



Hexachlororhodate(III) and the photocatalytic decomposition of chloroform

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ABSTRACT

Broadband ($\lambda > 320$ nm) irradiation of solutions of $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ in CHCl_3 exposed to air causes chloroform decomposition, with the production of HCl and substances, including phosgene and peroxides, capable of oxidizing iodide ion, and lesser amounts of CCl_4 and C_2Cl_6 . There is a short induction period as RhCl_6^{3-} is replaced by an unknown rhodium species, the spectrum of which is stable after 15 or 20 min. The rate of photodecomposition is reduced by the addition of chloride ion, and it ceases nearly completely in deoxygenated solutions or in CDCl_3 . Mechanistic possibilities in keeping with these observations include hydrogen atom transfer from chloroform during the primary photochemical step and a prior equilibrium involving chloride ion dissociation. A rhodium hydroperoxide offers one possible explanation for the required participation of O_2 .

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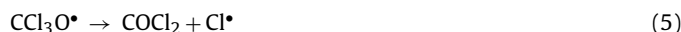
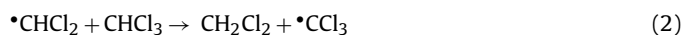
1. Introduction

Chloroform has been known to be light-sensitive for over a century, phosgene and hydrogen chloride being two of the products that have been used to gauge the extent of decomposition [1]. Its photosensitivity is such that commercial chloroform, even HPLC-grade, is very commonly supplied with up to 1% of a stabilizer to scavenge radicals produced by C–Cl bond homolysis. Because of its volatility and supposed sensitivity to sunlight, chloroform formed as a side product from water treatment is sometimes thought to present little problem for water reservoirs, in which a half-life of two days has been suggested [2]. Experimental results, however, indicate that the half-life of chloroform in natural waters is actually several months [3].

The reason for the persistence of chloroform, along with other chloroalkanes, is that its absorptivity within the solar spectrum is very small, in addition to which the rates of radical propagation reactions are greatly reduced in dilute aqueous solutions. Given that chloroform contamination of water supplies is a widespread problem [4,5], a means to accelerate its photodecomposition could be of considerable utility. In order to develop some insight into how photocatalysis might function, we have been examining chloroalkane decomposition in neat solvents in the presence of metal complexes, in particular chloro complexes [6–8].

When chloroform decomposes in the presence of air through absorption of UV light (generally <260 nm), a complex sequence of reactions leads eventually to CO_2 and HCl. The following steps, many of them suggested by experiments in the gas phase, may be

taken as a reasonable representation for this process.

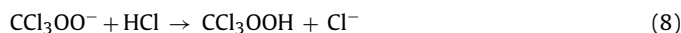


Bond homolysis yields chlorine atoms and dichloromethyl radicals, which abstract hydrogen from CHCl_3 to yield trichloromethyl radicals. These may self-terminate to form C_2Cl_6 , but in the presence of oxygen they readily form trichloromethylperoxy radicals [9–11]. $\text{CCl}_3\text{OO}^\bullet$ is a good one-electron oxidizing agent, particularly by electron transfer [12–19]. The concentration of peroxy radicals is limited by the self-reaction to form trichloromethoxy radicals [20], from which chlorine atoms rapidly dissociate [21], yielding phosgene. Given a source of hydrogen, $\text{CCl}_3\text{OO}^\bullet$ radicals also decompose to HCl and CO_2 by an incompletely characterized first-order mechanism [19]. Phosgene accumulates in irradiated chloroform [1], but in the presence of water, it slowly hydrolyzes [22,23].

Trichloromethylhydroperoxide is also known to accumulate in irradiated chloroform. Apparently this does not occur, as might be expected, through the abstraction of hydrogen by trichloromethylperoxy radicals, because the O–H bond energy in hydroperoxides, generally 370–380 kJ/mol [24], is less than the C–H bond energy in chloroform, 393 kJ/mol [25]. In the presence of an oxidizable substrate (S), CCl_3OOH can be expected to accumulate

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as a result of electron transfer.

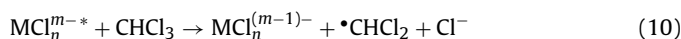


Trichloromethylhydroperoxide is itself a good oxidizing agent [16,26], generally reacting by breaking the O–O bond [27].

A chlorometallate complex might catalyze the photodecomposition, and spread the action spectrum toward or into the visible, by creating radicals that could initiate the formation of peroxy radicals. This could occur through homolytic photodissociation, photooxidation or photoreduction of the metal complex, or hydrogen atom transfer. Photodissociation yields chlorine atoms that can react as in Eq. (1).

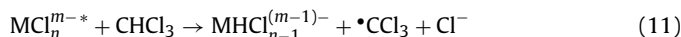


Photooxidation, with concomitant reduction of chloroform, has been implicated in some photocatalytic systems [28–30], and yields dichloromethyl radicals, beginning the sequence from Eq. (2).



Given that chloroform is not a good electron donor, photoreduction of a chlorometallate by electron transfer would normally require an additional substrate. Photodissociation may be thought of as a special case of photoreduction, with the role of substrate filled by a coordinated ligand.

Hydrogen atom transfer to metals that form metal–hydride bonds provides yet another means to generate radicals. The hydrogen may add to an unsaturated metal center or substitute for one of the coordinated ligands, as represented below.



In each case the resulting metal complex must return to its original form thermally (or, potentially, photochemically) in order to generate a sustainable cycle. Additional radicals may be generated in this process.

We have studied the ability of the hexachlororhodate(IV) ion to function as a photocatalyst for chloroform decomposition, with particular attention to the question of how the different pathways outlined above might be distinguished from each other experimentally.

2. Experimental

$(\text{Bu}_4\text{N})_3\text{RhCl}_6$ was prepared by dissolving K_3RhCl_6 (Sigma–Aldrich) and Bu_4NCl in water, mixing the two solutions, collecting the precipitate by filtration, and air-drying. Potassium chloride cocrystallized with $(\text{Bu}_4\text{N})_3\text{RhCl}_6$. Analysis. Calcd for $(\text{C}_{16}\text{H}_{36}\text{N})_3\text{RhCl}_6 \cdot 3\text{KCl}$: C, 45.51; H, 8.59; N, 3.32; Rh, 8.1; Cl, 25.2. Found: C, 44.93; H, 8.40; N, 3.38; Rh, 8.5, Cl, 25.3.

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 the cuvette 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. Deoxygenated samples were prepared by bubbling argon through the solution 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 Corp. XTI-5 column. The oven start temperature was 40 °C and a linear temperature gradient of 30 °C 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.

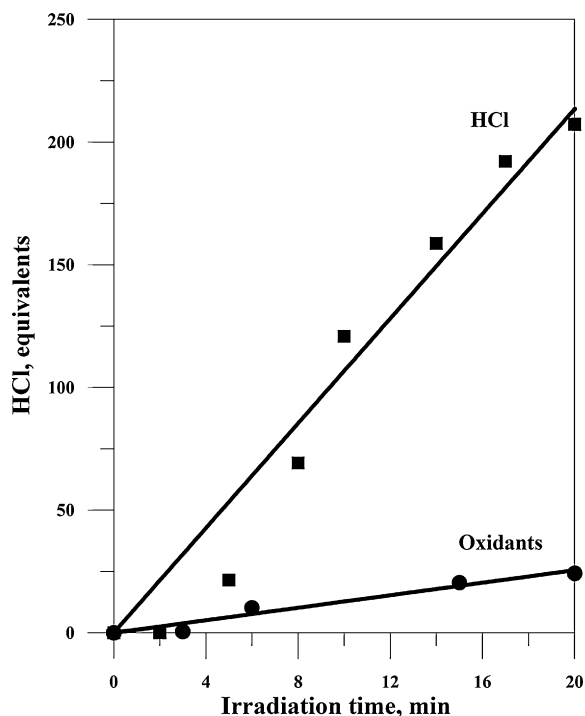


Fig. 1. Accumulation of HCl and oxidants (including CCl_3OOH and COCl_2) during the broadband ($\lambda > 320$ nm) irradiation of a 3.6×10^{-5} M solution of $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ in CHCl_3 exposed to air, in equivalents relative to $[\text{Rh}]$.

HCl production was measured by periodically removing 50 μL aliquots from the photolysate, and adding them 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 $\text{H}_4\text{TPP}^{2+}$ formed, by use of the extinction coefficients of the porphyrin species [31,32]. Protonation of H_2TPP yields $\text{H}_4\text{TPP}^{2+}$ in preference to H_3TPP^+ , even at low concentrations of acid [33].

The total oxidant concentration was determined by mixing 50 or 100 μL aliquots of the photolysate with 3.00 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 [34], correcting for the absorption from RhCl_6^{2-} . Iodide is oxidized by hydroperoxides with, experimentally, a 1:1 ratio of hydroperoxide reacted to triiodide ion formed [35]. Phosgene also produces triiodide in a 1:1 correspondence [36]. Another potential oxidant is Cl_2 ; however, GC–MS analysis showed the concentration of Cl_2 to be minor in comparison to the concentration of total oxidants.

The initial concentrations of $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ in chloroform solutions were calculated from absorption spectra, using the value of $3.27(\pm 0.06) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 269 nm, determined from a Beer's Law plot.

3. Results

Broadband irradiation ($\lambda > 320$ nm) of chloroform solutions containing $(\text{Bu}_4\text{N})_3\text{RhCl}_6$, at concentrations of 10–100 μM , exposed to air led to the continuous production of HCl and the accumulation of oxidant species, as shown in Fig. 1. Product formation was initially slow, but after several minutes it reached and maintained an approximately constant rate. In the absence of the hexachlororhodate, neither product was detectable under the same irradiation conditions.

During the photolysis the spectrum of the rhodium complex changed, the initial peak at 269 nm being replaced by a less intense peak at 321 nm with no isosbestic point, as can be seen in Fig. 2. In the visible, much less intense RhCl_6^{3-} peaks at 439 and 537 nm

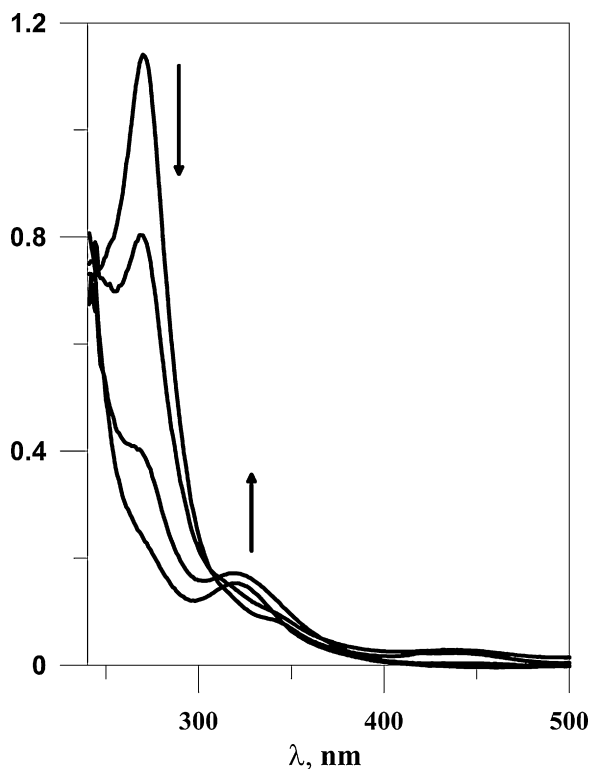


Fig. 2. Sequential spectra during the broadband irradiation of 3.3×10^{-5} M $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ in aerated chloroform (0, 6, 10, 15 min).

were replaced by a single peak at 512 nm. The conversion was gradual, requiring 15–20 min. Attempts to precipitate the rhodium species responsible for this spectrum by photolyzing solutions at higher concentrations and then reducing the solution volume were unsuccessful.

Deoxygenated solutions did not produce decomposition products, nor did the metal spectrum change.

In aerated solutions, besides HCl and oxidants (presumed to be phosgene and peroxides), the decomposition products included CCl_4 and C_2Cl_6 , which were readily detected by GC–MS, along with smaller amounts of $\text{C}_2\text{H}_2\text{Cl}_4$. A typical chromatogram is shown in Fig. 3.

Tetrabutylammonium chloride was added to some solutions to gauge the effect of chloride ion on the rate of the photoreaction. As can be seen in Fig. 4, Cl^- significantly retarded the reaction.

No decomposition products were observed when CDCl_3 was substituted for CHCl_3 and irradiation was carried out in aerated solutions under the same conditions.

Monochromatic irradiation of aerated $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ solutions in CHCl_3 at 313 nm was carried out in an attempt to relate the rate of the photochemical processes to the fraction of light absorbed by the rhodium complex. However, an unambiguous initial rate

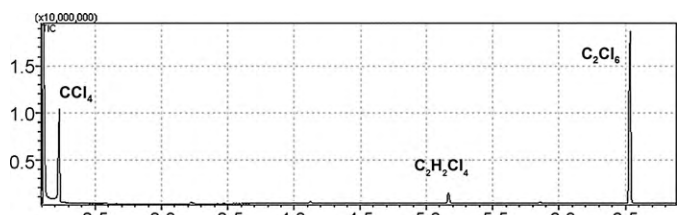


Fig. 3. GC–MS chromatogram of an aerated solution of $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ in chloroform following 20 min broadband irradiation.

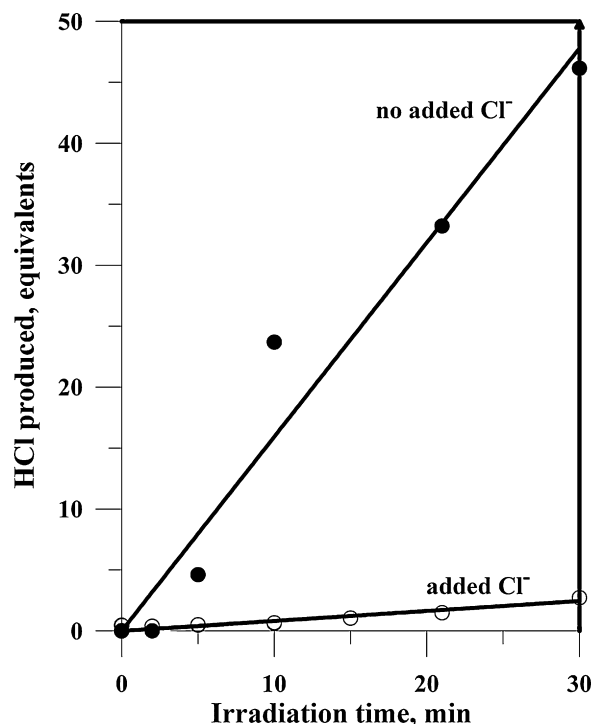


Fig. 4. Generation of HCl during the irradiation ($\lambda > 320$ nm) of a 7.3×10^{-5} M solution of $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ in CHCl_3 , with and without a tenfold excess of Bu_4NCl .

could not be determined, because of an induction period. Three such experiments are illustrated in Fig. 5.

The induction period was relatively insensitive to the concentration of RhCl_6^{3-} , while the subsequent rate of HCl formation appeared to be greater at lower rhodium concentrations within the range studied. On the other hand, under broadband irradiation the

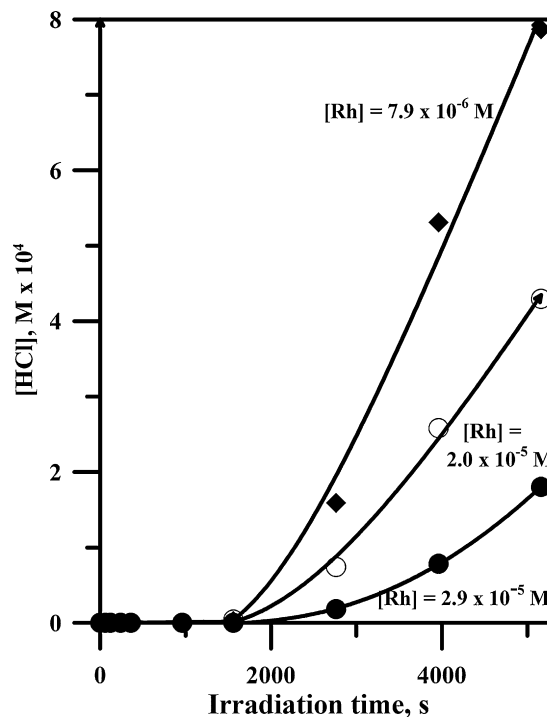


Fig. 5. Formation of HCl during the 313 nm irradiation of aerated solutions of $(\text{Bu}_4\text{N})_3\text{RhCl}_6$ in CHCl_3 . Data fitted to a double linear function, $y = e^{-ax}(bx + c)$; $R^2 > 0.995$ in each case.

HCl yield increased as the rhodium concentration was raised. It is impossible to calculate a quantum yield when the reaction rate is not directly proportional to the fraction of light absorbed, but as a point of comparison, the limiting slope of the curve for the solution shown in Fig. 5 in which $[\text{RhCl}_6^{3-}]$ is 7.9×10^{-6} M would correspond to an apparent quantum yield of 1.0 mol HCl produced per einstein absorbed. The apparent quantum yield at higher rhodium concentrations would, of course, be lower.

4. Discussion

The observations that must be accounted for in explaining the catalytic activity of RhCl_6^{3-} solutions in decomposing chloroform include

1. The induction period before a significant rate of decomposition set in.
2. The suppression of photodecomposition in CDCl_3 .
3. The retardation of photodecomposition by excess chloride ion.
4. The lack of any photodecomposition in the absence of oxygen.
5. The presence of CCl_4 among the most prevalent side products.
6. The apparent inverse relationship between $[\text{RhCl}_6^{3-}]$ and $d[\text{HCl}]/dt$ at concentrations near $100 \mu\text{M}$.

Since the induction period overlapped with spectral changes, it may be assumed that RhCl_6^{3-} is not itself the photocatalytically active species, or at least that its photocatalytic activity is much less than that of the species into which it is converted during photolysis. The complete loss of activity in deoxygenated solutions leads likewise to the conclusion that the active photocatalyst is an oxidized rhodium species.

One of the potential oxidized rhodium species is RhCl_6^{2-} . This complex has been reported several times in the literature [37–40], and there is even a reference to a commercial product [41], but Ellison and Gillard concluded that in each of these instances the complexes had been misidentified as hexachlororhodate(IV), being most probably a binuclear rhodium(III) complex bridged by a superoxo ligand [42]. Ellison and Gillard themselves did synthesize Cs_2RhCl_6 , but were unable to obtain a spectrum because of its instability in water [42].

4.1. Mechanistic implications

Of the potential pathways proposed in Section 1 by which a chlorometallate complex might catalyze the photodecomposition of chloroform, only one is consistent with the virtually complete cessation of the photoreaction in CDCl_3 , and that is hydrogen transfer from chloroform. Experimentally, the C–D bond in CDCl_3 has been found to be 25 kJ/mol stronger than the C–H bond in CHCl_3 [43]. From the very large isotope effect, one may infer that C–H bond breakage occurs during the primary photochemical step, so that deuteration renders this step unfeasible, or at least very slow. Considering that the rhodium species must be involved in a cycle, one might consider the alternative possibility that it is a thermal back-reaction that is hindered. However, since no spectral changes take place during the irradiation of RhCl_6^{3-} in CDCl_3 , it is reasonable to conclude that it is the primary photochemical process that is affected by deuteration.

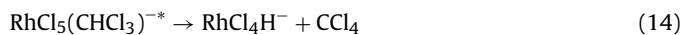
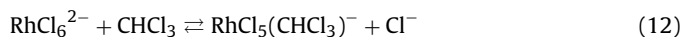
Alternative pathways can also be ruled out on other experimental grounds. For example, in the absence of oxygen, homolytic dissociation of a Rh–Cl bond would still lead to some HCl production, at least until the rhodium species had reacted stoichiometrically, contrary to observations. Electron transfer to chloroform by an excited state metal species would lead to a different distribution of haloalkane side products, since chloro-

form is reduced to chloride ion and dichloromethyl radicals. Experimentally, when chloroform reduction occurs as part of photodecomposition, chloroalkanes are typically found in the order $\text{C}_2\text{Cl}_6 > \text{CH}_2\text{Cl}_2 > \text{C}_2\text{HCl}_5 > \text{C}_2\text{H}_2\text{Cl}_4$ [29].

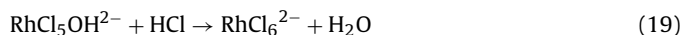
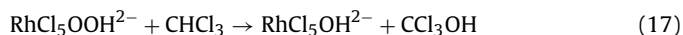
Yet another potential photocatalytic pathway is energy transfer to chloroform, which would be expected to lead to C–Cl bond homolysis, as observed in the classic study of benzene-catalyzed photodecomposition [44]. The subsequent accumulation of HCl would take place even in the absence of oxygen, again contrary to observations.

It is unlikely that C–H bond breakage occurs as a simple dissociation from the excited state complex, since the Rh–Cl and C–Cl bonds are weaker and would be considerably more likely to rupture under electronic excitation. Thus the carbon–hydrogen bond is likely to break as part of a concerted process with bond formation. The new bond could potentially be with rhodium, chlorine, or oxygen, and in Eq. (11) above, hydrogen atom transfer to form a metal hydride is illustrated. However, given that the Rh–H bond is considerably weaker than Cl–H or O–H [45], and also the observation that no reaction occurs in the absence of oxygen, we suggest that the hydrogen atom ends up on an oxygen, possibly by insertion of O_2 into a hydride intermediate, forming a rhodium hydroperoxide.

The retardation of the photodecomposition by chloride ion also suggests the existence of an equilibrium heterolytic dissociation process. Assuming for the moment that it is hexachlororhodate(IV), out of several possibilities, involved in this equilibrium and that chloride ion is replaced by chloroform, the equations below represent one way in which the mechanistic restrictions might be satisfied.



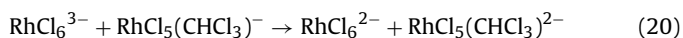
Although chloroform is generally considered too weak a ligand to compete for coordination sites, there is NMR evidence for the coordination of CHCl_3 to Co^{2+} and Ni^{2+} [46]. In Eq. (14) it is proposed that a coordinated chloride ion replaces hydrogen to create CCl_4 . Rhodium(III) hydroperoxides are known and isotope labelling studies show that they commonly react by oxygen atom transfer [47]. Oxygen atom transfer to chloroform would lead to the regeneration of the starting complex and the production of HCl through the eventual hydrolysis of phosgene.



The steps outlined would account for the catalytic production of HCl and CCl_4 , but not C_2Cl_6 , for which trichloromethyl radicals are required. These might be generated through a second reaction channel for the rhodium hydroperoxide, involving O–O bond homolysis to yield hydroxyl radicals, which in turn would generate CCl_3 radicals by hydrogen abstraction from chloroform or through a similar process involving CCl_3OOH , which is likely to be the major oxidizing species detected by iodide conversion to triiodide, or another peroxide species. Alternatively, the excited state complex could accept a hydrogen from CHCl_3 followed by dissociation of the CCl_3 radical without picking up a chlorine atom from the coordination sphere.

The experimental evidence does not justify further speculation, except on the question of the apparent inverse relationship

between the rhodium concentration and the photodecomposition yield. It should be noted that the retardation at higher concentrations applied only to the initial rate under monochromatic irradiation. Under those circumstances, most of the rhodium was still present as RhCl_6^{3-} . If this complex reacts with the subsequently formed photocatalytic rhodium species, or with one of the intermediate species, to deactivate it, an inverse relationship of the rate with the total rhodium concentration would be apparent over a certain concentration range. An example of such a reaction is the electron transfer process



4.2. The photocatalytic species

As is apparent from the foregoing discussion, we do not have enough information to identify the species that develops during the first 15–20 min of irradiation, with an invariant absorption spectrum thereafter. Possibilities include RhCl_6^{2-} , a hydroperoxide of either Rh(III) or Rh(IV), a peroxide or superoxide bridged species with Rh(III) or Rh(IV) centers, and others. We have illustrated potential mechanistic consequences as if RhCl_6^{2-} were the predominant species, but at this writing there is no authentic electronic spectral information with which to compare our own data. The existence of CCl_3 radicals during irradiation is shown by the formation of C_2Cl_6 as one termination product. Thus the reaction sequence shown in Eqs. (1)–(8) can be expected to occur, with the accumulation of some CCl_3OOH . This is a sufficiently good oxidizing agent that it seems reasonable to suspect that as its concentration builds up, all of the hexachlororhodate(III) would be oxidized, either to a rhodium(IV) species or to a hydroperoxide.

5. Conclusion

$(\text{Bu}_4\text{N})_3\text{RhCl}_6$ at concentrations of 10–100 μM catalyzes the photodecomposition of chloroform under broadband ($\lambda > 320 \text{ nm}$) irradiation. The photocatalysis is suppressed partially by adding chloride ion, and nearly completely by deoxygenation or the deuteration of the solvent. A mechanism in which hydrogen is transferred from chloroform to a rhodium species in the primary photochemical step appears to offer the best explanation for the results in CDCl_3 . A prior equilibrium involving replacement of a chloride ion by chloroform in the coordination sphere would be consonant with the added Cl^- data. The required O_2 presence might be explained by the generation of a hydroperoxide in conjunction with the hydrogen atom transfer step. This reasoning still leaves unexplained the nature of the photocatalytically active species, which supplants RhCl_6^{3-} after several minutes of irradiation.

Acknowledgements

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