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Simultaneous photooxidation of [Ru(bpy)$_2$Cl$_2$] and photoreduction of [Ru(bpy)$_2$Cl$_2$]$^+$ in several solvent systems

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Abstract

In a number of aerated solvent systems, [Ru(bpy)$_2$Cl$_2$] can be oxidized to [Ru(bpy)$_2$Cl$_2$]$^+$ under UV irradiation, in at least some of these solvents by a solvent-initiated radical chain reaction. Irradiation of [Ru(bpy)$_2$Cl$_2$]$^+$ in the blue or ultraviolet in some of the same solvents caused photoreduction to the Ru(II) complex. In some solvent systems a photostationary mixture was the end result of UV irradiation. In others the irradiated solution was either completely Ru(II) or completely Ru(III), depending on the temperature. The extreme temperature sensitivity is thought to depend on the oxygen concentration.

Keywords: Photoreduction; Photooxidation; Ruthenium complexes; Bipyridine complexes

1. Introduction

We recently reported on a bidirectional photoredox reaction between [Ru(bpy)$_2$Cl$_2$] and [Ru(bpy)$_2$Cl$_2$]$^+$ in CHCl$_3$ [1,2]; bpy = 2,2′-bipyridine. Among the peculiar characteristics of that reaction was the abrupt transition under irradiation as the temperature passed 59 °C, converting from Ru(III) to Ru(II) above that temperature and from Ru(II) to Ru(III) below. Since the temperature range for complete conversion in either direction was about one degree, it is appropriate to refer to a transition temperature for the system.

The main reason such a phenomenon can occur is that the oxidation and reduction reactions are not the reverse of each other. The photoreduction occurs through oxidation of ion-paired chloride ions by excited Ru(III), a typical photoredox process. The photooxidation, though it mimics reactions in which the metal complex is the photoactive species, is actually a chain reaction initiated by bond homolysis of the solvent. A key step in the proposed reaction sequence in chloroform was [1,2]

$$\text{CCl}_3\text{OO}^{\cdot} + \text{Ru(II)} \longrightarrow \text{CCl}_3\text{OO}^- + \text{Ru(III)} \qquad (1)$$
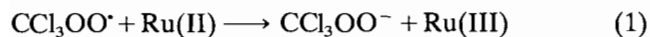
The trichloromethylperoxy radical is formed by reaction of oxygen with photochemically generated $^{\cdot}$CCl$_3$ [3,4],

which itself results from hydrogen abstraction from CHCl$_3$ by the radicals formed during bond homolysis.

$$^{\cdot}\text{CCl}_3 + \text{O}_2 \longrightarrow \text{CCl}_3\text{OO}^{\cdot} \qquad (2)$$

Among the stronger pieces of evidence for a chain reaction, with CCl$_3$OO$^{\cdot}$ as the dominant radical species, were the high (and concentration-dependent) quantum yield, typically between 10 and 20 mol/einstein, a square root dependence of the reaction rate on the light intensity, and the zero-order dependence on [O$_2$] in oxygenated solutions [1,2].

In oxygen-free solution, $^{\cdot}$CCl$_3$ is the radical in highest concentration during irradiation. In related systems, $^{\cdot}$CCl$_3$ has proved capable of chlorinating Ru(II) complexes without changing its oxidation state [5]. Irradiation of deaerated [Ru(bpy)$_2$Cl$_2$] in CHCl$_3$ caused no reaction.

The ruthenium(II) complex in Eq. (1) may also be regarded as photochemically generated, since it is likely that, in an aerated solution of either [Ru(bpy)$_2$Cl$_2$] or [Ru(bpy)$_2$Cl$_2$]$^+$, oxidation of Ru(II) and reduction of Ru(III) occur simultaneously. The latter process can be represented as

$$\{\text{Ru(III)} \cdot \text{Cl}^-\} \longrightarrow \text{Ru(II)} + \text{Cl}^{\cdot} \qquad (3)$$
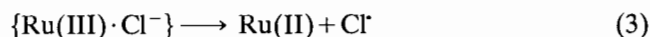
The proposed mechanism implies that the oxidant and reductant in Eq. (1) are photochemically generated

in separate processes, but at room temperature the oxidant is produced at a faster rate, so that Ru(II) is oxidized as rapidly as it is produced. The oxidant concentration is then limited by its self-decomposition processes. This situation is reversed at the transition temperature. The reductant is generated faster than the oxidant, until the excess of oxidant is consumed. There are several conceivable ways in which a reversal can take place, but the most likely in the chloroform system is the loss of oxygen near the boiling point, driven out by solvent vapor, retarding the formation of $CCl_3OO^{\cdot}$. Shortly after $CCl_3OO^{\cdot}$ begins to be formed more slowly than Ru(II), the composition of the solution changes completely to Ru(II).

Another means by which a sharp transition temperature may arise is through the crossing of the rates of oxidant and reductant generation due to the normal temperature dependence of the rate constants. In its simplest form, this might resemble a reversible thermal reaction in which the kinetics were zero order in both directions. Such a system would be characterized by the dominance of one side or the other, and a complete transformation whenever the magnitudes of the rate constants crossed because of a temperature change or other factors. Several complications mar this analogy, including some explicit concentration dependences and the generation of a radical initiator in the reduction process (Eq. (3)). Nevertheless, one might well expect at some point a complete alteration of the solution composition over a small temperature range if the rates of $CCl_3OO^{\cdot}$ formation (Eq. (2)) and Ru(II) formation (Eq. (3)) are similar.

In this communication we examine the behavior of the $[Ru(bpy)_2Cl_2]^{0/+}$ system in several solvents, with emphasis on the existence of a reproducible transition temperature and the characteristics of the transition. We have also examined the evidence that the photooxidation and photoreduction occur simultaneously.

2. Experimental

Solutions between 5×10^{-5} and 1×10^{-4} M in either $[Ru(bpy)_2Cl_2]$, $[Ru(bpy)_2Cl_2]^+$, or both were made up in chloroform, methylene chloride, 1,2-dichloroethane, ethyl chloroformate, benzyl chloride, allyl chloride, bromoform, methylene bromide, 1,2-dibromoethane, tetrahydrofuran (THF), nitromethane, acetone, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and some mixtures of these solvents. Without deoxygenation, these were irradiated with an Oriel 500-W Hg lamp, usually filtered only by water. Some experiments were carried out with monochromatic radiation by passing the light through a JY 100-mm monochrom-

ator. Changes in solution composition were monitored by UV–Vis spectrophotometry with a Hewlett-Packard 8451A diode array spectrometer. In the brominated solvents the ruthenium complexes were sensitive to room lights, so cuvettes were wrapped in foil during transfers to and from the spectrophotometer.

3. Results and discussion

In the solvents examined, the $[Ru(bpy)_2Cl_2]^{0/+}$ system exhibited one of several types of general behavior under irradiation from the full output of the mercury lamp.

(a) As in $CHCl_3$, irradiation of $[Ru(bpy)_2Cl_2]$ yielded $[Ru(bpy)_2Cl_2]^+$, but continued irradiation near the boiling point caused reduction back to $[Ru(bpy)_2Cl_2]$ (CH_2Cl_2 and $1,2\text{-}C_2H_4Cl_2$, CH_2CHCH_2Cl (only partial reduction)).

(b) Irradiation of $[Ru(bpy)_2Cl_2]$ yielded $[Ru(bpy)_2Cl_2]^+$, but no photoreduction occurred, even when the solution was boiling (EtOOCCl, CH_3NO_2).

(c) Irradiation of $[Ru(bpy)_2Cl_2]$ caused little or no change in solution composition (acetone, THF).

(d) Irradiation of $[Ru(bpy)_2Cl_2]$ led to substitution of Cl^- by solvent (DMF, DMSO).

(e) Irradiation of $[Ru(bpy)_2Cl_2]$ yielded $[Ru(bpy)_2Cl_2]^+$, and continued irradiation caused reduction at some higher temperature, but still well below the boiling point of the solvent (benzyl chloride, $CHCl_3$/mineral oil).

(f) Irradiation of $[Ru(bpy)_2Cl_2]$ yielded $[Ru(bpy)_2Cl_2]^+$, reversing under continued irradiation when Et_4NBr was added (brominated solvents).

(g) Irradiation of either $[Ru(bpy)_2Cl_2]$ or $[Ru(bpy)_2Cl_2]^+$ caused transformation to the other, but with little relationship to temperature, and producing after a few cycles a steady state mixture of the two; this mixture was richer in Ru(II) the more intense the irradiation, and was slowly moved towards Ru(III) in the dark (mixtures of brominated solvents with DMF or DMSO).

In type (a) systems, UV irradiation was necessary for photooxidation to occur. Rates showed the expected dependence on wavelength, matching the solvent absorption spectrum [5]. The same was generally true for other solvents.

The oxidizing species in the type (b) systems is unknown, and there are two possible explanations for the failure to observe photoreduction at the boiling point in these solvents. One is that there is no anionic species than can ion-pair with, and be reduced by, excited state $[Ru(bpy)_2Cl_2]^+$, the lifetime of which is probably too short to permit diffusion to a neutral reductant. The second explanation is that whatever the

actual oxidizing species is, external oxygen is not required for its generation, the rate of which could exceed that of photoreduction at all temperatures.

The behavior in benzyl chloride and in chloroform diluted by mineral oil suggests the possibility of the rate crossing mentioned in Section 1. In benzyl chloride (b.p. 179 °C) the first cycle (after initial conversion to Ru(III) at ambient temperature), from Ru(III) to Ru(II) and back again, occurred around 28 °C. Subsequent cycles took place at successively higher temperatures, usually about 5 °C higher for each cycle. Similar behavior was noted for chloroform/mineral oil mixtures in 1:1, 1:2 and 1:3 ratios (the ruthenium concentration was the same in all of these trials). The first cycle generally occurred between 30 and 40 °C, with subsequent transitions at higher temperatures.

Rate crossing due to the temperature dependence of the rate constants is not the cause of this behavior. It is more likely that in the Ru(III) state, conversion to Ru(II) occurs in part because of the depletion of O_2, much like chloroform near its boiling point. The higher viscosity [6] of benzyl chloride (and mineral oil) limits the diffusion of O_2 from the atmosphere, bringing the rate of production of $CCl_3OO\cdot$ near the rate of photoreduction. If O_2 is bubbled through the solution during irradiation, photoreduction of Ru(III) does not happen.

This is far from a complete explanation of the behavior in these solvent systems. If the diffusion of oxygen was the limiting factor in the generation of the oxidant, higher temperatures would bring an increase in the peroxy radical ($CCl_3OO\cdot$ in chloroform, $C_6H_5CHClOO\cdot$ in benzyl chloride) concentration, and conditions would be more favorable for Ru(III) formation. The photoreduction is expected to have little or no temperature dependence [1]. A perhaps more complete, though still problematic, hypothesis is that the hydroperoxide, rather than the peroxy radical, is the most important oxidizing agent. Its rate of formation would be linearly dependent on temperature, through the diffusion constant, which is to say it is nearly constant over the relatively small temperature range under consideration. Hydroperoxide decomposition proceeds by both unimolecular and bimolecular processes, and is known to be strongly temperature dependent [7].

When the solution is in the Ru(III) state (yellow) at room temperature, more of the hydroperoxide is present than is necessary to oxidize Ru(II) as fast as it is formed by photoreduction. The hydroperoxide concentration is limited primarily by its self-decomposition. As that decomposition rate increases with temperature, however, the concentration of the hydroperoxide eventually falls below the minimum necessary to oxidize all Ru(II) as formed. Then Ru(II) begins to accumulate and the hydroperoxide concentration continues to drop as it is used up in the oxidation.

The solution ends in the Ru(II) state (purple), with just enough Ru(III) present to yield a photoreduction rate equal to the rate of photooxidation. That subsequent cycles required higher temperatures may be due to the presence of several hydroperoxides (or other oxidizing species) in solution, reacting at different rates.

The behavior of $[Ru(bpy)_2Cl_2]^{0/+}$ in CH_2Br_2, $CHBr_3$ and 1,2-$C_2H_4Br_2$, though not exhibiting a transition temperature, is consistent with the picture of simultaneous photooxidation and photoreduction. Irradiation of Ru(II) yielded Ru(III), but addition of bromide ion with continued irradiation caused regeneration of Ru(II). There was no discernible temperature dependence for either process. After irradiation was stopped, Ru(II) was slowly converted to Ru(III) in a thermal reaction, even though no dark reaction occurred before the initial irradiation. Evidently the photooxidation, though still faster than photoreduction in the pure solvent, is not much faster, possibly because Br^- is a better reducing agent than Cl^-, though the ion-pair equilibrium would be more favorable with chloride ion. Adding bromide ion shifts the equilibrium towards the ion pair, allowing photoreduction to predominate.

In DMSO or DMF the solvent acts as a nucleophile towards the excited state Ru(II) complex. No oxidation takes place. With 5% of one of the brominated solvents added, photooxidation occurred, but the resulting solution was a mixture of Ru(II) and Ru(III). More Ru(II) was present the more intense the exciting light. When irradiation ceased, the Ru(II) was gradually depleted by a thermal reaction. Radicals would be generated at a slower rate in these solutions than in the pure brominated solvents, slowing the photooxidation to a rate comparable with photoreduction. In $CHCl_3$ the rate of photoreduction varied linearly with I_0, the incident light intensity, while the rate of photooxidation was proportional to $I_0^{1/2}$ [1,2]. If the same rate expressions hold in these mixed solvent systems, higher light intensity would favor photoreduction and a higher Ru(II) concentration in the apparent photostationary state (the photostationary state is only apparent since a net reaction occurs during a redox cycle, because the oxidation process is not the reverse of the reduction). We presume that, as in previous examples, the photooxidation is limited primarily by the diffusion of O_2 and the decomposition of the hydroperoxide. More than one oxidant appears to be at work, with a considerable difference in reaction rates.

4. Conclusions

Rate crossing caused by the temperature dependence of the rate constants for oxidation and reduction would

be predicted to favor Ru(III) at higher temperatures, whereas in all the systems displaying a temperature dependence in this study, Ru(II) was the high temperature species under irradiation. This is interpreted to mean that diffusion of oxygen and self-decomposition of the hydroperoxide oxidizing agent(s) are the processes limiting oxidation. In the brominated solvent systems no transition temperature was observed, yet the state of the system could be influenced by factors such as light intensity and bromide ion. This is consistent with a picture of photooxidation and photoreduction occurring simultaneously whatever the actual composition of the solution.

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