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Electron-Transfer Reactions between Vanadium(IV) and Manganese(III) Complexes of the EDTA Family

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The $Mn(EDTA)(H_2O)^-$ oxidations of $VO(H_2O)_5^{2+}$, $VO(HEDTA)^-$, $VO(EDTA)^{2-}$ and $VO(NTA)(H_2O)^-$ complexes have been studied. The complexes which possess an equatorial water molecule, $VO(H_2O)_5^{2+}$ and $VO(NTA)(H_2O)^-$, exhibit a rate law having an acid independent (k_0) path and an inverse acid (k_1) path. Kinetic parameters at 298 K were found to be $k_{0(NTA)} = 10.2\ M^{-1}\ s^{-1}$, $k_{1(NTA)} = 1.06 \times 10^{-2}\ s^{-1}$, $k_{0(H_2O)} = 7.78 \times 10^2\ M^{-1}\ s^{-1}$, and $k_{1(H_2O)} = 4.54\ s^{-1}$. The activation parameters for the $1/(H_3O^+)$ path of the aquo complex are $\Delta H_{1(H_2O)}^\ddagger = 11.5 \pm 1.0$ kcal/mol and $\Delta S_{1(H_2O)}^\ddagger = -17 \pm 3$ eu. Chelation by $HEDTA^{3-}$ or $EDTA^{4-}$ which excludes water from the equatorial positions of VO^{2+} causes a change in mechanisms for the Mn(III)/V(IV) aminocarboxylate redox reactions. The rate dependence for the $Mn(EDTA)(H_2O)^-/VO(HEDTA)^-$ system is dependent on $k_2[H_3O]^+$ with $k_2 = 3.50 \times 10^2\ M^{-2}\ s^{-1}$ at 298 K. The activation parameters for the first-order $[H_3O^+]$ path are $\Delta H^\ddagger = 11.8 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = -7 \pm 3$ eu. The rate of oxidation of $VO(HEDTA)^-$ at a given pH is relatively insensitive to $Mn(EDTA)(H_2O)^-$, $Mn(HEDTA)(H_2O)$, or $Mn(H_2O)_5(CH_3CO_2)^{2+}$ as its oxidant or to changes in ionic strength over the range of 0.10–0.50 in sodium acetate or phosphate buffers. Chloroacetate is oxidized by $Mn(HEDTA)(H_2O)$ rapidly but not by $Mn(EDTA)(H_2O)^-$. A contribution, $\Delta S_{CR}^\ddagger$, to $\Delta S_{tot}^\ddagger$ for the $Mn(EDTA)(H_2O)^-/VO(HEDTA)^-$ reaction is estimated to be 10 ± 6 eu attributable to differing solvation and coordination geometries of the incipient products. A binuclear complex is detected upon 1:1 combination of manganese(III) acetate and $VO(DTPA)^{3-}$. The binuclear species $[Mn^{III}, V^{IV}(DTPA)]$ undergoes intramolecular redox forming a binuclear $[Mn^{II}, V^{V}(DTPA)^{2-}]$ complex competitive with some ligand oxidation at the Mn(III) site. The product spectrum of the $[Mn^{II}, V^{V}(DTPA)^{2-}]$ complex was determined by ESR. The Mn(III)–V(IV) aminocarboxylate electron-transfer reactions appear to proceed by an outer-sphere mechanism.

Introduction

Ligand rearrangements and associated conformational changes which are coupled to redox events are likely to be an important biochemical control feature of metalloprotein redox processes.[1] The interconversion of various oxidation states of vanadium from V to III is important in the life cycle of tunicates.[2,3] The activation of small molecules on coordination and the effect of ligand chelation on redox reactivities of the metal centers are important topics. Haight has observed that the oxidation of VO^{2+}–ATP by H_2O_2 is much slower by a factor of 10^3 or more than the aquo complex.[4] The redox process is also catalytic for the hydrolysis of ATP which would imply a rather subtle coupling of an electron-transfer process to labilizing substitution at phosphorus in the ligand.[4] Shepherd and Kristine have observed that the intramolecular electron-transfer step in the V(HEDTA) (II, IV) binuclear ion to the stable (III, III) successor complex is limited by ligand rearrangement events.[5,6] We have extended the study of the effect of changing coordination geometries on redox processes by examining the oxidation of $VO(HEDTA)^-$ and related amino carboxylate complexes by $Mn(EDTA)(H_2O)^-$.

Hamm and Hunt have previously studied the oxidation of $VO(H_2O)_5^{2+}$ by $Mn(EDTA)(H_2O)^-$ and $Mn(CyDTA)(H_2O)^-$.[7] The rate law for the $Mn(EDTA)(H_2O)^-/VO(H_2O)_5^{2+}$ system exhibits parallel rate terms which are independent and inversely dependent in $[H_3O^+]$. The $1/[H_3O^+]$ path is favored by a factor of 60 relative to the acid independent path. Hamm and Hunt concluded that the mechanism for oxidation of $VO(H_2O)_5^{2+}$ by the Mn(III)–aminocarboxylate complexes is inner sphere on the basis of the enhancement from the hydroxy path,[8,9] but the effect is less than the 10^2–10^4 factor which is frequently observed with hydroxide bridging. Mn(III) and Mn(II) systems are labile with water exchange rate $\simeq 10^6$ and $10^7\ s^{-1}$, respectively.[10] No evidence from spectral data can be found which supports any detectable amounts of precursor or successor complexes in the $VO(H_2O)_5^{2+}/Mn(EDTA)(H_2O)^-$ reaction. This limitation is consistent with the labilities of Mn(III) and Mn(II). The $VO_2(H_2O)_4^+$ product has a cis configuration of the oxo ligands in contrast to the more common trans dioxo orientation as in MoO_2^{2+}, NpO_2^{2+}, and UO_2^{2+}.[11] Structural rearrangements in the oxidation of $VO(HEDTA)^-$ to $VO_2(HEDTA)^{2-}$ are likely to be more severe than for the oxidation of $VO(H_2O)_5^{2+}$ to $VO_2(H_2O)_4^+$.[12,13] We report here a reevaluation of the $Mn(EDTA)(H_2O)^-/VO(H_2O)_5^{2+}$ system at higher temperatures than were accessible to Hamm and Hunt and the alteration of the redox mechanisms when aminocaroxylate ligands are coordinated to the VO^{2+} center.

Experimental Section

Mn(III) was prepared in the form of $Mn(CH_3CO_2)_3$ anhydrous salt by the method of Brauer.[14] Solutions containing $Mn(EDTA)(H_2O)^-$ or $Mn(HEDTA)(H_2O)$ were prepared by complexation of analytically weighed amounts of $Mn(CH_3CO_2)_3$ and dissolution of the solid in 0.10 M ionic strength acetate or chloroacetate buffers containing the appropriate $HEDTA^{3-}$ or $EDTA^{4-}$ salts equal to the Mn(III) concentration. Spectra of the Mn(III) complexes were characterized by recording spectra on a Varian-Cary 118C spectrophotometer and comparing with the reported ϵ values of Hamm.[15,16] Chloroacetate buffer was found to be oxidized by $Mn(HEDTA)(H_2O)$; it was not used in this system. The pH measurements were made on the final reaction solutions and compared with identical buffer solutions at the given temperatures. The pH measurements were obtained on an Orion 601 Digital pH meter calibrated with commercial standards. Kinetic data were obtained on a Durrum D-110 stopped-flow spectrophotometer or in the repetitive scan mode of the Varian-Cary 118C. Thermal rates of Mn^{III} decomposition via solvent or ligand oxidations were determined to be less than 1% of the rate of the redox pathways for the V(IV) complexes. Temperature control was maintained to ±0.03 °C for the kinetic work on the stopped flow and ±0.1 °C for the Cary studies. The stopped-flow experiments were followed at 485 nm where the extinction coefficients are $168\ M^{-1}\ cm^{-1}$ for $Mn(HEDTA)(H_2O)$ and $466\ M^{-1}\ cm^{-1}$ for $Mn(EDTA)(H_2O)^-$. ESR spectra were obtained on a Varian E-4 instrument in the second derivative mode. Comparison spectra were obtained on $Mn(NTA)^-$ and $VO(HEDTA)^-$ at room temperature.

Results and Discussion

$Mn(EDTA)H_2O^-$ and $VO(H_2O)_5^{2+}$. Hamm and Hunt have shown that the stoichiometry for Mn(III):V(IV) is 1:1 for reaction 1 with Y = $EDTA^{4-}$ or $CyDTA^{4-}$. We have examined the $Mn(EDTA)(H_2O)^-/VO(H_2O)_5^{2+}$ reaction in the

$$MnY(H_2O)^- + VO(H_2O)_5^{2+} \rightarrow MnY(H_2O)^{2-} + VO_2(H_2O)_4^+ + 2H^+ \qquad (1)$$

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Table I. Kinetic Parameters for the $Mn(EDTA)(H_2O)^-$ Oxidation of $VO(H_2O)_5{}^{2+}$ [a]

T, °C	$10^{-1}k_1$ [b]	$-\ln k_1/T$	$10^3/T$	k_0
30.0	0.619	6.194	3.298	10.0
25.0	0.438	6.524	3.354	7.5
20.0	0.323	6.810	3.411	4.5
15.0	0.215	7.802	3.470	3.0

[a] $[VO(H_2O)_5{}^{2+}]_i = 9.64 \times 10^{-3}$ M, $[Mn(EDTA)(H_2O)^-]_i = 4.17 \times 10^{-4}$ to 4.31×10^{-4} M, pH 3.76, $[CH_3CO_2{}^-] = 0.10$ M, $[CH_3COOH] = 1.0$ M, $\mu = 0.12$. [b] Average of three or more traces; ±5% in k_1 and ±40% in k_0.

temperature range of 15.0–30.0 °C by the stopped-flow technique. The rate law of Hamm and Hunt given in eq 2 was confirmed by concentration-dependent studies. The

$$\frac{d[MnY(H_2O)^-]}{dt} = \left\{k_0 + \frac{k_1}{[H_3O^+]}\right\}[MnY(H_2O)^-][VO^{2+}] \quad (2)$$

temperature dependence of the k_1 and k_0 paths is shown in Table I. Their study was restricted to 1.7–7.0 °C for $Mn(EDTA)(H_2O)^-$ as the oxidant complex. The activation parameters which have been obtained for our experiments are reported in Table II. The results for the $Mn(EDTA)(H_2O)^-/VO(H_2O)_5{}^{2+}$ reaction are in very close agreement to the parameters determined by Hamm and Hunt for the $Mn(CyDTA)(H_2O)^-/VO(H_2O)_5{}^{2+}$ reaction[7] for the inverse hydrogen ion dependent path.

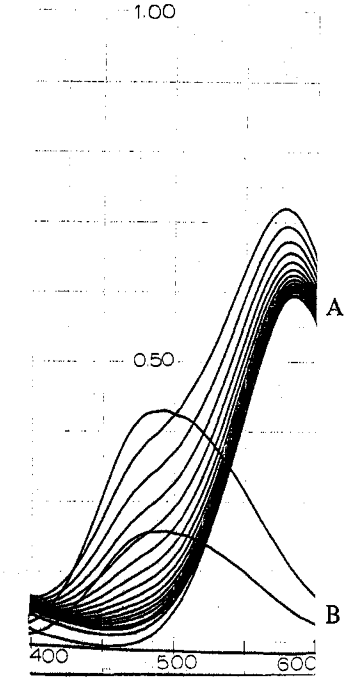


Figure 1. (A) Repetitive scan spectra of the $Mn(EDTA)(H_2O)^-/VO(EDTA)^{2-}$ reaction: $\mu = 0.12$, $b = 4.00$ cm, acetate buffer, $[Mn(III)]_i = 7.0 \times 10^{-4}$ M, $[V(IV)]_i = 1.45 \times 10^{-2}$ M, $T = 25.0$ °C. (B) $Mn(EDTA)(H_2O)^-$ thermal decay, $[Mn(III)]_i = 2.15 \times 10^{-4}$ M, $[V(IV)]_i = 0$, other conditions identical.

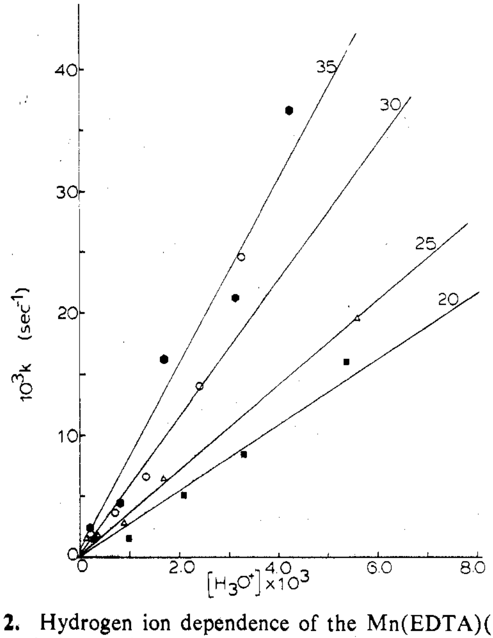


Figure 2. Hydrogen ion dependence of the $Mn(EDTA)(H_2O)^-/VO(HEDTA)^-$ reaction: $\mu = 0.12$ acetate or chloroacetate buffer, $[Mn(III)]_i = 2.15 \times 10^{-4}$ M, $[V(IV)]_i = 9.63 \times 10^{-3}$ M.

Manganese(III) and Vanadium(IV) Aminocarboxylate Monomeric Systems. The oxidation of $VO(HEDTA)^-$ or $VO(EDTA)^{2-}$ by $Mn(EDTA)(H_2O)^-$ proceeds according to eq 3. Spectra in the visible region confirm a 1:1 consumption

$$MnY(H_2O)^- + VOZ^- \rightarrow MnY(H_2O)^{2-} + VO_2Z^{2-} + 2H^+ \quad (3)$$

of the Mn(III) and V(IV) complex. The $Mn(EDTA)(H_2O)^-$ band at 497 nm and the $VO(HEDTA)^-$ bands at 578 and 775 nm are bleached to a constant final spectrum of $VO_2(HEDTA)^{2-}$ and $Mn(EDTA)(H_2O)^{2-}$. The repetitive scan spectra presented in Figure 1 illustrate the decay of both $Mn(EDTA)(H_2O)^-$ and $VO(EDTA)^{2-}$ under pseudo-first-order conditions in $VO(EDTA)^{2-}$. The shoulder at 485 nm bleaches to the zero absorbance contribution of $Mn(EDTA)(H_2O)^{2-}$ with an equimolar decrease in the $VO(EDTA)^{2-}$ band at 578 nm in ~86 min. The corresponding thermal decay of $Mn(EDTA)(H_2O)^-$ by means of ligand oxidation is shown by the overlapping $Mn(EDTA)(H_2O)^-$ spectra. Under identical conditions the thermal decomposition half-life is ca. 4.0 h ($k_{th} \simeq 4.8 \times 10^{-6}$ s^{-1}) which represents only 0.54% of the pseudo-first-order rate in the presence of $VO(EDTA)^{2-}$ at 1.0×10^{-2} M. The dependence of the aminocarboxylate reaction between Mn(III) and V(IV) conforms to the rate law given by eq 4 with Y or Z an

$$d[MnY(H_2O)^-]/dt = k_2[H_3O^+][MnY(H_2O)][VOZ] \quad (4)$$

aminocarboxylate of the EDTA family. The first-order dependence in $[H_3O^+]$ is shown in Figure 2. The absence of an intercept other than zero, within experimental error, and the first-order behavior in $[H_3O^+]$ support an elimination of the hydrolysis dependent and independent kinetic path which is observed in the $VO(H_2O)_5{}^{2+}$ oxidation. This is anticipated if all of the coordination positions on the V(IV) center are occupied by the chelating ligand. The acid-dependent path exhibits activation parameters of 11.8 ± 1.0 kcal/mol for $\Delta H^\ddagger$ and −7.2 ± 3 eu for $\Delta S^\ddagger$. The strikingly close correspondence to the value of $\Delta H^\ddagger$ for the inverse acid path in the $VO(H_2O)_5{}^{2+}$ is fortuitous in that the compositions of the activated

Table II. Activation Parameters for Mn(III) Complexes Oxidation of $VO(H_2O)_5{}^{2+}$ and $VO(HEDTA)^-$

System	Kinetic $[H_3O^+]$ dependence	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/(mol K)	Ref
$Mn(CyDTA)(H_2O)^-/VO(H_2O)_5{}^{2+}$	$[H_3O^+]^{-1.0}$	11.3 ± 1.6	−20.0 ± 6.0	4
$Mn(EDTA)(H_2O)^-/V(H_2O)_5{}^{2+}$	$[H_3O^+]^{-1.0}$	11.5 ± 1.0	−17.2 ± 3	This work
$Mn(EDTA)(H_2O)^-/VO(HEDTA)^-$	$[H_3O^+]^{1.0}$	11.8 ± 1.0	−7.2 ± 3	This work

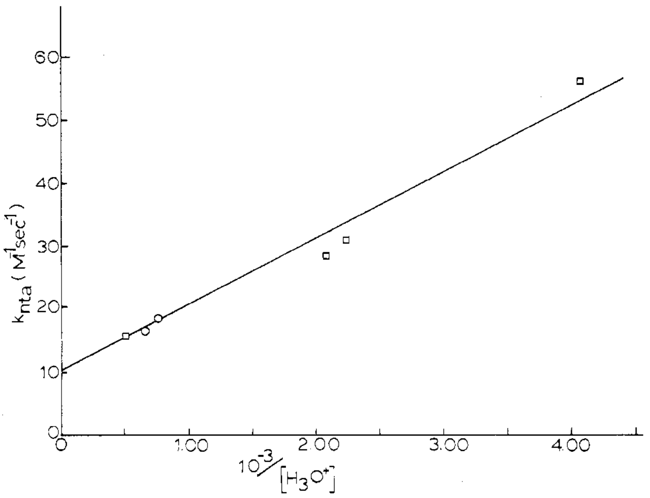


Figure 3. Hydrogen ion dependence of the $Mn(EDTA)(H_2O)^-$/$VO(NTA)(H_2O)^-$ reaction ($\mu = 0.10$, $T = 25.0$ °C): $[V(IV)]_i = 9.65 \times 10^{-3}$ M, $[Mn(III)]_i = (2.12–2.19) \times 10^{-4}$ M; □, points for acetate buffer; ○, points for chloroacetate buffer

complexes are quite different.

When all of the coordination positions on VO^{2+} are not fully coordinated in the strained $VO(NTA)(H_2O)^-$ complex, the rate law corresponds to the form given for the $VO(H_2O)_5^{2+}$ complex (eq 2) with the V(IV) concentration given by $[VO(NTA)(H_2O)^-]$. Figure 3 illustrates the $1/[H_3O^+]$ linear dependence for the $Mn(EDTA)(H_2O)^-/VO(NTA)(H_2O)^-$ reaction at 25 °C. The kinetic parameters are found in the $VO(NTA)(H_2O)^-$ and $VO(H_2O)_5^{2+}$ system to be the following: $k_{0(NTA)} = 10.2$ M^{-1} s^{-1}, $k_{1(NTA)} = 1.06 \times 10^{-2}$ s^{-1}, $k_{0(H_2O)} = 7.78 \times 10^2$ M^{-1} s^{-1}, $k_{1(H_2O)} = 4.54$ s^{-1}. The ratios of $k_{0(H_2O)}/k_{0(NTA)} \simeq 76$, $k_{1(H_2O)}/k_{1(NTA)} \simeq 430$, $k_{0(H_2O)}/k_{1(H_2O)} \simeq 171$, and $k_{0(NTA)}/k_{1(NTA)} \simeq 967$ reveal that the $1/[H_3O^+]$ and k_0 paths are both slower for the NTA complex by a magnitude of 10^2 and that the $1/[H_3O^+]$ path is more sensitive to the presence of the chelate by a factor of 5.6. The reduction in rate relative to the aquo complex may be rationalized on the basis of approach of anions in the $Mn(EDTA)(H_2O)^-/VO(NTA)(H_2O)^-$ reaction compared to approach of an anion and a cation for the $Mn(EDTA)(H_2O)^-/VO(H_2O)_5^{2+}$ reaction. The additional factor of 5.6 suggests that the water molecule on $VO(NTA)(H_2O)^-$ is less acidic than a water molecule on $VO(H_2O)_5^{2+}$, i.e., pK_a of $VO(NTA)(H_2O)^- = 6.19$, $\mu = 0.12$, and $VO(H_2O)_5^{2+} = 5.44$.[26]

The oxidation of vanadium(IV) aminocarboxylate complexes by Mn(III) is nearly independent of the charge product of the reactants. The rate is also relatively insensitive to the oxidizing potential of the Mn(III) complex or the number of aquo sites in the Mn(III) oxidant. These effects are shown by Table III. The $VO(EDTA)^{3-}$ species has a pK_a of 3.00 ± 0.05 ($\mu = 0.10$, 20 °C).[18] At pH 3.76, 17.5% and, at pH 3.00, 50.0% of the total $[VO(EDTA)^{2-}]$ are present as the protonated species $[VO(EDTA)H^-]$. Protonation occurs at one of the pendant carboxylate groups, so that the effective charge is similar to that for the $VO(HEDTA)^-$ system.

The spectrum of $Mn(EDTA)(H_2O)^-$ is independent of the presence or nature of monovalent anions ($CH_3CO_2^-$, $ClCH_2CO_2^-$, $H_2PO_4^-$). $Mn(HEDTA)(H_2O)$ is rapidly reduced to $Mn^{II}(HEDTA)^-$ in chloroacetate buffer while the EDTA complex was not affected by chloroacetate. The redox potentials for $Mn(EDTA)(H_2O)^-$ and $Mn(HEDTA)(H_2O)$ are comparable. Inner-sphere coordination of $ClCH_2CO_2^-$ must be necessary to initiate its oxidation and it seems reasonable that the neutrally charged $Mn(HEDTA)(H_2O)$ would associate more favorably with anions in the medium than the anionic $Mn(EDTA)(H_2O)^-$ complex. A few rate measurements were made in 0.10 and 0.50 M phosphate and acetate for the $Mn(HEDTA)(H_2O)/VO(EDTA)^{2-}$ reaction. The results are summarized in Table IV. In a given buffer the observed rate is relatively insensitive to an increase in the anion concentration of fivefold. This is expected for the $Mn(HEDTA)(H_2O)/VO(EDTA)H^-$ reactants. The slight increase with ionic strength suggests that the Mn(III) center has some positive character, rather than the formal 0 charge, as experienced by an approaching anionic $VO(EDTA)^{2-}$ or $VO(EDTA)H^-$. It may also be noted that increasing the anion concentration did not inhibit the rate. An equilibrium to form a complex of anion, A^-, with $Mn(HEDTA)(H_2O)$ as in eq 5

$$Mn(HEDTA)(H_2O) + A^- \overset{K_A}{\rightleftarrows} Mn(HEDTA)A^- + H_2O \tag{5}$$

would be expected to reduce an inner-sphere rate by a factor of $1/(1 + K_A[A^-])$.[27] The absence of any reduction with $A^- = CH_3CO_2^-$ or $H_2PO_4^-$ on increasing $[A^-]$ is ambiguous because almost no effect will be observed for any of the following reasons: (a) $K_A[A^-] \ll 1$ even at $[A^-] = 0.50$, (b) exchange at carboxylate is more rapid than the electron-transfer process, or (c) the reaction proceeds by an outer-sphere path. The values of K_A, on electrostatic grounds, for monovalent anions and cations with small effective positive charges ($\sim +1$) are normally about 0.20. The change in $1/(1 + K_A[A^-])$ is only 8% over the range of $[A^-] = 0.10–0.50$ with $K_A = 0.20$. Ligand exchange on Mn(III) as estimated by Davies is $\simeq 10^6$ s^{-1}.[10] Even if carboxylate exchange is slower by 10^4, the redox events are slower than the carboxylate exchange. Coordination of anions will not prevent an inner-sphere substitution on Mn(III). The monoazido complex of $Mn(EDTA)(H_2O)^-$ has a formation constant of 32.6 M^{-1}.[29] It would appear that the acetates and $H_2PO_4^-$ are less associated by at least $10^2–10^3$.

Table III. Observed Rate Constants for the Mn(III)–V(IV) Redox Systems at 25.0 °C[a]

Reaction	pH 3.76 10^2k,[b] M^{-1} s^{-1}	pH 3.00 $10k$,[b] M^{-1} s^{-1}	Charge product (approx)	$E°_{Mn}{}^{III/II}$, V (ref)
$Mn(HEDTA)(H_2O)/VO(HEDTA)^-$	6.66	4.20	0	0.782 (15)
$Mn(HEDTA)(H_2O)/VO(EDTA)^{2-}$		2.35	0	0.782 (15)
$Mn(EDTA)(H_2O)^-/VO(HEDTA)^-$	5.09	3.80	1	0.825 (15)
$Mn(EDTA)(H_2O)^-/VO(EDTA)^{2-}$	6.11		2	0.825 (15)
$Mn(H_2O)_5(CH_3CO_2)^{2+}$ or $Mn(H_2O)_4(CH_3CO_2)_2{}^+/VO(HEDTA)^-$		3.00	−1	1.49 (17)

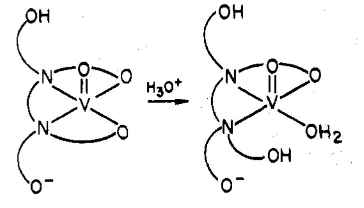
[a] $\mu = 0.10$ $NaCH_3CO_2$, $T = 25.0$ °C. [b] $k = k_2[H_3O^+]$, $[Mn(EDTA)(H_2O)^-] = 4.28 \times 10^{-4}$ M, $[Mn(HEDTA)(H_2O)] = 5.41 \times 10^{-4}$ M.

Table IV. $Mn(HEDTA)(H_2O)/VO(EDTA)^{2-}$ Reaction Ionic Strength and Counterion Effects[c]

Buffer	$[A^-]$, M	[HA], M	$10^{-2} \cdot k_{obsd}/[H_3O^+]$	Rel rate
$CH_3CO_2^-/CH_3CO_2H$	0.10	2.24[a]	2.35	
	0.50	11.2	2.63	1.12
$H_2PO_4^-/H_3PO_4$	0.07	0.036[b]	0.89	
	0.47	0.056	2.00	2.25

[a] pH 3.4. [b] pH 3.0. [c] $[Mn(HEDTA)(H_2O)] = 6.41 \times 10^{-4}$ M, $[VO(EDTA)^{2-}] = 1.45 \times 10^{-2}$ M, $T = 25$ °C.

The first-order dependence in $[H_3O^+]$ for the aminocarboxylate systems other than NTA suggests that conversion between structures A and B is required at the VO^{2+} center



A B

for formation of the V(V) product. Intermediates have not been detected for the relatively slow reaction of eq 3. The rate law is first order in Mn(III), assuring the presence of the Mn(III) moiety in the activated complex. Since substitution and water exchange on $Mn(EDTA)(H_2O)^-$ and $Mn(CyDTA)(H_2O)^-$ appear to be rapid compared to these redox events,[19,20] one cannot separate several kinetic possibilities which account for the $[H_3O^+]$ dependence. These correspond to two classes of reactions: (1) preequilibrium of the vanadyl complex with H_3O^+ followed by either inner- or outer-sphere rate limiting scavenging by the Mn(III) complex or (2) proton scavenging of a bridged V(IV)–Mn(III) intermediate. These are shown in Scheme I and II, respectively, with Z = $HEDTA^{3-}$ and Y = $EDTA^{4-}$. In these schemes Z'H represents a protonated structure similar to B. The preliminary equilibria with hydrogen ion schemes require $k_2 = kk_a$ or Kk_b; the proton scavenging of an inner-sphere complex requires $K'k_{lim}$. Therefore it remains undetermined whether ligand rearrangement occurs prior to bringing the reactant together as in Scheme I or after assembly of the Mn(III)–V(IV) reactant partners (Scheme II). Kristine and Shepherd have suggested eq 6 to account for the measured activation entropy for redox

$$\Delta S_{tot}^{\ddagger} = \Delta S_{form}^{\ddagger} + \Delta S_{ET}^{\ddagger} \tag{6a}$$

$$\Delta S_{ET}^{\ddagger} = \Delta S_{reorg}^{\ddagger} + \Delta S_{CR}^{\ddagger} \tag{6b}$$

systems that involve large amounts of ligand rearrangement.[6] $\Delta S_{ET}^{\ddagger}$ has been found to be zero for systems where ligand rearrangement is restricted to bond length readjustments.[21] We have attributed any additional effect on ligand rearrangement in the term $\Delta S_{CR}^{\ddagger}$. $\Delta S_{CR}^{\ddagger}$ is a rearrangement factor other than the costs of the initial aggregation of the reactant pairs and concomitant solvent reordering to achieve the activated complex which contribute to ΔS_{form} and $\Delta S_{reorg}^{\ddagger}$.

The contribution of $\Delta S_{CR}^{\ddagger}$ for the $Mn(EDTA)(H_2O)^-$/$VO(HEDTA)^-$ system may be estimated by comparison with the $Mn(EDTA)(H_2O)^-/VO(OH)(H_2O)_3^+$ system. $\Delta S_{tot}^{\ddagger}$ for the oxidation of $VO(OH)(H_2O)_3^+$ is −17 ± 3 eu which is in the range with the cost of −17 ± 3 eu to bring (−1)(−1) reactant partners together in the $VO(HEDTA)^-/V(HEDTA)^-$ cross-reaction.[6] $\Delta S_{tot}^{\ddagger}$ for the $Mn(EDTA)(H_2O)^-/VO(HEDTA)^-$ reaction is −7 ± 3 eu. If the contribution $\Delta S_{form}^{\ddagger}$ is estimated to be ≃−17 ± 3 eu, $\Delta S_{CR}^{\ddagger}$ is calculated to be +10 ± 6 eu for acid-catalyzed ring opening of $VO(HEDTA)^-$. This estimate seems compatible with the loss of one hydrate molecule from $H_5O_2^+$, somewhere else in the solvation shells of the reactants, or perhaps from the Mn(III) center. Amos and Sawyer have shown that conversion of the β-cis form of $VO_2(EDDA)^-$ to the α-cis form has a $\Delta S°$ of +7.8 eu.[28] The α-cis form has both oxo ligands in the equatorial plane and the β-cis form has one equatorial and one axial oxo ligand. Methylation or carboxylate substitution on the ethylenediamine nitrogens shifts the equilibrium completely in favor of the α-cis configuration. The α-cis form must have the greater absolute entropy and it was suggested that the α-cis and β-cis forms have different solvation spheres.[28] A rearrangement of structure B to an equatorial form similar to the α-*cis*-$VO_2(EDDA)^-$ structure in the activated complex should exhibit a positive contribution of ~8 eu to $\Delta S_{tot}^{\ddagger}$; this is certainly close to the calculated value of $\Delta S_{CR}^{\ddagger}$.

Scheme I

$$VOZ^- + H_3O^+ \overset{K}{\rightleftharpoons} VOZ'H(H_2O)$$

$$\text{(a)}\quad VOZ'H(H_2O) + MnY(H_2O)^- \overset{k_a}{\rightleftharpoons} VO_2Z^{2-} + 3H^+ + MnY(H_2O)^{2-}$$

$$\text{(b)}\quad VOZ'H(H_2O) + MnY(H_2O)^- \overset{k_b}{\rightleftharpoons} [(H_2O)VO(Z'H)MnY]^- + H_2O$$

$$[(H_2O)VOZ'HMnY]^- \xrightarrow{\text{fast}} VO_2Z^{2-} + 3H^+ + MnY(H_2O)^{2-}$$

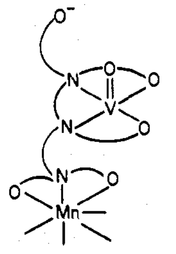
Scheme II

$$VOZ^- + MnY(H_2O)^- \overset{K'}{\rightleftharpoons} [MnYVOZ]^{2-} + H_2O$$

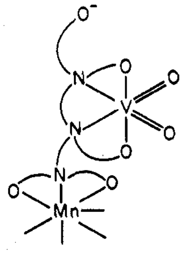
$$[MnYVOZ]^{2-} + H_3O^+ \xrightarrow{k_{lim}} VO_2Z^{2-} + 3H^+ + MnY(H_2O)^{2-}$$

Figure 4. Second-derivative ESR spectra: (A) Reaction product spectrum from 1:1 $Mn(CH_3CO_2)_3/VO(DTPA)^{3-}$ at 36 min: μ = 0.10, T = 25 °C, under N_2, pH 3.53 ($NaCH_3CO_2$, HCH_3CO_2), $[Mn(III)]_i$ = $[V(IV)]_i$ = 4.82 × 10^{-3} M, 50 mW, 9.47 GHz, 1000 Hz modulation, 100 kHz field modulation (4 G peak to peak); gain 1.6 × 10^3; dominant spectrum of [Mn^{II}, V^V(DTPA)]; minor spectrum of [V^{IV}DTPA]. (B) Spectrum for [$Mn^{II}(NTA)^-$]; pH 3.50; other conditions identical, gain 2 × 10^2, with A; $[Mn(II)]_{tot}$ = 4.82 × 10^{-3} M. (C) Spectrum for [$VO(DTPA)^{3-}$]; conditions the same as in B except $[V(IV)]_{tot}$ = 4.82 × 10^{-3} M

Mn(III)–V(IV) Binuclear Redox Systems. The ESR spectrum of $VO(DTPA)^{3-}$ is essentially the same as $VO(HEDTA)^-$. It may be concluded that there are two N and two carboxylate donors in the equatorial plane.[22] When $Mn(CH_3CO_2)_3$ is combined with $VO(DTPA)^{3-}$ under N_2 at 1:1 stoichiometry a rapid reaction occurs immediately after mixing followed by a slower bleaching of the V(IV) spectrum. The spectrum of the system in the visible range is approximated by the sum of $VO(HEDTA)^-$ and Mn(NTA) until the bleaching process is complete. The slower redox process occurs within 40 min at 25 °C. Mn(NTA) rapidly oxidizes its own ligand to produce Mn(II) under the same conditions. The Mn(III)–VO(DTPA) system would appear to rapidly form a binuclear complex C which decays by electron transfer to



C



D

D. The species with composition C is similar to the Cannon and Gardiner ion in which $Fe(H_2O)_6^{2+}$ is coordinated to the iminodiacetate fragment of carboxylate bound $Co(NH_3)_5NTA$.[23] The ESR spectrum of the reacting mixture (Figure 4) reveals the overlapping spectra of the VO^{2+} resonance of C with the Mn(II) resonance of D. As in the case of the MnNTA system alone, some competitive ligand oxidation or solvent oxidation also takes place. The final spectrum reveals a small amount of unconsumed V(IV) due to the thermal side reactions of the Mn(III) center in the binuclear complex. In the presence of O_2 there is a catalytic production of a peroxo species which is coordinated to the V(V) center. The induced formation of peroxo complexes is not observed for the oxidation of VO^{2+} amino carboxylate–Mn(III) aminocarboxylate monomeric complexes. Free radicals produced by competitive ligand oxidation at the Mn(III) center may be involved and the system is under investigation.[24] A peroxo complex is readily formed directly from $VO(DTPA)^{3-}$ and H_2O_2. It has a spectrum similar to the one reported by Tanaka et al. for $VO(O_2)(NTA)$.[25] No long-lived intermediates which might be attributed to a hydroxy or oxo bridged Mn(III)–V(IV) complex on the same $DTPA^{5-}$ ligand could be determined from the visible spectrum. Since the proximity effect should favor a higher concentration of a bridged species, these results suggest an outer-sphere mechanism for Mn(III)–V(IV) systems in aminocarboxylate environments.

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Registry No. $Mn(EDTA)(H_2O)^-$, 12318-32-0; $VO(EDTA)^{2-}$, 12276-03-8; $VO(HEDTA)^-$, 20648-99-1; $VO(NTA)(H_2O)^-$, 12347-63-6; $Mn(CH_3CO_2)_3$, 993-02-2; $VO(DTPA)^{3-}$, 65605-14-3; $Mn(HEDTA)(H_2O)^-$, 65545-48-4; $VO(H_2O)_5^{2+}$, 15391-95-4; chloroacetate, 14526-03-5.

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Trivalent Nickel Catalysis of the Autoxidation of Nickel(II) Tetraglycine

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Molecular oxygen reacts with nickel(II)–peptide complexes in aqueous solution by a facile autocatalytic process in which nickel(III) intermediates play a major role. With tetraglycine the formation of $Ni^{III}(H_{-3}G_4)^-$ initiates the reaction which results in the formation of carbon dioxide, triglycyl-*N*-(hydroxymethyl)amide, and glycinamide as the main products. The *N*-(hydroxymethyl)amide can further hydrolyze to produce triglycinamide and formaldehyde. When a free carboxylate group is adjacent to a deprotonated-peptide nitrogen (as in the tetraglycine complex), decarboxylation occurs and the autoxidation reactions are more rapid than for other peptide complexes. Initiation of the reaction by electrolytically prepared nickel(III)–peptide complexes is used to resolve the reaction order, which at low concentrations is first order in $[Ni^{II}G_4]_{total}$, in $[Ni^{III}(H_{-3}G_4)^-]$, and in $[O_2]$ but approaches zero order for each at higher concentrations.

Introduction

Autoxidation of *N*-alkylamides and *N*,*N*-dialkylamides is induced by either thermal[1-3] or photochemical[4] means to produce hydroperoxide intermediates by radical chain mechanisms. Transition-metal salts (e.g., Co(II), Fe(II), and Cu(I)) are often used to catalyze such O_2 reactions.[5] Ionizing radiation induces similar oxidation of oligopeptides.[6] These processes are slow, and the oxidation of oligopeptides is not self-sustaining in the absence of radiation.

Our laboratory has found that some copper(II) peptides[7,8] and nickel(II) peptides[9,10] react with oxygen in an autocatalytic manner with oxidation of the ligand. We have found recently that the trivalent oxidation states of copper[11,12] and nickel[13,14] are stabilized by deprotonated-peptide ligands. In the present