Photosubstitution of Diazidobis(bipyridine)ruthenium(II) through a Radical Mechanism

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Introduction

An earlier note described the initiation of photochemical oscillation between $[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_2Cl_2]^+$ by irradiation of a chloroform solution of $[Ru(bpy)_2(N_3)_2]$.[1] We report here details of the first step of this process, the photochemical conversion of the diazido to the dichloro complex.

Experimental Section

$[Ru(bpy)_2(N_3)_2]$ was prepared photochemically from $[Ru(bpy)_3](N_3)_2$ as previously described.[2] Irradiation was carried out in a stirred 1-cm rectangular cuvette in a water bath at 25 °C. In some experiments the solution was deoxygenated by bubbling N_2 through it or by adding a small amount of dry ice. The initial concentration of $[Ru(bpy)_2(N_3)_2]$ was determined from the extinction coefficient at 560 nm. An ISA 10-cm monochromator selected the irradiation wavelength from a 200-W high-pressure mercury lamp (Oriel 6137). A glass filter was used to reject higher order wavelengths. The light intensity was determined by ferrioxalate actinometry immediately following each run.[3-5] Concentrations of reactants and products were followed spectrophotometrically by use of a Hewlett-Packard Model 8451A diode array spectrometer.

Results and Discussion

Irradiation of an approximately 10^{-4} M solution of $[Ru(bpy)_2(N_3)_2]$ in $CHCl_3$ at either 546 or 436 nm caused no measurable reaction, although absorption occurs at both wavelengths. The charge-transfer band maximum for the complex lies at 560 nm. At 366 nm a very slow photoreaction did occur, but it amounted to less than 1% after 1 h. At 313 nm and below, photosubstitution occurred at measurable rates. Chloroform has a small absorbance at 313 nm ($A = 0.008$, measured against water). This raises the likelihood that it is $CHCl_3$, rather than Ru(II), that is the photoactive species. The C–Cl bond energy corresponds to a wavelength of approximately 365 nm, and bond homolysis is the expected photochemical outcome of $CHCl_3$ excitation.[6]

Conversion to the dichloro complex occurred in two distinct, slightly overlapping stages. When the course of the reaction was followed at 560 nm, for example, the absorbance first decreased and then increased until the spectrum of essentially pure $[Ru(bpy)_2Cl_2]$ resulted. The reaction could be stopped at any stage by removing the light source.

Figure 1 shows the first stage of this process, characterized by isosbestic points at 355, 441, and 484 nm. Figure 2 shows the second stage, characterized by isosbestic points at 336, 395, 476, and 567 nm. Several intermediate spectra, in which both processes occur, are omitted from the two figures. In solutions that had not been deaerated, a third stage occurred, the conversion of $[Ru(bpy)_2Cl_2]$ to $[Ru(bpy)_2Cl_2]^+$,[1] for which an isosbestic point at 342 nm was characteristic. When deaerated with carbon dioxide, a second intermediate appeared before conversion to $[Ru(bpy)_2Cl_2]$ was complete. It was not characterized.

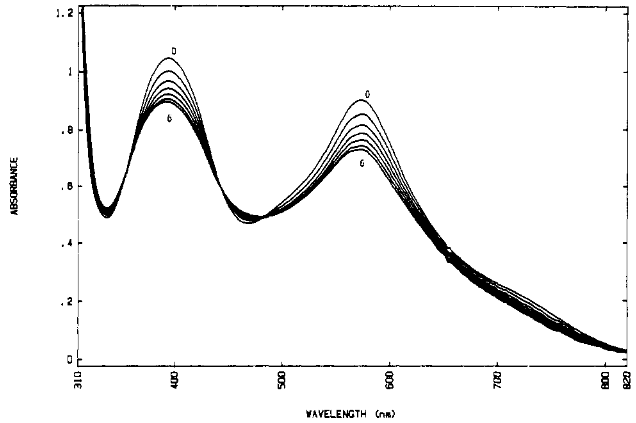

Figure 1. Results of irradiation of 1.312×10^{-4} M $[Ru(bpy)_2(N_3)_2]$ in $CHCl_3$ at an intensity of 2.2×10^{-9} einstein/s. Absorption spectra were taken at 1-min intervals. Absorbance changes at 560 nm are plotted in Figure 3.

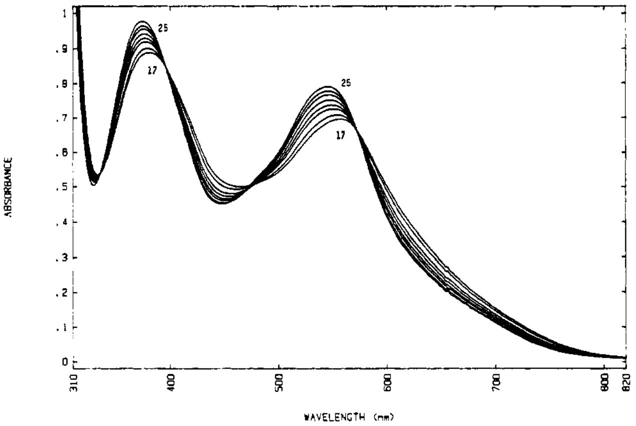

Figure 2. Results of irradiation of $[Ru(bpy)_2(N_3)_2]$ later in the course of the reaction. Absorption spectra are spaced at 1-min intervals, beginning at 17 min (spectrum for $t = 19$ min is missing). Absorbance changes at 560 nm are plotted in Figure 3.

For quantitative experiments a 1.312×10^{-4} M solution (determined spectrophotometrically) of $[Ru(bpy)_2(N_3)_2]$ was used. Initially, when the absorbance by the latter was 1.47 at 313 nm, the fraction of light absorbed by the chloroform was 0.005. It did not change greatly during irradiation, because the ruthenium(II) products have similar absorbances at 313 nm. The actinometrically determined incident light intensity was approximately 2.2×10^{-9} einstein/s in all experiments. The quantum yield ϕ was determined from the expression: Rate (M/s) = $[I_0(\text{einstein/s})]f[\phi(\text{mol/einstein})]/V(\text{L})$, where f is the fraction of light absorbed by the photoactive species, either $[Ru(bpy)_2(N_3)_2]$ ($f = f_{Ru}$) or the solvent ($f = f_S$).

In the first stage, conversion to the presumed $[Ru(bpy)_2(N_3)Cl]$ intermediate, the initial quantum yield, based on light absorbed by $CHCl_3$, was about 80 (as it was at 297 nm as well). In the early part of the reaction, the quantum yield for the first step decreased linearly with the $[Ru(bpy)_2(N_3)_2]$ concentration. This suggests a photoinitiated chain reaction. The first-order dependence on $[Ru(bpy)_2(N_3)_2]$ argues strongly against Ru(II) being the photoactive species. When the absorbance is that high, the fraction of light absorbed (f_{Ru}) changes little with concentration, so that a nearly zero-order dependence on $[Ru(bpy)_2(N_3)_2]$ would be expected if it were photoactive.

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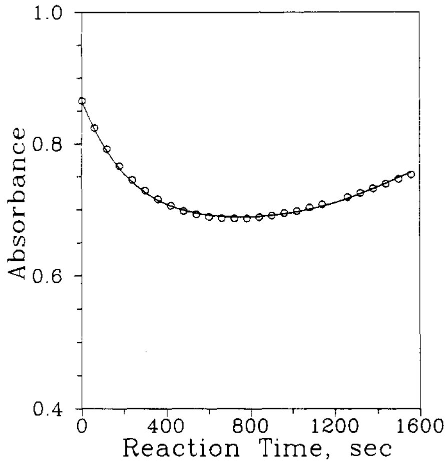

Figure 3. Absorbance at 560 nm of the solution resulting from the photolysis of $[Ru(bpy)_2(N_3)_2]$ in $CHCl_3$. Open circles are experimental points; the line was calculated numerically from eq 5, using $c_1 = 0.031$ s^{-1} and $c_2 = 0.0044$ s^{-1}.

The absorption of UV radiation by chloroform is accompanied by homolysis to $Cl^{\bullet}$ and $^{\bullet}CHCl_2$ radicals.[6] Both radicals can be expected to abstract a hydrogen upon encounter with the solvent, yielding $^{\bullet}CCl_3$ radicals, completing the initiation step. Propagation could occur in several ways, but one possibility is through hydrogen abstraction by the azido radical product.

$$^{\bullet}CCl_3 + [Ru(bpy)_2(N_3)_2] \rightarrow [Ru(bpy)_2(N_3)Cl] + :CCl_2 + {}^{\bullet}N_3 \quad (1)$$

$$^{\bullet}N_3 + CHCl_3 \rightarrow HN_3 + {}^{\bullet}CCl_3 \quad (2)$$

The same mechanism is presumed to apply to the second stage. It is also assumed that the termination steps operate to establish a steady-state concentration of $^{\bullet}CCl_3$ radicals that depends on the light intensity. If the process is represented as

$$\underset{A}{[Ru(bpy)_2(N_3)_2]} \xrightarrow{k_1} \underset{B}{[Ru(bpy)_2(N_3)Cl]} \xrightarrow{k_2} \underset{C}{[Ru(bpy)_2Cl_2]} \quad (3)$$

then

$$\frac{d[B]}{dt} = k_1[{}^{\bullet}CCl_3][A] \qquad \frac{d[C]}{dt} = k_2[{}^{\bullet}CCl_3][B] \quad (4)$$

The $[{}^{\bullet}CCl_3]$ concentration was expected to vary during the experiment with the fraction of light absorbed by $CHCl_3$, f_S. Introducing this proportionality,

$$\frac{d[B]}{dt} = c_1 f_S[A] \qquad \frac{d[C]}{dt} = c_2 f_S[B] \quad (5)$$

The constants c_1 and c_2 were optimized to fit the absorbance vs time data at 560 nm, approximating eq 5 numerically[7] and using the experimental extinction coefficients (M^{-1} cm^{-1}) at 560 nm of 6590 for A, 4450 for B, and 8440 for C. The resulting fit is shown in Figure 3, corresponding to $c_1 = 0.031(\pm 0.001)$ s^{-1} and $c_2 = 0.0044(\pm 0.0001)$ s^{-1}. It is not clear why the first reaction is faster, but this is responsible for the isosbestic points observed.

Chloride photosubstitution at a metal center in chlorinated solvents, without change of oxidation state, is not unknown,[8] but it is seldom attributed to direct homolysis of the solvent, unassisted by the metal. Excited-state metal complexes are also ordinarily invoked to explain photooxidation processes in chlorinated solvents.[9,10] The wavelength behavior often observed in these reactions makes it likely that at least some of them are actually initiated through direct homolysis of the solvent.

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