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Are excimers formed along with hydrated electrons in the UV excitation of cyanocuprate(I) ions in aqueous solution?

Kenneth L. Stevenson*, Jessica H. Jarboe

Department of Chemistry, Indiana University-Purdue University at Fort Wayne, Fort Wayne, IN 46805, USA

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Abstract

The three cyanocuprate(I) complexes, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$, photoeject electrons with high efficiency when excited in aqueous solution by 266 nm laser pulses of 7 ns duration with quantum yields of 0.37 ± 0.06, 0.224 ± 0.021, and 0.240 ± 0.005, for $Cu(CN)_2^-$ (at 2 M ionic strength), $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$ (both measured at 1 M ionic strength). Along with hydrated electrons, two transient intermediates, absorbing at 460 and 340 nm, respectively, form consecutively after excitation through bimolecular reactions with ground-state Cu(I) in solutions of $Cu(CN)_2^-$, and $Cu(CN)_3^{2-}$, but not in $Cu(CN)_4^{3-}$. All photoprocesses are essentially monophotonic. A mechanism is proposed that suggests the formation of a dinuclear excited-state complex such as an excimer. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrated electron; Excited-state; Excimer

1. Introduction

There have been numerous reports by us and others on the simultaneous formation of luminescent exciplexes and hydrated electrons in the UV-laser flash excitation of aqueous anionic Cu(I) complexes containing halo ligands [1–6] as well as in mixed-ligand halodicyanocuprate(I) complexes [3,7–12]. More recently, we have reported on the formation of dinuclear exciplexes or excimers having lifetimes in the microsecond range, accompanied by hydrated electron formation but not by luminescence, in the UV excitation of aqueous cationic Cu(I) complexes of ammonia [3,13,14], methylamine and ethylamine [14]. In the latter case, it appears that the dinuclear excimers or exciplexes must have a copper–copper bond because of the inability of the ammonia or amine nitrogen atom in such ligands to form bridged oligomers. In preliminary laser flash experiments with the anionic dicyanocuprate(I) complex it was observed that at higher concentrations of the copper, a transient absorbance band appears in the 400–500 nm region, which was the primary evidence for dinuclear excited-state species formation in the ammonia and amine complexes. Moreover, at all concentrations of complex, hydrated electrons are formed with a high quantum yield, which is consistent with earlier CW experiments [11]. We report here evidence that suggests that dinuclear excimers and hydrated electrons are simultaneously formed upon UV excitation of di- and tricyanocuprate(I), but that in tetracyanocuprate(I) only electrons are produced.

2. Experimental section

Solid potassium dicyanocuprate, which served as the starting material for the di-, tri-, and tetracyanocuprate(I) solutions, was prepared according to the method described by Horváth, et al. [11] from reagent grade potassium cyanide and Cu(I) cyanide. Aqueous solutions, which were prepared from triply-deionized water, contained sodium perchlorate to adjust the ionic strength, and potassium dicyanocuprate(I) and potassium cyanide were added in a 1:0, or 1:1 M ratio for studies of $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$, respectively. For study of $Cu(CN)_4^{3-}$, the concentration of added cyanide was increased to about 20 times that of $Cu(CN)_2^-$ to ensure that the residual concentration of $Cu(CN)_3^{2-}$ would be small compared to that of $Cu(CN)_4^{3-}$, owing to the latter's relatively small stepwise formation constant of 32 ± 18 in water [15]. After the solutions were prepared, they were bubble-degassed with argon for 30 min. A flow-through 1 cm cuvette was used for all laser measurements such that only fresh, oxygen-free solutions were exposed to the laser pulse. The Nd–YAG laser kinetic spectrometer system and the techniques for determining quantum yields have been described previously [1,16].

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* Corresponding author. Tel.: +1-219-481-6289; fax: +1-219-481-6070.
E-mail address: stevenso@ipfw.edu (K.L. Stevenson).

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3. Results and discussion

3.1. Dicyanocuprate(I)

3.1.1. Time-resolved spectra

The time-resolved spectra resulting from 266 nm excitation of dicyanocuprate(I) (2 M ionic strength) at low (1.0 mM) and high (7.0 mM) concentration are shown in Fig. 1. The dominant feature of both sets of spectra is the strong absorbance at 700 nm, especially at short delay times, and this can be attributed to that of the hydrated electron [17]. Although the intensity of this band at 10 ns band is slightly less in the 1 mM solution due to incomplete absorption of the laser pulse, the band disappears more quickly in the 7 mM solution because of scavenging by the dicyanocuprate(I) ion. The inset shows that the decay at 700 nm is not monoexponential as would be expected from the pseudo first-order kinetics that would result from Cu(I) scavenging, suggesting that other longer-decaying species (see the following sections) also absorb in this wavelength region. Another band, with maximum at 460 nm, appears after several tens of nanoseconds, and is much more obvious at higher concentration of dicyanocuprate(I). Moreover, it can be seen in the 7 mM solution that as this band decays there is a growing-in at 340 nm. This suggests there are three separate species associated with these bands: the electron, absorbing at 700 nm; a short-lived species, which we will identify as **I**, absorbing at 460 nm; and a longer-lived species, **II**, absorbing at 340 nm.

The maximum intensity of the 460 nm band, **I**, seems to appear at all copper concentrations after 100 ns, as seen in Fig. 2 which shows the 100 ns spectra for solutions in which

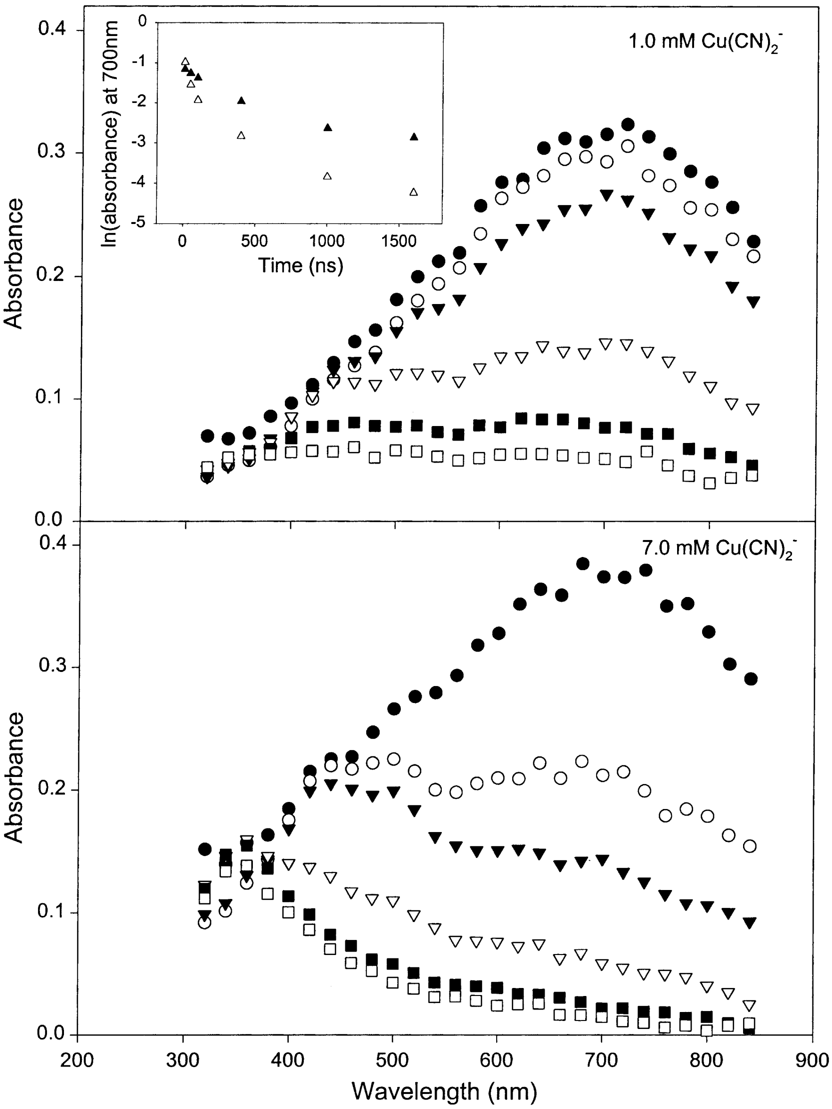


Fig. 1. Time-resolved absorbance spectra of solutions in 1 cm cuvette containing 2.0 M $NaClO_4$ and $Cu(CN)_2^-$ at 1.0 mM (top) and 7.0 mM (bottom) after being excited by 7 ns, 266 nm laser pulse, taken at time delays of (●) 10 ns, (○) 50 ns, (▼) 100 ns, (▽) 400 ns, (■) 1000 ns, and (□) 1600 ns. Inset, ln(absorbance) at 700 nm vs. time for (▲) 1 mM, and (△) 7 mM $Cu(CN)_2^-$ solutions.

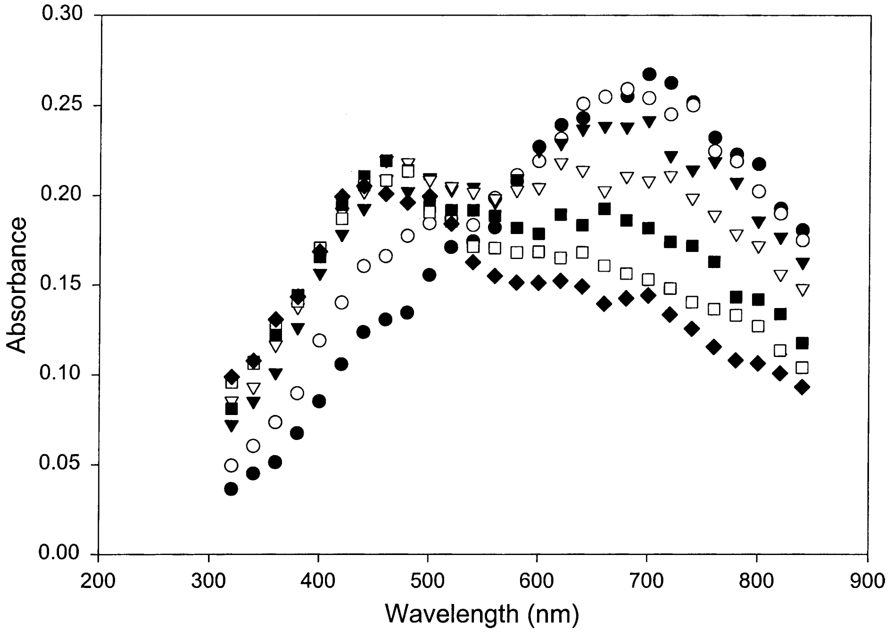


Fig. 2. Time-resolved absorbance spectra of solutions in 1 cm cuvette containing 2.0 M $NaClO_4$ and (●) 1.0 mM, (○), 2.0 mM, (▼) 3.0 mM ns, (▽) 4.0 mM, (■), 5.0 mM, (□) 6.0 mM, (◆) 7.0 mM $Cu(CN)_2^-$ 100 ns after being excited by 7 ns, 266 nm laser pulse.

the copper concentration was varied from 1.0 to 7.0 mM, keeping the laser energy constant. What is evident from this is that the intensity of the 460 nm band is sensitive to copper concentration at lower concentrations, but levels off at higher concentrations of copper. This is more clearly seen from the plots of Fig. 3, which compare the maximum intensity of the 700 nm band (at 10 ns) to that of the 460 nm band (at 100 ns). Although both bands increase with copper concentration and then level off, the ratio of the intensities of the 60–700 nm band also increase and level off, as seen at the bottom of Fig. 3, indicating that the 460 nm band intensity increase is caused by some concentration effect

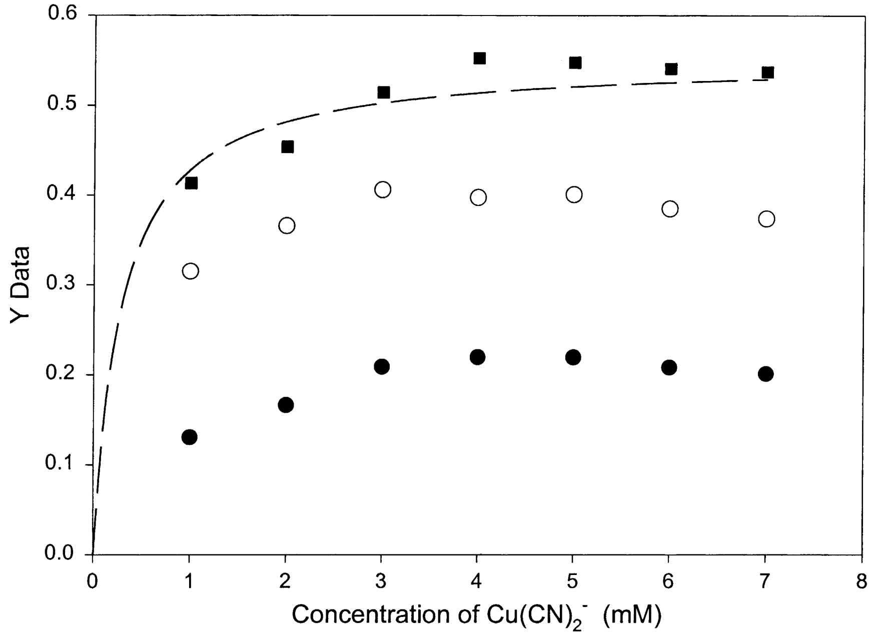


Fig. 3. Absorbance of (●) 460 nm band at 100 ns delay time, and of (○) 700 nm band at 10 ns delay time, after exposure of solutions containing 2.0 M $NaClO_4$ and $Cu(CN)_2^-$ to 7 ns, 266 nm laser pulse, as a function of copper concentration. Ratio (■) of these two absorbances as a function of copper concentration. (- - -) Fit to the ratio (see Eq. (3)).

in addition to the increasing absorbance of the sample at the laser wavelength. One plausible explanation for this is that a metastable excited-state, such as a triplet form of the dicyanocuprate(I), decays by two pathways, one of which is unimolecular and the other bimolecular, as follows:

$$^3\mathrm{Cu(CN)_2}^- \xrightarrow{k_1} \mathrm{Cu(CN)_2}^- \quad \text{thermal deactivation} \tag{1a}$$

and

$$^3\mathrm{Cu(CN)_2}^- + \mathrm{Cu(CN)_2}^- \xrightarrow{k_2} \mathbf{I} \tag{1b}$$

Such a decay should conform to the differential rate law:

$$\frac{-\mathrm{d}[^3\mathrm{Cu(CN)_2}^-]}{\mathrm{d}t} = k_1 + k_2[\mathrm{Cu(CN)_2}^-] \tag{2}$$

such that as the concentration of $\mathrm{Cu(CN)_2}^-$ increases the bimolecular reaction becomes dominant and the triplet is converted quantitatively into **I**.

3.1.2. Decay kinetics

Further evidence for a bimolecular formation reaction involving ground-state $\mathrm{Cu(CN)_2}^-$ can be obtained from the transient decay curves at 460 nm, a typical example of which is shown in Fig. 4. The complex curve can be resolved into a triexponential function consisting of: (1) a fast, 19 ns decay lifetime; (2) a fast, 44 ns growing-in lifetime; and (3) a slower, 928 ns decay lifetime. If we can identify the second and third components as the formation and decay of **I**, and the first component as some kind of fast ligand-exchange or reorganization reaction perhaps involving the Cu(II) species formed along with the electron, we can determine the rate constant for the bimolecular reaction (1b), from the dependence of the growing-in rate constant on copper concentration, the plot for which is shown in Fig. 5. The slope of the linear regression, forced through the origin, yields a value of $k_2 = 1.3 \times 10^{10}$ (±20%) $\mathrm{M^{-1}\,s^{-1}}$, which suggests this reaction is diffusion-controlled.

Because of the high error limits of this linear plot, it is not possible to obtain a reliable intercept that would give the first-order rate constant for the deactivation reaction (1a), but we can estimate its value using the behavior exhibited in Fig. 3. If we let C and D be concentration of products from reaction (1a and b), respectively, it is easy to show that at all times $C/D = k_1/k_2[\mathrm{Cu(CN)_2}^-]$. Moreover, we can assume that C is proportional to 0.55-R, and D is proportional to R, where R is the absorbance ratio of Fig. 3, and 0.55 is the approximate saturation value of R. Thus, we obtain the expression,

$$R = \frac{0.55k_2[\mathrm{Cu(CN)_2}^-]}{k_1 + k_2[\mathrm{Cu(CN)_2}^-]} \tag{3}$$

from which the fit (dashed line in Fig. 3) yields a value of $k_1 = 3.7 \times 10^6\,\mathrm{s^{-1}}$ (±50%).

The simultaneous decay of the 460 nm band with the growing-in of the 340 nm band is shown in Fig. 6 for a 5 mM solution of $\mathrm{Cu(CN)_2}^-$. That species **I** is the precursor of **II** is confirmed by the same linear dependence of their first-order rate constants, determined from biexponential fits to curves such as those in Fig. 6, on concentration of $\mathrm{Cu(CN)_2}^-$, as shown in Fig. 7. Thus, there is another bimolecular reaction, with rate constant determined from the slope of Fig. 7, $k_2' = 1.6 \times 10^8\,\mathrm{M^{-1}\,s^{-1}}$ (±30%), between **I** and $\mathrm{Cu(CN)_2}^-$ to form another species that has a characteristic absorption at 340 nm. The absorption spectrum of this species can be taken as that of the 1600 ns spectrum of the 7 mM $\mathrm{Cu(CN)_2}^-$

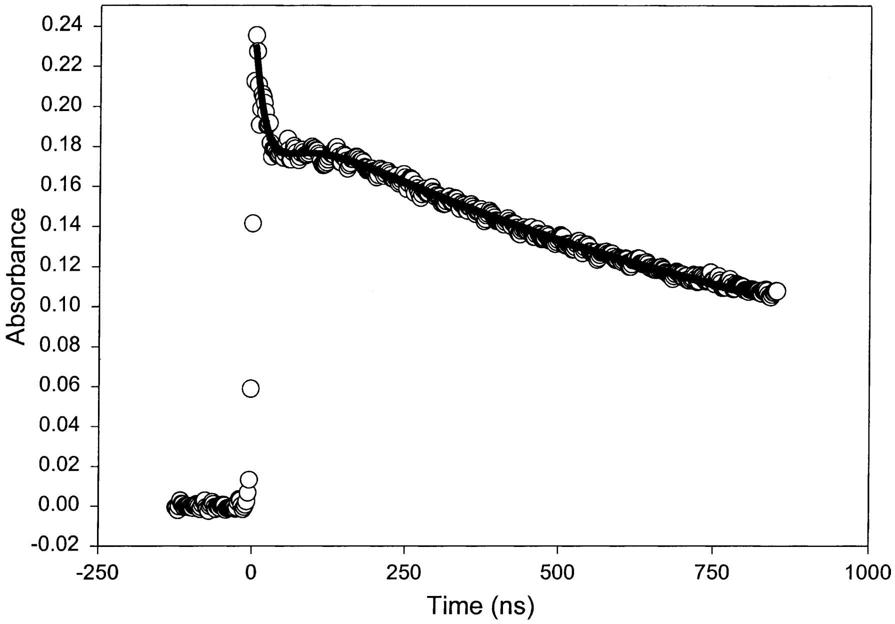


Fig. 4. Transient absorbance curve at 460 nm (○) along with triexponential fit for solution that is 3.0 mM $\mathrm{KCu(CN)_2}$ (—) in 2 M $\mathrm{NaClO_4}$ averaged over three exposures to a 7 ns, 266 nm laser pulse, 1 cm cuvette. Lifetimes of the three components are 19.0, 44 and 928 ns.

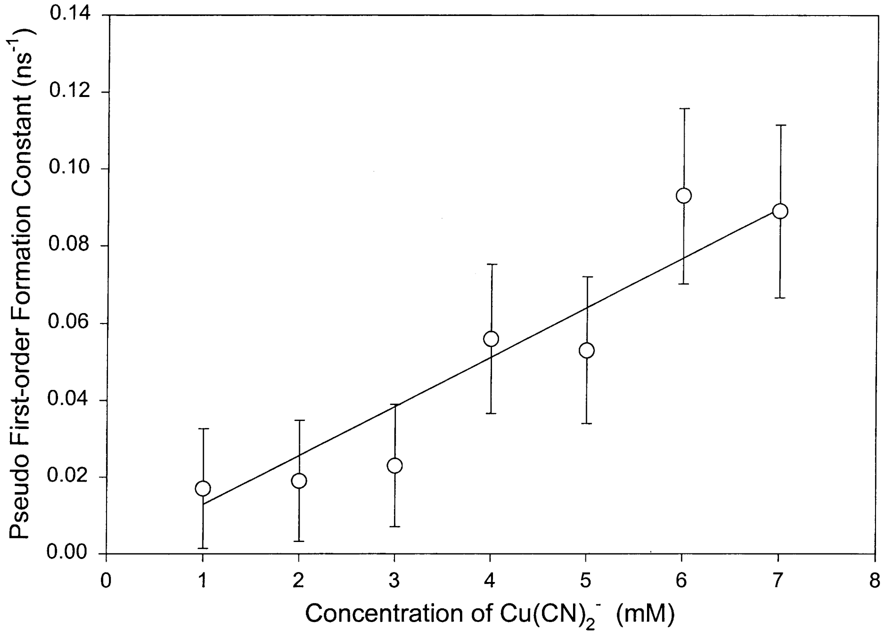


Fig. 5. Pseudo first-order rate constant for the growing-in components of the 460 nm absorbance transients, on 1 μs time scale (as in Fig. 4), for solutions containing 2.0 M $NaClO_4$ at varying concentration of $Cu(CN)_2^-$, after exposure to 7 ns, 266 nm laser pulse.

in Fig. 1, which shows a band at 340 nm and another very weak band at about 600 nm. The long decay of the 340 nm band has a lifetime of about 4 μs, which is the same as the second, long decay of the 460 nm band in Fig. 6, indicating that these represent the decay of the same species. Moreover, this long decay does not seem to correlate with concentration of $Cu(CN)_2^-$, suggesting that the **II** decays through a unimolecular thermal deactivation and/or decomposition.

3.1.3. Photonicity and quantum yield

If we can use the maximum absorbances at 670, 460 and 340 nm of plots like those in Fig. 6 as relative indicators

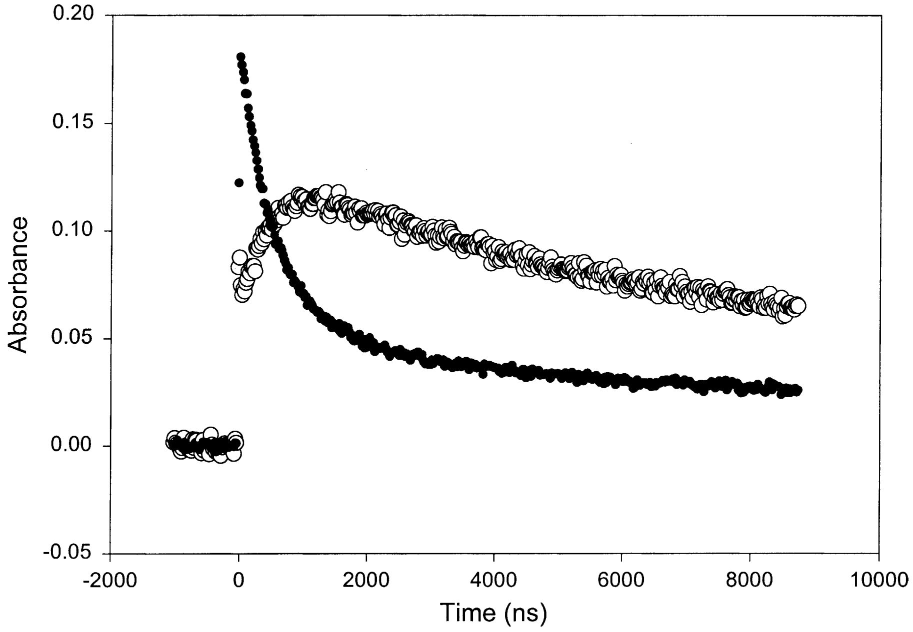


Fig. 6. Absorbance vs. time transients at (○) 340 nm and (●) 460 nm for is 5.0 mM $KCu(CN)_2$ in 2 M $NaClO_4$ averaged over three exposures to a 7 ns, 266 nm laser pulse, in a 1 cm cuvette.

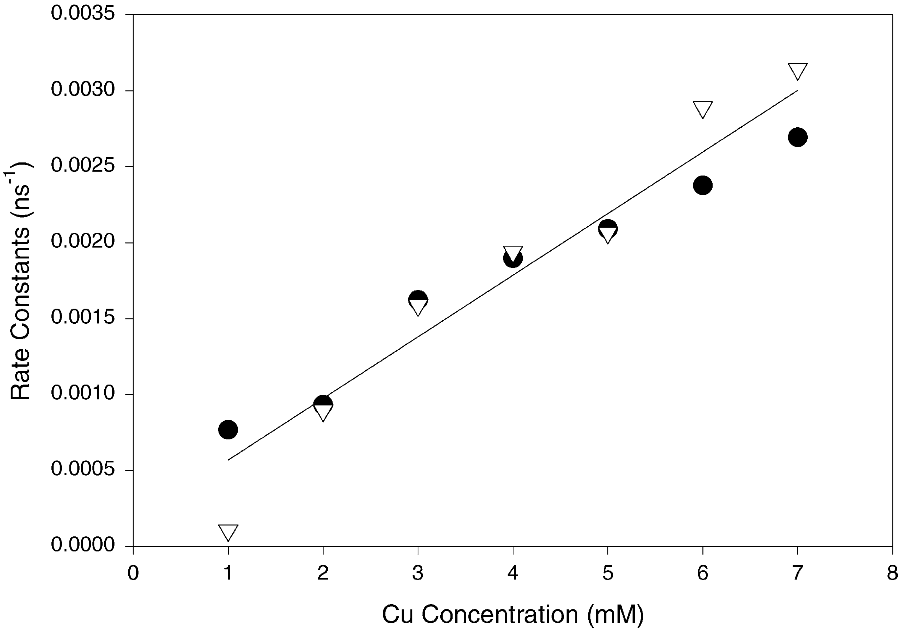


Fig. 7. Pseudo first-order rate constant for the growing-in components of the (▽) 340 nm and the first, long decay (●) at 460 nm absorbance transients, on 10 μs time scale (as in Fig. 6), for solutions containing 2.0 M $NaClO_4$ at varying concentration of $Cu(CN)_2^-$, after exposure to 7 ns, 266 nm laser pulse.

of the concentrations of hydrated electron, species **I** and **II**, respectively, formed after the excitation laser pulse, it is possible to do power studies to indicate the photonicity of the formation of each of these three species. Fig. 8 shows a double logarithmic plot of these maximum absorbances for a 7 mM solution of $Cu(CN)_2^-$ versus that at 670 nm for a solution of 1 mM sodium hexacyanoferrate(II), which can be used as an actinometer and is known to photoeject hydrated electrons when irradiated in the UV with a quantum yield of 0.52 [18]. The slopes of all three plots are 1.2 ± 0.1, 1.2 ± 0.1, and 1.1 ± 0.1, respectively, which leads to two conclusions: (1) the hydrated electron, and species **I** and **II**, all arise from a common precursor excited-state; and (2) the formation of this precursor is primarily monophotonic, with

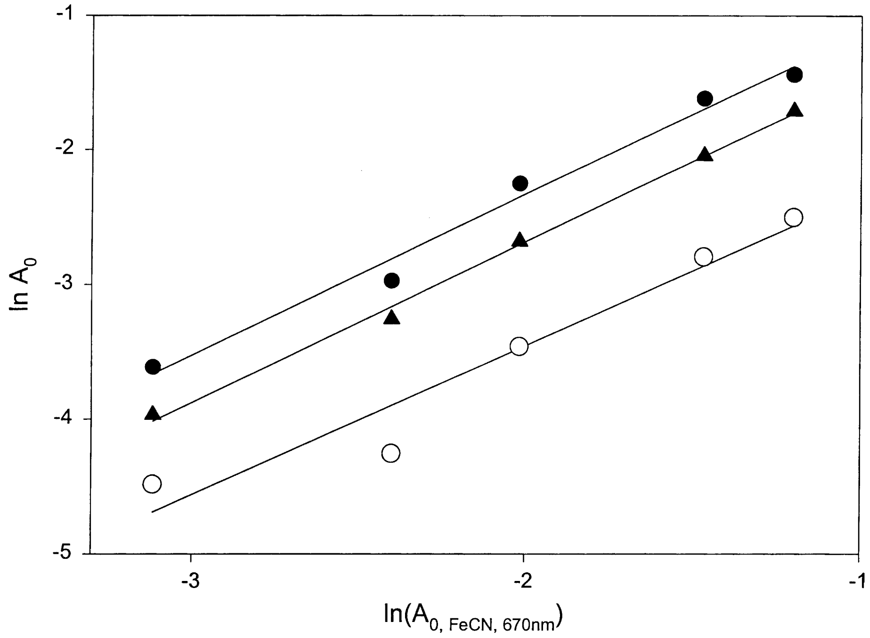
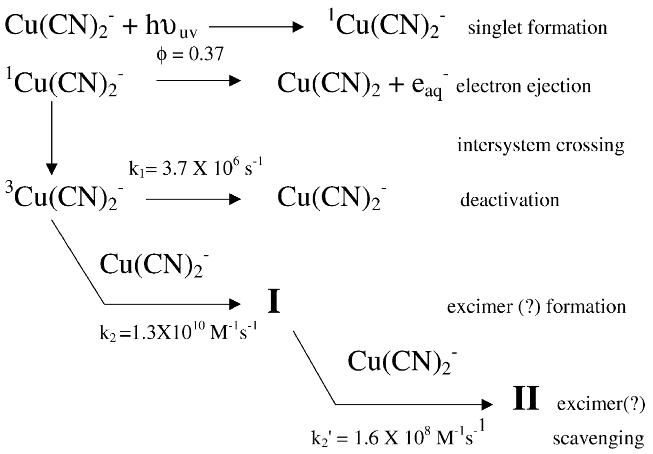


Fig. 8. Natural logarithm of maximum transient absorbance at (●) 670 nm (2 μs timescale), (▲) 460 nm (10 μs timescale), and (○) 340 nm (10 μs timescale) for solutions containing 2.0 M $NaClO_4$ and 7.00 mM $Cu(CN)_2^-$, after exposure to 7 ns, 266 nm laser pulse of varying pulse energy.

a small biphotonic component. Moreover, the average quantum yield of the electron formation, $\phi = 0.37 \pm 0.06$, is quite high, and therefore so must be its precursor. The most likely precursor excited-state has been previously characterized as a charge-transfer-to-solvent (CTTS) singlet state [11], which we denote as $^1Cu(CN)_2^-$.

3.1.4. Proposed mechanism

All of these results lead to a mechanism as outlined in Scheme 1. The initiation step is the 266 nm excitation of $Cu(CN)_2^-$, leading to the short-lived singlet, $^1Cu(CN)_2^-$. This singlet then undergoes two rapid, competing decays: (1) ejection of electron and formation of Cu(II) cyanide; and (2) intersystem crossing to form the longer-lived triplet, $^3Cu(CN)_2^-$ which may decay through a mono-exponential deactivation ($k_1 = 3.7 \pm 10^6\ s^{-1}$), such as a



Scheme 1.

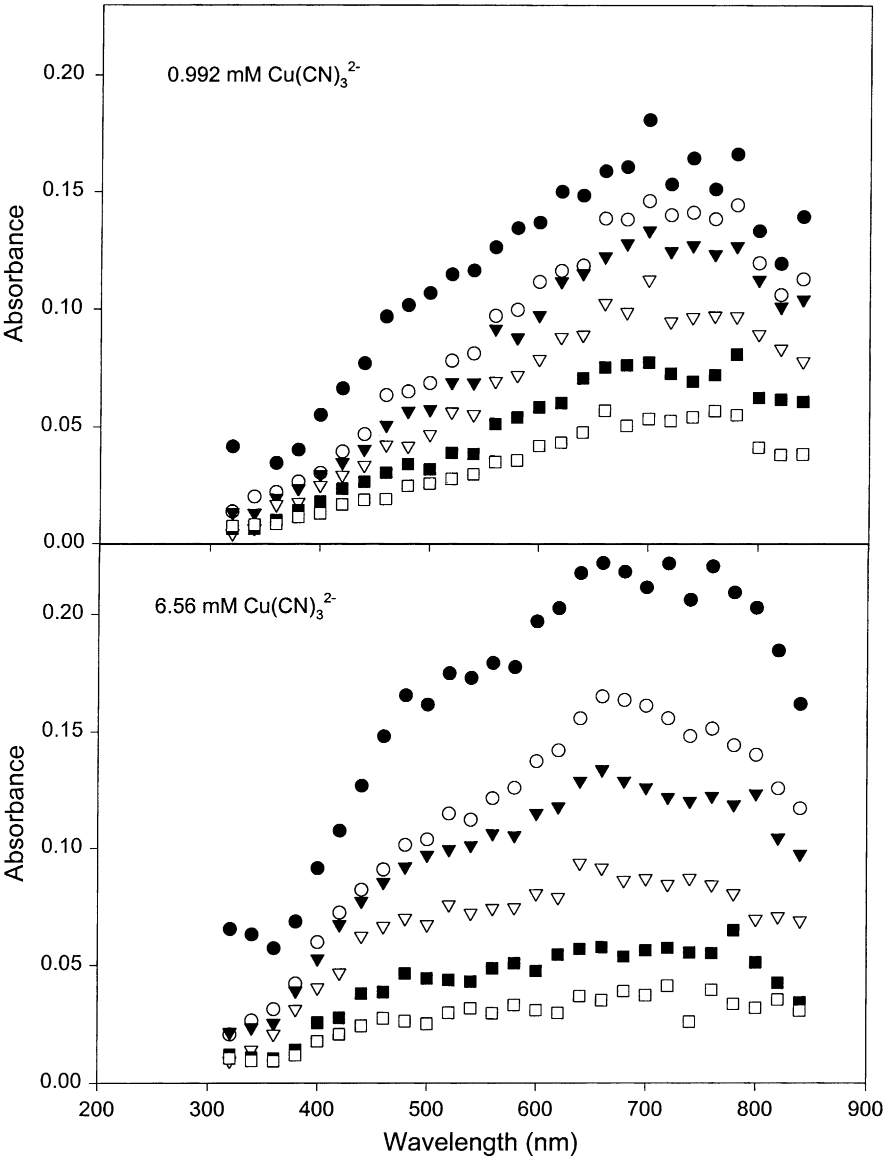


Fig. 9. Time-resolved absorbance spectra of solutions in 1 cm cuvette containing 1.0 M $NaClO_4$ and $Cu(CN)_3^{2-}$ at 0.992 (top) and 6.56 mM (bottom) after being excited by 7 ns, 266 nm laser pulse, taken at time delays of (●) 10 ns, (○) 50 ns, (▼) 100 ns, (▽) 400 ns, (■) 1000 ns, and (□) 1600 ns.

delayed electron ejection [1,2,13], or by bimolecular, diffusion-controlled reaction with ground-state $Cu(CN)_2^-$ ($k_2 = 1.3 \times 10^{10}\,M^{-1}\,s^{-1}$) to form **I**, which can react further with ground-state $Cu(CN)_2^-$ ($k'_2 = 1.6 \times 10^8\,M^{-1}\,s^{-1}$) forming species **II**.

What are the identities of species **I** and **II**? It is possible that **I** may actually be a stoichiometric mixture of $Cu(CN)_2^{2-}$ and $Cu(CN)_2$ formed in an electron-transfer reaction. If this were the case, the strong band at 460 would have to belong to one or both of these species. However, at low concentration of $Cu(CN)_2^-$ the 460 nm band does not seem to form as indicated in Fig. 1, although we should expect it to grow-in if $Cu(CN)_2^{2-}$ absorbs at this wavelength since it would be the primary product of the electron-scavenging by $Cu(CN)_2^-$. Furthermore, $Cu(CN)_2$ is formed along with the hydrated electron, yet the upper plot in Fig. 1 does not indicate any strong 460 nm band formed simultaneously with the electron. We suggest, therefore, that **I** is a dinuclear species, or excimer, possibly in the triplet state, such as in $^3Cu_2(CN)_4^{2-}$. The bonding between the two oligomers might be through a CN-bridge, or it is possible that a Cu–Cu bond forms, as we have suggested for dinuclear ammonia and amine Cu(I) excited-state complexes [3,13,14].

The identity of species **II** is a little more difficult to infer. If **I** is indeed an excimer, then **II** might be a mixed-valence, Cu(I)–Cu(II) dinuclear species formed by electron transfer between the excimer and the ground-state $Cu(CN)_2^-$. On the other hand, if **I** is a mixture of $Cu(CN)_2^{2-}$ and $Cu(CN)_2$, then **II** could be either of two mixed-valence dinuclear species, such as Cu(I)–Cu(II) or Cu(0)–Cu(I). In any case, further studies, such as time-resolved Raman spectroscopy, will be needed to confirm the nature of species **I** and **II**.

3.1.5. Tricyanocuprate(I)

Comparative time-resolved spectra for 0.992 and 6.56 mM $Cu(CN)_3^{2-}$ in 1 M ionic strength are shown in Fig. 9 for 10–1600 ns time delays. As in the case of dicyanocuprate, there is a species formed at higher copper concentrations that absorbs fairly strongly at 460 nm. The hydrated electron ($\lambda_{max} = 700$ nm) forms with a reasonably high quantum yield in either solution, but it does not decay as quickly as in the dicyanocuprate solutions, presumably due to the higher negative, repulsive charge on the complex. Moreover, both in the low and high copper concentrations there is a very short-lived species decaying in 10–50 ns and absorbing strongly at 460–480 nm, as in the dicyanocuprate system, but to a much greater degree. The fact that this short-decaying species appears in both the low and high copper concentrations, but the longer-lived 460 nm absorbing species seems to form more readily at high copper concentration is another indication that the former is probably a monomer and the latter may be an excimer, as was suggested for the dicyanocuprate system.

The ln–ln plots (not shown but similar to those for the dicyanocuprate system, Fig. 8) resulted in slopes of 1.08, 0.93, and 0.91 for the initial absorbances at 670, 460 and 340 nm, respectively, indicating that the species absorbing at all of these wavelengths are formed monophotonically. The quantum yield for electron production is 0.224 ± 0.021.

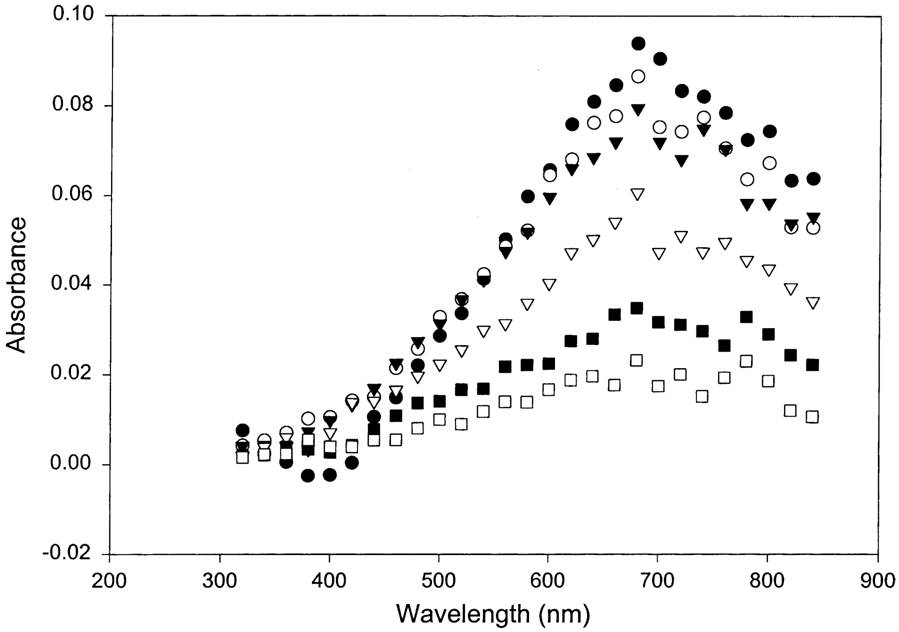


Fig. 10. Time-resolved absorbance spectra of solutions in 1 cm cuvette containing 1.0 M $NaClO_4$ and 6.17 mM $Cu(CN)_4^{3-}$ with 0.12 M excess CN^- after being excited by 7 ns, 266 nm laser pulse, taken at time delays of (●) 10 ns, (○) 50 ns, (▼) 100 ns, (▽) 400 ns, (■) 1000 ns, and (□) 1600 ns.

3.1.6. *Tetracyanocuprate(I)*

Since the stepwise formation constant [15] of $Cu(CN)_4{}^{3-}$ has a value of about 32 in water, solutions of CuCN in KCN were prepared to give an excess of about 0.12 M CN^- after formation of the complex. In this way, the ratio of tetra- to tricyanocuprate could be maintained at about 4:1 so that the primary absorbing species was the tetracyanocuprate. Fig. 10 shows the time-resolved spectra of a 6.17 mM tetracyanocuprate(I) solution containing 1 M $NaClO_4$ after exposure to the 266 nm pulse. Although the copper concentration is as high as it was in the di- and tricyanocuprate(I) solutions that showed clear formation of a 460 nm absorbing intermediate, no such intermediate absorbance is seen in these spectra; rather, only the broad electron absorbance band is observed. This suggests that the tetracyano complex is incapable of entering an excited-state that can form a dinuclear species, which is consistent with the fact that the Cu(I) is already coordinatively saturated by the cyano ligands and would not be able to form a dinuclear complex. We do notice some luminescence in the 10 ns spectrum at about 400 nm (seen as a negative absorbance), but this can be attributed to the excess CN^-, confirmed by the appearance of the same luminescence signal in a solution containing only KCN and $NaClO_4$.

The quantum yield of electron formation was calculated for this tetracyanocuprate(I) solution, yielding a value of 0.240 ± 0.005, indicating no significant difference in the ability of the $Cu(CN)_4{}^{3-}$ to photoeject electrons compared to $Cu(CN)_3{}^{2-}$.

4. Conclusions

1. All three cyanocuprate(I) complexes, $Cu(CN)_2{}^-$, $Cu(CN)_3{}^{2-}$, and $Cu(CN)_4{}^{3-}$, photoeject electrons with high efficiency when excited by 266 nm light.
2. Two intermediates, **I** and **II** (see Scheme 1), form after excitation through bimolecular reactions with ground-state Cu(I) in solutions of $Cu(CN)_2{}^-$, and $Cu(CN)_3{}^{2-}$, but not $Cu(CN)_4{}^{3-}$, suggesting the formation of dinuclear excited-state complexes such as excimers.
3. All photoprocesses are essentially monophotonic.

Acknowledgements

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