Table II. Variation of the Half-Wave Potential of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ in Acidic Melt Compositions at 40 °C^a

melt compn	pCl$^-$	$E_{1/2}$,^{b} V
1.05:1	11.2	0.352
1.1:1	11.6	0.374
1.25:1	12.2	0.411
1.5:1	12.9	0.433

^{a} Least-squares gradient 0.054 V/pCl$^-$; standard deviation 3 mV.
^{b} Vs. Al (2:1) reference.

ca. $(2.3RT/F)$ V per pCl$^-$ unit occurred (Table II). This value supports the loss of a single anionic ligand in the electron-transfer process, possibly a complexed heptachloroaluminate ion. One process (of many possible) consistent with this observed behavior is depicted in eq 4. The large positive shift of the half-wave potential in going from the 0.8:1 to the 2:1 melt, $\Delta E° \approx 1.32$ V, reveals that it is considerably easier to reduce the Ti(IV) complex in acidic melts. The polarizability of the bonds between the titanium and chloride or other anionic groups may be the most important factor affecting these standard reduction potentials, especially in the absence of molecular solvent capable of solvation. Nevertheless, it is possible too that the Lewis acid species may interact with the
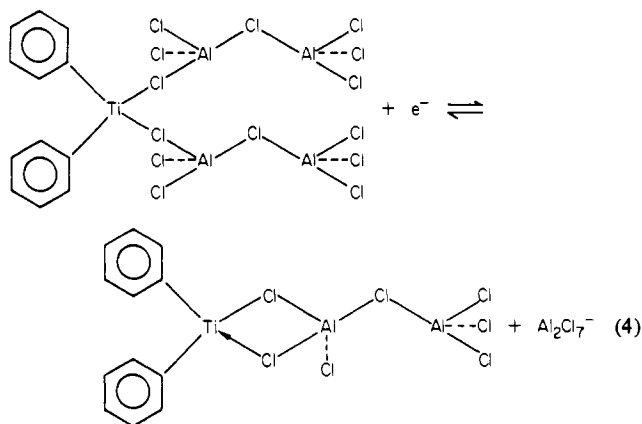
cyclopentadienyl π system such that the metal Ti(IV) center is less electronegative.

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Kinetics and Mechanisms of the Oxidation of Iodide by Copper(III)–Peptide Complexes

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Copper(III)–deprotonated peptide complexes react stoichiometrically with I$^-$ to give Cu(II) and I$_3^-$ via two reaction pathways. The rate of loss of Cu(III) equals $(2k_A[I^-] + 2k_B[I^-]^2)[Cu(III)]$. Linear free-energy relationships are observed for k_A and k_B with the variation of the reduction potentials for the Cu(III)–Cu(II) complexes from 0.62 to 0.81 V. Path A, which is first order in [I$^-$], has a slope of 0.56 for log k_A vs. $E_{III,II}/0.059$, suggesting that the rate is limited by the rate of electron transfer to form I·. Path B, which is second order in [I$^-$], has a corresponding slope of 0.95, indicating that the transition state for this pathway occurs after the electron transfer has taken place. Kinetic considerations indicate that the reduction potential for the I·/I$^-$ couple must be less than or equal to 1.2 V in 1 M NaClO$_4$.

Introduction

Copper(III)–deprotonated peptide complexes can easily be formed in aqueous solution by the chemical or electrochemical oxidation of the corresponding copper(II) complexes.[1-4] Many of the trivalent copper complexes are moderately stable in neutral solution when protected from light, and some are very stable.[5] In aqueous solution these complexes are mild to strong one-electron oxidizing agents. The copper(III, II) reduction potentials, $E_{III,II}$, are sensitive to the nature of the peptide ligand and span the range from 0.45 to 1.0 V (vs. NHE).[1] As would be expected on the basis of these potentials and that

for iodine ($E_{I_2/I^-}° = 0.62$ V), many of the copper(III)–peptide complexes are capable of oxidizing iodide to iodine and triiodide. Indeed, the oxidation of iodide has been used as one of several methods for the detection and characterization of chemically or electrochemically generated copper(III)–peptide complexes.[6] The kinetics of the complementary redox reactions between the copper(III)–peptide complexes Cu^{III}(H$_{-n}$L) and one-electron reducing agents such as IrCl$_6^{3-}$,[7] Co(phen)$_3^{2+}$,[8] and Cu(dmp)$_2^+$[9] have been investigated and have been shown to proceed both rapidly and quantitatively.

The oxidation of iodide ion to iodine involves the net transfer of two electrons. Copper(III)–deprotonated peptide complexes, Cu^{III}(H$_{-n}$L), oxidize iodide ion according to eq 1. In the present work the kinetics and mechanisms of the noncom-

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$$2Cu^{III}(H_{-n}L) + 2I^- \rightarrow 2Cu^{II}(H_{-n}L) + I_2$$

$$I_2 + I^- \rightleftharpoons I_3^- \tag{1}$$
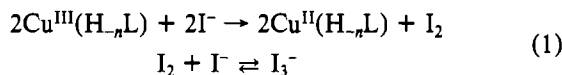
plementary redox reaction 1 are reported for six copper-(III)–peptide complexes $Cu^{III}(H_{-n}L)$, where n indicates the number of deprotonated peptide nitrogens coordinated to the copper center. The reactions proceed by two reaction paths, A and B, which conform to the rate expression given in eq 2.

$$-\frac{d}{dt}[Cu^{III}(H_{-n}L)] = 2(k_A[I^-] + k_B[I^-]^2)[Cu^{III}(H_{-n}L)] \tag{2}$$

At low iodide concentrations the rate of reaction 1 is dominated by reaction path A, which exhibits a first-order iodide dependence. Reaction path B exhibits a second-order iodide dependence and is the predominant pathway at high iodide concentrations.

Noncomplementary reactions such as eq 1 can involve either one-electron or two-electron transfer mechanisms. A pathway with a one-electron transfer reaction between Cu(III) and I⁻ generates Cu(II) and I· (or I_2^-), whereas, a two-electron pathway generates Cu(I) and I⁺ (or IOH_2^+, HOI, I_2). Both reactions are thermodynamically very unfavorable for the copper–peptide complexes, and neither appears to be a very attractive path. Our results indicate that the reactions proceed by the one-electron path with the generation of I· or, at higher I⁻ concentrations, the generation of I_2^-.

Experimental Section

The chromatographically pure peptides tri-L-alanine (A_3), tri-L-leucine (L_3), tetraglycinamide (G_4a), and tetraglycine (G_4) were obtained from Biosynthetika and Cyclo Chemical Co. Tri-α-aminoisobutyric acid (Aib_3) and N,N'-diglycyl-1,2-diaminoethane (DGEN) were synthesized as previously described.[5,10] A stock $Cu(ClO_4)_2$ solution was prepared from the twice recrystallized salt and was standardized by EDTA titration with use of a murexide indicator. All other chemicals were of analytical reagent grade.

Copper(II) complexes of the peptides were prepared in solution by using a 5–10% excess of the peptide. These solutions were adjusted to pH 10 in order to ensure the complete formation of the fully deprotonated complexes. Solutions of the corresponding copper-(III)–peptide complexes were then obtained from the copper(II) complexes by electrochemical oxidation by using a flow system that included a graphite-powder working electrode.[11] The resulting solutions were diluted to approximately 4×10^{-5} M and were deoxygenated by vigorous bubbling with Ar(g). The NaI solutions, which were freshly prepared prior to each experiment, were also deoxygenated and contained 2×10^{-3} M CyDTA (*trans*-1,2-diaminocyclohexane-tetraacetic acid) to inhibit trace metal catalysis of the autoxidation of iodide. In the final reaction mixtures Cu^{2+}(aq) is present as a result of some inefficiency in the electrochemical oxidation used to prepare the $Cu^{III}(H_{-n}L)$ reactants and because of the fact that Cu^{2+}(aq) is one of the reaction products resulting from the dissociation of the $Cu^{II}(H_{-n}L)$ species. CyDTA also prevented this Cu^{2+}(aq) from reacting with iodide.

Aminocarboxylates such as EDTA and CyDTA are known to react with iodine and triiodide.[12,13] This was observed as a slow reaction after the copper(III) oxidation of I⁻ to I_2 and I_3^-. The bleaching of the I_3^- product was, however, very slow at the CyDTA levels used and did not interfere with the reaction of interest.

The kinetics of the copper(III)–peptide oxidations of iodide were spectrophotometrically monitored by observing the appearance of I_3^- at 353 nm ($\epsilon = 2.64 \times 10^4$ M⁻¹ cm⁻¹),[14] where the molar absorptivity of the copper(III)–peptide complexes is less than 6×10^3 M⁻¹ cm⁻¹, by using a Durrum stopped-flow spectrometer with a 2.0-cm cell thermostated at 25.0 °C. In several cases, the reactions were also monitored by following the disappearance of the $Cu^{III}(H_{-n}L)$ species

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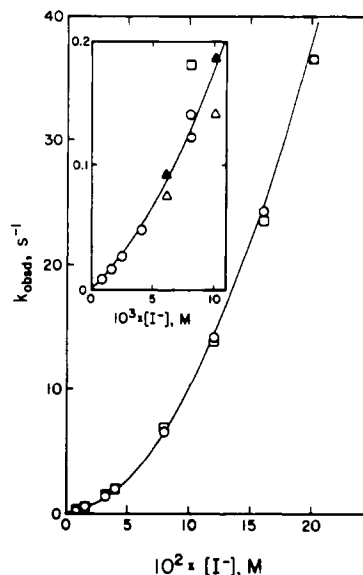(14) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1842.

Figure 1. Variation of the observed first-order rate constant, k_{obsd}, with the iodide concentration for the reaction of $[Cu^{III}(H_{-2}DGEN)]^+$ with iodide at $-\log [H^+] = 4.97$ (O), 6.79 (□), and 6.04 (△) and $-\log [D^+] = 6.01$ (▲).

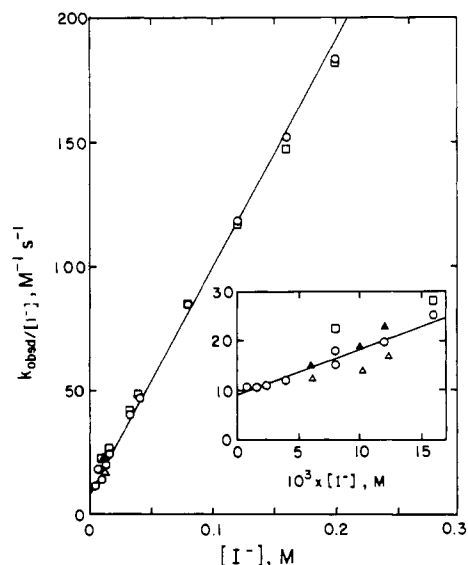**Figure 2.** Resolution of the rate constants k_A and k_B for the reaction of $[Cu^{III}(H_{-2}DGEN)]^+$ with iodide at $-\log [H^+] = 4.97$ (O), 6.79 (□), and 6.04 (△) and $-\log [D^+] = 6.01$ (▲) (intercept = $2k_A$, slope = $2k_B$).

$[Cu^{III}(H_{-2}DGEN)]^+$ ($\epsilon = 5.5 \times 10^3$ M⁻¹ cm⁻¹ at 390 nm) or $[Cu^{III}(H_{-2}Aib_3)]$ ($\epsilon = 5.3 \times 10^3$ M⁻¹ cm⁻¹ at 395 nm). The results obtained were independent of the monitoring wavelength. The absorbance data were collected and analyzed by using an on-line digital computer.[15] All reactions were run under irreversible, pseudo-first-order conditions ($[I^-]_{initial} \geq 25[Cu^{III}(H_{-n}L)]_{initial}$) at an ionic strength of 1.0 M ($NaClO_4 + NaI$). The hydrogen ion concentrations were determined from the measured pH after calibration of the pH meter with standard acid solutions of ionic strength 1.0 M ($NaClO_4$). The deuterium ion concentration was obtained by adding 0.40 to the $-\log [H^+]$ value. The reactions were observed to be pseudo first order for more than 4 half-lives and conformed to the rate expressions $-(d/dt)[Cu^{III}(H_{-n}L)] = k_{obsd}[Cu^{III}(H_{-n}L)]$. Each observed rate constant, k_{obsd}, is the mean of at least four kinetic runs. The relative standard deviations varied from 1% to 5%.

The stoichiometry of the reactions were spectrophotometrically confirmed to be that shown in eq 1. This stoichiometry was maintained

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Table I. Observed Pseudo-First-Order Rate Constants for the Oxidation of Iodide by Copper(III)–Deprotonated Peptide Complexes[a,b]

$-\log [H^+]$	$[I^-]$, M	k_{obsd}, s^{-1}	$-\log [H^+]$	$[I^-]$, M	k_{obsd}, s^{-1}
A. $[Cu^{III}(H_{-2}DGEN)]^+$					
4.98^d	8.0×10^{-4}	8.30×10^{-3}	6.04^c	6.15×10^{-3}	7.5×10^{-2}
4.96^d	1.6×10^{-3}	1.63×10^{-2}	6.80^c	8.0×10^{-3}	0.18
4.98^d	2.4×10^{-3}	2.63×10^{-2}	6.04^c	1.0×10^{-2}	0.14
4.96^d	4.0×10^{-3}	4.7×10^{-2}	6.04^c	1.23×10^{-2}	0.207
4.97^d	8.0×10^{-3}	0.12	6.80^c	1.6×10^{-2}	0.45
4.96	8.0×10^{-3}	0.14	6.80^c	3.2×10^{-2}	1.37
4.97^d	1.2×10^{-2}	0.236	6.80^c	4.0×10^{-2}	1.93
4.96	1.6×10^{-2}	0.40	6.79^c	8.0×10^{-2}	6.8
4.96	3.2×10^{-2}	1.28	6.79^c	0.12	14.0
4.96	4.0×10^{-2}	1.88	6.78^c	0.16	23.5
4.97	8.0×10^{-2}	6.7	6.78^c	0.20	36.4
4.97	0.12	14.2	6.01^h	6.05×10^{-3}	9.2×10^{-2}
4.95	0.16	24.3	6.01^h	1.00×10^{-2}	0.187
4.95	0.20	36.5	6.01^h	1.21×10^{-2}	0.27
B. $Cu^{III}(H_{-2}A_3)$					
5.12	1.2×10^{-2}	0.484	5.16^e	0.14	53
5.16	2.0×10^{-2}	1.17	5.13^e	0.16	58
5.15	4.0×10^{-2}	4.07	5.14^e	0.18	78
5.14	6.0×10^{-2}	9.4	5.14^e	0.20	94
5.14	0.10	27.0			
C. $Cu^{III}(H_{-2}L_3)$					
5.15	1.2×10^{-2}	0.228	5.16	0.10	11.5
5.18	2.0×10^{-2}	0.54	5.15	0.14	25.1
5.15	4.0×10^{-2}	1.94	5.15	0.18	38.2
5.16	6.0×10^{-2}	4.4	5.14	0.20	44.2
D. $Cu^{III}(H_{-3}G_4a)$					
5.11	2.0×10^{-2}	9.0×10^{-3}	5.14	0.20	0.598
5.13	4.0×10^{-2}	3.4×10^{-2}	5.15	0.28	1.05
5.12	8.0×10^{-2}	0.128	5.14	0.36	1.76
5.12	0.12	0.259	5.17	0.40	2.16
E. $Cu^{III}(H_{-2}Aib_3)^f$					
5.14	4.0×10^{-2}	1.46×10^{-2}	6.65^c	3.2×10^{-2}	9.2×10^{-3}
5.14	8.0×10^{-2}	5.55×10^{-2}	6.64^c	4.0×10^{-2}	1.43×10^{-2}
5.17	0.12	0.120	6.65^c	8.0×10^{-2}	5.04×10^{-2}
5.17	0.20	0.318	6.67^c	0.12	0.108
5.12	0.24	0.46	6.64^c	0.16	0.197
5.15^c	0.24	0.462	6.67^c	0.20	0.293
4.60	0.24	0.45			
5.66	0.24	0.457			
5.14	0.28	0.63			
5.13	0.36	1.01			
5.14	0.40	1.25			
F. $Cu^{III}(H_{-3}G_4)^-$					
6.83^c	4.0×10^{-2}	1.35×10^{-2}	5.73	0.28	0.308
6.85^c	8.0×10^{-2}	3.54×10^{-2}	5.75	0.32	0.368
6.85^c	0.16	0.109	5.76	0.36	0.452
6.86^c	0.24	0.219	5.74	0.40	0.556
6.85^c	0.32	0.365	4.65	4.0×10^{-2}	5.2×10^{-2}
6.83^c	0.40	0.541	4.64	0.14	0.208
5.77	4.0×10^{-2}	1.41×10^{-2}	4.63	0.20	0.305
5.76	0.14	9.57×10^{-2}	4.61	0.24	0.385
5.73	0.16	0.114	4.60	0.32	0.554
5.73	0.20	0.117	4.60	0.36	0.662
5.74	0.24	0.227	4.60	0.40	0.75

^{a} $[Cu^{III}]_T = 2 \times 10^{-5}$ M, $[CyDTA]_T = 1.0 \times 10^{-3}$ M; $\mu = 1.0$ (NaClO$_4$ + NaI); $T = 25.0$ °C. ^{b} [Acetate]$_T = 0.01$ M. ^{c} [PIPES]$_T = 0.01$ M.
^{d} $[Cu^{III}]_T = 3 \times 10^{-5}$ M. ^{e} $[Cu^{III}]_T = 4 \times 10^{-5}$ M. ^{f} $[Cu^{III}]_T = 1 \times 10^{-5}$. ^{g} [CyDTA]$_T = 2 \times 10^{-3}$ M. ^{h} $-\log$ [D$^+$].

at both high and low iodide concentrations.

Results

In all cases, the Cu^{III}(H$_{-n}$L) complex was the limiting reagent. Excellent pseudo-first-order plots of the absorbance data were obtained, indicating that the reactions were first order with respect to the [Cu^{III}(H$_{-n}$L)] concentration. The reaction order with respect to iodide was determined by varying the iodide concentration (Table I and Figure 1). The observed rate constant, k_{obsd}, exhibits both a first-order and a second-order dependence on [I$^-$] (Figure 2). The first-order [I$^-$] dependence dominates the observed reaction rates at low iodide

concentrations but decreases in importance as the iodide concentration increases (Figure 1), whereas the relative contribution of the second-order iodide term steadily increases. These variations are indicative of a reaction that proceeds by two different reaction pathways, one (path A) which exhibits a first-order [I$^-$] dependence and a second (path B) which exhibits an [I$^-$]^2 dependence. Hence, k_{obsd} is given by the expression $k_{obsd} = 2(k_A[I^-] + k_B[I^-]^2)$, where the factor of 2 arises as a consequence of the overall 2:1 ([Cu(III)]:[I$_2$]) reaction stoichiometry.

Copper(III)–deprotonated peptide complexes, like their copper(II) and nickel(II) counterparts, are capable of forming

Table II. pH Dependent Rate Constants for the Reaction of $Cu^{III}(H_{-3}G_4)^-$ with Iodide[a,b]

| $-\log [H^+]$	$k_A{}^0$, M^{-1} s^{-1}	$k_B{}^0$, M^{-2} s^{-1}
6.84	0.114 ± 0.005	1.42 ± 0.02
5.74	0.15 ± 0.01	1.35 ± 0.05
4.62	0.61 ± 0.01	0.83 ± 0.04

[a] $\mu = 1.0$ ($NaClO_4$); $T = 25.0$ °C. [b] $k_{obsd} = 2(k_A[I^-] + k_B[I^-]^2)$.

outside protonated species,[7,8,16-19] in which the peptide oxygen is protonated and the metal bond to the deprotonated peptide nitrogen remains intact. This outside protonation is rapid and results in equilibrations as shown in eq 3. For the tripeptide

$$Cu^{III}(H_{-3}G_4)^- + H^+ \xrightleftharpoons{K_{1H}} [Cu^{III}(H_{-3}G_4) \cdot H] \qquad (3)$$
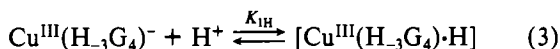
and peptide amide complexes $\log K_{1H}$ values are approximately 2,[17-19] while for $[Cu^{III}(H_{-3}G_4)]^-$, which can form an intramolecular hydrogen bond, the $\log K_{1H}$ value is 4.3.[8,16] The $[Cu^{III}(H_{-3}G_4)]^-$ and $[Cu^{III}(H_{-3}G_4) \cdot H]$ species are both present in appreciable concentrations at pH values of 4–7, and both are capable of oxidizing the iodide ion. As a consequence the observed pseudo-first-order rate constant, k_{obsd}, is pH dependent for the reaction of $Cu^{III}(H_{-3}G_4)^-$ with iodide (Table IF). However, in the same pH region, k_{obsd} for the reaction of the tripeptide complexes $[Cu^{III}(H_{-2}Aib_3)]$ and $[Cu^{III}-(H_{-2}DGEN)]^+$ (structures I and II) with iodide are pH in-

I. $[Cu^{III}(H_{-2}DGEN)]^+$

II. $Cu^{III}(H_{-2}Aib_3)$
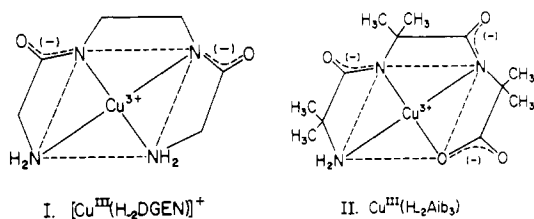
dependent (Table IA,E). Similar pH effects have previously been observed in the copper(III)–peptide oxidations of Co^{II}-$(phen)_3{}^{2+}$,[8] $Cu^I(dmp)_2{}^+$,[9] and $IrCl_6{}^{3-}$.[7]

The pH-dependent rate constants $k_A{}^0$ and $k_B{}^0$ that were obtained for the $Cu^{III}(H_{-3}G_4)^-$–iodide reaction are given in Table II. The rate constants k_A and k_B, which refer specifically to the $Cu^{III}(H_{-3}G_4)^-$ species, were resolved by using eq 4 for k_A. The rate constant k_B was resolved in a completely

$$k_A{}^0 = (k_A + k_A{}^H k_{1H}[H^+])/(1 + K_{1H}[H^+]) \qquad (4)$$

analogous manner. Below $-\log [H^+] = 4$ the kinetics of the copper(III) tetraglycine oxidation of iodide become more complex, and simple first-order and second-order iodide dependences (eq 2) are no longer observed. Consequently, while the rate constants k_A and k_B can be reliably evaluated by an analysis based on eq 4, the rate constants $k_A{}^H$ and $k_B{}^H$, which refer to the reactions of the outside protonated species $[Cu^{III}(H_{-3}G_4)H]$, are less accurately evaluated. In spite of this difficulty, the data in Table II clearly show that the rate constant for reaction by path A, $k_A{}^0$, increases as the acidity increases, while the opposite trend is observed for reaction via path B. Such a dichotomy has not been previously observed within one system. The pH dependences for the redox reaction of $Co(phen)_3{}^{2+}$ with the copper(III) complexes of tetraglycine and tetra-L-alanine[8] do exhibit opposite pH trends, although they are much smaller than in the present case. The relative reactivities of a $Cu^{III}(H_{-n}L)$ complex and its outside protonated form are determined by a balancing of thermodynamic and
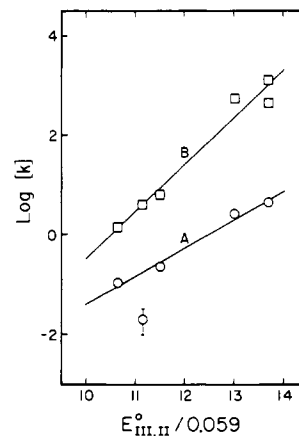

Figure 3. Correlation between the rate constants for the two reaction pathways, A and B, and the copper(III)–copper(II) reduction potentials, $E_{III/II}$. $k_A = K_0 k_1$ and $k_B = K_0 k_2$; see eq 5–7. The deviation from line A occurs for $Cu^{III}(H_{-2}Aib_3)$.
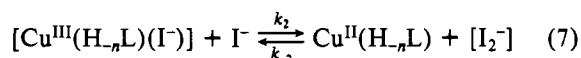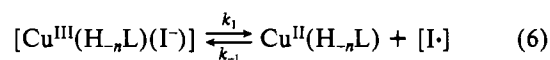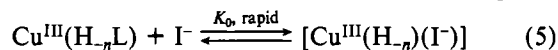
electrostatic effects.[8] The effect of protonation on the rate of reaction path A is in the direction expected on the basis of electrostatics. For path B the opposite trend is observed. The reason for this is not presently clear.

At $-\log [H^+] = 1.3$ two distinct reactions are observed for the reaction of copper(III) tetraglycine with iodide. In acid media the decomposition of $Cu^{III}(H_{-3}G_4)^-$ also exhibits two distinct first-order reactions. These acid decomposition reactions have been interpreted as sequential reaction steps.[16] A doubly outside protonated $[Cu^{III}(H_{-3}G_4) \cdot 2H]^+$ species forms very rapidly and rearranges with a rate constant of 0.3 s^{-1} to give a rearranged form, $[Cu^{III}(H_{-2}G_4) \cdot H]^+$ with one less nitrogen coordinated to Cu(III). This is followed by a slower reaction that corresponds to a redox decomposition process in which Cu(II) and oxidized peptide are formed.[16] Both the $[Cu^{III}(H_{-3}G_4) \cdot 2H]^+$ species and its rearranged form are capable of oxidizing iodide, and therefore two distinct reactions are observed for the oxidation of iodide by copper(III) tetraglycine in acid solution.

The resolved rate constants, k_A and k_B, for all of the $Cu^{III}(H_{-n}L)$ complexes investigated are given in Table III. Both k_A and k_B become larger as the copper(III, II) reduction potential, $E_{III,II}$, and hence the equilibrium constant for the overall reaction (eq 1), increases. The free-energy rate constant correlations for the two reaction paths, which are illustrated in Figure 3, are $\log k_A = (-7.0 \pm 0.4) + (0.56 \pm 0.03)(E_{III,II}/0.059)$ and $\log k_B = (-10 \pm 1) + (0.95 \pm 0.09)(E_{III,II}/0.059)$. The only deviation from these correlations occurs for k_A with the $Cu^{III}(H_{-2}Aib_3)$ complex (Figure 3, structure II). The reactions of $Cu^{III}(H_{-2}Aib_3)$ with $Cu^I(2,9-Me_2-1,10-phen)_2{}^+$ and $Co^{II}(phen)_3{}^{2+}$ are also slower than expected,[20] while those with $IrCl_6{}^{-}$[21] and other $Cu^{II}(H_{-2}L)^{20}$ complexes do not deviate from the appropriate free-energy correlations. Steric factors may be the cause of some of these deviations.

Discussion

Proposed Mechanism. The mechanism proposed for the copper(III)–peptide oxidations of iodide is given in eq 5–7.

$$Cu^{III}(H_{-n}L) + I^- \xrightleftharpoons{K_0, rapid} [Cu^{III}(H_{-n})(I^-)] \qquad (5)$$

$$[Cu^{III}(H_{-n}L)(I^-)] \xrightleftharpoons[k_{-1}]{k_1} Cu^{II}(H_{-n}L) + [I \cdot] \qquad (6)$$

$$[Cu^{III}(H_{-n}L)(I^-)] + I^- \xrightleftharpoons[k_{-2}]{k_2} Cu^{II}(H_{-n}L) + [I_2^-] \qquad (7)$$

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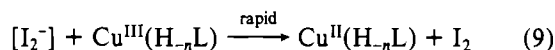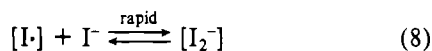(18) Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 497.
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(The overall charge, which depends on the identity of the ligand, L, and the number, n, of deprotonated peptide nitrogens, is omitted.) The radical products of reactions 6 and 7 rapidly react by eq 8–10 to produce the final products of the

$$[I \cdot] + I^- \underset{\text{rapid}}{\overset{}{\rightleftharpoons}} [I_2^-] \qquad (8)$$

$$[I_2^-] + Cu^{III}(H_{-n}L) \xrightarrow{\text{rapid}} Cu^{II}(H_{-n}L) + I_2 \qquad (9)$$

$$I_2 + I^- \underset{\text{rapid}}{\overset{}{\rightleftharpoons}} I_3^- \qquad (10)$$

overall reaction (eq 1). In terms of this mechanism, the rate constants for the two reaction pathways, A and B, are $k_A = K_0 k_1$ and $k_B = K_0 k_2$.

The [Cu^{III}(H$_{-n}$L)(I$^-$)] complex produced in eq 5 is present as a steady-state species rather than a transient intermediate. The initial absorbance obtained by extrapolating the absorbance–time traces to zero time and the absorbance expected from simple mixing of the reactants were found to be in agreement. If a transient intermediate was being formed in appreciable concentrations, such agreement would not be anticipated. In addition, the copper(III)–deprotonated peptide complexes, which are low-spin d^8, square-planar complexes,[1] do not readily add additional ligands. In fact, in aqueous solution not even the solvent ligates the axial coordination sites of the square-planar Cu^{III}(H$_{-n}$L) complexes.[22] Hence, the equilibrium constant K_0 (eq 5) is expected to be relatively small. On the basis of the observation that the [I$^-$]^2 dependence of k_{obsd} is maintained even at iodide concentrations of 0.2–0.4 M, K_0 must be less than 1 M^{-1}.

The copper(III) complexes under consideration behave as net one-electron oxidizing agents, while iodide undergoes a net two-electron oxidation to iodine (eq 1). The rate-determining reaction steps for the oxidation of iodide by metal and nonmetal oxidants have been proposed to occur via both one-electron[23-25] and two-electron transfers.[26,27] For noncomplementary redox reactions such as reaction 1 both one-electron and two-electron transfers must be considered as possible elementary steps in the reaction mechanism. We have considered an extensive set of two-electron reaction mechanisms as possible alternatives to the one-electron transfer mechanism proposed in eq 5–7. All of the conceivable two-electron mechanisms, which involved the initial oxidation of I$^-$ to I$_2$, H$_2$OI$^+$, HOI, or OI$^-$ and the reduction of the Cu^{III}(H$_{-n}$L) complexes to various copper(I) species, proved to be unable to account for the observed kinetic results. These mechanisms fit the kinetic data only if the copper(II, I) reduction potential, $E_{II,I}$, is more positive than +0.1 V. For a wide range of nitrogen donor chelate and macrocyclic complexes of copper(II), $E_{II,I}$ is known to vary from −0.16 to −0.64 V (vs. NHE).[28] Also, the two-electron transfer mechanisms that involved the formation of HOI or OI$^-$ and various protonated copper(I)

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(25) (a) Adedinsewo, C. O.; Adegite, A. *Inorg. Chem.* **1979**, *18*, 3597. (b) Ige, J.; Ojo, J. F.; Obubuyide, O. *Can. J. Chem.* **1979**, *57*, 2065. (c) Kimura, M.; Wada, G. *Inorg. Chem.* **1978**, *17*, 2239.
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Table III. Resolved Rate Constants for the Oxidation of Iodide by Copper(III)–Deprotonated Peptide Complexes[a]

complex	$E_{III,II}/$ 0.059	k_A, M^{-1} s^{-1} [b]	k_B, M^{-2} s^{-1} [b]
Cu^{III}(H$_{-2}$A$_3$)	13.69	4.5 ± 0.4	(1.28 ± 0.01) × 10^3
Cu^{III}(H$_{-2}$DGEN)$^+$	13.69	4.50 ± 0.02	(4.54 ± 0.02) × 10^2
Cu^{III}(H$_{-2}$L$_3$)	13.02	2.6 ± 0.2	(5.54 ± 0.04) × 10^2
Cu^{III}(H$_{-3}$G$_4$a)	11.49	0.23 ± 0.01	6.25 ± 0.05
Cu^{III}(H$_{-2}$Aib$_3$)	11.16	(2 ± 1) × 10^{-2}	3.86 ± 0.05
Cu^{III}(H$_{-3}$G$_4$)$^-$	10.65	0.10 ± 0.01	1.4 ± 0.1

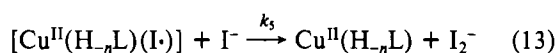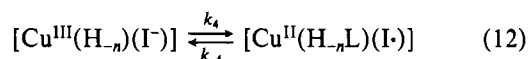[a] $\mu = 1.0$ (NaClO$_4$); $T = 25.0$ °C. [b] Error limit is 1 σ. $k_A = K_0 k_1$ and $k_B = K_0 k_2$; see eq 5–7.

Table IV. Reduction Potentials for Cu(III)–Deprotonated Peptide and Iodide Couples in Aqueous Solution

half-reaction	$E°$, V (vs. NHE)
Cu^{III}(H$_{-2}$DGEN)$^+$ + e$^-$ = Cu^{II}(H$_{-2}$DGEN)	0.81
Cu^{III}(H$_{-2}$A$_3$) + e$^-$ = Cu^{II}(H$_{-2}$A$_3$)$^-$	0.81[a]
Cu^{III}(H$_{-2}$L$_3$) + e$^-$ = Cu^{II}(H$_{-2}$L$_3$)$^-$	0.77[a]
Cu^{III}(H$_{-3}$G$_4$a) + e$^-$ = Cu^{II}(H$_{-3}$G$_4$a)$^-$	0.68[a]
Cu^{III}(H$_{-2}$Aib$_3$) + e$^-$ = Cu^{II}(H$_{-2}$Aib$_3$)$^-$	0.66[b]
Cu^{III}(H$_{-3}$G$_4$)$^-$ + e$^-$ = Cu^{II}(H$_{-3}$G$_4$)$^{2-}$	0.63[a]
I$_2$(aq) + 2e$^-$ = 2I$^-$	0.6197[c]
I$_3^-$ + 2e$^-$ = 3I$^-$	0.534[c]
HOI + 2e$^-$ + H$^+$ = I$^-$	0.99[c]
OI$^-$ + 2e$^-$ + H$_2$O = I$^-$ + 2OH$^-$	0.49[c]
H$_2$OI$^+$ + 2e$^-$ = I$^-$	0.94[d]
I$_2$(aq) + e$^-$ = I$_2^-$	⩾0.32[e]
I$_2^-$(aq) + e$^-$ = 2I$^-$	⩽0.9[f]
I$\cdot$(aq) + e$^-$ = I$^-$	⩽1.2[g]

[a] Reference 1. [b] Reference 5. [c] Latimer, W. M. "Oxidation Potentials", 2nd ed; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 64. [d] Calculated by using K(HOI + H$_3$O$^+$ $\rightleftharpoons$ H$_2$OI$^+$) = 35 M^{-1}: Bell, R. P.; Gelles, E. *J. Chem. Soc.* **1951**, 2734. [e] Calculated from E_{I_2/I^-} and $E_{I_2^-/I^-}$. [f] Calculated from $E_{I\cdot/I^-}$ by using K(I$\cdot$ + I$^-$ $\rightleftharpoons$ I$_2^-$) = 1.1 × 10^5 M^{-1}: Baxendale, J. H.; Bevan, P. L. T.; Scott, D. A. *Trans. Faraday Soc.* **1968**, *64*, 2389. [g] Upper limit based on kinetic data. See text.

species would be expected to exhibit solvent isotope effects. No appreciable difference in reaction rate was observed when the solvent was changed from H$_2$O to D$_2$O (Table IA, Figure 1). Hence, a two-electron transfer path does not provide a viable mechanistic description for the oxidation of iodide by the copper(III)–peptide complexes.

Reaction Path A. The potential for the reduction of the iodine radical (eq 11), I$\cdot$, has been estimated on the basis of

$$I\cdot(aq) + {}^1/_2 H_2(g) = I^-(aq) + H^+(aq) \qquad (11)$$
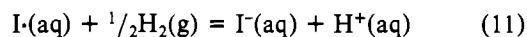
the appropriate thermodynamic cycles to be 1.4 V.[29,30] With use of this potential in conjunction with the copper(III, II) potentials (Table IV) and the measured rate constants, k_A (Table III), the rate constant, k_{-1}, for the reverse of reaction 6 can be calculated. The calculated values of k_{-1} vary from a low of 9 × 10^{10} M^{-1} s^{-1} for the Cu^{III}(H$_{-2}$A$_3$) and [Cu^{III}-(H$_{-2}$DGEN)]$^+$ complexes to a high of 2 × 10^{12} M^{-1} s^{-1} for the [Cu^{III}(H$_{-3}$G$_4$)]$^-$ complex. These values exceed the diffusion-controlled limit of 3 × 10^9 M^{-1} s^{-1} [31] by nearly 3 orders of magnitude and indicate that either (1) the I$\cdot$ radical produced in eq 6 is stabilized by complexation, and, hence, the effective I$\cdot$/I$^-$ potential is reduced, or (2) the I$\cdot$/I$^-$ potential is substantially less than 1.4 V. Complex formation between I$\cdot$ and a copper(II)–peptide complex or an anion (e.g., ClO$_4^-$) is the only likely means of stabilizing the I$\cdot$ radical.

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Table V. Ionic Strength and Anion Effects on the Reaction of [Cu^{III}(H$_{-2}$DGEN)]$^+$ with Iodide^a

ionic strength, M	medium	$10^3 \times$ [I$^-$], M	$10^2 k_{obsd}$, s^{-1}
1.0	NaCl	2.0	5.0 ± 0.1
1.0	NaNO$_3$	2.0	2.42 ± 0.03
1.0	NaClO$_4$	2.0	2.59 ± 0.04
0.5	NaClO$_4$	2.0	3.8 ± 0.1
0.2	NaClO$_4$	2.0	5.53 ± 0.07
0.1	NaClO$_4$	2.0	6.9 ± 0.1
0.1	NaClO$_4$	1.2	4.17 ± 0.09
0.1	NaClO$_4$	4.0	15.4 ± 0.1
0.1	NaClO$_4$	6.0	26.4 ± 0.4

^{a} [Cu^{III}(H$_{-2}$DGEN)]$_T$ = 4.0 × 10^{-5} M; −log [H$^+$] = 5.2; λ = 390 nm; T = 25.0 °C.

Stabilization of the I· radical by complexation with a copper(II)–peptide complex could be accommodated in the proposed mechanism by replacing eq 6 by eq 12 and 13. The

$$[Cu^{III}(H_{-n})(I^-)] \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Cu^{II}(H_{-n}L)(I\cdot)] \qquad (12)$$

$$[Cu^{II}(H_{-n}L)(I\cdot)] + I^- \overset{k_5}{\longrightarrow} Cu^{II}(H_{-n}L) + I_2^- \qquad (13)$$

rate constant k_5 may be as large as 10^9 M^{-1} s^{-1}. In order to explain the observed first-order [I$^-$] dependence of reaction path A, the condition that $k_5[I^-] \gg k_{-4}$ must be fulfilled. This means that k_{-4} must be less than 10^8 s^{-1}, and therefore, the equilibrium constant K (=[Cu^{II}(H$_{-n}$L)(I$^-$)]/[Cu^{II}(H$_{-n}$L)][I$^-$]) must be greater than 10^4 M^{-1}. The equilibrium constant K' (=[Cu(en)$_2$I$^+$]/[Cu(en)$_2$$^{2+}$][I$^-$]) for the formation of [Cu(en)$_2$I]$^+$ from Cu(en)$_2$$^{2+}$ and iodide has been determined to be 10^2 M^{-1}.[32] Since the I· radical is a weaker Lewis base than the iodide ion, K will not exceed 10^2 M^{-1}. However, eq 12 and 13 are consistent with the observed kinetic results only if K is greater than 10^4 M^{-1}. Therefore, if $E_{I\cdot/I^-}$ is 1.4 V, eq 12 and 13 can be eliminated as a possible mechanistic alternative to reaction 6.

Anion binding to halogen and pseudohalogen radicals (eq 14) is a general phenomenon that has been directly observed
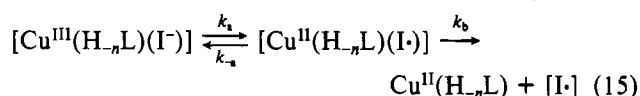
$$Y\cdot + X^- \rightleftharpoons YX^- \qquad (14)$$

and quantitated in a number of pulse radiolysis studies.[33] The transient formation of ICl$^-$ and IBr$^-$ radical anion intermediates has been proposed in order to explain the Cl$^-$ and Br$^-$ catalysis of the oxidation of iodide by Fe(phen)$_3$$^{3+}$.[23b] The effect of changing the ionic strength and the anion on the rate of the [Cu^{III}(H$_{-2}$DGEN)]$^+$ oxidation of iodide is shown in Table V. Changing the anion from 1.0 M ClO$_4$$^-$ to 1.0 M Cl$^-$ caused only a very minor rate enhancement. Moreover, the ionic strength effect on k_{obsd} is that expected for a reaction of the +1, −1 charge type (Table V). Both of these observations indicate that anion binding to the I· radical is not kinetically significant in perchlorate media.

Since complexation of I· neither by the Cu^{II}(H$_{-n}$L) species nor by anions can account for the kinetic results, the only plausible explanation is that the I·/I$^-$ reduction potential, $E_{I\cdot/I^-}$, is less than 1.4 V. An upper limit for the value of $E_{I\cdot/I^-}$ can be calculated from the kinetic results by *assuming* that the rate constant k_{-1} (eq 6) for the Cu^{II}(H$_{-3}$G$_4$)$^{2-}$/I· reaction pair is near to the diffusion-controlled limit (i.e., $k_{-1} \lesssim 1 \times 10^9$ M^{-1} s^{-1}). The result of this calculation is that $E_{I\cdot/I^-} \lesssim 1.22$ V. The

source of the discrepancy between this value of $E_{I\cdot/I^-}$ (1.2 V) and that calculated from the appropriate thermodynamic cycles (1.4 V) is not known. However, in the latter estimation it was necessary to approximate the free energy of solvation of I·(g) by $\Delta G_{solv}°$ for Xe(g), and this could be a source of error.

The copper(III)–iodide reactions are not unique in requiring that $E_{I\cdot/I^-}$ is less than 1.4 V. For the oxidation of I$^-$ by Os(bpy)$_3$$^{3+}$ the reverse rate constant was found to be 2 × 10^{10} M^{-1} s^{-1} in 1 M NaCl, and $E_{I\cdot/I^-}$ was estimated to be 1.38 V.[24d] The kinetics of the oxidation of iodide by Fe(phen)$_3$$^{3+}$, Fe(bpy)$_3$$^{3+}$, and IrCl$_6$$^{2-}$ have been investigated by a number of workers.[24] When $E_{I\cdot/I^-}$ = 1.4 V is used to calculate the reverse rate constant, k_{-1}, for these systems, it is found to exceed the diffusion-controlled limit. However, when a value of 1.2 V is used for $E_{I\cdot/I^-}$, the calculated values of k_{-1} are of a more reasonable magnitude.

In order to determine whether the rate of the copper(III)–I$^-$ reactions that proceed via path A are limited by the rate of electron transfer, it is convenient to view reaction 6 as being composed of the two sequential steps given in eq 15. An

$$[Cu^{III}(H_{-n}L)(I^-)] \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [Cu^{II}(H_{-n}L)(I\cdot)] \overset{k_b}{\longrightarrow}$$
$$Cu^{II}(H_{-n}L) + [I\cdot] \qquad (15)$$

electron transfer occurs during the first step, k_a, in eq 15. The products of the electron transfer diffuse apart in the second, k_b, step. The rate constant k_A is then given by eq 16. The

$$k_A = K_0 k_a k_b/(k_{-a} + k_b) \qquad (16)$$

reaction steps described by K_0 (eq 5) and k_b involve only diffusion or substitution processes, and therefore the magnitudes of K_0 and k_b are independent of the copper(III, II) reduction potential. The ratio (k_a/k_{-a}), which is the equilibrium constant for the electron-transfer step, is directly dependent on the thermodynamic driving force of the redox step and is related to $E_{III,II}$ by the relation log (k_a/k_{-a}) = ($E_{III,II}/0.059$) + C, where C is a constant. The rate constant k_a for the electron-transfer step also depends on the thermodynamic driving force.[34] Over an extended range of copper(III, II) reduction potentials (e.g., 0.6 V < $E_{III,II}$ < 1.8 V), this interdependence can be approximated by the expression log k_a = 0.5($E_{III,II}/0.059$) + C'. When k_b is less than k_{-a}, electron transfer is not rate limiting, and k_A is equal to K_0· (k_a/k_{-a})k_b. Under these circumstances a plot of log k_A vs. $E_{III,II}/0.059$ will have a slope of unity. If k_b is larger than k_{-a}, k_A is equal to $K_0 k_a$, electron transfer is rate determining, and a plot of log k_A vs. $E_{III,II}/0.059$ will have a slope of 0.5. The actual plot of log k_A vs. $E_{III,II}/0.059$ (Figure 3) has a slope of 0.56 ± 0.03. Therefore, the rate of the electron-transfer step (k_a in eq 16) determines the rate of reaction via reaction path A and k_A = $K_0 k_a$.

Electron-transfer reactions can proceed by either innersphere or outer-sphere mechanisms. Both types of mechanism can exhibit free-energy correlations similar to that observed for reaction path A. Whether path A occurs by an innersphere or an outer-sphere mechanism requires some additional information. In aqueous solution copper(III)–peptide complexes do not form axially coordinated inner-sphere complexes with additional ligands,[22] while nickel(III)–peptide and –macrocycle complexes do form inner-sphere complexes with amines[35] and halides.[36] Nevertheless, it has been suggested that the oxidation of iodide by Ni(cyclam)$^{3+}$, where cyclam

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is 1,4,8,11-tetraazacyclotetradecane, proceeds by an outer-sphere mechanism.[36] Also, the oxidation of iodide by Co^{3+}(aq) is believed to be an outer-sphere process, although the oxidation of Br^- and NCS^- occur by substitution-controlled inner-sphere pathways.[23] On the other hand, the oxidation of $IrCl_6^{3-}$ by $Cu^{III}(H_{-n}L)$ complexes appears to require an inner-sphere bridging chloride,[7,9,20,21] which suggests that the oxidation of iodide may also be inner sphere. Thus, there is presently no definitive evidence requiring that the oxidations of iodide by copper(III) be either inner-sphere or outer-sphere processes.

Reaction Path B. The slope of the plot of log k_B vs. $E_{III,II}/0.059$ is 0.95 ± 0.09 (Figure 3). Arguments similar to those presented for path A can be used to show that the slope of 0.95 indicates that reaction path B is not limited by the rate of electron transfer. They also show that for path B the reaction sequence given in eq 12 and 13 is not a possible alternative to the reaction proposed in eq 7.

A lower limit of the equilibrium constant K_B ($=K_0k_2/k_{-2}$) for reaction path B (eq 5 and 7) can be calculated from the reduction potentials in Table IV. The principle of microscopic reversibility[37,38] can then be used to evaluate a maximum value for k_{-2}, which is $(1.0 \pm 0.5) \times 10^5 \ M^{-1} \ s^{-1}$. This value of k_{-2} is substantially less than might be expected for a diffusion- or substitution-limited reaction of I_2^- with $Cu^{II}(H_{-n}L)$. It is, however, consistent with the rate constants k_{ox}, which have been measured by pulse radiolysis for the oxidation of the copper(II) macrocyclic complexes $Cu^{II}Z^{2+}$ and $Cu^{II}Z'^{2+}$ (where Z is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and Z' is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) by the Cl_2^- and Br_2^- radical anions. For the reaction of $Cu^{II}Z'^{2+}$ with Cl_2^- k_{ox} is $3.2 \times 10^8 \ M^{-1} \ s^{-1}$ and with Br_2^- k_{ox} is $1 \times 10^7 \ M^{-1} \ s^{-1}$.[39] These

results suggest that the oxidation of copper(II)–macrocycle and –peptide complexes by halogen radical anions undergo a rate-limiting structural or electronic activation step prior to electron transfer. The copper(II)–peptide complexes are tetragonally distorted with water molecules in the axial coordination sites, while the copper(III)–peptide complexes have square-planar coordination geometries. Desolvation of the copper(II) complexes must occur in the course of their oxidation by the radical anions. This reaction also involves the breaking of the I–I bond of the I_2^- radical anion. Both the desolvation of the copper(II) complex and the breaking of the I–I bond will make significant contributions to the rate-limiting activation process. For the reverse reaction, namely, the oxidation of iodide to I_2^- by copper(III) in eq 7, the same (de)activation process is of necessity rate limiting and occurs after the electron transfer has been accomplished. That is, the transition state for reaction path B occurs at a point near the product (Cu(II) and I_2^-) end of the reaction coordinate.

Conclusions

The copper(III)–deprotonated peptide complexes behave both thermodynamically and kinetically as one-electron oxidizing agents in their reactions with iodide. These reactions occur by two kinetic pathways. Path A exhibits a first-order iodide dependence, and its rate is limited by the rate of electron transfer. Path B exhibits a second-order iodide dependence, and its rate is not electron transfer limited. The measured rate constants for reaction path A and microscopic reversibility considerations indicate that the reduction potential for the $I\cdot/I^-$ couple is less than or equal to 1.2 V.

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Reactions of Hydrogen Peroxide with Metal Complexes. 5.[1] Mechanism of the Peroxo Complex Formation of (Nitrilotriacetato)dioxovanadate(V) As Studied by a High-Pressure Stopped-Flow Technique

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A high-pressure stopped-flow apparatus has been exploited which enables us to follow reactions with a half-life longer than 0.1 s under pressure up to 1600 kg cm^{-2}. The rate for the formation of the peroxo complex of (nitrilotriacetato)dioxovanadate(V) $(VO_2(nta)^{2-})$ is expressed as $d[VO(O_2)(nta)^{2-}]/dt = (k_1 + k_2[H^+])[VO_2(nta)^{2-}][H_2O_2]$, where $k_1 = 7.05 \ m^{-1} \ s^{-1}$, $k_2 = 1.46 \times 10^4 \ m^{-2} \ s^{-1}$ at 25 °C and $I = 1.05 \ m$ at atmospheric pressure and the volumes of activation for the k_1 and k_2 paths are -3.4 ± 0.5 and $1.5 \pm 0.5 \ cm^3 \ mol^{-1}$, respectively. An associative mechanism is most probably operative.

Introduction

Flow techniques have been introduced more than 50 years ago by Hartridge and Roughton.[2] The stopped-flow method has been utilized for studies of many kinds of reactions. We

have developed a highly sensitive stopped-flow technique by use of a computer-assisted signal averaging device.[3] In contrast to the relaxation techniques, the application of the stopped-flow techniques is not limited to reversible reactions. Both techniques are complementary for studies of reactions in solution. Measurement of activation volumes is important

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