Prompt and Delayed Photoejection of Electrons in Aqueous Solution

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The hydrated electron was first observed and characterized in pulsed radiolysis studies,[1] but subsequently it has been observed in numerous photochemical systems as well. Besides the inorganic anions[2] such as Cl^-, Br^-, I^-, and SCN^-, a number of transition metal complexes with reducing metal centers,[3] such as $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $Ru(CN)_6^{4-}$, as well as low-valent metal cations[4] like Fe^{2+}, Cr^{2+}, and Ce^{3+}, all eject hydrated electrons in aqueous solution when irradiated in the ultraviolet region. Efficient electron photoejection has also been observed in aqueous solutions of copper(I) complexes,[5] such as CuX_3^{2-} (X = Cl, Br, I, CN), $Cu(CN)_2^-$, $Cu(CN)_2X^{2-}$,[6] and $Cu(NH_3)_3^+$.[7] Recently, attention has been focused on the ability of the copper(I) anionic complexes, in the presence of high concentration of halide ligands, to form blue−green emitting, presumably, triplet exciplexes after photoexcitation into the initial charge transfer state.[8] In our laser flash photolysis studies of the luminescence and transient absorption dynamics of copper(I) species forming exciplexes we noticed that flashed systems in which the luminescence lifetime is relatively short (ca. 100 ns or less) the electron absorption signal in the red is not a simple first- or second-order decay, but rather a biexponential function consisting of growing-in and decay terms. In this paper we wish to explain this behavior by pointing out that besides the ejection of an electron from the primary charge transfer excited state there is a secondary, very efficient delayed escape of the electron.

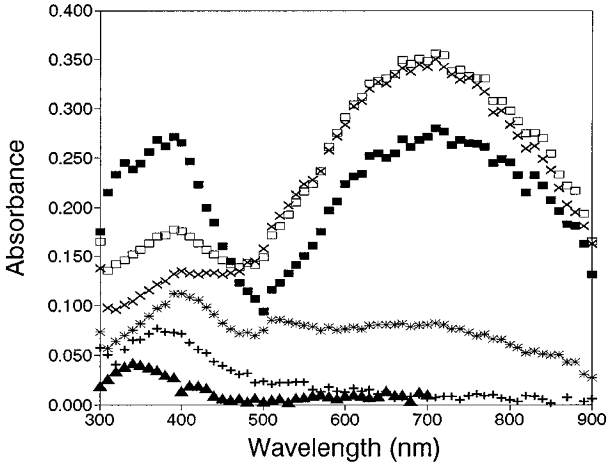

Figure 1. Time-resolved spectra of 266-nm pulsed solution containing 2.7×10^{-4} M CuCl and 5 M NaCl. Time delays: (■) 10 ns, (□) 100 ns, (×) 200 ns, (*) 1200 ns, (+) 4 μs, (▲) 17 μs.

Figure 1 shows the transient absorption spectra, at delay times ranging from 10 ns to 17 μs, in a solution of $CuCl_3^{2-}$ in 5 M NaCl (pH = 7, ambient temperature) flashed with a 266-nm, 7-ns pulsed laser. The formation of hydrated electron is confirmed by the strong 720-nm absorption band,[9] which becomes smaller and decays faster in the presence of electron scavengers such as H^+, N_2O, NO_3^-, and methyl viologen. Figure 1 clearly indicates that the electron band first appears to increase and then to decrease over time while the absorption between 300 and 400 nm only decreases. Because of the existence of the temporary isosbestic point at 460 nm, it is apparent that the delayed escape of the electron proceeds concomitantly with the initial part of the decay of short-wavelength absorption. Moreover, the short-wavelength decay lifetime is the same as that of the luminescence decay at any ligand concentration or solvent medium, confirming that the luminescent molecular entity identified as an exciplex has an absorption band peaking at about 390 nm.[10] Figure 2 shows a comparison of a luminescence decay signal (at 475 nm) with the transient absorption at 700 nm, from which has been extracted, using component-stripping analysis or iterative reconvolution,[11] the exponential growing-in component, suggesting that the delayed electron escape has about the same lifetime as the exciplex decay.

We have shown in earlier studies of anionic copper(I) systems very similar to this one that excitation of ground-state species

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[10] There are apparently two other bands appearing in the 300−400-nm range at longer times after the disappearance of the isosbestic point. These can be identified with (1) a copper(0) complex absorbing at 380 nm (cf. Sukhov, N. L.; Akinshin, M. A.; Ershov, B. G. *High Energy Chem.* **1986**, *20,* 303) formed by the scavenging of electrons by Cu(I) complex and (2) the Cl_2^- radical absorbing at 340 nm (cf. Jayson, G. G.; Parsons, B. J.; Swallow, A. J. *Faraday Trans. 1* **1973**, *69,* 1597) formed by a uni- or bimolecular reaction of excited copper(I) complex.

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in equilibrium, such as

$$\mathrm{CuY_2}^- + \mathrm{X}^- \rightleftarrows \mathrm{CuY_2X}^{2-} \tag{1}$$

where Y is cyano or halo and X is a halo ligand, results in singlet excited states (assigned as CTTS or d^9s^1 Rydberg states) of either complex, from which hydrated electrons are ejected. Moreover, we have confirmed that a competing pathway to electron ejection is the formation through intersystem crossing from the singlet species of long-lived triplets, which themselves rapidly establish an equilibrium,

$$^3\mathrm{CuY_2}^- + \mathrm{X}^- \rightleftarrows {}^3\mathrm{CuY_2X}^{2-} \tag{2}$$

The tricoordinated triplet, which is luminescent,[8a,f] has been termed an exciplex because of its ability to be formed by reaction of an excited state species with a ground-state ligand. Because this equilibration process occurs much faster than the decay of either species, they will disappear at the same rate, which is governed by the position of the excited-state equilibrium and the decay constants of $^3\mathrm{CuY_2}^-$ and $^3\mathrm{CuY_2X}^{2-}$. Since, in general, the decay constant for the former species is much greater than the latter, the observed decay lifetime increases with ligand concentration. The inset to Figure 2A, in which luminescence lifetimes for the chlorocuprate(I) system are plotted versus chloro ligand concentration, illustrates this behavior. Moreover, electron absorbance growing-in lifetimes are plotted on the same figure confirming that the emission and delayed electron ejection originate from the same species, which is $^3\mathrm{CuCl_3}^{2-}$. The inset to Figure 2A extrapolates to about 7−8 ns which is the lifetime of the dicoordinated triplet, the luminescence of which cannot be detected at room temperature.

Estimates of quantum yields for prompt and delayed electron ejection can be obtained from maximum absorbance values in transient signals like those of Figure 2B, resulting in comparable values, in the range of 0.2−0.3 (±10%), for both the prompt and delayed electron ejection. This confirms that the intersystem crossing to the triplet species must be a very efficient process. Furthermore, since maximum absorbance values for both prompt and delayed electron ejection are comparable even at low values of [Cl$^-$], it is reasonable to suppose that $^3\mathrm{CuCl_2}^-$ also decays through the delayed electron ejection mechanism.

We believe this is the first example of photochemical hydrated electrons being produced concurrently from two distinct types of excited states. Prompt ejection occurs immediately after the excitation from a very short-lived singlet CT state of high energy, whereas the delayed electron originates from a low-lying triplet level. While both the di- and tricoordinated species have this ability, the potential barriers are different for these two species. In principle, the formation of solvated electron can be described by an electron transfer from the potential minimum to another trap site in the nearby solvent through a potential barrier which is created by the negative charge-induced attractive polarization of the anion. The triplet excited state is naturally lower in energy than the singlet, so it would be expected to have a slower rate of "dissociation" to give the solvated electron. The coordination of the third halide ligand deepens the polarization well further resulting in the still slower electron escape of that triplet state complex. It is reasonable to assume that this property is not limited to the trichlorocuprate(I) ion alone, as we have observed similar behavior in other copper(I) anionic complexes having cyano and halo ligands. The only requirement is that halo ligands must be present, and this is precisely the condition for formation of the luminescent exciplex species in all cases.

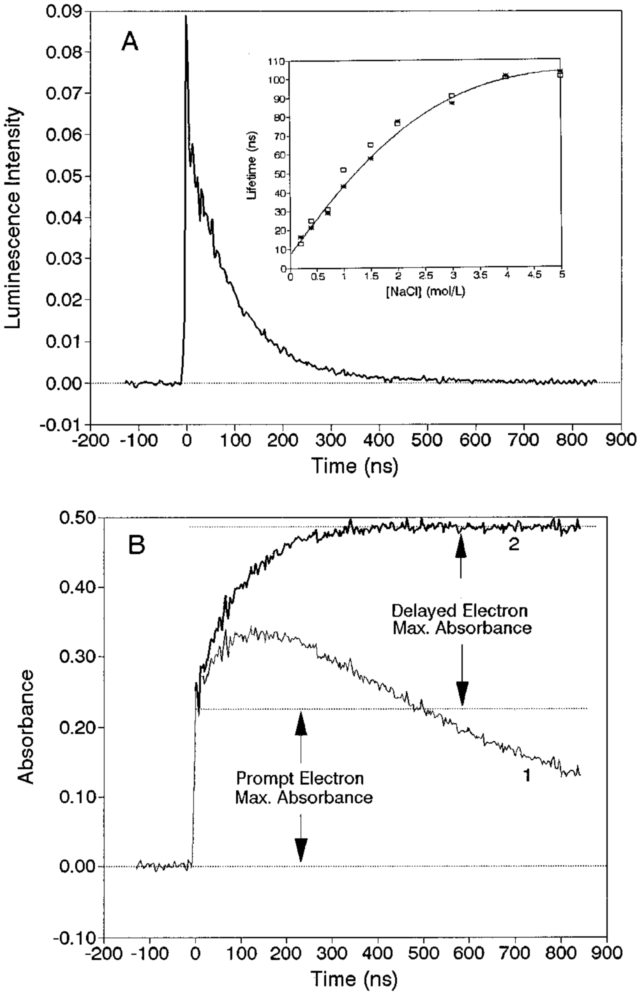

Figure 2. (A) Luminescence intensity signal, at 475 nm, for same flashed solution as in Figure 1. Inset: lifetimes of (*) luminescence decay and (☐) 700-nm absorbance growing-in in 2 × 10^{-4} M CuCl in neutral solutions of varying [NaCl] at constant 5 M ionic strength, $\mathrm{NaClO_4}$ medium, after absorption of 266-nm laser pulse. (B) (1) transient absorbance signal at 700 nm for same solution as in Figure 1; (2) growing-in signal extracted from (1).

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