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Kinetics and Mechanism of the Photooxidation of Bis(bipyridine)dichlororuthenium(II) and the Photoreduction of Bis(bipyridine)dichlororuthenium(III) in Chloroform

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In air-saturated $CHCl_3$ irradiation of $[Ru(bpy)_2Cl_2]^{0/+}$ (bpy = 2,2′-bipyridine) with the full UV output of a 200-W mercury lamp converted the Ru(II) complex completely to Ru(III) at or below 58 °C, and converted the Ru(III) complex completely to Ru(II) at or above 60 °C. No thermal reaction occurred in either direction. The photooxidation takes place through a radical chain mechanism initiated by absorption of light by chloroform followed by C−Cl bond homolysis. This leads to the formation of trichloromethylperoxy radicals, each of which can cause the oxidation of two molecules of $[Ru(bpy)_2Cl_2]$. The mechanism proposed is consistent with the experimental rate law, $d[Ru(III)]/dt = a\{fI_0[Ru(II)]\}^{1/2}$. The photoreduction in deoxygenated solution takes place through direct excitation of $[Ru(bpy)_2Cl_2]^+$, which then oxidizes Cl^- to Cl atoms. Because of its short lifetime, only the Ru(III) complexes that are ion-paired with chloride ion can react.

Introduction

In an earlier report[1] we noted that, when irradiated with broad band UV/visible light, unstirred solutions of $[Ru(bpy)_2(N_3)_2]$ in $CHCl_3$ were converted to $[Ru(bpy)_2Cl_2]$ and then oscillated once or twice between $[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_2Cl_2]^+$, each change being complete. Subsequently, we presented evidence that the initial conversion of the diazido- to the dichlororuthenium(II) species was initiated through homolysis of a C−Cl bond in $CHCl_3$ by UV light, followed by conversion of the initial radicals formed to $^{\bullet}CCl_3$. The trichloromethyl radical then attacks the diazido complex to convert it to $[Ru(bpy)_2Cl_2]$ in two separate stages, each first order in the Ru(II) complex.[2] That neither $[Ru(bpy)_2(N_3)_2]$ nor $[Ru(bpy)_2(N_3)Cl]$ were photoactive in this reaction may seem suspect, in light of the voluminous literature on Ru(II) photochemistry.[3,4] Yet the rate of reaction was inversely correlated with the $[Ru(bpy)_2(N_3)_2]$ absorption spectrum, while the quantum yield based on chloroform absorption was virtually the same at two different wavelengths, and the reaction did not occur at all with visible light.

In this paper we examine the kinetics of the photochemical oxidation of $[Ru(bpy)_2Cl_2]$ to $[Ru(bpy)_2Cl_2]^+$ and the photochemical reduction of $[Ru(bpy)_2Cl_2]^+$ to $[Ru(bpy)_2Cl_2]$. We also explore the reasons for the rudimentary photooscillatory behavior previously observed.

Experimental Section

Materials. Spectrophotometric grade chloroform was obtained from Aldrich. The absorption spectrum was measured with water as a blank. The absorbance above 350 nm was less than 0.003, and between 310 and 330 nm it was approximately 0.008. For some experiments it was purified according to the method of Morgan and Lowry,[5] by first washing it several times with concentrated sulfuric acid, then with dilute sodium hydroxide, and finally with ice water. It was dried over potassium carbonate, stored in a completely filled brown bottle, and distilled shortly before use.

cis-Dichlorobis(2,2′-bipyridine)ruthenium(II) hydrate was also obtained from Aldrich and was used without further purification. No impurities were found when a chloroform solution was passed through a $CHCl_3$-equilibrated Sephadex LH-20 column. $[Ru(bpy)_2Cl_2]Cl{\cdot}2H_2O$ was prepared by the method of Bottomley and Mukaida.[6]

Physical Measurements. UV−visible absorption spectra were recorded with a Hewlett-Packard Model 8451A diode array spectrophotometer. The spectrum of chloroform was measured against water, and the ruthenium solution spectra were measured against chloroform. Infrared spectra of solutions (in a KBr cell) and solids (in KBr disks) were measured with a Mattson Galaxy Model 2020 FT-IR spectrometer.

The mass spectra were measured on a Hewlett-Packard Model 5890 Series II gas chromatograph, equipped with a flame ionization detector and a capillary column. The resolution of the peaks by the mass spectrometer was 0.5 amu (fwhm). About 2 μL of the solution was injected for analysis and the oven temperature was increased from 30 to 150 °C at a rate of 2°/min.

The temperature inside the 1.0 cm photolysis cuvette was measured with an Omega HH81 digital thermometer with a Type-K probe.

Photolyses. In experiments to characterize products or induce oscillation an approximately 2.0×10^{-4} M $[Ru(bpy)_2Cl_2]{\cdot}H_2O$ solution or a 1.0×10^{-4} M $[Ru(bpy)_2Cl_2]Cl{\cdot}H_2O$ solution in chloroform was used unless otherwise mentioned. Irradiation was carried out with an unfiltered 500 or 200-W mercury lamp in Oriel housings. The sample was placed in a rectangular 1.0-cm spectrophotometer cell, and no water bath was used. In some experiments the solution was deoxygenated by bubbling N_2 gas through it for 10 min prior to photolysis.

All kinetic experiments were performed under monochromatic irradiation with a 500-W high pressure mercury lamp in an Oriel housing. The light then passed through a water cell with two quartz windows, an ISA 10-cm monochromator, and a quartz lens. The sample was placed in a 1.0-cm rectangular quartz spectrophotometer cell, and was suspended in an aluminum water bath with quartz windows. When the sample was irradiated above 330 nm, a glass filter was placed in front of the quartz window to reject higher order wavelengths. The temperature of the water bath was maintained by the circulation of water from an external thermostated bath. During the experiment both the water bath and the sample were stirred. Incident light intensities were measured by ferrioxalate actinometry.[7,8]

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Photooxidation. Crystalline [Ru(bpy)$_2$Cl$_2$]·H$_2$O was dissolved in chloroform in a 1.0-cm rectangular spectrophotometer cell just prior to irradiation. The complex concentrations were between 10^{-5} and 2×10^{-4} M. The rate of disappearance of the Ru(II) species was monitored by following the change in absorbance at 556 nm, where the [Ru(bpy)$_2$Cl$_2$]$^+$ absorbance is negligible. Each experiment was repeated several times to check reproducibility.

The Ru(III) photoproduct was less soluble in chloroform than [Ru(bpy)$_2$Cl$_2$], and irradiation of an approximately 5×10^{-4} M [Ru(bpy)$_2$Cl$_2$] solution caused a brown solid to form at the bottom of the cuvette, which was found to be [Ru(bpy)$_2$Cl$_2$]Cl·H$_2$O. Anal. Calcd for [Ru(C$_{10}$H$_8$N$_2$)$_2$Cl$_2$]Cl·2H$_2$O: C, 43.22; H, 3.63; N, 10.08; Cl, 19.13. Found: C, 43.31; H, 3.69; N, 9.70; Cl, 18.92.

Photoreduction. Since the solubility of [Ru(bpy)$_2$Cl$_2$]Cl in chloroform is very low, the crystals were dissolved by stirring for two hours in the dark, and the excess was filtered out before use. The concentration of the solution was calculated from the extinction coefficient at 384 nm (6.07×10^3 M^{-1} cm^{-1}). To monitor the photoreaction, the solution was pipetted into a 1.0-cm spectrophotometer cell and nitrogen gas was passed through the solution for 10 min just prior to irradiation. The rate of formation of Ru(II) was followed by monitoring the growth of the 556 nm peak.

Results

The Bidirectional Photoredox Process. No measurable dark reaction was observed in either oxygenated or deoxygenated solutions of [Ru(bpy)$_2$Cl$_2$] and [Ru(bpy)$_2$Cl$_2$]$^+$ at temperatures from 10 to 60 °C.

Because we first observed the oxidation of [Ru(bpy)$_2$Cl$_2$] followed by reduction of [Ru(bpy)$_2$Cl$_2$]$^+$ in experiments in which [Ru(bpy)$_2$(N$_3$)$_2$] was the starting material, and bidirectional behavior had not been observed in other bis(bipyridine) complexes of Ru(II) by the many investigators who have studied such complexes in chloroform or other chlorinated solvents,[9-12] an initial hypothesis was that azide ion was uniquely responsible at least for the oscillatory behavior in this system. However, both the photooxidation and the photoreduction occur with no azide ion present, and the rates are independent of azide ion concentration. An alternative explanation for the failure by others to observe oscillation is that the illumination intensity or the temperature was never high enough, or deoxygenated solutions were always used, precluding oxidation.

To test the effect of temperature on the oxidation and reduction photoreactions, a stirred, air-saturated solution of [Ru(bpy)$_2$Cl$_2$] was irradiated with an unfiltered 200-W mercury lamp at full power, while the temperature was monitored by a digital thermocouple, placing the thermocouple probe out of the light beam. The solution lightened, and conversion to yellow [Ru(bpy)$_2$Cl$_2$]$^+$ was complete in about 1 min. No further reaction occurred until the temperature reached 58 °C (heated primarily by the absorbed visible and UV light). Conversion of the Ru(III) complex to violet Ru(II) was complete by the time the temperature had reached 60 °C. A plate was then used to block part of the light, causing the solution to cool. At approximately 59 °C, again over a span of 1 or 2 °C, the Ru(II) complex was completely converted to Ru(III). This process could be repeated for several cycles by removing and inserting the plate, and the transition temperature was always 59 °C in both directions (in this paper the term transition temperature will only be used to describe a bidirectional process). Above 60 °C, no Ru(III) could be detected spectrophotometrically, and below 58 °C no Ru(II) could be detected.

The phenomenon of a sharp transition temperature makes some of the initial observations on this system more understandable. In a typical experiment an open cell containing Ru(II) was suspended in an unthermostatted water bath, initially at 20–25 °C, with no stirring. Irradiation would convert this to the cold-stable Ru(III) species within 1 min. Continued irradiation would warm the solution in the cell past 59 °C in spite of the water bath, causing a transition back to Ru(II). The amount of light absorbed by the Ru(II) complex from the mercury lamp output is apparently less than that absorbed by the Ru(III) complex, because the latter has a higher extinction in much of the UV. If the water bath had not warmed sufficiently, the temperature in the cell would drop below 59 °C again, causing a further transformation to Ru(III), which then warmed up, possibly repeating the process until a steady-state temperature was reached. The steady state was probably delayed by convection currents that built up in the cell.

In air-saturated solution, [Ru(bpy)$_2$Cl$_2$] was oxidized to [Ru(bpy)$_2$Cl$_2$]$^+$ under irradiation, but only below 59 °C. [Ru(bpy)$_2$Cl$_2$]$^+$ was reduced under irradiation to [Ru(bpy)$_2$Cl$_2$], but only above 59 °C. When the solution was deoxygenated by bubbling N$_2$ through it for 5 min, [Ru(bpy)$_2$Cl$_2$] could not be photooxidized. [Ru(bpy)$_2$Cl$_2$]$^+$ was photoreduced, and reduction occurred at any temperature. The same results were obtained when these experiments were repeated with CHCl$_3$ that had been purified and distilled. Addition of small amounts of water had no effect.

When neat, air-saturated chloroform was irradiated with an unfiltered 200-W mercury lamp, the resulting solution was able to oxidize [Ru(bpy)$_2$Cl$_2$] thermally to [Ru(bpy)$_2$Cl$_2$]$^+$, even the next day. No reaction occurred when the Ru(II) complex was added to preirradiated deoxygenated chloroform. No reaction occurred when the Ru(III) complex was added to preirradiated chloroform solution, deoxygenated or not. This suggests that excited state Ru(II) is not involved in the formation of the oxidizing agent, since Ru(II) could be oxidized to Ru(III) without further irradiation. It also suggests that Ru(III) is involved directly in the initiation of the reduction process, since no agent capable of reducing Ru(III) is generated by photolysis of chloroform alone.

Since oxygen is required for the photooxidation, the active oxidizing agent in irradiated chloroform was suspected to be CCl$_3$OOH,[13,14] formed through hydrogen abstraction by the trichloromethylperoxy radical, which has been extensively studied in the gas-phase photooxidation of chloroform in the presence of oxygen.[15-18] CHCl$_3$ was irradiated with an unfiltered 200-W mercury lamp at full power for 5 min, and an infrared spectrum was recorded against unirradiated chloroform. A peak at 876 cm^{-1} is characteristic of the O–O stretching vibration in hydroperoxides,[19] and is assigned to CCl$_3$OOH. Other IR peaks reported for CCl$_3$OOH in CHCl$_3$ [13] were also present. Solutions of I$_2$ ($\approx 10^{-4}$M) in CHCl$_3$ were decolorized

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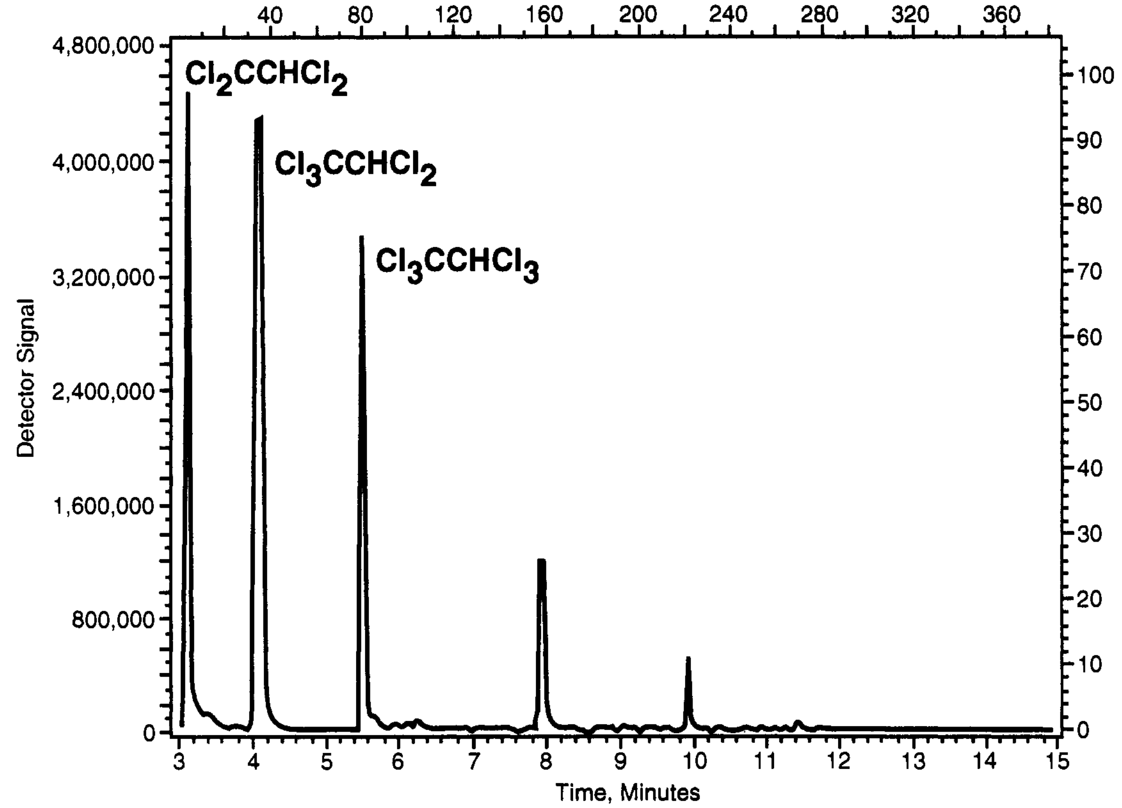

Figure 1. Gas chromatogram of the photolysate from the irradiation of neat $CHCl_3$ with a water-filtered 200-W mercury lamp for 1 h.

when added to irradiated chloroform. When irradiated solutions were titrated with I_2, they were found to have concentrations of oxidizing agent of a few millimolar, which did not decrease substantially when left overnight in the dark.

Identification of CCl_3OOH by GC/mass spectrometry was not successful, because its molecular weight is close to that of the chloroform solvent, and perhaps because the compound may not survive electron impact in the mass spectrometer. However, secondary oxygenated fragments were identified at high retention time when the chloroform solution was irradiated with a small amount of the metal complex. The gas chromatograms following photolysis in the absence and the presence of [Ru(bpy)$_2$Cl$_2$] are shown in Figures 1 and 2, respectively. In the absence of the Ru(II) complex, the termination products resulting from nonoxygenated radicals predominated over oxygenated products. Figure 2b is the mass spectrum of the major oxygenated product from the photolysis in the presence of Ru(II). The parent molecular ion, which may have been $ClCO_2CO_2CH_3^+$, was evidently destroyed before reaching the detector.

Similar reactions have been found to occur in other halogenated solvents.[20] The transition temperature was usually, though not always, close to the boiling point.

Photooxidation of [Ru(bpy)$_2$Cl$_2$]. When a 4.5×10^{-5} M [Ru(bpy)$_2$Cl$_2$] solution was irradiated at 313 nm with a 500-W mercury lamp, isosbestic points were observed at 283, 306, and 341 nm in the sequential spectra and were constant throughout the reaction. After one reaction was ca. 50% complete, the photolysate was passed through a $CHCl_3$-equilibrated Sephadex LH-20 column. The first, violet band was identified as the starting [Ru(bpy)$_2$Cl$_2$] complex, and the second, yellow band was identified as [Ru(bpy)$_2$Cl$_2$]$^+$ by comparison with the UV spectra of authentic samples. No other colored species could be seen on the column.

Table 1. Comparison of Quantum Yields for the Photooxidation of [Ru(bpy)$_2$Cl$_2$] Based on Absorption by Ruthenium(II) and by Chloroform[a]

λ_{exc}, nm	f_2[b]	$\phi_{Ru(II)}$[c]	f_c[b]	ϕ_c[c]
313	0.75	0.15	0.008	13
297	0.98	0.07	0.003	24

[a] Initial concentration of [Ru(bpy)$_2$Cl$_2$] was approximately 1.6×10^{-4} M; $T = 25$ °C; $I_0 = 1.6 \times 10^{-8}$ einstein s^{-1}. [b] f_2 = fraction of incident light intensity absorbed by Ru(II); f_c = fraction absorbed by $CHCl_3$. [c] $\phi_{Ru(II)}$ = quantum yield calculated based on light absorbed by Ru(II); ϕ_c = quantum yield based on light absorbed by $CHCl_3$.

Solutions of [Ru(bpy)$_2$Cl$_2$] in chloroform were irradiated at the mercury lamp wavelengths 546, 436, 366, 313, 297, and 254 nm. Irradiation at 546 nm, although this wavelength is strongly absorbed by [Ru(bpy)$_2$Cl$_2$], caused no measurable reaction. The same was true under 436 nm irradiation, while at 366 nm an extremely slow reaction did occur, with an absorbance change of less than 0.01 after 1 h. Irradiation at 313 nm and below caused a measurable reaction. Table 1 shows data gathered at two wavelengths after the lamp power was adjusted so that the incident light intensities were nearly the same. The quantum yield, calculated as if [Ru(bpy)$_2$Cl$_2$] were the photoactive species, went down from 313 to 297 nm. When calculated as if chloroform were the photoactive species, the quantum yield was higher at 297 nm than at 313 nm (note that, although the $CHCl_3$ absorbance is slightly higher at 297 nm than at 313 nm, the fraction of light absorbed was smaller because of the much greater absorbance by the ruthenium complex).

The rate of the reaction was followed for several initial concentrations of [Ru(bpy)$_2$Cl$_2$]. In each case, plots (Figure 3) of log[Ru(II)] vs time appeared to be linear, indicating a first-order dependence on the ruthenium(II) concentration. The observed rate constants, k_{obs}, were approximately inversely proportional to the square root of the initial concentration of

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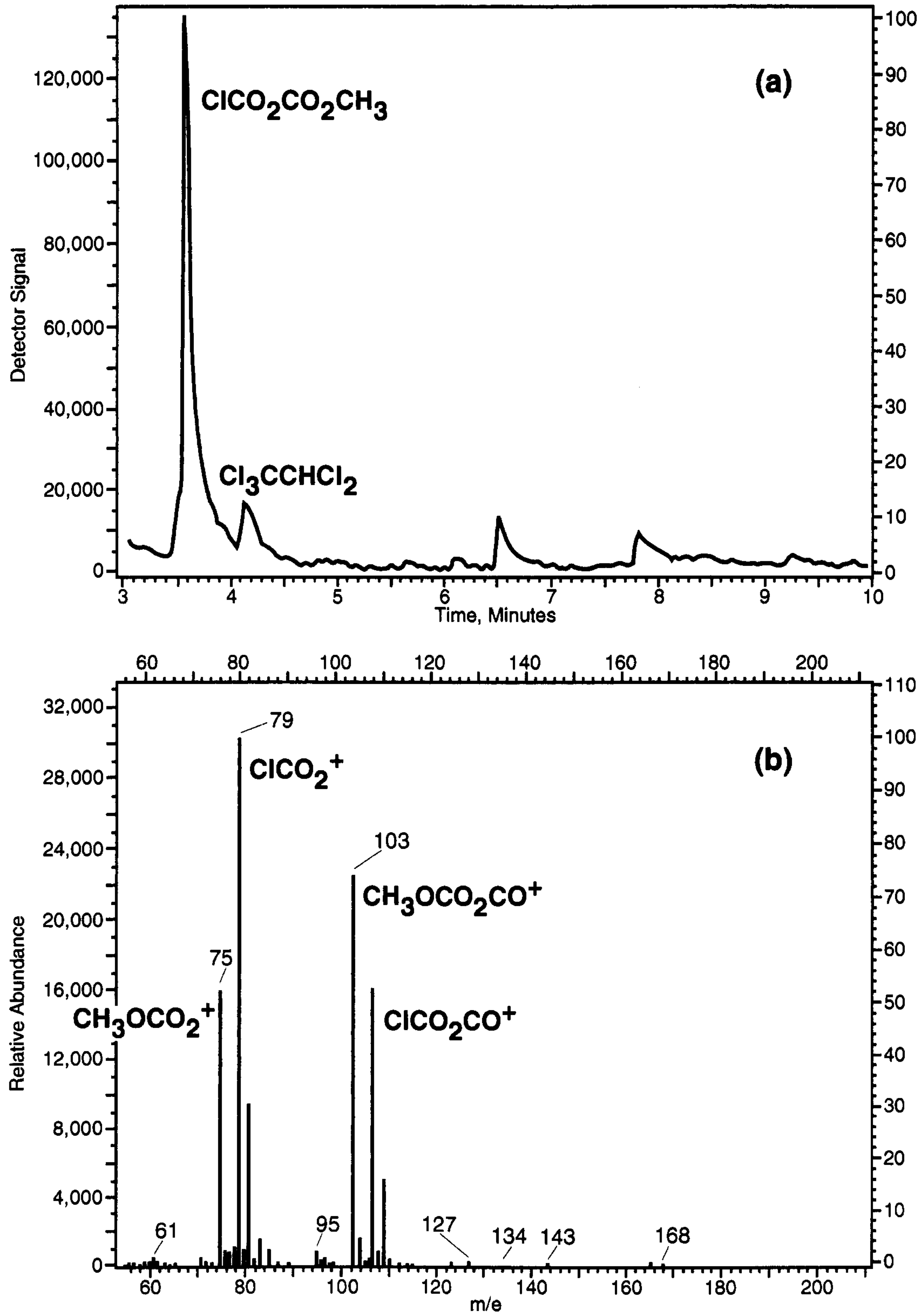

Figure 2. Gas chromatogram (a) of the photolysate from the irradiation of $CHCl_3$ with dissolved $[Ru(bpy)_2Cl_2]$ with a water-filtered 200-W mercury lamp for 1 h and mass spectrum (b) of the material from the largest peak in part a; formulas attached to major peaks are suggested, but not confirmed.

the Ru(II) complex. Because spectrophotometric grade chloroform is stabilized with ethanol, it was expected that there would be an induction period while the ethanol was being consumed, but none was evident. No difference was observed when purified and distilled $CHCl_3$ was used.

At four different light intensities the reaction still appeared to be first-order in Ru(II). The observed rate constants are shown in Table 2, and are approximately proportional to the square root of the incident light intensity.

The rate of photooxidation was compared in air-saturated and O_2-saturated solutions. The concentration of oxygen was calculated from the Ostwald coefficient of 0.217 at 25 °C.[21] In deoxygenated solution no photoreaction takes place. The rates in air- and oxygen-saturated solution were, within experimental error, the same (Table 3). The calculated concentration of

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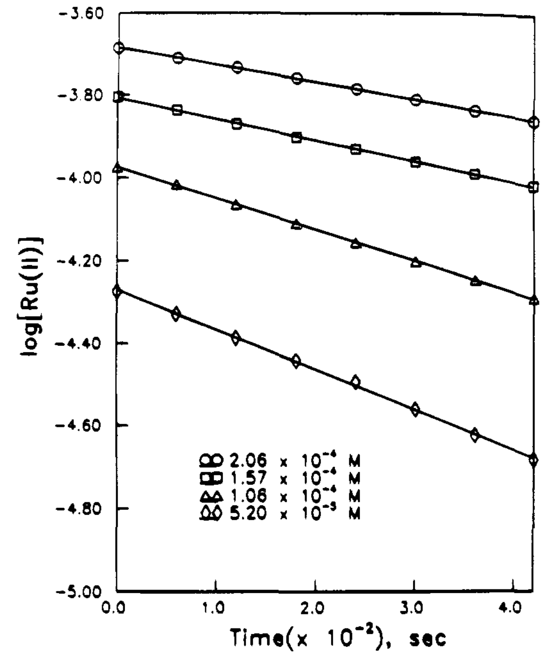

Figure 3. First-order plot of the kinetic data for the photooxidation of $[Ru(bpy)_2Cl_2]$ at 25 °C and $I_0 = 3.8 \times 10^{-9}$ einstein s^{-1}.

Table 2. Observed First-Order Rate Constants for the Photooxidation of $[Ru(bpy)_2Cl_2]$ in $CHCl_3$ at Various Light Intensities[a]

light intensity, einsteins $s^{-1} \times 10^9$	k_{obs}, $s^{-1} \times 10^4$	$k_{obs}/(I_0)^{1/2}$, $einstein^{-1/2}\,s^{-1/2}$
7.05	4.23 ± 0.04	5.04 ± 0.07
5.06	3.30 ± 0.02	4.64 ± 0.04
2.18	2.24 ± 0.04	4.80 ± 0.12
1.40	1.85 ± 0.02	4.94 ± 0.07

[a] $T = 25$ °C; concentration of $[Ru(bpy)_2Cl_2]$ was 1.85×10^{-4} M.

Table 3. Observed First-Order Rate Constants for the Photooxidation of $[Ru(bpy)_2Cl_2]$ in Deoxygenated, Air-Saturated, and O_2-Saturated $CHCl_3$[a]

$[O_2]$, M	k_{obs}, s^{-1}
0	no reaction
1.86×10^{-3}	$9.10 \pm 0.23 \times 10^{-4}$
8.88×10^{-3}	$8.69 \pm 0.12 \times 10^{-4}$

[a] Concentration of $[Ru(bpy)_2Cl_2] = 8.85 \times 10^{-5}$ M; $T = 25$ °C; $\lambda_{exc} = 313$ nm; $I_0 = 3.90 \times 10^{-8}$ einstein s^{-1}.

oxygen was approximately 20 times greater than the initial concentration of ruthenium(II) in air-saturated chloroform.

The quantum yield (based on light absorption by $CHCl_3$) for photooxidation was measured at several temperatures between 10 and 55 °C. The quantum yield increased with temperature up to 35 °C, and then remained approximately constant. A plot of log(ϕ) vs $1/T$ for the photooxidation reaction is shown in Figure 4. Between 10 and 35 °C it shows an Arrhenius-like dependence, with an apparent activation energy of 18 kJ/mol. This need not correspond to the activation energy for any single process.

Photoreduction of $[Ru(bpy)_2Cl_2]^+$. When an approximately 4×10^{-5} M $[Ru(bpy)_2Cl_2]Cl$ solution was irradiated with a 500-W mercury lamp at 366 nm, in the absence of oxygen, the same three isosbestic points were observed as in the photooxidation of $[Ru(bpy)_2Cl_2]$. In the presence of oxygen no measurable reaction was observed under irradiation at 25 °C, so all the measurements reported below were made on deoxygenated solutions. The only photoproduct was $[Ru(bpy)_2Cl_2]$, identified chromatographically.

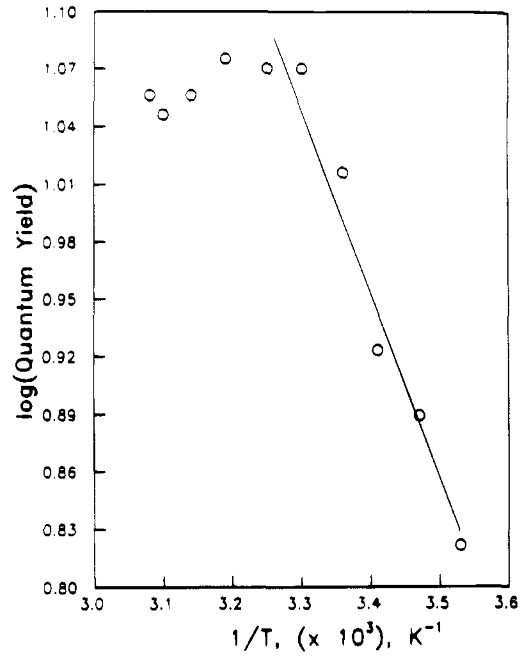

Figure 4. Initial quantum yield for the photooxidation of $[Ru(bpy)_2Cl_2]$ as a function of temperature. $I_0 = 1.1 \times 10^{-9}$ einstein s^{-1}.

Table 4. Quantum Yields for the Photoreduction of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$ Based on Absorption by Ru(III) and by Chloroform[a]

irradiation wavelength, nm	$\phi_{Ru(III)}$	ϕ_{CHCl_3}
366	0.008	1.5
313	0.009	1.0
297	0.008	2.0

[a] Initial concentration of $[Ru(bpy)_2Cl_2]Cl = 8.0 \times 10^{-5}$ M; $T = 25$ °C; $I_0 \approx 3.5 \times 10^{-8}$ einstein s^{-1}.

Unlike the photooxidation reaction, irradiation at 366 and 436 nm caused a measurable reaction. The calculated quantum yields based on Ru(III) absorption, and alternatively on chloroform absorption, are reported for a series of wavelengths in Table 4. The Ru(III)-based quantum yield was approximately constant with wavelength, and was about 0.01. The chloroform-based quantum yield was inconsistent, and we conclude that $[Ru(bpy)_2Cl_2]^+$ is the photoactive species.

The reaction rate of an approximately 5×10^{-5} M $[Ru(bpy)_2Cl_2]Cl$ solution was followed during irradiation at 366 and 313 nm. At 366 nm, a linear plot of 1/[Ru(III)] vs time implied a second-order dependence of the rate on the Ru(III) concentration during the course of a single photolysis (Figure 5). At 313 nm, on the other hand, a first-order dependence on Ru(III) concentration fit the data better, as shown in Figure 6. In both cases the observed rate constant was independent of the initial concentration of $[Ru(bpy)_2Cl_2]^+$.

The rate of photoreduction of a 5×10^{-5} M solution of $[Ru(bpy)_2Cl_2]Cl$ in chloroform was measured at 366 nm at three different light intensities. The observed second order rate constants were directly proportional to the intensity, as shown in Table 5.

The addition of chloride ion (from the tetrapropylammonium salt) increased the rate of the photoreduction reaction. $[Ru(bpy)_2Cl_2]$ was still the only ruthenium photoproduct found by Sepahadex LH-20 chromatography. The best fit to the kinetic data was to a rate law first order in both $[Cl^-]$ and [Ru(III)], yielding linear plots of $\log([Cl^-]/[Ru(III)])$ vs $([Cl^-]_0 -$

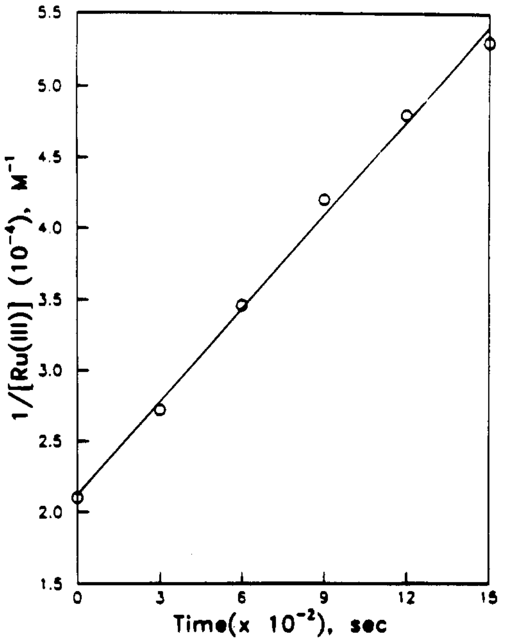

Figure 5. Second-order plot of the kinetic data for the photoreduction of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$ under 366 nm irradiation. $I_0 = 5.7 \times 10^{-8}$ einstein s^{-1}.

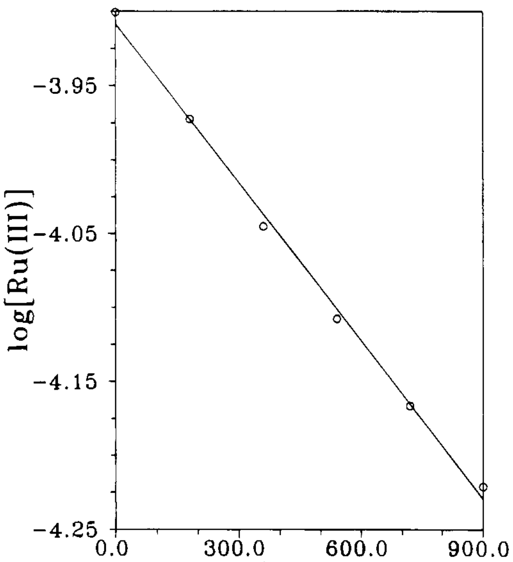

Figure 6. First-order plot of the kinetic data for the photoreduction of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$ under 313 nm irradiation. $I_0 = 3.9 \times 10^{-8}$ einstein s^{-1}.

$[Ru]_0)t$.[22] The chloride ion dependence of the initial quantum yield (based on the light absorbed by Ru(III)) is displayed in Figure 7.

The rate of the reaction was independent of the temperature between 10 and 55 °C.

Discussion

Photooxidation of $[Ru(bpy)_2Cl_2]$. Perhaps the most important question to be decided is whether the ruthenium complex or the chloroform is the photoactive species. Some of the relevant experimental observations are (a) preirradiated chloroform oxidizes Ru(II) to Ru(III) in the absence of light, (b) the apparent quantum yield based on the fraction of incident light absorbed by $[Ru(bpy)_2Cl_2]$ changes with wavelength, exhibits an inverse correlation with the absorption spectrum of the ruthenium complex, and is nearly zero above 366 nm, and (c) the quantum yield based on chloroform absorption was typically between 10 and 30 for 313 nm irradiation at the Ru(II) concentrations and light intensities used in this study.

Table 5. Observed Second-Order Rate Constants for the Photoreduction of $[Ru(bpy)_2Cl_2]Cl$ in $CHCl_3$ under 366 nm Irradiation[a]

light intensity, einstein $s^{-1} \times 10^8$	k_{obs} M^{-1} s^{-1}	k_{obs}/I_0, M^{-1} einstein$^{-1} \times 10^{-8}$
3.98	21.9 ± 0.69	5.51 ± 0.18
1.82	8.88 ± 0.20	4.88 ± 0.11
0.67	3.49 ± 0.14	5.21 ± 0.21

[a] Initial concentration of $[Ru(bpy)_2Cl_2]Cl \approx 5 \times 10^{-5}$ M; $T = 25$ °C.

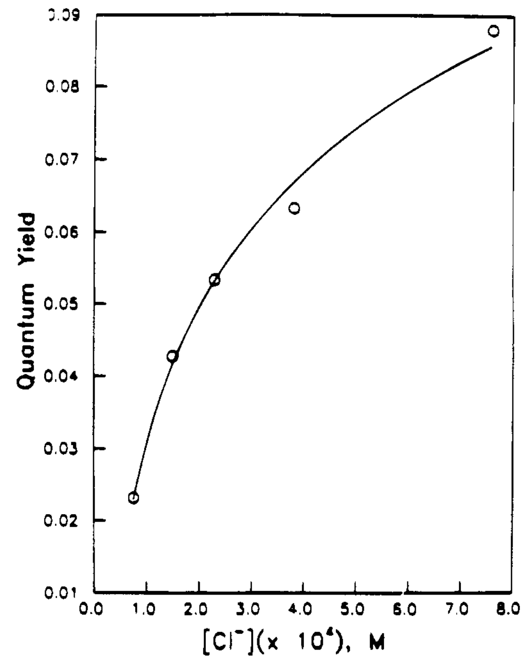

Figure 7. Observed quantum yield for the photoreduction of $[Ru(bpy)_2Cl_2]^+$ under 366 nm irradiation as a function of chloride ion concentration. $I_0 = 3.5 \times 10^{-8}$ einstein s^{-1}.

The first two observations suggest that the ruthenium complex plays no direct role in the photochemistry and only the absorption by solvent initiates the process. If $[Ru(bpy)_2Cl_2]$ were the photoactive species, one would expect the lowest excited state to be primarily responsible for reactivity, because it is the only state likely to have a long enough lifetime to undergo a bimolecular reaction. Yet neither of the charge transfer to ligand bands in the visible and near-UV regions leads to electron transfer upon irradiation. If a higher excited state of $[Ru(bpy)_2Cl_2]$ is photoactive, one would expect that the quantum yield would be constant with wavelength, or perhaps increase with decreasing wavelength if the photoactive band is farther in the UV.

We therefore assume that chloroform is photoactive, which implies that the reaction is radical-initiated. The quantum yield based on chloroform is also not constant, however this is common in radical chain reactions. The mechanism to be proposed below predicts that the quantum yield should increase with decreasing intensity of absorbed light.

Several observations must be accounted for in a proposed mechanism for the photooxidation of $[Ru(bpy)_2Cl_2]$: (a) oxygen is required for the oxidation process, (b) at higher oxygen concentrations (ambient air pressure and above), the rate of disappearance of $[Ru(bpy)_2Cl_2]$ is independent of $[O_2]$, (c) the

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[22] Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981, Chapter 2.

rate of the reaction appears to be first-order in [Ru(II)] during the reaction, (d) the observed first-order rate constant is approximately proportional to the square root of the intensity of the incident light, and (e) the observed first-order rate constant is inversely proportional to the square root of the initial concentration of the Ru(II) complex. That the rate appears first order in [Ru(II)], rather than nearly zero order, at high ruthenium concentration is further evidence that $[Ru(bpy)_2Cl_2]$ is not the photoactive species.

The large quantum yield (based on $CHCl_3$ absorption) suggests a radical-initiated chain pathway. It is known that the photolysis of chloroform first yields a dichloromethyl radical and a chlorine atom, and those subsequently undergo hydrogen abstraction.[15,23] The resulting trichloromethyl radicals are expected to react with O_2 to form trichloromethylperoxy radicals. Observable transients in both solution and gas phase have been assigned to this species.[17,24-28]

$$CHCl_3 + h\nu \xrightarrow{I_0f_c\phi_c/V} {}^{\bullet}CHCl_2 + Cl^{\bullet} \tag{1}$$

$$Cl^{\bullet} + CHCl_3 \xrightarrow{k_2} HCl + {}^{\bullet}CCl_3 \tag{2}$$

$${}^{\bullet}CHCl_2 + CHCl_3 \xrightarrow{k_3} CH_2Cl_2 + {}^{\bullet}CCl_3 \tag{3}$$

$${}^{\bullet}CCl_3 + O_2 \xrightarrow{k_4} CCl_3OO^{\bullet} \tag{4}$$

In step 1, I_0 is the incident light intensity, f_c the fraction of light absorbed by $CHCl_3$, and ϕ_c the quantum yield for C−Cl bond homolysis. The dichloromethyl radical may react with oxygen before it abstracts a proton. Thus $CCl_3OO^{\bullet}$ when referred to below may include some $CHCl_2OO^{\bullet}$.

The first-order behavior of the photooxidation exhibited in Figure 3 is deceptive. If Ru(III) were produced along a single, unbranched pathway, the rate could be expressed as $I_0f_c\phi/V$, where ϕ is the overall quantum yield. Though the chloroform absorbance can be treated as a constant, the fraction of light absorbed by chloroform (f_c) depends on the concentrations of Ru(II) and Ru(III). The dependence of the rate of formation of Ru(III) on the concentration of Ru(II) thus derives both from f_c and from the explicit dependence on [Ru(II)], if any. We therefore expect the rate law to have the form

$$\frac{d[Ru(II)]}{dt} = a(f_cI_0)^m[Ru(II)]^n \tag{5}$$

Given the observed dependence of the rate on the square root of the light intensity, a plot (Figure 8) was made of $(d[Ru(II)]/dt)/(f_cI_0)^{1/2}$ as a function of [Ru(II)], combining kinetic runs at different light intensities and different starting concentrations of $[Ru(bpy)_2Cl_2]$. The fraction of light absorbed by chloroform was determined from the solution absorbance at the irradiation frequency (313 nm). An optimization based on eq 5, with $m = 1/2$, yielded a value of 0.6 for n, based on the data from Figure 8. From this a rate law of the form

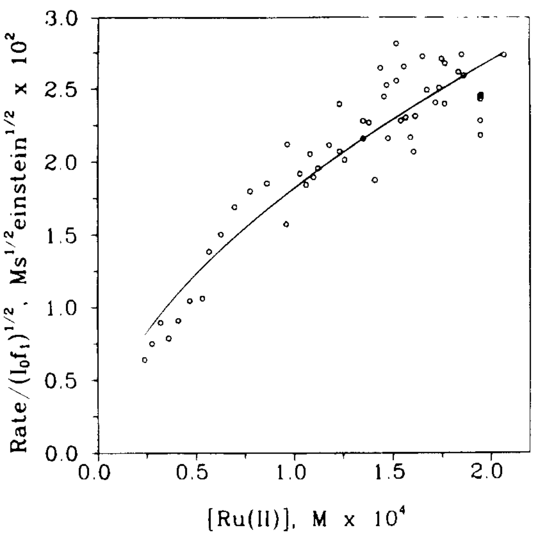

Figure 8. Plot of $f_c^{-1/2}I_0^{-1/2}\Delta[Ru(III)]/\Delta t$ as a function of the Ru(II) concentration in the 313 nm photolysis of $[Ru(bpy)_2Cl_2]$ in $CHCl_3$. Data from several runs with different light intensities and initial concentrations of Ru(II) are mixed, and points are included from each measurement in the run. The curve is from eq 21, with $\phi_c = 1.0$, $k_7k_{15}^{-1/2} = 6.83$, and $k_{17}/k_{16} = 3.93 \times 10^{-4}$ M.

$$\frac{d[Ru(II)]}{dt} = af^{1/2}I_0^{1/2}[Ru(II)]^{1/2} \tag{6}$$

can reasonably be inferred. The mean value of a was 0.98 ± 0.03 $M^{1/2}$ $einstein^{-1/2}$ $s^{-1/2}$.

The precision of the data is not sufficient to rule out other forms of the rate law, for example, $a/(1 + b[Ru(II)])$. The data of Figure 8 can even be fit quite well with a logarithmic dependence on concentration. However, eq 6 is the only form consonant with the expected behavior of photochemical reactions.

Consider first two possible routes to the oxidation of $[Ru(bpy)_2Cl_2]$ by $CCl_3OO^{\bullet}$. Step 7 shows direct oxidation by $CCl_3O_2^{\bullet}$, by means of electron transfer, yielding the trichloromethylperoxide ion.

$$CCl_3OO^{\bullet} + Ru(II) \xrightarrow{k_7} Ru(III) + CCl_3O_2^- \tag{7}$$

Steps 8 and 9 represent oxidation by CCl_3OOH, formed through hydrogen abstraction by the peroxy radical. Hydroperoxides are expected to react with O−O bond cleavage,[29,30] yielding in this case the trichloromethoxide ion.

$$CCl_3OO^{\bullet} + CHCl_3 \xrightarrow{k_8} CCl_3OOH + {}^{\bullet}CCl_3 \tag{8}$$

$$CCl_3OOH + Ru(II) \xrightarrow{k_9} Ru(III) + CCl_3O^- + {}^{\bullet}OH \tag{9}$$

$$CCl_3O^- \xrightarrow{k_{10}} Cl^- + CCl_2O \tag{10}$$

$${}^{\bullet}OH + CHCl_3 \xrightarrow{k_{11}} H_2O + {}^{\bullet}CCl_3 \tag{11}$$

The dissociation of CCl_3O^- (step 10) is expected to be rapid. Phosgene will be hydrolyzed by water (from step 11 or from the starting Ru(II) complex) to HCl and CO_2.

CCl_3OOH is stable for weeks in chloroform, even at moderate concentrations.[13] The ability of preirradiated $CHCl_3$ to oxidize

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$[Ru(bpy)_2Cl_2]$ implies that the hydroperoxide pathway is feasible. Though the reaction of CCl_3OOH with $[Ru(bpy)_2Cl_2]$ is immediate, it cannot be concluded that this is a competitive pathway under irradiation.

Note that oxidation through the hydroperoxide pathway (beginning with step 8) generates two $^\bullet CCl_3$ radicals to propagate the chain. How many chain carriers are generated in the peroxy radical pathway (step 7) depends on what happens to the trichloromethylperoxide ion. It appears not to be stable enough to precipitate with the $[Ru(bpy)_2Cl_2]^+$ cation, since only the chloride salt was recovered. Two possibilities may be considered. One is elimination of dioxygen to leave a chloride ion and dichlorocarbene.

$$CCl_3O_2^- \xrightarrow{k_{12}} Cl^- + {:}CCl_2 + O_2 \qquad (12)$$

We tested for the presence of dichlorocarbene by adding bicyclo[2.2.1]hept-2-ene during the oxidation process.[31-33] The insertion product, $C_8H_{10}Cl_2$, was observed by GC/mass spectrometry, by which *m/e* peaks at 176 and 141 were found, corresponding to $C_8H_{10}Cl_2^+$ and $C_8H_{10}Cl^+$ for the ^{35}Cl isotope, with the ^{37}Cl peaks in the correct ratios. When chloroform was irradiated with the alkene but without ruthenium present, the insertion product was not formed. Of course, this does not show that the $:CCl_2$ was generated from $CCl_3O_2^-$. Dichlorocarbene may insert into $CHCl_3$ to form pentachloroethane, which was detected in gas chromatograms, both with and without $[Ru(bpy)_2Cl_2]$.

The second possibility is that $CCl_3O_2^-$ may function as a Brønsted base, reacting with chloroform or with HCl or H_2O.

$$CCl_3O_2^- + CHCl_3 \xrightarrow{k_{13}} CCl_3OOH + Cl^- + {:}CCl_2 \qquad (13)$$

$$CCl_3O_2^- + HCl \xrightarrow{k_{14}} CCl_3OOH + Cl^- \qquad (14)$$

The first of these leads to dichlorocarbene, through the same CCl_3^- intermediate as in step 12. A similar route to $:CCl_2$ in solutions of O_2^- and $CHCl_3$ in benzene has been postulated.[34] Any trichloromethylhydroperoxide formed would be available to oxidize another Ru(II) molecule (step 9), generating a chain-carrying radical (step 11). Trichloromethylperoxide ions reacting by step 12 would generate no chain carriers.

The absence of a kinetic dependence on $[O_2]$ implies that most $^\bullet CCl_3$ radicals are converted to $CCl_3OO^\bullet$ before they can self-terminate, and it is the termination of the trichloromethylperoxy radicals that governs the steady state and the rate law (at lower oxygen concentrations, the termination of $^\bullet CCl_3$ with $CCl_3OO^\bullet$ and the self-termination of $^\bullet CCl_3$ would become important). The square root dependence on f_cI_0 (eq 6) indicates that this is predominantly a self-termination, rather than a reaction with another species. In the gas phase this termination results in the elimination of dioxygen and formation of trichloromethoxy radicals,[15,17,18] and it is likely that this occurs in solution as well.

$$2CCl_3OO^\bullet \xrightarrow{k_{15}} 2CCl_3O^\bullet + O_2 \qquad (15)$$

A reaction of this type is also dictated by the kinetic dependence on $[Ru(II)]^{1/2}$. If $CCl_3OO^\bullet$ self-terminated predominantly into nonradical products, there would be a first or second order dependence on the Ru(II) concentration. The observed square root dependence implies that there must be a step in which a product formed in the self-termination of $CCl_3OO^\bullet$ oxidizes Ru(II) to Ru(III). The trichloromethoxy radical can undergo electron transfer to form the trichloromethoxide ion, which should decompose as in step 10.

$$CCl_3O^\bullet + Ru(II) \xrightarrow{k_{16}} Ru(III) + Cl^- + CCl_2O \qquad (16)$$

$$CCl_3O^\bullet + CHCl_3 \xrightarrow{k_{17}} CCl_2O + HCl + {}^\bullet CCl_3 \qquad (17)$$

In gas phase reactions, $CCl_3O^\bullet$ terminates unimolecularly to CCl_2O and $Cl^\bullet$,[15] which would lead to HCl and $^\bullet CCl_3$ by hydrogen abstraction if it occurred in solution. Step 17 leads to the same products by the somewhat more likely route, in solution, of initial hydrogen abstraction. Step 16 generates no additional chain carriers, but step 17 generates one.

Steps 15 through 17 introduce an inverse dependence on [Ru(II)] for the steady-state concentration of $CCl_3O^\bullet$, and potentially an inverse square root dependence on [Ru(II)] for the steady-state concentration of $CCl_3OO^\bullet$. This would yield the necessary square root dependence of the total reaction rate on [Ru(II)] if step 7 (oxidation of Ru(II) by electron transfer to $CCl_3OO^\bullet$) dominates over the hydroperoxide pathway. The only way that the steady-state concentration of $CCl_3OO^\bullet$ can be completely determined by steps 15−17, while step 7 proceeds at a rate sufficiently rapid to determine the form of the net rate law, is for step 7 to produce exactly one chain carrier. Step 7 then has no influence on the steady-state concentration of $CCl_3O_2^\bullet$, since every $CCl_3O_2^\bullet$ radical that is reduced in step 7 is regenerated. The decomposition of the $CCl_3O_2^-$ product by step 12 yields no chain carriers, but protonation (step 13 or 14) leads to oxidation of a second Ru(II) (step 9) by CCl_3OOH, which generates one carrier.

Although the rate of hydrogen abstraction by $CCl_3O_2^\bullet$ (step 8) is reasonably fast,[14] oxidation of Ru(II) by the hydroperoxide through that pathway yields an incompatible rate expression (because there are two chain carriers), and we conclude that it can be neglected for the reaction occurring under irradiation. Nevertheless, since CCl_3OOH is generated after the initial peroxy radical oxidation, hydroperoxide oxidation (step 9) occurs anyway. Oxidation by the peroxy radical pathway (step 7), assuming protonation of $CCl_3O_2^-$ mainly by HCl, yields the net stoichiometry

$$O_2 + CHCl_3 + 2\,Ru(II) \rightarrow 2\,Ru(III) + 2\,Cl^- + HCl + CO_2 \qquad (18)$$

If the peroxy radical pathway is followed as described above (steps 7, 14, 9, 10, 11, 15, 16, and 17), then, under steady-state conditions for all radical intermediates, the steady-state concentrations of $CCl_3O^\bullet$ and $CCl_3O_2^\bullet$ are

$$[CCl_3O^\bullet] = \frac{2I_0f_c\phi_c}{k_{16}[Ru(II)]V} \qquad (19)$$

$$[CCl_3OO^\bullet] = \left\{\frac{I_0f_c\phi_c}{k_{15}V}\left(1 + \frac{k_{17}}{k_{16}[Ru(II)]}\right)\right\}^{1/2} \qquad (20)$$

The net rate of reaction is

$$\frac{d[Ru(III)]}{dt} = \frac{2I_0f_c\phi_c}{V} + 2k_7\left(\frac{I_0f_c\phi_c}{k_{15}V}\right)^{1/2}\left(1 + \frac{k_{17}}{k_{16}[Ru(II)]}\right)^{1/2}[Ru(II)] \qquad (21)$$

Under the assumption that $k_{17} \gg k_{16}[Ru(II)]$, i.e., that $CCl_3O^\bullet$

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decomposes faster than it oxidizes Ru(II), and $2I_0f_c\phi_c/V$ is smaller than the remainder of the right side of eq 21, i.e., the rate of Ru(II) oxidation greatly exceeds the rate of C–Cl bond homolysis, a square root dependence on the ruthenium(II) concentration and on absorbed light intensity results. A value of 1.0 was assigned to ϕ_c, the quantum yield for bond homolysis in $CHCl_3$, to generate the curve in Figure 8. The constants in eq 21 were found to be too strongly correlated to determine any of values uniquely.

The fraction of light absorbed by chloroform is

$$f_c = (1 - 10^{-A_T})A_c/A_T \tag{22}$$

where A_c is the chloroform absorbance and A_T the total absorbance, equal to $A_c + \epsilon_{II}[Ru(II)] + \epsilon_{III}[Ru(III)]$ (ϵ_{II} and ϵ_{III} are the extinction coefficients, at the irradiation wavelength, of Ru(II) and Ru(III), respectively, and a path length of one centimeter is assumed). The chloroform absorbance is quite small (0.008) at 313 nm. Neglecting it, the total absorbance can also be expressed as $A_T = \epsilon_{III}C_{Ru} - (\epsilon_{III} - \epsilon_{II})[Ru(II)]$, where C_{Ru} is the total ruthenium concentration. At 313 nm, $\epsilon_{III} = 4.2\epsilon_{II}$. The experimental rate law, $R = aI_0^{1/2}f_c^{1/2}[Ru(II)]^{1/2}$, becomes, with the approximation that $1 - 10^{-A_T} \approx 1$

$$\frac{d[Ru(III)]}{dt} = \frac{aI_0^{1/2}A_c^{1/2}[Ru(II)]^{1/2}}{\{\epsilon_{III}C_{Ru} - (\epsilon_{III} - \epsilon_{II})[Ru(II)]\}^{1/2}} = a\left(\frac{I_0A_c[Ru(II)]}{\epsilon_{III}(C_{Ru} - 0.76[Ru(II)])}\right)^{1/2} \tag{23}$$

The inverse relationship between the initial concentration of $[Ru(bpy)_2Cl_2]$, C_{Ru}, and the reaction rate can be seen in eq 23. This equation also shows that the reaction rate decreases more rapidly than the square root of the ruthenium(II) concentration, which may be why it appeared to be first order when ln[Ru(II)] was plotted against time.

Photoreduction of $[Ru(bpy)_2Cl_2]^+$. That the photoreduction is initiated by the direct absorption of light by $[Ru(bpy)_2Cl_2]^+$ is suggested by the observations that no reduction of Ru(III) was observed with preirradiated, deoxygenated chloroform and the initial quantum yield for photoreduction based on absorption by Ru(III) was approximately constant with wavelength.

The following features must be accounted for in a proposed mechanism: (a) the rate of reduction of $[Ru(bpy)_2Cl_2]^+$ is chloride ion-dependent, (b) under 366 nm irradiation, the rate of reaction appears to be second order in Ru(III) (with no additional chloride), while 313 nm irradiation yields a first-order Ru(III) dependence, and (c) the second-order rate constant is directly proportional to the incident light intensity.

The dependence on chloride concentration of the quantum yield for the formation of $[Ru(bpy)_2Cl_2]$, as shown in Figure 7, suggests an ion-pairing mechanism for the reduction of $[Ru(bpy)_2Cl_2]^+$.

$$Ru(III) + Cl^- \xrightleftharpoons{K_{ip}} Ru(III){\cdot}Cl^- \tag{24}$$

$$Ru(III){\cdot}Cl^- \xrightarrow{h\nu,\phi_{ip}} Ru(II) + Cl^{\bullet} \tag{25}$$

K_{ip} is the ion-pair formation constant, and ϕ_{ip} is the quantum yield for the photoreduction of the ion-paired complex. Free $[Ru(bpy)_2Cl_2]^+$ is presumed to be unreactive, because the excited state lifetime is too short for diffusion to a chloride ion or other potential reductants in solution. The reduction potential of ground state $[Ru(bpy)_2Cl_2]^+$ in CH_2Cl_2 is +0.24 V (vs SCE).[35] With up to an additional three volts at 400 nm, oxidation of Cl^- by excited state $[Ru(bpy)_2Cl_2]^+$ is quite feasible.

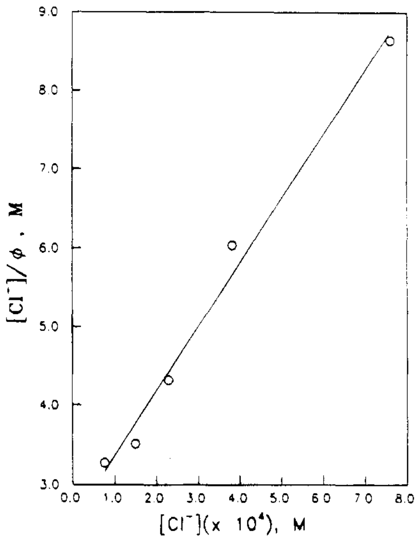

Figure 9. Plot of $[Cl^-]/\phi$ vs $[Cl^-]$ for the photoreduction of $[Ru(bpy)_2Cl_2]^+$ in $CHCl_3$ under 366 nm irradiation. $I_0 = 3.5 \times 10^{-8}$ einstein s^{-1}.

The observed quantum yield, ϕ, for the formation of Ru(II) will depend on what fraction of the total light absorbed by Ru(III) is absorbed by the ion pair. Light absorption by the ion-paired and free complexes is assumed to be the same, so

$$\phi = \phi_{ip}f_{ip} \tag{26}$$

where f_{ip} is the fraction of Ru(III) in the ion-paired form, $K_{ip}[Cl^-]/(1 + K_{ip}[Cl^-])$. Therefore

$$\frac{[Cl^-]}{\phi} = \frac{1}{\phi_{ip}}\left(\frac{1}{K_{ip}} + [Cl^-]\right) \tag{27}$$

and a plot of $[Cl^-]/\phi$ vs $[Cl^-]$ should produce a straight line with a slope $1/\phi_{ip}$ and an intercept $1/\phi_{ip}K_{ip}$. The corresponding plot is shown in Figure 9, yielding $K_{ip} = 3270 \pm 234$ and $\phi_{ip} = 0.12 \pm 0.02$. With no added chloride ion, a 5×10^{-5} M solution of $[Ru(bpy)_2Cl_2]^+$ should be 15% ion-paired, with the apparent quantum yield reduced proportionately.

The experimental rate law, which is consistent with eq 27, can be expressed as

$$\frac{d[Ru(II)]}{dt} = \frac{I_0f_3\phi_{ip}K_{ip}[Cl^-]}{1 + K_{ip}[Cl^-]} \tag{28}$$

In eq 28, f_3 is the fraction of the incident light absorbed by Ru(III).

The observed dependence of the rate on $[Ru(III)]^2$ at 366 nm and on [Ru(III)] at 313 nm derives from the fraction of light absorbed

$$f_3 = \frac{(1 - 10^{-\{A_c+\epsilon_{II}[Ru(II)]+\epsilon_{III}[Ru(III)]\}})\epsilon_{III}[Ru(III)]}{A_c + \epsilon_{II}[Ru(II)] + \epsilon_{III}[Ru(III)]} \tag{29}$$

The chloroform absorbance, A_c, will be neglected. At 366 nm the absorbance of a 5×10^{-5} M solution of $[Ru(bpy)_2Cl_2]^+$ is less than 0.5, and making use of the the approximation $1 - 10^{-x} \approx 2.3x$ for small x, f_3 becomes approximately $2.3\epsilon_{III}[Ru(III)]$. Letting $1 + K_{ip}[Cl^-] \approx 1$, the approximate rate law is

$$\frac{d[Ru(II)]}{dt} = \frac{2.3\phi_{ip}I_0\epsilon_{III}K_{ip}[Ru(III)][Cl^-]}{V} \tag{30}$$

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[35] tom Dieck, H.; Kollvitz, W.; Kleinwächter, I. *Inorg. Chem.* **1984**, *23*, 2685.

This results in second-order behavior (with no added Cl^-), because $[Cl^-] = [Ru(III)]$. $K_{ip}\phi_{ip}$ can be determined from the slope of a plot of k_{obs} vs I_0. The value derived from this plot was $140 \pm 9\ M^{-1}$. The difference between this and the value obtained from a plot of $[Cl^-]/\phi$ vs $[Cl^-]$ ($392\ M^{-1}$) can be ascribed to the serious approximations made to put the rate law into the form of eq 30.

At 313 nm the total absorbance of a 5×10^{-5} M solution of $[Ru(bpy)_2Cl_2]^+$ is greater than 1.5. If the approximation is made that the total fraction absorbed ≈ 1, the fraction of light absorbed by Ru(III) is $\epsilon_{III}[Ru(III)]/\{\epsilon_{II}[Ru(II)] + \epsilon_{III}[Ru(III)]\}$. At 313 nm $\epsilon_{III} = 4.2\epsilon_{II}$, so as a rough approximation (which gets worse the farther the reaction progresses) the [Ru(II)] term can be neglected, so that $f_3 \approx 1$. Again approximating $1 + K_{ip}[Cl^-]$ as 1, the rate law at 313 nm is

$$\frac{d[Ru(II)]}{dt} = \frac{\phi_{ip}I_0K_{ip}[Cl^-]}{V} \tag{31}$$

Since $[Ru(III)] = [Cl^-]$ when no chloride is added, approximate first-order behavior should be observed.

All the measurements for the photoreduction reaction were made on deoxygenated solutions. Oxygen quenching can be ruled out as a reason for the complete lack of reactivity of $[Ru(bpy)_2Cl_2]^+$ in air-saturated solutions below 59 °C. The theoretical bimolecular quenching constant, k_q, is approximately $10^{10}\ M^{-1}\ s^{-1}$ for a noncharged quencher.[36] This yields a value of about $10^7\ s^{-1}$ for $k_q[O_2]$. Even recognizing that O_2 may quench more strongly than the theoretical value of k_q would predict, it is unlikely that quenching competes with, much less dominates, nonradiative relaxation if $Ru(III)^*$ is unable to diffuse far enough to be reduced by Cl^- unless it is ion-paired.

A more reasonable explanation is that any reduction of $Ru(III)^*{\cdot}Cl^-$ in solutions with oxygen is followed by back-reaction of Ru(II) with $CCl_3OO^\bullet$ or CCl_3OOH. The quantum yield of the photooxidation was found to be about one thousand times greater than that of the photoreduction under typical reaction conditions. The chlorine atom produced in the photoreduction will be converted to $CCl_3OO^\bullet$ (steps 2 and 4) when oxygen is present. Each $CCl_3OO^\bullet$ can reoxidize two molecules of $[Ru(bpy)_2Cl_2]$ according to the mechanism proposed above, and enough CCl_3OOH should build up for the reoxidation to be rapid.

Conclusions

The rate of the photooxidation of $[Ru(bpy)_2Cl_2]$ in $CHCl_3$ was found experimentally to take the form $I_0^{1/2}f_c^{1/2}[Ru(II)]^{1/2}$. This was found to be consistent with a chain mechanism initiated by C−Cl bond homolysis in which each $CCl_3OO^\bullet$ oxidant is responsible for the oxidation of two ruthenium(II) molecules. The photoreduction of $[Ru(bpy)_2Cl_2]^+$ can be explained as the reaction of the excited state ion pair, $[Ru(bpy)_2Cl_2]^{+*}{\cdot}Cl^-$ to yield the Ru(II) complex and a chlorine atom.

The noteworthy observation is that in air-saturated solutions the photooxidation takes place only above 59 °C, while the photoreduction takes place only below 59 °C. This temperature-hypersensitive behavior is not a natural consequence of the temperature dependence of these reactions below 59 °C. The photoreduction rate was found to be independent of temperature, while the photooxidation rate *increased*, rather than decreased, with temperature up to 35 °C, then was constant, or fell only slightly with temperature until a few degrees below the transition temperature.

We conclude that in chloroform the sharp transition temperature results from a reversible loss of solution oxygen near the boiling point as it is driven out by solvent vapor. The existence of sharp transition temperatures for the photoconversion of $[Ru(bpy)_2Cl_2]^{0/+}$ well below the boiling point in benzyl chloride and in chloroform diluted with alkanes[20] does show that other mechanisms are possible.

Although photoreduction below 59 °C was observed only with deoxygenated solutions, we do not conclude that it does not take place in oxygenated solution, but rather that it is overwhelmed by photooxidation. At any temperature, it may be presumed that both processes take place simultaneously. This may help to rationalize the lack of an induction period due to dissolved ethanol. Ethanol may be oxidized catalytically, with no net conversion of Ru(II) to Ru(III), too rapidly to be seen on the time scale for Ru(III) formation.

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