(58) C. K. Jörgensen, "Modern Aspects of Ligand-Field Theory", American-Elsevier, New York, N.Y., 1971.
(59) Reference 44, p 225.
(60) (a) D. Heinert and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 3933 (1959); (b) C. M. Harris, R. J. Johnson, and D. E. Metzler, *Biochim. Biophys. Acta*, **421**, 181 (1976).
(61) M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **12**, 253 (1958).
(62) K. Fukushima, T. Onishi, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **15**, 236 (1959).
(63) G. C. Percy, *J. Inorg. Nucl. Chem.*, **37**, 2071 (1975).
(64) H. A. O. Hill and N. Zarb-Adami, *J. Inorg. Nucl. Chem.*, **37**, 2443 (1975).
(65) G. C. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, **34**, 3369 (1972).
(66) E. P. Dudek and G. Dudek, *Inorg. Nucl. Chem. Lett.*, **3**, 241 (1967).
(67) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4528 (1961).
(68) S. Mizushima, I. Ichishima, I. Nakagawa, and J. V. Quagliano, *J. Phys. Chem.*, **59**, 293 (1955).
(69) D. M. Sweeny, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6521 (1955).
(70) M. E. Farago, M. M. McMillan, and S. S. Sabir, *Inorg. Chim. Acta*, **14**, 207 (1975).
(71) L. G. Hulett and D. A. Thornton, *Spectrochim. Acta, Part A*, **27**, 2089 (1971).
(72) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1970.
(73) G. S. Shephard and D. A. Thornton, *J. Mol. Struct.*, **16**, 321 (1973).
(74) R. C. Burrows and J. C. Bailar, *J. Am. Chem. Soc.*, **88**, 4150 (1966).
(75) F. T. Helm, Ph.D. Dissertation, Georgia Institute of Technology, 1973.
(76) S. Yamada, Y. Kuge, and T. Yamayoshi, *Inorg. Chim. Acta*, **9**, 29 (1974).
(77) S. Yamada, H. Kuma, and K. Yamanouchi, *Inorg. Chim. Acta*, **10**, 151 (1974).
(78) S. Yamada, Y. Kuge, T. Yamayoshi, and H. Kuma, *Inorg. Chim. Acta*, **11**, 253 (1974).
(79) J. T. Wrobleski and G. J. Long, in preparation.
(80) M. Ando and S. Emoto, *Bull. Chem. Soc. Jpn.*, **42**, 2628 (1969).
(81) M. Ando and S. Emoto, *Bull, Chem. Soc. Jpn.*, **48**, 1655 (1975).
(82) T. Ueki, T. Ashida, Y. Sasada, and M. Kakudo, *Acta Crystallogr.*, **22**, 870 (1967).

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Photostimulated Solvolytic Reactions of a Macrocyclic Copper Complex[1a]

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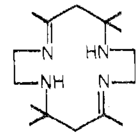
The photochemical behavior of $Cu([14]dieneN_4)^{2+}$ was studied under various experimental conditions for excitations in the region of the charge-transfer transitions. Two processes, ligand hydrolysis in aqueous solutions and formation of reduced copper(I) species in methanol, were detected as the photochemical modes of reaction for this ion. A ketone–amine intermediate product was characterized in the aqueous photoreaction and a precursor, possibly a carbinolamine species ($t_{1/2} \simeq 0.03$ s), was observed by means of flash photolysis. The slow formation of Cu(I) was observed in neat methanol by a second-order reaction ($k = 2.2 \times 10^4$ M^{-1} s^{-1}). A mechanism based on a common precursor with ligand and metal reaction centers was proposed.

Introduction

Since copper complexes often serve as labile mediators of redox reactions, one might expect photoredox reactions of copper complexes to be of some potential significance. Yet there have been few systematic studies.[2-7] Among the recent studies, those of Davis and Stevenson[2] and of Kutal and co-workers[3] are of interest in that they attempt to use copper complexes to produce the conversion of solar to storable chemical energy. Several years ago, Wehry proposed a direct photooxidation of solvent species, water or methanol, by copper(II) phenanthroline complexes[4] while Lintvedt and DeGraaf and their co-workers had found evidence that photoredox processes in other copper chelates involved production of radical ligand species, followed by often complex and rapid radical reactions with solvent and/or substrate.[5,6]

In this report we describe our photochemical studies of $Cu([14]dieneN_4)^{2+}$.[8] It seemed possible that the macrocyclic $[14]dieneN_4$ ligand would be stable to the complexities introduced by radical reactions of more labile ligand systems and that one might be enabled to observe simple intermolecular reactions between the excited copper complex and solvent species.



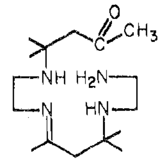
$[14]dieneN_4$

Experimental Section

Continuous irradiations were performed using either resonance emission lines of Philips Zn, Cd, and Hg spectral lamps or spectral bands from a medium-pressure Hg lamp (1 kW). The source was arranged on an optical bench with a collimating lens system, slits, a water filter plus the interference filter, and sample cell as appropriate to the experiment. Ferrioxalate[9] and uranyloxalate[10] were used as the primary actinometric references. The light intensity for a given source was checked frequently with $Co(NH_3)_5Cl^{2+}$ or $Co(NH_3)_5Br^{2+}$.[11]

Solutions were deaerated either with streams of nitrogen (Cr^{2+} scrubbed) or by four freeze–pump–thaw cycles. The latter procedure was used for determinations of the quantum yields in methanolic solutions owing to the reactivity of the copper(I) product with dioxygen. An analytical procedure for this species was developed in order to minimize loses. Oxidation of the cuprous species in the photolyte was carried out with a vacuum deaerated solution of Fe^{3+} (10^{-4} M) placed in a detachable side arm of the reaction cell. Solutions were mixed under vacuum, and the Fe^{2+} was analyzed with 1,10-phenantroline.[12] Unphotolyzed solutions, handled in the same manner, were used as references. Copper(II) was analyzed with rubeanhydridic acid (ditizone).[13] Tests for primary amines, methyl ketones, and formaldehyde were performed according to literature descriptions.[14] The search for pseudo-macrocyclic complexes was carried out with appropriate $Cu^{2+}(aq)$ reagents in acid medium (0.1–0.05 M I^- or ditizone).

Flash irradiations[15] of $Cu([14]dieneN_4)^{2+}$ in methanolic media were performed on solutions degassed by four freeze–pump–thaw cycles. Transfer to the flash photolysis cell was carried out under an argon atmosphere in a gas-tight apparatus. Aqueous solutions were liberated of oxygen with nitrogen (scrubbed in towers filled with chromous solutions). Literature procedures were used for the synthesis of $[Cu([14]dieneN_4)](ClO_4)_2$[16] and $[Cu(8\text{-en-2-one}N_4)](ClO_4)_2$.[8,17]



$8\text{-en-2-one}N_4$

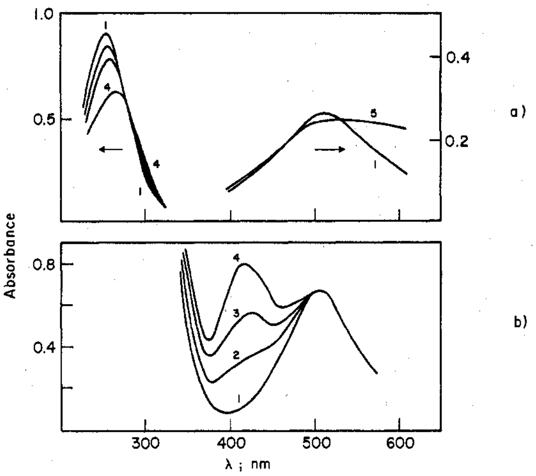


Figure 1. Spectral change during photolysis of Cu([14]dieneN$_4$)$^{2+}$. (a) Aqueous solutions saturated in boric acid (pH $\simeq$6.0), λ 254 nm, $I_0 = 5.0 \times 10^{-4}$ einstein/(L min). Irradiation time (min): 1, 0; 2, 30; 3, 60; 4, 120; 5, 240. (b) Vacuum deaerated methanolic solutions, λ 254 nm, $I_0 = 5.0 \times 10^{-4}$ einstein/(L min). Irradiation time (min): 1, 0; 2, 30; 3, 60; 4, 90.

The [14]dieneN$_4$ complex was recrystallized several times from hot water by addition of 5.0 M HClO$_4$. Two further recrystallizations were carried out from distilled water. Tests for small amounts of copper complexes with open cycle ligands were negative in the purified compound. The infrared and visible–ultraviolet spectra of the compounds agreed well with literature reports.[16-19]

Spectroquality methanol was used without further purification. The alcohol exhibited no significant absorbance in the 200–400-nm region. Other materials used were reagent grade and they were handled without extra purifications.

Visible and ultraviolet spectra were recorded with a Perkin-Elmer 450 or Cary 14 spectrophotometer. Infrared spectra were obtained in a Perkin-Elmer 621 spectrophotometer and pH measurements were performed with a Radiometer pH meter with suitable scale expansions.

Stopped-flow experiments were performed using an Aminco stopped-flow apparatus.

Results

(A) Continuous Irradiations. (1) Reaction Products. Irradiations of the Cu([14]dieneN$_4$)$^{2+}$ complex were carried out under various experimental conditions in the region of the charge-transfer transitions (λ ≤400 nm). A new Cu(II) species, the Cu(8-en-2-oneN$_4$)$^{2+}$, was produced when the medium of the reaction was buffered at pH 6 (boric acid saturated solutions) while its hydrolysis fragments, Cu^{2+}(aq), mesityl oxide, and ethylenediamine were obtained in more acid solutions (HClO$_4$ 2.0 to 10^{-3} M). The identification of the reaction product was performed by comparing the absorption spectra of the irradiated samples (see Figure 1a) with solutions prepared with appropriate concentrations of the substrate and Cu(8-en-2-oneN$_4$)$^{2+}$. Reduced species reaction products were not found in aqueous solutions deaerated by means of either nitrogen purge or freeze–thaw cycles. However, different results were obtained when photolyses were performed in pure methanolic solvent media. Charge-transfer irradiations in such media produced a highly reducing product, identified as Cu([14]dieneN$_4$)$^+$ by means of absorption spectra (Figure 1b), and formaldehyde. The estimated extinction coefficient (ϵ 5.0 × 10^3 M^{-1} cm^{-1} at λ_{max} 415 nm), obtained from the spectra of irradiated samples, agreed well with values reported by different authors.[20] A search for additional reaction products by ionic exchange chromatography did not provide reliable information as a consequence of the narrow range of conditions permitted in these experiments. The absorption spectra of irradiated samples (5.0 × 10^{-3} M Cu[(14)dieneN$_4$]$^{2+}$, neat methanol) showed that variations of the optical density were smaller than those expected at λ ≥540 nm, and this suggested that Cu([14]dieneN$_4$)$^+$ was not the only reaction product. Complexes with open cycle ligands were not found in these irradiated samples.

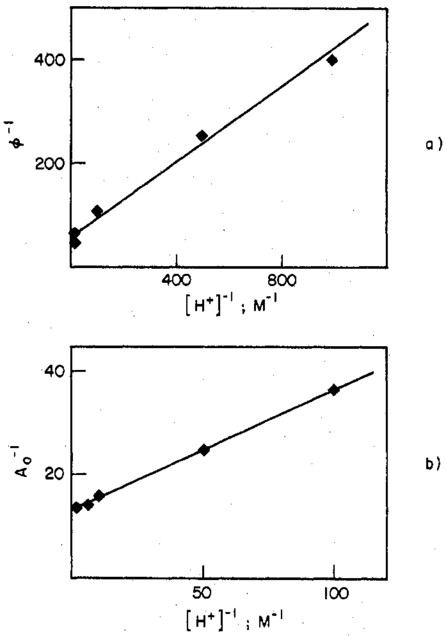


Figure 2. Variation of the yield for the hydrolyzed product with acid concentration. (a) Quantum yields for irradiations at 254 nm (I_0 = 5.0 × 10^{-5} einstein/(L min)). (b) Absorption of the carbinolamine extrapolated to zero time. Flash-photolyzed solutions were 6.0 × 10^{-6} M in substrate and acidities were adjusted with HClO$_4$ [(HClO$_4$) + (NaClO$_4$) = 2.0 M].

(2) Quantum Yields. Quantum yields for the photochemical reactions, obtained under distinct conditions, for various excitation wavelengths, are collected in Table I and Figure 2a.

The results, obtained for photolyses of the Cu(II) complex in aqueous solutions, show that the presence of moderate concentrations of radical scavengers ([2-propanol] = 0.5 M or O$_2$ saturated solutions) neither affects the efficiency of the hydrolytic process nor leads to reduced species. In addition, the yield for the hydrolyzed product was found largely dependent on the hydrogen ion concentration (Figure 2a). The Cu([14]dieneN$_4$)$^+$ yield in methanol was diminished by salts (LiClO$_4$; NaOCOCH$_3$) or water present in the medium but products of solvolysis were only observed in mixed aqueous methanolic solutions.

Similar irradiations of Ni([14]dieneN$_4$)$^{2+}$ produced no evidence of reaction ($\phi < 10^{-5}$).

(B) Flash Photolysis. Flash photolyses of acidic aqueous solutions (10^{-2} M ≤ [HClO$_4$ ≤ 2.0 M) of Cu([14]dieneN$_4$)$^{2+}$ produced transient absorptions in the region 280–340 nm (Figure 3a) that decayed through two successive steps. A half-life ($t_{1/2} \simeq 0.03$ s) independent of both the pH of the solution and the initial concentration of the transient was found for the faster stage while the next presented a half-life time dependent on the hydrogen ion concentration (Table II). Further, a linear dependence of the initial absorbance on flash energy and also on hydrogen ion concentration was obtained (Figure 2b).

Absorptions were observed in flash photolyses of vacuum deaerated methanolic solutions that agreed with the formation of Cu([14]dieneN$_4$)$^+$ (see Figure 2b). The reaction was followed at 415 nm, and the results of these experiments may be summarized as follows. The rate of formation of Cu([14]dieneN$_4$)$^+$ was found to be first order in the flash energy for a series of experiments with 2.0 × 10^{-5} M substrate. The rate constant of the first-order process, at a given flash output

Table I. Quantum Yields for Cu([14]dieneN_4)$^{2+}$

λ, nm	$10^5 I_0$, einstein/(L min)	$10^2\phi$			Conditions^a
		Cu(II)^b	A^c	Cu(I)^d	
340	5.3 ± 0.2	0.09 ± 0.01 (4)			$HClO_4$, 0.1 M
295	8.7 ± 0.3	0.16 ± 0.04 (3)			$HClO_4$, 0.1 M
				0.05 ± 0.02 (3)	MeOH; vacuum
254	5.0 ± 0.3	2.3 ± 0.3 (2)			$HClO_4$, 2.0 M
		2.0 ± 0.2 (3)			$HClO_4$, 2.0 M
		2.3 ± 0.3 (5)	2.5 ± 0.3 (4)	<0.13 (3)^f	$HClO_4$, 0.1 M
		0.93 ± 0.04 (4)			$HClO_4$, 0.01 M
		0.43 ± 0.03 (3)			$HClO_4$, 0.002 M
		0.25 ± 0.03 (4)			$HClO_4$, 0.001 M
		2.3 ± 0.2 (3)			$HClO_4$, 0.1 M; O_2^{e}
		2.1 ± 0.3 (2)		<0.13 (5)^f	$HClO_4$, 0.1 M; vacuum
		2.1 ± 0.2 (3)			$HClO_4$, 0.1 M; 2-propanol, 0.5 M
	2.7 ± 0.3			0.26 ± 0.02	MeOH; vacuum
229	2.6 ± 0.4	3.0 ± 0.3 (6)	2.9 ± 0.4 (5)	<0.13 (3)^f	$HClO_4$, 0.1 M
				<0.13 (3)^f	$HClO_4$, 0.1 M; vacuum
		3.0 ± 0.3 (2)		<0.13 (3)^f	$HClO_4$, 0.5 M
		3.0 ± 0.3 (2)		<0.13 (6)^f	$HClO_4$, 0.1 M; 2-propanol, 0.5 M
	3.6 ± 0.2			1.1 ± 0.2 (2)	MeOH; vacuum
214	1.3 ± 0.1			2.1 ± 0.2 (2)	MeOH; vacuum
				1.3 ± 0.1 (3)	MeOH; H_2O, 1.1 M
				0.83 ± 0.02 (2)	MeOH; H_2O, 3.2 M; vacuum
		0.17 ± 0.09 (3)		0.60 ± 0.02 (3)	MeOH; H_2O, 5.5 M; vacuum
		0.90 ± 0.06 (5)		0.25 ± 0.02 (3)	MeOH; H_2O, 10 M; vacuum
				1.20 ± 0.03 (2)	MeOH; $LiClO_4$, 0.05 M; vacuum
				0.90 ± 0.04 (3)	MeOH; $LiClO_4$, 0.1 M; vacuum
				0.34 ± 0.04 (2)	MeOH; $LiClO_4$, 0.2 M; vacuum
				<0.01	MeOH; $LiClO_4$, 0.35 M; vacuum
				0.14 ± 0.03 (2)	MeOH; NaOAc, 0.1 M; vacuum
				0.14 ± 0.03 (2)	MeOH; NaOAc, 0.01 M; vacuum

^{a} Deaeration with streams of nitrogen unless otherwise stated. ^{b} Quantum yield for the total amount of hydrolyzed product. ^{c} Yields determined by measurement of the absorbance of the irradiated solutions at 254 nm. ^{d} Quantum yields for the reduced species, Cu([14]dieneN_4)$^+$. ^{e} Oxygen-saturated solutions. ^{f} Upper limit for Cu(I) detection in our experimental conditions.

Table II. Rates of Hydrolysis of Cu(8-en-2-oneN_4)$^{2+}$ in Acid Solutions

[H^+],^{a} mol/L	$t_{1/2}$, s	
	Flash photolysis^b	Stopped flow^c
1.6	1.5 ± 0.2	1.4 ± 0.3
0.8	1.8 ± 0.2	1.6 ± 0.3
0.4	4.5 ± 0.3	4.0 ± 0.5
0.2	7.7 ± 0.3	8.0 ± 0.7
0.02	>10	>10

^{a} [$HClO_4$] + [$NaClO_4$] = 2.0 M. ^{b} Flash photolytically generated species in 6.0 × 10^{-6} M Cu([14]dieneN_4)$^{2+}$ solutions. Energy/flash: 250 J. ^{c} The hydrolytic reaction was followed by a stopped-flow technique in 5 × 10^{-4} to 1 × 10^{-4} M Cu(8-en-2-oneN_4)$^{2+}$ solutions.

(250 J/flash), was linearly dependent on substrate concentration (Figure 4).

These experimental results have been expressed as the integrated rate law (eq 1) for Cu(I) formation.

$$[\mathrm{Cu}([14]\mathrm{dieneN_4})^+] = [\mathrm{Cu}([14]\mathrm{dieneN_4})^+]_\infty (1 - e^{-kt}) \qquad (1)$$
$$k \simeq (2.2 \times 10^4)[\mathrm{Cu}([14]\mathrm{dieneN_4})^{2+}]\ \mathrm{s}^{-1}$$

Precursors of the product were observed at 320 nm as small absorptions not clearly defined and developed within the flash lifetime.

(C) Stopped Flow. A comparison between the kinetics of the last step observed in our flash photolysis experiments and the acid hydrolysis of Cu(8-en-2-oneN_4)$^{2+}$ was carried out in order to elucidate the nature of the transient species. Solutions of the ketone–amine complex (5.0 × 10^{-4} to 1.0 × 10^{-4} M) in 2.0 M $NaClO_4$ were mixed with appropriate solutions of $HClO_4$ ([$HClO_4$] + [$NaClO_4$] = 2.0 M), and the hydrolysis of the complex was followed at 290 nm (see Table II).

Discussion

In this study we have found reasonably efficient photoinduced reactions of Cu([14]dieneN_4)$^{2+}$. By contrast, the relative photoinsensitivity of the nickel(II) analogue and the generation of copper(I) in methanolic media indicate that these reactions are mediated by the metal. That the copper(I) species are generated slowly enough for their formation to be observed in flash photolysis demonstrates that these species are not primary photoredox products and suggests some sort of complex radical mechanism (see below). As a consequence the type of mechanism proposed by Wehry, the direct formation of Cu^I and oxidized solvents as primary products does not apply to the Cu([14]dieneN_4)$^{2+}$ complex. Since, as indicated below, there is reason to suspect that the reactions of excited Cu([14]dieneN_4)$^{2+}$ with solvent are due to reactivity of the Cu–imine moiety, the Wehry mechanism may not even be applicable to the polypyridyl complexes for which it was proposed.

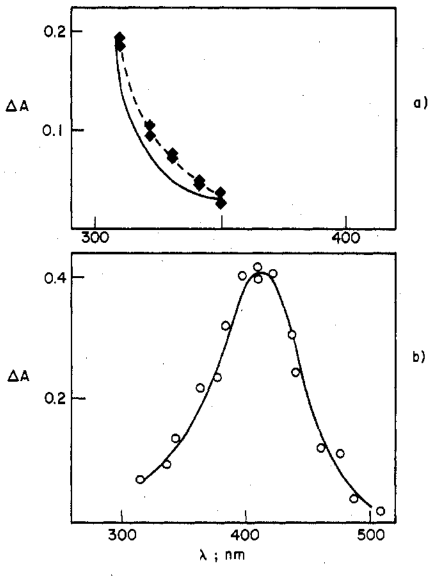


Figure 3. Spectra of the species generated in flash irradiations. (a) Absorptions developed 100 μs after the flash in aqueous solutions of $Cu([14]dieneN_4)^{2+}$ (1.6×10^{-5} M) in 0.02 M $HClO_4$: —, substrate absorption; - - -, transient absorption. (b) Differential absorptions between the substrate and the species generated 1 s after the flash in vacuum-deaerated methanolic solutions: $[Cu([14]dieneN_4)]^{2+}] = 1.0 \times 10^{-5}$ M; energy/flash = 250 J.

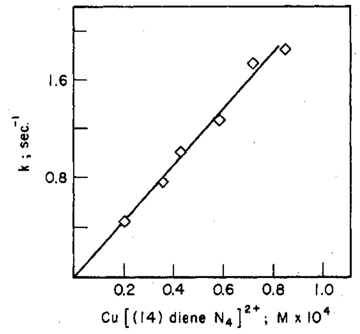
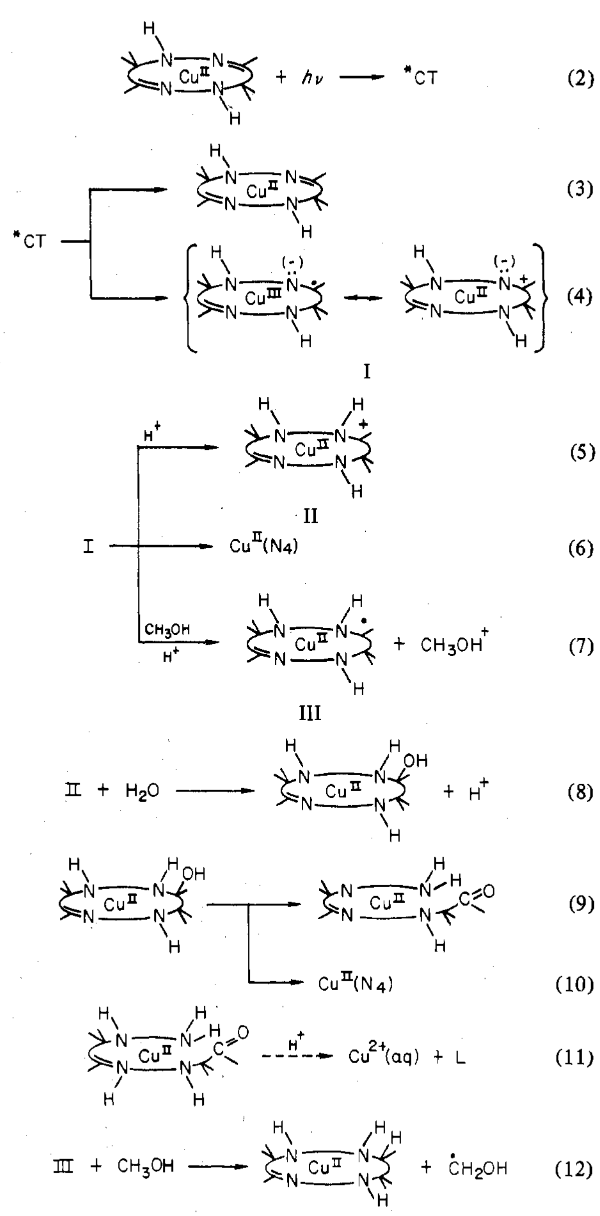


Figure 4. Dependence of the rate constant for the formation of $Cu([14]dieneN_4)^+$ in vacuum-deaerated methanolic solutions with substrate concentration, energy/flash = 250 J.



$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH + H^+ + \dot{C}H_2OH \qquad (13)$$

$$\dot{C}H_2OH + Cu^{II}(N_4) \longrightarrow Cu^{I}(N_4) + CH_2O + H^+ \qquad (14)$$

Our observation that the products of irradiation of $Cu([14]dieneN_4)^{2+}$ vary with the medium, ligand hydrolysis products in water or copper(I) products in methanol, is mechanistically significant since the photoreactions must have similar excited-state precursors. In fact, the photoactivity appears to be associated with irradiations of an absorption band which is assigned as metal to ligand charge transfer.[19,21] This fact, the features of the hydrolysis process, and the slow reaction generating copper(I) all strongly implicate the imine moiety in the reaction and are suggestive of the reactions of imine complexes of trivalent metals with bases.[22,26] Our observations on the photochemistry of $Cu([14]dieneN_4)^{2+}$ may be accounted for by a mechanistic scheme such as in eq 2–14. The experimental evidence indicates the formation, during the flash pulse, of metastable intermediate species in water and in methanol; the amount of the initial intermediate formed in aqueous media increases with $[H^+]$ (Figure 1). We propose that these intermediates are formed in scavenging reactions of H^+ and CH_3OH for a very reactive primary photoproduct (the scavenging for the reactive excited state, *CT, might also be considered; however, this species is likely to be very short lived) as in eq 4 and 6 or 5 and 9. Thus, it seems most plausible that the immediate precursor to the $Cu(8\text{-en-2-one}N_4)^{2+}$ complex is the corresponding carbinolamine (eq 7) and that the copper(I) products are formed by means of the rapid reaction of substrate (or other copper(II) complexes) with $\cdot CH_2OH$.[27] To account for the transient kinetics observed in flash photolysis merely requires that eq 9 or eq 11 describe the slow steps in aqueous or methanolic media, respectively.

The striking inhibition of the formation of copper(I) by various salts is consistent with a reaction such as eq 5, scavenging for a very short-lived transient intermediate, since ion pairing would have the effect of desolvating the copper(II) complex (see ref 19 for a discussion of evidence of such desolvating effects even in aqueous media). If such a desolvating effect were to account for the decrease in copper(I) yields, one would have to infer that the species scavenged by methanol cannot survive many collisions.

Registry No. $Cu([14]dieneN_4)^{2+}$, 33727-13-8; $Cu(8\text{-en-2-one}N_4)^{2+}$, 63883-54-5; $Cu([14]dieneN_4)^+$, 47105-27-1.

References and Notes

(1) (a) Partial support of this research by the National Institutes of Health is gratefully acknowledged. (b) Author to whom correspondence should be addressed at The Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556. Contributor from Wayne State University and Universidad Tecnica del Estado. (c) Wayne State University.

(2) K. L. Stevenson and D. D. Davis, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, No. INOR 15.

(3) C. Kutal, D. P. Schwendiman, and P. Gratsch, private communication from C.K., 1976.

(4) S. Sundarajan and E. J. Wehry, *J. Phys. Chem.*, **76**, 1528 (1972).

(5) (a) R. L. Lintvedt, "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, Chapter 7, p 299; (b) H. D. Gafney and R. L. Lintvedt, *J. Am. Chem. Soc.*, **92**, 1623 (1971).

(6) (a) J. Y. Morimoto and B. A. DeGraaff, *J. Phys. Chem.*, **79**, 326 (1975); (b) *ibid.*, **76**, 1387 (1972).

(7) D. R. McMillan and M. T. Backner, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, No. INOR 35.

(8) Ligand abbreviation: [14]dieneN$_4$ = 5,7,7,12,14,14,-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; 8-en-2-oneN$_4$ = 14-amino-4,4,9,11,11-pentamethyl-5,8,12-triazatetradeca-8-en-2-one.

(9) C. A. Parker and G. E. Hatchard, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

(10) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966; (b) J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **95**, 630 (1973).

(11) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975).

(12) J. K. Kochi et al., *J. Am. Chem. Soc.*, **84**, 2121 (1962).

(13) J. Fries, "Analysis of Traces", E. Merk, Darmstad, 1971.

(14) A. E. Vogel, "Elementary Practical Organic Chemistry", Longmans, London, 1958. For formaldehyde analysis: "Methods in Carbohydrate Chemistry", Vol. 1, Academic Press, London, 1962.

(15) For descriptions of flash photolysis techniques see G. J. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973).

(16) N. Sadasivan and J. R. Endicott, *J. Am. Chem. Soc.*, **88**, 5468 (1966); N. F. Curtis and R. W. Hay, *Chem. Commun.*, 524 (1966).

(17) N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1358 (1972).

(18) N. F. Curtis et al., *J. Chem. Soc. A*, 1075 (1966).

(19) J. F. Endicott, J. M. Palmer, and E. Papaconstantinou, *Inorg. Chem.*, **8**, 1516 (1969).

(20) The spectra of Cu([14]dieneN$_4$)$^+$ were described previously by several authors; see ref 19, 21, and 27. The chemical stability of this species, generated in our experimental conditions, agreed with those reported in ref 19 and 21. Apparent discrepancies with the reactivity reported in ref 27 were probably caused by a different nature in the proton donor.

(21) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **10**, 463 (1971).

(22) R. D. Gillard, *Coord, Chem. Rev.*, **16**, 67 (1975).

(23) G. Nord and O. Wernberg, *J. Chem. Soc., Dalton Trans*, 845 (1975).

(24) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci., U.S.A.*, **72**, 2858 (1975).

(25) J. DelGaudio and G. N. LaMar, *J. Am. Chem. Soc.*, **98**, 3014 (1976).

(26) R. H. Yamada, T. Kato, S. Shimizu, and S. Fukui, *Biochim. Biophys. Acta*, **117**, 13 (1966).

(27) A. M. Tait, M. Z. Hoffman, and E. Hayon, *Inorg. Chem.*, **15**, 934 (1976). These authors report $k \simeq 9 \times 10^8$ M^{-1} s^{-1} for the $\cdot CH_2O^-$ reduction of Cu([14]dieneN$_4$)$^{2+}$ and that they were unable to detect the $\cdot CH_2OH$ reduction of the copper(II) complex. Their data seem to be consistent with $k_{11} \le 10^6$ M^{-1} s^{-1}; we have found a value of 2.2×10^4 M^{-1} s^{-1} which could correspond to reductions of Cu([14]dieneN$_4$)$^{2+}$ by either $\cdot CH_2OH$ or CH_2O^- in neutral solution.

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Photoredox Energetics of Transition Metals. Redox and Nitrene Pathways in Azidopentaamminechromium(III)[1]

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The charge-transfer photochemistry of $Cr(NH_3)_5N_3^{2+}$ has been studied in detail under a variety of conditions. Both redox and nitrene pathways have been found. The redox and nitrene quantum yields have been obtained as a function of irradiation wavelength and they both show definite threshold energies which are in agreement with previous results and proposed models. The actual yields of products are diminished due to complicating secondary reactions of radical scavenging species. Scavenger concentration studies show that the $\phi_{Cr(II)}$ increases in deaerated solutions. Flash photolyses of acidic solutions of the complex imply the production of $\cdot N_3$ radical. A mechanistic scheme is proposed to explain the primary steps induced by photolysis and the secondary thermal reactions. The lowest charge-transfer excited state which is photoactive toward both the redox and nitrene reactive pathways is most likely a L → M state. The photochemistry of $Cr(NH_3)_5N_3^{2+}$ is compared with that of the azido complexes of other transition metals.

Introduction

The photochemical behavior of transition-metal azide complexes has long been a subject of interest.[2] Renewed interest has followed the discovery by Basolo and co-workers[3] of an efficient photoinduced coordinated nitrene pathway in iridium(III) and rhodium(III) azidopentaammine complexes, eq 1. This dominance of the nitrene pathway for the

$$M(NH_3)_5N_3^{2+} \xrightarrow[H^+]{h\nu} M(NH_3)_5NH^{3+} + N_2 \qquad (1)$$

heavy-metal complexes[3,4] contrasts strikingly with the observation of photoredox modes, eq 2, for the analogous co-

$$Co(NH_3)_5N_3^{2+} \xrightarrow[H^+]{h\nu} Co^{2+} + 5NH_4^+ + {}^3/_2N_2 \qquad (2)$$

balt(III) complexes.[2,4,5] This contrast in photochemical behavior of the various azido complexes has been very puzzling. It has been variously proposed that the difference in photochemical behavior may be attributed to:[6] (1) the involvement of metal-to-ligand charge-transfer states;[7] (2) differences in the efficiencies of internal conversion processes populating ligand centered states;[3] or (3) differences in the metal-to-ligand back-bonding interactions in the charge transfer to metal excited state.[3b,4] Miskowski et al.[8] have recently found evidence that direct excitation of apparently ligand-centered bands of $M(CN)_5N_3^{3-}$ (M = Ir, Rh) complexes does not lead to detectable nitrene formation, but rather only azide photoaquation was found for those complexes.[9]

It has previously been reported by Vogler[11] that the ligand-field excitations of $Cr(NH_3)_5N_3^{2+}$ lead to efficient ammonia aquation while charge-transfer photolysis produces redox decomposition as the only reaction with a high quantum yield. We began investigating the photochemistry of $Cr(NH_3)_5N_3^{2+}$ as a part of our systematic examination of the charge-transfer photochemistry of Cr(III) complexes[10] and while these studies were in progress we learned of independent studies demonstrating a coordinated nitrene product following 313-nm irradiations.[12] These observations and our concern over the fact that the charge-transfer photochemistry of $Cr(NH_3)_5N_3^{2+}$ is different in many regards from that of the other acidopentaamminechromium(III) complexes have led us to examine this system very critically. As a result of our