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Prompt and Delayed Electron Ejection from Photoexcited Aqueous Bromo- and Chlorocuprate(I) Complexes

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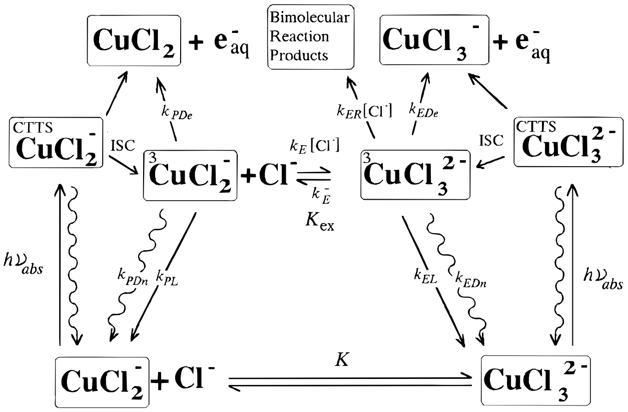
Two different routes for ejection of hydrated electrons by photoexcited $CuCl_2^-$ and $CuCl_3^{2-}$ have been observed: (1) a prompt (i.e. within the 5-ns laser pulse width) ejection directly from the charge-transfer excited states (characterized as CTTS or Rydberg states), and (2) a delayed ejection, with lifetimes of up to 105 ns, from the triplet states of the two complexes. These two processes have rather high quantum yields: 0.30−0.40 for the prompt ejection and 0.25−0.33 for the delayed ejection for the chlorocuprate(I) complexes. The delayed ejection process is the primary decay route for the two triplet species, $^3CuCl_2^-$ and $^3CuCl_3^{2-}$, which are formed by intersystem crossing from the charge-transfer excited states formed by absorption of light by the bis- and triscoordinated complexes in equilibrium in the ground state. Both of the chlorocuprate triplet excited states are weakly luminescent species. The triplet tris species, $^3CuCl_3^{2-}$, has a strong absorption band at 390 nm ($\epsilon \approx 27\,000$ M^{-1} cm^{-1}), and the biscoordinated species, $^3CuCl_2^-$, probably absorbs in the same region as well. Other intermediates such as Cu(0) complexes and $Cl_2^{\bullet-}$ radicals have also been observed as decay products. Prompt and delayed electron ejection has also been observed in $CuBr_3^{2-}$ with quantum yields of 0.25 and 0.18, respectively. A mechanism that incorporates a triplet excited state equilibrium is invoked to account for these observations.

Introduction

The formation of hydrated electrons by ultraviolet irradiation of the charge-transfer-to-solvent (CTTS)[1] bands of halocuprate(I), cyanocuprate(I), and dicyanohalocuprate(I) complexes in aqueous solution has been well-established by both continuous-wave (CW) scavenging studies and direct observation of the time-resolved hydrated electron spectrum in laser flash photolysis experiments.[1−6] Moreover, it has been observed[6−9] that such excitation simultaneously promotes the formation of a weakly luminescent species under conditions of high ligand concentration and high ionic strength with an emission band Stokes-shifted by about 200 nm from the photoactive absorption band centered at 270−280 nm common to all the complexes. Recent studies of the dependence of the luminescence quantum yield and lifetime on ligand concentration [9−11] have suggested that the luminescence is emitted by a triscoordinated triplet state formed either by intersystem crossing from the initial trihalo- or dicyanohalocuprate(I) excited state, which may be characterized as either a CTTS or metal-centered Rydberg state of d^9s^1 or d^9p^1 configuration, or by the rapid equilibration with a triplet biscoordinated excited state, itself formed by intersystem crossing from the charge-transfer excited state of the dihalo- or dicyanocuprate(I) complex. Although the bulk of the reported kinetic studies were in mixed-ligand dicyanohalocuprate systems, it has recently been demonstrated[12] that the luminescence of the trihalocuprate(I) complex, $CuBr_3^{2-}$, conforms to the same triplet tris complex formation and decay mechanism. Recent studies on the chlorocuprate(I) complexes, $CuCl_2^-$ and $CuCl_3^{2-}$, indicate that they also exhibit such triplet tris complex formation and decay behavior and that a major route of decay of the triplet tris complex and its triplet bis precursor is via delayed electron ejection.[13] Moreover, it now appears that luminescence is characteristic of *both* of the triplet intermediates. Scheme 1 presents the mechanism for formation and decay of the triplet species and for prompt and delayed electron ejection for the $CuCl_3^{2-}$ system, according to our present state of knowledge. This paper will present detailed evidence to support these assertions, to characterize several other intermediates that arise in the $CuCl_3^{2-}$ system during the first several microseconds after absorption of a photon, and to demonstrate that $CuBr_3^{2-}$ also conforms to Scheme 1.

SCHEME 1



Experimental Section

Copper(I) chloride or bromide, prepared as described earlier,[1] was the source of the bromo- and chlorocuprate(I) complexes

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in all of the solutions. Stock solutions were prepared from reagent grade sodium chloride, sodium bromide, hydrochloric acid, hydrobromic acid, or sodium perchlorate and standardized by density. In studies of the dependence of decay lifetimes on concentration of ligand, or H^+, etc., solutions were prepared directly in 1-cm cuvets using micropipets to deliver aliquots of stock solutions. The cuvettes were then bubble-degassed with Ar for 40 min, after which a small aliquot of a concentrated (0.01−0.02 M), degassed stock solution of CuCl in 5 M NaCl or CuBr in 5 M NaBr was introduced, followed immediately by the laser flash photolysis.

Transient absorbance and luminescence signals were obtained on such samples using the Nd:YAG laser system described previously.[11] For signals that were obviously monoexponential decays, lifetimes were determined by linear regression analysis of plots of the natural logarithm of absorbance or luminescence intensity vs time, using QuattroPro 3.0. For transient signals that were polyexponential, Sigmaplot 3.0 was used to fit the appropriate exponential equation to the data and determine the lifetimes and constants in the equation.

For the measurement of time-resolved spectra, a large amount of the solution to be irradiated was placed in a vessel and bubble-degassed, after which a weighed sample of CuCl was added. This solution was drawn through a flow-through cuvette, and at wavelength increments it was flashed, producing transient signals from which absorbances could be extracted at predetermined time delays. These were stored in the computer for subsequent reconstruction of the spectra. The path of the laser beam was either at a right angle or collinear with respect to the analyzing light beam.

Quantum yields of hydrated electron production were obtained in a given sample by comparing the electron absorbance signal at 700 nm, extrapolated to $t = 0$, to that of a reference chlorocuprate(I) solution flashed under identical conditions of laser power, wavelength, cuvette, geometric configuration of laser and analyzing beam, and optical density at the laser wavelength. Two methods were used for determining the reference quantum yield. In the first method, five solutions in which [CuCl] varied from 5.4×10^{-5} to 1×10^{-3} M were prepared in 5 M NaCl, and A_0 was measured using collinear beams, where A_0 is the electron absorbance obtained by extrapolating the ln(absorbance) plot back to $t = 0$. It was observed that A_0 leveled off to a value of 0.65 at the three highest concentrations of CuCl, for which the optical density at the laser wavelength of 266 nm varied from about 1 to 3.5. Thus, it was assumed that 0.65 was the absorbance of both prompt and delayed electrons produced when all the laser light was absorbed by the sample. The total number of photons of laser light absorbed by the reference sample was determined by exposing actinometric solutions of potassium tris(oxalato)ferrate(III) in the reaction cuvette to 10, 20, and 30 pulses of the laser beam at 266 nm. The solutions were developed with phenanthroline according to the accepted procedure,[15] which yielded 2.28×10^{-8} einsteins per shot. The total number of hydrated electrons produced by the absorbed laser photons could be calculated using the extinction coefficient of the hydrated electron, 19 000 cm^{-1} mol^{-1} L,[16] and the measured volume of the irradiated sample obtained from the dimensions of the cuvette and the beam diameter, and a quantum yield of 0.57 was obtained for the reference chlorocuprate(I) sample.

In the second method solutions of varying concentrations of sodium hexacyanoferrate(II) were flashed in the reaction cuvette with a laser beam at a right angle to the analyzing beam. The quantum yield of a reference chlorocuprate(I) sample with the same optical density at 266 nm as the hexacyanoferrate(II) sample could be obtained by comparison of its maximum absorbance signal at 700 nm to that of the flashed hexacyanoferrate(II) solution using the reported quantum yield, 0.52, for production of hydrated electrons by hexacyanoferrate(II) at 266 nm,[17] again resulting in a value of 0.57 for the chlorocuprate(I) quantum yield.

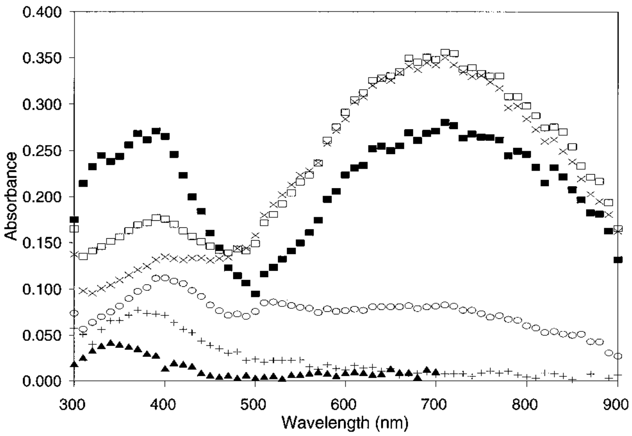

Figure 1. Time-resolved spectra of 266-nm pulsed solution containing 2.7×10^{-4} M CuCl and 5 M NaCl. Time delays: (■) 10 ns, (□) 100 ns, (×) 200 ns, (○) 1200 ns, (+) 4 μs, (▲) 17 μs.

Results and Discussion

Chlorocuprate(I) System. The time-resolved absorbance spectra of 266-nm laser-flashed CuCl in 5 M NaCl solution are shown in Figure 1 at a variety of delay times from 10 ns to 17 μs. The 17-μs spectrum was taken in a separate time-resolved experiment in which the wavelength range was 300−700 nm, rather than the 300−900-nm range that was used for the shorter delay times. There are two wavelength regions of interest in these spectra: (1) the 500−900-nm region having a peak at about 700 nm that can be ascribed to the absorbance of the hydrated electron;[18] and (2) the 300−400-nm region showing rather complex decay kinetics that will be assigned to the decay of several intermediates.

Hydrated Electron Ejection. It can be seen from the time dependence of the absorbances at 700 nm in Figure 1 that following the prompt, initial formation of hydrated electrons (10 ns) there is a secondary growing-in of the electron signal peaking at about 200 ns, followed by the decay. This is more clearly indicated by the 700-nm transient absorbance signal of Figure 2. Such a signal can be understood in terms of consecutive processes: a prompt ejection of electrons within the duration of the laser pulse followed by a delayed ejection of more electrons, simultaneous to the decay of all electrons over a longer time span. The kinetics of such a process is well-described[19] by a biexponential rate law in which the coefficient of the growing-in term is negative. Fitting the biexponential rate equation to absorbance transients yields both the electron growing-in and decay lifetimes, and such fits are shown on the transients in Figure 2 for both a 5-μs and 1-μs (inset) time scale.

The biexponential nature of the electron signal can be explained in terms of the mechanism of Scheme 1. After absorption of the photon by the copper(I) species the promptly ejected electron and the triplet excited states are formed simultaneously in the subnanosecond time regime. The subsequent reactions, which occur on the nanosecond time scale, are

$$e^{-}_{aq} + S \xrightarrow{k_2 = k_S[S]} S^{-} \tag{1a}$$

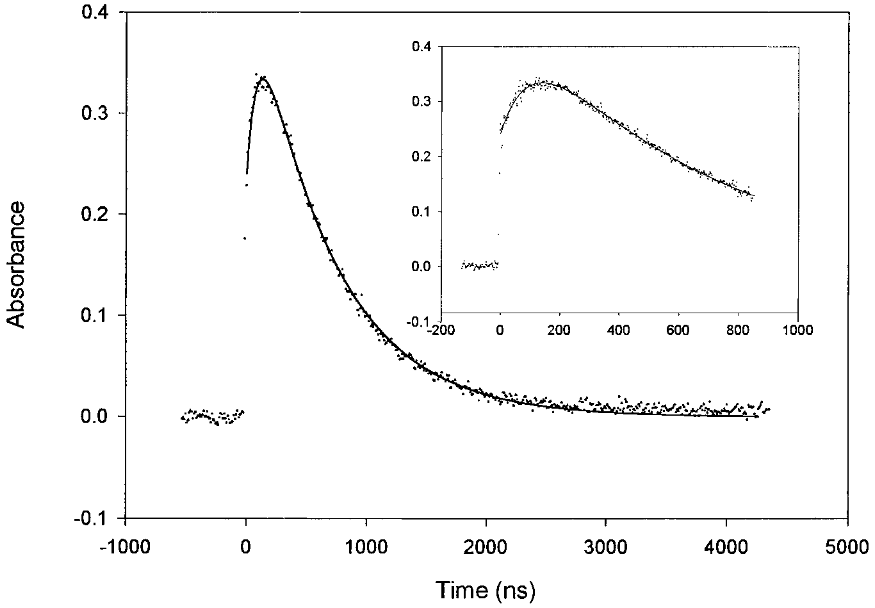

Figure 2. Measured absorbance at 700 nm vs time for the same solution as in Figure 1, and calculated absorbance signal using fit of data to eq 5. Inset: Higher time-resolution signal at 700 nm for the same sample as in Figure 1, and biexponential fit.

scavenging of hydrated electrons by H^+ and Cu(I) species;

$$^3\mathrm{Cu(I)} \xrightarrow{k_\mathrm{L}} \mathrm{Cu(I)} \tag{1b}$$

net emission (radiative decay) of both copper(I) triplet states;

$$^3\mathrm{Cu(I)} \xrightarrow{k_\mathrm{NR}} \mathrm{Cu(I)} \tag{1c}$$

net nonradiative decay of both copper(I) triplet states; and

$$^3\mathrm{Cu(I)} \xrightarrow{k_0} \mathrm{Cu(II)} + \mathrm{e_{aq}}^- \tag{1d}$$

net delayed electron ejection from both triplet states.

The net rate law for decay of the two triplet states should thus be

$$\mathrm{d}[^3\mathrm{Cu(I)}]/\mathrm{d}t = -(k_\mathrm{L} + k_\mathrm{NR} + k_0)[^3\mathrm{Cu(I)}] = -k_1[^3\mathrm{Cu(I)}] \tag{2}$$

and that for the change in hydrated electron concentration should be

$$\mathrm{d}[\mathrm{e_{aq}}^-]/\mathrm{d}t = k_0[^3\mathrm{Cu(I)}] - k_2[\mathrm{e_{aq}}^-] \tag{3}$$

The integrated forms of eqs 6 and 7 can be combined to give

$$[\mathrm{e_{aq}}^-] = [\mathrm{e_{aq}}^-]_0\mathrm{e}^{-k_2t} + \frac{k_0[^3\mathrm{Cu(I)}]_0}{k_2 - k_1}(\mathrm{e}^{-k_1t} - \mathrm{e}^{-k_2t}) \tag{4}$$

where $[\mathrm{e_{aq}}^-]_0$ and $[^3\mathrm{Cu(I)}]_0$ are initial concentrations of hydrated electrons and both triplet excited states, respectively. If we recognize that $[\mathrm{e_{aq}}^-]_0$ is the concentration of the prompt electrons, and $[^3\mathrm{Cu(I)}]_0k_0/k_1$ is the total concentration of electrons that are ejected by the delayed process, then it is possible to substitute absorbances, A_p and A_d, respectively, for these electron concentrations, and eq 4 reduces to the simple biexponential expression in terms of measured electron absorbances,

$$A = (A_\mathrm{p} + B)\exp(-k_2t) - B\exp(-k_1t) \tag{5}$$

where $B = -k_1A_\mathrm{d}/(k_2 - k_1)$.

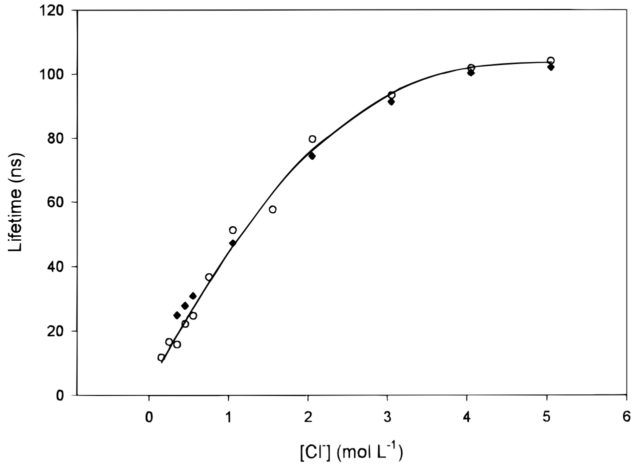

Figure 3. Lifetimes of (○) luminescence decay and (◆) 700-nm absorbance growing-in in 2×10^{-4} M CuCl in neutral solutions of varying [NaCl] at constant 5 M ionic strength, $NaClO_4$ medium, after absorption of a 266-nm laser pulse. The curve is at least squares fit to eq 7.

The lifetimes of the hydrated electron growing-in and decay were measured at a variety of scavenger and ligand concentrations. In all cases, the delayed electron ejection lifetime was virtually identical to that for emission at 480 nm, as is illustrated by their dependencies on chloride concentration, shown in Figure 3. Thus it must be concluded that the source of the delayed electron is the emitting species.

The dependence of the luminescence lifetime on ligand concentration of Figure 3 strongly resembles that observed in similar systems of copper(I) complexes with halo and cyano ligands.[9−12] In such systems the behavior was rationalized by assuming that the triplet tris complex is luminescent and that there is a rapid equilibration between the two triplets, which decay to ground-state species, as shown in Scheme 1. It was shown[12] that the observed luminescence decay constant for such a kinetic system at or near equilibrium should be given by the expression

$$k_\mathrm{obs} = k_\mathrm{D} + \frac{k_\mathrm{PD} - k_\mathrm{D}}{1 + K_\mathrm{ex}[\mathrm{Cl}^-]} \tag{6}$$

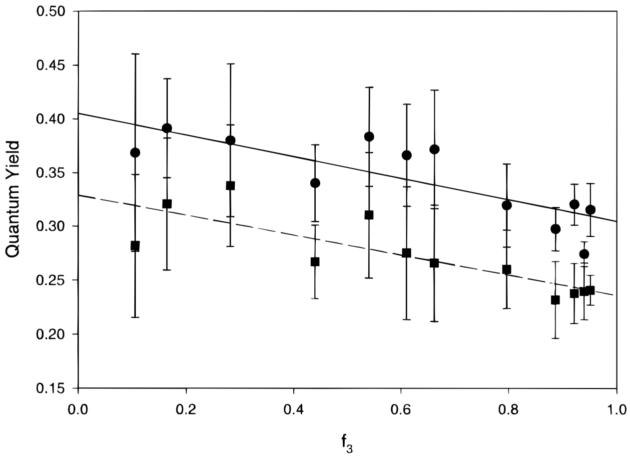

Figure 4. Quantum yields for (●) prompt electron ejection and (■) delayed electron ejection in solutions of 2 × 10^{-4} M CuCl at constant 5 M ionic strength vs the fraction of light absorbed by $CuCl_3^{2-}$.

where K_{ex} is the excited-state equilibrium constant (i.e. k_E/k_{E}^{-}) k_{PD} is the net decay constant (i.e., $k_{PL}+ k_{PDn} + k_{PDe}$) for the triplet bis complex, and k_D is the net decay constant (i.e., $k_{EL}+ k_{EDn} + k_{EDe}$) of the triplet tris complex. For the chlorocuprate(I) system, an attempt at fitting eq 6 to the luminescence lifetime values of Figure 3 was made, but it was found that a much better fit could be obtained if a bimolecular rate term, $k_{ER}[Cl^-]$, were introduced into the original expressions,[20] resulting in the modified equation

$$k_{obs} = k_D + k_{ER}[Cl^-] + \frac{k_{PD} - k_D - k_{ER}[Cl^-]}{1 + K_{ex}[Cl^-]} \qquad (7)$$

The resulting values of the constants, which must be considered to be only rough estimates with about 50% error limits, are $K_{ex} = 12\ mol^{-1}\ L$, $k_{PD} = 2.6 \times 10^8\ s^{-1}$, $k_D = 7.8 \times 10^5\ s^{-1}$, and $k_{ER} = 9.1 \times 10^5\ mol^{-1}\ L\ s^{-1}$. The curve drawn through the points in Figure 3 was calculated from these constants.

Figure 4 shows the quantum yields of prompt electron ejection, obtained from values of A_p vs the fraction of light absorbed by ground-state $CuCl_3^{2-}$ complex, f_3, where

$$f_3 = \epsilon_3 K[Cl^-]/(\epsilon_2 + \epsilon_3 K[Cl^-]) \qquad (8)$$

K is the equilibrium constant for the ground-state reaction

$$CuCl_2^- + Cl^- = CuCl_3^{2-} \qquad (9)$$

with a value of 0.648,[1,7] and ϵ_2 and ϵ_3 are the extinction coefficients (642 and 3889 $M^{-1}\ cm^{-1}$, respectively) of the two complexes at the laser wavelength. The quantum yields at different chloride concentrations were corrected for the total fraction of light absorbed by the sample at 266 nm. Since the net quantum yield for a product being formed from two excited species is the sum of the products of the mole fraction of each excited species times its individual quantum yield,[7] and since the mole fractions of CTTS excited state for the bis- and triscoordinated species are given by the fraction of light absorbed by each (eq 8), it follows that the quantum yield for prompt electron ejection is given by

$$\phi_p = (1 - f_3)\phi_{2p} + f_3\phi_{3p} \qquad (10)$$

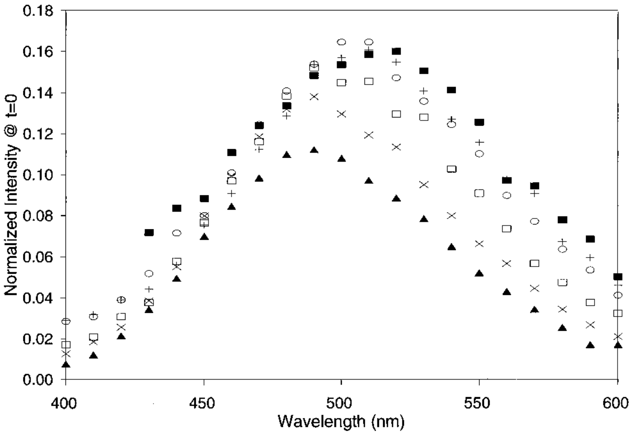

Figure 5. Time-resolved relative emission spectra, normalized to $t = 0$ and equal absorbance of the laser pulse, for 2 × 10^{-4} M CuCl in 5 M ionic strength ($NaClO_4$ medium) solutions containing NaCl at molar concentrations of (■) 0.1, (+) 0.3, (○) 0.5, (□) 1.0, (×) 3.0, and (▲) 5.0.

where ϕ_{2p} and ϕ_{3p} are the individual quantum yields for $CuCl_2^-$ and $CuCl_3^{2-}$, respectively. Extrapolation to $f_3 = 0$ and $f_3 = 1$ results in values of the prompt electron quantum yields $\phi_{2p} = 0.40 \pm 0.08$ and $\phi_{3p} = 0.30 \pm 0.05$, respectively.

Although the concentration of $^3CuCl_2^{2-}$ is so much greater than that of $^3CuCl_2^-$ at any chloride concentration since $K_{ex} \gg 1$, the fact that $k_{PD} \gg k_D$ means that nearly all of the observed delayed electrons emanate from the triplet bis complex. For example, even at 5 M chloride concentration, the electron ejection rate from the triplet tris is only 0.17 that from the triplet bis complex, using the values from Figure 3 for the rate and equilibrium constants. Thus, the quantum yield of delayed electrons is a measure of how efficient the intersystem crossing from either of the two CTTS excited singlet species to the triplet states is. These quantum yields have also been plotted in Figure 4, and the intercepts at $f_3 = 0$ and $f_3 = 1$ (0.33 and 0.25, respectively) suggest that both the bis and tris CTTS states are rather efficient in crossing over to the triplet states. The smaller intercept at $f_3 = 1$ compared to $f_3 = 0$ can be partly explained by the competition of the bimolecular reaction pathway, represented by $k_{ER}[Cl^-]$ in Scheme 1, with the electron ejection from the tris triplet species.

We had suggested in all of the systems studied that the source of the luminescence is the triscoordinated triplet species, on the basis of our earlier observations that the steady-state luminescence intensity decreases to virtually nothing as the ligand concentration is decreased from 5 M to about 0.1 M at constant ionic strength.[7,10,12] However, in view of the fact that the luminescence lifetimes also decrease with ligand concentration, as in Figure 3, and since quantum yield is determined by the populations of the excited states as well as the rate constants for radiative decay, it seemed necessary that some time-resolved luminescence spectra be taken at different ligand concentrations to determine if the triplet bis complex also emits. Such time-resolved spectra were obtained at a series of chloride concentrations ranging from 0.1 to 5 M, constant ionic strength ($NaClO_4$ medium), using delay times at a given concentration ranging from about 0 ns to about twice the lifetime given in Figure 3. Using the first-order rate law, the spectral intensities were normalized to $t = 0$ and then normalized again to adjust for the fraction of light absorbed by the sample at the laser wavelength, 266 nm. The resulting spectra are shown in Figure 5 on a relative intensity scale. The interesting result is that not only does the luminescence intensity increase slightly at lower ligand concentrations but there is a red shift of about 20 nm in the peak of the emission band, suggesting that the biscoordinated triplet is also luminescent. The radiative decay constants of

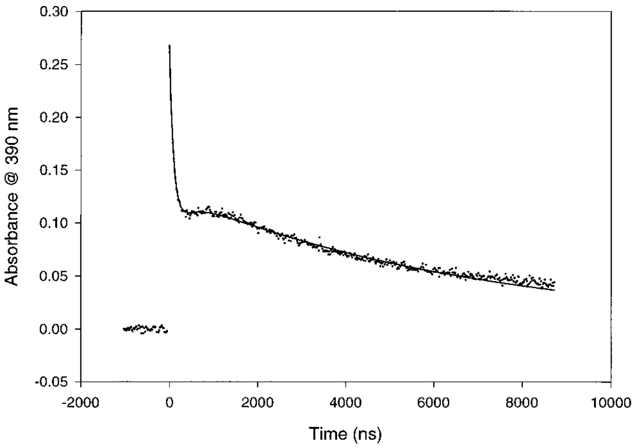

Figure 6. Absorbance and triexponential fit at 390 nm for the same solution as in Figure 1.

the two triplets must be considerably smaller than those for electron ejection since the quantum yields for the former process are so much smaller than for the latter (for example, 0.0036[7] vs 0.25 for $CuCl_3^{2-}$). The red shift can be explained by the fact that although the equilibrium constant between the triplet states suggests a deeper potential energy well for the tris complex, the vertical transitions that occur in the bis complex are less energetic because the minimum in the potential well of the triplet bis complex is at a considerably shorter Cu−Cl distance from that of the ground state compared to the situation for the tris complex. This is due to the fact that the more positive metal center caused by excitation of copper(I) from a d to a p or s orbital will attract two chloro ligands to a greater extent than three ligands. The very small quantum yield for luminescence[7] and the rather high delayed electron ejection quantum yields suggest that the major pathway for decay of the two equilibrated triplet complexes is through this latter process. More evidence for this is given, below, in the time-resolved absorbance data in the 300−400-nm region.

Other Intermediates. Figure 1 reveals that the temporal behavior in the 300−400-nm wavelength range is rather complex; that is, it appears that more than one species with an absorption band in this region forms and decays. This is demonstrated further by the 290-nm transient absorbance signal shown in Figure 6, which suggests that during the laser pulse a strongly absorbing species forms and then decays after about 200 ns, followed by a slower growing-in of another species, most likely a copper(0) species, which decays over a period of several tens of microseconds. The decay lifetime of the first species can be estimated from a simple ln(A)-vs-t plot, and the result is almost identical to the luminescence decay lifetime, suggesting that the initial absorbance is that of the triplet tris complex, $^3CuCl_3^{2-}$. This was further supported by noting that the lifetime of this absorption has the same dependence on chloride concentration as does the luminescence and delayed electron ejection. Moreover, the appearance of a temporary (i.e. up to about 300 ns) isosbestic point at 480 nm strongly suggests that the decay of this band is directly correlated to the growing-in of the 700-nm band, further evidence that the triplet tris complex decays primarily through delayed electron ejection, indicated in Scheme 1. Some time-resolved spectral data (not shown) at low chloride concentration suggest that the biscoordinated excited state, $^3CuCl_2^-$, also has an absorption band in this same wavelength region.

The species that grows in at 380 nm and then decays is probably a Cu(0) complex. Figure 7 shows time-resolved spectra in a solution that has been made acidic enough (0.008 M HCl) such that electrons are scavenged on a much shorter time scale primarily by H^+, but not enough to decrease significantly the lifetime of the luminescent complex since the second-order rate constant for reaction of H^+ with electrons is about 5.5×10^9 s^{-1} M^{-1} at 5 M ionic strength[3] versus 5.8×10^8 s^{-1} M^{-1} for reaction with the luminescent species.[7] The 380-nm band is considerably simpler, devoid of any growing-in and longer decay of a copper(0) species. In neutral solution the primary electron scavengers are the ground-state copper(I) complexes themselves,

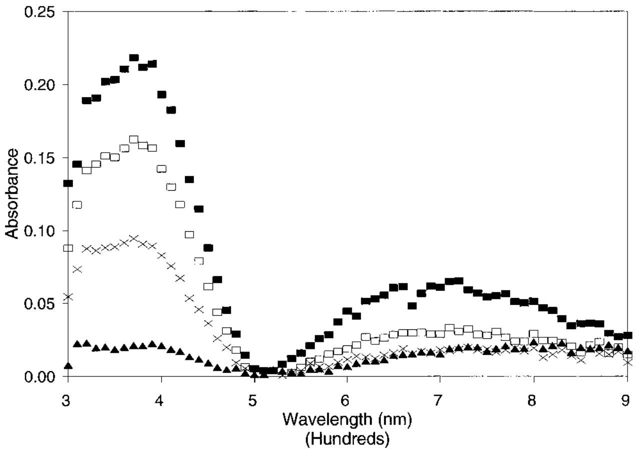

Figure 7. Time-resolved spectra of 266-nm pulsed solution containing 5×10^{-4} M CuCl, 5 M NaCl, and 0.008 M HCl. Time delays: (■) 20 ns, (□) 50 ns, (×) 100 ns, (▲) 900 ns.

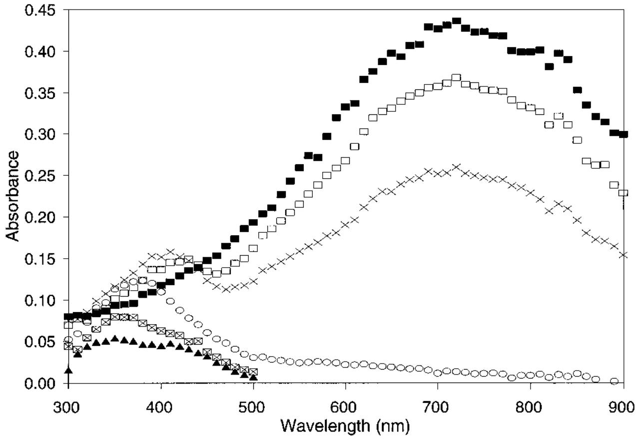

Figure 8. Time-resolved spectra of 266-nm pulsed solution containing 2×10^{-4} M CuCl and 1 M NaCl. Time delays: (■) 10 ns, (□) 100 ns, (×) 200 ns, (○) 1200 ns, (⊡) 4 μs, (▲) 17 μs.

$$CuCl_3^{2-} + e_{aq}^- \rightarrow CuCl_3^{3-} \qquad (11a)$$

or

$$CuCl_2^{-} + e_{aq}^- \rightarrow CuCl_2^{2-} \qquad (11b)$$

whereas in acid solution electrons are scavenged mostly by H^+,

$$H^+ + e_{aq}^- \rightarrow H^\bullet \qquad (12)$$

The rather clean UV bands, then, in Figure 7, peaking at 380 nm can be attributed solely to the triplet tris complex, $^3CuCl_3^{2-}$. From the quantum yield results for delayed electron ejection, above, and from the 10-ns spectrum of Figure 1, a lower limit to the extinction coefficient of the triplet tris complex at 380 nm can be estimated, yielding a value of 27 000 cm^{-1} M^{-1}.

Figure 8 gives us a better picture of the absorption band of the copper(0) species. Here the chloride concentration and ionic

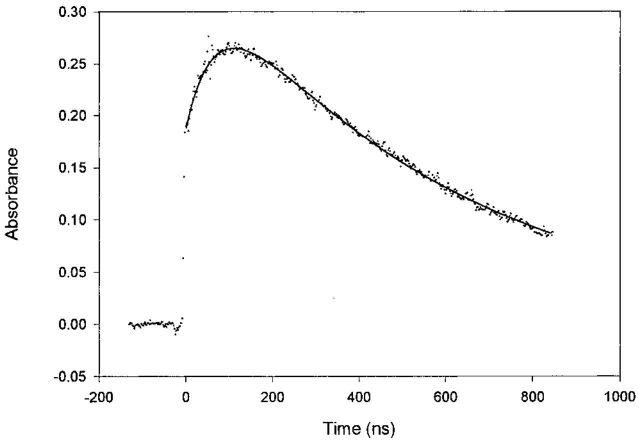

Figure 9. Transient absorbance and biexponential fit at 700 nm for 2 × 10^{-4} M $CuBr_3^{2-}$ in 0.4 M NaBr solution, 5 M ionic strength, $NaClO_4$ medium, flashed at 266 nm.

strength have been reduced to 1 M, a condition in which luminescence is not observed, and hence the triplet complex concentrations must be small. Again one sees an isosbestic point, at about 440 nm, but this time reversed with respect to the one seen in Figure 1; that is, as the electron band decays, the band at 380−400 nm grows in at the same rate. This band is easier to visualize after the electron decays, as shown in the 1200-ns spectrum, which gives a maximum wavelength at 390 nm. This observation is consistent with the fact that chlorocuprate(0) complexes absorbing in this region have also been observed after electron formation in pulse radiolysis studies of CuCl in NaCl solutions.[21]

After 17 000 ns there is still a residual absorbance with a peak at about 340 nm, and this is most likely due to the dichloride radical, $Cl_2^{\bullet-}$,[22] which could be formed in a variety of ways, such as from chlorine radicals released in the prompt electron ejection,

$$^{*}CuCl_3^{2-} \rightarrow CuCl_2^{-} + Cl^{\bullet} + e_{aq}^{-} \qquad (13)$$

or by bimolecular reactions of triplet species with the chloride ion mentioned earlier,

$$^{3}CuCl_3^{2-} + Cl^{-} \rightarrow CuCl_2^{2-} + Cl_2^{\bullet-} \qquad (14a)$$

or

$$^{3}CuCl_3^{2-} + Cl^{-} \rightarrow CuCl_3^{3-} + Cl^{\bullet} \qquad (14b)$$

Such reactions probably occur in the bromocuprate system as well.[12] Since the decay of the dihalide radical is a very slow second-order process, it is simply the only observable species left after such a long time.

Bromocuprate(I) System. In our previous paper on the transients in the flash photolysis of $CuBr_3^{2-}$ in solution,[12] we did not report any delayed electron ejection because most of the transient absorbance measurements at 700 nm were made at 5 M NaBr concentration, where the electron decay and luminescence decay lifetimes are about the same (700−900 ns), resulting in a signal that did not show any growing-in, as in Figure 3. Noting, however, that the luminescence lifetime decreases with decreasing ligand concentration because the bromocuprate(I) system obeys the same triplet tris complex mechanism as in Scheme 1, we subsequently realized that at low [Br^-] there should be a large enough difference between k_1 and k_2 in eq 5 that a growing-in should be observed. Figure 9 shows such a signal for 2 × 10^{-4} M $CuBr_3^{2-}$ in 0.5 M NaBr, at 5 M ionic strength, and it is obvious that there is indeed such a delayed ejection signal. The lifetimes of delayed ejection are compared in Table 1 to those of luminescence for a series of low-[Br^-] solutions, indicating that the triplet tris complex decay is consistent with delayed electron ejection. Because the bromocuprate(I) system has higher equilibrium constants for both the ground state[23] ($K = 9.45$) and the triplet excited state[12] ($K_{ex} = 73$) than does the chlorocuprate(I) system, it is more difficult to shift either the ground or excited state equilibria toward the dibromo species; therefore only the quantum yields for $CuBr_3^{2-}$ can be reliably measured, yielding values of 0.25 ± 0.03 and 0.18 ± 0.02 for the prompt and delayed ejection, respectively. Nevertheless, it is reasonable to assume that the bromocuprate(I) system also conforms to Scheme 1.

TABLE 1: Comparison of Luminescence Decay and Electron Growing-in Lifetimes for Solutions of 2 × 10^{-4} M $CuBr_3^{2-}$ in Varying [Br^-] at 5 M Ionic Strength

[Br^-]	luminescence[12] lifetime (ns)	growing-in lifetime (ns)
0.08		23
0.1	17	24
0.2	35	35
0.3		44
0.4	71	83
0.7	135	
1.0	223	215

Conclusions

There appear to be two different routes for ejection of hydrated electrons by photoexcited $CuCl_2^-$ and $CuCl_3^{2-}$: (1) a prompt (i.e. within the 5-ns laser pulse width) ejection directly from the CTTS excited states, and (2) a delayed ejection, with lifetimes of up to 105 ns, from the triplet states of the two complexes. These two processes have rather high quantum yields: 0.30−0.40 for the prompt ejection and 0.25−0.33 for the delayed ejection for the chlorocuprate(I) complexes. For $CuBr_3^{2-}$, the delayed ejection has longer lifetimes, again consistent with the luminescence lifetimes, with quantum yields for prompt and delayed ejection of 0.25 and 0.18, respectively. Both of the chlorocuprate triplet excited states are weakly luminescent species. The triplet tris species, $^3CuCl_3^{2-}$, has a strong absorption band at 390 nm ($\epsilon \approx 27\,000$ M^{-1} cm^{-1}), and the biscoordinated species, $^3CuCl_2^-$, probably absorbs in the same region as well.

We have previously called the species, $^3CuCl_2^-$, and similar triplet tris complexes *exciplexes*. We are aware that this is viewed by some photochemists (including our referees) as an incorrect assignment since an exciplex is an excited-state complex that exists only in the excited state and is dissociative in the ground state. But, what does it mean for the ground-state to be dissociative? It can often be demonstrated that the formation constant of a ground-state species is very small ($K \ll 1$), but can one confirm that it is absolutely 0? The crucial point of the definition is that the formation constant in the excited state is larger than in the ground state so that the deactivation of an excited associated species results in a ground-state system in which dissociation must occur in order to achieve equilibrium. In the chloro- and bromocuprate(I) systems described here the excited-state equilibrium constants are an order of magnitude larger than the ground-state constants, justifying, we believe, our assignments of the triplet tris species as exciplexes. This less rigid view of what constitutes an exciplex has some precedent in the literature.[24−26]

Since their discovery in 1962,[27] hydrated electrons have been the subject of intense investigation. Although they were originally observed in pulse radiolysis experiments, there have been many examples of their photochemical generation by irradiation of a wide variety of organic and inorganic compounds and water itself.[28] We believe that $CuCl_3^{2-}$ and $CuBr_3^{2-}$ are the first examples of the photogeneration of hydrated electrons from a chemical species through both prompt and delayed ejection processes.

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