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Notes

Photochemistry of Iodocuprate(I) Complexes

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Along with the increase of interest in the photochemistry of coordination compounds of the past several decades,[2] many important photochemical features of copper complexes have surfaced.[3] Among those complexes which have been thoroughly studied are the halo and pseudohalo complexes of copper(I), specifically with the ligands Cl^-, Br^-, and CN^-. It now appears that there are two kinds of luminescence arising from ultraviolet excitation of such complexes: (1) emission in the 470–480-nm range observed in the triscoordinated halocuprate(I) complexes, with lifetimes of 105 ns (for $CuCl_3^{2-}$ in 5 M NaCl) and 710 ns (for $CuBr_3^{2-}$ in 5 M NaBr);[4,5] (2) emission in the biscoordinated cyanocuprate(I) $Cu(CN)_2^-$ at much shorter wavelengths, peaking at about 400 nm.[6] Interestingly, the photoluminescence properties of the mixed-ligand complex $Cu(CN)_2Cl^{2-}$ are nearly the same as those of $CuCl_3^{2-}$.[7]

The other important feature of the halo- and cyanocuprate(I) complexes studied so far is the ejection of a hydrated electron when these complexes are irradiated by light in the UV range. The efficiency of this process proved to be highest for the complexes with only two ligands (compared to three or four) in the chloro-,[3,8–10] bromo-,[5] and cyanocuprate(I)[11] systems. In acidic solutions of halocuprates(I), the overall photoreaction produces H_2 gas and Cu(II) species, but hydrido complexes as intermediates were also detected in these systems.[12–15]

In spite of the detailed investigations of the chloro- and bromocuprates(I) published so far, little attention has been paid to the photoactivity of the corresponding iodo complexes, other than a study of the iodine formation observed in the irradiation of $Cu_2I_3^-$ in saturated KI solution with low quantum yield[16] and the observation of photoluminescence in benzene solutions of $Cu_4I_4(pyridine)_4$.[17–19] In this paper, we present the first results of studies of the primary photoreactions of the iodocuprates(I), and we compare the photophysical and photochemical properties of these complexes to those of the chloro-, bromo-, and cyanocuprate(I) complexes.

Experimental Section

Reagent grade NaI, $NaClO_4$, $HClO_4$, and KNO_3 were used for the preparation of stock solutions, from which solutions of desired ligand concentration, ionic strength, and H^+ or NO_3^- concentration could be prepared. Water was deionized and purified by a Millipore Milli-Q system containing a 0.4-μm filter at the outlet. Weighed samples of CuCl solid, which was synthesized as described previously,[8] were added to the argon bubble-degassed solutions. Since the copper(I) concentration was several orders of magnitude lower than that of I^- in all experiments and because the formation constants for the iodocuprates(I) are considerably higher than those for the chloro complexes,[20] it was assumed that CuCl could be used instead of CuI as the source of Cu(I). Typically, the photochemical measurements were carried out using 3 mL of solution in a 1-cm quartz cuvette.

Luminescence spectra were taken on optically dense samples with a Shimadzu RF-540 spectrofluorimeter, utilizing the emission from the front surface of the sample. Absorption spectra were taken in a Beckman ACTA M-VI spectrometer in a cuvette of path length 0.001 27 cm (Hellma Cells).

Time-resolved spectra, transient absorbances, and luminescence lifetimes were determined by several laser systems. The fluorescence lifetime was measured by the single-photon-counting method using a frequency-doubled dye laser (λ_{exc} = 295 nm, 20-ps pulse width) pumped with an Ar^+ laser.[21] Flash photolysis experiments were carried out by using a XeCl excimer laser (Lambda Physik EMG 101 MSC, λ_{exc} = 308 nm, 20-ns pulse width, 120 mJ/pulse) for excitation and a kinetic spectrometer system involving a 150-W Xe–Hg lamp (Oriel), a Jarrel-Ash monochromator, a Hamamatsu R955 photomultiplier, and a Hewlett-Packard 54510A digitizing storage oscilloscope. Although there is an overlap between the UV absorption of the iodocuprate(I) complexes and the excess iodide ligand in water, the difference in cutoff wavelengths of about 300 nm for I^- and 320 nm for the copper complex creates a favorable window for selective excitation of the iodocuprate(I) species by the 308-nm output of the excimer laser. This is illustrated by the fact that the molar absorbance of I^- at 308 nm is only 0.016 M^{-1} cm^{-1} while that for the iodocuprate(I) complexes is about 1000 M^{-1} cm^{-1}, and thus for solutions with 0.4 total absorbance (against water) the portion of the absorbance due to Cu(I) species is 96% in 1 M NaI. Such light absorption fractions were taken into account in calculating quantum yields. Aberchrome-540 was employed as an actinometer.[22]

Results and Discussion

Absorption and Luminescence. A solution of Cu(I) in 1–5 M NaI contains mostly CuI_3^{2-} and CuI_4^{3-} [20] and displays a strong absorption band in the ultraviolet range at 275–285 nm (Figure 1). The wavelength of this band depends very little on which of the halo ligands in the series Cl^-, Br^-, and I^- is bound to the

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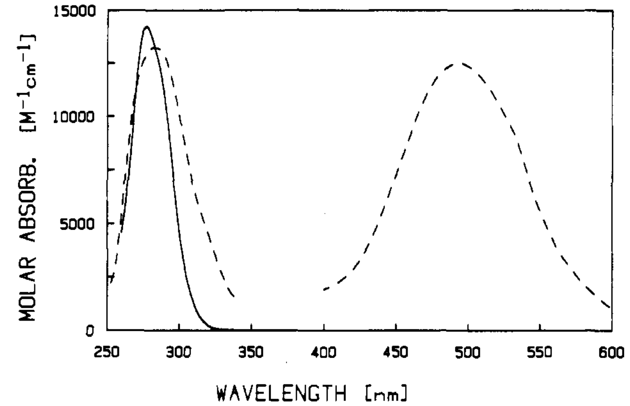

Figure 1. Molar absorption spectrum (—) and front-surface excitation (λ_{em} = 490 nm) and emission (λ_{exc} = 278 nm) spectra (- - -) of 0.02 M CuCl in 2.0 M NaI in a 1-cm cuvette. The luminescence spectra are normalized to the molar extinction scale.

Table I. Molar Absorbances (ϵ_{max}) at λ_{max}, Excitation (λ_{exc}) and Emission (λ_{em}) Maxima, Fluorescence Lifetimes (τ), and Rate Constants for Luminescence Quenching by H$^+$ (k_H) for CuX_3^{2-} Complexes at 5 M Ionic Strength

ligand	ϵ_{max}, M^{-1} cm^{-1}	λ_{exc}, nm	λ_{em}, nm	τ, ns	k_H, M^{-1} s^{-1}
Cl^{-a}	4.9×10^3	275	475	105	5.8×10^8
Br^{-b}	9.4×10^3	279	465	710	6.2×10^8
I$^-$	1.7×10^4	284	493	14.3	7.8×10^9

[a] From ref 4. [b] From ref 5.

Cu(I), indicating that the energy of the corresponding transition (probably CTTS, on the basis of earlier studies)[4,8] is determined by the metal center. From the position of this band, an ionization energy of about 290 kJ/mol can be estimated for the central metal in these complexes using the Mulliken theory.[2d] On the other hand, the intensity of this band is very ligand sensitive, in the order of I$^-$ > Br$^-$ > Cl$^-$, as indicated by the molar absorbances of the corresponding trihalocuprates(I) at 5 M ionic strength, shown in Table I. This strong ligand effect may be attributed to the different polarizabilities of the halo ions.

The steady-state luminescence properties of the iodo complexes are also consistent with those of other halocuprates(I). Similarly to the absorption band at 275–285 nm, the excitation and emission spectra (Figure 1) show peaks only slightly red-shifted compared to the corresponding chloro and bromo systems.[4,5] The fluorescence lifetime, however, proved to be much shorter (14.3 ± 0.3 ns) than those in the other halo systems at 5 M ligand concentration (Table I). It does not show a significant sensitivity to [I$^-$] above 1 M (e.g. τ = 16.4 ns in 1 M NaI), strongly differing from the behavior in the chlorocuprate(I) system in which τ decreases from 105 ns in 5 M NaCl to 9.8 ns in 1 M NaCl.[4] As in the case of other halocuprates(I), the luminescence of the iodo complexes is quenched by the hydronium ion, giving a linear Stern–Volmer dependence (not shown). The rates of this process, however, were found to be extremely fast, compared to those of the other systems (Table I), and suggest that the reaction of the emitting species with H$^+$ may be diffusion-controlled.

Photochemistry. In neutral 1 M NaI solution of copper(I) ($C = 2 \times 10^{-4}$ M), 308-nm laser irradiation resulted in the formation and decay of several intermediates with different lifetimes and spectra. Figure 2 shows the transient absorption spectra recorded 20 ns after the laser pulse and, in the 450–850-nm range, is identical to that of the hydrated electron.[23] A typical decay curve recorded at the absorption maximum at 700 nm is shown in Figure 3 and unambiguously obeys a pseudo-first-order rate law with a lifetime of 0.6 ± 0.04 μs under the conditions above. Scavenging experiments with NO$_3^-$ and H$^+$ gave rate constants in agreement with those in the literature for the reactions between e_{aq}^- and these ions.[24,25] Therefore, the primary photochemical reaction can be described as

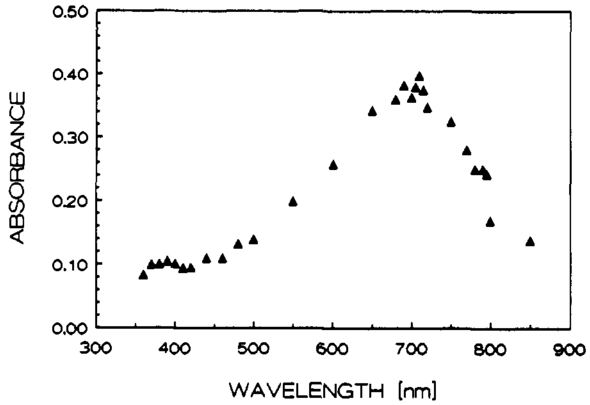

Figure 2. Transient absorption spectrum recorded ca. 20 ns after a 308-nm laser pulse in 1 M NaI solution containing 2×10^{-4} M CuCl in a 1-cm cuvette.

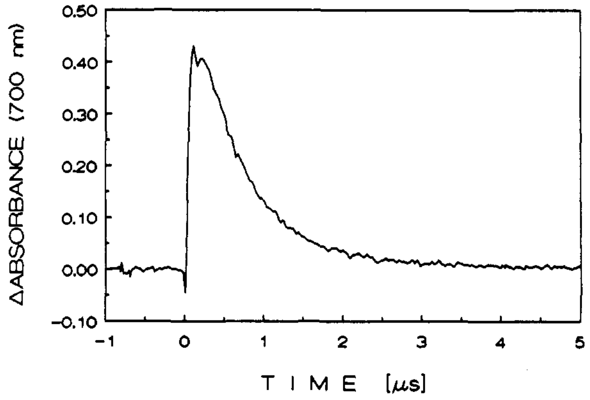

Figure 3. Transient absorption at 700 nm (conditions as in Figure 2).

$$CuI_3^{2-} \xrightarrow{h\nu} CuI_3^- + e_{aq}^- \qquad (1)$$

which is analogous to the reactions of the other halo- and pseudohalocuprate(I) complexes.[4,5,26] Variation of the laser pulse energy resulted in a proportional change in the value of A_{700}, verifying the single-photon nature of the process. From the fact that $\epsilon_{700} = 1.5 \times 10^4$ M^{-1} cm^{-1} for the hydrated electron,[23] the quantum yield for its formation was determined to be 0.28 ± 0.015 in 1 M NaI. Of course, it is well-known that hydrated electrons are produced by UV photolysis of aqueous I$^-$,[27] and in fact, we did observe the hydrated electron transient absorbance when 1 M NaI solutions not containing copper(I) were irradiated by the 308-nm laser pulse, but the peak value of the 700-nm transient was only 10% of the value measured in the same solution containing iodocuprate(I) complexes with an absorbance of 0.4. Thus, the quantum yield for the formation of e_{aq}^- by iodocuprate(I) was always corrected for this baseline transient.

The disappearance of e_{aq}^- in the absence of H$^+$ or NO$_3^-$ can take place via either geminate pair recombination or scavenging by a Cu(I) species in the solution. At increasing copper(I) concentration, the latter process becomes predominant, resulting in a shortening of the lifetime of the hydrated electron, as was recently observed in other halo- and cyanocuprate(I) systems.[5,28,29] A linear regression of the plot of the pseudo-first-order rate

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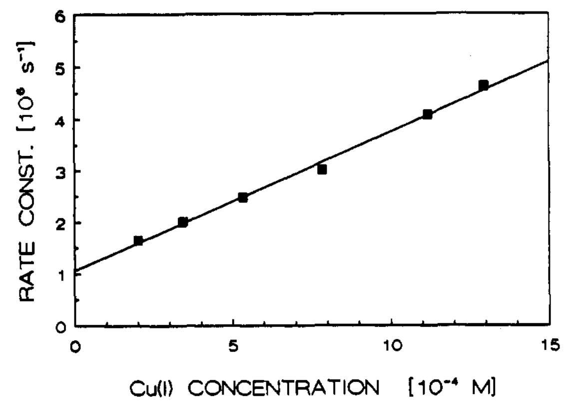

Figure 4. Hydrated electron decay constant vs copper(I) concentration in a solution containing 1 M NaI.

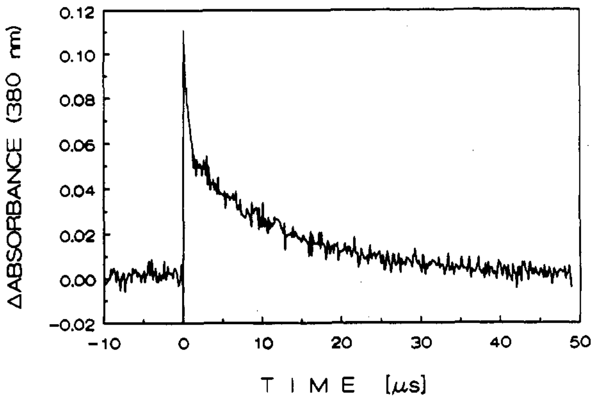

Figure 5. Transient absorption at 380 nm (conditions as in Figure 2).

constant for the absorption decay at 700 nm versus [Cu(I)] (Figure 4) results in the rate constant for the reaction

$$\mathrm{Cu(I)} + e_{aq}^{-} \xrightarrow{k_{Cu}} \mathrm{Cu(0)} \qquad (2)$$

yielding a value of (2.7 ± 0.1) × 10^9 M^{-1} s^{-1} in 1 M NaI solution. The good linear fit suggests that the recombination reaction

$$\mathrm{Cu(II)} + e_{aq}^{-} \rightarrow \mathrm{Cu(I)} \qquad (3)$$

has a rate which is essentially constant in this concentration range, and thus the lifetime of the photoejected electron can be estimated by extrapolation to [Cu(I)] = 0 M, yielding τ_0 = 0.95 ± 0.05 μs.

The short-wavelength band peaking at 380–390 nm in the spectrum of Figure 2 can be associated with an intermediate which is different from the hydrated electron, as confirmed in Figure 5, which shows the slow decay of this band compared to the spiked, hydrated electron decay right after the laser pulse. The time-resolved spectrum taken 18 μs after the laser pulse, long after the decay of the e_{aq}, is shown in Figure 6, revealing a strong band at 380–390 nm and a much weaker one in the 700–800-nm range. On the basis of the positions and the ratio of the intensities of these bands, the spectrum can be attributed to the I_2^- radical,[30] which could be formed via reduction of Cu(II) produced in the primary photochemical reaction

$$\mathrm{CuI_3^{-}} + 2\mathrm{I^{-}} \rightarrow \mathrm{CuI_3^{2-}} + \mathrm{I_2^{-}} \qquad (4)$$

The decay of the 380-nm absorbance (preceded by the spike) obeys pseudo-first-order kinetics, probably because of the reaction of I_2^- with excess Cu(I) and/or Cu(0), with a rate constant of 6.1 × 10^4 s^{-1}, and, on the basis of Figure 5, appears to start right after the pulse. In fact, a small growing-in can be seen immediately after the peak of the 700-nm absorbance in Figure 3, and although this local maximum only slightly exceeds the electronic noise, it suggests that I_2^- forms somewhat later than e_{aq}^-. This is further supported by Figure 7, which shows the disappearance of the electron signal by the addition of acid and the decay of the intermediate over a long time scale. The growing-in of the I_2^- transient can clearly be seen in Figure 8, which is a 50-fold expansion on the time scale of Figure 7. The time at which the peak in such a transient absorption signal occurs varies with iodide concentration, increasing from 150 ns in 1 M NaI solutions to 1 μs in 0.2 M NaI (at constant copper(I) concentration of 2 × 10^{-4} M), an inverse dependence consistent with eq 4. It has been shown[31] that the time of maximum concentration of a transient

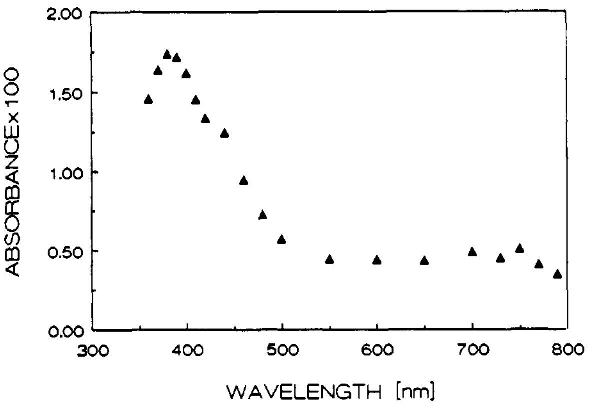

Figure 6. Transient absorption spectrum recorded 18 μs after the laser pulse (conditions as in Figure 2).

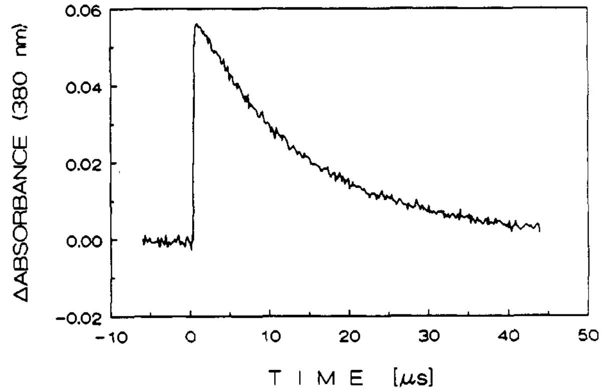

Figure 7. Transient absorption at 380 nm in 1 M solution of NaI containing 2 × 10^{-4} M CuCl and 0.1 M H^+ over a 50-μs time scale after the laser pulse.

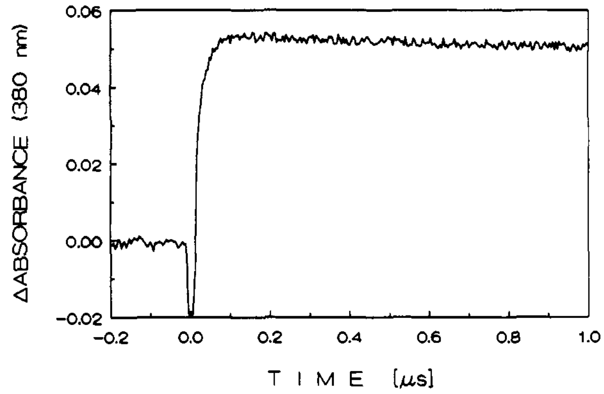

Figure 8. Transient signal of Figure 7 expanded to the first microsecond after the laser pulse.

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which forms and decays by first-order processes is given by

$$t_{\max} = [\ln (k_d/k_f)]/(k_d - k_f) \qquad (5)$$

where k_f and k_d are the rate constants for formation and decay of the transient, respectively. From the rate constant for the decay of I_2^- (6.1×10^4 s^{-1}) and the value of 150 ± 50 ns for $t_{\max}$, and assuming reaction 4 is pseudo-first-order (since $[I^-] \gg [CuI_3^-]$), an estimate of the rate constant for the formation of I_2^- was made, yielding a value of $(4.4 \pm 2.6) \times 10^7$ s^{-1} at 1 M NaI. This shows that reaction 2 is much slower than one which is diffusion-controlled, in accordance with other observations of the overall reaction between Cu(II) and I^- in 1 M NaCl.[32] It should be mentioned that, in the transient spectrum determined about 20 ns after the pulse (Figure 2), A_{380}/A_{700} is somewhat lower (i.e. about 56%) than what one would expect for a 1:1 molar ratio of I_2^- to e_{aq}^-, further demonstrating that formation of I_2^- is delayed with respect to formation of e_{aq}^-.

The primary products of electron-scavenging by the Cu(I) complexes, as shown in eq 2, are Cu(0) complexes or colloidal copper, as was recently suggested in the photolysis of bromo-,[5] chloro-, and cyanocuprate(I) systems.[29] The spectra of such species are essentially structureless, with a decreasing absorbance from 340 nm out to about 500 nm, and are very similar to those detected in acidic solutions of halocuprate(I) complexes irradiated in the UV[12-15] and attributed to Cu(0), Cu(I)-hydrogeno, and Cu(II)-hydride intermediates. Unfortunately, spectral verification of Cu(0) in the iodocuprate(I) system reported here is not possible because such a spectrum is masked by the I_2^- intermediate formed on the short time scale and by I_3^-, which is formed by reduction of Cu(II) by I^- or I_2^-.

Summary

Iodocuprate(I) complexes in aqueous solutions luminesce when excited in the UV region (275–290 nm), emitting in the visible region ($\lambda_{\max}$ = 493 nm), with a very short lifetime of about 14 ns which is independent of ligand concentration in the range 1–5 M iodide ion. Luminescence quenching by H^+ follows a Stern–Volmer relationship.

Photolysis into the UV absorption band also produces hydrated electrons, which decay through scavenging by iodocuprate(I) itself or through recombination with the Cu(II) species formed in the primary step, similarly to the chloro- and bromocuprates(I).

Also observed was the time-resolved spectrum of the transient I_2^-, which is apparently formed by reaction of the iodide ion with Cu(II) formed in the primary electron ejection step. The rate constant for the formation of I_2^- in 1 M NaI is estimated to be 4.4×10^7 s^{-1}.

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