August, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *55*, *2673—2674 (1982)* 2673

Photoredox Chemistry of Copper(II) Perchlorate in Methanolic Medium

Paulo Augustro Correa da Silva and Pazhayirayyathu Geeverghese David*
Departamento de Quimica, Universidade de Brasilia, Brasilia-DF, Brazil

(Received November 16, 1981)

Synopsis. Ultraviolet irradiation of copper(II) perchlorate in methanol yields copper(I) and formaldehyde as the products. The primary photoprocess is believed to be the homolytic cleavage of copper(II)-methanol bond. Secondary reactions of oxidized solvent species with copper(II), copper(I), and solvent molecules affect the product quantum yields. Variation of the quantum yield for copper(I) as a function of irradiating wavelength indicates the existence of methanol-to-copper(II) charge transfer band in the 200—250 nm region.

Most of the reports on the photochemistry of copper(II) salts such as copper(II) chloride, bromide, perchlorate, *etc.*, describe only qualitative observations. Eventhough the observation of the photoxidation of organic solvents by copper(II) chloride dates back to 1804,[1] no report on the quantitative aspects has appeared hitherto. Kochi reported the use of UV irradiation of methanolic solutions of copper(II) chloride in the chlorination of organic compounds.[2] Qualitative observation of the photochemistry of methanolic solutions of copper(II) perchlorate to 254 nm radiations were reported by Murai and Tsutsumi.[3] The present report deals with the quantitative aspects of the photoreduction of copper(II) perchlorate in methanolic medium.

Experimental

Copper(II) perchlorate hexahydrate (Alfa Inorganics) and benzoic acid were purified by recrystallization from hot water and dried under vacuum. Methanol and methyl methacrylate were purified by published procedures.[4–6] Copper(I) solution was prepared by exhaustive photolysis of methanolic solution of copper(II) perchlorate (2.0×10^{-3} M, 1 M = 1 mol dm^{-3}) deaerated by bubbling oxygen-free nitrogen. A Rayonet Photochemical Reactor fitted with RPR 2540 Å lamps was used for this photolysis. All the quantum yields were determined at 25 ± 0.2 °C using deaerated solutions. Photochemical techniques[4] and chemical scavenging experiments[4–6] have been described. Copper(I) was determined spectrophotometrically as the $[Cu(dmp)_2]^+$ complex (dmp = 2,9-dimethyl-1,10-phenanthroline). Formaldehyde and ethylene glycol were determined by the literature procedures.[7,8]

Results and Discussion

The electronic absorption spectrum of copper(II) perchlorate in anhydrous methanol is presented in Fig. 1 along which the variation of quantum yields for the formation of copper(I) ($\Phi_{Cu(I)}$) and formaldehyde (Φ_{CH_2O}) as a function of irradiating wavelength. Being a weak ligand coordination of ClO_4^- to copper(II) may be excluded and, hence, the broad absorption in the 200—250 nm region may reasonably be attributed to the charge transfer from methanol to copper(II). The existence of the CT absorption in this region is substantiated by the variation of the photoredox quantum yield as a function of irradiating wavelength (Fig. 1). The quantum yields show a tendency to level off for $\lambda<230$ nm and exhibit a threshold energy at approximately 333 nm.

In addition to copper(I), formaldehyde was formed during the irradiation at all wavelengths studied and its quantum yield was half of that of copper(I). It is important to point out that, contrary to the report of Murai and Tsutsumi,[3] we did not detect the formation of any precipitate of copper metal during or after the irradiations. It is quite probable that the disproportionation of copper(I) reported by these authors might be a consequence of its higher concentration (approximately 0.5 M copper(I) produced by exhaustive photolysis of copper(II) perchlorate). Copper(I) is apparently stable in methanol at the lower concentrations ($<10^{-1}$ M) encountered in our system.[9]

The primary photoprocess in the photolysis of methanolic solutions of copper(II) perchlorate may be represented as given below.

$$[Cu(CH_3OH)_6]^{2+} \longrightarrow [Cu(CH_3OH)_5]^+ + [CH_3OH]^+ \quad (1)$$

The $[CH_3OH]^+$ may be converted to $CH_3O\cdot$ or $\cdot CH_2OH$ by the following reactions.

$$[CH_3OH]^+ \longrightarrow CH_3O\cdot + H^+ \quad (2)$$

$${}^*CH_3O\cdot + CH_3OH \longrightarrow {}^*CH_3OH + \cdot CH_2OH \quad (3)$$

The formation of $CH_3O\cdot$ during the photolysis of copper(II) perchlorate in methanol has been substantiated by Murai and Tsutsumi,[3] while our chemical scavenging experiments using methyl methacrylate clearly indicate the incorporation of $-CH_2OH$ end group in the polymer as was shown by the strong positive test for the OH end group in the photopolymer obtained by irradiating methanolic solutions of copper(II) perchlorate at 254 nm in the presence of methyl methacrylate. Polymer obtained from methanol solution which did not contain copper(II) perchlorate gave a negative test for OH end group.

In addition to Reaction 3, $CH_3O\cdot$ radical may disproportionate according to Reaction 4. Since Reaction 4 is second order, it may be considered insignificant due to the insufficient rate of production of $CH_3O\cdot$ during the photolysis of methanolic solutions of copper(II) perchlorate. Hence, we consider that Reaction 3 is the only significant thermal reaction in which $CH_3O\cdot$ disappears.

$$2CH_3O\cdot \longrightarrow CH_2O + CH_3OH \quad (4)$$

In methanolic medium $\cdot CH_2OH$ may dimerize, disproportionate, or reduce copper(II).[10,11] Ethylene glycol was not detected in our system after the photolysis and, hence, Reaction 5 may be considered insignificant. It is known that Reaction 6 has a second order rate constant slower than that of Reaction 5 by approximately a factor of ten.[12] Consequently, we consider the disproportionation reaction (6) insignificant. Therefore, the principal reaction of the reducing radical $\cdot CH_2OH$ is (7) leading to the formation of copper(I) and formaldehyde. This is further substantiated by our quantum yield data in the

$$2\cdot CH_2OH \longrightarrow (CH_2OH)_2 \quad (5)$$

$$2\cdot CH_2OH \longrightarrow CH_2O + CH_3OH \quad (6)$$

$$\cdot CH_2OH + [Cu(CH_3OH)_6]^{2+} \longrightarrow [Cu(CH_3OH)_6]^+ + CH_2O + H^+ \quad (7)$$

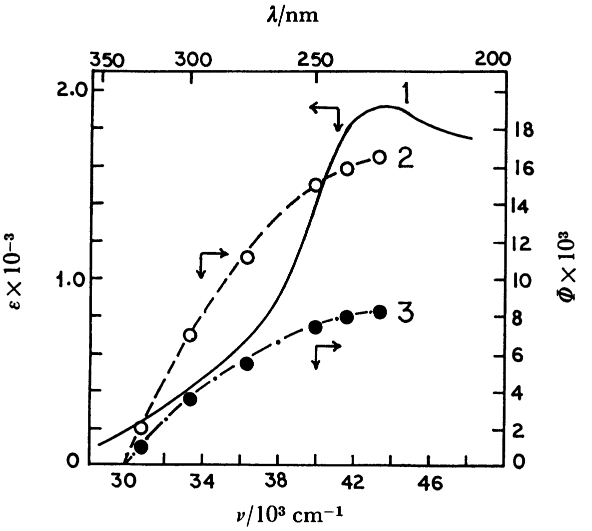

Fig. 1. Electronic absorption spectrum of copper(II) perchlorate in methanol (1), and the quantum yields for the formation of copper(I) (2), and formaldehyde (3) as a function of wavelength of irradiation. The quantum yields were determined for an initial concentration of copper(II) perchlorate 2.0×10^{-3} M, incident intensity $1.5\pm0.1\times10^{14}$ photons s^{-1}, and time of irradiation 10 h.

presence of added concentrations of benzoic acid for an initial concentration of copper(II) perchlorate 2.0×10^{-3} M, wavelength of irradiation 300 nm, incident intensity 1.5×10^{14} photons s^{-1}, and time of irradiation 10 h. The 300 nm irradiating wavelength was chosen to avoid the partial absorption of light by benzoic acid which absorbs at $\lambda<300$ nm. Gradual decreases in $\Phi_{Cu(I)}$ and Φ_{CH_2O} occur with increase in the concentration of benzoic acid. At benzoic acid concentrations 0.05 M or higher $\Phi_{Cu(I)}$ dropped to half of the value 0.007 obtained in the absence of benzoic acid and the Φ_{CH_2O} dropped to zero. This is in agreement with our prediction that, in the absence of benzoic acid which is known to act as a scavenger for $CH_3O\cdot$ and $\cdot CH_2OH$ radicals,[5] $\cdot CH_2OH$ reacts with copper(II) leading to copper(I) and formaldehyde (Reaction 7). If the thermal reactions (2), (3), and (7) follow Reaction 1, Φ_{CH_2O} should be half of $\Phi_{Cu(I)}$. Suppression of Reaction 7 by added $\cdot CH_2OH$ scavengers will affect $\Phi_{Cu(I)}$ and Φ_{CH_2O} and their relative values. Complete scavenging of $\cdot CH_2OH$ by benzoic acid will lead to $\Phi_{CH_2O}=0$ and $\Phi_{Cu(I)}$ equal to half of that in the absence of added radical scavengers, as was observed.

Quantum yields (wavelength of irradiation 250 nm, incident intensity 1.5×10^{14} photons s^{-1}, and time of irradiation 5 h) for the formation of copper(I) for initial concentrations of copper(II) perchlorate ($M\times10^5$) 1000, 500, 100, 50, 10, and 5 were, respectively, 0.006, 0.010, 0.016, 0.030, 0.102, and 0.120 (all± 0.002). The decrease in the product quantum yield with the increase in the initial copper(II) concentration suggests the importance of the reoxidation of copper(I) by the radicals generated in the reaction. Assuming a steady-state concentration for $CH_3O\cdot$ (or $[CH_3OH]^+$), the recombination $Cu^+ + CH_3O\cdot + H^+ \rightarrow [Cu(CH_3OH)]^{2+}$ (or $Cu^+ + [CH_3OH]^+ \rightarrow [Cu(CH_3OH)]^{2+}$) depends on the effective concentration of Cu^+. Increase in the concentration of copper(II) increases the absorbed intensity of light and/or decreases the pathlength of the solution absorbing light. This amounts to the increase in the photoreduction and/or restriction of the photoreduction to a narrower and narrower region of the photolysis cell nearest to the source (depth effect) with the consequent increase in the effective concentration of Cu^+. We have also observed decreases in the product quantum yields with the increase in time of irradiation indicating further the probable importance of the reoxidation of copper(I) by $CH_3O\cdot$ or $[CH_3OH]^+$. For 250 nm irradiating wavelength (incident intensity 1.5×10^{14} photons s^{-1} and initial concentration of copper(II) perchlorate 2.0×10^{-3} M) $\Phi_{Cu(I)}$ for time of irradiation 5, 10, 15, 20, and 40 h were, respectively, 0.014 (6.27), 0.012 (10.76), 0.010 (13.45), 0.008 (14.34), and 0.005 (17.93), the numbers in parentheses indicating the concentrations ($\mathrm{mmol}\times10^5$) of copper(I) in 4.5 cm^3 of the solution after the irradiation. As we may observe, increase in the copper(I) concentration occurs with increasing time of irradiation, thus rendering the second order recombination (see above) more probable.[4] The quantum yields determined in the presence of added initial concentrations of copper(I) ($\mathrm{mmol}\times10^5$) 0, 5, 10, 15, 20, and 25 in 4.5 cm^3 of the solution (other experimental conditions remaining same as indicated above) support this hypothesis. The quantum yields ($\Phi_{Cu(I)}$) were, respectively, 0.014, 0.012, 0.008, and 0.002 (all±0.002) for the first four solutions while it was zero for the last two. Photolysis appears to reach a steady-state for copper(I) concentrations higher than 1.5×10^{-4} mmol in 4.5 cm^3 (3.33×10^{-5} mol dm^{-3}).

The authors thank the National Research Council of Brazil (CNPq) for partial support to this work.

References

1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York (1970).

2) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 2121 (1962).

3) S. Murai and T. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **39**, 198 (1966).

4) F. David and P. G. David, *J. Phys. Chem.*, **80**, 579 (1976).

5) P. G. David and E. L. Wehry, *Mol. Photochem.*, **5**, 21 (1973).

6) P. G. David, J. G. Richardson, and E. L. Wehry, *J. Inorg. Nucl. Chem.*, **34**, 1333 (1972).

7) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

8) N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley-Interscience, New York (1980).

10) W. Brackman, F. V. D. Craats, and P. J. Smit, *Recueil*, **83**, 1253 (1964).

11) G. E. Adams and J. H. Baxendale, *J. Am. Chem. Soc.*, **80**, 4215 (1958).

12) F. S. Dainton, G. A. Salmon, and P. Wardman, *Proc. R. Soc. London, Ser. A*, **313**, 1 (1969).