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Photooxidation of Dichloro- and Trichlorocuprate(I) Ions in Acid Solution[1a]

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Abstract: Photooxidation of the dichloro- and trichlorocuprate(I) ions in aqueous acidic media produces chlorocuprate(II) ions and hydrogen with quantum yields approaching unity. The photolysis of $CuCl_3^{2-}$ at 274 nm shows a linear dependence for the reaction $Cu(I) + H^+ \rightarrow Cu(II) + \frac{1}{2}H_2(g)$ on the square root of scavenger (H^+) concentration within a range of scavenger concentrations greater than 10^{-2} M and less than 2 M. The square-root dependence as well as the response at high and low scavenger concentrations is explained by invoking a Noyes-geminate-pair scavenging mechanism. The charge transfer to solvent (CTTS) character of the transition, and the dependencies of ϕ on $[H^+]$, ionic strength, temperature, and on the presence of acetone as an electron scavenger, are used as evidence for the production of an electron in the primary step. In addition, laser flash photolysis experiments at 265 nm have confirmed the production of the hydrated electron in a neutral solution of di- and trichlorocuprate ion, containing no known efficient electron scavengers. An unusual dependence of ϕ on chloride ion concentration was observed, and this is explained in terms of a salt effect. In the absence of efficient scavengers the hydrated electron is the primary product. The equilibrium constant for the reaction $CuCl_2^- + Cl^- = CuCl_3^{2-}$ and the resolved spectra for the two complexes were measured at 3 M ionic strength. The association constant obtained was 1.1 ± 0.1. $CuCl_3^{2-}$ exhibits a band at 274 nm, believed to be CTTS because of its behavior in different solvents, while $CuCl_2^-$ is transparent at this wavelength. Both complexes absorb at 230 nm, but the nature of this band is unclear. An overall mechanism is proposed and the implications of this system for solar energy conversion are discussed.

In spite of the fact that copper(I) chloride has been used for a great number of photocatalyzed organic reactions, the photochemical behavior of copper(I) complexes in solution has been given very little attention. Recently it has been reported by Hurst et al.[2] and by McMillin et al.[3] that excitation of metal–ligand charge transfer bands of Cu(I) complexes results

in an electron transfer reaction between Cu(I) and a Co(III) metal center.

During our work on photochemical hydrogen production for solar energy conversion,[4,5] we observed that when acidified aqueous chloride or bromide ion solutions of CuCl or CuBr are irradiated with UV light of wavelength shorter than 320 nm, hydrogen gas is evolved according to the stoichiometry

$$Cu(I) + H^+ \rightarrow Cu(II) + \frac{1}{2}H_2(g) \qquad (1)$$
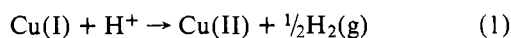
There are a number of other ions which undergo a similar photoredox reaction in acid solution with H_2 production, namely, Cr^{2+},[6,7] Fe^{2+},[8-11] V^{2+},[9] Eu^{2+},[12-14] Ce^{3+},[15] and Co^{2+}.[9,16] For the anions Cl^-,[17] Br^-,[17] I^-,[18] and $Fe(CN)_4{}^{4-}$ [11,19,20] it has been proposed, and indeed confirmed in nearly all cases,[21] that hydrated electrons are produced by the absorption of a photon. In the systems we studied, the copper is undoubtedly coordinated in anionic halo complexes, and for the chloro complexes in particular, there is ample evidence that at the concentrations we used, $CuCl_2{}^-$ and $CuCl_3{}^{2-}$ are present,[22,23] but there is some disagreement in the literature about the existence of $CuCl_4{}^{3-}$.[22,23] Thus it seems plausible that reaction 1 might involve a hydrated electron.

The purpose of this paper is to report our findings regarding the anionic species present and the mechanism for the photoinduced electron transfer from Cu(I) to proton in aqueous chloride ion solution.

Experimental Section

Cuprous chloride was prepared by dissolving reagent grade cupric sulfate in 12 M HCl, adding a stoichiometric amount of copper powder, diluting the supernate with water until a white precipitate formed, filtering with suction, rinsing with 0.1 M HCl and acetone, and drying in vacuo. The moisture-sensitive powder was stored in air in a desiccator.

Solutions of CuCl in various solvents, usually water, containing various concentrations of H^+, Cl^-, Na^+, $ClO_4{}^-$, or other solutes were prepared by placing a test tube containing preweighed CuCl inside a flask containing the rest of the solution, degassing through a septum and adding Ar or N_2, and finally tipping the flask to allow the CuCl to mix and dissolve after all the air had been removed. The concentrations of Cu(I) were fixed by weight, but were checked in many cases both by Ce(IV) titration and by atomic absorption, which confirmed the purity of CuCl as well as the effectiveness of the degassing procedure in keeping copper in the 1+ oxidation state.

Photolyses were carried out in a 1-cm quartz cuvette under inert atmosphere. The solutions, usually 0.01 M in total copper, were introduced into the cuvettes through a septum using syringe techniques. During irradiation the solutions were stirred continuously with magnetic stir bars and thermostated in water-cooled brass or aluminum blocks. The rates of reaction were followed by measuring evolved hydrogen using an automatic recording gas volumeter described previously.[24] In the initial experiments we confirmed the production of hydrogen mass spectrometrically.

The irradiation source was either a 200-W high-pressure mercury arc lamp (Oriel) for qualitative work or a 1000-W high-pressure mercury-xenon system (Schoeffel) for quantum yield determinations at specific wavelengths. The wavelengths were isolated via a 0.25-m grating monochromator (Jarrell-Ash) using 5-mm slits. The combination of slit width and line output of the source resulted in bandwidths at all irradiating wavelengths of less than 6 nm. Light intensities were determined for all wavelengths using the potassium trioxalatoferrate(III) actinometer.[25] We used the actinometer below its calibration limit at 254 nm and assumed that its quantum yield was at least as high down to 235 nm as at 254 nm.

The spectra of the solutions were determined using a Beckman Acta M-VI UV-vis spectrometer. The cell path length was 0.05 cm, which eliminated the necessity for dilution of solutions prepared for photolysis runs.

Results and Discussion

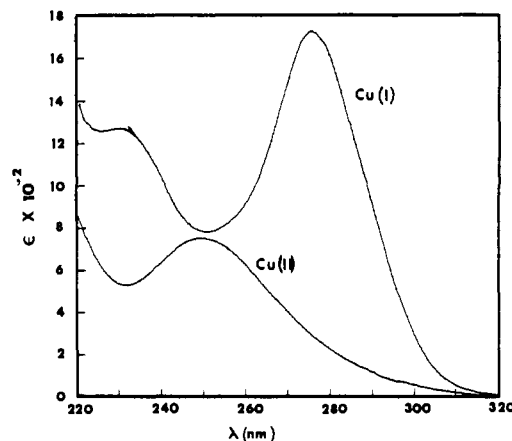**1. Spectra of Complexes.** Figure 1 shows spectra of 0.01 M

Figure 1. UV spectra of 0.01 M CuCl in 1 M HCl (a) before and (b) after complete photolysis with 200-W lamp.

CuCl in 1 M HCl before and after complete photolysis. The spectrum of the oxidized species appears to be that of $CuCl^+$ and other Cu(II)-chloro complexes in equilbrium.[26] In the Cu(I) spectrum, there is good agreement that the band at 274 nm belongs only to $CuCl_3{}^{2-}$,[23,27] while the band at 230 nm has been attributed to both $CuCl_2{}^-$ and $CuCl_3{}^{2-}$.[23]

We undertook to confirm the presence of the two complexes, $CuCl_2{}^-$ and $CuCl_3{}^{2-}$, by an analysis of the spectra of CuCl in solutions of variable chloride concentration. The spectra of ten solutions of 0.01 M CuCl were taken with $[Cl^-]$ varying from 0.25 to 1.70 M, using HCl, NaCl, $HClO_4$, and $NaClO_4$ to maintain an ionic strength of 3.0 M and a hydrogen ion concentration of 1.0 M. By applying the graphical technique of Coleman et al.[28] it was clearly established that there are indeed only two complexes in these solutions. Assuming, then, that the equilibrium system consists of the di- and trichlorocuprate ions, the measured extinction coefficient, $\bar{\epsilon}$, can be written as

$$\bar{\epsilon} = \epsilon_2 \frac{\epsilon_2 - \epsilon_1}{1 + \beta[Cl^-]} \qquad (2)$$

where ϵ_1 and ϵ_2 are the molar extinction coefficients of the di- and trichlorocuprate complexes, respectively, at any given wavelength, and β is the association constant:

$$\beta = \frac{[CuCl_3{}^{2-}]}{[CuCl_2{}^-][Cl^-]} \qquad (3)$$

In order to determine β, least-squares plots of $\bar{\epsilon}$ vs. $1/(1 + \beta[Cl^-])$ were computed for trial values of β until the best linear fit was obtained, as determined by a minimum probable error in the slope. The wavelength chosen was 273 nm, at the center of the band whose intensity was the most sensitive to $[Cl^-]$. From this we obtained a value of 1.1 ± 0.1 for β, from which values of ϵ_1 and ϵ_2 were obtained at the rest of the wavelengths using linear plots as defined by eq 2. Figure 2 shows these plots for a selection of wavelengths. The fact that a constant value of β gives good straight lines at all wavelengths further supports the assumption that only two complexes are in equilibrium.

The resolved spectra of the two complexes are shown in Figure 3. The shapes of these spectra are very similar to those published by Sugasaka and Fujii,[23] although there are some differences in ϵ values, as shown in Table I. Also, our value of β of 1.1 is to be compared to their value of 1.8, but their work was done at a higher ionic strength (5 vs. 3 M). Thus we agree that only $CuCl_3{}^{2-}$ has a band centered at 273 nm, while both complexes absorb at about 230 nm (appearing as a shoulder for $CuCl_3{}^{2-}$).

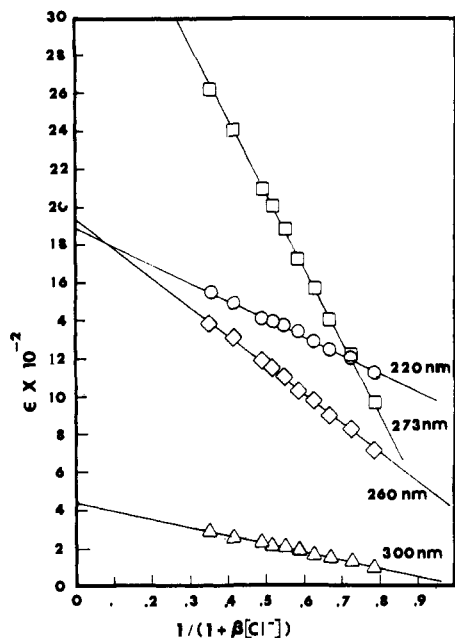In order to assess the nature of these transitions, in particular, to test for charge transfer to solvent (CTTS) character,

Figure 2. Plot of $\bar{\epsilon}$ vs. $1/(1 + \beta[Cl^-])$, where $\beta = 1.1 \pm 0.1$, at a series of wavelengths for the system, 0.01 M CuCl, 1.0 M H$^+$, 3 M ionic strength.

Table I

λ_{max}, nm	ϵ_1 (this work)	ϵ_1 (ref 23)	ϵ_2 (this work)	ϵ_2 (ref 23)
233		800 ± 20		1450 ± 10
230	1060 ± 30		1550 ± 10	
273	140 ± 30	0 ± 80	3980 ± 10	3330 ± 50

spectra were taken in various solvent systems. According to a detailed analysis of CTTS bands by Blandemer and Fox[29] there are a number of unique characteristics which can be used to diagnose such a transition. Among these are (1) a blue shift of several nanometers when changing the solvent from H_2O to D_2O; (2) a very slight red shift as the temperature is raised; (3) blue shifts when organic solutes and solvents are added; and (4) a blue shift for large increases in ionic strength. Table II lists the results of our application of tests for such properties in this system.

These results strongly suggest that for $CuCl_3^{2-}$, the band at 273 nm is CTTS, whereas the nature of the band at 230 nm is not clear for either complex. It is plausible to suggest that the 230-nm transition may be an atomic transition in both complexes, and that the 273-nm band is forbidden in the $CuCl_2^-$ ion. This, however, would not rule out the accessibility of the CTTS state in $CuCl_2^-$ via an internal transition from the atomic level, and if the CTTS state is the chemically reactive one, then photochemical activity could occur in $CuCl_2^-$ by absorption in the 230-nm band. It is postulated, then, that the primary step in the photolysis of $CuCl_3^{2-}$ at 273 nm is the formation of an excited CTTS state, and that this process may follow the absorption of light in the 230-nm band of either complex.

2. Photokinetics. We established, at the outset, using neutral density filters, that the photolysis rate was proportional to light intensity in the range of 275–320 nm. We also observed that at low concentrations of CuCl, in which only part of the incident light was absorbed, the rate at 275 nm was proportional to the fraction of incident light absorbed. Thus the system obeys the usual photochemical rate law

$$-d[Cu(I)]/dt = I_0\phi(1 - 10^{-A})S/V \qquad (4)$$

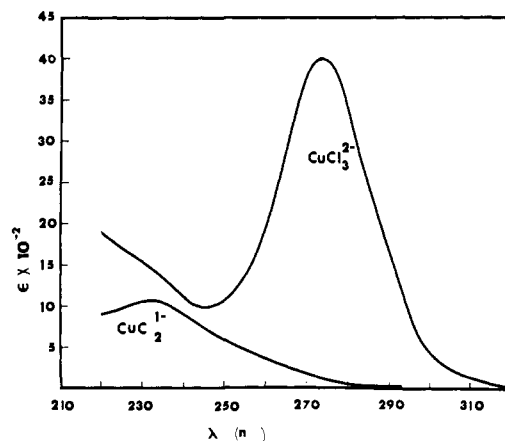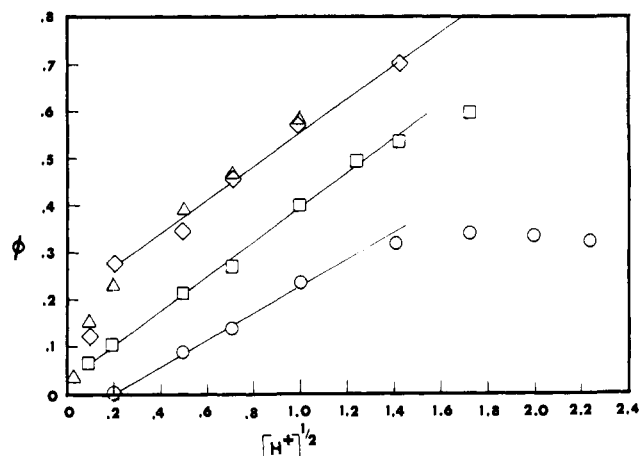Figure 3. Spectra of $CuCl_2^-$ and $CuCl_3^{2-}$ in 1.0 M H$^+$, 3.0 M ionic strength.

Figure 4. ϕ vs $[H^+]^{1/2}$ for 0.01 M solutions of CuCl in 1 M Cl$^-$ solutions. $[ClO_4^-] = \mu - 1$, $[Na^+] = \mu - [H^+]$, λ 274 nm, ionic strengths, $\triangle$, 1 M; $\diamond$, 2 M; $\square$, 3 M; $\bigcirc$, 5 M.

where I_0 = incident light intensity in einsteins cm^{-2} s^{-1}, ϕ = quantum yield defined as (mol Cu(I) oxidized)/einsteins absorbed, A = optical density, S = area of incident beam in cm^2, and V = volume of solution in liters. It was assumed that this law was obeyed at all other conditions studied.

3. Ionic Strength and Hydrogen Ion Dependence. A series of runs were made at 274 nm in which ionic strength was varied from 1 to 5 M, and hydrogen ion was varied from 0.01 M up to the limit of ionic strength. The results are summarized in Figure 4, in which ϕ is plotted vs $[H^+]^{1/2}$.[30] Such a plot was made in order to test for a Noyes type of scavenging mechanism.[31,32] In such a mechanism, the primary photoprocess results in a primary radical pair in close contact, which can either recombine or diffuse apart slightly to a secondary geminate pair, which also can undergo either recombination or diffusion into the bulk of the solution. The mathematical treatment[31] results in the expression

$$d\phi/d[S]^{1/2} = 2a(2\Pi k_s)^{1/2} \qquad (5)$$

where S is a reactive radical scavenger, a is a diffusion parameter, and k_s is the bimolecular scavenging rate constant. Noyes estimated that this type of behavior should be apparent above scavenger concentrations of 10^{-2} M. Our data do indeed show this linear relationship at all ionic strengths studied. Noyes also predicted[31] that at high scavenger concentrations all secondary pairs would be scavenged, and a leveling off in

Table II

solute	test	spectral result
0.01 M CuCl 0.25 M Cl⁻ 0.20 M Li⁺ 0.05 M NH₄⁺	solvent changed from H_2O to D_2O	$\nu 1l_{max}$ shifted from 274 to 271 nm, and 231 to 230 nm
0.01 M CuCl 1.0 M Cl⁻ 0.05 M NH₄⁺ 0.95 M Li⁺	solvent changed from H_2O to methanol	λ_{max} shifted from 276 to ca. 269 nm, no shift of band at 230 nm
0.01 M CuCl 1.0 M Cl⁻ 1.0 M H⁺	sucrose dissolved to 1 M	λ_{max} shifted from 276 to 273 nm, no apparent shift at 230 nm
0.01 M CuCl 1.0 M Cl⁻ 1.0 M H⁺	temperature raised from 25 to 70 °C	no detectable shift in either band, slight broadening of 273-nm transition
0.01 M CuCl 1.0 M Cl⁻ 1.0 M H⁺	addition of 2 M $NaClO_4$	λ_{max} shifted from 276 to 273 nm, and 232 to 226 nm

Table III. Effect of Ionic Strength on Parameters in Equation 5

μ, M	slope, $M^{-1/2}$	ϕ_{max}	$k_s \times 10^{-10}$, $M^{-1} s^{-1}$ Noyes	J–O–S
1.0	0.43	~0.85	0.3	0.8
2.0	0.36	~0.85	0.2	0.8
3.0	0.37	0.6	0.2	1.1
5.0	0.27	0.34	0.11	1.9

the ϕ vs. $[S]^{1/2}$ plot would occur, and this is observed in Figure 4, partly at 3 M ionic strength, and especially at 5 M ionic strength. Thus the leveled value of ϕ can be associated with the fraction of the primary pairs resulting in secondary pairs, i.e., the number escaping primary recombination. Table III gives the slopes and the maximum or estimated maximum values for ϕ at four ionic strengths. These slopes allow the calculation of the quantity $a(k_s)^{1/2}$. Noyes[31] has estimated that a reasonable value for a is $1.6 \times 10^{-6} s^{1/2}$, from which the values for k_s in Table III were calculated.

The later treatment by Jortner, Ottolenghi, and Stein (J–O–S)[18] yields the expression

$$\phi = \phi_0 + \alpha\Gamma[S]^{1/2} \qquad (6)$$

where ϕ_0 is the residual yield of pairs escaping both primary and secondary recombination without competitive scavenging by the scavenger, $\alpha = 2a(\Pi k_s)^{1/2}$, and Γ is the yield of primary pairs escaping primary recombination only. If we associate Γ with our estimated values for ϕ_{max}, we obtain the J–O–S values for k_s in Table III.

For the scavenging reaction

$$H^+ + H\cdot \rightarrow H_2^+ \qquad (7)$$

the rate constant is of the order of 10^4 $M^{-1} s^{-1}$.[18] On the other hand, pulse radiolysis has been used to measure accurately the rate constant for

$$H^+ + e_{aq}^- \rightarrow H\cdot \qquad (8)$$

and a value of 2.2×10^{10} $M^{-1} s^{-1}$ has been reported.[33] This is clearly in the range of k_s that we estimate, and hence we conclude that eq 8 is the scavenging reaction, and that hydrated electrons are therefore produced in this photoredox reaction.
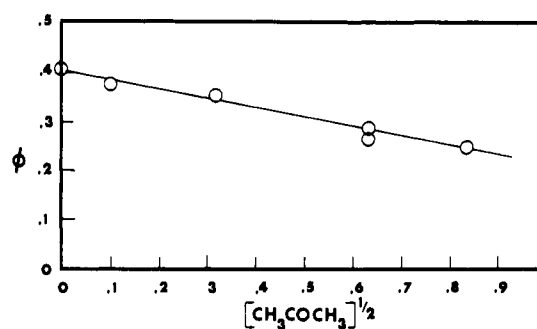
Recently, we have confirmed the production of hydrated

Figure 5. Plot of ϕ for H_2 production vs $[(CH_3)_2CO]^{1/2}$, 1 M HCl, 3 M ionic strength, 0.01 M CuCl, λ 274 nm.

electrons in a $CuCl_2^-$, $CuCl_3^{2-}$ solution containing no efficient electron scavengers, utilizing the laser flash apparatus of Grossweiner and Baugher.[34] After irradiation of a 3.8×10^{-4} M solution of CuCl in 1 M NaCl with the 17-ns, 265-Å pulse, a transient, with half-life of about 10^{-7} s, and with absorbances at 640, 550, 450, and 350 nm corresponding to the hydrated electron spectrum,[18] was observed. When the solution was saturated with N_2O the transient absorption disappeared entirely, further confirming the hydrated electron. The quantum yield for the formation of hydrated electron was estimated to be about 0.7, which is about the same as that for the reduction of H^+ in 0.01 M CuCl in 1 M HCl. In fact, when a solution of CuCl in 1 M HCl was laser photolysed, a longer lived transient, with half-life of about 1 μs, appeared, but it did not disappear upon saturation with N_2O, and therefore it could not be identified with the hydrated electron. This, of course, is as one would expect since H^+ would scavenge electrons too rapidly to allow their observation. We can only speculate as to the nature of this transient, which might be a hydride intermediate. Another transient, which appeared after the decay of the electron in the NaCl solution, was observed, with a half-life of about 1 μs. We intend to investigate the nature of these two transients further.[39]

4. Effect of Added Scavenger. Acetone, a known electron scavenger, was added to solutions containing 1 M HCl at $\mu = 3$ M. The plot in Figure 5 shows an inhibition of ϕ, measured by H_2 production and corrected for partial absorption of light by acetone at the irradiating wavelength of 274 nm. The rate
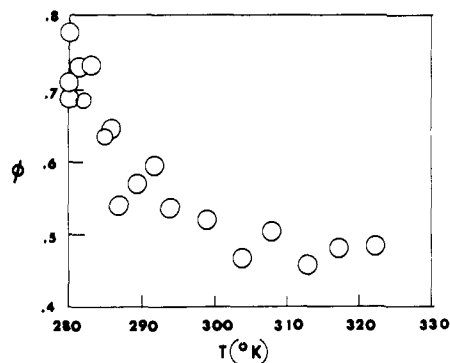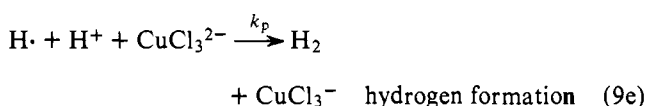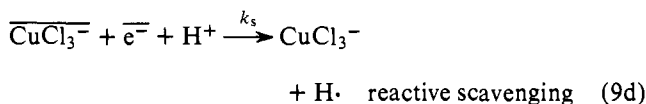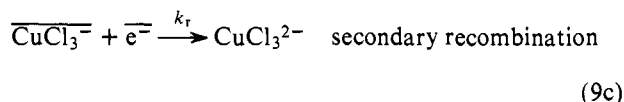
Figure 6. The quantum yield, ϕ, of 0.01 M CuCl in 1.0 M HCl, μ = 1 M, vs. temperature, K.

Figure 7. ϕ vs. [Cl⁻] in solutions which are 0.01 M CuCl, 1 M H⁺, μ = 3 M at wavelengths of O, 235 nm; □, 274 nm; △, 296 nm; ◊, 313 nm.

constant for scavenging of electrons by acetone has been reported as 5.6×10^9 M⁻¹ s⁻¹,[35] certainly within the range of being competitive with scavenging by hydrogen ion.

5. Effect of Temperature. The temperature dependence of ϕ at 274 nm, 1 M HCl, 0.01 M CuCl, and unit ionic strength is shown in Figure 6. The quantum yield drops from 0.78 at 280 K to ca. 0.47 at temperatures greater than 300 K. The leveling off of ϕ at higher temperatures to a value approximating half the maximum observed at lower temperatures suggests that the recombination of secondary pairs increases with temperature more than does the reactive scavenging and that a point is reached where they occur at the same rate which is clearly controlled by diffusion. Noyes[31,32] has shown that the secondary pair recombination probability is dependent not only on the rate of reencounter, but on a reaction probability at each reencounter. This reaction probability might be very sensitive to temperature if the partners have a Coulombic energy barrier. If the mechanism is as follows:

$$CuCl_3{}^{2-} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} \overline{CuCl_3{}^{-} \cdot e^{-}} \quad \text{primary pair} \quad (9a)$$

$$\overline{CuCl_3{}^{-} \cdot e^{-}} \overset{k_D}{\longrightarrow} \overline{CuCl_3{}^{-}} + \overline{e^{-}} \quad \text{secondary pair} \quad (9b)$$

$$\overline{CuCl_3{}^{-}} + \overline{e^{-}} \overset{k_r}{\longrightarrow} CuCl_3{}^{2-} \quad \text{secondary recombination}$$

$$(9c)$$

$$\overline{CuCl_3{}^{-}} + \overline{e^{-}} + H^{+} \overset{k_s}{\longrightarrow} CuCl_3{}^{-}$$

$$+ H \cdot \quad \text{reactive scavenging} \quad (9d)$$

$$H \cdot + H^{+} + CuCl_3{}^{2-} \overset{k_p}{\longrightarrow} H_2$$

$$+ CuCl_3{}^{-} \quad \text{hydrogen formation} \quad (9e)$$
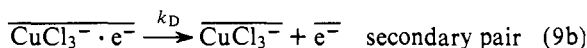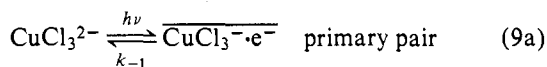
then step 9c is indeed a recombination between repulsive partners. Such a temperature effect would therefore appear only in electron formation from anions with a charge equal to or more negative than −2. The behavior of this system is to be contrasted to that of I⁻, which exhibits an increase in quantum yield of $e_{aq}{}^{-}$ production with temperature.[17] That system would involve recombination of I· and e⁻, which does not have a Coulombic barrier. The temperature dependence for photolytic hydrated electron production has been studied for Fe(CN)$_6{}^{4-}$,[36] and although it is positive, it is believed that hydrated electron production follows a MLCT absorption, through a somewhat different mechanism than that proposed here.

6. Effects of Wavelength and Chloride Ion. We observed that decreasing [Cl⁻] at μ = 3 M generally increased ϕ at a variety of wavelengths, as shown in Figure 7. The temptation is strong
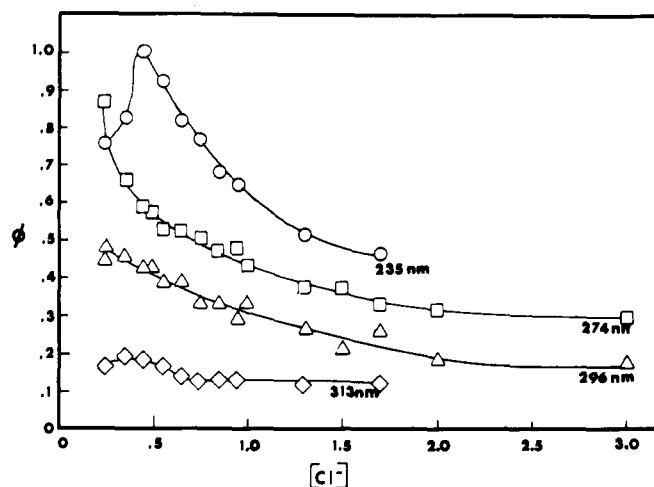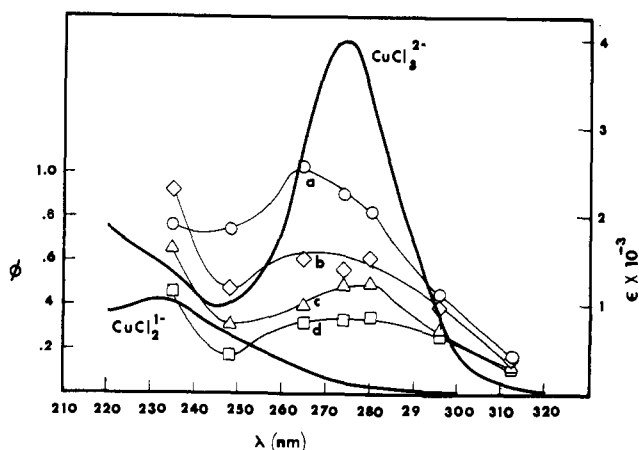

Figure 8. ϕ vs. λ for 0.01 M CuCl in solutions of μ = 3 M at chloride concentrations of (a) 0.25, (b) 0.55, (c) 0.85, and (d) 1.7 M. Spectra of Figure 3 are superimposed.

to explain this behavior in terms of a shift in equilibrium to the $CuCl_2{}^{-}$ ion, which might react with a higher value of ϕ than $CuCl_3{}^{2-}$. This cannot be the case if one accepts the spectra of Figure 3, since $CuCl_3{}^{2-}$ is absorbing most of the light at 274 nm even at the lowest chloride concentration, and at 295 nm it is the only absorbing species at all chloride concentrations. Even if the spectra of Figure 3 were incorrect one could not use equilibrium shifting to explain these effects since it is quite clear that the band at 274 nm intensifies at higher rather than lower [Cl⁻] and hence must correspond to the trichloro complex.

The most likely cause of this behavior is a salt effect. Even though μ was constant for all these runs, $ClO_4{}^{-}$ and Cl⁻ were being interchanged, and since increased ionic strength does inhibit the reaction, chloride ion may simply have a stronger effect than perchlorate, owing to its higher charge density, and therefore its stronger tendency to form ion pairs and to change the nature of the solvent. Salt effects on this and similar phtolyses are a current area of investigation in these laboratories.

Figure 8 shows the wavelength dependence of ϕ at several values of [Cl⁻] ranging from 0.25 to 1.7 m, with the absorption spectra of the two complexes superimposed. As the wavelength was decreased from 313 nm down to the middle of the $CuCl_3{}^{2-}$ CTTS transition at about 265 nm, the quantum yield increased presumably because of the increasing amount of excess energy

favoring diffusion to the secondary pairs. Below 265 nm the absorbing species is shifting from primarily $CuCl_3^{2-}$ to $CuCl_2^-$, especially at low $[Cl^-]$. For example, at $[Cl^-] = 1.7$ M the fraction of light absorbed by $CuCl_2^-$ is 0.050, 0.275, and 0.285 at 265, 246, and 235 nm, respectively, and at $[Cl^-] = 0.25$ M the fractions are 0.263, 0.721, and 0.731, respectively. Indeed, in order for the value of ϕ to be so large at 0.25 M chloride concentration and at 235 nm, one is compelled to assume that $CuCl_2^-$ must be undergoing photolysis. This could then explain the dips in the curves at 246 nm, since this wavelength might correspond to a trailing off of ϕ for $CuCl_2^-$ at longer wavelengths. Although this argument is rather qualitative, an estimate of the quantum yields for $CuCl_2^-$ at 235 nm can be made on the assumption that the quantum yield for $CuCl_3^{2-}$ at this wavelength is about the same as it is at 274 nm. These values turn out to be about 0.7, 1.2, 0.8, and 0.7 at $[Cl^-] = 0.25, 0.55, 0.95,$ and 1.7 M, respectively. Although these values have rather large error limits, at least ±50%, they are in the same range as those for the photolysis of $CuCl_3^{2-}$, and it seems reasonable to suppose that a similar mechanism obtains.

7. Implications for Solar Energy Conversion. Using values reported in the literature for stability constants of $CuCl_3^{2-}$ [22,37] and for $CuCl_3^-$,[26,38] and the standard oxidation potential for Cu^+ of -0.153 V, the value of $\Delta G°$ at 298 K is about 11 kcal/mol for the reaction

$$CuCl_3^{2-} + H^+ \xrightarrow{h\nu} CuCl_3^- + \tfrac{1}{2}H_2(g) \qquad (10)$$
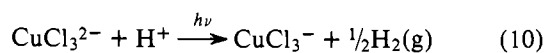
From the maximum value of ϕ we measured for $CuCl_3^{2-}$ of about 0.8 at 265 nm, we obtain an energy conversion efficiency at this wavelength of 8%. This efficiency reduces to about 2% at the absorption cutoff at 320 nm. Since the insolation spectrum cuts off at around 285 nm, there is a narrow band of the solar spectrum capable of promoting this reaction, and we have demonstrated[5] that it can indeed be carried out in sunlight. The integrated efficiency over the entire solar spectrum is quite low because of the lack of any absorption of visible light. In spite of this, photoredox reactions involving the two oxidation states of copper may offer certain advantages such as low cost, low toxicity, and high stability of the two states. And it may be that the spectral efficiency may be much improved by consideration of MLCT transitions.

References and Notes

(1) (a) Presented, in part, at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977, and the International Conference on the Photochemical Conversion and Storage of Solar Energy, London, Ontario, Canada, Aug 1976. (b) New Mexico State University. (c) Indiana-Purdue University of Fort Wayne.
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(39) **Note added in proof.** After acceptance of this article, independent confirmation of the formation of aquated electrons from the photolysis of $CuCl_3^{2-}$ and evidence for a long-lived copper hydride intermediate was published by G. Ferraudi, *Inorg. Chem.*, **17**, 1370 (1978).