# Prompt and Delayed Electron Photoejection from Triamminecopper(I) and Formation of a Dinuclear Excited State Complex in Aqueous Solution

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We have previously reported the prompt and delayed UV photoejection of hydrated electrons from aqueous solutions of di- and trihalo anionic complexes of copper(I) with chloro[1,2] and bromo[2] ligands. The source of the prompt electron is attributed to direct ejection following excitation into the charge-transfer-to-solvent (CTTS) states of the complexes, whereas the delayed electron is ejected from two weakly luminescent, triplet, excited-state equilibrated species, a short-lived dihalo and a longer-lived trihalo complex, designated an exciplex.[3−6] Similarly to the halocuprate systems, copper(I) forms di- and triammine complexes, according to the equilibrium[7−9] ($K = 0.040$)

$$Cu(NH_3)_2^+ + NH_3 \rightleftharpoons Cu(NH_3)_3^+ \quad (1)$$

In an equilibrated mixture of these complexes, only the triammine species absorbs the laser UV output at 266 nm appreciably, also resulting in the ejection of hydrated electrons but without any accompanying luminescence.[7,9] Earlier laser flash studies at 266 nm revealed, along with the time-resolved spectrum of hydrated electrons, some other long-lived intermediate absorbing at about 400 nm.[9] We report in this paper the surprising result that the cationic triamminecopper(I) complex also produces delayed ejection of electrons after excitation in the UV through an equilibrium between an excited monomer, a ground-state monomer, and a dinuclear exciplex, an excited-state equilibrium that is rather different from that observed in the halocuprate(I) systems.

Figure 1 shows two time-resolved spectra taken at different time delays, and at different concentrations of $CuClO_4$ in 3.04 M $NH_3$. Spectrum 1 was taken 50 ns after the 266-nm, 7-ns laser flash in a solution containing 0.00386 M $CuClO_4$ (prepared by reacting $Cu(ClO_4)_2$ with Cu powder in 3.04 M $NH_3$ under argon). The absorption peak at about 720 nm is clearly that of the hydrated electron,[10] and by comparison of this peak to the electron signal produced by a ferrocyanide actinometer solution[11] the quantum yield for this prompt electron photoejection is estimated to be about 0.3. Since earlier CW experiments[7,9] showed that the species oxidized by UV light in a solution of copper(I) in ammonia is the triamminecopper(I) cation, the primary photochemical step

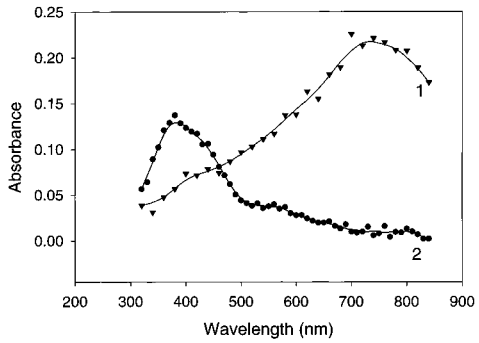


**Figure 1.** Time-resolved (and smoothed) spectra taken after 266-nm flash in a 1-cm cuvette of solution which is 3.04 M $NH_3$ and contains $CuClO_4$. Curve 1 (▼): delay time = 50 ns, $[CuClO_4] = 0.00386$ M. Curve 2 (●): delay time = 500 ns, $[CuClO_4] = 0.0150$ M.

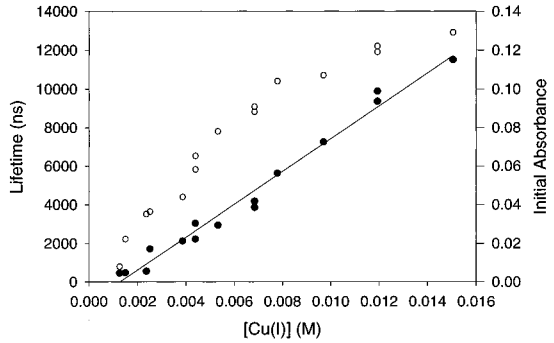


**Figure 2.** (●) First-order lifetime (ns) of the 400-nm transient vs $[CuClO_4]$ (M) for 3.04 M $NH_3$ solution flashed in a flow-through 1-cm cuvette. The linear regression line is also shown. (○) Initial absorbance of the 400-nm transient vs $[CuClO_4]$ (M).

is absorption into the CTTS (or Rydberg d → s or d → p) state and prompt ejection of an electron,

$$Cu(NH_3)_3^+ \xrightarrow{h\nu} e_{aq}^- + Cu(NH_3)_3^{2+} \quad (2)$$

The electron is scavenged by the two copper(I) ammine complexes presumably forming copper(0) ammine species which appear to absorb around 400 nm, similarly to their halocuprate counterparts.[2,3] At very low or very high copper concentrations the electron decay is simple first order, but there is an intermediate range of copper concentrations where the signal becomes biexponential (see below). The initial decay lifetime of this electron signal decreases as the copper(I) concentration is increased, and from the slope of a plot of the observed electron decay constant vs [Cu(I)] (not shown) we obtain, at this ammonia concentration, the second-order scavenging constant of $3.0 \times 10^9$ $M^{-1}$ $s^{-1}$.

At higher copper(I) concentrations, where the electron signal becomes biexponential, another intermediate with a spectrum like that shown in Figure 1, spectrum 2 (taken 500 ns after the laser pulse on a sample that is 0.015 M $CuClO_4$ in 3.04 M $NH_3$), forms immediately after the pulse and decays with a first-order lifetime that increases nearly linearly with respect to copper(I) concentration, as shown in Figure 2. The amount of transient formed increases with copper(I) concentration, as indicated by the initial absorbance of the 400-nm signals, also shown in Figure 2. Spectrum 2 of Figure 1 is observed consistently over a wide variety of copper(I) and ammonia concentrations, indicating that there is probably only one absorbing long-lived intermediate (besides the hydrated electron) formed promptly after absorption of the laser pulse. It appears that the lifetime of this species is very sensitive to the concentration of $Cu(NH_3)_2^+$ and/or $Cu(NH_3)_3^+$ but not to that of the ligand, $NH_3$. The most reasonable

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explanation for this behavior is that there is a prompt establishment of an equilibrium,

$$\underset{[I]}{*Cu(NH_3)_3^+} + Cu(NH_3)_2^+ \rightleftharpoons \underset{[II]}{*Cu_2(NH_3)_5^{2+}} \quad (3)$$

between monomeric copper(I) species, one of which is an excited state, [I], and a dinuclear excited species, [II], which is an *exciplex*. The lack of sensitivity of decay lifetime to ammonia concentration implies that the ground-state species forming the exciplex is $Cu(NH_3)_2^+$ rather than $Cu(NH_3)_3^+$ since the relative concentration of the former is little affected by ammonia concentration whereas that of the latter is strongly affected (see eq 1). Although the kinetics of such coupled systems can be analyzed in detail,[2,5,12] the linearity and near zero intercept[13] of lifetime-vs-copper(I) concentration plot of Figure 2 can be interpreted in terms of the rapidly equilibrated system of eq 3 decaying primarily through the rate-controlling decay of species [I]. Thus the rate of decay of [II] should follow that of [I], which would be given by $k_{[I]}$-$[*Cu(NH_3)_3^+]$, where $k_{[I]}$ is the first-order decay constant of [I], which may decay by radiationless deactivation, and/or by the ejection of electron,

$$*Cu(NH_3)_3^+ \rightarrow e_{aq}^- + Cu(NH_3)_3^{2+} \quad (4)$$

Using the excited-state equilibrium constant, $K_{ex}$, one can show that the lifetime of the decay is given by $K_{ex}[Cu(NH_3)_2^+]/k_{[I]}$. Since the experimental slope in Figure 2 is $8.5 \times 10^{-4}$ s $M^{-1}$, it becomes apparent that the value of $K_{ex}$ must be very large, suggesting that the dinuclear excited species is quite stable.

If the concentration of Cu(I) is low enough to result in an electron decay lifetime of several hundreds of nanoseconds but high enough to produce a strong absorbance by the excited dinuclear complex, the 700-nm decay signal becomes biexponential as shown by Figure 3C, which is to be compared to the simple monoexponential decay at a lower copper concentration in Figure 3A. The decay of the dinuclear species at the same copper concentration as in Figure 3C is shown by the 400-nm absorbance signal in Figure 3B, producing a biexponential decay the first lifetime of which is about the same as the second decay lifetime in Figure 3C, suggesting that the latter corresponds also to the decay of the dinuclear intermediate. To verify that this secondary decay of the 700-nm signal is consistent with eq 4, Figure 4 shows the time-resolved spectra taken at the time delays marked in Figure 3C. At 50 ns delay time the spectrum is dominated by that of the promptly ejected hydrated electron, with a small shoulder at 400-nm corresponding to the dinuclear complex. At 600 ns, however, the prompt electron should have decayed to less than 8% of its original concentration (from the 235-ns lifetime of the initial decay in Figure 3C), yet the 700-nm absorbance of the electron is clearly stronger than this. Even at 2000 ns, where the prompt electron should have decayed to 0.02% of its original concentration, its band can clearly be seen. Moreover, during the secondary decay region the ratios of the electron absorbance at 700 nm to the absorbance of the dinuclear complex at 400 nm remain roughly constant, indicating a steady-state electron concentration decaying simultaneously with that of the dinuclear complex. Thus, we conclude that the long-lifetime component of the biexponential 700-nm decay is at least partially due to the delayed ejection of electrons, according to eq 4.

Reports of inorganic excimers[14−16] and dinuclear exciplexes[17−20] are rare. McMillin et al. have reported extensively on excited cationic diimine complexes of copper(I) forming exciplexes with Lewis bases,[21−24] but this is the first example to our knowledge of a dinuclear copper(I) exciplex, as well as the first example of a cationic inorganic complex that undergoes delayed electron photoejection.

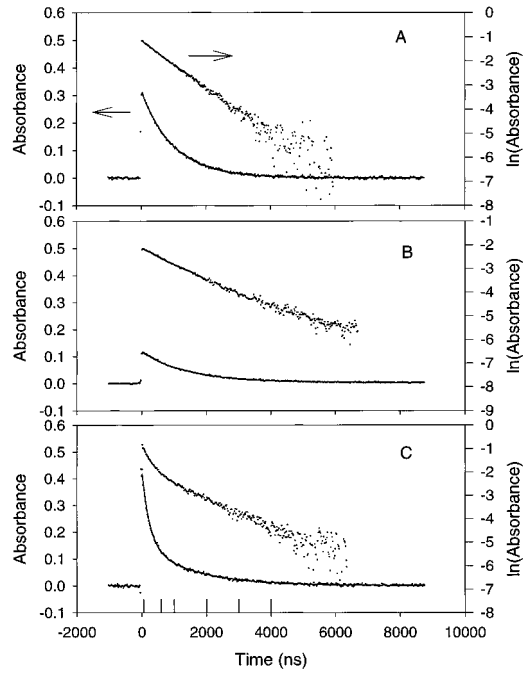


**Figure 3.** Transient absorbance (with mono- or biexponential fit) and ln(absorbance) vs time for solutions of $CuClO_4$ in 2.0 M $NH_3$ flashed in a 5-cm cuvette at 266 nm: (A) [Cu] = 0.00133 M measured at 700 nm; (B) [Cu] = 0.00186 M measured at 400 nm; (C) [Cu] = 0.00186 M measured at 700 nm. Markers show delay times for spectra in Figure 4.

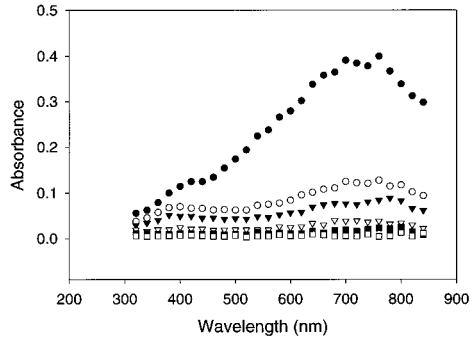


**Figure 4.** Time-resolved spectra of the same solution as in Figure 3B,C with delay times of (●) 50, (○) 600, (▼) 1000, (▽) 2000, (■) 3000, and (□) 4000 ns.

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