen carbonate complex ion formation with chromium(III) species. Thus the rate constants for both the forward and reverse reactions, which make up the composite rate constant for the approach to equilibrium, must have the same dependences upon the concentrations of hydrogen ion and carbon dioxide. The data do not rule out an additional rate law term involving $[H^+]^{-1}$ and with no dependence upon $[CO_2]$, but the correlation of data with the proposed rate law is sufficiently good to discourage adding another adjustable parameter. In the range of acidity studied, the relative importance of transition states with net charges 2+ and 1+ varies from 38% and 13% at the highest acidity to 33% and 59% at the lowest acidity.

Hydrogen carbonate ion is isoelectronic with nitrate ion, and a rough comparison of the labilizing effects of these two ligands for the displacement of coordinated water by dimethyl sulfoxide can be made. The earlier study³ gives the first-order rate constant k , for the rate law term $k[Cr(OH_2)_5ONO_2^{2+}]$ for $Z \approx 0.012$, $10^2 k = 6.9 \pm 0.5 \text{ s}^{-1}$. (Apparent lack of dependence of the rate upon the concentration of dimethyl sulfoxide is consistent with the occurrence of outer-sphere association of the chromium(III) species with dimethyl sulfoxide, a characteristic of this system suggested also by other data.²) To estimate the value of the corresponding rate constant for the hydrogen carbonate system, $k[Cr(OH_2)_5OCO_2H^{2+}]$, from the value $k_1 = 3.7 \times 10^{-6} \text{ s}^{-1}$ requires an estimation of the stability of the hydrogen carbonate complex. A formation constant $K \approx 90 \text{ L mol}^{-1}$ has been esti-

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mated for the iron(III) hydrogen carbonate complex²⁸ and use of this value allows estimation of the value $k \approx 9 \times 10^{-2} \text{ s}^{-1}$ for the reaction of (hydrogen carbonate)chromium(III) ion with dimethyl sulfoxide at $Z = 0.01$. Thus, the magnitude of the labilization by coordinated hydrogen carbonate ion is similar to that of coordinated nitrate ion.

The labilization of chromium(III) ion by carbon dioxide through the formation of carbonate or hydrogen carbonate

containing transition states for substitution reactions suggests that carbon dioxide may be a useful catalyst in procedures for forming complexes of chromium(III).²⁹

Registry No. Cr(ONO₂)(H₂O)₅²⁺, 17500-09-3; (CH₃)₂SO, 67-68-5; Cr(OH₂)₆³⁺, 14873-01-9; hydrogen sulfite, 15181-46-1; hydrogen carbonate, 71-52-3; Cr(H₂O)(OS(CH₃)₂)₅³⁺, 24269-28-1; Cr(H₂O)₅(OS(CH₃)₂)³⁺, 24283-89-4.

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Reactions of Hexafluoroacetone with Sulfur-Containing Compounds

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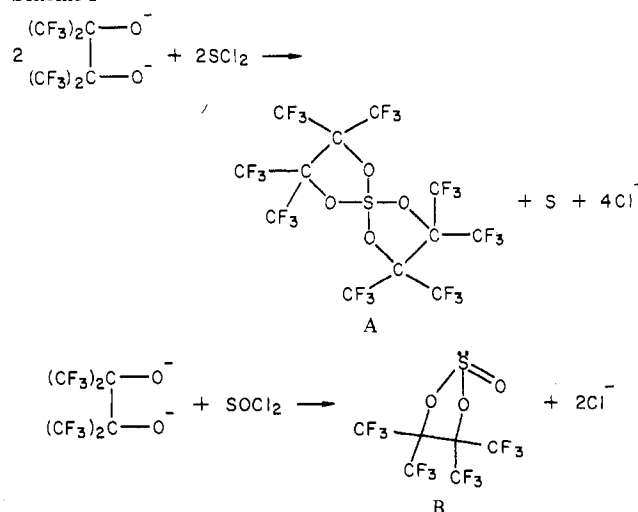
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Reactions of hexafluoroacetone with simple alkyl sulfides were studied. With trimethylene sulfide, a concerted addition reaction resulted in the formation of a six-membered ring, (CF₃)₂COSCH₂CH₂CH₂; with tetramethylene sulfide, dimethyl sulfide, or dimethyldisulfane, insertion into the α position occurred to give SCH[C(OH)(CF₃)₂]CH₂CH₂CHC(OH)(CF₃)₂, HO(CF₃)₂CCH₂SSCH₂C(CF₃)₂OH, and HO(CF₃)₂CCH₂SSCH₂C(CF₃)₂OH, respectively. With thiophosphoryl chloride, where no α -hydrogen is present, oxidative addition at sulfur (II) gave OC(CF₃)₂C(CF₃)₂OS=PCl₃. No reaction was observed with *F*-alkyl sulfides under the conditions used, with the exception that those with active functional groups such as NH₂ behave as primary aliphatic amines in their reactions with hexafluoroacetone; e.g., with H₂N(CF₃)COCH₂CH₂O and H₂N(CF₃)CSCH₂CH₂S, (CF₃)₂C=N(CF₃)COCH₂CH₂O, (CF₃)₂C=N(CF₃)CSCH₂CH₂S, and HO(CF₃)₂CNH(CF₃)CSCH₂CH₂S were obtained. No reaction was observed when a sulfur-phosphorus mixed ligand such as SCH₂C-H₂SPSCH₂CH₂SPSCH₂CH₂S or ethylene sulfide was reacted with hexafluoroacetone. When (CF₃)₂C(OH)SH was mixed with SCl₂ and Cl₂, compounds such as HO(CF₃)₂CSSSC(CF₃)₂OH and HO(CF₃)₂CSSC(CF₃)₂OH were formed, respectively. The latter two compounds as well as (CF₃)₂C(OH)SH, when reacted with SF₄, gave hexafluorothioacetone. (CF₃)₂C(OH)SH also was reacted with ClF in Pyrex glass to give (CF₃)₂C(OH)₂.

The reactions of hexafluoroacetone (HFA) with various phosphites and phosphines have been examined extensively as a synthetic route to cyclic phosphoranes.¹⁻⁴ Sulfur analogues such as the spirothiophane A and the monocyclic thionyl compound B were obtained from reactions of an *F*-pinacol salt with SCl₂⁵ and SOCl₂,⁶ respectively (Scheme I).

Although a modified synthesis of sulfurane A has appeared in the literature recently,⁷ use of the extremely toxic *F*-pinacol was still required. We have investigated reactions between HFA and simple sulfur compounds as a route to make cyclic sulfuranes. A dipolar 1:1 adduct has been postulated as the intermediate in the synthesis of cyclic phosphoranes,^{8a} and it

Scheme I



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is likely that the same mechanism also applies in reactions with sulfur-containing compounds. In order to stabilize such an intermediate, the sulfur atom must be rich in electron density. Indeed, we found that no reaction occurred with *F*-alkyl sulfides, such as CF₃SSCF₃, CF₂SCF₂S, etc., under the conditions used. In the case of nonfluorinated sulfides, with two exceptions, substitution into the α position by HFA was the reaction mode. However, when hexafluoroacetone was reacted with thiophosphoryl trichloride, where no α -hydrogen was