Research Note

Photocatalysis of Chloroform Decomposition by Hexachloroosmate(IV)

Laura A. Peña and Patrick E. Hoggard*

Department of Chemistry, Santa Clara University, Santa Clara, CA Received 20 July 2009, accepted 9 October 2009, DOI: 10.1111/j.1751-1097.2009.00669.x

ABSTRACT

Hexachloroosmate(IV) effectively catalyzes the photodecomposition of chloroform in aerated solutions. The decomposition products are consistent with a mechanism in which excited state $OsCl_6^{2-}$ reduces chloroform, rather than one involving photodissociation of chlorine atoms. Trace amounts of ethanol or water in the chloroform lead to photosubstitution to form $OsCl_5(EtOH)^-$ or $OsCl_5(H_2O)^-$, neither of which is photocatalytically active.

INTRODUCTION

Chloroform and other trihalomethanes that find their way into drinking water primarily through municipal disinfection (1,2) have half-lives of months in aqueous environments even exposed to the sun (3). Chloroform is one of the water pollutants most commonly found to exceed regulatory guidelines (1,4,5). Materials that could heterogeneously catalyze the photodecomposition of chloroform by means of sunlight would have the potential to effect passive remediation; however, it is not yet clear how such a catalyst might function. We have examined several metal complexes that homogeneously catalyze chloroalkane decomposition in the neat solvent. Some of these function through photodissociation of a chlorine atom (6,7), which generally requires irradiation into ligand-to-metal charge transfer (LMCT) bands, which facilitate metal-ligand bond homolysis (8-11). An alternative route to photodegradation consists of the photoreduction of the chloroalkane (12-16). In either case, radicals are created that react with oxygen to form peroxy radicals and hydroperoxides, leading to further decomposition through a chain process (17). Yet another means to effect photodecomposition is for the catalyst to undergo photoreduction by oxidizing a counterion or another substrate to create radicals, following which the catalyst is restored by a thermal process that may generate additional radicals (18). To function in aqueous environments, coordinated chlorides, at least some of them, should resist hydrolysis. This eliminates chloro complexes of first-row transition metals as candidates.

In this study, we examined $OsCl_6^{2-}$ as a potential photocatalyst in chloroform. The near-UV spectrum of hexachloroosmate(IV) is dominated by intense LMCT bands (19) although lower energy d-d excited states are also present, and internal conversion to this manifold could lead to different primary photochemical events, or none at all. The chlorine atoms formed by photodissociation can initiate radical chain processes in which an organic substrate is degraded, potentially to CO₂ and HCl.

MATERIALS AND METHODS

 $(Bu_4N)_2OsCl_6$ was prepared by dissolving K_2OsCl_6 (Sigma-Aldrich) and Bu_4NBr in water, mixing the two solutions, collecting the precipitate by filtration, and air-drying. Chloroform (J.T. Baker reagent grade) was prepared by shaking with an equal volume of water five times to remove the ethanol stabilizer. It was then dried over anhydrous calcium chloride.

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 or a 100-W mercury lamp (Oriel) with a Schott WG-320 cutoff filter, which may be characterized approximately as passing wavelengths above 320 nm. Some samples were deoxygenated by bubbling argon through the cuvette for 10 min. UV-visible spectra were monitored with a Cary 50 spectrophotometer. GC-mass spectrometry was carried out with a Shimadzu QP-5000 instrument with a Restek XTI-5 column. The over start temperature was 40°C and a linear temperature gradient of 30° min⁻¹ was applied to 250°C. Injection was carried out with a 1:1 split ratio. Chlorine-containing species were identified from their mass spectra.

HCl production was measured by periodically removing 50 μ L aliquots from the photolysate, and adding them to 3.0 mL of a solution of tetraphenylporphyrin (H₂TPP) in CHCl₃, the spectrum of which was then measured to determine the amount of H₄TPP²⁺ formed, by using the extinction coefficients of the porphyrin species (20,21). Protonation of H₂TPP yields H₄TPP²⁺ in preference to H₄TPP⁺, even at low concentrations of acid (22).

Peroxide concentrations were estimated by mixing 50 or 100 μ L aliquots of the photolysate with 3.00 mL of approximately 0.01 M Bu₄NI in CHCl₃ and determining the resulting I₃⁻ concentration from the extinction coefficient, 2.50 × 10⁴, at 365 nm (23), correcting for the absorption from OsCl₆²⁻ and taking into account the experimental 1:1 ratio of hydroperoxide reacted to triiodide ion formed (24). Triiodide ion is also formed by the reaction of I⁻ with Cl₂, although GC-MS analysis showed the concentration of Cl₂ to be minor in comparison to the concentration of total oxidants.

The initial concentrations of $(Bu_4N)_2OsCl_6$ in chloroform solutions were calculated from absorption spectra, using the value of 9.78 $(\pm 0.01) \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$ at 341 nm, determined from a Beer's Law plot.

RESULTS AND DISCUSSION

Hexachloroosmate dissolved in chloroform did catalyze its photodecomposition. Figure 1 shows HCl produced during

^{*}Corresponding author email: phoggard@scu.edu (Patrick E. Hoggard) © 2009 The Authors. Journal Compilation. The American Society of Photobiology 0031-8655/10



Figure 1. Accumulation of HCl and peroxide (in equivalents relative to Os) during the broadband ($\lambda > 320$ nm) irradiation of a 2×10^{-4} m solution of (Bu₄N)₂OsCl₆ in chloroform that was exposed to air and from which ethanol was removed.

the irradiation of a typical aerated sample. In the absence of the osmium complex, no HCl was detected after 40 min of irradiation. During the course of irradiation, the spectrum of the $OsCl_6^{2-}$ ($\lambda_{max} = 341$ and 375 nm) did not change. Chlorine atoms generate HCl through hydrogen abstraction; thus the result is consistent with a photodissociation mechanism:

$$\operatorname{OsCl}_{6}^{2-} \xrightarrow{hv} \operatorname{OsCl}_{5}^{2-} + \operatorname{Cl} \bullet \tag{1}$$

$$Cl \bullet + CHCl_3 \longrightarrow HCl + \bullet CCl_3 \tag{2}$$

In aerated solutions, however, HCl can also be generated in a chain process through the formation of a hydroperoxide, which also constitutes a means of regenerating the $OsCl_6^{2-}$ starting material.

$$\bullet CCl_3 + O_2 \longrightarrow CCl_3OO \bullet \tag{3}$$

$$CCl_3OO \bullet + CHCl_3 \longrightarrow CCl_3OOH + \bullet CCl_3$$
 (4)

$$\operatorname{CCl_3OOH} + \operatorname{OsCl_5^{--}} \longrightarrow \operatorname{CCl_3O\bullet} + \operatorname{OsCl_5(OH)^{2--}} (5)$$

$$OsCl_5(OH)^{2-} + HCl \longrightarrow OsCl_6^{2-} + H_2O$$
 (6)

$$\operatorname{CCl}_3\operatorname{O} \bullet \longrightarrow \operatorname{COCl}_2 + \operatorname{Cl} \bullet$$
 (7)

$$\text{COCl}_2 + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + 2 \,\text{HCl}$$
 (8)

Since hydroperoxides can be formed from the reaction of any radical with oxygen, it cannot be concluded from this experiment alone that HCl is formed through photochemical Os–Cl homolytic bond cleavage. An alternative, based on several observations of the photoreduction of chloroalkanes by metal complexes (25–28) proceeds as follows:

$$OsCl_6^{2-} + CHCl_3 \xrightarrow{hv} OsCl_6^{-} + \bullet CHCl_2 + Cl^{-}$$
(9)

$$\bullet CHCl_2 + CHCl_3 \longrightarrow CH_2Cl_2 + \bullet CCl_3 \tag{10}$$

GC-MS analysis of photolysates provides evidence that photoreduction, Eqs. (9) and (10), constitute a more likely mechanism for chloroform photodecomposition than photodissociation (Eqs. [1] and [2]). From the generation of dichloromethyl radicals by photoreduction, as in Eq. (9), one would expect to find CH₂Cl₂ from hydrogen abstraction, as in Eq. (10), along with C₂H₂Cl₄, C₂HCl₅ and C₂H₆ from the termination of •CHCl₂ and •CCl₃ radicals, respectively. All three of these products were found in significant amounts in photolysates. Typically, the concentrations of CH2Cl2, C2H2Cl4 and C₂HCl₅ were approximately 20%, 10% and 40% of the concentration of C₂Cl₆. From the photodissociation mechanism, C₂Cl₆ is the only chloroethane termination product expected and experimentally this is what is observed in systems in which chloroform is known to be degraded through the photodissociation of chlorine from a metal complex (7).

Another prediction from the two proposed mechanisms would be that in deoxygenated solutions some HCl would still be produced through Eq. (2) if photodissociation occurred, while from photoreduction either a much smaller amount of HCl would be produced or none at all, depending on how the OsCl₆⁻ intermediate is reduced (*vide infra*). In fact, no HCl at all was detected in irradiated deoxygenated solutions.

The $OsCl_6^{2-}$ spectrum remained essentially unchanged under irradiation ($\lambda > 320$ nm); thus, no significant amount of $OsCl_6^-$ accumulated and it must have been rapidly reduced. Given the relative difficulty of oxidizing chloroform by electron transfer, chloride ion (from the reduction of CHCl₃, Eq. [9]) is the most probable substrate. One possibility, observed in some other photocatalytic systems (16,18), is for chloride ion to be oxidized to chlorine radicals. This would lead to some HCl formation through hydrogen abstraction by chlorine atoms, which was not observed. This is consistent with the experimental value for the $OsCl_6^{-/2-}$ half-wave potential, 1.52 V (*vs.* NHE) in CH_2Cl_2 (29), whereas the Cl/Cl^- potential (in water) is 2.5 V (30). An alternative is a two-electron oxidation to Cl₂, which may require the participation of a coordinated chloride, *i.e.*

$$\operatorname{OsCl}_{6}^{-} + \operatorname{Cl}^{-} \longrightarrow \operatorname{OsCl}_{5}^{2-} + \operatorname{Cl}_{2}$$
(11)

$$OsCl_5^{2-} + CHCl_3 \longrightarrow OsCl_6^{2-} + CHCl_2$$
 (12)

In Eq. (12) the osmium(III) intermediate is presumed to reduce chloroform in order to be restored to $OsCl_6^{2-}$ to complete the cycle. Experimentally, Cl_2 was found in photolysates by GC-MS. This offers some experimental support for the suggested mechanism, whereby it must be noted that an analogous cycle has been reported by Maverick *et al.* for hexachlororhenate(IV), in which $ReCl_6^{2-}$ is photooxidized to $ReCl_6^{-}$, which is then reduced by Cl^- , yielding Cl_2 . The reaction was proposed to pass through a Cl_2^{-} intermediate:

$$\operatorname{ReCl}_{6}^{-} + 2\operatorname{Cl}^{-} \longrightarrow \operatorname{ReCl}_{6}^{2-} + \operatorname{Cl}_{2}^{-}$$
(13)

$$2 \operatorname{Cl}_2^- \longrightarrow \operatorname{Cl}_2 + 2 \operatorname{Cl}^- \tag{14}$$

Replacing Re by Os, this presents a reasonable alternative to Eqs. (11) and (12), and from either cycle it would be predicted that no HCl would form. It is not entirely clear how the three reactants in Eq. (13) could combine to yield the proposed products, for which reason we have suggested that one of the two chlorides to be oxidized might be taken from the coordination sphere.

The lack of a significant photodissociation pathway, given that absorption takes place into LMCT charge transfer bands, is not difficult to reconcile with the electronic structure in $OsCl_6^{2^-}$. Whereas $FeCl_4^-$, for comparison, does undergo photodissociation (7) and also has LMCT bands in the near-UV and ligand field (LF) bands at lower energy, the coupling between LMCT and LF bands is quite strong in the osmium complex (19). As a consequence one expects internal conversion from LMCT to LF states to be considerably more rapid in $OsCl_6^{2^-}$, so that the lifetimes of the LMCT states would be shorter and the excited states correspondingly less reactive.

When ethanol was not completely removed from the chloroform, a photosubstitution reaction took place, yielding $OsCl_5(C_2H_5OH)^-$, verified from its UV spectrum (31). Photosubstitution of chloride in $OsCl_6^{2-}$ by one solvent molecule has been observed in coordinating solvents (32). While photosubstitution was taking place, the rate of HCl production decreased, reaching zero with complete substitution. Likewise, traces of water in the chloroform led to photosubstitution to form, as verified by its UV spectrum (31,32), $OsCl_5(H_2O)^-$. It too was photocatalytically inert.

The failure of the aquapentaammineosmium(IV) complex to catalyze chloroform photodecomposition is quite consistent with the known inverse effect of coordinated water molecules on excited state lifetimes (33), which is based on the increase in the rate of nonradiative relaxation caused by high-frequency O–H or N–H vibrations in coordinated groups (34). Because of the shorter excited state lifetime for $OsCl_5(H_2O)^-$ compared with $OsCl_6^{2-}$, the bimolecular rate constant for Eq. (9) can be expected to be correspondingly lower.

CONCLUSION

While $OsCl_6^{2-}$ has shown itself to be quite effective in catalyzing the photodecomposition of chloroform under near-UV irradiation, ligand exchange occurs in the presence of even trace amounts of water, completely quenching the catalysis. In the absence of available ligands, *i.e.* in pure chloroform, photodecomposition occurs in a process that begins with the reduction of CHCl₃ by excited state OsCl₆²⁻. Because photosubstitution takes place rapidly in the presence of water, OsCl₆²⁻ would be unsuited for halocarbon remediation in aqueous systems.

Acknowledgement—This work was supported by the National Science Foundation through Grant CHE-0749681.

REFERENCES

- U.S. Environmental Protection Agency (1975) Preliminary Assessment of Suspected Carcinogens in Drinking Water [Report to Congress]. EPA Document 560475003; 120 pp.
- U.S. Environmental Protection Agency disinfection byproducts: A reference resource. Available at: http://www.epa.gov/enviro/html/ icr/gloss_dbp.html. Accessed November, 2009.
- Pavelic, P., P. J. Dillon and B. C. Nicholson (2006) Comparative evaluation of the fate of disinfection byproducts at eight aquifer storage and recovery sites. *Environ. Sci. Technol.* 40, 501–508.
- U.S. Environmental Protection Agency. (1999) Ambient Water Quality Criteria for Chloroform. EPA Document 440/5-80-033.

- U.S. Environmental Protection Agency. (2002) National primary drinking water standards. EPA Document 816-F-01-007.
- Doyle, K. J., H. Tran, M. Baldoni-Olivencia, M. Karabulut and P. E. Hoggard (2008) Photocatalytic degradation of dichloromethane by chlorocuprate(II) Ions. *Inorg. Chem.* 47, 7029–7034.
- Hoggard, P. E., M. Gruber and A. Vogler (2003) The photolysis of iron(III) chloride in chloroform. *Inorg. Chim. Acta* 346, 137–142.
- Horvath, O. and A. Vogler (1993) Photoredox chemistry of chloromercurate(II) complexes in acetonitrile. *Inorg. Chem.* 32, 5485–5489.
- Oldenburg, K. and A. Vogler (1993) Electronic spectra and photochemistry of tin(II), lead(II), antimony(III), and bismuth(III) bromide complexes in solution. Z. Naturforsch., B: Chem. Sci. 48, 1519–1523.
- Oldenburg, K. and A. Vogler (1996) Photoredox chemistry of bismuth trichloride in benzene. J. Organomet. Chem. 515, 245–248.
- Vogler, A. and A. Paukner (1989) Photoredox chemistry of chloro complexes of antimony(III) and (V). *Inorg. Chim. Acta* 163, 207– 211.
- Pena, L. A., A. J. Seidl, L. R. Cohen and P. E. Hoggard (2009) Ferrocene/ferrocenium ion as a catalyst for the photodecomposition of chloroform. *Transition Met. Chem. (Dordrecht, Neth.)* 34 135–141.
- Traverso, O., R. Rossi and V. Carassiti (1974) Improved photochemical method for obtaining ferricenium cation. *Synth. React. Inorg. Met.-Org. Chem.* 4, 309–315.
- Wilputte-Steinert, L. (1978) Photoinduced catalysis—Hydrogen transfer reactions catalyzed by ferrocene and/or ferric chloride. J. Mol. Catal. 4, 113–123.
- Gasyna, Z., W. R. Browett and M. J. Stillman (1984) One-electron, visible-light photooxidation of porphyrins in alkyl chloride solutions. *Inorg. Chem.* 23, 382–384.
- Muñoz, Z., A. S. Cohen, L. M. Nguyen, T. A. McIntosh and P. E. Hoggard (2008) Photocatalysis by tetraphenylporphyrin of the decomposition of chloroform. *Photochem. Photobiol. Sci.* 7, 337– 343.
- Cohen, L. R., L. A. Peña, A. J. Seidl, J. M. Olsen, J. Wekselbaum and P. E. Hoggard (2009) The photocatalytic decomposition of chloroform by tetrachloroaurate(III). *Monatsh. Chem.* 40, 1159– 1165.
- Cohen, L. R., L. A. Pena, A. J. Seidl, K. N. Chau, B. C. Keck, P. L. Feng and P. E. Hoggard (2009) Photocatalytic degradation of chloroform by bis (bipyridine)dichlororuthenium(III/II). J. Coord. Chem. 62, 1743–1753.
- Allen, G. C., R. Al-Mobarak, G. A. M. El-Sharkawy and K. D. Warren (1972) Electronic spectra of the hexahalo anions of osmium(IV) and iridium(IV). *Inorg. Chem.* 11, 787–796.
- Du, H., R.-C. A. Fuh, J. Li, L. A. Corkan and J. S. Lindsey (1998) Photochem CAD: A computer-aided design and research tool in photochemistry. *Photochem. Photobiol.* 68, 141–142.
- Lindsey, J. S., PhotochemCAD spectra recorded by Junzhong Li and Richard W. Wagner. http://omlc.ogi.edu/spectra/PhotochemCAD/html/index.html. Accessed November 2009.
- Stone, A. and E. B. Fleischer (1968) The molecular and crystal structure of porphyrin diacids. J. Am. Chem. Soc. 90, 2735– 2748.
- Solis Montiel, E. and J. A. Solano (1986) Spectrophotometric analysis for chlorine by the extraction of triiodide formed in chloroform solution of tetrabutylammonium perchlorate. *Ingenieria y Ciencia Quimica* 10, 45–48.
- Hicks, M. and J. M. Gebicki (1979) A spectrophotometric method for the determination of lipid hydroperoxides. *Anal. Biochem.* 99, 249–253.
- Horvath, A. and S. Papp (1987) Photooxidation of hexacyanoferrate(II) and pentacyanotributylphosphinoferrate(II) in chloroform. *Acta Chim. Hung.*, **124**, 765–771.
- Ng, W. and P. E. Hoggard (2001) Kinetics of the photoreduction of bis(2,4-pentanedionato)copper(II) in chloroform. *Inorg. Chim. Acta*, 321, 1–4.
- Traverso, O. and F. Scandola (1970) Photooxidation of ferrocene in halocarbon solvents. *Inorg. Chim. Acta*, 4, 493–498.

- Yao, Q. and A. W. Maverick (1986) One- and two-electron photooxidation of a molybdenum(III) thiocyanate complex. *J. Am. Chem. Soc.*, 108, 5364–5365.
- Heath, G. A., K. A. Moock, D. W. A. Sharp and L. J. Yellowlees (1985) The orderly progression of redox behavior of 4d- and 5dhexachlorometallate complexes. J. Chem. Soc., Chem. Commun. 1503–1505.
- Thornton, A. T. and G. S. Laurence (1973) Kinetics of oxidation of transition metal ions by halogen radical anions. II. Oxidation of cobalt(II) by dichloride ions generated by flash photolysis. *J. Chem. Soc., Dalton Trans.* 1632–1636.
- Maiboroda, A., G. Rheinwald and H. Lang (2000) Synthesis and reaction of the novel complex [AsPh₄][OsCl₅(H₂O)]. X-ray struc-

ture analysis of [AsPh₄][OsCl₅(H₂O)]·2EtOH and [AsPh₄] [OsCl₅(EtOH)]·EtOH. *Inorg. Chem.*, **39**, 5725–5730. 32. Hasenpusch, W. and W. Preetz (1977) Photochemical ligand

- Hasenpusch, W. and W. Preetz (1977) Photochemical ligand exchange of hexahaloosmates(IV). Zeitschrift fuer Anorganische und Allgemeine Chemie 432, 107–114.
- Supkowski, R. M. and W. D. Horrocks Jr (2002) On the determination of the number of water molecules, q, coordinated to europium(III) ions in solution from luminescence decay lifetimes. *Inorg. Chim. Acta* 340, 44–48.
- Kuehn, K., F. Wasgestian and H. Kupka (1981) The role of hydrogen vibrations in the radiationless deactivation of chromium(III)-alkylamine complexes in their lowest doublet state. *J. Phys. Chem.* 85, 665–670.