

Photochemical Properties of Copper(II)-Amino Acid Complexes

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The photochemistry of copper(II)-amino acid complexes (amino acid = glutamic acid, β -alanine, or glycine) has been investigated by continuous and flash photolysis. The charge-transfer irradiations induce the oxidation of the ligand and the reduction of copper(II) to copper(I). Transients observed in flash photolysis have been assigned as copper-alkyl complexes. Moreover, other copper-alkyl species are produced when carbon-centered radicals react with excess of copper(II) complexes. The photochemical properties of the copper(II)-amino acid complexes are discussed in terms of the population of charge transfer to copper excited states.

Introduction

The photochemistry of copper(II) complexes with carboxylate ligands has been previously investigated.²⁻⁷ Irradiations at wavelengths of the charge-transfer bands induce redox transformations of the ligands. Although these redox processes normally produce the decarboxylation of the ligand, the formation of copper(I) complexes is not a general result.^{2,3} Indeed, the reoxidation of the cuprous species by carbon-centered radicals can be responsible for the disappearance of the photoproducts. Such reoxidations involve, at least in some cases, the formation of copper-alkyl intermediates by an intermolecular attack of the free radical on $\text{Cu}^+(\text{aq})$ or by an intramolecular reorganization of a copper(I)-ligand radical complex.^{2,4} Also, reactions of cupric complexes with carbon-centered radicals, namely, radicals generated in the decarboxylation of the ligand, have been detected in the photochemical transformations of copper(II) complexes.^{4,8}

The photoredox properties of copper(II)-carboxylate complexes have been attributed to photoactive carboxylate to copper(II) charge-transfer states.²⁻⁴ However, some copper(II)-carboxylate complexes seem to have unreactive charge-transfer states which do not produce photoredox transformations, e.g., complexes of EDTA^{2-} and HCO_2^- .^{5,6}

Charge-transfer states have also been regarded as reactive intermediates in the photochemistry of amino complexes of copper(II).⁹ Two photoactive states can be populated in $\text{Cu}(\text{N}_4)\text{X}^+$ (N_4 = amino tetraaza ligand and $\text{X} = \text{Cl}^-, \text{Br}^-$). These states involve the electronic density of the amino nitrogens and the electronic density of the amino ligand, X^- . Amino acid complexes of copper(II) have charge-transfer states with different features, namely, carboxylate to copper(II) and amino to copper(II) charge-transfer. We have investigated in this work the photochemical behavior of the amino acid complexes of the glycine, β -alanine, and glutamic acid and their photochemical relationships with other amino and carboxylate complexes.

Experimental Section

Photochemical Procedures. Continuous-wave irradiations were carried out with a high-pressure xenon lamp, Eimac Vix-300, coupled with collimating lenses, a high-intensity monochromator, and a photocell-microvoltmeter apparatus. The photocell-microvoltmeter apparatus was used for the determination of relative values of the light intensity. Absolute values were obtained with tris(oxalato)ferrate.¹⁰ Some irradiations at 254 nm were carried out with a

low-pressure mercury lamp, GE 4T4.1.

Quantum yields were obtained from the slope of product concentration vs. irradiation time plots. The photolyte solutions were stirred with magnetic bars during the irradiation. Concentrations were adjusted in order to absorb more than 99.9% of the incident light.

Flash irradiations were carried out with an experimental setup, which has been described elsewhere.¹¹ The waveform recorder, Biomation 805, was interfaced to a Digital PDP-8L processor. The raw data, stored in digital form in the waveform recorder, was processed in the PDP-8L in order to obtain either rate constants or spectral information. Solutions were irradiated at preselected wavelengths by using appropriate cutoff filters.

Analytical Procedures. Carbon dioxide was determined by gas chromatography according to a procedure indicated below. Solutions of the complexes were deaerated by three freeze-thaw cycles. The carbon dioxide was distilled under vacuum from the acidic irradiated solutions, namely, pH ≤ 6 . Moreover, irradiated basic solutions, pH ≥ 6 , were acidified with 6.0 M HClO_4 before the vacuum distillation of CO_2 in a gastight apparatus.

Copper(I) was determined with 1,10-phenanthroline.¹² The syringe procedure was used for mixing irradiated solutions of the photolyses with argon-deaerated solutions of the analytical reactants. Determinations, carried out under vacuum in a gastight apparatus, gave results indistinguishable from those obtained with the syringe procedure.

Qualitative determinations of amines were carried out according to procedures reported elsewhere.¹³

Materials. The copper(II)-amino acid complexes were precipitated from aqueous solutions that contain copper(II) perchlorate and an excess of the ligand at pH ≥ 6 . The solids were recrystallized from neutral solutions that contained an excess of the amino acid.¹⁴

Other chemicals were analytical grade and were used without further purification.

Results

Species in Solution. The distribution of the various species was investigated in order to characterize the labile copper(II)-amino acid complexes at acid and copper(II) concentrations used for photochemical experiments. The relative concentration of each copper(II)-amino acid species was determined as a function of the solution's pH. Equilibrium constants reported elsewhere were used for these calculations.¹⁵ The equations for the complexation equilibria were treated by mathematical procedures already described in the literature; see ref 16 and Appendix I. Figure 1 shows a typical distribution of the more significant species in the $\text{Cu}(\text{II})$ - β -alanine and $\text{Cu}(\text{II})$ -glycine equilibria at acid concentrations used for the photochemical work.

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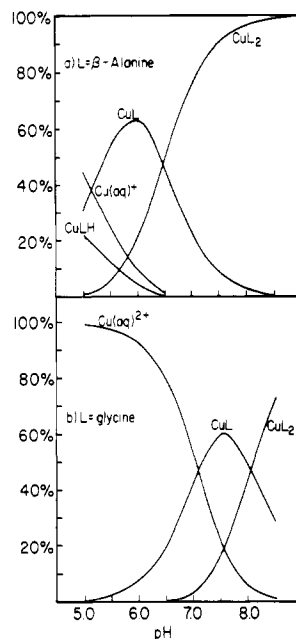


Figure 1. Distribution of the significant species in the complexation equilibria of (a) Cu(II)- β -alanine and (b) Cu(II)-glycine complexes at the hydrogen concentrations of the photochemical experiments.

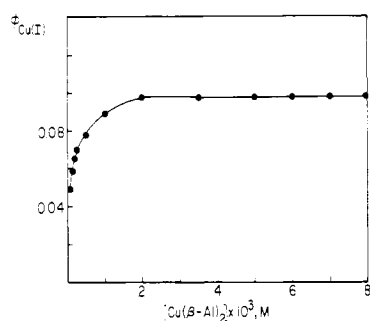


Figure 2. Dependence of the copper(I) yield on the concentration of Cu(β -Al) $_2$ in 254-nm photolyses; $I_0 = 1.5 \times 10^{-4}$ einstein/(L·min), at pH 8.

Continuous Photolysis. Ultraviolet irradiations of the amino acid complexes in aqueous solutions produce copper(I) and carbon dioxide. Moreover, a qualitative analysis of the reaction products reveals the formation of amines in the photoinduced decarboxylation of the amino acid complexes.

The concentrations of carbon dioxide and copper(I) increase linearly with irradiation time. However, extended irradiations, namely, photolyses for conversions larger than 5%, produce a solid precipitate which seems to be a mixture of metallic copper and cuprous oxide. The precipitation of solid material was avoided in the determination of the carbon dioxide and copper(I) quantum yields by using conversions to products smaller than 1%.

The copper(I) yields, determined for 254-nm irradiations of Cu(β -Al) $_2$ in deaerated solutions at pH ≥ 7 , increase with complex concentrations (Figure 2). Limiting yields of copper(I), $\phi_{\text{Cu(I)}}^L$, were obtained for excitations at given wavelengths with concentrations of Cu(β -Al) $_2$ larger than or equal to 10^{-3} M (Table I). Carbon dioxide is produced with a quantum yield that is independent of the complex concentration and pH of the solution, for pH ≥ 6.0 . The carbon dioxide yield has a smaller value than the limiting yield of copper(I) (Table I and Appendix II).

The ultraviolet irradiations of Cu(Glu) $_2$ in deaerated aqueous solutions produce copper(I) with a yield that is independent of the complex concentration for concentrations

Table I. Quantum Yields of Copper(II)-Amino Acid Complexes

λ_{excit} , nm	I_0 , einstein/ (L·min)	$\Phi_{\text{Cu(I)}}$	Φ_{CO_2}	conditions	
				[Cu(II)], M	pH
Glutamic Acid ^a					
350	3.0×10^{-5}	0.070 ± 0.005	0.26 ± 0.03	1.0×10^{-2}	7.5
290	1.4×10^{-5}	0.073 ± 0.005		1.0×10^{-2}	7.5
254	8.9×10^{-6}	0.067 ± 0.003	0.25 ± 0.02	5.0×10^{-3}	7.5
254	1.5×10^{-4}	0.067 ± 0.004		5.0×10^{-3}	7.5
254	1.5×10^{-4}	0.073 ± 0.004	0.25 ± 0.02	1.0×10^{-2}	7.5
254	1.5×10^{-4}	0.067 ± 0.006		1.0×10^{-3}	7.5
220	2.4×10^{-6}	0.073 ± 0.003		5.0×10^{-3}	7.5
β -Alanine ^{a,b}					
350	3.0×10^{-5}	0.097 ± 0.005	0.066 ± 0.005	1.0×10^{-3}	7.0
290	1.4×10^{-5}	0.097 ± 0.005		1.0×10^{-3}	7.2
254	1.5×10^{-4}	0.097 ± 0.003	0.064 ± 0.003	1.0×10^{-3}	8.0
254	1.5×10^{-4}	0.097 ± 0.003	0.067 ± 0.004	7.0×10^{-4}	8.0
254	1.5×10^{-4}	0.097 ± 0.002		5.0×10^{-4}	8.0
254	1.5×10^{-4}	0.089 ± 0.003		1.0×10^{-4}	8.0
254	1.5×10^{-4}	0.077 ± 0.002		5.6×10^{-5}	8.0
254	1.5×10^{-4}	0.071 ± 0.002		2.1×10^{-5}	8.0
254	1.5×10^{-4}	0.058 ± 0.004		1.1×10^{-5}	8.0
220	2.4×10^{-6}	0.099 ± 0.005		1.0×10^{-3}	8.0

^a pH adjusted with 0.1 M NaOH. ^b Photolysis in the presence of 10^{-2} M β -alanine.

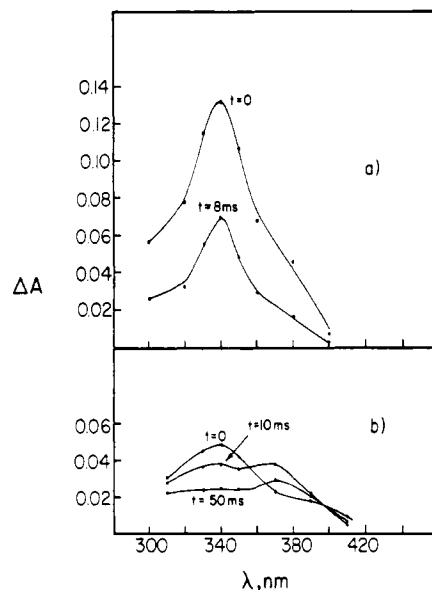


Figure 3. Transient spectra obtained in flash photolyses of deaerated solutions of Cu(Glu) $_2$ at (a) pH 8 and (b) pH 5.5; irradiations with 250 J/pulse at $\lambda_{\text{excit}} \geq 240$ nm.

larger than 10^{-3} M. Moreover, the yield of carbon dioxide is larger than the limiting yield of copper(I) (Table I).

Yields of copper(I) were determined for photolyses of the amino acid complexes Cu(β -Al) $_2$ and Cu(Glu) $_2$ at various excitation wavelengths. The copper(I) yields are independent of the excitation wavelength in the region of the charge-transfer absorptions. No photoredox transformations were observed for irradiations in the dd bands, namely, $\phi_{\text{Cu(I)}} \leq 10^{-5}$ for $\lambda_{\text{excit}} \leq 500$ nm.

Flash Photolysis. Transient spectra, $\lambda_{\text{max}} \sim 340$ nm, were determined in flash irradiations of Cu(Glu) $_2$, $\lambda_{\text{excit}} \geq 240$ nm, in deaerated solutions with pH ≥ 7.0 (Figure 3a). These transients disappear with a rate that exhibits a first-order dependence in transient concentration. However, the time-resolved spectrum, obtained for irradiations of Cu(Glu) $_2$ in acidic solutions where the concentrations of Cu(Glu) and Cu $^{2+}$ (aq) are large, shows a more complex behavior (Figure 3b). The transient spectrum at reaction times shorter than

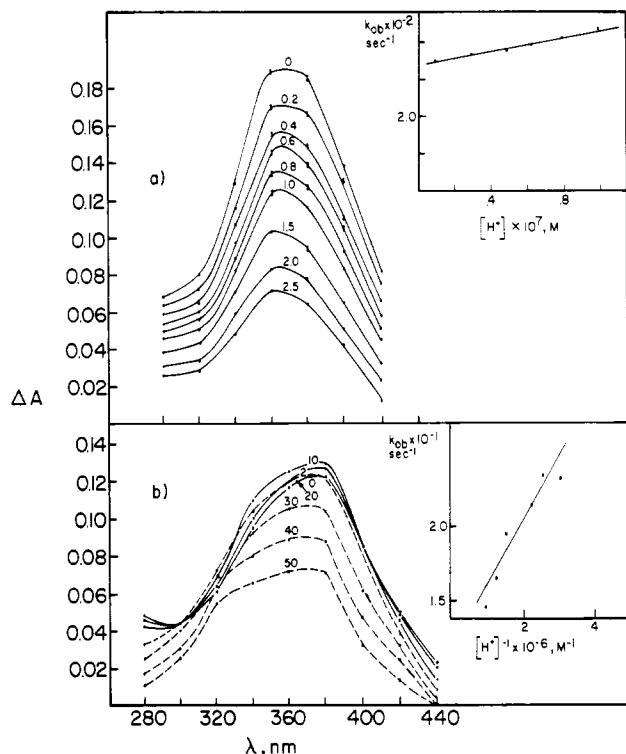


Figure 4. Transient spectra determined in flash irradiations of $\text{Cu}(\beta\text{-Al})_2$ at (a) pH 8 and (b) pH 7.0 in deaerated solutions containing 10^{-2} M β -alanine. Numbers indicate the reaction times in milliseconds. Insets show the dependence of the corresponding decay rate constants on $[\text{H}^+]$ (top) and $[\text{H}^+]^{-1}$ (bottom).

1 ms has the features of the transient spectrum obtained in more basic solutions (see above). New absorptions with $\lambda_{\text{max}} \sim 380$ nm were observed for reaction times longer than 1.0 ms (Figure 3b). The rate of the 370-nm absorbance growth in Figure 3b is the same as the 340-nm absorbance decay for reaction times shorter than 1.0 ms. This observation suggests that the second species, $\lambda_{\text{max}} \sim 370$ nm, is generated at the expense of the intermediate with $\lambda_{\text{max}} \sim 340$ nm.

The flash irradiations of $\text{Cu}(\beta\text{-Al})_2$, $\lambda_{\text{excit}} \geq 240$ nm, produce transient transformations, which have some of the features indicated above for the irradiations of $\text{Cu}(\text{Glu})_2$ (Figure 4). Absorbances with $\lambda_{\text{max}} \sim 340$ nm were observed for flash irradiations of $\text{Cu}(\beta\text{-Al})_2$ in deaerated solutions with pH ≥ 7.0 (Figure 4a). Such absorbances disappear with a rate that has a first-order dependence on transient concentration at a given pH. Moreover, the rate of the absorbance decay increases with acid concentration for pH ≥ 8 (Figure 4a). Flash irradiations of $\text{Cu}(\beta\text{-Al})_2$, $\lambda_{\text{excit}} \geq 240$ nm, in deaerated acidic solutions produce a transient spectrum which is different from the spectrum obtained in more basic solutions (Figure 4b). A transient growth of the absorbance is observed at $300 \leq \lambda \leq 400$ nm for reaction times shorter than 10 ms (Figure 4b). The rate of disappearance of the transient absorbances at reaction times longer than 20 ms exhibited a first-order dependence on transient concentration. Moreover, the rate of disappearance increases with pH, namely, for $5 \leq \text{pH} \leq 7$ (Figure 4b).

The copper(II)–glycine complex behaves as a copper(II)– β -alanine complex in flash irradiations. A transient spectrum with $\lambda_{\text{max}} \leq 300$ nm was observed in flash photolysis (Figure 5). The rate of the absorbance decay has a first-order dependence on transient concentration. A rate constant $k = 1.5 \times 10^1 \text{ s}^{-1}$ was determined for solutions with pH > 6 .

The presence of oxygen in solutions of the photolytes greatly affects the transient transformations induced in flash irradiations of the copper(II)–amino acid complexes. The new

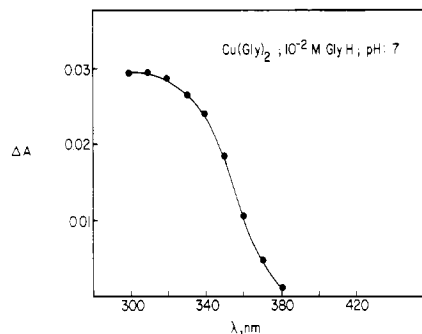


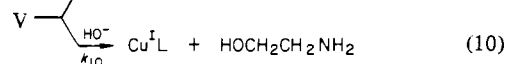
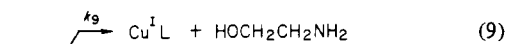
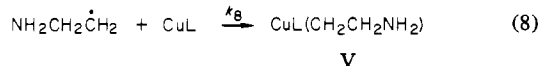
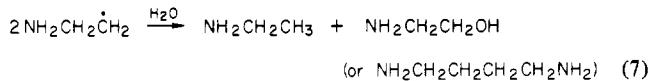
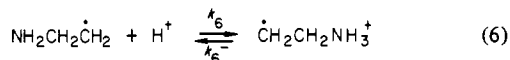
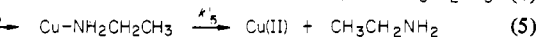
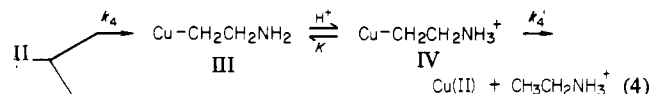
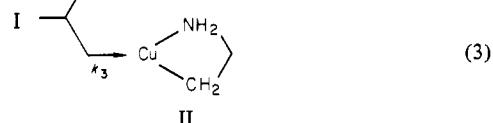
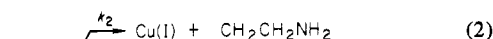
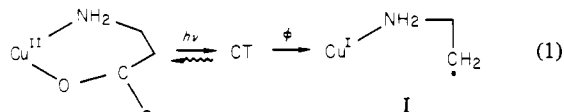
Figure 5. Transient spectrum determined at zero reaction time in flash photolysis of deaerated solutions of $\text{Cu}(\text{Gly})_2$ (pH 7); irradiations with 250 J/pulse flashes at $\lambda_{\text{excit}} \geq 240$ nm.

transient absorbances, under aerobic conditions, can be attributed to peroxo or superoxo species.

Acrylamide was used as a scavenger of photochemically generated radicals. Increasing concentrations of acrylamide failed to change the rate of decay of the transient absorbances generated in flash photolysis of deaerated solutions. However, the yields of the intermediates decrease with increasing concentrations of the scavenger.

Discussion

The charge-transfer irradiations of copper(II)–amino acid complexes induce the redox decomposition in copper(I), carbon dioxide, and various amino products. The overall photochemical transformation to products proceeds through several intermediates, which were observed in flash photolysis. These transients can be assigned as copper–alkyl complexes that are formed in secondary reactions between copper(I) or copper(II) species and carbon-centered radicals (eq 1–10). Similar



metastable species have been reported to mediate in redox reactions of carbon-centered radicals with copper(I) and copper(II) complexes.^{4,8} In this regard, the transient absorbances in basic solutions (Figures 3–5) are proposed to be copper–alkyl derivatives generated by reoxidation of copper–

(I)-ligand radical intermediates, namely II in eq 3. The decay of such absorbances can be attributed to hydrolyses of these species, e.g., eq 4 and 5. If the various copper-alkyl derivatives have similar absorptivities at the wavelength of observation, namely, the CT region, the decay rate constant can be expressed by means of two contributions (eq 11 and Appendix III).

$$k_1 = k_4 + k_5 \quad k_{II} = k_4'K[H] \quad (11)$$

The dependence of the decay rate constant on acid concentration, pH ≥ 6 , gives $k_4 + k_5 = 3.4 \times 10^2 \text{ s}^{-1}$ and $k_4'K = 7.9 \times 10^8 \text{ M s}^{-1}$ for the intermediates generated in flash irradiations of $\text{Cu}(\beta\text{-Al})_2$. Moreover, the results obtained in flash irradiations of $\text{Cu}(\text{Glu})_2$ gave the relationships $k_4 + k_5 = 2.02 \text{ s}^{-1}$ and $k_4'K = 4.28 \times 10^6 \text{ M s}^{-1}$. Differences of nearly 2 orders of magnitude can be observed between the rate constants of the transients generated in photolyses of $\text{Cu}(\beta\text{-Al})_2$ and $\text{Cu}(\text{Glu})_2$. Such a disparity probably reflects the distinctive structure of the decarboxylated amino acids, as in species II in eq 3–5. The photogeneration of a precursor of species II, namely, I in eq 2 and 3, is indicated by the reduction of the copper-alkyl yield as acrylamide concentration increases. Moreover, the values of the carbon dioxide and copper(I) yields give an indication of the reactivity of intermediate I (see Appendix II). Product yields in Table I give ratios $k_3/k_2 \sim 0.32$ for the β -alanine complex and $k_3/k_2 \sim 6.1$ for the glutamic acid complex. These results suggest that the species generated by decarboxylation of the glutamate complex has a larger tendency to form a copper-alkyl intermediate, II in eq 4 and 5, than the one produced by decarboxylation of the β -alanine complex. This behavior is in good agreement with the reactivity of intermediate II, measured by means of the combined rate constants, i.e., $k_4 + k_5$ (see above).

The transient spectrum observed for flash irradiations of $\text{Cu}(\beta\text{-Al})_2$ at pH < 6 has been attributed to copper-alkyl intermediates, e.g., intermediate V. Such intermediates are generated in reactions of carbon-centered aminoalkyl radicals with excess copper(II) complexes, eq 8–10. Aqueous copper(II) complexes, namely, $\text{Cu}^{2+}(\text{aq})$ and $\text{Cu}(\text{H}_2\text{O})_2(\beta\text{-Al})^+$ (see Figure 1), are very likely the scavengers of the aminoalkyl radicals. Similar copper-alkyl species have been previously proposed as intermediates in redox reactions between carbon-centered radicals and copper(II) complexes.¹⁷ Moreover, transient species observed in the pulse radiolysis and flash photolysis have been assigned as copper-alkyl complexes.⁴ The pH dependence of the copper-alkyl disappearance has been explained in terms of two parallel processes: eq 9 and 10, with $k_9 = 1.2 \times 10^5 \text{ s}^{-1}$ and $k_{10} = 4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The base-assisted hydrolysis, eq 10, can be regarded as a substitution process in a coordination complex.^{18,19} However, the nucleophilic attack of hydroxide ions at the coordinated carbon is also a possible mechanism for the disappearance of the covalent copper-alkyl species.

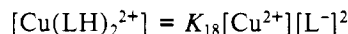
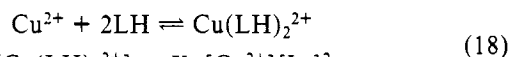
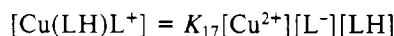
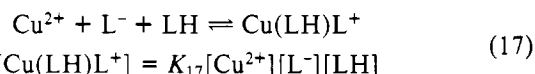
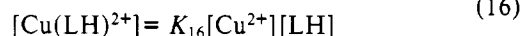
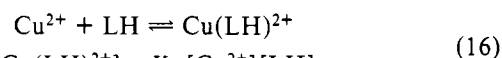
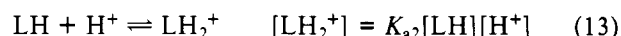
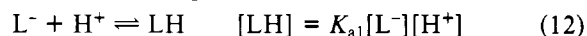
The redox photochemistry of the copper(II)-carboxylate complexes, e.g., $\text{Cu}(\text{CH}_3\text{CO}_2)^+$ and $\text{Cu}(\text{malonate})_2^{2-}$, has been associated with the population of reactive carboxylate to copper(II) charge-transfer states.²⁴ Similar assignments can be proposed for the photochemistries of the amino acid complexes. Moreover, the independence of the carbon dioxide and copper(I) yields on excitation wavelength suggests that other excited states, namely, amino to copper(II) charge-transfer

states, are not photoreactive.^{20–22} Such a behavior contrasts with that of copper(II) macrocyclic complexes where two photoreactive charge-transfer states have been characterized.⁹ This disparity in the photochemical reactivity probably indicates that some carboxylate to copper(II) charge-transfer states are placed at lower energies than the amino to copper(II) charge-transfer states.²² The optical electronegativities of the amino and carboxylate ligands suggest that a charge transfer involving π electrons of the carboxylate group takes place at lower energies than a transfer involving σ electrons of the amino group.²² Therefore, the upper charge-transfer states, σ amino and/or σ carboxylate, must undergo an efficient conversion into the photoreactive π carboxylate to copper(II) charge-transfer states.

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Appendix I

The complexation of copper(II) by β -alanine can be described by means of eq 12–18, where $\text{L}^- = \beta$ -alanine. The



corresponding equilibrium equations, eq 12–18, were combined with corresponding mass balances of the copper(II) and ligand, eq 19 and 20. The ligand mass balance, eq 20, was obtained

$$C_{\text{Cu}} = [\text{Cu}^{2+}] + [\text{CuL}^+] + [\text{CuL}_2] + [\text{Cu}(\text{LH})^{2+}] + [\text{Cu}(\text{LH})\text{L}^+] + [\text{Cu}(\text{LH})_2^{2+}] \quad (19)$$

$$C_{\text{L}} \sim [\text{L}^-] + [\text{LH}] + [\text{LH}_2^+] \quad (20)$$

under the condition that the concentration of ligand in excess, C_{L} , is much larger than the concentration of complex, C_{Cu} . Substitution of eq 12 and 13 into eq 20 allows expression of the concentration of the ligand L as a function of the solution's

(20) Symmetry considerations²¹ show that orbitally allowed-spin allowed charge-transfer transitions to the following states are possible: $^2\text{A}_g \rightarrow ^2\text{B}_{1g} (\pi \rightarrow \text{Cu})$, $^2\text{A}_g \rightarrow ^2\text{B}_{2g} (\sigma_{\text{N}} \rightarrow \text{Cu})$, $^2\text{A}_g \rightarrow ^2\text{B}_{3u} (\sigma_{\text{N}} \rightarrow \text{Cu})$, $^2\text{A}_g \rightarrow ^2\text{B}_{3u} (\sigma_{\text{N}} \rightarrow \text{Cu})$, $^2\text{A}_g \rightarrow ^2\text{B}_{2u} (\sigma_{\text{O}} \rightarrow \text{Cu})$, $^2\text{A}_g \rightarrow ^2\text{B}_{3u} (\sigma_{\text{O}} \rightarrow \text{Cu})$. Symbols between parentheses indicate that charge is transferred from σ or π orbitals of carboxylate (O subscript) or amino (N subscript) ligands. The copper(II)-amino acid complex has been assumed to have a D_{2h} point group symmetry.²¹

(21) Cotton, F. A. "Chemical Applications of Group Theory"; Wiley-Interscience: New York, 1971.

(22) An average optical electronegativity $\chi = 3.12$ has been reported for a carboxylate ligand.^{23–25} Orbitally assigned optical electronegativities for the carboxylate group are $\chi_{\pi} = 3.0$ for the highest filled π orbital and $\chi_{\sigma} = 3.4$ for the σ orbital.^{24,25} The reported value for the optical electronegativity of the amino ligand is $\chi \approx 3.28$. These optical electronegativities show that charge-transfer transitions $\pi_{\text{O}} \rightarrow \text{Cu}$ are placed around $8.4 \times 10^3 \text{ cm}^{-2}$ lower than $\sigma_{\text{N}} \rightarrow \text{Cu}$ transitions.²⁰ It is feasible that a similar ordering is valid for the thermally equilibrated excited states.

(23) For a definition of the optical electronegativities see: Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968; Chapter 7.

(24) Endicott, J. F. "Concepts in Inorganic Photochemistry"; Adamson, A., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 3.

(25) Ferraudi, G.; Muralidharan, S. *Coord. Chem. Res.* **1981**, 36, 45.

(17) For a general survey of the oxidation-reduction reactions of free radicals and complex ions see: Kochi, J. K. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 11.

(18) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1967.

(19) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes"; Allyn and Bacon Inc.: Boston, 1974; Chapter 4.

pH (eq 21). Moreover, the substitution of eq 14-18 and 21

$$[L] = \frac{C_L}{1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2} \quad (21)$$

into eq 19 gives the distribution of $\text{Cu}^{2+}(\text{aq})$ with solution's pH, eq 22. The fractions of the other species were obtained

$$\alpha = [\text{Cu}^{2+}]/C_{\text{Cu}} = 1/[1 + (K_{14} + K_{16}K_{a1}[H^+]) \times [L] + (K_{15}K_{14} + K_{17}K_{21}[H^+] + K_{18}K_{a1}^2[H^+]^2)[L]^2] \quad (22)$$

by combining eq 22 and eq 14-18.

The $\text{Cu}(\text{II})$ -glycine and $\text{Cu}(\text{II})$ -glutamic acid equilibria were treated by similar procedures.

Appendix II

The mechanism described by eq 1-10 predicts different formation rates for CO_2 and $\text{Cu}(\text{I})$ (eq 23 and 24). Such rates

$$\frac{\partial[\text{CO}_2]}{\partial t} = \phi I_0 \quad (23)$$

$$\frac{\partial[\text{Cu}(\text{I})]}{\partial t} = k_2[\text{I}] + (k_9 + k'_{10})[\text{V}] \quad (24)$$

are determined by the light intensity, I_0 , and the concentrations of intermediates II and V (see eq 1-5). The dependence of the copper(I) rate law on irradiation time, eq 25, was obtained

$$\begin{aligned} \frac{\partial[\text{Cu}(\text{I})]}{\partial t} = \phi I_0 \left(\frac{k_2}{k_2 + k_3} \right) + \left(\frac{K}{K + [H^+]} \right) \left\{ \left[\left(\frac{k_8(K + [H^+])[\text{Cu}(\text{II})]}{4Kk_7} \right)^2 - \frac{\phi I_0(K + [H^+])^2 k_2}{2K^2 k_7(k_2 + k_3)} \right]^{1/2} - \frac{k_8(K + [H^+])[\text{Cu}(\text{II})]}{4Kk_7} \right\} k_8[\text{Cu}(\text{II})] \quad (25) \end{aligned}$$

by introducing the steady-state concentrations of the intermediates I, V, and aminoalkyl radicals, e.g., $\text{CH}_2\text{CH}_2\text{NH}_2$,

in eq 24. Such a rate law can be simplified if the concentration of copper(II) is large or the light intensities are small. The rate of copper(I) formation is given by eq 26 under these two

$$\frac{\partial[\text{Cu}(\text{I})]}{\partial t} = 2\phi \frac{k_2}{k_2 + k_3} I_0 \quad (26)$$

limiting conditions. Moreover, the yields of carbon dioxide and copper(I) (eq 23 and 26) give an indication of the relative reactivity of intermediate I (eq 27).

$$\frac{\phi_{\text{Cu}(\text{I})}}{\phi_{\text{CO}_2}} = 2 \frac{k_2}{k_2 + k_3} \quad (27)$$

Appendix III

The decay of the copper-alkyl intermediate in neutral to basic solutions exhibited a linear dependence on acid concentration. Such a behavior is explained by means of eq 3-5 in the proposed mechanism, eq 1-10. Indeed, the rate of decay of the transient absorbance, ΔA , can be described by using the rate of decay of intermediates II, III, and IV, eq 28, where

$$\frac{\partial \Delta A}{\partial t} = \epsilon_1 \frac{\partial[\text{II}]}{\partial t} + \epsilon_2 \frac{\partial[\text{III}]}{\partial t} + \epsilon_3 \frac{\partial[\text{IV}]}{\partial t} \quad (28)$$

ϵ_1 , ϵ_2 , and ϵ_3 are the extinctions of the transients. Equation 28 can be reduced to eq 29 by assuming that the equilibrium

$$\frac{\partial \Delta A}{\partial t} = \epsilon_1(k_4 + k_5)[\text{II}] + \left(\frac{\epsilon_2 + \epsilon_3 K[H^+]}{1 + K[H^+]} \right) \frac{\partial C}{\partial t} \quad (29)$$

$$C = [\text{III}] + [\text{IV}]$$

between III and IV is rapid. A further reorganization of eq 29 is obtained by assuming that species III and IV have nearly the same extinctions at the monitoring wavelength (eq 30).

$$\frac{\partial \Delta A}{\partial t} = \epsilon_1(k_4 + k_5)[\text{II}] + \epsilon_2 k_4' K[H^+] C \quad (30)$$

The different contributions to the rate of the absorbance decay can be separated under appropriate experimental conditions.

Registry No. $\text{Cu}(\beta\text{-Al})_2$, 14040-31-4; $\text{Cu}(\text{Glu})_2$, 15169-63-8; $\text{Cu}(\text{Gly})^+$, 15841-47-1.

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Kinetic Studies of the Oxidation of Horse Heart Ferrocyanochrome c by $[\text{Ru}(\text{NH}_3)_5\text{py}]^{3+}$ at Low pH

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The kinetics of the oxidation of ferrocyanochrome c by $[\text{Ru}(\text{NH}_3)_5\text{py}]^{3+}$ have been studied over the pH range 1.25-6.8 at 25 °C. An increase in the rate of oxidation was observed between pH values of 4.0 and 3.0. Very little change in the rate was found below pH 2.5 and above 4.5. Analysis of this pH-rate profile yields second-order rate constants of 6.0×10^3 and $3.77 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the oxidation of ferrocyanochrome c and a monoprotonated species (H^+ -ferrocyanochrome c), respectively, with the equilibrium constant for protonation being $1.40 \times 10^3 \text{ M}^{-1}$. It is suggested that a small structural change is induced in the region of the protein redox center in H^+ -ferrocyanochrome c, thereby allowing easier reagent access to the heme c group. Comparison of NMR titration data and the kinetic results indicates that H^+ -ferrocyanochrome c is protonated at His-26.

Introduction

Analysis of the kinetics of oxidation of horse heart ferrocyanochrome c by inorganic complexes such as $[\text{Co}(\text{phen})_3]^{3+}$, $[\text{Co}(\text{dipic})_2]^-$, and $[\text{Ru}(\text{NH}_3)_5\text{py}]^{3+}$ suggests that electron transfer occurs at a site near the partially exposed edge of the

heme c group.¹⁻⁵ This interpretation of the electron-transfer pathway is appropriate for the protein in its native confor-

(1) Mauk, A. G.; Scott, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 4360.