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Photocatalysis of Chloroform Decomposition by Tetrachlorocuprate (II) on Dowex 2-X8

Brent M. Harvey and Patrick E. Hoggard*

Department of Chemistry, Santa Clara University, Santa Clara, CA, USA

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ABSTRACT

Heterogenized on a polystyrene anion exchange resin and in the presence of oxygen, $CuCl_4^{2-}$ catalyzes the photodecomposition of chloroform at wavelengths above 345 nm with greater efficiency than an equivalent amount in homogeneous solution. The reaction is proposed to proceed in two stages, the first stage yielding CCl_4 and HO_2^- as products, the second consisting of a chain reaction resulting from the $CuCl_4^{2-}$-catalyzed photodissociation of CCl_4, yielding phosgene with CCl_3 radicals as chain carriers. Photodecomposition is retarded by added Cl^-, CH_3CN, C_6H_{12} or C_2H_5OH, which is ascribed to the displacement of $CHCl_3$ molecules from the vicinity of the copper by attraction to the polystyrene matrix or to the alkylammonium cation sites.

INTRODUCTION

The tetrachlorocuprate(II) ion acts as a homogeneous catalyst for the photodecomposition of dichloromethane (1). In that system, the photocatalytically active species is not $CuCl_4^{2-}$, but rather $Cu_2Cl_6^{2-}$, the two species being in rapid equilibrium in CH_2Cl_2 (1).

$$2CuCl_4^{2-} \rightleftharpoons Cu_2Cl_6^{2-} + 2Cl^- \quad (1)$$

During the course of photodecomposition, net reduction to copper(I) is observed, which is later reversed. The reversal is attributed to a buildup of oxidizing species such as the hydroperoxide $CHCl_2OOH$ (1).

When heterogenized on a Dowex anion exchange resin, $CuCl_4^{2-}$ loses its ability to catalyze the photodecomposition of CH_2Cl_2 (2), possibly because the equilibrium with $Cu_2Cl_6^{2-}$ is unfavorable on the surface of the anion exchange resin. We find, however, that heterogenized $CuCl_4^{2-}$ does catalyze the photodecomposition of chloroform, which is the subject of this study.

The thermal decomposition of chloroform yields almost exclusively HCl and CCl_2 (3), the least endergonic of the possible decomposition products (3). Studies of chloroform photolysis, however, have invariably found that the primary photochemical step is carbon–chlorine bond fission (4–6). This is due to excitation to an $n(Cl) \rightarrow \sigma^*$ (C–Cl) excited state (7), which leads to C–Cl bond homolysis with essentially unit efficiency (4). The remaining steps in the decomposition of $CHCl_3$ by direct photolysis in the gas phase, which takes place only at wavelengths below approximately 260 nm, have been worked out reasonably well (8). Hydrogen abstraction by each of the photogenerated radicals leads to the formation of phosgene and hydrogen chloride.

$$CHCl_3 \xrightarrow{h\nu} {}^{\bullet}CHCl_2 + Cl^{\bullet} \quad (2)$$

$$^{\bullet}CHCl_2 + CHCl_3 \rightarrow CH_2Cl_2 + CCl_3 \quad (3)$$

$$Cl^{\bullet} + CHCl_3 \rightarrow HCl + CCl_3 \quad (4)$$

$$^{\bullet}CCl_3 + O_2 \rightarrow CCl_3OO^{\bullet} \quad (5)$$

$$2CCl_3OO^{\bullet} \rightarrow 2CCl_3O^{\bullet} + O_2 \quad (6)$$

$$CCl_3O^{\bullet} \rightarrow COCl_2 + Cl^{\bullet} \quad (7)$$

Trichloromethyl radicals formed by hydrogen abstraction react with oxygen to yield trichloromethylperoxy radicals (9–11). Their self-reaction results in trichloromethoxy radicals (12), which in the gas phase are unstable with respect to dissociation to phosgene and chlorine atoms (13). Eqs. (4)–(7) constitute a radical chain with the net stoichiometry

$$CHCl_3 + \frac{1}{2}O_2 \rightarrow COCl_2 + HCl \quad (8)$$

In solution, the much higher rates of collision may make hydrogen abstraction by trichloromethoxy radicals competitive with unimolecular dissociation.

$$CCl_3O^{\bullet} + CHCl_3 \rightarrow CCl_3OH + {}^{\bullet}CCl_3 \quad (9)$$

From theoretical calculations by Sun and Bozzelli, ΔH° for this reaction in the gas phase is approximately -65 kJ mol^{-1} (14). Trichloromethanol is, however, unstable with respect to dissociation into hydrogen chloride and phosgene (15), thus hydrogen abstraction yields a stoichiometry identical with that of Eq. (8).

The absorption spectrum of $CuCl_4^{2-}$ in the blue and near-UV consists principally of ligand-to-metal charge transfer (LMCT) bands (16,17). This suggests chlorine atom dissociation as a potential mechanism for the initiation of the radical chain represented by Eqs. (4)–(7).

$$CuCl_4^{2-} \xrightarrow{h\nu} CuCl_3^{2-} + Cl^{\bullet} \quad (10)$$

This would lead to the stoichiometry of Eq. (8) and the prediction that the yields of HCl and $COCl_2$ would be

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*Corresponding author email: phoggard@scu.edu (Patrick E. Hoggard) approximately equal. Given a reoxidation of Cu(I) to complete a catalytic cycle, however, the ratio of HCl to $COCl_2$ could change. One possibility, not, however, observed during the homogeneous catalysis of dichloromethane decomposition by $(Et_4N)_2CuCl_4$ in solution (1), is the reduction of chloroform by the predominant copper(I) species, here taken to be $CuCl_3^{2-}$ for convenience:

$$CuCl_3^{2-} + CHCl_3 \rightarrow CuCl_4^{2-} + {}^{\bullet}CHCl_2 \qquad (11)$$

Following hydrogen abstraction by the resulting dichloromethyl radical as in Eq. (3), the overall stoichiometry would be little changed, but some quantity of dichloromethane would be expected.

If, on the other hand, reoxidation were effected by a hydroperoxide, CCl_3OOH, *e.g.* (18), some alteration in the ratio of HCl to $COCl_2$ would be expected.

$$CuCl_3^{2-} + CCl_3OOH \rightarrow CuCl_3(OH)^{2-} + CCl_3O^{\bullet} \qquad (12)$$

$$CuCl_3(OH)^{2-} + HCl \rightarrow CuCl_4^{2-} + H_2O \qquad (13)$$

$$CCl_3O^{\bullet} \rightarrow COCl_2 + Cl^{\bullet} \qquad (14)$$

Reoxidation by this mechanism would produce phosgene with no increase in hydrogen chloride. This might or might not be noticeable, depending on the length of the radical chain represented by Eqs. (4)–(7).

Given these considerations, our initial hypothesis was that chloroform would be photodecomposed in a process initiated by $CuCl_4^{2-}$ as in Eq. (10), producing HCl and $COCl_2$ at approximately equal rates by the chain process of Eqs. (4)–(7), but with potentially more $COCl_2$ should Cu(I) be reoxidized primarily by hydroperoxide. We also expected the side products to be dominated by C_2Cl_6 from the self-termination of the CCl_3 radical chain carriers in Eqs. (4)–(7).

MATERIALS AND METHODS

Chloroform (J. T. Baker, ACS Grade) was washed seven times with an equal volume of water to remove the ethanol stabilizer, after which 4A molecular sieves were added to remove dissolved water.

Because the chloride form of Dowex 2-X8 catalyzes the photodecomposition of chloroform (19), it was desirable to remove Cl^- entirely when heterogenizing $CuCl_4^{2-}$. The resin was first converted to the perchlorate form, which is photocatalytically inactive (19), by passing a 1M aqueous solution of $NaClO_4$ through a column containing the chloride form of the resin (Bio-Rad AG2-X8,) until the eluate was chloride-free by $AgNO_3$ test, then rinsing with water and air-drying. The tetrachlorocuprate catalyst was made by dissolving 0.54 g of $(Et_4N)_2CuCl_4$ (Sigma-Aldrich) in 50 mL of acetonitrile, adding 1.00 g of the ClO_4^- form of Dowex 2-X8, and stirring for 24 h, at which time the liquid phase was nearly colorless. After filtering the resin and rinsing with CH_3CN, the resin was soaked in chloroform for 1 hr to remove traces of acetonitrile, then filtered and air-dried. Based on the stated resin capacity of 3.2 mequiv per dry gram (Cl^- form) (20), which corresponds to 2.7 mequiv g^{-1} in the perchlorate form, approximately 87% of the cationic resin sites were occupied by $CuCl_4^{2-}$ ions. The $CuCl_4^{2-}$ loading was 1.1 mmol per gram of dry resin.

Photodegradation experiments were generally performed with 1.0 mL portions of chloroform with a stirred suspension of the $CuCl_4^{2-}$/Dowex catalyst in a 1 cm fused silica cuvette. A balloon containing air or O_2 was affixed to the cuvette with a plastic pipet. Light from an Oriel 350-W mercury lamp was passed through a 345 nm longpass filter and directed to the sample slightly defocused, so as to irradiate most of the sample. A fan was used to maintain the temperature in the cuvette at 22 ± 2°C.

HCl in the photolysate was measured by adding aliquots (between 10 and 100 μL) to 3.00 mL portions of tetraphenylporphyrin (H_2TPP, Frontier Scientific, chlorin-free) dissolved in destabilized chloroform. The absorbance increase at 446 nm, with the aid of extinction coefficients for H_2TPP and H_4TPP^{2+} in chloroform (21,22), was used to determine the concentration of $[H_4TPP^{2+}]$ formed through the protonation of the remaining porphyrin nitrogens:

$$2HCl + H_2TPP \rightleftharpoons \{H_4TPP^{2+}; 2Cl^-\} \qquad (15)$$

The intermediate H_3TPP^+ is unstable to disproportionation and can be neglected (23), simplifying the analysis. Although the equilibrium constant for Eq. (15) is very large, the reaction is not quite stoichiometric (24). While readings can, in principle, be corrected for this by taking measurements with two different ratios of photolysate to H_2TPP (24), deviations in duplicate measurements with the same amount of photolysate were greater than the calculated corrections; therefore, corrections were not applied and instead repeated measurements with different amounts of photolysate were simply treated as independent measures of the HCl concentration.

Phosgene concentrations in the photolysate were measured by adding methanol (50 μL) to the TPP solution containing an aliquot of the photolysate, immediately following the HCl determination. Alcoholysis of phosgene to form methyl chloroformate was generally complete within 2 min and the liberated HCl was measured by means of the additional H_4TPP^{2+} formed. Alcoholysis of the second chlorine, *i.e.* of methyl chloroformate, is much slower and did not interfere with measurements made within 30 min.

A parallel analysis for phosgene was conducted by adding an aliquot from the photolysate to a 3.00 mL solution of approximately 0.01 M Bu_4NI in $CHCl_3$ from which ethanol had been removed. After 2 min, the absorbance at 365 nm was used to determine the concentration of I_3^- (25), arising from the reaction (26)

$$COCl_2 + 2I^- \rightarrow CO(g) + I_2 + 2\ Cl^- \qquad (16)$$

and the subsequent formation of I_3^- by reaction of the iodine with iodide in solution. Triiodide reduces a number of potential species in solution aside from phosgene, including peroxides; thus, a higher result than that from the TPP test would indicate the presence of oxidizing species other than phosgene.

UV–visible spectra were recorded with a Cary 50 spectrophotometer. UV–visible reflectance spectra were recorded on an Ocean Optics USB4-UV-VIS spectrophotometer with an Ocean Optics R400-7 reflectance probe, using the Cl^- form of the resin as a baseline. GC-MS measurements were carried out with a Shimadzu QP-5000 instrument with an Agilent DB624 column (30 m, 0.32 mm × 1.8 μm cyanopropylphenyl/dimethyl polysiloxane film). The oven start temperature was 40°C and a 20°C min^{-1} linear temperature gradient was applied to a final temperature of 240°C. A 10:1 split ratio was applied to sample injections. Species were identified from their mass spectra and peak areas were used to determine concentrations. Before injection, 50 μL of ethanol, containing a standard concentration of xylene as an internal standard, was mixed with 500 μL of the photolysate. Ethyl chloroformate, formed from the alcoholysis of phosgene, was then used as the analytical standard in place of phosgene. Without added ethanol, phosgene was readily identifiable in the gas chromatogram, as was its complete disappearance and conversion to ethyl chloroformate in the presence of ethanol. Analyses had to be undertaken within a few hours to avoid further alcoholysis to diethyl carbonate.

RESULTS AND DISCUSSION

Reaction products

When chloroform was exposed to broadband irradiation ($\lambda > 345$ nm) in the presence of the $CuCl_4^{2-}$/Dowex catalyst, HCl and $COCl_2$ accumulated in solution, although it can be assumed that both escaped into the gas phase to some extent. Figure 1 shows a typical 30-min experiment. A short induction period is evident, following which $COCl_2$ increased steadily, while HCl formation, from the beginning slower than that of

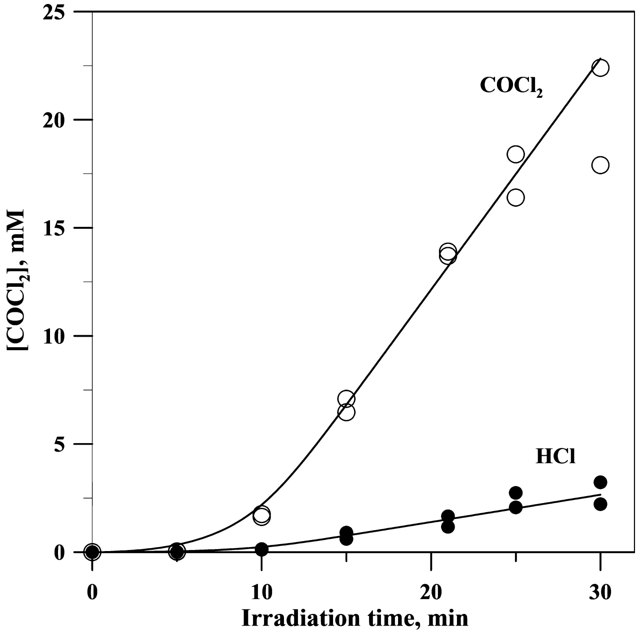

Figure 1. Products formed during the broadband (λ > 345 nm, 350-W Hg lamp) irradiation of 2 mL of chloroform with 29 mg of $CuCl_4^{2-}$/Dowex exposed to air. Solid lines are fits to Eqs. (28) and (29) in text.

$COCl_2$, appeared to level off. The considerably greater rate of $COCl_2$ formation might be consistent with peroxide or hydroperoxide reoxidation of Cu(I), and certainly rules out reoxidation by chloroform as a major pathway. However, the $COCl_2$ to HCl ratio was much higher than would be predicted for decomposition initiated by chlorine atom photodissociation from $CuCl_4^{2-}$.

A 3-hr irradiation was undertaken in order to be able to detect minor products by GC-MS, and the results are shown in Table 1, which also includes a comparison of the three methods used to determine the phosgene yield.

While the TPP and triiodide tests gave similar estimates of the phosgene concentration in solution, the concentration by GC-MS was approximately 25% smaller. It is possible that the discrepancy is due to the evaporation of phosgene during sample handling and further evaporation into the head space of the sample vial while waiting to be processed. The high volatility of $COCl_2$ in chloroform was tested by expressing into methanol the contents of an air balloon that had been connected to the sample during irradiation, converting much of the phosgene to methyl chloroformate and releasing HCl in the process. This served only to establish a lower limit for the $COCl_2$ in the vapor phase, since it can be assumed that some of the phosgene escaped without reacting with methanol. As shown in Table 1, the vapor phase contained on the order of half as much phosgene as was present in the chloroform solution.

The discrepancies between the phosgene concentration determined by GCMS and by the TPP test were much smaller for shorter irradiation times, which is consistent with a greater loss of volatile phosgene into the head space from solutions of high $COCl_2$ concentration (ca. 0.5M after the 3-hr radiation reported in Table 1) during irradiation and sample handling for the analyses (1–2 hr). On the other hand, the difference between the TPP and iodide tests was persistent, often greater than that shown in Table 1. Since the iodide test responds to many oxidizing species, it can be concluded that oxidants other than phosgene are produced during irradiation and build up in solution along with phosgene.

Table 1. Product yields following a 180-min irradiation (λ > 345 nm, 350-W Hg lamp) of a suspension of 30 mg of $CuCl_4^{2-}$/Dowex in 1 mL of $CHCl_3$ exposed to air.

Product	Yield, μmol
HCl	10
$COCl_2$ (GCMS)	260
$COCl_2$ (TPP test)	345
$COCl_2$ (I^- test)	360
$COCl_2$ in balloon*	150
CCl_4	235
C_2Cl_6	3
CH_2Cl_2	1

*TPP test.

The longer irradiation confirms the decline in the rate of HCl production intimated in Fig. 1, while the rate of $COCl_2$ formation increased further, compared to the rate during the first 30 min. Unexpectedly, given the presumed mechanism from Eqs. (3)–(7), a large amount of CCl_4 was also found, far exceeding the amount of HCl. On the other hand, there were only trace quantities of C_2Cl_6, the expected termination product from the CCl_3 radicals that were presumed to be chain carriers. These results are in distinct conflict with our initial hypothesis of chlorine atom photodissociation from $CuCl_4^{2-}$.

Control experiments

Table 2 shows a comparison of chloroform decomposition yields in the presence of the $CuCl_4^{2-}$ form of the Dowex 2-X8 resin, the perchlorate form from which it was prepared, and the chloride form, which has been shown to be photocatalytically active (19), all under irradiation above 345 nm. While the perchlorate form showed no activity whatever, the resin in the chloride form was even more active than the resin with $CuCl_4^{2-}$. This difference may be attributable to the considerably higher concentration of anion sites per gram in the chloride form, but the complex relationship between the quantity of a photocatalyst and its activity (27) permits only the broadest comparisons. No decomposition of chloroform occurred in the presence of $CuCl_4^{2-}$/Dowex in the dark. There was also no decomposition of pure chloroform under irradiation for 60 min in the absence of a catalyst.

Reflectance spectra

Because $Cu_2Cl_6^{2-}$, in equilibrium with $CuCl_4^{2-}$ as in Eq. (1), was found to be the photocatalytically active species in homogeneously catalyzed CH_2Cl_2 photodecomposition, reflectance spec-

Table 2. Product yields (in μmol) following 60-min irradiation (λ > 345 nm, 350-W Hg lamp, O_2 balloon) of a suspension in 1 mL $CHCl_3$ of 31 mg of Dowex 2-X8 resin in the $CuCl_4^{2-}$, ClO_4^-, or Cl^- form.

	HCl	$COCl_2$*
$CuCl_4^{2-}$	6.3	322
ClO_4^-	0.0	0
Cl^-	35	489

*Methanol/TPP test.

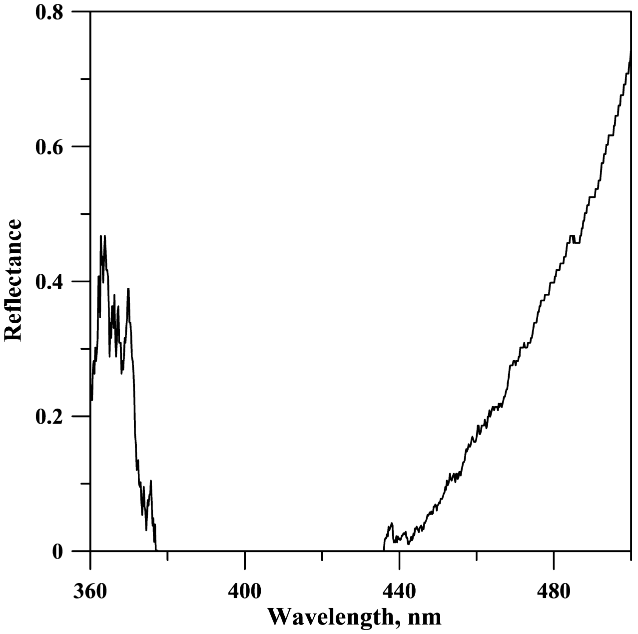

Figure 2. Reflectance, Kubelka–Munk function (60,61), of $CuCl_4^{2-}$/Dowex, relative to Cl^-/Dowex.

tra were taken both before and after irradiation to determine whether any detectable amount of $Cu_2Cl_6^{2-}$ might be present. In CH_2Cl_2 solution, $CuCl_4^{2-}$ was characterized by a peak at 409 nm, while $Cu_2Cl_6^{2-}$ had an almost equally intense peak at 475 nm (1). By reflectance (Fig. 2) we could see that the resin absorbed strongly between 380 and 440 nm, but could not find the exact peak position. Nevertheless, there was no evidence of an absorbance peak near 475 nm, and it appears that all the copper was in the form of $CuCl_4^{2-}$. This did not change after irradiation; thus, if $Cu_2Cl_6^{2-}$ does participate in the process, its existence is transitory.

Oxygen dependence

Although the mechanism described by Eqs. (4)–(7) is clearly at odds with the experimental product distribution, the formation of the trichloromethylperoxy radical as in Eq. (5) could still be a key step. If so, a dependence of the overall photodecomposition rate on the rate of Eq. (5), and thus on the photostationary state concentration of CCl_3, would lead to the prediction that as the partial pressure of O_2 increased, the photodecomposition rate would be higher, asymptotically approaching the condition in which essentially all CCl_3 radicals reacted with oxygen and additional O_2 yielded no increase in rate.

Experimentally, as seen in Table 3, photodecomposition proceeded much more rapidly under an atmosphere of pure oxygen than under air. The yield of phosgene was approximately proportional to the O_2 percentage, as was the HCl yield, although very small. Because of this, most of the tests conducted were under an oxygen atmosphere. No asymptotic behavior was observed.

Photodecomposition in the presence of cyclohexane and ethanol

When photodecomposition was carried out as in Table 3, irradiating for 60 min, but with 30 μL of cyclohexane added to the 1.00 mL of chloroform, no detectable amount of either HCl or phosgene was obtained (< 0.1 μmol). This result was unexpected, because Cl atoms from the dissociation of $CuCl_4^{2-}$, Eq. (10), would be expected to abstract hydrogen from both chloroform and cyclohexane, the C–H bond enthalpies being similar in these two molecules (28,29). No bicyclohexyl or other cyclohexyl products were seen by GC-MS; thus, it appears that the quenching is not a result of radical scavenging by C_6H_{12}.

Table 3. Product yields (in μmol) following 60-min irradiation (λ > 345 nm, 350-W Hg lamp) of a suspension of 31 mg $CuCl_4^{2-}$/Dowex in 1 mL $CHCl_3$ with an air or an oxygen balloon.

	21% O_2	100% O_2
HCl	1.0	6.3
$COCl_2$*	68	348

*Iodide test.

Table 4. Product yields (in μmol) following 60-min irradiation (λ > 345 nm, 350-W Hg lamp, O_2 balloon) of a suspension of 31 mg $CuCl_4^{2-}$/Dowex in 1 mL $CHCl_3$ with and without the addition of acetonitrile.

	no CH_3CN	3% CH_3CN
HCl	6.3	0.3
$COCl_2$*	322	32
$COCl_2$†	348	115

*Methanol/TPP test. †Iodide test.

Photodecomposition was also completely quenched when irradiation was carried out on stabilized chloroform, containing approximately 1% ethanol. Again, despite the well-known role of ethanol as a radical scavenger, quenching was not attributable to this mechanism, since the products from hydrogen abstraction from the α-carbon, primarily acetaldehyde (30), but potentially 2,3-butanediol (31), were not found.

Photodecomposition in the presence of acetonitrile

In the presence of 3% acetonitrile, the photodecomposition of chloroform catalyzed by $CuCl_4^{2-}$/Dowex slowed, but was not quenched entirely, as can be seen in Table 4. In addition, there was a discrepancy in the phosgene determined by the methanol/TPP test and by the iodide test. Since in the iodide test, triiodide is also formed by reaction with peroxides, it is possible that CCl_3OOH or related species accumulated in solution during irradiation.

Photodecomposition in the presence of added chloride ion

The addition of Bu_4NCl to chloroform drastically lowered the rate of photodecomposition, as can be seen in Table 5. This suggests that there may be an equilibrium step in the photodecomposition in which Cl^- is a product, although there are other explanations for the retardation of the photodecomposition rate that may be considered (*vide infra*).

Catalyst surface area

It was expected that increasing the surface area of the $CuCl_4^{2-}$/Dowex catalyst would increase the rate of photodecom-

Table 5. Product yields (in μmol) following 60-min irradiation (λ > 345 nm, 350-W Hg lamp, O_2 balloon) of a suspension of 31 mg $CuCl_4^{2-}$/Dowex in 1 mL $CHCl_3$ with and without the addition of chloride ion.

	no Bu_4NCl	5 mg Bu_4NCl
HCl	6.3	1.0
$COCl_2$*	322	6

*Methanol/TPP test.

Table 6. Product yields (in μmol) following 60-min irradiation (λ > 345 nm, 350-W Hg lamp, O_2 balloon) of a suspension in 1 mL $CHCl_3$ of 3.5 mg of $CuCl_4^{2-}$/Dowex, normal (16-50 mesh) or powdered.

	HCl	$COCl_2$*
Normal	0.4	8
Powdered	107	1100

*Iodide test.

Table 7. Product yields (in μmol) following 60-min irradiation (λ > 345 nm, 350-W Hg lamp, O_2 balloon) of 2×10^{-3} mol of $CuCl_4^{2-}$ in 1 mL of $CHCl_3$ in a homogeneous solution and in a heterogeneous suspension.

Catalyst	HCl	$COCl_2$
$(Et_4N)_2CuCl_4$ in solution	14	300
$CuCl_4^{2-}$ on Dowex 2-X8	35	490

position and, as Table 6 shows, this was decidedly true in the comparison of 3.5 g of the normal resin (16–50 mesh) with the same amount of powdered resin. The dramatic increase in yield can be ascribed to the much lower transmittance of the suspension, and thus higher probability of absorption, with the smaller particles (27).

Heterogeneous *vs* homogeneous catalysis

Heterogenization of a homogeneous photocatalyst generally results in a lower catalytic activity for an equivalent amount of catalyst, due to less efficient light absorption in the solid state (32). There are, however, examples where only a small loss of activity is observed (33,34), or even an increase in activity (35), due predominantly to the stabilization of intermediate species by the solid matrix (36).

A comparison was made between the homogeneous photocatalytic activity of $(Et_4N)_2CuCl_4$ and the heterogeneous activity of $CuCl_4^{2-}$ on Dowex 2-X8, the results of which are shown in Table 7. Unexpectedly, the heterogenized form exhibited somewhat higher yields of both HCl and $COCl_2$.

Mechanism 1—Photodissociation of a chlorine atom

Our initial hypothesis was that the photocatalytic activity of $CuCl_4^{2-}$ on Dowex was due to the photodissociation of a chlorine atom through irradiation into the Cu(II) LMCT bands in the visible and near-UV, as in Eq. (10), which would be consonant with the common understanding of the photochemistry of chlorocopper(II) complexes in organic solvents (37–40), specifically including $CuCl_4^{2-}$ (41).

For several reasons, this mechanism can be ruled out. One consideration is that as a homogeneous photocatalyst for dichloromethane decomposition, the tetrachlorocuprate ion is not itself active, but is in equilibrium with the hexachlorodicuprate ion, as in Eq. (1), which is photoactive (1). The photocatalytic activity of the $Cu_2Cl_6^{2-}$ ion may be due, in part, to stabilization of photodissociated chlorine atoms by the chloride ions in solution as a result of the equilibrium of Eq. (1), whereby the resulting Cl_2^- ion prevents recombination sufficiently to allow diffusion out of the solvent cage (1). From the reflectance spectrum of $CuCl_4^{2-}$ on Dowex 2-X8, there was no detectable $Cu_2Cl_6^{2-}$ peak; thus, the formation of the dimer as in Eq. (1) is greatly suppressed on the ion exchange resin, if it takes place at all.

Experimentally, this mechanism is directly contradicted by the finding that only a very small quantity of C_2Cl_6 is produced. When chlorine atoms abstract hydrogen from chloroform to make CCl_3 radicals, as in Eq. (4), the trichloromethyl radicals self-terminate to make C_2Cl_6 the major side product when chlorine atoms initiate the photodecomposition of chloroform (42). The small amount of HCl produced in our experiments is even more direct evidence that the photodissociation of chlorine atoms from $CuCl_4^{2-}$/Dowex does not occur under the conditions of this study. What HCl was found can potentially be ascribed to phosgene hydrolysis, water being formed when peroxides or hydroperoxides react by breaking the O–O bond (43), *vide infra,* Eqs. (26) and (27).

Is dichlorocarbene produced in the primary photochemical step?

Given the lack of evidence for the photodissociation of chlorine atoms from either $CuCl_4^{2-}$ or from $CHCl_3$ directly, one possibility is that under visible irradiation in the presence of $CuCl_4^{2-}$ chloroform decomposes to HCl and CCl_2, as it does in uncatalyzed thermal degradation (3). This can be ruled out from the low yield of HCl and the absence of the typical CCl_2 secondary products in chloroform, C_2Cl_4 and C_2HCl_5 (3).

Mechanism 2—Photocatalysis by Cl^-/Amberlite in equilibrium with $CuCl_4^{2-}$

As shown in Table 2, the chloride form of the anion exchange resin is an efficient catalyst for the decomposition of chloroform, possibly more efficient than the $CuCl_4^{2-}$ form of the resin. Because of the potential lability of chloride ions in copper(II) complexes, this raises the question of whether the photocatalytic activity of $CuCl_4^{2-}$ on Dowex 2-X8 is actually due to dissociated chloride ions. Hypothetically, a ligand dissociation equilibrium populates a certain fraction of resin sites with chloride ions, that is

$$(R^+)CuCl_4^{2-}(R^+) \rightleftharpoons (R^+)CuCl_3^- + (R^+)Cl^- \qquad (17)$$

where R^+ represents the cationic resin sites, which have the structure $R\text{-}CH_2N^+(CH_3)_2(C_2H_4OH)$ in Dowex 2-X8 (20). If this hypothesis were correct, the observed photocatalytic activity would actually result from light absorption by the resin in the vicinity of chloride ions rather than by $CuCl_4^{2-}$ complexes.

This mechanism is consistent with the high ratio of CCl_4 to C_2Cl_6 observed. The mechanism for the photocatalysis of chloroform decomposition by the chloride form of the resin appears to comprise two sequential photochemical processes, the first of which leads to CCl_4 (19):

$$(R^{+})\mathrm{Cl}^{-} + \mathrm{CHCl_3} + \mathrm{O_2} \xrightarrow{hv} (R^{+})\mathrm{HO_2^{-}} + \mathrm{CCl_4} \qquad (18)$$

The second process, representing the major decomposition pathway for chloroform, would then be the chain reaction Eqs. (4)–(7), initiated by the photodissociation of CCl_4.

The reflectance spectrum, on the other hand, does not support this hypothesis, because no trace of the trigonal $CuCl_3^-$ ion spectrum (44) can be found. This is not conclusive in itself, however, since the Cu^{2+} ion may remain four-coordinate even after dissociation of a chloride ion, through coordination of chloroform molecules (*vide infra*). A weightier argument against the mechanism is that even if the dissociation equilibrium, Eq. (17), lay completely to the right, still only half of the resin cation sites would have chloride ions. Furthermore, for wavelengths above 345 nm the tetrachlorocuprate(II) ion absorbs much more strongly than the polystyrene resin, greatly reducing net light absorption by the resin. It seems unlikely that there would be significant energy transfer from the copper (II) to the resin, given the low-lying $CuCl_4^{2-}$ ligand field excited states (45). It is difficult to see how under these circumstances a photodecomposition efficiency could result that was two-thirds as great as that achieved when all the resin sites are occupied by Cl^-.

Experimentally, the Cl^- and $CuCl_4^{2-}$ forms of the resin also exhibit different relationships between photocatalytic activity and the partial pressure of oxygen. The resin excited state is quenched by O_2, which with the Cl^-/Amberlite catalyst causes an asymptotic increase in the photochemical yield with the partial pressure of oxygen (19). In contrast, the $CuCl_4^{2-}$/Dowex system exhibits a direct proportionality between O_2 partial pressure and photochemical yield up to 1 atm, thus no quenching of the excited state within this range of partial pressures.

A further incompatibility with this hypothesis is furnished by the behavior with added chloride ion. Additional chloride ion would not be expected to alter the equilibrium of Eq. (17), unless one or the other of the two copper complexes could be displaced by Cl^-, for which there was no spectrophotometric evidence. Chloride could, however, displace some of the small fraction of perchlorate ions (~13% of the resin sites) remaining after preparation of the $CuCl_4^{2-}$ form of the resin. Thus, if there were any effect, it would be expected to be that of enhancement of the reaction rate through the additional Cl^- sites on the resin, whereas a decrease in yield was observed experimentally.

Mechanism 3—Chlorine atom transfer with photoreduction of O_2

Consider a process similar to that of Eq. (18) in which immobilized $CuCl_4^{2-}$ is the photoactive species:

$$(R^{+})\mathrm{CuCl_4^{2-*}}(R^{+}) + \mathrm{CHCl_3} \xrightarrow{\mathrm{O_2}} \mathrm{CCl_4} + (R^{+})\mathrm{HO_2^{-}} + (R^{+})\mathrm{CuCl_3^{-}} \qquad (19)$$

It is doubtful that this could take place as a single step, and it is not clear what the mechanistic steps would be, but we suggest that chloroform displaces some fraction of the coordinated chloride ions in an equilibrium process, possibly assisted by the geometry of the resin cation sites.

$$(R^{+})\mathrm{CuCl_4^{2-}}(R^{+}) + \mathrm{CHCl_3} \leftrightarrows (R^{+})\mathrm{CuCl_3(Cl_3CH)^{-}}(R^{+})\mathrm{Cl^{-}} \qquad (20)$$

Chloride ions in solution would suppress this equilibrium by displacing coordinated chloroform, thereby hindering further reaction. When copper with chloroform in the first coordination sphere absorbs light, the excited state would then be able to react with oxygen, leading to the peroxide.

$$\begin{aligned}[(R^{+})\mathrm{CuCl_3(Cl_3CH)^{-}}(R^{+})\mathrm{Cl^{-}}]^{*} + \mathrm{O_2} \rightarrow \\ (R^{+})\mathrm{HO_2^{-}} + (R^{+})\mathrm{CuCl_3^{-}} + \mathrm{CCl_4}\end{aligned} \qquad (21)$$

Chloroform is not normally considered as a potential ligand (46), but in fact there is NMR evidence of chloroform coordination with first-row transition metal ions (47).

The tetrachlorocuprate(II) ion would be regenerated following the protonation of the hydrogen peroxide anion by hydrogen chloride.

$$\mathrm{HCl} + (R^{+})\mathrm{HO_2^{-}} \rightarrow (R^{+})\mathrm{Cl^{-}} + \mathrm{H_2O_2} \qquad (22)$$

$$(R^{+})\mathrm{Cl^{-}} + (R^{+})\mathrm{CuCl_3^{-}} \rightarrow (R^{+})\mathrm{CuCl_4^{2-}}(R^{+}) \qquad (23)$$

As with the photodecomposition of chloroform in the presence of Cl^- on Amberlite IRA-900 (19), phosgene would be formed through the subsequent catalyzed photodissociation of CCl_4, with CCl_3 radicals as chain carriers. This could conceivably occur in exactly the same way through absorption of light by the polystyrene resin at sites with Cl^- ions, achieved through the equilibrium of Eq. (20). However, the presumably small value for the equilibrium constant of Eq. (20), together with the much higher fraction of light absorbed by $CuCl_4^{2-}$, leads to the supposition of an analogous process involving $CuCl_4^{2-}$ and a $CuCl_5^{2-}$ intermediate.

$$(R^{+})\mathrm{CuCl_4^{2-*}}(R^{+}) + \mathrm{CCl_4} \rightarrow (R^{+})\mathrm{CuCl_5^{2-}}(R^{+}) + {}^{\bullet}\mathrm{CCl_3} \qquad (24)$$

$$(R^{+})\mathrm{CuCl_5^{2-}}(R^{+}) + \mathrm{CHCl_3} \rightarrow (R^{+})\mathrm{CuCl_4^{2-}}(R^{+}) + \mathrm{HCl} + {}^{\bullet}\mathrm{CCl_3} \qquad (25)$$

Trichloromethyl radicals can react with oxygen to generate phosgene as in Eqs. (4)–(7), and in addition, hydrogen peroxide can react with CCl_3 radicals, breaking the O–O bond (48) and propagating the chain:

$$\mathrm{H_2O_2} + {}^{\bullet}\mathrm{CCl_3} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{CCl_3OH}(\rightarrow \mathrm{HCl} + \mathrm{COCl_2}) \qquad (26)$$

$${}^{\bullet}\mathrm{OH} + \mathrm{HCl} \rightarrow \mathrm{H_2O} + {}^{\bullet}\mathrm{Cl} \qquad (27)$$

As water builds up, it can be expected to hydrolyze phosgene to yield carbon dioxide and water. If the rate of Eq. (26) is high enough, it prevents the self-termination of CCl_3 radicals, which would explain the low quantities of C_2Cl_6 found.

ΔH^o for the reaction represented by Eq. (26) is estimated to be -160 kJ mol^{-1}, using the gas phase data for H_2O_2 in preference to the highly hydrogen-bonded liquid phase, and using the value of -261 kJ mol^{-1} inferred from *ab initio* calculations for CCl_3OH (15). Trichloromethanol decomposes rapidly to hydrogen chloride and phosgene (15,49), with ΔH^o of approximately -50 kJ mol^{-1} (15). As water builds up, it can be expected to hydrolyze phosgene to yield carbon dioxide and hydrogen chloride.

In the process described above, the photocatalytic activity of $CuCl_4^{2-}$ appears to be exerted with no involvement of Cu(I), at odds with generally accepted models for copper complex redox photochemistry (50). However, the reaction shown in Eq. (21) could be a multistep process involving a copper(I) intermediate. In any case, it seems likely that the reaction would proceed through a charge transfer to solvent (CTTS) excited state (51–53). CTTS states have specifically been implicated in the photooxidation of various substrates by Cu(II) complexes in chloroform and other halocarbon solvents (54).

The time sequence data in Fig. 1 can be fit reasonably well to a simple model for two sequential photochemical processes, the first of which produces CCl_4, both induced by excited state tetrachlorocuprate(II), here represented as Cu*.

$$Cu* + CHCl_3 \rightarrow CCl_4 \qquad (28)$$

$$Cu* + CCl_4 \rightarrow n\,COCl_2 \qquad (29)$$

Differential equations for these two steps were modeled numerically using small time intervals and the rate constants were adjusted to yield the fit in Fig. 1. This should not be considered evidence offered in proof of this interpretation, because there are other models that are also consonant with the data of Fig. 1, *e.g.* one in which CCl_4 undergoes photodissociation directly.

The net reaction predicted by Eqs. (20) and (21) is

$$CHCl_3 + O_2 + HCl \xrightarrow{h\nu,(R^+)_2CuCl_4} CCl_4 + H_2O_2 \qquad (30)$$

The overall reaction is exothermic by approximately 40 kJ mol^{-1} (again using gas phase data for H_2O_2), although one or more of the steps implied by Eq. (21) must be endothermic, requiring light. Eqs. (26) and (27), together with Eq. (4), constitute a radical chain with net stoichiometry

$$CHCl_3 + H_2O_2 \rightarrow HCl + H_2O + COCl_2 \qquad (31)$$

The net reaction is exothermic by approximately 300 kJ mol^{-1} (using H_2O and H_2O_2 gas phase data), and each of the three steps is also exothermic.

CONCLUSIONS

Virtually all of the experimental observations find an explanation with the steps outlined above for Mechanism 3. The low ratio of hydrogen chloride to phosgene can be attributed to the protonation of hydrogen peroxide anions, Eq. (22), and hydroxyl radicals, Eq. (27), by HCl. The suppression of photodecomposition by ethanol and acetonitrile, without either acting as a radical scavenger, can be ascribed to the same process by which chloride ions retard the reaction, that is, by suppressing the complexation of chloroform, Eq. (20), preferentially occupying copper(II) coordination sites in place of the weaker ligand chloroform. Both acetonitrile and ethanol may also displace chloroform from the photoactive sites indirectly because of strong intermolecular attractions to the polystyrene chain or to the cation resin sites, or both. The attraction of the resin to ethanol may be particularly enhanced by hydrogen bonding with the 2-hydroxyethyltrialkylammonium moieties that constitute the resin cation sites (55), which might explain why ethanol suppressed photodecomposition more effectively than acetonitrile.

The importance of matrix effects is underscored by the quenching of the photodecomposition in the presence of cyclohexane. Since there is no evidence of any hydrogen abstraction from cyclohexane, its quenching function must also result from the displacement of chloroform from the photoactive sites, presumably through the strong London forces shared with the polystyrene matrix.

The discrepancy between the TPP test and the iodide test for phosgene was ascribed to the presence of oxidizing species other than phosgene in irradiated solutions. While hydroperoxides, formed by the reaction of CCl_3 radicals with O_2 followed by hydrogen abstraction, may account for some of these oxidizing equivalents, hydrogen peroxide, if formed as in Eqs. (21) and (22), would presumably be the predominant species of this type.

The direct proportion observed between the photodecomposition rate and the partial pressure of oxygen is also explained better by Mechanism 3. In the other mechanisms considered, O_2 reacts with CCl_3 to produce CCl_3OO radicals, leading to an expected asymptotic variation of the decomposition rate with the O_2 partial pressure, a relationship that has been observed in other systems involving trichloromethylperoxy radicals (56). In Mechanism 3, O_2 reacts with a chlorocopper(II) excited state complex to which chloroform is coordinated. Given the expected high rate of deexcitation of the Cu(II) excited state, saturation of the photochemical reaction channel with O_2 would not be expected.

Finally, consider how it can be that equivalent molar quantities of $CuCl_4^{2-}$ catalyze the photodecomposition of chloroform better when immobilized on an anion exchange resin than in homogeneous solution. This can be ascribed to a matrix effect in which the chloroform molecules are brought into the vicinity of $CuCl_4^{2-}$ for a longer duration, promoting coordination as in Eq. (20), which we suggest is a prerequisite for the excited Cu(II) species to react with O_2. $CHCl_3$ molecules are attracted by London forces to the polystyrene, but also by ion-dipole forces to the tetraalkylammonium cation sites, which is consistent with an enforced proximity to the $CuCl_4^{2-}$ anions and a shift of the equilibrium in Eq. (20) toward the chloroform complex.

In water, $CuCl_4^{2-}$ is rapidly aquated, which rules this complex out as a means to catalyze the photodegradation of halocarbons in water by means of sunlight, the goal of a number of ongoing research efforts (57–59). However, the ability of $CuCl_4^{2-}$ to catalyze chloroform photodegradation with near-UV irradiation plus the relatively low cost and low toxicity of copper, compared to the heavy metals most commonly under investigation (57), suggest that related copper complexes that are not susceptible to ligand displacement may prove useful.

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