$VO(OH)_2$ precipitation. $(VOOH)_2^{2+}$ and $VO(OH)_2$ are EPR silent at room temperature presumably because of their polynuclear structures. The gentle slope between pH 5.0 and 6.0 is probably due to the onset of amphoterism, e.g., $VO(OH)_3^-$ formation, which offsets the formation of $VO(OH)_2$.

At a pH of approximately 6.7 the solution starts becoming a golden brown color indicative of formation of a new species. As the pH is raised well into the alkaline range, the $VO(OH)_2$ precipitate dissolves. At pH 11.5 with no precipitate present a strong eight-line EPR spectrum with $A_0 = 87.3 \times 10^{-4}$ cm^{-1} and $g_0 = 1.969$ is observed. These values are in good agreement with those reported for the recently well-characterized $VO(OH)_3^-$ species.[15]

In protein studies at physiological pH in the absence of chelating buffers, one does not observe an EPR spectrum of VO^{2+} unbound to the protein. Our studies indicate that under these conditions most of the uncoordinated vanadyl ion exists as a suspension of $VO(OH)_2$.

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Registry No. $VOSO_4$, 27774-13-6; NaOH, 1310-73-2; $VO(H_2O)_5^{2+}$, 15391-95-4; $VO(OH)_2$, 30486-37-4.

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Contribution from the Departments of Chemistry,
University of Colorado, Boulder, Colorado 80302,
and Iowa State University, Ames, Iowa 50010

Rapid Reaction of Dimethyl Sulfoxide with Nitratopentaaquochromium(III) Ion[1,2]

Mike L. Mitchell, Theresa Montag,[3a] James H. Espenson,[3b] and Edward L. King*[3c]

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The replacement of water in the first coordination shell around chromium(III) in hexaaquochromium(III) ion by dimethyl sulfoxide is very slow, having a half-time of ~380 hr at 25° at 0.705 mole fraction of dimethyl sulfoxide.[4] It is interesting to report, therefore, that this same process (replacement of coordinated water by dimethyl sulfoxide) occurs for nitratopentaaquochromium(III) ion with a half-time of ~10 sec at 25° at 0.004–0.04 mole fraction of dimethyl sulfoxide.

Table I. Rate of Replacement of Water in $Cr(OH_2)_5ONO_2^{2+}$ by Dimethyl Sulfoxide (25°, $[Cr^{III}] = 0.016\ M$)^a

Z^b	$10^2 k_{obsd}{}^c$/sec^{-1}	Z^b	$10^2 k_{obsd}{}^c$/sec^{-1}
0.0036^d	7.9 ± 0.4	0.034	8.0 ± 0.3
0.012	6.9 ± 0.5	0.045^e	8.6 ± 0.3

^{a} $k_{obsd} = -d \ln (A_\infty - A)/dt$. ^{b} Z = mole fraction of dimethyl sulfoxide in solvent, calculated with no allowance for solute species. ^{c} Three to five runs at each set of concentration conditions. ^{d} $[Cr^{III}] = 0.0197\ M$. ^{e} At this solvent composition, other concentrations of chromium(III) were studied; at 0.0087 M Cr^{III}, $10^2 k = 9.4 \pm 1.3$ sec^{-1}; at 0.0035 M Cr^{III}, $10^2 k = 10.4 \pm 0.3$ sec^{-1}.

Labilizing effects of other coordinated oxy anions are known for reactions of chromium(III),[5-8] but the real precedent for the present study was the remarkable labilizing effect of nitrate ion upon the rate of loss of ammonia by nitratopentaamminechromium(III) observed by Guastalla and Swaddle.[9] In this study the two isomeric aquodihydroxytriamminechromium(III) ions are produced but only *cis*-aquohydroxytetraamminechromium(III) ion is produced. These authors suggest that ammonia located cis to the coordinated nitrate ion is displaced by the nitrate to produce a transient bidentate nitrato intermediate which opens with introduction of water into the coordination shell. This loss of ammonia by nitratopentaamminechromium(III) ion is powers of 10 faster than the corresponding reaction of hexaamminechromium(III) ion. The rapid changes which occur when nitratopentaaquochromium(III) ion (hereafter called nitratochromium(III) ion) is added to acidic aqueous dimethyl sulfoxide are reactions analogous to those observed by Guastalla and Swaddle.[9]

Experimental Section

Reagents. Hexaaquochromium(III) perchlorate was prepared from reagent grade chromium trioxide and hydrogen peroxide as already described.[4] Nitratochromium(III) ion in perchloric acid solution was prepared as described by Swaddle.[10] Reagent grade Dowex 50W resin in the hydrogen ion form was treated before use as described earlier.[11] Other chemicals were reagent grade and were used without further purification.

Spectral Measurements. Upon adding an acidic aqueous solution of nitratochromium(III) ion to acidic aqueous dimethyl sulfoxide, a rapid color change (gray-blue to green) occurs. Coordinated nitrate is lost in a much slower reaction. The spectra of solutions of various composition taken after the rapid chemical change are consistent with substitution of water by dimethyl sulfoxide in the inner coordination shell of nitratochromium(III) ion. Positions of maxima and corresponding molar absorbancy index values for the two peaks in the visible region of the spectrum for various solvent mixtures [given as mole fraction of dimethyl sulfoxide, λ_{max} (nm), $\tilde{a}$ $(=(\log (I_0/I))/([Cr^{III}] \times \text{cell length}))$ are as follows: 0.0104, 410 (19.9), 578 (17.2); 0.0215, 414 (21.0), 582 (18.1); 0.0395, 416 (22.1), 588 (18.9); 0.0816, 423 (24.5), 599 (21.9); 0.144, 429 (27.2), 607 (24.9); 0.276, 436 (30.2), 616 (28.2); 0.374, 438 (32.4), 618 (30.8); 0.600, 442 (35.1), 622 (33.5).

Kinetic Measurements. Two types of kinetic measurements have been made. The rapid changes which are the primary subject of this note were studied using a Durrum stopped-flow spectrophotometer with a Kel-F mixing block and a 2-cm optical path. In these experiments, equal volumes of (1) an aqueous solution of chromium(III) perchlorate and perchloric acid (1.00 M) and (2) a 1.00 M perchloric acid in a binary dimethyl sulfoxide–water solvent mixture were mixed. The spectral change followed at 440 nm conformed to first-order kinetics, log $(A_\infty - A_t)$ being a linear function of time. Runs over a fivefold range of concentrations of chromium(III) (0.0163–0.0035 M) gave within experimental error the same value of k_{obsd}, the first-order rate constant for the approach to equilibrium ($k_{obsd} = d \ln (A_\infty - A_t)/dt$. Values of k_{obsd} are presented in Table I.

Much slower than this rapid change was the loss of nitrate co-

Table II. Rate of Loss of Nitrate Ion by Nitratochromium(III) Ion ($I = 1.00\,M$, $[H^+] = 1.0\,M$)[a,b]

$T/°C$	Z	$10^6 k'/sec^{-1}$
25	0.403	8.81
35	0	210[c]
	0.134	100
	0.268	29
	0.403	29[d]

[a] $[CrONO_2^{2+}]_0 \simeq 5 \times 10^{-3}\,M$. [b] $k' = -d \ln [CrONO_2^{2+}]/dt$. [c] A run in water ($Z = 0$) at $[H^+] = 0.11\,M$ gave $k' = 2.70 \times 10^{-4}$ sec^{-1}. In water, Swaddle[10] determined the rate constant for aquation of nitratochromium(III) ion at 35° to be 2.40×10^{-4} sec^{-1} ($[H^+] = 0.97\,M$) and 2.7×10^{-4} sec^{-1} ($[H^+] = 0.17\,M$). [d] Four experiments with $[H^+] = 0.12$–$1.0\,M$.

ordinated to chromium(III), which was followed by analysis of reaction mixtures by ion-exchange procedures. The elution of nitratochromium(III) ion by 0.5 *M* sulfuric acid occurs much more readily than elution of species of charge 3+ from which nitrate ion has been lost. The labilizing effect of coordinated nitrate ion is manifested in the ease of elution of nitratochromium(III) ion. Since the elution rate for nitratochromium(III) ion is observed to be greater than that expected for an ion of charge 2+, it seems likely that chromium(III) ion coordinated to nitrate ion is present in 0.5 *M* sulfuric acid as a mixture of species of charge 2+ ($Cr(OH_2)_5ONO_2^{2+}$), 1+ ($Cr(OH_2)_4(OSO_3H)(ONO_2)^+$), and 0 ($Cr(OH_2)_4(OSO_3)(ONO_2)$), and possibly anionic species. On the time scale of the elution, these species would be in equilibrium with each other. The elution profiles of reaction mixtures at various times show the presence of more than one chromium(III) species of charge 3+. Although separation of all possible aquo(dimethyl sulfoxide)chromium(III) species is possible,[12] complete resolution of the species of charge 3+ resulting from the loss of coordinated nitrate ion was not attempted in the present study. Only the rate of disappearance of nitratochromium(III) ion was of concern; values of $k'_{obsd} = -d \ln [CrONO_2^{2+}]/dt$ as a function of solvent composition are given in Table II. (In these experiments, the concentration of nitratochromium(III) ion extrapolated to zero time was significantly smaller than the value expected on the basis of the concentration of stock solution employed. Appreciable heat is generated when water and dimethyl sulfoxide are mixed.)

Discussion

The labilizing effect of coordinated nitrate ion prevents use of ion-exchange procedures to separate and identify the differently solvated nitratochromium(III) ions. The question of whether nitrate ion has labilized the trans site, the cis sites, or all sites may be settled with reasonable satisfaction by consideration of the spectrum of nitratochromium(III) in the various mixed solvents. If an average environment approximation[13] is applied to the species $Cr(OH_2)_{5-d}(OS(CH_3)_2)_dONO_2^{2+}$, the average number of bound molecules of dimethyl sulfoxide, $\bar{d}$, is related to the spectral peak position by the equation

$$\bar{d} = 6(\nu - \nu_1)/(\nu_2 - \nu_3)$$

in which ν, ν_1, ν_2, and ν_3 are the energies corresponding to peak positions for nitratochromium(III) in the mixed solvent, nitratopentaquochromium(III) ion, hexakis(dimethyl sulfoxide)chromium(III) ion, and hexaaquochromium(III) ion, respectively. These peak positions are as follows: nitratopentaaquochromium(III) ion, 408 and 574 nm; hexakis(dimethyl sulfoxide)chromium(III) ion,[14] 444 and 634 nm; hexaaquochromium(III) ion 406 and 570 nm. Applying the equation just given to the data obtained in this study gives the following values of $\bar{d}$ as a function of Z (given as Z, $\bar{d}$): 0.0104, 0.38; 0.0215, 0.92; 0.0395, 1.38; 0.0816, 2.47; 0.144, 3.32; 0.276, 4.25; 0.374, 4.49; 0.600, 4.92. (These values of $\bar{d}$ are the averages from the two peak positions; the average difference between values calculated for the two peaks was 0.3 unit of $\bar{d}$.) This calculation is based upon the assumption that no loss of nitrate has occurred at the time of measurement, an assumption which is not correct. However, the errors introduced are not expected to be large. If nitrate ion was lost before the remaining five sites equilibrated, the observed spectra would be unduly weighted with species having peaks at lower frequency than corresponds to equilibrated chromium(III). If nitrate ion was lost after all of the sites had equilibrated, the value of $\bar{d}$ for the mixture of species ($Cr(OH_2)_{6-d}(OS(CH_3)_2)_d^{3+}$) arising in this way would be expected to be six-fifths greater than the value for the corresponding mixture of species $Cr(OH_2)_{5-d}(OS(CH_3)_2)_dONO_2^{2+}$. The uncertainties associated with the value of $\bar{d}$ calculated from the position of the spectral peaks are not sufficient to mar the derived result, namely, that the value of $\bar{d}$ exceeds 4 and approaches 5 as the solvent becomes rich in dimethyl sulfoxide. The coordinated nitrate ion labilizes all five of the other coordination sites. Presumably this labilization occurs by a mechanism proposed by Guastalla and Swaddle[9] in which a transient bidentate nitrate ion steps about the coordination sites, labilizing them as it goes.

The values of $\bar{d}$ obtained from the spectral peak positions can be used to calculate a "discrimination factor" which is a measure of the relative tendency for the nitratochromium(III) unit to coordinate dimethyl sulfoxide compared to water. This quotient $[\bar{d}/(5 - \bar{d})]/[Z/(1 - Z)]$ varies from ~8 at $Z = 0.01$ to ~15 at $Z = 0.37$. Over the same range of Z the value of an analogous quotient $[\bar{n}/(6 - \bar{n})]/[Z/(1 - Z)]$ for chromium(III) at 35° varies from ~2.9 to ~4.5. This comparison supports the notion that all five of the sites in nitratochromium(III) are essentially at equilibrium with the solvent medium.

The rate constant for equilibration of the five coordination sites, $k_{obsd} \simeq 8 \times 10^{-2}$ sec^{-1} at 25°, is remarkably high. In the absence of coordinated nitrate, the corresponding rate constant is $k \simeq 2 \times 10^{-5}$ sec^{-1} at 60°. If an activation energy for this latter reaction is assumed to be 26 kcal mol^{-1}, this value would become $k \simeq 2 \times 10^{-7}$ sec^{-1} at 25°. The rate enhancement caused by the coordinated nitrate is $\sim 4 \times 10^5$, a value comparable to that for the coordinated chloromethyl group.[15]

Registry No. $Cr(OH_2)_5ONO_2^{2+}$, 17500-09-3; dimethyl sulfoxide, 67-68-5.

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