Photocatalysis of Chloroform Decomposition by the Hexachlororuthenate (IV) Ion

Alissa M. Chan, Laura A. Peña, Rosa E. Segura, Ramya Auroprem, Brent M. Harvey, Caroline M. Brooke and Patrick E. Hoggard*

Department of Chemistry, Santa Clara University, Santa Clara, CA Received 8 August 2012, accepted 1 October 2012, DOI: 10.1111/php.12005

ABSTRACT

Dissolved hexachlororuthenate(IV) effectively catalyzes the photodecomposition of chloroform to hydrogen chloride and phosgene under near-UV ($\lambda > 345$ nm) irradiation, whereby RuCl_{6}^{2-} is not itself photocatalytically active, but is photochemically transformed into a species that is active, possibly RuCl₅(CHCl₃)⁻. Conversion to a photoactive species during irradiation is consistent with the acceleration of the decomposition rate during the early stages and with the apparent inverse dependence of the decomposition rate on the initial concentration of RuCl_6^{2-} . The displacement of Cl^- by CHCl_3 in the coordination sphere to create the photoactive species is consistent with the retardation of photodecomposition by both Cland H₂O. The much smaller photodecomposition rate in CDCl₃ suggests that C-H bond dissociation occurs during the primary photochemical event, which is also consistent with the presence of a CHCl₃ molecule in the first coordination sphere.

INTRODUCTION

Several chlorometallate complexes have been found to catalyze the photodecomposition of liquid chloroform (1-4), effectively raising the threshold wavelength for decomposition from ca 260 nm for neat chloroform, in some cases to well above 400 nm (5). Although the mechanism of catalysis appears to vary among the chlorometallate complexes, most of the mechanisms have in common the production of a radical, leading to the sequence of steps shown below.

$$R^{\bullet} + \mathrm{CHCl}_3 \to \mathrm{RH} + {}^{\bullet}\mathrm{CCl}_3 \tag{1}$$

$$^{\bullet}\mathrm{CCl}_3 + \mathrm{O}_2 \to \mathrm{CCl}_3\mathrm{OO}^{\bullet} \tag{2}$$

$$2\text{CCl}_3\text{OO}^\bullet \to 2\text{CCl}_3\text{O}^\bullet + \text{O}_2 \tag{3}$$

$$CCl_3O^{\bullet} + CHCl_3 \rightarrow CCl_3OH + {}^{\bullet}CCl_3$$
 (4)

$$CCl_3OH \rightarrow HCl + COCl_2$$
 (5)

Equations (2)–(4) constitute a radical chain, for which C_2Cl_6 can be expected to be the major termination product. This sequence differs from that accepted for the gas-phase decomposition (6-9), in which the trichloromethoxy radical is proposed to decompose to COCl₂ and Cl atoms (10), leaving the latter to abstract hydrogen from chloroform. The net reaction is the same in either case:

$$2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl \tag{6}$$

In condensed phase, hydrogen abstraction by the CCl₃O radical is presumed to be faster than unimolecular decomposition (11), leading to the formation of trichloromethanol, whose decomposition, Eq. (5), has a half-life of about 100 s in the gas phase (12).

The existence of trichloromethanol as an intermediate makes possible an additional side reaction leading to carbon tetrachloride:

$$\operatorname{CCl}_{3}\operatorname{OH} + 2\operatorname{HCl} \to \operatorname{CCl}_{4} + \{\operatorname{H}_{3}\operatorname{O}^{+}; \operatorname{Cl}^{-}\}$$
(7)

Recent theoretical calculations have predicted that CCl₃OH will decompose more rapidly in the presence of hydrogen halides (13). Reaction with a single HCl molecule to make CCl_4 and H_2O is not energetically favorable (14), but protonation of the water by a second HCl molecule greatly increases the driving force.

There are several ways the radical required for Eq. (1) can be generated with the help of a chlorometallate catalyst. One very direct way is by photodissociation of a chlorine atom, as is presumed to occur with FeCl_4^- (15,16):

$$\operatorname{FeCl}_{4}^{-} \xrightarrow{n_{V}} \operatorname{FeCl}_{3}^{-} + \operatorname{Cl}^{\bullet}$$
 (8)

To complete the cycle, the iron must be reoxidized, from which process more radicals may be generated. A second route to radicals is the photoreduction of the solvent, which is thought to occur with $OsCl_6^{2-}$ as the catalyst (3):

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

As a consequence of the generation of dichloromethyl radicals, termination products are expected to include C2H2Cl4 and C_2HCl_5 when this mechanism is operative.

Another route to chloroform decomposition can arise from the photooxidation of a counterion. This is more readily accomplished when the counterion is negatively charged; thus, chlorometallates would not normally be candidates for this mechanism. A complex that does appear to catalyze chloroform decomposition in this way is [Ru(bpy)₂Cl₂]⁺, which, when excited, apparently oxidizes Cl- to Cl• (17).

^{*}Corresponding author email: phoggard@scu.edu (Patrick E. Hoggard) © 2012 Wiley Periodicals, Inc. Photochemistry and Photobiology © 2012 The American Society of Photobiology 0031-8655/13

While these and other (1,4) mechanisms lead to photocatalyzed decomposition, the situation is often complicated by a transformation of the original chlorometallate complex to another species under irradiation (2-4,18), which can greatly obscure mechanistic conclusions.

In this study, we examine the photodecomposition of chloroform catalyzed homogeneously by the hexachlororuthenate(IV) ion, with a number of tests designed to unravel mechanistic details.

MATERIALS AND METHODS

Chloroform (J. T. Baker, ACS Grade) was washed seven times with an equal volume of water to remove the ethanol stabilizer, the absence of which was verified by GC-MS. Molecular sieves (5A; Sigma-Aldrich) were added to remove water.

Attempts to prepare a tetraalkylammonium hexachlororuthenate(IV) salt were unsuccessful because either no precipitate formed (*e.g.* with Bu_4N^+) or, when precipitation did occur (*e.g.* with Hx_4N^+), it had a waxy consistency that made isolation and purification impractical. Instead, the hexachlororuthenate(IV) ion was solubilized in chloroform by first mixing aqueous solutions of $(NH_4)_2RuCl_6$ and Bu_4NCl in an approximately 1:5 mole ratio, then extracting $(Bu_4N)_2RuCl_6$ into an equal volume of chloroform. The UV–Visible spectrum was not significantly different from that of $(NH_4)_2RuCl_6$ in water, and therefore extinction coefficients from aqueous solution were used to estimate concentrations in chloroform.

UV–Visible spectra were recorded with a Cary 50 spectrophotometer. GC-MS measurements were carried out with a Shimadzu QP-5000 instrument with an Agilent DB624 column (30 m, 0.32 mm × 1.8 μ m 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. For all quantitative measurements, 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 μ L of ethanol, containing xylene as an internal standard, was mixed with 500 μ L of the photolysate. The ethanol converted phosgene to ethyl chloroformate; thus, this compound was taken as the analytical standard for phosgene. Phosgene was readily identifiable in the gas chromatogram when no ethanol was added, and its complete disappearance and conversion to ethyl chloroformate was likewise readily observable. Analyses had to be undertaken within a few hours to avoid further condensation of ethyl chloroformate with ethanol to give diethyl carbonate.

Photodecomposition was generally carried out on 2.0 mL portions of chloroform containing a known concentration of $(Bu_4N)_2RuCl_6$ in a fused silica spectrophotometer cuvette with stirring. The cuvette was loosely capped, leaving approximately 2 mL of head space. Light from an Oriel Q Series housing with a 100-W mercury lamp was passed through a 345 nm highpass filter and focused on the sample. Balloons were sometimes used to control the composition of the atmosphere above the reaction. A fan was used to maintain the temperature in the cuvette at $22 \pm 2^{\circ}C$.

HCl production was measured by taking aliquots of the photolysate (between 20 and 100 μ L, after diluting with chloroform when necessary) and adding them to 3 mL portions of tetraphenylporphyrin (H₂TPP; Frontier Scientific) in CHCl₃. The absorbance change at 446 nm and extinction coefficients for H₂TPP and H₄TPP²⁺ (19,20) were used to determine the concentration of [H₄TPP²⁺] formed through the protonation of the remaining porphyrin nitrogens:

$$2\text{HCl} + \text{H}_2\text{TPP} \rightleftharpoons \{\text{H}_4\text{TPP}^{2+}; 2\text{Cl}^-\}$$
(10)

While the intermediate H_3TPP^+ species can be neglected (21), Eq. (10) is not completely stoichiometric at the typical concentrations of HCl and H_2TPP used, and an approximation to the true value can, in principle, be made by measuring the absorbance of a second solution with a smaller volume of the analyte solution (22). It was found, however, that the magnitude of the corrections made was smaller than the variability of repeated measurements. Therefore, corrections were not made and each analyte dilution was treated as an independent measurement. Because of this, the analyses for both HCl and COCl_2 (see below) can be assumed to underestimate the total amount actually produced. To this discrepancy may be added that from the evaporation of both substances from chloroform solutions.

Phosene was measured by taking advantage of its condensation with methanol, which was found to be complete within 2 min under the conditions employed:

$$\text{COCl}_2 + \text{MeOH} \rightarrow \text{ClCO(OMe)} + \text{HCl}$$
 (11)

After adding an aliquot of the photolysate to H_2TPP and measuring the absorbance change at 446 nm, a 50 μ L portion of MeOH was injected and, after 2 min, the absorbance was remeasured to find the amount of HCl formed by the condensation. This was done likewise with the second, smaller aliquot, and Eq. (11) was also applied to these data.

RESULTS AND DISCUSSION

Variation in product yield with time

Broadband irradiation ($\lambda > 345$ nm) of chloroform containing (Bu₄N)₂RuCl₆ caused chloroform decomposition, generating HCl and COCl₂, as can be seen in Fig. 1. Although a 1:1 ratio of these two products would be expected from Eq. (6), in fact considerably more phosgene was produced. An induction period is evident, after which the two products grow approximately linearly with time, COCl₂ about eight times as fast as HCl.

Chloroform photodecomposition was accompanied by significant spectral changes, as shown in Fig. 2. Over a period of 20–30 min, a substance with an intense UV absorption peak at 274 nm accumulated in solution. In relatively dilute solutions, this was accompanied by a general decrease in intensity in the visible spectrum; however, with more concentrated solutions



Figure 1. HCl and COCl₂ produced during the irradiation ($\lambda > 345$ nm) of a 2 × 10⁻⁴ M solution of (Bu₄N)₂RuCl₆ in CHCl₃. Solid lines are fits as described in text. The yield of COCl₂ at 36 min corresponds to approximately 60 equivalents, based on Ru.



Figure 2. Spectral changes at 3 min intervals during the irradiation $(\lambda > 345 \text{ nm})$ of $2 \times 10^{-4} \text{ M} (\text{Bu}_4\text{N})_2\text{RuCl}_6$ in CHCl₃.

 $({\sim}5\times10^{-4}{\rm M})$ approximate isosbestic points developed at about 380 and 480 nm, the absorbance decreasing between those two wavelengths.

The time scale for the spectral changes rather naturally gives rise to the supposition that they are related to the observed induction period for photodecomposition. In fact, a conceptually (although not mathematically) simple model can account quite well for the temporal development. Although the ruthenium speciation may be more complex, we assume for this purpose that a reactant A is photochemically converted to B, and that only B can catalyze the photodecomposition of chloroform. The rate of conversion of A to B is taken to be proportional to the fraction of light absorbed by A, f_A , whereas the rate of formation of HCl and COCl₂ are likewise taken to be proportional to the fraction of light absorbed by B, f_B . These fractions are given by (23)

$$f_{\rm A} = \left(1 - e^{-2.303(\varepsilon_{\rm A}[{\rm A}] + \varepsilon_{\rm B}[{\rm B}])}\right) \frac{\varepsilon_{\rm A}[{\rm A}]}{\varepsilon_{\rm A}[{\rm A}] + \varepsilon_{\rm B}[{\rm B}]}$$
(12)

$$f_{\rm B} = \left(1 - e^{-2.303(\varepsilon_{\rm A}[{\rm A}] + \varepsilon_{\rm B}[{\rm B}])}\right) \frac{\varepsilon_{\rm B}[{\rm B}]}{\varepsilon_{\rm A}[{\rm A}] + \varepsilon_{\rm B}[{\rm B}]}$$
(13)

Note that these equations are actually valid only for a specific wavelength. The true fractions of light absorbed would be a weighted average over all wavelengths. In Eqs. (12) and (13), ε_A and ε_B are the extinction coefficients at the hypothetical single wavelength. Given this fairly drastic simplification, the rate equations can then be written as follows:

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \alpha f_{\mathrm{A}} \tag{14}$$

$$\frac{\mathrm{d[HCl]}}{\mathrm{d}t} = \beta_{\mathrm{l}} f_{\mathrm{B}} \tag{15}$$

$$\frac{\mathrm{d}[\mathrm{COCl}_2]}{\mathrm{d}t} = \beta_2 f_\mathrm{B} \tag{16}$$

While none of these can be integrated in closed form, they are readily integrated numerically, by computing incremental concentration changes over small time intervals. The solid lines in Fig. 1 were obtained by this procedure, optimizing the fit to the experimental data. In general terms, the induction period arises when the inactive complex A is converted to the catalytically active B. whereby the extinction coefficient of A is considerably higher than that of B. This would mean that even after a relatively large fraction of A had been converted to B, A could still be absorbing more light than B, with the result that HCl and COCl₂ would still be forming at a relatively low rate. Only later, when there was very little A remaining, would B be absorbing more light than A. At this point, the rate of decomposition would be approaching a constant value. Given the decrease in solution absorbance during irradiation at wavelengths above 345 nm, this corresponds qualitatively to what was observed.

Control experiments

Irradiation under identical conditions of neat chloroform yielded no detectable quantity of HCl or $COCl_2$, nor were these products obtained from chloroform solutions of $(Bu_4N)_2RuCl_6$ kept in the dark for 6 h.

Variation in product yield with RuCl₆²⁻ concentration

The rate of chloroform photodecomposition varied considerably with the concentration of the RuCl_6^{2-} , in a manner that might at first seem peculiar. The yield of COCl_2 from several experiments in which only the concentration of RuCl_6^{2-} was changed are shown in Fig. 3. Notable is a steep decline in yield above a ruthenium concentration of about 1 x 10^{-5} M.

While this behavior appears to be that of an inhibitor rather than a catalyst, in fact it fits well with the hypothesis presented above. When the concentration of RuCl_6^{2-} (A) is high enough that most of the photons capable of causing conversion to the active ruthenium species (B) are absorbed, higher concentrations do not increase the rate of conversion substantially, but a smaller fraction of the absorbed photons go into the excitation of the active ruthenium species, thus slowing the photodecomposition. The solid line in Fig. 3 was achieved by a numerical fit of Eqs. (12) through (16) to the experimental data.

Effect of ethanol, cyclohexane and water on the rate of photodecomposition

No photodecomposition was observed in stabilized chloroform (~0.75% EtOH) in the presence of RuCl_6^{2-} . Likewise no decomposition took place when 10 μ L of cyclohexane was added to 2 mL of chloroform, nor when 0.5 μ L of water was added. Although ethanol (24) and cyclohexane (25) are frequently used as radical scavengers and can be expected to quench the photodecomposition through hydrogen abstraction, water would not be expected to react with any of the radicals in the schemes above. It may act through ligand substitution on the ruthenium (*vide infra*).



Figure 3. Phosgene concentration following 20 min broadband irradiation ($\lambda > 345$ nm) of chloroform, shown in relation to the concentration of RuCl₆^{2–}. Solid line is a numerical fit to Eqs. (12)–(16), with $\varepsilon_{\rm A} = 20\varepsilon_{\rm B}$ and $\beta = 100\alpha$.

Effect of added chloride ion

The addition of 5 mg of Bu_4NCl to 2 mL of chloroform reduced the rate of photodecomposition catalyzed by $RuCl_6^{2-}$ by approximately 90%, whereas photodecomposition was unmeasurable with 10 mg of Bu_4NCl . This suggests the suppression of an equilibrium, or pseudo-equilibrium, process, which we suggest may involve the coordination of a molecule of chloroform, the forward step being photochemical and the reverse step thermal.

$$\operatorname{RuCl}_{6}^{2-} + \operatorname{CHCl}_{3} \xrightarrow{h_{\nu}} \operatorname{RuCl}_{5}(\operatorname{CHCl}_{3})^{-} + \operatorname{Cl}^{-}$$
(17)

Chloroform is seldom considered as a potential ligand (4), but in fact there is NMR evidence of chloroform coordination in some systems (26). The replacement of a -2 ion by two -1 ions potentially adds to the driving force in a low polarity medium. Although RuCl₅(CHCl₃)⁻ may not be the photocatalytically active species, the presence of CHCl₃ in the inner sphere of the ruthenium(IV) does present possibilities beyond those available for outer sphere encounters.

If RuCl₅(CHCl₃)⁻ is the photoactive species, the induction period can be ascribed to the relatively slow approach to the photostationary state presupposed by Eq. (17). Moreover, the photostationary state can be expected to shift toward the right as HCl is generated, due to the favorable equilibrium in moderately polar solvents for the formation of HCl_2^- (18,27), removing chloride ion.

$$\mathrm{HCl} + \mathrm{Cl}^{-} \rightleftharpoons \mathrm{HCl}_{2}^{-}$$
 (18)

The equilibrium in Eq. (17) also presents a ready explanation for the quenching of the photodecomposition by water, as H₂O is a considerably stronger ligand than CHCl₃ and would readily displace chloroform from RuCl₅(CHCl₃)⁻.

Deuterated chloroform

Under otherwise identical conditions, $CDCl_3$ decomposed less than 5% as rapidly as $CHCl_3$. The most likely explanation lies in the anomalously large effect of deuteration on the C–H(D) bond energy, which is about 25 kJ mol⁻¹ greater in deuterated chloroform (28), with the implication that C–H bond breakage occurs as part of the primary photochemical process. Coordination of $CHCl_3$ to ruthenium presents more possibilities for the C–H bond to break, including stabilization of the hydrogen as a bound hydride.

Effect of O₂

Except at very low concentrations of O_2 , the yield of phosgene was, within experimental error, independent of the percentage of oxygen in contact with the solution, as can be seen in Fig. 4. This argues against a photodecomposition mechanism in which a radical is generated by the excited state ruthenium complex followed by the chain sequence described in Eqs. (1) through (5). This sequence, in combination with an appropriate termination step (*e.g.* the formation of C_2Cl_6 from the encounter of two CCl₃ radicals), yields a linear dependence on O_2 concentration.

A product yield that approaches an asymptotic maximum implies that an intermediate reacts with O_2 to yield products in competition with a nonproductive step, for example, deactivation of an excited state.

$$\operatorname{Ru} \xrightarrow{hv} \operatorname{Ru}^*$$
 (19)



Figure 4. Phosgene concentration in 2 mL of CHCl₃ with $\sim 2 \times 10^{-4}$ M RuCl₆^{2–} following 20 min broadband ($\lambda > 345$ nm) irradiation. Gas in contact with the solution was a mixture of Ar and air or air and O₂. Solid line is a fit of the experimental data to the expression $a[O_2]/(1 + b[O_2])$. Each point is an average of three separate measurements.

$$\operatorname{Ru}^* \xrightarrow{k_1} \operatorname{Ru}$$
 (20)

$$\operatorname{Ru}^* + \operatorname{O}_2 \xrightarrow{k_2} \operatorname{Products}$$
 (21)

Expressing the rate of Step (19) as $I_0 f/V$, where I_0 is the incident light intensity, f the fraction of light absorbed and V the sample volume, the steady-state rate of product formation becomes

$$\frac{d[Products]}{dt} = \frac{k_2 I_0 f[O_2]}{V(k_1 + k_2 [O_2])} = \frac{a[O_2]}{1 + b[O_2]}$$
(22)

This function was used to fit the data in Fig. 4.

Side Products

GC-MS analysis of photolysates revealed only CCl₄ and C₂Cl₆ as minor products, in approximately equal amounts. The failure to find any detectable amounts of $C_2H_2Cl_4$ or C_2HCl_5 rules out both the photoreduction of chloroform and energy transfer to chloroform followed by bond homolysis as primary photoprocesses, as both would yield CHCl₂ radicals.

The detection of C_2Cl_6 confirms the expected role of CCl_3 as chain carrier, whereas the presence of substantial amounts of CCl_4 requires a reaction other than the termination of Cl atoms with CCl_3 , which cannot be competitive with the self-termination of the chain carrier CCl_3 .

CONCLUSION

The mechanism by which RuCl_6^{2-} acts to catalyze the photodecomposition of chloroform must conform to the following observations:

- 1. The induction period before significant decomposition takes place.
- 2. The retardation of photodecomposition at higher concentrations of ${\rm RuCl_6}^{2-}$
- 3. The retardation of photodecomposition by added chloride ion.
- 4. The suppression of photodecomposition in CDCl₃.
- The formation of CCl₄ as a side product in amounts approximately equivalent to those of C₂Cl₆.
- The asymptotic increase in the decomposition rate with O₂ concentration.

The induction period, the inverse dependence on the ruthenium concentration in more concentrated solutions, and the retardation by Cl⁻ were proposed to result from the photochemical formation of a CHCl₃ complex together with a thermal backreaction as in Eq. (17). The rate of chloroform decomposition would then increase as the concentration of RuCl₅(CHCl₃)⁻, the photocatalytically active species, increases. The maximum concentration of this species, dictated by the photostationary state from Eq. (17), is predicted to increase as HCl is generated, removing chloride ion, whereas the maximum concentration would be reduced, as observed, by the addition of chloride.

The remainder of the observations are consistent with a mechanism involving hydride formation from the excited state ruthenium complex followed by the insertion of O_2 to form a ruthenium hydroperoxide.

$$\operatorname{RuCl}_{5}(\operatorname{CHCl}_{3})^{-} \xrightarrow{hv} \operatorname{RuCl}_{4}\operatorname{H}^{-} + \operatorname{CCl}_{4}$$
(23)

$$RuCl_4H^- + Cl^- \rightleftharpoons RuCl_5H^{2-}$$
(24)

$$RuCl_5H^{2-} + O_2 \rightarrow RuCl_5OOH^{2-}$$
(25)

Within this mechanism, the very slow reaction in deuterochloroform is consistent with C–H bond breakage in Eq. (23), requiring an additional 25 kJ mol⁻¹ with CDCl₃ (28), and also consistent with the accumulation of CCl₄, also by virtue of Eq. (23). The asymptotic dependence on the oxygen concentration will arise as long as $\text{RuCl}_5\text{H}^{2-}$ can return unproductively to the original ruthenium complex. This is shown in Eqs. (23) and (24) by reverse steps, but in fact the entire sequence could well occur in a more concerted fashion.

Ruthenium hydroperoxides have been postulated for a variety of catalytic sequences involving ruthenium complexes, including several involving coordinated chloride ions (29–31). Isotope labeling studies indicate that heavy metal hydroperoxides generally react by oxygen atom transfer (32), from which the following sequence of steps can be hypothesized.

$$RuCl_5OOH^{2-} + CHCl_3 \rightarrow RuCl_5OH^{2-} + CCl_3OH$$
 (26)

$$CCl_3OH \rightarrow HCl + COCl_2$$
 (27)

$$RuCl_5OH^{2-} + HCl \rightarrow RuCl_6^{2-} + H_2O$$
(28)

The stoichiometry of the catalyzed photodecomposition by this sequence of steps, standing in contrast with that predicted (and observed) for the decomposition mechanism postulated in the Introduction, Eq. (6), is as follows:

$$2CHCl_3 + O_2 \rightarrow CCl_4 + COCl_2 + H_2O \tag{29}$$

Experimentally, five to ten times more COCl_2 than HCl was observed, which is more consistent with this mechanism than with that of Eqs. (1)–(5), which predicts equimolar yields. In addition, water was often found to form as droplets on the cuvettes following long (>45 min) irradiation. As phosgene is slowly hydrolyzed by water (12,33), the ruthenium hydroperoxide mechanism could conceivably account for the HCl observed as well as COCl_2 . However, the presence of C_2Cl_6 among the side products is a clear indication that radical chemistry also takes place.

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