metry at +1.1 V confirmed that the reversible oxidation is a one-electron process and that the dication is stable for several hours at least. Other workers[11,12] have been able to obtain the dication Ni(IV) species in highly purified acetonitile, and their results show that the Cp_2Ni^{2+} ion is a highly reactive entity undergoing rapid nucleophilic attack by water. The strictly anhydrous nature of the acidic $AlCl_3$–BPC melt precludes the presence of water as a nucleophilic scavenger.

Spectral Investigations. Visible absorption spectra of nickelocene species in the II, III, and IV oxidation states are shown in Figure 4. Although the major features of the spectra were reproducible (in the 1:1 region), a slight deviation from the neutral point toward either the acidic or basic compositions caused the spectra to contain features appropriate for the oxidized Cp_2Ni^+ ion or for the basic melt species, respectively. The d^6 metallocenes such as ferrocene commonly exhibit two low-intensity bands in the visible region which are generally assigned to d–d transitions.[13] Nickelocene in the neutral melt region has a spectrum that resembles the electronic spectra for Cp_2Ni in isooctane solution;[14] however, the d–d transitions at ca. 660 nm are resolved into three bands and the peak at ~435 nm has similar intensity to a shoulder at ~365 nm. In the basic melt, the spectrum of nickelocene is similar to that in the neutral region for the visible frequencies but a strong peak which appears in each of the other spectra at 320 ± 5 nm is shifted to ~360 nm. In aqueous chloride solutions, the Cp_2Ni^+ ion has absorption bands at approximately 300, 358, and 389 nm,[15] whereas Cp_2Ni^+ ion in ethanolic $HClO_4$ has two broad peaks at 300 and 434 nm.[16] This latter result more closely resembles the spectrum of Cp_2Ni^+ ion in the acidic molten salt. The 300–400-nm regions of these spectra seem to be sensitive to solvent interactions or chloride complex charge-transfer transitions,[16] and the interpretation of these spectra will be restricted to this general comparison. A spectrum of the dication Cp_2Ni^{2+} has not been reported previously and bands at 412, 438, and 532 nm are resolved (in an acidic melt composition).

Experimental Section

Nickelocene was prepared by a modification of the method of Cordes,[17] entailing a 3-h reflux in THF and extraction with petroleum ether (bp 30–60 °C). It was stored under argon at 0 °C. The preparation of $AlCl_3$–1-butylpyridinium chloride was similar to that described earlier.[6] All electrochemical experiments were done in a drybox under purified argon atmosphere. Cyclic voltammetry and chronoamperometry were performed with use of a PAR 175 Universal Programmer, PAR 173 potentiostat and Model 179 digital coulometer, a PAR RE0074 X-Y recorder, and a Tektronix 561A oscilloscope. Working electrodes were polished vitreous carbon (Atomergic Chemetals) of areas 0.0573 and 0.0855 cm^2, and an Al wire comprised the reference electrode in the 2:1 molar ratio $AlCl_3$–BPC melt, respectively (+0.15 V vs. SCE). Visible spectra were recorded in quartz 1-cm path length cells (filled and sealed in the drybox) on a Varian Techtron Model 635 spectrometer.

Acknowledgment. Support funds were provided by the Solar Energy Research Institute under Contract XP-9-8002-9, awarded to J. DuBow, R. Krisnan, and R. Job.

Registry No. Cp_2Ni, 1271-28-9; Cp_2Ni^+, 11091-00-2; Cp_2Ni^{2+}, 75365-53-6; 1-BPC, 1124-64-7; $AlCl_3$, 7446-70-0.

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Metallocene Electrochemistry. 3. Reduction–Oxidation Study of Dicyclopentadienyl Compounds of Ruthenium and Titanium in Lewis Acid–Base Molten Salts

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Received June 3, 1980

Voltammetry at vitreous C electrodes of $Ru(\eta^5\text{-}C_5H_5)_2$ and $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ in the 0.8:1 molar ratio $AlCl_3$–1-butylpyridinium chloride melt reveals an irreversible oxidation ($E_{p/2}$ = +0.68 V, 100 mV s^{-1}) and a reversible 1e reduction ($E_{1/2}$ = –0.65 V vs. SCE), respectively. These electrode potentials are comparable to those found for each species in nonaqueous, organic electrolytes. In the acidic melts (excess $AlCl_3$), $Ru(\eta^5\text{-}C_5H_5)_2$ is oxidized by multistep pathways sensitive to the melt composition, while the $Ti(\eta^5\text{-}C_5H_5)^{2+}$ dication is reduced by a reversible 1e step ($E_{1/2}$ = +0.67 V vs. SCE, 2:1 mole ratio melt) in a pCl$^-$ dependent process. Electrochemical behavior of each of these metallocenes in neutral 1:1 molar ratio melts is complicated.

Introduction

The electrochemistry and photochemistry of the metallocenes recently have been attracting attention because they represent well-characterized organometallic model compounds and because they have possible applications in solar energy conversion systems.[2-5] Our studies of their electrochemistry in the room temperature $AlCl_3$–1-butylpyridinium chloride melts have been pursued for four reasons in particular: (i) redox potentials of couples may be determined in the absence of polar solvent molecules, (ii) uncommon oxidation states of the metal center can be stabilized in the highly aprotic, ionic environment,[6] (iii) nucleophilic attack by chloride ion or the formation and stability of anionic complexes may be investigated, e.g., ref 7, and (iv) metal electrodeposition processes may be possible via cyclopentadienyl metal complexes, e.g., Zr and V.[8]

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The electrochemistry of ruthenocene, $Ru(\eta^5\text{-}C_5H_5)_2$, and the effects of ring substitutents have been studied previously in mixed aqueous–organic and organic-based electrolytes. Page and Wilkinson[9] investigated the dc polarography of the $Ru(\eta^5\text{-}C_5H_5)_2/Ru(\eta^5C_5H_5)_2^+$ ion couple in 90% EtOH/0.1 M $NaClO_4$/0.01 M $HClO_4$ supporting electrolyte and reported a well-defined 1e oxidation at +0.26 V vs. SCE. Kuwana et al.[10,11] have determined a chronopotentiometric $E_{\tau/4}$ value of 0.693 V vs. SCE (0.2 M $LiClO_4/CH_3CN$ electrolyte) for a 2e oxidation of $Ru(\eta^5\text{-}C_5H_5)_2$ at Pt electrodes. Similarly, Gubin and co-workers[12] reported a 1e oxidation of $Ru(\eta^5\text{-}C_5H_5)_2$ at 0.36 V vs. SCE at the DME and an irreversible 2e process at 0.78 V vs. SCE on Pt in aprotic 0.1 M Bu_4NBF_4/CH_3CN. However, in a later paper,[13] it was proposed that the electrochemical oxidations at Hg electrodes involve dissolution of the electrode and the formation of electroactive salts of the type $[Ru(\eta^5\text{-}C_5H_5)_2]_2Hg(BF_4)_2$. For photoelectrochemical cell applications, the thermal stability and photostability for each oxidation state of a particular couple are important, in addition to the energetics of the electron-transfer process. Unless stabilized by adducts, the $Ru(\eta^5\text{-}C_5H_5)_2^{2+}$ ion formed irreversibly at Pt electrodes is unstable in acetonitrile.[11,13] On the other hand, Borrell and Henderson[14] have established that d^6 18-electron $Ru(\eta^5\text{-}C_5H_5)_2$ is stable to photolysis at 254-nm radiation in cyclohexane solution.

Titanocene dianion electrochemistry has been investigated fairly thoroughly. A well-defined polarographic wave at −0.44 V vs. SCE for the reduction of yellow $[Ti(\eta^5\text{-}C_5H_5)_2(ClO_4)_2]$ to a green product ion in aqueous 0.1 M $NaClO_4$/0.1 M $HClO_4$ was obtained by Wilkinson and Birmingham,[16] while in nonaqueous 0.2 M $NaClO_4$/formamide electrolyte a poorly defined reduction wave was obtained at −0.62 V vs. SCE at the DME.[17] These systems have been resolved by Valcher and Mastragostino,[18] who undertook a detailed polarographic study of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ in both aqueous and nonaqueous media. In aqueous 1 M LiCl, a deformed cathodic wave was obtained at −0.48 V vs. SCE, in agreement with the earlier value;[19] however, the number of electrons involved in the electron-transfer process was determined to be 1, contrary to the figure given by Korshunov and Malyugina. The reaction mechanism in buffered aqueous electrolytes showed a pH dependency and can be represented by eq 1. In anhydrous DMF, $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ is reduced reversibly to a green Ti(III) complex and the half-wave potential is affected by the concentration of Cl^- ion. The slope of the line, $E_{1/2}/\log C_{Cl^-}$, indicated a difference of one chloride ion between the oxidized and reduced forms of the complex (see eq 2). The half-wave potential was −0.63 V vs. SCE at the mercury electrode, and two anodic waves appeared at −0.22 V and +0.19 V, with Et_4NClO_4 as the supporting electrolyte. The latter waves were used to obtain kinetic data for the dissociation of the complex (eq 3).

$$Ti(\eta^5\text{-}C_5H_5)_2OH^+ + H^+ + e^- \rightleftarrows Ti(\eta^5\text{-}C_5H_5)_2^+ + H_2O \tag{1}$$

$$Ti(\eta^5\text{-}C_5H_5)_2Cl_2 + e^- \rightleftarrows Ti(\eta^5\text{-}C_5H_5)_2Cl + Cl^- \tag{2}$$

$$Ti(\eta^5\text{-}C_5H_5)_2Cl_2 \xrightarrow{k} Ti(\eta^5\text{-}C_5H_5)^{2+} + 2Cl^- \tag{3}$$

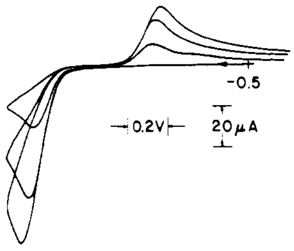

Figure 1. Voltammetry of $Ru(\eta^5\text{-}C_5H_5)_2$ 22.2 mM in a 0.8:1 melt (40 °C; ν = 10, 50, and 100 mV s^{-1}; area (C electrode) = 0.057 cm^2).

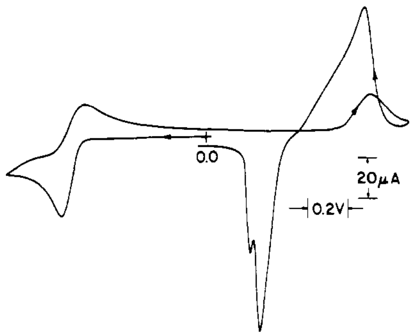

Figure 2. Cyclic voltammogram of $Ru(\eta^5\text{-}C_5H_5)_2$ in neutral region (40 °C; ν = 50 mV s^{-1}).

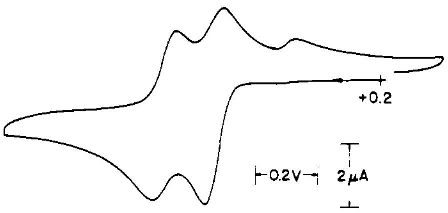

Figure 3. Voltammetry of $Ru(\eta^5\text{-}C_5H_5)_2$ 6.6 mM in a 1.2:1 melt (40 °C; ν = 20 mV s^{-1}).

In this paper we report the electrochemical behavior of the parent species $Ru(\eta^5\text{-}C_5H_5)_2$ (Pressure Chemical Co.) and $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ (Strem Chemicals, Inc.). Experimental procedures and techniques were similar to those described in earlier publications.[5-7]

Results and Discussion

Ruthenocene. A cyclic voltammogram of $Ru(\eta^5\text{-}C_5H_5)_2$ added to a basic 0.8:1 melt at 40 °C is illustrated in Figure 1. At the slowest scan rate, an irreversible oxidation peak appeared at 0.57 V vs. Al (2:1) reference and shifted negative to 0.63 V with a 10-fold increase in ν. For an irreversible charge-transfer reaction the shift should be $30/\alpha n$ mV, or $\alpha = 0.25$, on the assumption of a 2e oxidation process. Attempts to confirm the number of electrons involved in this oxidation by constant potential coulometry were not successful (cf. ref 13). With the analysis of Reinmuth for the foot of the wave current response,[15] the kinetic parameters were found to be $\alpha = 0.22 \pm 0.03$ and $k_s = 6 \times 10^{-8}$ cm s^{-1}, consistent with an irreversible oxidation process. A broad, two-component reduction wave appears on the reverse scan with peaks at ca. 0.0 and −0.24 V vs. Al (2:1) reference.

If the basic melt containing $Ru(\eta^5\text{-}C_5H_5)_2$ is adjusted to the 1:1 molar ratio composition, a small cathodic peak appears at approximately −0.8 V, followed by a large cathodic peak on the return scan and two sharp anodic peaks at ca. −0.26 and −0.22 V (Figure 2). It is possible that a conductive layer

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Table I

electrolyte	electrode	$E_{1/2}$, V/SCE[a]	n	ref
	$Ru(\eta^5\text{-}C_5H_5)_2$			
ethanolic $HClO_4$	Hg	+0.26	1	9
CH_3CN/0.2 M $LiClO_4$	Pt	+0.69	2	10, 11
basic 0.8:1 melt	C	+0.68[b]	2	this work
	$Ti(\eta^5\text{-}C_5H_5)_2{}^{2+}$			
aqueous $HClO_4$	Hg	−0.44	1	16
aqueous 1 M LiCl	Hg	−0.47	1	18
formamide/0.2 M $NaClO_4$	Hg	−0.62	1	17
DMF/Et_4NClO_4	Hg	−0.63	1	18
basic 0.8:1 melt	C	−0.65	1	this work
acidic 2:1 melt	C	+0.67	1	this work

[a] 0.0 V Al (2:1) reference equivalent to +0.15 V SCE. [b] Approximate $E_{p/2}$ value for irreversible wave (100 mV s^{-1}).

of ruthenium is deposited initially which passivates, and then aluminum or a catalytic decomposition product is codeposited on the return sweep. However, because of the complex nature of the voltammograms, no further investigations were made regarding the nature of these electrode processes, or the deposits. Under neutral conditions, the oxidation process described for the 0.8:1 melt shifts positive slightly and appears to change to a distorted 1e system.

The electrochemical behavior of $Ru(\eta^5\text{-}C_5H_5)_2$ in the acidic melt compositions was extremely complex also. Figure 3 illustrates a cyclic voltammogram obtained in a 1.2:1 molar ratio melt. Two oxidation waves are resolved at approximately 0.76 and 0.93 V vs. Al (2:1) reference, possibly the result of a 1e oxidation process followed by a chemical step and further 1e charge transfer (ECE mechanism). A small feature at 0.55 V might be associated with the species equilibria or an absorption phenomenon. Just prior to the background oxidation of the melt, a multielectron, irreversible oxidation wave could be resolved at 1.76 V. The reverse voltammetric scans contained three reduction waves at approximately 0.86, 0.71, and 0.47 V vs. Al (2:1) reference (ν = 20 mV s^{-1}). In the 2:1 molar ratio melt, the first oxidation peak was shifted positive to approximately 1.08 V and followed by several poorly resolved waves. The reduction waves were also shifted to 0.95, 0.81, and 0.50 V (ν = 20 mV s^{-1}). In both the basic and acidic solvents, the reduction processes appear to be hindered relative to the oxidative reactions.

As the positions of the peak potentials for the 2e processes in CH_3CN and the basic melt are almost coincident (Table I), these results may be interpreted by assuming that in the presence of excess chloride ion the dication species is relatively stable. Denisovich et al.[13] reached a similar conclusion. In the acidic media, the electron-transfer processes are sensitive to the $AlCl_4^-/Al_2Cl_7^-$ ion ratios, and this suggests that an interaction may occur between the Lewis acid species, $Al_2Cl_7^-$, with either the cyclopentadienyl groups or the central metal atom. Both the nature of the electron-transfer processes and the chemical stability of intermediates can be modified by the solvent environment.

Titanium Dicyclopentadienyl Dichloride. The electrochemistry of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ in both the basic and acidic melts was simpler than that of $Ru(\eta^5\text{-}C_5H_5)_2$. It dissolved in the basic 0.8:1 melt to give a red solution and a (slightly distorted) reversible 1e reduction wave at $E_{1/2}$ = −0.803 V vs. Al (2:1) reference. This potential lies in the range of those found for the reduction of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ in DMF,[18] but an attempt to see if the half-wave potential was pCl^- dependent in melts was inconclusive. A slight shift, perhaps ca. $0.5(2.3RT/F)$ V per pCl^- unit, seemed to occur between the 0.95:1 and 0.8:1 compositions; however, the accessible range of pCl^- was insufficient to establish whether or not a linear relation exists. Figure 4 contains the absorption spectra of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ in 0.8:1 melt. Peaks are resolved at 394 and 529 nm, close to those assigned to charge-transfer transitions of the d^0 Ti(IV) formal complex at 392 and 521 nm in $CHCl_3$.[2,20] Constant potential electrolysis at −0.9 V proceeded fairly cleanly to produce a blue solution and confirm the charge-transfer process as 1e. Breslow and Newburg[21] have proposed that a blue compound formed between $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $(C_2H_5)_2AlCl$ contains a double chlorine bridge between the titanium and aluminum atoms. Such compounds are important Ziegler-type catalysts for the polymerization of ethylene. A similar structure might be possible if the reduced titanium complex in the basic melt is complexed to a chloroaluminate species. Additionally, this anion exchange might explain the failure of the half-wave potential to shift in a regular way with pCl^-. A possible structure for the Ti(III) complex, I, is consistent with the well-known propensity of Al(III) to form $AlCl_4^-$ tetrahedra in chloride melts and in solid and gaseous compounds. Green titanocene chloride apparently exists as a dimer in the solid and in nonpolar solvents,[22-25] and the blue color of I may be a consequence of Ti–Cl–Al bridge chromophoric interactions. In the neutral composition region, the voltammetry of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ becomes complicated and was not investigated in detail. Acid–base equilibria evidently cause irreversibility of the charge-transfer processes that are reversible in the acidic and basic melts.

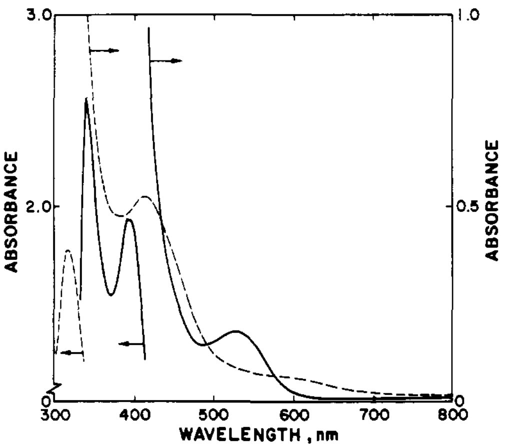
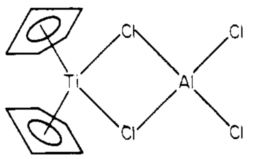


Figure 4. Absorption spectra of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ added to a basic 0.8:1 melt, 16.7 mM (solid line), and 1.2:1 melt, 0.33 mM (broken line).



I

If $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ is dissolved in acidic melts, a green solution is obtained of a disparate species which presumably has lost one or both of the complexed chloride ions. The absorption spectrum shown in Figure 4 contains peaks at 308, 414, and 590 nm that are red shifted relative to the basic melt species. This green species reduces by a reversible 1e process; however, in acidic melts from 1.05:1 to 2:1 molar ratios the mean half-wave potentials derived from cyclic voltammograms were a function of the electrolyte composition. A positive shift of

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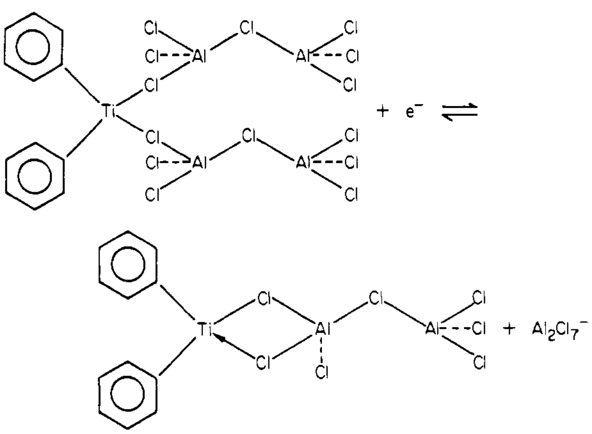
Table II. Variation of the Half-Wave Potential of $Ti(\eta^5-C_5H_5)_2Cl_2$ in Acidic Melt Compositions at 40 °C[a]

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.



(4)

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.

Acknowledgment. Support funds were provided by the Solar Energy Research Institute under Contract No. XP-9-8002-9, awarded to Drs. J. DuBow, K. Rajeshwar, and R. Job.

Registry No. $Ru(\eta^5-C_5H_5)_2$, 1287-13-4; $Ti(\eta^5-C_5H_5)_2Cl_2$, 1271-19-8; $AlCl_3$, 7446-70-0; 1-butylpyridinium chloride, 1124-64-7.

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

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Received April 22, 1980

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 $I\cdot/I^-$ 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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