© 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 3566—3569 (1985) [Vol. 58, No. 12

Photoredox Chemistry of Chloro and Bromo Complexes of Copper(II) in Methanolic Medium

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(Received August 20, 1984)

Investigation of the photoreduction of copper(II) to copper(I) in methanolic solutions of copper(II) chloride and copper(II) bromide indicates the halide-to-copper(II) charge-transfer (CT) responsible for the photoreduction. Quantum yields for the formation of copper(I) as a function of irradiating wavelength and copper(II) halide concentration show that $[Cu(CH_3OH)_5Cl]^+$ and $[Cu(CH_3OH)_4Cl_2]$ have identical photoreaction efficiency, while $[Cu(CH_3OH)_4Br_2]$ is more photoreactive than $[Cu(CH_3OH)_5Br]^+$. In the copper(II) chloride system the chloride-to-copper(II) CT band centered around 272 nm appears to be responsible for the photoreaction, while the bromide-to-copper(II) CT band centered around 245 nm effects the photoreaction in copper(II) bromide system.

Qualitative aspects of the photochemistry of copper(II) salts in organic solvents have been investigated[1] since 1804. We have reported recently the quantitative aspects of the photoredox chemistry of copper(II) perchlorate in methanolic medium;[2] the primary photoprocess is the homolytic cleavage of copper(II)–methanol bond caused by the broad methanol-to-copper(II) charge-transfer absorption with λ_{max} at 235±2 nm. Kochi[3] employed copper(II) chloride in the chlorination of organic compounds. The primary photoprocess was proposed to be the redox reaction of chloro complexes of copper(II), forming copper(I) and Cl atoms. The present work deals with the quantitative aspects of the photoredox chemistry of chloro and bromo complexes of copper(II) in methanolic medium.

Experimental

Copper(II) perchlorate (Alfa Inorganics) was purified by recrystallization from hot water and dried under vacuum. Copper(II) chloride, copper(II) bromide, lithium chloride, and lithium bromide were reagent grade chemicals (BDH) and were dried under vacuum before use. Methanol and methyl methacrylate were purified by published procedures.[4]

Gross irradiations, from which no quantum yield data were desired, were carried out in a Rayonet photochemical reactor fitted with RPR 3500 Å lamps. Photochemical irradiations, from which quantum yields were to be determined, were performed with a Hanovia 901C-1 150 W xenon lamp dispersed through a Bausch and Lomb 33-86-40 monochromator. Intensity reductions were accomplished by Baird-Atomic neutral density filters. Samples were irradiated in a 1-cm rectangular cell (volume 4.5 cm^3) fitted with ground joint and teflon stopper. The cell was thermostated at 25±0.1 °C by circulating water through the cell holder from a constant-temperature water bath. All methanolic copper(II) solutions were deaerated by bubbling oxygen-free dry nitrogen. Manipulations of methanol and methanolic solutions were carried out in a dry box in an oxygen-free dry-nitrogen atmosphere.

Source intensities were measured by potassium trioxalatoferrate(III) actinometry.[5] Copper(I) was determined spectrophotometrically as the $[Cu(dmp)_2]^+$ complex (dmp=2,9-dimethyl-1,10-phenanthroline) which has a characteristic absorption maximum at 450 nm (ε=7530 $dm^3\,mol^{-1}\,cm^{-1}$ in methanol). A large excess of dmp was always employed. Absorption due to $[Cu(dmp)_2]^{2+}$ at 450 nm (ε=150 $dm^3\,mol^{-1}\,cm^{-1}$ in methanol) was taken into consideration in computing the concentration of copper(I). Formaldehyde formed during the photolysis was determined by the published procedure.[2] Techniques utilized in chemical scavenging experiments with methyl methacrylate have been described.[6]

Results and Discussion

Irradiation of methanolic solutions of copper(II) chloride and copper(II) bromide at 350 nm resulted in the formation of copper(I) and formaldehyde as the products, the concentration of formaldehyde being always half of that of copper(I). At this wavelength the predominant light absorbing species are the halo complexes of copper(II). The results obtained are shown in Table 1. These results are identical to those reported earlier by us for the photolysis of methanolic solution of copper(II) perchlorate[2] in which the photoactive species is $[Cu(CH_3OH)_6]^{2+}$. However, the photopolymer obtained in the radical scavenging experiments using methyl methacrylate yielded positive tests for both the hydroxyl and halogen end

TABLE 1. STOICHIOMETRIC RELATION BETWEEN COPPER(I) AND FORMALDEHYDE IN THE PHOTOLYSIS OF COPPER(II) HALIDES IN METHANOL MEDIUM

$[CuX_2]$	$[Cu^+]$	$[CH_2O]$	$[Cu^+]$ / $[CH_2O]$
1.0×10^{-2}*	8.04×10^{-4}	4.03×10^{-4}	1.99
1.0×10^{-2}	7.60×10^{-3}	3.80×10^{-3}	2.00
7.0×10^{-3}*	5.22×10^{-4}	2.60×10^{-4}	2.01
7.0×10^{-3}	4.15×10^{-4}	2.10×10^{-4}	1.98
4.0×10^{-3}*	3.31×10^{-4}	1.66×10^{-4}	1.99
4.0×10^{-3}	2.55×10^{-4}	1.28×10^{-4}	1.99
1.0×10^{-3}*	1.00×10^{-4}	5.00×10^{-5}	2.00
1.0×10^{-3}	8.60×10^{-5}	4.28×10^{-5}	2.01
1.0×10^{-4}*	8.95×10^{-6}	4.50×10^{-6}	1.99
1.0×10^{-4}	9.50×10^{-6}	4.80×10^{-6}	1.98

All the concentrations are in mol dm^{-3}. Wavelength of irradiation 350 nm. Time of irradiation was adjusted to maintain the photolysis between 5—10% of the initial copper(II) concentration. Copper(II) halide concentrations before the photolysis are indicated. Asterisks indicate copper(II) chloride solutions and the others copper(II) bromide.

groups for the chloride and bromide salts.[7] As the concentration of methyl methacrylate was increased (at constant initial concentration of 0.001 mol dm^{-3} for the copper(II) halides) the concentration of OH end group decreased, while the concentration of halogen end group increased. At [methyl methacrylate]> 0.1 mol dm^{-3}, the concentration of halogen end groups was large and unaffected by further increases in the concentration of methyl methacrylate, while the concentration of OH end group was virtually zero. These results indicate that the halogen atoms are produced in the primary photoreaction and the $\cdot CH_2OH$ radicals[8] are formed as product of secondary reactions of halogen atoms with methanol. If $\cdot CH_2OH$ were a primary product, with X· being formed *via* scavenging of $\cdot CH_2OH$ by X^-, the opposite result would be expected. The observation suggests instead that methyl methacrylate and methanol are competitive scavengers of halogen atoms. Hence, we suggest the homolytic cleavage of Cu(II)–X producing Cu(I) and X· as the primary photoprocess. The halogen atom may reoxidize copper(I) to copper(II) or may be scavenged by CH_3OH yielding $\cdot CH_2OH$ and HX. It has been reported that the principal reaction of the radical $\cdot CH_2OH$ is reduction of copper(II) leading to copper(I) and formaldehyde.[2] This is in agreement with the present result $[Cu^+]/[CH_2O]=2.0$ (Table 1). The following Eqs. may summarize the above observations.

$$CuX^+ (\text{or } CuX_2) \xrightarrow{h\nu} [Cu^+\cdot X] \quad (\text{or } [CuX\cdot X]) \tag{1}$$

$$[Cu^+\cdot X] (\text{or } [CuX\cdot X]) \longrightarrow Cu^+ + \cdot X \quad (\text{or} \quad Cu^+ + X^- + \cdot X) \tag{2}$$

$$\cdot X + CH_3OH \longrightarrow \cdot CH_2OH + HX \tag{3}$$

$$\cdot CH_2OH + Cu^{2+} \longrightarrow Cu^+ + HCHO + H^+ \tag{4}$$

Quantum yields for the formation of copper(I) in the photoreduction of copper(II) chloride as a function of initial copper(II) chloride concentration are presented in Table 2. For [copper(II) chloride]<0.002 mol dm^{-3} the light absorption was incomplete (pathlength 1.0 cm) and was taken into account in calculating the quantum yields. Manahan and Iwamoto have shown that in methanol $[Cu(CH_3OH)_5Cl]^+$ and $[Cu(CH_3OH)_4Cl_2]$ are the predominant species.[9] The absorption spectra of these species in methanol are not known. However, the work of Baaz *et al.* has proved that in acetonitrile medium the mono- and dichlorocopper(II) complexes have nearly identical absorption spectra with absorption maximum at 310 nm.[10] We repeated the work of Baaz *et al.* in methanol medium using $Cu(ClO_4)_2$ and LiCl. Addition of LiCl to methanolic solution of $Cu(ClO_4)_2$ (5.0×10^{-4} mol dm^{-3}) gave rise to an absorption with maximum at 272 nm. This absorption centered around 272 nm increased until the ratio $[Cu(ClO_4)_2]/[LiCl]=1.0$. Further increase in LiCl concentration produced a slow and steady decrease in the absorption. This agrees with the findings of Baaz *et al.* that the mono- and dichlorocopper(II) complexes have nearly identical absorption spectra. Also the present results indicate that the molar absorptivity of the dichlorocopper(II) complex is less than that of the monochloro complex. The spectra of copper(II) chloride obtained as a function of concentration corroborate the above observations. An increase in ε for the band centered around 272 nm is observed upto a copper(II) chloride concentration 3.0×10^{-4} mol dm^{-3}. Further increase in concentration showed a decrease in these ε values. This indicates that $[Cu(CH_3OH)_6]^{2+}$ and $[Cu(CH_3OH)_5Cl]^+$ are at equilibrium at concentrations of copper(II) chloride $\leq 3.0\times10^{-4}$ mol dm^{-3}, while $[Cu(CH_3OH)_5Cl]^+$ and $[Cu(CH_3OH)_4Cl_2]$ are at equilibrium for higher concentrations of copper(II) chloride. The constancy of the quantum yields for the concentration range $1.0\times10^{-4}-2.0\times10^{-3}$ mol dm^{-3} (Table 2) indicates that the monochloro and the dichlorocopper(II) complexes have nearly identical photoreduction efficiency. This behavior is different from that observed for the photoreduction of copper(II) bromide (see below). The decrease in quantum yields for concentrations higher than 2.0×10^{-3} mol dm^{-3} (Table 2) is probably a consequence of depth effect,[2] or reoxidation of copper(I) by Cl_2^- radicals. Increase in the concentration of copper(II) chloride increases the concentration of free Cl^- which may compete with methanol in scavenging Cl atoms. The Cl_2^- species may reoxidize copper(I) with consequent reduction in quantum yield, or may be scavenged by methanol producing $\cdot CH_2OH$ and HCl. However, the final products and the ratio $[Cu^+]/[CH_2O]$ will be unaffected by these reactions. Quantum yield for the formation of copper(I) as a function of irradiating wavelength (Fig. 1) indicate that a charge-transfer band centered around 272 nm is, in fact, responsible for the photoreduction of copper(II) in methanolic solution of copper(II) chloride.

TABLE 2. QUANTUM YIELD FOR THE FORMATION OF COPPER(I) IN METHANOLIC SOLUTIONS OF COPPER(II) CHLORIDE

$[CuCl_2]$ / mol dm^{-3}	$\Phi^{a)}$	$[CuCl_2]$ / mol dm^{-3}	$\Phi^{a)}$
6.0×10^{-5}	0.077	3.0×10^{-3}	0.060
1.0×10^{-4}	0.079	4.0×10^{-3}	0.041
2.5×10^{-4}	0.077	6.0×10^{-3}	0.030
5.0×10^{-4}	0.080	8.0×10^{-3}	0.025
1.0×10^{-3}	0.078	1.0×10^{-2}	0.022
2.0×10^{-3}	0.079	1.5×10^{-2}	0.020

a) All±0.001; irradiating wavelength 300 nm; incident intensity $6.67\pm0.01\times10^{14}$ q s^{-1}.

Photoredox chemistry of copper(II) bromide does not parallel that of copper(II) chloride. Quantum yields as a function of initial concentration of copper(II) bromide (Table 3) show that higher concentrations are more effective. The quantum yield values in the concentration range 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3} are similar to those reported for the photoreduction of copper(II) perchlorate in methanol.[2] A substantial

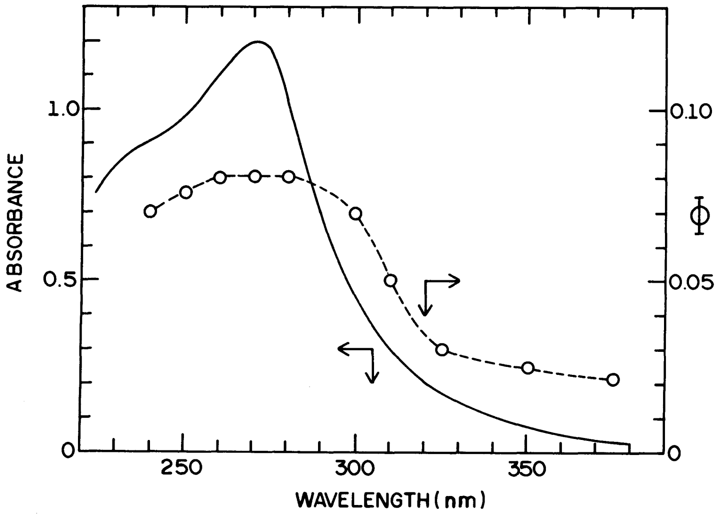

Fig. 1. Electronic absorption spectrum of 5.0×10^{-4} mol dm^{-3} copper(II) chloride in methanol (continuous line), and the variation of quantum yield for the formation of copper(I) as a function of irradiating wavelength (broken line). Initial copper(II) chloride concentration employed for the irradiations was 5.0×10^{-4} mol dm^{-3}.

Table 3. Quantum yield for the formation of copper(I) in methanolic solutions of copper(II) bromide

[CuBr$_2$] mol dm^{-3}	$\Phi^{a)}$	[CuBr$_2$] mol dm^{-3}	$\Phi^{b)}$
5.0×10^{-5}	0.110	1.0×10^{-2}	0.40
1.0×10^{-4}	0.087	2.0×10^{-2}	0.60
2.0×10^{-4}	0.055	3.0×10^{-2}	0.85
5.0×10^{-4}	0.028	4.0×10^{-2}	1.10
8.0×10^{-4}	0.024	5.0×10^{-2}	1.40
1.0×10^{-3}	0.035	6.0×10^{-2}	1.35
2.0×10^{-3}	0.052	8.0×10^{-2}	1.30
4.0×10^{-3}	0.105	1.0×10^{-1}	1.15
8.0×10^{-3}	0.150		

a) All±0.001. b) All±0.01; irradiating wavelength 250 nm; incident intensity $2.32\pm0.01\times10^{14}$ q s^{-1}.

increase in the quantum yields occurs for [copper(II) bromide]$>8.0\times10^{-4}$ mol dm^{-3}. We have reported recently[11] that only [Cu(CH$_3$OH)$_6$]$^{2+}$, [Cu(CH$_3$OH)$_5$Br]$^+$, and [Cu(CH$_3$OH)$_4$Br$_2$] are important in methanolic medium at low concentrations of copper(II) (3.0×10^{-4} mol dm^{-3}) and [LiBr] up to 0.1 mol dm^{-3}. In methanol the monobromo and dibromo complexes of copper(II) have distinctly different spectra and, hence, their formation can be identified.[11] Spectral identification of the monobromo- and dibromocopper(II) complexes in methanolic solutions of copper(II) bromide was carried out in the concentration range 5.0×10^{-5}—8.0×10^{-3} mol dm^{-3}. A graph of molar absorptivity *vs.* wavelength showed an increase in molar absorptivity for $\lambda>235$ nm and a decrease for $\lambda<235$ nm with an isosbestic point at 235 nm in the concentration range 5.0×10^{-5}—5.0×10^{-4} mol dm^{-3}. In agreement with our earlier work[11] this result shows an equilibrium involving [Cu(CH$_3$OH)$_6$]$^{2+}$ and [Cu(CH$_3$OH)$_5$Br]$^+$. For concentrations higher than 5.0×10^{-4} mol dm^{-3} a general increase in molar absorptivity was observed for all wavelengths in the range 400—220 nm, the increases being larger for $\lambda<290$ nm. These results indicate the increasing formation of [Cu(CH$_3$OH)$_4$Br$_2$] at the expense of the other two species when the [copper(II) bromide]$>5.0\times10^{-4}$ mol dm^{-3}. The increase in quantum yields for [copper(II) bromide]$>8.0\times10^{-4}$ mol dm^{-3} shows that [Cu(CH$_3$OH)$_4$Br$_2$] is more photoactive than the other two species. Also a quantum yield which exceeds unity indicates that the deactivation reactions are less efficient in the photolysis of [Cu(CH$_3$OH)$_4$Br$_2$] in comparison to that of [Cu(CH$_3$OH)$_5$Br]$^+$. The principal deactivation processes may be represented by the reverse of Eq. 1 (primary cage recombination) and the reoxidation of copper(I) by ·X (secondary recombination) represented by Eq. 5.

$$\mathrm{Cu^+ + \cdot X \xrightarrow{X^-} CuX^+(or\ CuX_2)} \qquad (5)$$

Since for every copper(I) ion formed photochemically (Eq. 1) another copper(I) is formed thermally (Eq. 4), a quantum yield of 2.0 is attainable if Eqs. 1—4 represent entirely the photoreaction and the ensuing thermal reactions. However, the fact that this value is not attained experimentally indicates the importance of deactivation processes.

The nearly identical quantum yield values for the photoreduction of copper(II) perchlorate and copper(II) bromide in the concentration range 5.0×10^{-5}—5.0×10^{-4} mol dm^{-3} (compare this work with the results of Ref. 2) may indicate either that [Cu(CH$_3$OH)$_6$]$^{2+}$ and [Cu(CH$_3$OH)$_5$Br]$^+$ have nearly identical photoreduction efficiency or [Cu(CH$_3$OH)$_5$Br]$^+$ is photochemically inactive. The former seems more plausible. Since [Cu(CH$_3$OH)$_5$Br]$^+$, which is in equilibrium with [Cu(CH$_3$OH)$_6$]$^{2+}$ at this concentration range, is respon-

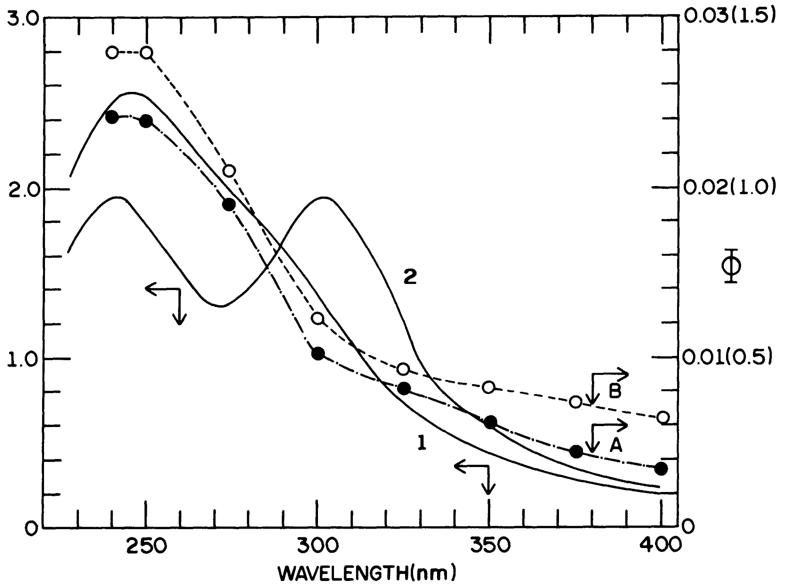

Fig. 2 Electronic absorption, spectra of $[Cu(CH_3OH)_5Br]^+$ and $[Cu(CH_3OH)_4Br_2]$ (1 and 2, respectively) in methanol, and variation of quantum yields as a function of irradiating wavelength (A and B). Curve A is for an initial concentration of copper(II) bromide 8.0×10^{-4} mol dm^{-3} and curve B for 5.0×10^{-2} mol dm^{-3}. The numbers in parentheses (right ordinate scale) are for curve B.

sible for the absorption of a significant part of the incident light its photoinertness could signify a reduction in quantum yield in comparison to that of copper(II) perchlorate solution in which the only light absorbing species is $[Cu(CH_3OH)_6]^{2+}$. Hence, the nearly identical quantum yields in the two solutions signify, quite probably, that the two species, $[Cu(CH_3OH)_6]^{2+}$ and $[Cu(CH_3OH)_5Br]^+$, have nearly identical photoreduction efficiency. The decrease in quantum yield for copper(II) bromide concentrations higher than 5.0×10^{-2} mol dm^{-3} is similar to that observed for copper(II) chloride solutions and, hence, could be the consequence of depth-effect,[2] or reoxidation of copper(I) by Br_2^- radicals.[2,12] Quantum yields as a function of irradiating wavelength (Fig. 2) shows that charge-transfer transitions occurring at wavelengths below 300 nm is in fact responsible for the photoreduction. This points to $[Cu(CH_3OH)_4Br_2]$ as the photoactive species which has the CT band centered around 245 nm.

A plausible explanation for the difference in the photoreactivities of $[Cu(CH_3OH)_5Br]^+$ and $[Cu(CH_3OH)_4Br_2]$ is that the Cu–Br distances are different in the two species. Barnes and Day[13] have showed that an increase in the internuclear distance increases the energy of the charge-transfer transition. Hence, the high energy charge-transfer transition in the dibromo complex (Fig. 2) may signify a longer Cu–Br bond in this compound in comparison to that of the monobromo complex.[14] This could mean a larger distance between Cu(I) and ·Br in the excited state of the dibromo complex and, hence, could render their separation more efficient (and cage-recombination less probable) leading to an increase in the product quantum yield.

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14) The bromide-to-copper(II) CT transition is centered around 300 nm in the monobromo complex; the band centered around 240 nm could be methanol-to-copper(II) CT band. The absorption centered around 245 nm in the dibromo complex represents, quite probably, two CT bands (bromide-to-copper and methanol-to-copper) superimposed one over the other.