Inorg. Chem. **2008**, *47*, 7029−7034

Inorganic Chemistry
Article

Photocatalytic Degradation of Dichloromethane by Chlorocuprate(II) Ions

Kevin J. Doyle, Huy Tran, Miguel Baldoni-Olivencia, Merve Karabulut, and Patrick E. Hoggard*

Department of Chemistry, Santa Clara University, Santa Clara, California 95053

Received April 16, 2008

Near UV irradiation of aerated solutions of $(Et_4N)_2[CuCl_4]$ in dichloromethane causes the decomposition of CH_2Cl_2, as evidenced by the buildup of HCl, $C_2H_2Cl_4$, and peroxides. A net reduction to $[CuCl_2]^-$ occurs in the early stages, but is later reversed. In CH_2Cl_2, $[CuCl_4]^{2-}$ is in equilibrium with $[Cu_2Cl_6]^{2-}$, and only the latter species is photoactive. The decomposition is initiated by the photodissociation of chlorine atoms, which propagate to peroxy radicals, $CHCl_2OO$. Experimental evidence, including a linear dependence of the decomposition rate on the incident light intensity and on the fraction of light absorbed by $[Cu_2Cl_6]^{2-}$, is consistent with a mechanism in which $CHCl_2OO$ is reduced by electron transfer from $[CuCl_2]^-$, following which protonation yields $CHCl_2OOH$. The hydroperoxide accumulates during irradiation and it too can reoxidize $[CuCl_2]^-$. The quantum yield for HCl production at the outset of irradiation at 313 nm is 1.3 mol/einstein, based on the fraction of light absorbed by $[Cu_2Cl_6]^{2-}$.

I. Introduction

Halomethanes pose environmental concerns that include chronic toxicity, mutagenicity, and carcinogenicity.[1] Dichloromethane, due to its low absorption cross-section for solar radiation, also has the potential to deliver chlorine to the stratosphere and has a half-life in the troposphere estimated to be several months.[1] The main source for dichloromethane and other halomethanes in drinking water supplies is municipal disinfection.[2] A heterogeneous catalyst that could promote decomposition of CH_2Cl_2 and other halomethanes by solar radiation could prove very beneficial, and the present study was initiated in an attempt to understand how such a catalyst might function.

Under aerobic conditions, thermal or photochemical homolysis of a C−Cl bond in dichloromethane causes decomposition to HCl and CO.[3,4] Wavelengths below approximately 225 nm are required to have significant absorption of light by CH_2Cl_2. In the presence of TiO_2 and other heterogeneous catalysts, decomposition of dichloromethane to HCl and CO_2 can be accomplished with UV irradiation above 300 nm.[5–12]

The individual steps of the decomposition process in the gas phase have been investigated by several groups,[4,13–16] and may be represented as follows.

$$CH_2Cl_2 \xrightarrow{h\nu} Cl + CH_2Cl \tag{1}$$

$$Cl + CH_2Cl_2 \xrightarrow{k_2} HCl + CHCl_2 \tag{2}$$

$$CH_2Cl + CH_2Cl_2 \xrightarrow{k_3} CH_3Cl + CHCl_2 \tag{3}$$

$$CHCl_2 + O_2 \xrightarrow{k_4} CHCl_2OO \tag{4}$$

---

* To whom correspondence should be addressed. E-mail: phoggard@scu.edu.

(1) U.S. Environmental Protection Agency. *Ambient water quality criteria for halomethanes*; EPA 440 5−80−051; 1980.
(2) U.S. Environmental Protection Agency. *Preliminary assessment of suspected carcinogens in drinking water [Report to Congress]*; EPA 560475003, 1975.
(3) Hoare, M. R.; Norrish, R. G. W.; Whittingham, G. *Proc. R. Soc. (London)* **1959**, *A250*, 197–211.
(4) Sanhueza, E.; Heicklen, J. *J. Phys. Chem.* **1975**, *79*, 7–11.
(5) Borisch, J.; Pilkenton, S.; Miller, M. L.; Raftery, D.; Francisco, J. S. *J. Phys. Chem. B* **2004**, *108*, 5640–5646.
(6) Calza, P.; Minero, C.; Pelizzetti, E. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3765–3771.
(7) Gutierrez-Ortiz, J. I.; Lopez-Fonseca, R.; Aurrekoetxea, U.; Gonzalez-Velasco, J. R. *J. Catal.* **2003**, *218*, 148–154.
(8) Halmann, M.; Hunt, A. J.; Spath, D. *Sol. Energy Mater. Sol. Cells* **1992**, *26*, 1–16.
(9) Hsiao, C. Y.; Lee, C. L.; Ollis, D. F. *J. Catal.* **1983**, *82*, 418–423.
(10) Pinard, L.; Magnoux, P.; Ayrault, P.; Guisnet, M. *J. Catal.* **2004**, *221*, 662–665.
(11) Sabin, F.; Tuerk, T.; Vogler, A. *J. Photochem. Photobiol., A* **1992**, *63*, 99–106.
(12) Tanguay, J. F.; Suib, S. L.; Coughlin, R. W. *J. Catal.* **1989**, *117*, 335–347.
(13) Catoire, V.; Lesclaux, R.; Schneider, W. F.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 14356–14371.
(14) Hisatsune, I. C.; Heicklen, J. *Can. J. Spectrosc.* **1973**, *18*, 77–81.
(15) Rayez, J. C.; Rayez, M. T.; Halvick, P.; Duguay, B.; Lesclaux, R.; Dannenberg, J. J. *Chem. Phys.* **1987**, *116*, 203–213.
(16) Sheps, L.; Crowther, A. C.; Elles, C. G.; Crim, F. F. *J. Phys. Chem. A* **2005**, *109*, 4296–4302.

10.1021/ic800684v CCC: $40.75

$$2\mathrm{CHCl_2OO} \xrightarrow{k_5} 2\mathrm{CHCl_2O} + \mathrm{O_2} \qquad (5)$$

$$\mathrm{CHCl_2O} \xrightarrow{k_6} \mathrm{CHClO} + \mathrm{Cl} \qquad (6)$$

$$\mathrm{CHClO} \xrightarrow{k_7} \mathrm{HCl} + \mathrm{CO} \qquad (7)$$

Light-induced dissociation is followed by hydrogen abstraction,[16] leaving dichloromethyl radicals, which add O_2 to form dichloromethylperoxy radicals.[13] These decompose bimolecularly to form dichloromethoxy radicals,[13] which expel chlorine atoms,[15] leaving HClO. Formyl chloride decomposes to CO and HCl with a half-life of 10 min at room temperature.[14]

Another potential reaction that must be considered is hydrogen abstraction by the peroxy radical.

$$\mathrm{CHCl_2OO} + \mathrm{CH_2Cl_2} \xrightarrow{k_8} \mathrm{CHCl_2OOH} + \mathrm{CHCl_2} \qquad (8)$$

Because the O−H bond energy in hydroperoxides is generally between 370 and 380 kJ/mol,[17,18] hydrogen abstraction from carbon is competitive with termination and other reactions only for relatively weak C−H bonds.[19] The C−H bond energy in CH_2Cl_2 is reported to be 402.5 kJ/mol;[20] thus, the abstraction in eq 8 is unfavorable and, in fact, is not observed in the gas phase.[4,13] Nevertheless, it should be considered as a potential reaction in the liquid phase. Hydroperoxides normally oxidize substrates by breaking the O−O bond,[21–23] and the resulting dichloromethoxy radicals would decay as in eqs 6 and 7.

We wish to intervene in this process using longer wavelength irradiation. We have observed the photodegradation of chloroform to be catalyzed by iron(III) chloride with visible light.[24] Irradiation of $FeCl_3$ solutions causes chlorine atom dissociation and reduction to Fe(II), which is then reoxidized thermally by CCl_3OOH, an intermediate in the chloroform degradation process that begins with hydrogen abstraction from chloroform by the chlorine radicals.[24] The C−H bond energy is smaller in chloroform than it is in dichloromethane,[25] which might explain why the hydroperoxide accumulates in irradiated chloroform.[26]

Several photoreactions of copper(II) complexes in organic solvents are known in which reduction to copper(I) occurs,[27–31] including several studies of copper(II) chloride and chlorocuprate(II) complexes.[23,32–37] If the chlorocuprate(I) product from the photolysis of $CuCl_4^{2-}$ in a halocarbon could be reoxidized to copper(II), as occurs with iron(II/III), the net result of an oxidation−reduction cycle would be the degradation of the halocarbon. We undertook an investigation of this process in dichloromethane, with the assumption that absorption into the ligand-to-metal charge transfer (LMCT) bands of $CuCl_4^{2-}$, which extend from the UV into the blue part of the spectrum,[38,39] would cause chlorine atom dissociation, initiating the decomposition process (eq 9).

$$[\mathrm{CuCl_4}]^{2-} \xrightarrow{h\nu} [\mathrm{CuCl_3}]^{2-} + \mathrm{Cl} \qquad (9)$$

To complete this cycle, copper(I) might be reoxidized by the peroxy radical or, if it is formed at all in dichloromethane, the hydroperoxide.

II. Experimental Section

Tetraethylammonium tetrachlorocuprate(II), 1,1,2,2-tetrachloroethane, hexachloroethane, and HPLC-grade dichloromethane, stabilized with ~0.1% amylenes, were obtained from Aldrich. For most experiments, the stabilizer was removed by shaking the dichloromethane with 1 M aqueous sulfuric acid, then a sodium carbonate solution, and finally several times with water. Measurements of HCl production could not be done accurately with stabilized CH_2Cl_2 because it added to the alkene on a time scale of minutes.[40,41]

Photolyses were carried out by pipetting 3.0 mL of a solution into a fused silica cuvette and irradiating it with either a 350-W mercury lamp (Oriel) with a Schott WG-320 or WG-395 cutoff filter, or a 500-W Hg/Xe lamp (Oriel) passed through a 25 cm monochromator. Light intensities were measured with an Oriel 70260 radiant power meter. UV−visible spectra were monitored with a Cary 50 spectrophotometer or an HP 8453 diode array spectrometer. GC-mass spectrometry was carried out with a Shimadzu QP-5000 with a Restek Corp. XTI-5 column. The oven start temperature was 40 °C and a linear temperature gradient of 20° $\mathrm{min^{-1}}$ was applied to 260 °C. The instrument was operated in splitless injection mode. Chlorine-containing species were identified from their mass spectra.

Two methods were used to measure HCl production during photolysis: (1) 200 μL aliquots were removed periodically from the photolysate and shaken with 3.0 mL of DI water that had been

---

(17) Benson, S. W.; Shaw, R. *Adv. Chem. Ser.* **1968**, *75*, 288–294.
(18) Kondo, O.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6675–6680.
(19) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413–513.
(20) Seetula, J. A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3069–3078.
(21) Coffman, D. D.; Jenner, E. L. *J. Am. Chem. Soc.* **1958**, *80*, 2872–2877.
(22) Kharasch, M. S.; Fono, A. *J. Org. Chem.* **1959**, *24*, 72–78.
(23) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 2121–2127.
(24) Hoggard, P. E.; Gruber, M.; Vogler, A. *Inorg. Chim. Acta* **2003**, *346*, 137–142.
(25) Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.* **1987**, *19*, 15–24.
(26) Gäb, S.; Turner, W. V. *Angew. Chem.* **1985**, *97*, 48.
(27) Gafney, H. D.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 1623–1628.
(28) Matsushima, R.; Ichikawa, Y.; Kuwabara, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1902–1907.
(29) Ng, W.; Hoggard, P. E. *Inorg. Chim. Acta* **2001**, *321*, 1–4.
(30) Sundararajan, S.; Wehry, E. L. *J. Phys. Chem.* **1972**, *76*, 1528–1536.
(31) Tanaka, K. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2999–3001.
(32) Cervone, E.; Camassei, F. D.; Giannini, I.; Sykora, J. *J. Photochem.* **1979**, *11*, 321–332.
(33) Horvath, E.; Sykora, J.; Gazo, J. *Z. Anorg. Allg. Chem.* **1978**, *442*, 235–244.
(34) Horvath, O. *J. Photochem. Photobiol., A* **1989**, *48*, 243–248.
(35) Sykora, J.; Horvath, E.; Gazo, J. *Z. Chem.* **1978**, *18*, 346–347.
(36) Sykora, J.; Giannini, I.; Diomedi Camassei, F. *J. Chem. Soc., Chem. Commun.* **1978**, 207–208.
(37) Sykora, J.; Jakubcova, M.; Cvengrosova, Z. *Collect. Czech. Chem. Commun.* **1982**, *47*, 2061–2068.
(38) Sharnoff, M.; Reimann, C. W. *J. Chem. Phys.* **1967**, *46*, 2634–2640.
(39) Desjardins, S. R.; Penfield, K. W.; Cohen, S. L.; Musselman, R. L.; Solomon, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 4590–4603.
(40) Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 42854293.
(41) Pocker, Y.; Stevens, K. D.; Champoux, J. J. *J. Am. Chem. Soc.* **1969**, *91*, 4199–4205.

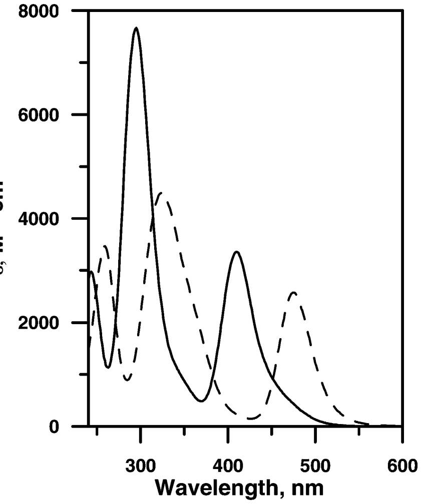

Figure 1. Spectra of $CuCl_4^{2-}$ (solid line) and 1/2 × $Cu_2Cl_6^{2-}$ (dashed line) in CH_2Cl_2; $CuCl_4^{2-}$ spectrum in presence of excess Cl-, $Cu_2Cl_6^{2-}$ in presence of excess HCl.

boiled to expel CO_2, after which the pH of the aqueous phase was recorded; (2) 50 μL aliquots were removed periodically and added to 3.0 mL of a solution of tetraphenylporphyrin (H_2TPP) in $CHCl_3$, the spectrum of which was then measured to determine the amount of H_4TPP^{2+} formed, by use of the extinction coefficients of the porphyrin species.[42,43] The equilibria strongly favor the diprotonated over the monoprotonated porphyrin.[44] There was good agreement between the two methods, but the TPP method had better reproducibility, provided the stabilizer was removed from the dichloromethane, because dissolved CH_2Cl_2 remaining in the aqueous phase caused the pH meter to drift.

Peroxide concentrations were measured by mixing 1.00 mL of the photolysate with 2.00 mL of approximately 0.01 M Bu_4NI in $CHCl_3$ and determining the resulting I_3^- concentration from the extinction coefficient, 2.50 × 10^4, at 365 nm.[45]

The concentration of $C_2H_2Cl_4$ in photolysates was determined from the peak area in the gas chromatogram relative to an internal C_2Cl_6 standard.

III. Results

A. Chlorocopper Complex Speciation. UV–visible absorption spectra of solutions of $(Et_4N)_2[CuCl_4]$ in CH_2Cl_2 did not follow Beer's Law. Peaks were apparent in the spectrum at approximately 251, 300, 409, and 474 nm. When an excess of Et_4NCl was added, the spectrum was altered to one with peaks at 233, 294, and 410 nm (Figure 1). This spectrum did follow Beer's Law throughout and can readily be identified as $CuCl_4^{2-}$ by comparison with both solid state[39,46] and solution[47] spectra. This suggests that a rapid dissociation equilibrium is operative. Dissociation of $CuCl_4^{2-}$ has also been observed by Golubeva et al. in chlorobenzene solutions.[47,48]

Anhydrous HCl was added to solutions of $(Et_4N)_2[CuCl_4]$ in CH_2Cl_2, with the expectation that H_2CuCl_4 (in which the protons would be associated with one or more chloride ligands) would be formed, analogous to the protonation observed with $PdCl_4^{2-}$ in chloroform,[49] with a spectrum shifted somewhat from that of $\{2Et_4N^+;CuCl_4^{2-}\}$. Instead, the peaks associated with $CuCl_4^{2-}$ disappeared, while peaks at 259, 324, and 475 nm remained. This spectrum, shown in Figure 1, obeyed Beer's Law at different copper concentrations and matched that of the $Cu_2Cl_6^{2-}$ ion in the solid state[50,51] and in solution.[47] This implies a strong association beween HCl and chloride ion and, in fact, the equilibrium constant constant for the process

$$HCl + Cl^- \rightleftharpoons HCl_2^- \tag{10}$$

in CH_3NO_2 has been suggested to be so large that the association is virtually stoichiometric.[41] It may be presumed that the anions in eq 10 are predominantly associated with Et_4N^+ cations but, for simplicity, the ion pair notation will not be used.

The spectrum of $Cu_2Cl_6^{2-}$ shown in Figure 1 was arrived at by determining the extinction coefficient at 1 nm intervals from spectra at six concentrations by linear regression. In each case, after adding HCl and recording the spectrum, more HCl was bubbled into the solution to ensure that the spectrum was constant. The spectrum of $CuCl_4^{2-}$ was also arrived at from the spectra at several concentrations. However, it was found that addition of too much chloride ion caused reduction to occur thermally by a process not understood, but alluded to in the literature for Cu^{2+} with excess halide ions.[52] Consequently, Cl^- was added in small portions until the 474 nm band, characteristic of $Cu_2Cl_6^{2-}$, just disappeared, with isosbestic points still intact, before net reduction to $CuCl_2^-$, which lowered the absorbance at all wavelengths. Prepared thusly, we found that Beer's Law with respect to the copper concentration was adhered to very well, and R^2 for the linear regression exceeded 0.99 at all wavelengths except between 550 and 600 nm, where the absorbance is very low.

The concentrations of $CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$ in solutions of $(Et_4N)_2[CuCl_4]$ in CH_2Cl_2 were determined from absorption spectra by multicomponent analysis. The apparent equilibrium constant for the dissociation process,

$$2CuCl_4^{2-} \rightleftharpoons Cu_2Cl_6^{2-} + 2Cl^- \tag{11a}$$

decreased with increasing copper concentration. Extrapolated to zero concentration, K was 5 × 10^{-5}, about ten times greater than the value found for chlorobenzene solutions.[47] The equilibrium shifted with temperature, favoring dissociation at higher T. A plot of ln K versus $1/T$ (Supporting

---

(42) Du, H.; Fuh, R.-C. A.; Li, J.; Corkan, L. A.; Lindsey, J. S. *Photochem. Photobiol.* **1998**, *68*, 141–142.

(43) Lindsey, J. S., PhotochemCAD, spectra recorded by Junzhong Li and Richard W. Wagner. http://omlc.ogi.edu/spectra/PhotochemCAD/html/index.html (accessed Mar 15, 2007).

(44) Stone, A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 2735–2748.

(45) Solis Montiel, E.; Solano, H. J. A. *Ingenieria y Ciencia Quimica* **1986**, *10*, 45–48.

(46) Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93–158.

(47) Kharitonov, D. N.; Golubeva, E. N. *Kinet. Catal.* **2003**, *44*, 513–517.

(48) Golubeva, E. N.; Kokorin, A. I.; Kochubei, D. I.; Pergushov, V. I.; Kriventsov, V. V. *Kinet. Catal.* **2002**, *43*, 408–411.

(49) Le, A. L.; Hoggard, P. E. *Photochem. Photobiol.* **2008**, *84*, 86–89.

(50) Desjardins, S. R.; Wilcox, D. E.; Musselman, R. L.; Solomon, E. I. *Inorg. Chem.* **1987**, *26*, 288–300.

(51) Willett, R. D.; Liles; O, L., Jr. *Inorg. Chem.* **1967**, *6*, 1666–1669.

(52) Furlani, C.; Sgamellatti, A.; Ciullo, G. *Ric. Sci., Rend.* **1964**, 49–60.

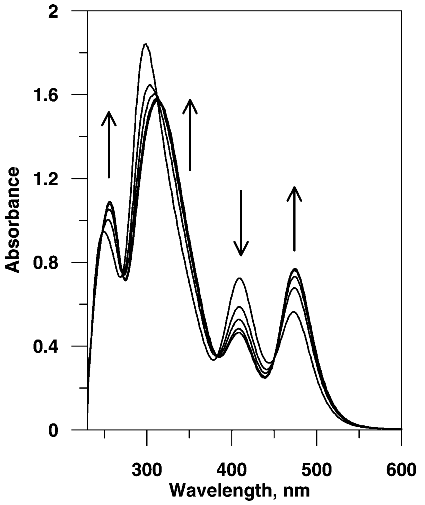

Figure 2. UV−visible spectral changes during the irradiation of a 3.8 × 10^{-4} M solution of $(Et_4N)_2CuCl_4$ in aerated CH_2Cl_2 (350-W Hg lamp, 320-nm cutoff filter, 1-min irradiation intervals).

Information, Figure S1) yielded 69 kJ/mol for ΔH and 166 J/mol·K for ΔS.

B. Chlorocopper Photochemical Changes. Irradiation ($\lambda > 320$ or 395 nm) of deaerated solutions of $(Et_4N)_2[CuCl_4]$ in CH_2Cl_2 led to the loss of spectral features above 250 nm, with the growth of a peak at 234 nm (see Supporting Information, Figure S2). An isosbestic point was maintained at 239 nm. The final spectrum was consistent with that of $CuCl_2^-$.[53] Very little HCl was produced during the photoreduction. After complete reduction to $CuCl_2^-$ in eight separate experiments, a maximum of 0.1 equiv of HCl, scaled against the total copper present, was found in the solution. We were unable to detect any $C_2H_2Cl_4$ by GC-MS, which implies that no significant formation of $CHCl_2$ radicals occurred, as would be expected if Cl atoms had formed and abstracted hydrogen.

When aerated solutions of $(Et_4N)_2CuCl_4$ in CH_2Cl_2 were exposed either to $\lambda > 320$ nm or to $\lambda > 395$ nm broadband irradiation, a series of spectral changes ensued, depicted in Figure 2. Initially, the 474 nm peak, due to $Cu_2Cl_6^{2-}$, increased in intensity while the 404 nm peak, due to $CuCl_4^{2-}$, decreased in intensity, and isosbestic points at 235, 247, 271, 312, 383, and 450 nm corresponded to the wavelengths at which the extinction coefficients of $(1/2)Cu_2Cl_6^{2-}$ and $CuCl_4^{2-}$ (Figure 1) are equal.

After a period of conversion of $CuCl_4^{2-}$ to $Cu_2Cl_6^{2-}$, continued irradiation of aerated solutions led to a loss of the initial isosbestic points and net reduction to $CuCl_2^-$, similar to the reaction occurring in deaerated solution. However, the reduction eventually halted and reversed, regenerating Cu(II) as $Cu_2Cl_6^{2-}$ (see Supporting Information, Figure S3). The presence of an isosbestic point at 240 nm during the reoxidation suggests that the only copper-containing species present were $CuCl_2^-$ and $Cu_2Cl_6^{2-}$. Further irradiation led to no spectral changes as long as access to air was allowed. When cuvettes were stoppered at this point, continued irradiation eventually led to rereduction to $CuCl_2^-$.

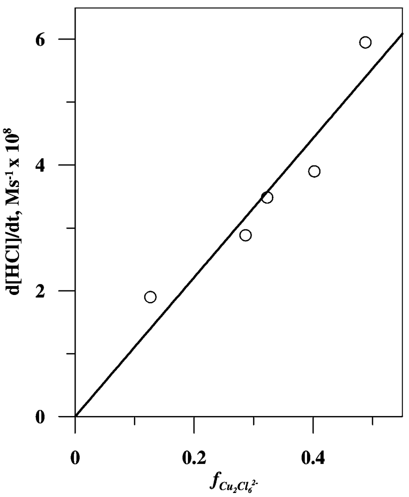

Figure 3. Initial rate of HCl formation in solutions of $(Et_4N)_2CuCl_4$ in unstabilized CH_2Cl_2, irradiated at 313 nm, as a function of the fraction of light absorbed by the $Cu_2Cl_6^{2-}$ component; $I_0 = 5.4 \times 10^{-10}$ einstein/s, $R^2 = 0.99$.

When an aerated sample of $(Et_4N)_2CuCl_4$ with an excess of Et_4NCl was irradiated under the same conditions, the photoreaction was completely suppressed. The $CuCl_4^{2-}$ spectrum remained unaltered, and no HCl was formed. On the other hand, when the dissociation equilibrium was shifted almost completely toward $Cu_2Cl_6^{2-}$ by addition of anhydrous HCl, irradiation caused reduction, followed by reoxidation.

The initial conversion to $Cu_2Cl_6^{2-}$ can readily be ascribed to the photoproduction of HCl which, as discussed above, shifts the dissociation equilibrium.

$$2CuCl_4^{2-} + 2HCl \rightleftharpoons Cu_2Cl_6^{2-} + 2HCl_2^- \qquad (11b)$$

C. Dichloromethane Decomposition Products. The initial rate of HCl formation under 313 nm irradiation, determined by adding small aliquots from the photolysate to a solution of H_2TPP, was measured over a range of starting concentrations of $(Et_4N)_2[CuCl_4]$. The rates correlated well with the fraction of light absorbed by $Cu_2Cl_6^{2-}$, as shown in Figure 3. The concentrations of $Cu_2Cl_6^{2-}$ and $CuCl_4^{2-}$ in each solution were determined by fitting the absorption spectrum to the spectra of the pure components.

The initial rate of HCl formation was also studied as a function of the incident light intensity. The rate varied linearly with intensity, as shown in Figure 4. The slope corresponded to a quantum yield, φ, of 0.6, based on the total light absorbed, but based only on the fraction of light absorbed by $Cu_2Cl_6^{2-}$, φ was 1.3.

Upon extended broadband ($\lambda > 320$ nm) irradiation in unstabilized CH_2Cl_2, HCl continued to form, the development being approximately linear well beyond stoichiometric quantities, regardless of whether Cu(I) or Cu(II) predominated in the solution, as shown for one example in Figure 5. In the presence of the amylene stabilizer, there was a considerable induction period, following which HCl formed at approximately the same rate as in unstabilized dichloromethane.

Several halocarbon products were identified from GC-MS analysis of photolysates at various reaction times, most

---

(53) Stevenson, K. L.; Braun, J. L.; Davis, D. D.; Kurtz, K. S.; Sparks, R. I. *Inorg. Chem.* **1988**, *27*, 3472–3476.

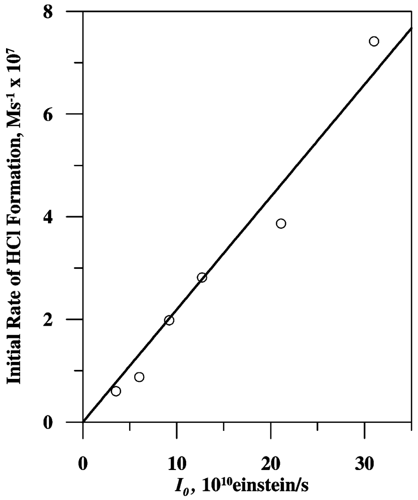

Figure 4. Initial rate of HCl formation in a 5 × 10^{-4} M solution of $(Et_4N)_2[CuCl_4]$ in unstabilized CH_2Cl_2 as a function of the incident light intensity. The slope is 2.2 × 10^2 M/einstein; $R^2 = 0.99$.

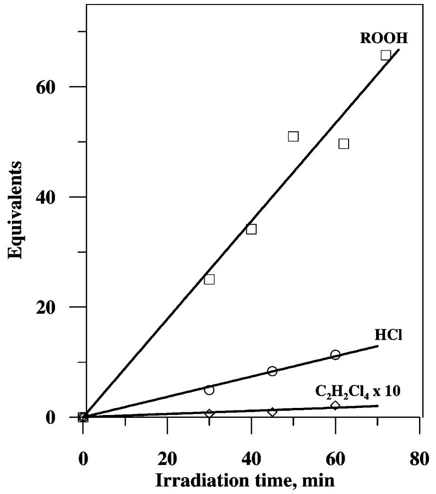

Figure 5. Evolution of HCl, peroxide, and $C_2H_2Cl_4$ during irradiation (λ > 320 nm) of a solution of $(Et_4N)_2CuCl_4$ in aerated, unstabilized CH_2Cl_2. Concentrations are relative to [Cu] = 6.0 × 10^{-5} M.

prominently 1,1,2,2-tetrachloroethane, 1,1,2,3,3-pentachloropropane, and chloroform. The concentration of $C_2H_2Cl_4$ as a function of irradiation time is also shown in Figure 5. Although its concentration increased approximately linearly with irradiation time, the relatively small yield compared to other products implies that dimerization of $\cdot CHCl_2$ is not the major radical termination step.

A key question with respect to photodecomposition in liquid dichloromethane is whether it proceeds through a hydroperoxide, as is known to occur with chloroform,[26] despite the apparently unfavorable energetics for the formation of the hydroperoxide by hydrogen abstraction from CH_2Cl_2. Although we were unable to analyze specifically for this compound (it eluted with the solvent under all GC-MS conditions that were tried), an analysis of total peroxide was performed by the oxidation of iodide to triiodide.[45] Hydroperoxides other than $CHCl_2OOH$ could in any case function in like manner to reoxidize Cu(I) to Cu(II). To test whether iodide might have been oxidized by Cl_2 rather than hydroperoxides, cyclohexene was added to a photolysate. A small amount of 1,2-dichlorocyclohexane was formed, but the peak area was less than 1% of that of chlorocyclohexane, formed by HCl addition. We conclude that Cl_2 was a minor contributor to iodide oxidation. Figure 5 shows the total peroxide concentration as a function of irradiation time. The hydroperoxide did not reach a steady state during any of the photolyses for which we tracked its concentration.

The buildup of (presumably) $CHCl_2OOH$ can be expected eventually to be limited by slower thermal[54] and acid-catalyzed[55] hydroperoxide decomposition routes, but no decrease in rate was evident during the up to 2 h irradiation times employed in this study.

No reaction was observed to take place (by GC-MS, UV spectral changes, or HCl production) in neat, aerated CH_2Cl_2 under any of our experimental conditions,.

IV. Discussion

The most direct way to effect photoreduction and initiate decomposition of CH_2Cl_2 would be by the photodissociation of $CuCl_3^-$ to produce $CuCl_2^-$ and a chlorine radical. Though it is possible that $Cu_2Cl_6^{2-}$ is in rapid equilibrium with $CuCl_3^-$, it seems more likely that fragmentation occurs after excitation of $Cu_2Cl_6^{2-}$,

$$Cu_2Cl_6^{2-} \xrightarrow{h\nu} CuCl_3^- + CuCl_2^- + Cl \qquad (12)$$

followed by association of $CuCl_3^-$ ions to reconstitute $Cu_2Cl_6^{2-}$. Chlorine atoms may then initiate decomposition as in eqs 1–7. The rate for this step may be expressed as $I_0 f_R \varphi / V$, where I_0 is the incident light intensity, f_R the fraction of light absorbed by the reactant, $Cu_2Cl_6^{2-}$, φ the quantum yield for bond homolysis, and V the solution volume.

The linear dependence of the initial rate of HCl formation on the incident light intensity and on the fraction of light absorbed by the $Cu_2Cl_6^{2-}$ species implies that there is a radical termination pathway other than dimerization because a biradical termination alone would lead to a square root dependence of the reaction rate on the absorbed light intensity. Such a pathway exists if the peroxy radicals (eq 4) oxidize Cu(I) back to Cu(II) by electron transfer.

$$CHCl_2OO + CuCl_2^- \xrightarrow{k_{13}} CHCl_2OO^- + CuCl_2 \qquad (13)$$

$$CHCl_2OO^- + HCl \xrightarrow{k_{14}} CHCl_2OOH + Cl^- \qquad (14)$$

$$CuCl_2 + Cl^- \xrightarrow{k_{15}} CuCl_3^- \qquad (15)$$

Hydroperoxides generally react with oxidizable substrates by breaking the O−O bond.[21–23] Dichloromethylhydroperoxide can thus serve as a second oxidant for $CuCl_2^-$, yielding thereby dichloromethoxy radicals, which decompose unimolecularly[15] (eq 6).

---

(54) Kirillov, A. I. *Zh. Org. Khim.* **1965**, *1*, 1226–1230.

(55) Kharasch, M. S.; Fono, A.; Nudenberg, W. *J. Org. Chem.* **1950**, *15*, 748–752.

$$\mathrm{CHCl_2OOH + CuCl_2^- \xrightarrow{k_{16}} CuCl_2(OH)^- + CHCl_2O} \quad (16)$$

$$\mathrm{CuCl_2(OH)^- + HCl \xrightarrow{k_{17}} CuCl_3^- + H_2O} \quad (17)$$

Given some dimerization of $CHCl_2$ radicals, as was found experimentally,

$$\mathrm{2CHCl_2 \xrightarrow{k_{18}} C_2H_2Cl_4} \quad (18)$$

a steady state in all intermediates except $CHCl_2OOH$ leads to the relationship

$$\frac{\mathrm{d[HCl]}}{\mathrm{d}t} + \frac{\mathrm{d[CHCl_2OOH]}}{\mathrm{d}t} = \frac{I_0 f_R \phi}{V} \quad (19)$$

Thus, the sum of HCl and $CHCl_2OOH$ is predicted to grow in direct proportion to the incident light intensity and the fraction of light absorbed by the photoactive copper species. Assuming this mechanism to be operative, the fractions of HCl and $CHCl_2OOH$ produced are controlled by the relative rates of peroxy radical formation (eq 4) and biradical termination (eq 18). A faster termination step is predicted to lead to a greater fraction of HCl while a more rapid $CHCl_2OO$ formation step is predicted to lead to a higher fraction of $CHCl_2OOH$. The latter condition was observed experimentally, which is consistent with the low rate observed for the formation of the $C_2H_2Cl_4$ termination product.

Once the copper species reach a photostationary state, the mechanism predicts that the concentration of $CuCl_2^-$ should be inversely proportional to the hydroperoxide concentration. This is consistent with the observed behavior in which reduction of copper(II) to $CuCl_2^-$ upon irradiation is reversed, eventually reverting almost completely to the +2 state as the concentration of the hydroperoxide increases.

Although eq 19 is consistent with our observation for aerated solutions, it does not account for the lack of stoichiometric HCl production in deoxygenated CH_2Cl_2, and this remains unexplained.

V. Conclusion

Under near-UV, and even visible, irradiation, dissolved $(Et_4N)_2[CuCl_4]$ catalyzes the decomposition of CH_2Cl_2, the photoactive species being $Cu_2Cl_6^{2-}$. The photodissociation of a chlorine atom initiates the decomposition. During the process, a great deal of the hydroperoxide $CHCl_2OOH$ builds up, even though abstraction of hydrogen by peroxy radicals is unfavorable. It is proposed that the hydroperoxide is formed instead through electron transfer from copper(II) to the peroxy radical, followed by protonation of the resulting peroxide anion.

Acknowledgment. This work was supported by the US National Science Foundation through grants CHE-0079152 and CHE-0453460 (REU).

Supporting Information Available: Figures showing the temperature dependence of the dimerization equilibrium constant, sequential spectra from the irradiation of a deoxygenated solution of $(Et_4N)_2[CuCl_4]$ in CH_2Cl_2, and sequential spectra from the irradiation of an aerated solution, showing the conversion of Cu(II) to Cu(I) and back to Cu(II) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC800684V