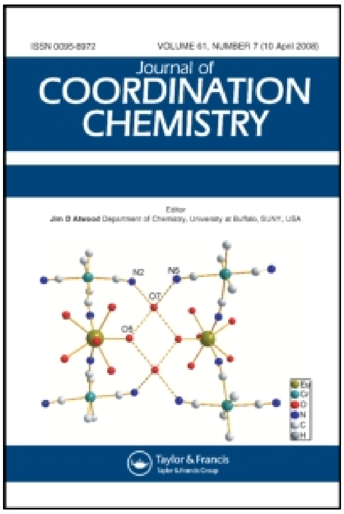

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Photocatalytic degradation of chloroform by *bis*(bipyridine)dichlororuthenium(III/II)

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Broadband ($\lambda > 320\,\mathrm{nm}$) irradiation of chloroform solutions of either [Ru(bpy)$_2$Cl$_2$] or [Ru(bpy)$_2$Cl$_2$]Cl exposed to air led to a photostationary state, in which [Ru(bpy)$_2$Cl$_2$]$^+$ predominated, and to the continuous decomposition of CHCl$_3$, as evidenced by the accumulation of HCl, hydroperoxides (CCl$_3$OOH and CHCl$_2$OOH), and tetra-, penta-, and hexachloroethane. The addition of Cl$^-$ increased the rate of photodecomposition, while the replacement of Cl$^-$ by F$^-$ greatly decreased the rate. The observations are consistent with a photocatalytic cycle in which [Ru(bpy)$_2$Cl$_2$]$^+$ is photochemically reduced to [Ru(bpy)$_2$Cl$_2$], which is thermally reoxidized by CCl$_3$OO or CCl$_3$OOH. In the absence of air a much slower photodecomposition reaction takes place leading to continuously increasing concentrations of chloroethanes. The data are consistent with a catalytic cycle in which [Ru(bpy)$_2$Cl$_2$]$^+$ is photoreduced, as in aerated solutions, while [Ru(bpy)$_2$Cl$_2$] is photooxidized with chloroform as the substrate.

Keywords: *Bis*(bipyridine)dichlororuthenium(II); *Bis*(bipyridine)dichlororuthenium(III); Photocatalyzed degradation; Chloroform; Photolysis

1. Introduction

Halomethanes, particularly trihalomethanes, are introduced into drinking water supplies by municipal disinfection [1, 2]. They have half-lives of months or years, even in bodies of water exposed to the sun [3], and pose significant environmental concerns [4, 5]. A heterogeneous catalyst that promoted the decomposition of trihalomethanes by sunlight could be useful in remediation, and this study was undertaken both to assess the potential of the [Ru(bpy)$_2$Cl$_2$]$^{+/0}$ couple as a photocatalyst and to attempt to understand how such a photocatalyst might function.

In chloroform, [Ru(bpy)$_2$Cl$_2$] can be converted to [Ru(bpy)$_2$Cl$_2$]$^+$ by irradiating solutions exposed to air at 254 nm [6]. The photooxidation occurs through absorption of light by CHCl$_3$, causing C–Cl bond homolysis, which leads to peroxy radicals and hydroperoxide by the following route.

$$\mathrm{Cl}\cdot + \mathrm{CHCl_3} \rightarrow \mathrm{HCl} + \cdot\mathrm{CCl_3} \tag{1}$$

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$$\cdot CHCl_2 + CHCl_3 \rightarrow CH_2Cl_2 + \cdot CCl_3 \tag{2}$$

$$\cdot CCl_3 + O_2 \rightarrow CCl_3OO\cdot \tag{3}$$

$$CCl_3OO\cdot + CHCl_3 \rightarrow CCl_3OOH + \cdot CCl_3 \tag{4}$$

The primary radicals are converted by energetically favorable hydrogen abstraction to trichloromethyl radicals, which react with oxygen to form trichloromethylperoxy radicals [7–9]. CCl_3OO is a good oxidizing agent [10–17], as is CCl_3OOH [17, 18].

On the other hand, deoxygenated solutions of $[Ru(bpy)_2Cl_2]Cl$ irradiated at 313 or 365 nm are reduced to $[Ru(bpy)_2Cl_2]$ through oxidation of chloride ion by excited state $[Ru(bpy)_2Cl_2]^+$ [6].

$$\left\{\left[Ru(bpy)_2Cl_2\right]^{+*}; Cl^-\right\} \rightarrow \left[Ru(bpy)_2Cl_2\right] + Cl\cdot \tag{5}$$

This raises the possibility that the chlorine atom produced during the photoreduction could generate a sufficient amount of CCl_3OOH through the sequence outlined in equations (1)–(4) that oxidation from $[Ru(bpy)_2Cl_2]$ to $[Ru(bpy)_2Cl_2]^+$ could take place without the direct photolysis of $CHCl_3$. Irradiation in the near-UV would then establish a cycle consisting of a photoreduction followed by thermal reoxidation, in the course of which chloroform would be decomposed without having to photolyze $CHCl_3$ directly. A potential difficulty is that the photoreduction of $[Ru(bpy)_2Cl_2]^+$ was only observed to occur in deoxygenated solutions, whereas O_2 is clearly required to build the hydroperoxide. This study was undertaken with the hypothesis that reduction of $[Ru(bpy)_2Cl_2]^+$ also takes place in solutions exposed to air, but with no net reduction. If this proved to be true, a photocatalytic cycle in which the solvent is degraded while the ruthenium complex cycles between Ru(II) and Ru(III) could, in principle, proceed indefinitely.

2. Experimental

2.1. *Materials*

$[Ru(bpy)_2Cl_2]$, tetrahexylammonium chloride, tetrabutylammonium iodide, and HPLC-grade $CHCl_3$ and CH_2Cl_2 were obtained from Aldrich, as were all chloroalkanes. For all photochemical experiments, ethanol was removed from the chloroform by washing four times with water and drying over molecular sieves. The absence of ethanol was verified by GC-MS. Dichloromethane was treated with 1 M H_2SO_4 in order to hydrate the alkene stabilizer, which otherwise reacts with HCl as it is produced by the photochemical reaction.

$[Ru(bpy)_2Cl_2]Cl$: A total of 0.3 g of $[Ru(bpy)_2Cl_2]$ was suspended in about 80 mL of CH_2Cl_2 and stirred. Chlorine gas (from MnO_2 and 6 M HCl) was bubbled into the purple solution, which turned yellow within a few seconds. Bubbling was discontinued, while the solution was stirred until all traces of solid $[Ru(bpy)_2Cl_2]$ were gone (less than a minute). The dichloromethane and residual Cl_2 were evaporated, leaving a dark red solid, which was washed with acetone and air-dried. Found: C, 42.8; H, 3.54;

N, 10.2; Cl, 19.8. Calcd for $[Ru(C_{10}H_8N_2)_2]Cl \cdot 2H_2O$: C, 43.2; H, 3.62; N, 10.1; Cl, 19.1. The fluoride salt was made by passing an aqueous solution of $[Ru(bpy)_2Cl_2]Cl$ through a Biorad AG 2-X8 anion exchange resin in the F^- form.

Solutions of $[Ru(bpy)_2Cl_2]Cl$ in chloroform were prepared by stirring for a minimum of 2 h, followed by syringe filtration to remove undissolved solids. $[Ru(bpy)_2Cl_2]F$ was somewhat more soluble, but solutions were prepared in the same manner.

2.2. *Photolysis and analytical methods*

Photolyses were performed on solutions in 1-cm rectangular fused silica cuvettes. Broadband irradiation was done with an Oriel 350 W or 100 W mercury lamp passed through a Schott long pass filter (generally a WG320, which can be characterized approximately as passing $\lambda > 320$ nm). Monochromatic irradiation was carried out with an Oriel 500W mercury/xenon lamp and a 25 cm monochromator. Intensities were measured with a Thermo Oriel Model 70260 radiant power meter. Absorption spectra were recorded on a Cary 50 spectrophotometer.

HCl in irradiated solutions was determined by adding an aliquot, usually 50 µL, to a 3.0 mL solution of tetraphenylporphyrin (H_2TPP) in $CHCl_3$. The equilibrium constant for the protonation of H_2TPP to H_4TPP^{2+} is very large [19], and it can be assumed that the reaction with HCl is complete as long as sufficient H_2TPP remains unprotonated. The H_4TPP^{2+} concentration was determined from the absorbance at 446 or 660 nm using literature values for the extinction coefficients in chloroform [20, 21].

Concentrations of $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 in irradiated solutions were determined from peak areas in GC-MS chromatograms using C_2Cl_4 as an internal standard (no C_2Cl_4 was observed in photolyzed solutions). The instrument was a Shimadzu QP-5000 with a Restek XTI-5 column. The oven start temperature was 40°C and a temperature gradient of $30\,\mathrm{min}^{-1}$ was applied. A split ratio of 1 : 1 was applied to the injection.

The concentration of Cl_2 was estimated by adding cyclohexene to an aliquot of the photolysate and measuring the amount of 1,2-dichlorocyclohexane by GC-MS against a C_2Cl_4 internal standard. Because Cl_2 at low concentrations gradually oxidizes $[Ru(bpy)_2Cl_2]$, when Cl_2 was detected the amount measured decreased with time, and reported concentrations should be considered to be minimum values.

The total peroxide concentration was determined by mixing 1.00 mL of a photolysate with 2.00 mL of approximately 0.01 M Bu_4NI in $CHCl_3$ and determining the resulting I_3^- concentration from the extinction coefficient (2.50×10^4) at 365 nm [22] using the experimental 1 : 1 stoichiometric ratio of hydroperoxide to I_3^- [23]. Iodide ion reduces $[Ru(bpy)_2Cl_2]^+$ to $[Ru(bpy)_2Cl_2]$; therefore, the absorption at 365 nm had to be corrected for the $[Ru(bpy)_2Cl_2]$ present and the measured $[I_3^-]$ had to be corrected for the amount of ruthenium reduced in order to derive a valid hydroperoxide concentration. While the peroxide was rapidly reduced, complete reduction of $[Ru(bpy)_2Cl_2]^+$ required several minutes; thus, the tri-iodide concentration was measured 10 min after mixing.

Extinction coefficients for $[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_2Cl_2]^+$ were determined from 250 to 600 nm in order to calculate concentrations in solutions. Those for $[Ru(bpy)_2Cl_2]$ in $CHCl_3$ were obtained by recording spectra for solutions of known concentration

Table 1. Extinction coefficients of $[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_2Cl_2]^+$ peaks.

Species	λ_{max} (nm)	ε ($M^{-1}\,cm^{-1}$) $[Ru(bpy)_2Cl_2]$	ε ($M^{-1}\,cm^{-1}$) $[Ru(bpy)_2Cl_2]^+$
$[Ru(bpy)_2Cl_2]$	379	$8.32\ (\pm 0.20) \times 10^3$	$5.53\ (\pm 0.13) \times 10^3$
	557	$8.16\ (\pm 0.18) \times 10^3$	$0.02\ (\pm 0.02) \times 10^3$
$[Ru(bpy)_2Cl_2]^+$	384	$8.23\ (\pm 0.20) \times 10^3$	$5.72\ (\pm 0.13) \times 10^3$

Table 2. Products from the irradiation ($\lambda > 320$ nm) of a 3×10^{-5} M deoxygenated solution of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$.

Irradiation time (min)	$[C_2H_2Cl_4]$ equiv	$[C_2HCl_5]$ equiv	$[C_2Cl_6]$ equiv	[HCl] equiv
10	0.16	0.14	0.23	1.12
20	0.08	0.38	0.45	1.15

Note: Concentrations relative to [Ru].

and computing the slope (absorbance *vs*. concentration) at each wavelength. Because of the difficulty in dissolving $[Ru(bpy)_2Cl_2]Cl$ in chloroform, and the resulting uncertainties in concentration, $[Ru(bpy)_2Cl_2]$ solutions of known concentration were converted to $[Ru(bpy)_2Cl_2]^+$ and Cl^- by photolysis in order to determine extinction coefficients. Values of ε at the absorbance maxima for $[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_2Cl_2]^+$ are listed in table 1.

3. Results

3.1. $[Ru(bpy)_2Cl_2]^+$ *in deoxygenated chloroform*

Irradiation ($\lambda > 320$ nm) of deoxygenated solutions of $[Ru(bpy)_2Cl_2]Cl$ in chloroform led to complete reduction to $[Ru(bpy)_2Cl_2]$ within 20 min (approximately 50% reduction after 4 min) and the formation of approximately one equivalent of HCl along with, initially, approximately half an equivalent of $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 taken together (table 2). After complete conversion to $[Ru(bpy)_2Cl_2]^+$, the HCl concentration did not increase significantly, while the concentration of the radical termination products crept higher. No Cl_2 was detected. No tri-iodide was formed after adding Bu_4NI to the photolysate, confirming the absence of peroxide or Cl_2 in the samples. Irradiation of neat, deoxygenated chloroform under the same conditions yielded no detectable HCl or chloroethanes. Neither were decomposition products observed from neat, deoxygenated chloroform when a 285 nm cutoff filter was substituted for the 320 nm filter used in most experiments. The product distribution may be compared with that observed following 15 min irradiation of neat, deoxygenated $CHCl_3$ with an unfiltered 100-W mercury lamp: approximately 10 times the yield of HCl and chloroethanes as that reported in table 2, with a very similar distribution of chloroethane products.

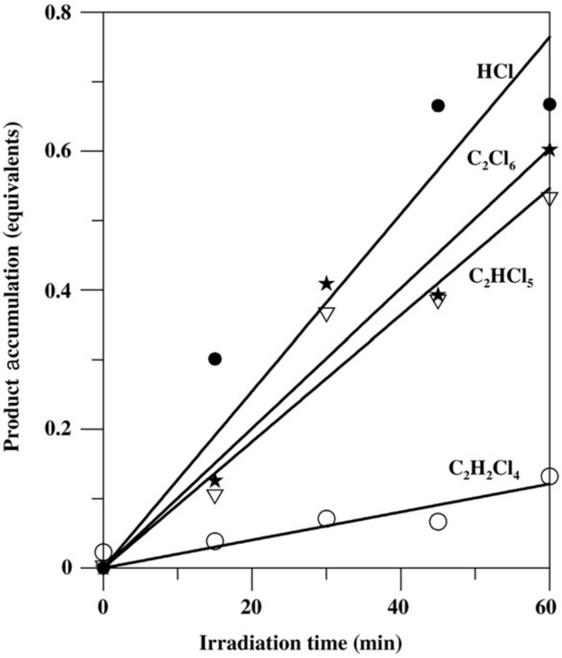

Figure 1. Production of HCl, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 from the irradiation ($\lambda > 320$ nm) of deoxygenated solutions, approximately 8×10^{-5} M, of $[Ru(bpy)_2Cl_2]$ in $CHCl_3$.

When a solution of $[Ru(bpy)_2Cl_2]F$ in $CHCl_3$ was irradiated ($\lambda > 320$ nm) for 30 min, reduction to $[Ru(bpy)_2Cl_2]$ took place at a rate about 10% of that exhibited by $[Ru(bpy)_2Cl_2]Cl$. Some HCl was formed, as evidenced by the conversion of cyclohexene to chlorocyclohexane as well as the protonation of H_2TPP, in approximate proportion to the extent of reduction of the Ru(III).

3.2. *[Ru(bpy)$_2$Cl$_2$] in deoxygenated chloroform*

Irradiation ($\lambda > 320$ nm) of deoxygenated solutions of $[Ru(bpy)_2Cl_2]$ in chloroform for one hour caused no change to the absorption spectrum of the irradiated solution. Nevertheless, a steady increase in chloroethane products (figure 1) was observed, pointing to the generation of $\cdot CHCl_2$ and CCl_3 radicals. HCl was also formed, while no Cl_2 was detected in any of the samples. The peroxide tests were negative, confirming the displacement of O_2 from all samples.

No HCl was formed upon irradiation under the same conditions in the absence of $[Ru(bpy)_2Cl_2]$.

3.3. *[Ru(bpy)$_2$Cl$_2$] in chloroform solutions exposed to air*

Irradiation ($\lambda > 320$ nm) of solutions of $[Ru(bpy)_2Cl_2]$ in chloroform exposed to air led to the oxidation of $[Ru(bpy)_2Cl_2]$ in less than 2 min. $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 were generated, along with HCl and peroxide, and concentrations continued to increase after conversion to Ru(III), as shown in figure 2. In the absence of

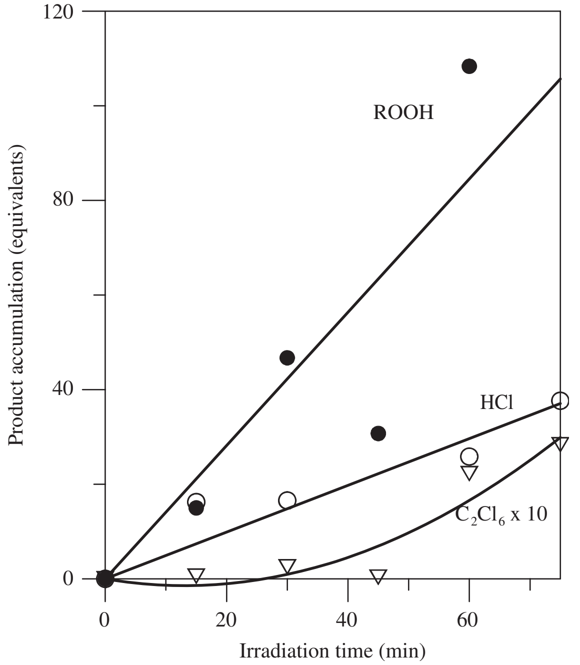

Figure 2. Production of peroxide (ROOH), HCl, and C_2Cl_6 during irradiation ($\lambda > 320$ nm) of an approximately 1×10^{-4} M solution of $[Ru(bpy)_2Cl_2]$ in $CHCl_3$, exposed to air, relative to total Ru. Arbitrarily, ROOH and HCl fit with straight lines and C_2Cl_6 with a quadratic.

$[Ru(bpy)_2Cl_2]$ no decomposition products were detected. When irradiated for 15 min with an unfiltered 100-W mercury lamp, neat, aerated chloroform yielded HCl at a rate similar to that shown in figure 2, with other products in the following ratios to HCl: C_2HCl_5 (0.04), C_2Cl_6 (0.1), and ROOH (0.4).

Experiments were undertaken to determine the dependence of the rate of HCl production under 313 nm irradiation on the fraction of light absorbed by $[Ru(bpy)_2Cl_2]$, f_R. Irradiation of aerated $[Ru(bpy)_2Cl_2]$ solutions in $CHCl_3$ caused an approximately linear increase in HCl concentration over an hour. A threefold increase in f_R was accompanied by a *decrease* in the rate by 20%. The situation is complicated by the almost complete conversion of Ru(II) to Ru(III) during irradiation. Furthermore, after photooxidation to $[Ru(bpy)_2Cl_2]^+$ in more concentrated solutions, the solution absorbance at 313 nm was much higher than expected from conversion to Ru(III) as a result of a strong tail from deeper in the UV, possibly from highly chlorinated alkanes.

Because the rate of HCl production under 313 nm irradiation, at least initially, was not proportional to the fraction of light absorbed by the Ru(II) and Ru(III) species, the quantum yield is undefined. Nevertheless, in order to compare $[Ru(bpy)_2Cl_2]^{+/0}$ with other potential photocatalysts, for the specific concentration 6×10^{-5} M $[Ru(bpy)_2Cl_2]$, the rate of HCl production corresponded to an apparent quantum yield of approximately 0.01 mol/einstein.

Approximately 50 mL of 5×10^{-5} M $[Ru(bpy)_2Cl_2]$ was put into a stoppered flask and exposed to sunlight. After 1 day the solution had turned yellow, due to complete oxidation to $[Ru(bpy)_2Cl_2]^+$. After 1 week, five equivalents of HCl were produced.

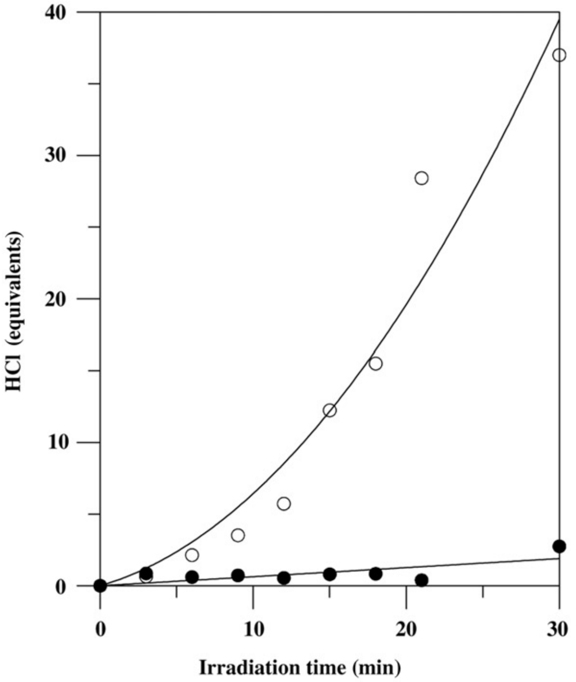

Figure 3. Production of HCl in irradiated ($\lambda > 320\,\text{nm}$) 3×10^{-5} M solutions of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$ with (open circles) and without (closed circles) 0.006 M Cl^-. The added chloride data were arbitrarily fit to a quadratic.

3.4. *$[Ru(bpy)_2Cl_2]^+$ in chloroform solutions exposed to air*

No net reduction of $[Ru(bpy)_2Cl_2]^+$ occurred upon irradiation ($\lambda > 320\,\text{nm}$) of chloroform solutions of $[Ru(bpy)_2Cl_2]Cl$ exposed to air for periods up to 30 min. Peroxide and HCl were formed continuously and in approximately the same quantities as in the $[Ru(bpy)_2Cl_2]$ photolysis. In stark contrast, however, no $C_2H_2Cl_4$, C_2HCl_5, or C_2Cl_6 was detected in any samples. On the other hand, Cl_2 occurred in all irradiated samples, as much as 1.5 equivalents after 30 min of exposure.

The addition of chloride ion in the form of tetrahexylammonium chloride had a marked effect on the rate of HCl formation. Figure 3 shows an initial fourfold increase in the rate from a 200-fold excess of chloride ion, but this accelerated to a factor of 20 after 30 min irradiation.

The rate of formation of peroxide was influenced by HCl concentration. When anhydrous HCl was bubbled into a solution of $[Ru(bpy)_2Cl_2]$ in $CHCl_3$, the yield of peroxide after 5 min irradiation was greater by a factor of three than the yield with no HCl added.

3.5. *$[Ru(bpy)_2Cl_2]$ in dichloromethane*

The rate of HCl formation was compared in $CHCl_3$ and CH_2Cl_2 solutions of $[Ru(bpy)_2Cl_2]$ having the same concentration and exposed to air. At each concentration tested, HCl was produced approximately 2.5 times faster in chloroform.

4. Discussion

4.1. *Chloroform decomposition in the absence of oxygen*

In earlier work we observed photoreduction of $[Ru(bpy)_2Cl_2]^+$ to $[Ru(bpy)_2Cl_2]$ from near-UV irradiation in deoxygenated chloroform [6], and suggested that this occurred through the oxidation of ion-paired chloride ions to chlorine atoms by excited state $[Ru(bpy)_2Cl_2]^+$ as in equation (5) [6].

This hypothesis is supported by analysis of the products formed in the course of the photoreduction. Hydrogen abstraction from chloroform by the photogenerated chlorine atoms would be expected to generate one equivalent of HCl, and this is essentially what was observed. Self-termination of the CCl_3 radicals left after hydrogen abstraction should yield 0.5 equivalents of C_2Cl_6. Only half that was observed, although C_2HCl_5 and $C_2H_2Cl_4$ were also formed, the total amounting to approximately half an equivalent. These products appear to be associated with the photolysis of $[Ru(bpy)_2Cl_2]$ (*vide infra*).

Further confirmation that chloride ion acts as the reducing agent comes from the substitution of F^- for Cl^-, which reduced the photoreduction rate by 90%, as well as the rate of formation of HCl and chloroalkanes. It should be noted that some chloride ion will still be present in chloroform solutions because of halogen exchange between F^- and $CHCl_3$ [24]. Given the expectation that $[Ru(bpy)_2Cl_2]^+$ must be ion-paired with Cl^- in order to oxidize it, the excess of F^- greatly reduces the fraction of $[Ru(bpy)_2Cl_2]^+$ ion-paired with Cl^-, which is consonant with the observed decrease in rates.

Because the known route for the photooxidation of $[Ru(bpy)_2Cl_2]$ to $[Ru(bpy)_2Cl_2]^+$ is a solvent-initiated process requiring oxygen, to which excited state $[Ru(bpy)_2Cl_2]$ does not contribute [6], we did not expect to see any chloroform decomposition upon irradiation of the Ru(II) species at wavelengths above 320 nm, to which $CHCl_3$ is essentially transparent. Nevertheless, decomposition did take place at a slow rate. Our conclusion is that excited state $[Ru(bpy)_2Cl_2]$ can reduce chloroform to yield $[Ru(bpy)_2Cl_2]^+$, but so slowly as to be insignificant when aerated solutions are irradiated at wavelengths that can excite chloroform.

$$\left[Ru(bpy)_2Cl_2\right]^* + CHCl_3 \rightarrow \left[Ru(bpy)_2Cl_2\right]^+ + \cdot CHCl_2 + Cl^- \qquad (6)$$

The quantum yield for photoxidation of $[Ru(bpy)_2Cl_2]$ by this route would have to be much smaller than that for photoreduction of $[Ru(bpy)_2Cl_2]^+$ in order for the photostationary state to have so little of the Ru(III) complex as to be unobservable.

Dichloromethyl radicals can abstract hydrogen from chloroform because of the weaker C–H bond in $CHCl_3$ than in CH_2Cl_2 [25, 26], and rapid hydrogen abstraction would convert all $CHCl_2$ radicals to CCl_3. However, the observation of $C_2H_2Cl_4$ and, especially, C_2HCl_5 in amounts similar to those of C_2Cl_6 indicates that for the $CHCl_2$ radicals produced through reaction (6), termination is competitive with hydrogen abstraction from chloroform.

4.2. *Chloroform decomposition in the presence of oxygen*

The catalytic generation of HCl, peroxide, and chloroalkanes upon exposure of chloroform solutions of either $[Ru(bpy)_2Cl_2]$ or $[Ru(bpy)_2Cl_2]^+$ to broadband excitation is consistent with the hypothesized cycle in which $[Ru(bpy)_2Cl_2]^+$ is reduced photochemically as in reaction (5) while $[Ru(bpy)_2Cl_2]$ is oxidized thermally by either CCl_3OO radicals or CCl_3OOH, created in a chain process by reactions (1)–(4), initiated by chlorine radicals from reaction (5). We have proposed that oxidation by trichloromethyl radicals proceeds by electron transfer [6],

$$CCl_3OO + [Ru(bpy)_2Cl_2] \rightarrow CCl_3OO^- + [Ru(bpy)_2Cl_2]^+ \tag{7}$$

while oxidation by trichloromethylhydroperoxide normally proceeds with O–O bond breaking [27].

$$CCl_3OOH + [Ru(bpy)_2Cl_2] \rightarrow \left\{[Ru(bpy)_2Cl_2]^+; OH^-\right\} + CCl_3O\cdot \tag{8}$$

$$\left\{[Ru(bpy)_2Cl_2]^+; OH^-\right\} + HCl \rightarrow \left\{[Ru(bpy)_2Cl_2]^+; Cl^-\right\} + H_2O \tag{9}$$

Beginning with either $[Ru(bpy)_2Cl_2]$ or $[Ru(bpy)_2Cl_2]Cl$ in chloroform, after irradiating for a few minutes, a photostationary state was reached that consisted almost entirely of $[Ru(bpy)_2Cl_2]^+$. It was easier to start with $[Ru(bpy)_2Cl_2]$ because of its relatively high solubility in $CHCl_3$. The predominance of Ru(III) in the photostationary state can be attributed to a buildup of CCl_3OOH, so that $[Ru(bpy)_2Cl_2]$ produced by photoreduction is reoxidized very soon after its formation.

Based on the dependence of the rate of photoreduction of $[Ru(bpy)_2Cl_2]^+$ in deoxygenated solutions on the chloride ion concentration, the ion-pair formation constant for $\{[Ru(bpy)_2Cl_2]^+; Cl^-\}$ in $CHCl_3$ has been determined to be 3×10^3 [6], from which it can be calculated that a 3×10^{-5} M solution of $[Ru(bpy)_2Cl_2]Cl$ should be approximately 8% ion-paired. This is quite consistent with the observed increase in the rate of HCl formation with added chloride seen in figure 3.

The increase in the rate of peroxide formation upon addition of anhydrous HCl is probably related to the formation of HCl_2^-.

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

Hydrogen dichloride anions occur in the solid state [28], and in nitromethane; the equilibrium constant for HCl_2^- formation has been suggested to be large enough that association is practically stoichiometric [29]. On the other hand, NMR measurements were used to estimate a value of 600 for the formation constant for HCl_2^- in tetrachloroethane [30], which at an HCl concentration of 10^{-3} M would mean that about half of the chloride ions were converted to HCl_2^-. In any case, the net result of adding HCl is to replace Cl^- by HCl_2^- and to replace $\{[Ru(bpy)_2Cl_2]^+; Cl^-\}$ ion pairs by $\{[Ru(bpy)_2Cl_2]^+; HCl_2^-\}$. The photodecomposition rate would be affected by either a change in the ion-pair formation constant with HCl_2^- or the ease of oxidation of HCl_2^- compared to Cl^-.

At first glance, it may seem strange that no chloroethane products were detected when aerated solutions of $[Ru(bpy)_2Cl_2]Cl$ were irradiated, while irradiation of aerated $[Ru(bpy)_2Cl_2]$ solutions produced tetra-, penta-, and especially hexachloroethane. This can be ascribed to the lower concentrations of $[Ru(bpy)_2Cl_2]^+$ used, due to the low solubility of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$. The absence of chloroethanes in this case implies that competition between the self- and cross-termination of $CHCl_2$ and CCl_3 radicals and the addition of oxygen to form peroxy radicals, reaction (3), favors the latter process given sufficient O_2. Low concentrations of $[Ru(bpy)_2Cl_2]^+$ do not significantly deplete the dissolved oxygen. By contrast, the generally more concentrated solutions of $[Ru(bpy)_2Cl_2]$ employed by us produced only small concentrations of chloroethanes at first, possibly due to the photooxidation of $[Ru(bpy)_2Cl_2]$, as observed in deoxygenated solutions. The significantly higher concentrations of C_2Cl_6 observed after 45–60 min of broadband irradiation may result from a decrease in the O_2 concentration with irradiation time.

4.3. *Catalysis of dichloromethane photodecomposition*

The significantly slower rate of photocatalyzed decomposition in CH_2Cl_2 solutions containing $[Ru(bpy)_2Cl_2]$ and exposed to broadband ($\lambda > 320\,nm$) irradiation, compared to $CHCl_3$, was not investigated further, but is probably ascribable to a smaller ion-pair formation constant for $\{[Ru(bpy)_2Cl_2]^+; Cl^-\}$ in the more polar dichloromethane.

5. Conclusions

In aerated solutions, the data are consistent with the proposed cycle involving photochemical reduction of $[Ru(bpy)_2Cl_2]^+$ and thermal reoxidation, reactions (5), (7), and (8). Because photoreduction appears to take place only through oxidation of Cl^- within ion pairs, increasing the chloride ion concentration increases the rate of photodecomposition, while replacing Cl^- by F^- reduces the photodecomposition rate correspondingly. In deoxygenated solutions, hydroperoxides and peroxy radicals are unavailable to oxidize $[Ru(bpy)_2Cl_2]$, but a much slower photooxidation takes place, with reduction of chloroform.

The low solubility of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$, while a hindrance to the study of its homogeneous photocatalysis, may actually be useful when we proceed towards heterogenization.

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