

## Spectra and Photochemistry of the Chloro Complexes of Copper(I)

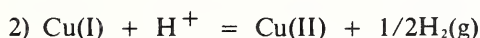
KRISTINE S. KURTZ AND KENNETH L. STEVENSON  
Department of Chemistry  
Indiana University-Purdue University at Fort Wayne  
Fort Wayne, Indiana 46805

### Introduction

Previous studies (9,8,7,4,1) have shown that in aqueous chloride media, the two copper(I) complexes shown in the following equation are in equilibrium:



The purposes of this study were to achieve the following measurements of this system at 5M ionic strength: 1) verification of the equilibrium constant measured by Ahrland and Tagesson (1), 2) to resolve the ultraviolet charge-transfer-to-solvent (CTTS) spectra of these two complexes, and 3) to determine the quantum yields of the following photoredox reaction:



for each of the two complexes at several wavelengths in the CTTS absorption region.

### Procedure

Seven solutions in which chloride ion concentration varied from 0.2M to 5M at constant ionic strength of 5M and constant hydrogen ion concentration of 1M were prepared using analytical grade reagents (perchloric acid, sodium perchlorate, sodium chloride, and hydrochloric acid) and deionized water. Since Cu(I) solutions are readily oxidized by air, the 0.01M cuprous chloride solutions were prepared by inserting test tubes containing preweighed amounts of cuprous chloride into the flasks containing the solutions, above, and bubble-degassed with argon through septums in the top of the flasks. The flasks were then tipped and the solid dissolved.

The absorbance spectra of the equilibrated solutions were measured in the 200-340 nm range where the two complexes exhibit CTTS absorption (4). A Beckman ACTA M-VI spectrometer interfaced with a HP-86 microcomputer allowed the spectra to be stored on disk for subsequent spectral computations.

The photochemical setup consisted of a Schoeffel 1000-watt mercury-xenon high pressure arc lamp, a Jarrell Ash quarter meter monochromator, a thermostated 1-cm cuvette, and a recording gas volumeter (3) for measuring the evolved hydrogen gas. Light intensities were measured in the cuvette with the potassium trioxalatoferate (III) actinometer (5). Volumeter chart traces were digitized and integrated rates determined with the computer.

### Results and Discussion

Figure 1 shows the molar extinction absorption spectra of the seven solutions of varying chloride ion concentration. The increase in peak absorption at 274 nm with increase in  $[\text{Cl}^-]$  indicates that the trichloro species has a stronger absorption in this region. Since there are only two complexes in equilibrium in this system, one can show (4) that the measured extinction coefficient is a function of the extinction coefficient

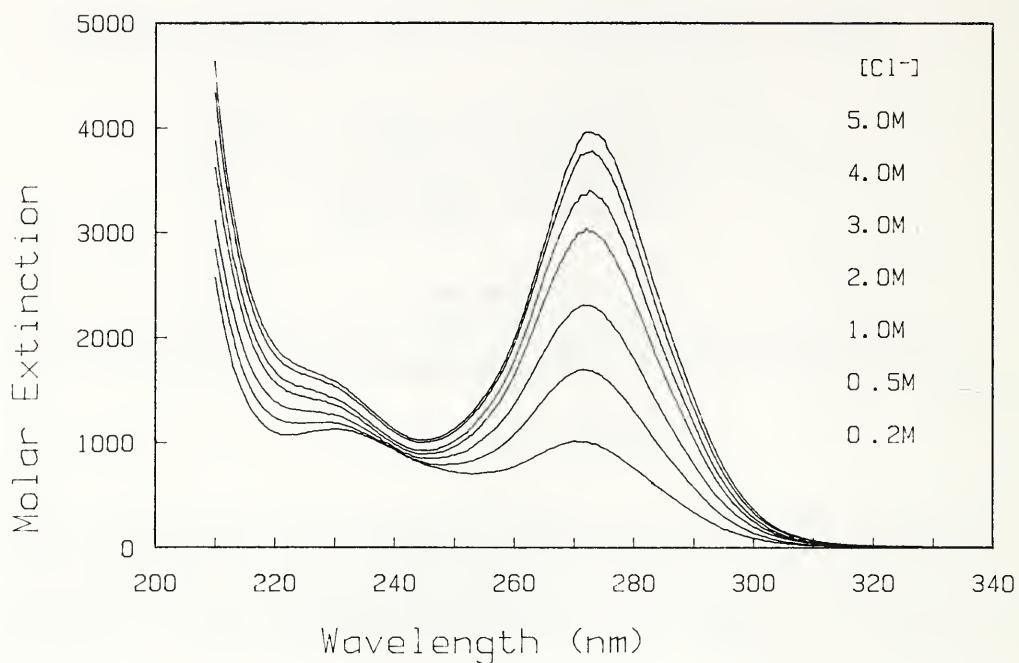


FIGURE 1. Molar extinction spectra of 0.01M CuCl in 5M ionic strength medium in which  $0.2 < [\text{Cl}^-] < 5.0\text{M}$ , at  $25^\circ\text{C}$ .

icients of di- and trichloro complexes,  $e_2$  and  $e_3$ , and the equilibrium constant,  $K$ , for equation 1, as follows:

$$3) e = e_3 + (e_2 - e_3)/(1 + K[\text{Cl}^-])$$

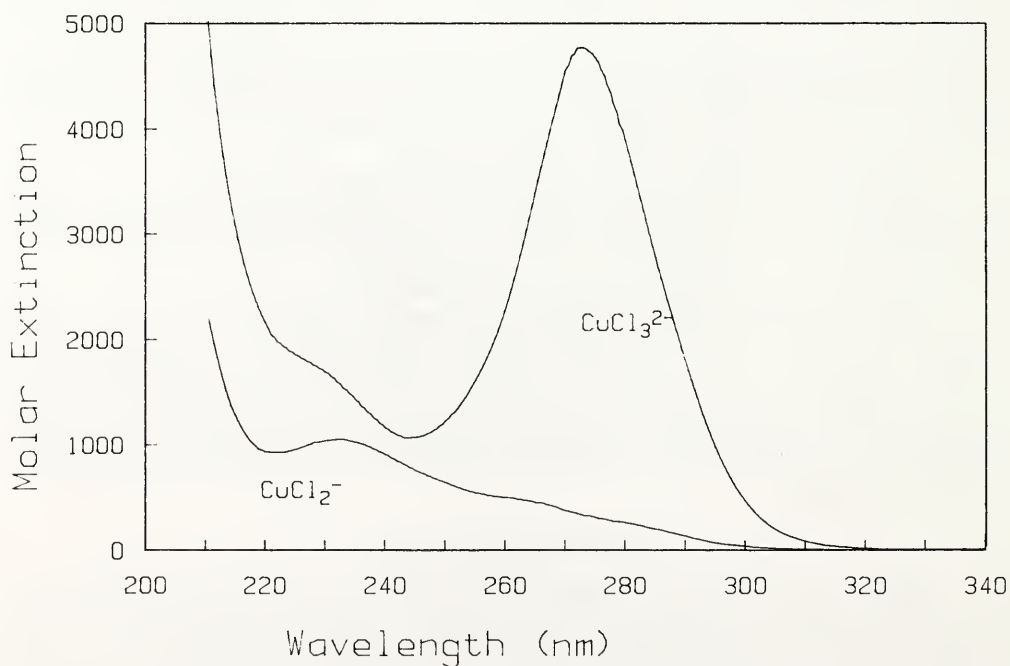


FIGURE 2. Resolved molar extinction spectra of  $\text{CuCl}_2^-$  and  $\text{CuCl}_3^{2-}$  at 5M ionic strength,  $25^\circ\text{C}$ , assuming  $K = 0.72$ .

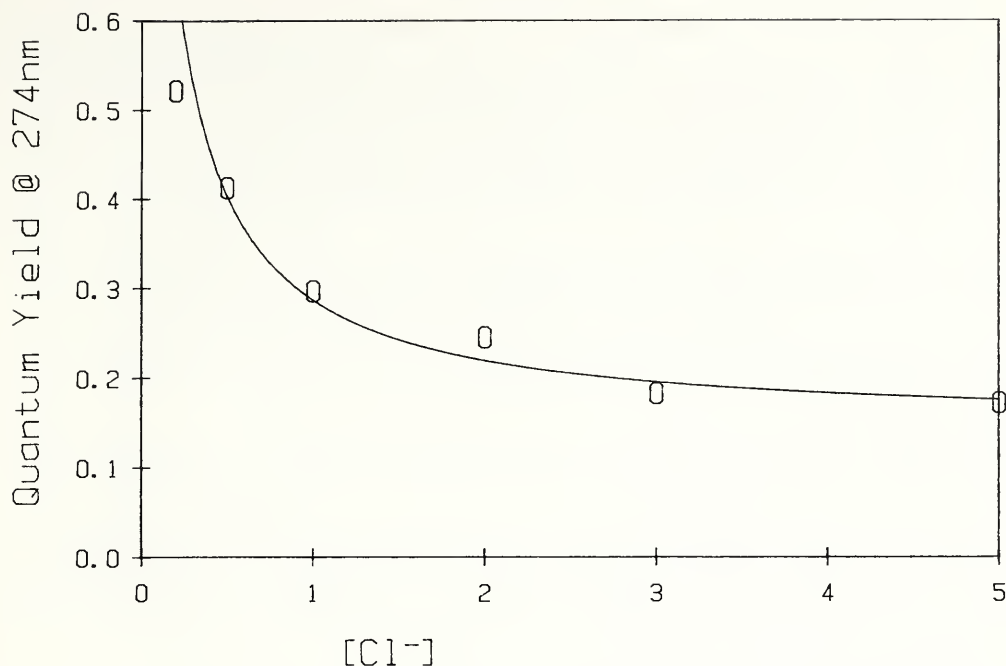


FIGURE 3. Quantum yield of photooxidation of aqueous CuCl versus chloride ion concentration, at 274 nm irradiating wavelength, 25°C, 5M ionic strength.

The computer was used to find the value of  $K$  which gave the best linear fit of  $e$  vs.  $1/(1 + K[Cl^-])$  in the 271 to 281 nm region where the spectra are most sensitive to chloride ion concentration. This gave an average value of  $K$  of  $0.72 \pm 0.08$ , which compares favorably to the value of  $0.76 \pm 0.07$  determined by Ahrlund and Tagesson from electrochemical measurements (1). Using our value of  $K$  the computer then calculated  $e_2$  and  $e_3$  from equation 3 at all wavelengths, resulting in the resolved spectra for the two complexes, as shown in Figure 2. It is noteworthy that the trichloro complex has a strong band at 274 nm compared to a weak shoulder somewhat blue shifted in the dichloro species, whereas both exhibit transitions more nearly equal in the 230-235 nm region.

Figure 3 indicates that the quantum efficiency of photolysis into the band at 274 nm is depressed by increasing chloride ion concentration. This would imply that the trichloro species has a lower quantum efficiency than the dichloro complex. One can show, using Beer's law, that the net quantum yield,  $\phi$ , is related to individual quantum yields of the di- and trichloro complexes,  $\phi_2$  and  $\phi_3$  as follows:

$$4) \quad \phi = \phi_3 + \frac{(\phi_2 - \phi_3) e_2}{(e_2 + e_3 K [Cl^-])}$$

A suitable linear plot of this function at 274 nm is shown in Figure 4, resulting in resolved quantum yields for the two complexes. Equation 4 was used for the curve-fit in Figure 3 using the results of the linear regression. These quantum yields and those determined at two other wavelengths are shown in Table 1.

These results show that the quantum yields bear an inverse relationship to molar extinction coefficients, since the trichloro complex, which has the larger absorbance, has the smaller quantum yield. This may be rationalized by the fact that lifetime of

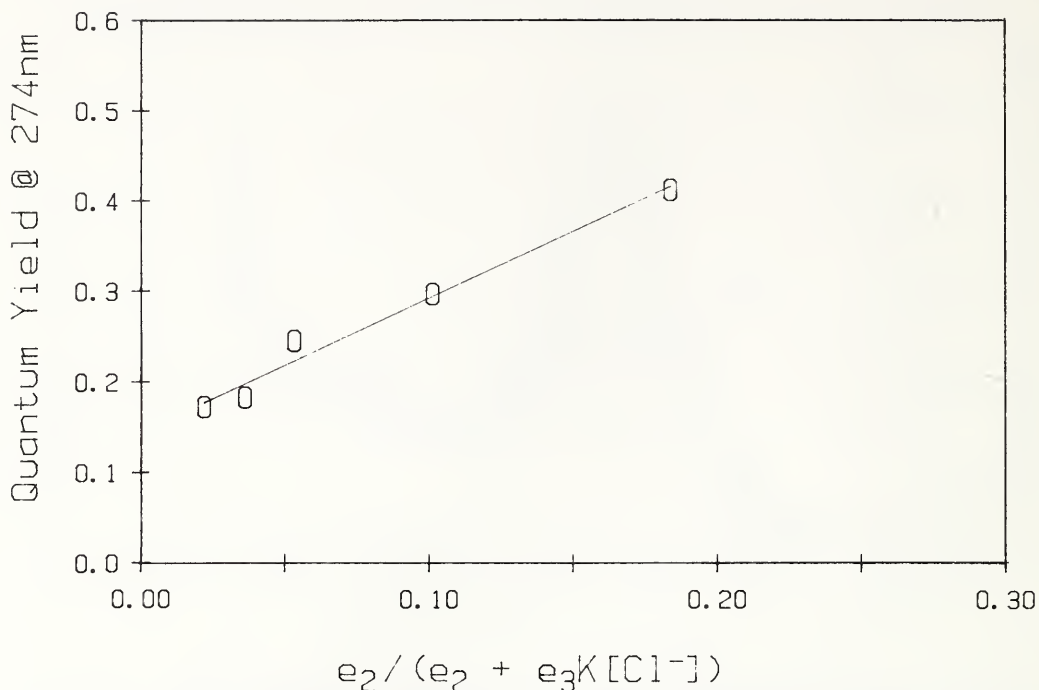


FIGURE 4. Quantum yield of photooxidation of aqueous CuCl versus the function,  $e_2/(e_2 - e_3K[Cl^-])$ , at same conditions as Figure 3.

any excited state is inversely proportional to the oscillator strength (2). The dichloro species, which has the lower absorbance, and hence lower oscillator strength, would have a longer excited state lifetime, thus resulting in a greater probability for the hydrated electron produced by the photolysis to be scavenged by hydrogen ion (6). Further experiments are in progress, with the intent of discerning similarities or contrasts with spectral and photochemical properties of other halo complexes, and what role stereochemistry plays in these properties.

#### Acknowledgment

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

#### Literature Cited

1. Ahrlund, A., and Tagesson, B. 1977. Thermodynamics of Metal Complex Formation in Aqueous Solution. XII. Equilibrium Measurements on the Copper(I) Bromide, Iodide and Thiocyanate Systems. *Acta. Chem. Scand.*, A31(8):615.
2. Calvert, J.G. and Pitts, Jr., J. N. *Photochemistry*. John Wiley & Sons, Inc., New York, 1966, 173-174 pp.

TABLE 1: Quantum Yields

| Wavelength (nm) | Quantum Yield |               |
|-----------------|---------------|---------------|
|                 | $CuCl_2^-$    | $CuCl_2^{2-}$ |
| 265             | 1.30 ± 0.12   | 0.178 ± 0.010 |
| 274             | 1.62 ± 0.28   | 0.144 ± 0.010 |
| 296             | 1.47 ± 0.25   | 0.275 ± 0.010 |

3. Davis, D.D., and Stevenson, K.L. 1977. A Recording Gas Microvolumeter. *J. Chem. Educ.*, 54: 394.
4. Davis, D.D., Stevenson, K.L., and Davis, C.R. 1978. Photooxidation of Dichloro- and Trichlorocuprate(I) Ions in Acid Solution. *J. Amer. Chem. Soc.*, 100(17): 5344.
5. Hatchard, C.G., and Parker, L.A. 1956. A New Sensitive Chemical Actinometer II. Potassium Ferrioxalato as a Standard Chemical Actinometer. *Proc. Roy. Soc. London*, A235: 518.
6. Stevenson, K.L., Kaehr, D.M., Davis, D.D., and Davis, C.R. 1980. Long-Lived Intermediates in the Production of Hydrogen from Ultraviolet Photolysis of Acidic Di- and Trichlorocuprate(I) Ions. *Inorg. Chem.*, 19(3): 782.
7. Sugasaka, K. and Fujii, A. 1976. A Spectrophotometric Study of Copper (I) Chloro-Complexes in Aqueous 5M Na(Cl,ClO<sub>4</sub>) Solutions. *Bull. Chem. Soc. Japan*, 49(1): 82.
8. Sukhova, T.G., Temkin, O.N., and Flid, R.M. 1970. Electronic Absorption Spectra of Chloro-complexes of Univalent Copper in Aqueous Solution. *Russ. J. Inorg. Chem.*, 15(7): 949.
9. Sukhova, T.G., Temkin, O.N., Flid, R.M., and Kaliya, T.K. 1968. Determination of the Composition and Stability Constants of Chlorocuprate (I) Complexes in Concentrated Solutions. *Russ. J. Inorg. Chem.*, 13(8): 1072.

