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The Stoichiometry and Kinetics of the Electron-Transfer Reactions between Vanadium(IV) and the Manganese(III) Complexes of *trans*-1,2-Diaminocyclohexanetetraacetic Acid (CyDTA) and Ethylenediaminetetraacetic Acid (EDTA) in Acidic Solution[1]

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Kinetic studies have been carried out on the reaction vanadium(IV) and the manganese(III) complexes of *trans*-1,2 diaminocyclohexanetetraacetate ($Mn^{III}CyDTAH_2O^-$) and ethylenediaminetetraacetate ($Mn^{III}EDTAH_2O^-$). The rate law for either $Mn^{III}CyDTAH_2O^-$ or $Mn^{III}EDTAH_2O^-$ reacting with vanadium(IV) is first order with respect to each reactant and second order overall. Both reactions proceed by parallel paths, one path with inverse hydrogen ion dependence (k_1) and the other path with acid independence (k_0). At 7.0° with $I = 1.0\ M$, the rate constants were $k_0 = 65\ M^{-1}\ sec^{-1}$, $k_1 = 0.53\ sec^{-1}$ for $Mn^{III}CyDTAH_2O^-$ and $k_0 = 173\ M^{-1}\ sec^{-1}$, $k_1 = 0.71\ sec^{-1}$ for $Mn^{III}CyDTAH_2O^-$. Activation parameters found for the reaction of $Mn^{III}CyDTAH_2O^-$ and vanadium(IV) were $\Delta H_0^* = 13.1 \pm 1.1$ kcal mol^{-1}, $\Delta S_0^* = -3.4 \pm 3.8$ eu, $\Delta H_1^* = 11.3 \pm 1.6$ kcal mol^{-1}, and $\Delta S_1^* = -20.0 \pm 6.0$ eu. An inner-sphere electron transfer process is proposed to account for reactions of the chelated manganese(III).

Introduction

The question of an inner-sphere mechanism as opposed to an outer-sphere mechanism for an electron-transfer reaction is one of considerable interest today as indicated by the number of reviews discussing the subject.[2-8] This question is a particularly difficult one to answer whenever both reactants are substitution labile on the time scale for electron transfer.

The reactions of manganese(III) in aqueous solution have been the subject of a recent review article,[9] in which the lability of $MnOH_{aq}^{2+}$ has been estimated at $1 \times 10^6\ sec^{-1}$. This value is in agreement with the value $\geq 10^4\ sec^{-1}$ inferred for manganese(III) water exchange using the temperature-jump measurements of Diebler and Eigen.[10]

The intimate details of manganese(III) functioning as an oxidizing agent remain an unsettled problem due to the uncertainty of the rate of water substitution. Arguments based on isotope effects have been used in support of an outer-sphere mechanism for the oxidation of sterically hindered alcohols.[11] Likewise the close parallel in rate between manganese(III) oxidation of iron(II) and vanadium(IV) has been used to advocate an outer-sphere electron-transfer reaction for these reactions.[12]

Inner-sphere mechanisms have been postulated for several reactions involving hexaaquomanganese(III) where evidence of complexation prior to electron transfer is based largely on effects of acid variation and changes in spectral properties during the course of the reaction.[13] Reactions of cobalt(II)–EDTA and cobalt(II)–CyDTA with $Mn^{III}EDTAH_2O^-$ and $Mn^{III}CyDTAH_2O^-$ have also been interpreted in terms of an inner-sphere process.[14]

Oxygen-17 nuclear magnetic resonance studies indicate that $VO(H_2O)_5^{2+}$ has two types of coordination sites, axial and equatorial, with the axial site exchanging with a residence time of about 10^{-11} sec.[15,16] It would seem that only those reactions between vanadium(IV) and manganese(III) which are diffusion controlled have no chance of proceeding by an inner-sphere mechanism.

The reaction between vanadium(IV) and the hexaaquomanganese(III) ion has recently been investigated.[17] A study of the reaction between CyDTA and EDTA complexes of manganese(III) and the oxy cation VO^{2+} would be of interest for several reasons. First of all, it seems likely that the reaction mechanism for the chelated manganese(III) complexes would be quite similar to that of the hexaaquomanganese(III), provided an inner-sphere pathway is available to both species. Second, if the mechanisms are very much alike, one should be able to make a direct comparison between the reaction of the six-coordinate hexaaquomanganese(III) complex and the presumably seven-coordinate chelated manganese(III) complexes.[18] Finally, the ambiguity[13] regarding the participation of Mn_{aq}^{3+} and $MnOH_{aq}^{2+}$ which exists for the oxidation of hydrazines,[19,20] the hydroxylamines,[20,21] and nitrous acid[21] does not exist for the CyDTA and EDTA complexes of manganese(III).

Experimental Section

Materials.—All chemicals used for preparation of compounds, analytic procedures, and kinetic studies were of reagent quality unless otherwise specified. The potassium salts of *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III) and ethylenedi-

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aminetetraacetatomanganate(III) were prepared as before.[18,22] Vanadyl sulfate was of purified grade obtained from the Fisher Scientific Co. Vanadyl sulfate solutions were standardized with standard potassium permanganate in dilute sulfuric acid. Titration was to the first permanent pink coloration of the solution. Ionic strength was maintained at 1.0 *M* with lithium perchlorate and pH was adjusted using a chloroacetate–chloroacetic acid buffer system. The pH was in general measured with a Beckman research pH meter equipped with a calomel electrode filled with 4 *M* sodium chloride before a kinetic experiment, with VO^{2+} missing, and after the reaction was completed and found to be invariant in the pH range studied. Water used for all experiments was distilled deionized water redistilled from an alkaline permanganate solution. Lithium perchlorate was prepared by neutralization of 70% perchloric acid with carbonate-free lithium hydroxide.

Stoichiometry.—The stoichiometry of the $Mn^{III}CyDTAH_2O^-$ and the $Mn^{III}EDTAH_2O^-$ ions reaction with VO^{2+} was determined spectrophotometrically at the appropriate wavelength maximum for each complex (510 nm for $Mn^{III}CyDTAH_2O^-$ and 497 nm for $Mn^{III}EDTAH_2O^-$). Excess manganese(III) complex was added to a known amount of VO^{2+}, and the absorbance was measured after the reaction was complete. After correction was made for the absorbance of V(V) (510 nm, 23 M^{-1} cm^{-1}; 497 nm, 20 M^{-1} cm^{-1}), these measurements gave a ratio of (manganese(III) consumed)/(vanadium(IV) consumed) = 1.0 ± 0.1 for both reactions.

Kinetics.—For all kinetic runs the cell was filled with a solution containing the manganese(III) complex, buffer, and $LiClO_4$ and was placed in the constant-temperature block of the Cary 14 spectrophotometer through which water from a thermostated water bath was being circulated. The temperature was monitored by thermometers both in the block and in the bath. The thermometers had been calibrated at the ice point. The VO^{2+} solution was taken from a bottle submerged in the constant-temperature bath by syringe which had also been temperature equilibrated and was immediately emptied into the cell. The decrease in manganese(III) concentration was followed with time at the appropriate wavelength. Reactant concentrations were approximately 10^{-4} *M*, and hydrogen ion concentration was varied 20-fold and 90-fold for $Mn^{III}EDTAH_2O^-$ and $Mn^{III}CyDTAH_2O^-$, respectively.

Results and Discussion

The overall stoichiometry for the reaction of either manganese(III) complex was found to be as given in eq 1, where $Y^{4-} = CyDTA^{4-}$ or $EDTA^{4-}$.

$$Mn^{III}YH_2O^- + VO^{2+} (+H_2O) = Mn^{II}YH_2O^{2-} + VO_2^+ (+2H^+) \quad (1)$$

Linear plots of log $(V - x)/(M - x)$ *vs.* time, where V is the initial concentration of vanadium(IV), M is the initial concentration of manganese(III) complex, and x is the amount of manganese(III) complex that had been consumed at time t,[23] were obtained for both manganese(III) complexes.

Linearity of such plots indicates that the reaction is second-order overall and first-order with respect to each reactant. The apparent rate constant was obtained from the slope of these plots using the relationship $k_{app} = 2.303(\text{slope})$.

The apparent rate constant was found to be a linear function of the inverse hydrogen ion concentration as indicated in Table I. Each of the values shown in Table I resulted from two or more individual runs. The standard deviation calculated on all multiple runs (70 runs, 39 degrees of freedom) was 0.12×10^2 M^{-1} sec^{-1}. The standard deviation for the runs shown in Table I was 0.10×10^2 M^{-1} sec^{-1}.

TABLE I

THE INCREASE OF THE APPARENT RATE CONSTANT WITH DECREASING HYDROGEN ION CONCENTRATION FOR THE REACTION BETWEEN VANADIUM(IV) AND THE MANGANESE(III) COMPLEXES OF CyDTA AND EDTA AT 7.0 ± 0.1° AND I = 1.0 *M*

$Mn^{III}CyDTAH_2O^-$			$Mn^{III}EDTAH_2O^-$		
pH	$10^{-1}[H^+]^{-1}$, M^{-1}	$10^{-2}k_{app}$, M^{-1} sec^{-1}	pH	$10^{-1}[H^+]^{-1}$, M^{-1}	$10^{-2}k_{app}$, M^{-1} sec^{-1}
1.90	7.94	1.24	1.50	3.16	1.90
2.10	12.6	1.31	7.94	7.94	2.48
2.52	33.2	2.48	2.10	12.6	2.55
2.84	69.2	4.20	2.30	20.0	3.09
2.94	87.0	5.20			

The form of the rate law was therefore the same for the CyDTA and EDTA complexes and may be represented by eq 2. The rate constants k_0 and k_1 were

$$\frac{-d[Mn^{III}YH_2O^-]}{dt} = \left[k_0 + \frac{k_1}{[H^+]}\right][Mn^{III}YH_2O^-][VO^{2+}] \quad (2)$$

found not to be affected by manganous ion or vanadium(V) being present initially in an experiment.

The rate law represented by eq 2 can be explained in terms of a mechanism involving path a

$$Mn^{III}YH_2O^- + VO^{2+} \rightleftharpoons MnYH_2OVO^+ \quad (\text{rapid}, K) \quad (3)$$

$$MnYH_2OVO^+ \longrightarrow \text{products} \quad (\text{slow}, k_0') \quad (4)$$

where $k_0 = Kk_0'$ and path b

$$VOH_2O^{2+} \rightleftharpoons VOOH^+ + H^+ \quad (\text{rapid}, K_h) \quad (5)$$

$$Mn^{III}YH_2O^- + VOOH^+ \rightleftharpoons MnYVOOH \quad (\text{rapid}, K_1) \quad (6)$$

$$MnYVOOH \longrightarrow \text{products} \quad (\text{slow}, k_1') \quad (7)$$

where $k_1 = K_1k_1'K_h$.

The presence of hydrolyzed and unhydrolyzed species of vanadium(IV) in the pH range studied, pH 1.5–3.0, readily accounts for the increase in k_{app} with decreasing $[H^+]$ and appears reasonable in light of the fact that a value of $K_h = 3.6 \times 10^{-6}$ at 25° and $I = 0.10$ *M* has been reported.[24] Minimal hydrolysis of VO^{2+} should give rise to linear plots of k_{app} *vs.* $[H^+]^{-1}$. Hydrolysis of $Mn^{III}CyDTAH_2O^-$ would not be expected to be as important as vanadium(IV) hydrolysis in view of the pK_a of 8.1.[25] The situation is not nearly as clean cut with the EDTA complex, where $pK_a = 5.5$,[22] and hydrolysis of $Mn^{III}EDTAH_2O^-$ may be as important as that of vanadium(IV) in this reaction.

Activation parameters for the reaction of $Mn^{III}CyDTAH_2O^-$ and VO^{2+} were evaluated using a linear least-squares data treatment with equal weighting of data points. Because of the limited range of temperature available, due to the speed of the reaction, the activation parameters for the reaction of $Mn^{III}EDTAH_2O^-$ are not reported. Values of the data used are given in Table II. Experimental error on these data was about ±10%. For the $Mn^{III}CyDTAH_2O^-$ complex the values found were $\Delta H_0^* = 13.1 \pm 1.1$ kcal mole^{-1}, $\Delta S_0^* = -3.4 \pm 3.8$ eu, $\Delta H_1^* = 11.3 \pm 1.6$ kcal mole^{-1}, and $\Delta S_1^* = -20.0 \pm 6.0$ eu.

The fact that values for k_1 given in Table II for the reaction with $Mn^{III}EDTAH_2O^-$ are roughly twice

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TABLE II

RATE DATA OBTAINED AS A FUNCTION OF TEMPERATURE FOR THE REACTION OF VANADIUM(IV) WITH THE MANGANESE(III) COMPLEXES OF CyDTA AND EDTA

$Mn^{III}CyDTAH_2O^-$			$Mn^{III}EDTAH_2O^-$		
$10^{-2}k_0$, M^{-1} sec^{-1}	k_1, sec^{-1}	Temp, °C	$10^{-2}k_0$, M^{-1} sec^{-1}	k_1, sec^{-1}	Temp, °C
1.25	0.74	13.9	1.73	0.71	7.0
0.87	0.66	11.2	1.30	0.68	4.3
0.65	0.53	7.0	0.78	0.47	1.7
0.50	0.37	3.4			
0.40	0.29	1.7			

those for $Mn^{III}CyDTAH_2O^-$ under identical conditions may be indicative of two parallel paths (*i.e.*, a reaction proceeding either through a hydrolyzed vanadium or a hydrolyzed manganese). An alternate possibility is the steric effect of the bulky cyclohexane ring to hamper intermediate formation compared to the ethylene backbone in EDTA.

The ratio of the rate constants for the hydroxo and aquo pathways, k_{OH}/k_{H_2O}, at 1.7° and pH 2.10 was $\sim$72 for the CyDTA complex and $\sim$60 for the EDTA complex. These values are in accordance with the general observation of greater reactivity, 10^2 to 10^4, of a hydroxy-bridged path over a water-bridged path for inner-sphere electron-transfer reactions.[7,26-28] Such an enhancement in rate does not seem to occur for outer-sphere reactions. A comparison of reduction reactions of VO^{2+} with Cu^+, V^{2+}, Cr^{2+}, and Fe^{2+} illustrates the importance of dinuclear hydroxy-bridged species as intermediates.[29]

Vanadium(IV) is sufficiently labile to react by an inner-sphere mechanism[15,16] in agreement with oxidation–reduction studies.

All oxidation–reduction reaction rates of manganese(III) studied to date are within the estimated time scale for the rate of water exchange. Davies has suggested that the rate of water loss is rate determining even for the fastest reactions that have been observed.[9] In view of the large discrimination between hydroxide and water for the reactions studied, we propose that both $Mn^{III}CyDTAH_2O^-$ and $Mn^{III}EDTAH_2O^-$ are reacting by an inner-sphere mechanism. The situation for the reaction between hexaaquomanganese(III) and VO^{2+}, which shows only a slightly favored hydroxide pathway,[12] is still uncertain.

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Structure and Reactivity in Octahedral Complexes. XIII. Trans-to-Cis Isomerizations and Hydrolysis Reactions of Some Chromium(III) Anionic Complexes[1]

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The kinetics of isomerization and hydrolysis reactions of some anionic complexes of chromium(III) have been investigated. The results obtained for the trans-to-cis isomerizations of $Cr(ox)_2(OH_2)_2^-$, $Cr(ox)_2(OH_2)OH^{2-}$, and $Cr(ox)_2(OH)_2^{3-}$ are interpreted in terms of one-ended dissociation of the oxalato ligand. In contrast, the similar malonato series reveals a breakdown in the kinetic pattern, which suggests a change in mechanism for the aquohydroxo and diaquo forms involving the primary dissociation of a water molecule. The hydrolysis of *trans*-$Cr(ox)_2(OAc)_2^{3-}$ occurs at a rate independent of pH in the range pH 2–11, with retention of geometrical configuration. The pH ranges related to the hydrolysis of the aquoacetato or the hydroxoacetato complexes are below 6.8 and above 10.8, respectively; the hydrolysis of the former is acid catalyzed. The final product of all these reactions is *cis*-$Cr(ox)_2(OH_2)_2^-$ or its conjugate bases. The mechanism of the hydrolysis is discussed in the light of the isomerization behavior of the related species above, of the activation parameters, and, in part, of the stereochemical results. A common feature is the tendency to a dissociation mechanism as a function of the overall negative charge of the complex.

Introduction

Most studies on the reactivity of octahedral complexes concern cationic species, especially those involving Co(III) as the transition metal. Much less information is available on anionic complexes.

In hydrolysis reactions cationic Co(III) complexes display a dissociative mechanism. In acid solution aquation takes place by a first-order process.[2] Although base hydrolysis of such complexes as $Co(NH_3)_5Cl^{2+}$ shows second-order kinetics, provided that acidic protons in the ligands are available, the mechanism still involves a dissociative path *via* the conjugate base.[2] A clear proof of a dissociative mechanism with this general type of complex was obtained when acidic protons were absent in the substrate structure; thus with $Co(dipy)_2(OAc)_2^+$, first-order kinetics were observed.[3] However, the existence of an associative mechanism is also well-established, particularly with the octahedral complexes of the second- and third-row metals, such as Rh(III) and Ir(III).[4]

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