ARTICLES

An Iridium–Bipyridine Complex as a Photosensitizer for the Bromide Oxidation to Bromine by Oxygen

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An iridium(III)-bipyridine complex, $[Ir(C^3, N'-bpy)(bpy)_2]^{2+}$, was used as a photosensitizer in aqueous bromide solutions. Steady-state photolysis of oxygenated solutions by near-ultraviolet and visible light produces equal concentrations of Br₃⁻ and H_2O_2 . The quantum yield of Br_3^- equivalents depends on pH, illumination dose, and bromide concentration. The initial yield (extrapolated) reaches a value of 0.08. A mechanism involving two exciplexes and the transients Br₂- and HO₂ is proposed, based on products analysis, steady-state emission, and pulsed laser experiments.

Introduction

Watts, Ford, and Finlayson¹ reported the use of $[Ir(C^3, N'$ $bpy)(bpy)_2|^{2+}$ as a photosensitizer for electron-transfer reactions with a variety of quenchers. In all these systems, the excited state of the Ir-bipyridine complex appears as an electron acceptor, resulting in the formation of the corresponding Ir(II) complex. The latter is known as a strong reducing agent, capable of H_2 liberation from aqueous solutions.² $[Ir(C^3, N'-bpy)(bpy)_2]^{2+*}$ has been reported to luminesce, peaking at 482 and 518 nm. The lifetime of the excited state depends on the concentration of the ground state and equals 12.2 μ s in dilute (10⁻⁵ M) solutions at pH 1.³ The ground state has strong optical absorption in the UV region, extending to the blue part of the visible range.³ Thus, the photophysical properties of $[Ir(C^3, N'-bpy)(bpy)_2]^{2+}$ make it a suitable photosensitizer for the investigations of model systems for the photochemical storage of light energy by redox systems.

The present manuscript describes the photochemistry of [Ir- $(C^3, N'$ -bpy)(bpy)₂]²⁺ aqueous solutions containing bromide ions and oxygen, using this sytem as a model for the oxidation of bromide ions to bromine, photosensitized by visible light.

In addition to the basic interest in photochemical oxidations of systems which possess large redox potentials, such processes, particularly those involving halide ions, may be of considerable

practical importance in the commercial production of bromine and chlorine. Therefore, extensive work has been carried out on oxidations of halides (especially bromide and chloride) in both thermal and photochemical systems (mostly in the UV range). Photochemical oxidations of bromide, and of chloride, involve anthraquinonesulfonates,⁴ TiO_2 ,⁵ and platinized TiO_2^6 as photosensitizers. An interesting system is $FeBr_3^7$ which produces in aqueous solution FeBr₂ and Br₂ upon visible light absorption. Except for the platinized TiO₂ powder, which was reported to product Br_3^- with an initial quantum yield of about 0.3,⁶ other systems were reported to produce relatively low yields of Br_2 (or Cl₂), of a few percent. Yields higher than 5% are observed in photoassisted electrolysis of halide ion solutions with n-Si electrodes.⁸ Halide ions are also oxidized in illuminated silver zeolite suspensions in water.⁹ Several groups have used n-MoSe₂ with various combinations of halides and solvents for conversion of light to electricity.¹⁰ A photoelectrochemical halogen storage cell (using MoSe₂) has recently been reported.¹¹

Experimental Section

Materials. $[Ir(C^3, N'-bpy)(bpy)_2]Cl_2 \cdot 3H_2O$ was prepared by following the procedure of Watts, Harrington, and Van Houten.³

IrCl₃ (Aldrich), 2,2'-bipyridine (Sigma), KI (Merck, analytical reagent), KBr (Baker analyzed), HClO₄ (Merck analytical

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⁽¹⁾ Watts, J.; Ford, P. C.; Finalyson, M. F. "Book of Abstracts", 4th Interntional Conference on Photochemical Conversion and Storage of Solar Energy, Israel, 1982. (b) Bergeron, S. F.; Watts, R. J. J. Am. Chem. Soc. **1979**, 101, 3151. This complex was first synthesized by Watts et al.³ who suggested that one of the bpy ligands acts as a monodentate. In a recent study, Nord et al. (Nord, G.; Hazell, A. C.; Hazell, R. G.; Farver, O. *Inorg. Chem.* **1983**, 22, 3429) determined in an X-ray study the structure of the parent compound $[Ir(N,N' bpy)_2(C,N bpy)^{-1}^2+$ in which one of the bpy groups is bound to the iridium by one nitrogen and one carbon-metal bond. They suggested that Watt's complex is best described as $[Ir(N,N'-bpy)_2(C^3,N'$ bpy)-H₃O+]³⁻

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reagent), and uranyl oxalate (BDH, analytical) were used as received.

Illumination. The light source was a 100-W super high pressure Hg lamp (Osram HBO $100/w_2$). A water filter was placed between the lamp and the irradiation cell in order to absorb the infrared emission of the lamp.

The excitation wavelengths were selected by appropriate filters. Samples were illuminated at 20 ± 0.1 °C and were stirred during illumination by means of a Teflon-coated magnetic stirrer. Oxygenated samples were bubbled for 20 min prior to the illumination. The quartz cells were filled with 6.2 cm³ of the solution, above which was a 7.7-cm³ gas phase, all closed by a glass stopcock with Teflon o-ring. The light intensity was monitored with the aid of a small solar cell which absorbed a small fraction of the excitation light. The light signal of the monitor was found to be linear with light intensity in the range used. Actinometry was carried out using uranyl oxalate.¹² Optimal absorbance and slow kinetics were measured with the aid of a Bausch & Lomb Spectronic 2000 spectrophotometer. Emission was measured by an SLM 4800 spectrofluorimeter: excitation slits at 2 nm; emission slits at 1 nm.

Kinetic measurement of emission as well as transient absorption measurements were carried out using a Nd:YAG laser. The laser excitation beam, 10-mm high and 2-mm wide (by means of a cylindrical lens), entered the sample solutions at 90° to the analytical light. The analytical light source was a 150-W Xe lamp. The light signals were digitized and analyzed with the aid of a Biomation Model 8100 and Nicolet 1170. An IP28 photomultiplier and a B&L monochromator were used. Excitation wavelength was 355 nm. The time resolution was 50 ns. In order to avoid biphotonic effects a 4-cm cell with cobalt perchlorate solution transmitting 7% of the light at 355 nm was used between the laser and irradiation cell.

Analysis. As will be reported later, both Br_3^- and H_2O_2 were produced in our Br⁻ systems. The analysis of these species was based on their reaction with I⁻. A KI solution, buffered at pH 4.5 (acetate-acetic acid) was added to the test solution (I⁻ was 0.1-0.5 M). Under these conditions, Br3⁻ quickly oxidized I⁻ to I_3^- , and the absorption of I_3^- at 350 nm ($\epsilon = 2.64 \times 10^4 \text{ M}^{-1}$ cm^{-1})¹³ followed. H₂O₂ oxidizes I⁻ considerably slower. The final absorbance (after about 30 min) was used to determine the sum $[H_2O_2] + [Br_3]$, while the "initial" absorbance, obtained by extrapolation to the time of mixing gave the $[Br_3]$ alone. As will be discussed later, H₂O₂ slowly oxidizes Br⁻ ions.¹⁴ This reaction takes place, in part, during the time of illumination. Therefore, the concentrations of Br_3^- which we determined by the above procedure are consistently higher by up to 10% than those of H_2O_2 . The yield of Br_3^- and H_2O_2 reported in the following are based on the assumption that initially exactly equal concentrations of H₂O₂ and Br₃⁻ were produced. Appropriate control experiments which were carried out prove the reliability of this analytical method.

Analysis of H_2O_2 prepared from a stock solution (in the absence of Br⁻ and Br₃⁻) was carried out by the addition of FeSO₄ (10 mM) in 0.8 N H₂SO₄. The concentration of H₂O₂ was determined from the absorbance of Fe(III) which was produced by the oxidation of Fe(II). This method gave results identical with the iodide method. Control experiments for Br₃⁻ were also carried out. Br₂ was produced by Br⁻ oxidation with permanganate and the concentrations of Br₂ was determined with the aid of fluorescein.¹⁵ These results were identical with those from the iodide method.

Finally control solutions containing both H_2O_2 and Br_3^- were prepared from appropriate analyzed stock solutions of H_2O_2 and Br^-/Br_3^- . Analysis of the mixed solution with the aid of the iodide



Figure 1. Effect of the irradiation time on the quantum yield of Br_3^- : •, oxygenated solutions; O, aerated solutions. Illumination intensity 1.6 × 10^{-3} einstein/(L min); 3.5×10^{-5} M $[Ir(C^3, N'-bpy)(bpy)_2]^{2+}$; 0.64 M KBr, pH 1.5 (HClO₄); excitation wavelength 365 nm.



Figure 2. Effect of [Br⁻] on the quantum yield of Br₃⁻. Illumination time 15 min at λ (excitation) = 365 nm; 3.5 × 10⁻⁵ M [Ir(C^3 , N'-bpy)-(bpy)₂]²⁺; pH 1.5 (HClO₄), Θ_2 saturated. A: 1.61 × 10⁻³ einstein/(L min); B: 7 × 10⁻³ einstein/(L min).

method showed that the concentrations of H_2O_2 and Br_3^- in the mixed solutions could be determined with an accuracy of 2%. Control experiments also showed that the presence of the Ir complex did not interfere with the analysis. Unless otherwise stated, steady-state excitation was at 365 nm. Excitation light intensity was carried in the range 2×10^{-4} -7 $\times 10^{-3}$ einstein L⁻¹ min⁻¹ with the aid of neutral density filters.

Results

Steady-State Photolysis. When a solution containing $[Ir-(C^3, N'-bpy)(bpy)_2]^2+$ absorbs light in the presence of both Br⁻ ions and oxygen, Br₃⁻ and H₂O₂ are formed with a yield depending on pH, [Br⁻], [O₂], and the irradiation dose. The quantum yield of Br₃⁻ (calculated as the number of Br₂ + Br₃⁻ equivalents produced by one photon) decreases with the time of illumination, undoubtedly due to accumulation of products which participate in reactions competing with additional product formation. This effect is shown in Figure 1 for aerated and oxygenated solutions. Note that changing the light intensity by applying neutral filters while maintaining the same amount of total absorbed light has no effect on the quantum yield.

The quantum yield of Br^- decreases with the irradiation time, and the effect is more remarkable in the aerated solutions. Note that at very short irradiation times the quantum yield seems to be higher in the presence of air. The effect of $[Br^-]$ on the "initial" quantum yield of Br_3^- , at a constant radiation time, is demonstrated in Figure 2 (pH 1.5, HClO₄). The quantum yield observed

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Figure 3. Effect of pH on the quantum yield of Br_3^- . 3.5×10^{-5} M $[Ir(C^3,N'-bpy)(bpy)_2]^{2+}$; 0.64 M Br^- , O₂ saturated; illumination at 365 nm for 15 min; illumination intensity 1.6×10^{-3} einstein/(L min).



Figure 4. Emmision spectra at different Br⁻ concentrations (not corrected). Excitation at 355 nm. 3.5×10^{-5} M $[Ir(C^3, N'-bpy)(bpy)_2]^{2+}$; pH 1.5, He saturated. (---) no Br⁻; (--) 6.4×10^{-3} M Br⁻; (**m**) 1 M Br⁻; (--) 2 M Br⁻.

increases steadily with $[Br^-]$. Br^- , however, has no effect on the absorption spectrum of the ground state of the Ir complex.

The effect of pH on the quantum yield of Br_3^- is demonstrated in Figure 3, showing a decrease of the quantum yield when the pH is raised above 1.5. A relatively small yield $(6 \pm 1) \times 10^{-4}$ of Br_3^- is still observed at pH 4. The results correspond to an apparent pK of about 2.6. The quantum yield of Br_3^- is unaffected by variations in the concentration of the Ir complex ((3-14) × 10^{-5} M). It is unaffected also by the wavelength of the excitation light in the range 365-435 nm.

The iridium complex seems to be stable with respect to bromination. This conclusion is based on experiments carried out with oxygenated solutions containing 0.64 M Br⁻ in the presence of the iridium complex at pH 1. After 18 h of illumination at 365 nm, NaBH₄ was added to reduce the Br₃⁻ and H₂O₂ products. The spectrum of the illuminated solution was then taken and found to be identical with that observed in a control solution, indicating no net changes of the iridium complex.

Emission Measurements. Emission spectra at various Br^- concentrations are shown in Figure 4. At relatively low [Br^-] (<10 mM), the emission spectrum is practically identical with that observed in the absence of Br^- . There are two peaks, at 483 and 513.5 nm, in fair agreement with previously reported data.¹



Figure 5. Time profiles of typical emission signals; excitation at 355 nm, emission at 480 nm. 3.5×10^{-5} M $[Ir(C^3, N'-bpy)(bpy)_2]^{2+}$, pH 1.5, deoxygenated. A, no Br⁻ added; B, 6×10^{-3} M Br⁻; C, 2.5×10^{-1} M Br⁻. Emission vertical scale (arbitrary) is the same for A, B, and C. Vertical scale expanded by a factor of 2.15 in insert C.

Br⁻ quenches the emission, as can be seen from Figure 4. At relatively high [**Br**⁻] (>0.1 M) in addition to the quenching of most of the emission, a different spectrum is observed with two peaks at 488 and 525.6 nm and a shoulder at 511 nm. We assign the emission spectrum observed at concentrations of 1-2 M Br⁻ to the emission spectrum of the ([Ir(C^3 ,N'-bpy)(bpy)₂]Br₂⁻)* exciplex as will be explained later.

The Nd:YAG laser was employed for time-resolved measurements of the emission. Typical emission time profiles at 482 nm are shown in Figure 5. The decay of emission in the absence of Br⁻ is first order, yielding the natural (no quencher) reaction rate constant, $k_N = 1.43 \times 10^5 \text{ s}^{-1}$, at $3.5 \times 10^{-5} \text{ M} [\text{Ir}(C^3, N'$ byy)(byy)₂]²⁺ compared to $k_N = 8.20 \times 10^4 \text{ s}^{-1}$ at $1.0 \times 10^{-5} \text{ M}$ of the Ir complex which was reported by Watts et al.¹ Upon addition of $<10^{-2} \text{ M Br}^-$ the lifetime of the emission is shortened. The first-order nature of the decay is maintained, and the initial emission intensity is unchanged. The results agree with the assumption that dynamic quenching of the excited Ir(III) complex by Br⁻ takes place. At higher [Br⁻] two decay processes are observed; both show a first-order rate law. The rate of the faster process (in the following, the fast decay) is linear with [Br⁻], and corresponds to the rate at the low Br⁻ concentrations when only one reaction is observed.

The quenching rate constant of the Ir(III) emission by Br⁻, $k_q = (2.4 \pm 0.1) \times 10^7$ M⁻¹ s⁻¹, is obtained from the average of eight different Br⁻ concentrations in the range of 3 mM to 0.25 M. The fraction of the slower reaction (in the following, the slow decay), which increases steadily with [Br⁻], reaches a limiting value of 0.15 at >0.1 M Br⁻. It decays away according to a first-order rate law, the rate of decay increasing slightly with Br⁻. The results correspond to a decay of an additional Ir(III) excited state with a self-decay rate constant of $(1.5 \pm 0.4) \times 10^5$ s⁻¹. This excited state is also quenched by Br⁻, with a reaction rate constant of $(1.6 \pm 0.4) \times 10^5$ s⁻¹. The results are summarized in Table I.

Excitation spectra (1 M Br⁻) were also taken by using the spectrofluorimeter. The excitation spectra were identical, in the range 315-420 nm, with the absorption spectrum.

Absorption Measurements of Transients Formed in Experiments with a Pulsed Laser. Following a pulse of the Nd: YAG

TABLE I: Pulsed Laser Measurements of the Emission Intensities and Quenching Rates^a

	initial emission ^b	$k_2[Br^-],^d s^{-1}$	residual emission ^c	$k_{4},^{e} s^{-1}$
0	34	1.4×10^{5}		
3×10^{-3}	33	1.8×10^{5}		
6×10^{-3}	32	2.3×10^{5}		
10-2	30	3.6×10^{5}		
5×10^{-2}	30	1.6×10^{6}	(0.14)	1.5×10^{5}
10-1	30	3.3×10^{6}	(0.15)	
2.5×10^{-1}	31	7.8×10^{6}	(0.20)	2.1×10^{5}
5.0×10^{-1}	34	1.8×10^{7}	(0.14)	
7.5×10^{-1}			0.14	2.6×10^{5}
1.0			0.13	3.2×10^{5}

 $^{a}3.5 \times 10^{-5}$ M $[Ir(C^{3},N'-bpy)(bpy)_{2}]^{2+}$, pH 1.5, deaerated solutions. ^bArbitrary units. ^cAs a fraction of the initial emission. ^d"fast" process. ^eSlow" process.

laser at 355 nm, a solution containing 3.5×10^{-5} M of the Ir(III) complex and 0.6 M Br⁻, air-saturated at pH 1.5, showed a small absorption at 360 nm which decayed away in the time range of milliseconds. If this absorption is attributed to Br₂⁻, it corresponds to a quantum yield of 0.023 ($\epsilon_{Br_2}^{360}$ = 13 000 M⁻¹ cm⁻¹).¹⁶ This yield is comparable to the yield of Br₃⁻ in the steady-state experiments, and will be discussed later. No absorption was observed in identical solutions which contain 6 mM Br⁻.

Discussion

Loeff, Treinin, and Linschitz^{4a} measured the quenching of 9,10-anthraquinone-2-sulfonate by various inorganic anions, including halides. They found no product formation at relatively low halide concentrations, although their halide concentrations were sufficient to suppress the triplet state of the quinone. At relatively high halide concentrations, optical absorptions due to short-lived transients were observed and attributed to electron-transfer transients. These results were interpreted by assuming two exciplexes involving Br atom and Br_2^{-} anion radical, respectively, bound to the semiquinone.

According to Treinin, Loeff, Hurley, and Linschitz,¹⁷ the probability of product separation depends on the intraradical spin-orbit coupling, so that an exciplex with Br atom is quickly converted to the ground-state initial reactants while the second exciplex (with Br_2^{-}) lives sufficiently long and may produce the radical species Br_2^{-} and the semiquinone.

Our results support the work of these authors.^{4a,17} The emission spectrum of $[Ir(C^3, N'-bpy)(bpy)_2]^{2+*}$ is attributed to the lowest "triplet" state. Br⁻ reacts with the triplet and produces an exciplex, according to eq 2. The exciplex on the right-hand side of eq 2,

$$[\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]^{2+} \xrightarrow{h_{\nu}} [\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]^{2+*} (1)$$

 $[Ir(C^{3},N'-bpy)(bpy)_{2}]^{2+*} + Br^{-} \rightarrow ([Ir(C^{3},N'-bpy)(bpy)_{2}]Br)^{+*} (2)$

in the following, "the Br exciplex" does not emit light, but rather decays quickly to produce the ground-state reactants according to eq 3. At higher Br^- concentrations, reaction 4 competes with

$$([Ir(C3,N'-bpy)(bpy)_2]Br)^{+*} \rightarrow [Ir(C3,N'-bpy)(bpy)_2]^{2+} + Br^{-}$$
(3)

$$([Ir(C^{3},N'-bpy)(bpy)_{2}]Br)^{+*} + Br^{-} \rightarrow ([Ir(C^{3},N'-bpy)(bpy)_{2}]Br_{2}^{-})^{*} (4)$$

reaction 3. The product on the right-hand side of eq 4 (in the following, "the Br_2^- exciplex") is responsible for the slower reaction observed when the emission is measured at high [Br⁻] (Figure 5).

Indeed, the emission spectrum of $[Ir(C^3, N'-bpy)(bpy)_2]^{2^*}$ which is observed in the absence of Br⁻ as well as at low [Br⁻] (Figure 4), is different from the emission of $([Ir(C^3, N'-bpy)(bpy)_2]Br_2^{-})^*$ which is taken at high [Br⁻] (Figure 4). (At 1–2 M, the emission of $[Ir(C^3, N'-bpy)(bpy)_2]^{2^{+*}}$ is totally suppressed.) Although these spectra were recorded in steady-state measurements it is clear that these are two different emitting species. The combination of the steady-state results with the kinetic measurements of the emission (Figure 5 and Table I) is in accord with the suggestion for the nature of the emitting species.

The assignment of the long-lived emission to the Br_2^{-} exciplex is not the only possibility to explain the results. In fact, it raises some questions. First, the lifetimes of most exciplexes are shorter by several orders of magnitude. Second, the long lifetime would give the exciplex time to dissociate Br_2^{-} and thus the Br_2^{-} quantum yield might be expected to be higher compared with the observed quantum yield. Alternatively, a complex between Br_2^{-} and the iridium complex might exist. In the absence of clear evidence, we will discuss the system in terms of the "exciplex model".

From Table I, $k_2 = (2.4 \pm 0.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The specific rates of reactions 3 and 4 cannot be determined due to insufficient time separation between reaction 2 and 4 and the much stronger emission of the Ir triplet as compared to the Br₂⁻ exciplex. However since the Br₂⁻ exciplex is observed at >10⁻² M Br⁻, we can roughly estimate $k_3 < 10^8 \text{ s}^{-1}$ (based on the upper limit of $k_4 = 10^{10} \text{ M}^{-1}$). Br⁻, at concentrations up to 2 M, does not quench the excited singlet state of the $[\text{Ir}(C^3, N' \text{-bpy})(\text{bpy})_2]^{2+*}$. This is evident since the initial intensity of the emission (measured at or extrapolated to time zero) does not depend on [Br⁻].

The effect of Br^- concentration on the lifetime of the slow emission, Figure 5, and on the yield of Br_3^- in the steady-state photolysis experiments indicates that a further reaction of the $Br_2^$ exciplex with Br^- occurs. As the mechanism of formation of $Br_3^$ probably involves Br_2^- as an intermediate, we propose the following additional reactions as an explanation of the experimental observations.

$$([\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]\operatorname{Br}_2^{-})^* \rightarrow [\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]^+ + \operatorname{Br}_2^{-} (5)$$

$$([\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]\operatorname{Br}_2^{-})^* \rightarrow [\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]^{2+} + 2\operatorname{Br}^{-}(6)$$

$$([Ir(C^{3},N'-bpy)(bpy)_{2}]Br_{2}^{-})^{*} \rightarrow [Ir(C^{3},N'-bpy)(bpy)_{2}]^{2+} + 2Br^{-} + h\nu \quad (7)$$

$$([\operatorname{Ir}(C^{3}, N' \operatorname{bpy})(\operatorname{bpy})_{2}]\operatorname{Br}_{2}^{-} \cdot)^{*} + \operatorname{Br}^{-} \rightarrow ([\operatorname{Ir}(C^{3}, N' \operatorname{bpy})(\operatorname{bpy})_{2}]\operatorname{Br})^{*} + \operatorname{Br}_{2}^{-} \cdot \rightarrow [\operatorname{Ir}(C^{3}, N' \operatorname{bpy})(\operatorname{bpy})_{2}]^{+} + \operatorname{Br}_{2}^{-} \cdot + \operatorname{Br}^{-} (8)$$

$$Br_2 \cdot + Br_2 \cdot \rightarrow Br + Br_3 \tag{9}$$

$$k_9 = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$
 (ref 16)

Reaction 9 is followed by equilibrium (reaction 10), $K_{10} = 16.9$.¹⁶

$$Br_2 + Br^- \rightleftharpoons Br_3^- \tag{10}$$

Reaction 5, which represents the unimolecular formation of Br_2^- from the Br_2^- exciplex competes with reactions 6 and 7. Reaction 5 may account for the relatively small yields of Br_3^- observed at relatively low $[Br^-]$, such as $10^{-2}-10^{-1}$ M (see Figure 2), where reaction 8 is still unimportant. Reaction 8 probably involves a bromide atom transfer between Br_2^- and Br^- , followed by fast deactivation. It accounts for the continuous increase in the yield of Br_3^- (and Br_2^-) with Br^- even at the highest Br^- concentrations. If reaction 8 did not take place the yield of Br_3^- would be expected to level off at the highest Br^- concentrations, contrary to our observations.

In the steady-state photolysis, H_2O_2 is observed along with Br_3^- . Since H_2O_2 is known to slowly oxidize $Br^{-,14}$ the yield of Br_3^- is always higher than the yield of H_2O_2 . However, from results at short times, we conclude that initially equal concentrations of $Br_3^$ and H_2O_2 are produced.

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The formation of H_2O_2 involves reactions 11 and 12. Reaction

$$[Ir(C^{3}, N'-bpy)(bpy)_{2}]^{+} + O_{2} \xrightarrow{H_{3}O^{+}} [Ir(C^{3}, N'-bpy)(bpy)_{2}]^{2+} + HO_{2^{*}} (11)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
(12)

11 was measured to be very fast.¹⁹ The product, HO₂, is an acid, pK = 4.75.²⁰ At pH <3, $K_{12} = 7.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ Another expected reaction of HO₂· is the oxidation of Br₂⁻ according to reaction 13, $k_{13} = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²⁰

$$HO_2 + Br_2 \rightarrow \xrightarrow{H^*, Br^-} H_2O_2 + Br_3 \qquad (13)$$

Reaction 13 is expected to contribute to additional formation of Br_3^- . Br_2^- ion radicals reacting according to reaction 9 produce one equivalent of Br_3^- while Br_2^- reacting according to reaction 13 produces two equivalents of Br_3^- . The reaction rate constants k_9 , k_{12} , and k_{13} predict that only a fraction of the Br_2^- will react with HO₂. Comparison between the Br_2^- yield at the end of reaction 8 (pulsed laser experiments) and the yield of Br_3^- in the steady-state illuminations (extrapolated to time zero, O₂ saturated, 0.64 M Br⁻) suggests that the yield of Br_3^- equivalents is somewhat higher than the yield of Br_2^- . This indicates that reaction 13 does contribute to the reaction mechanism. The accuracy of our measurements and a possible effect of impurities in the steady-state experiments does not enable quantitative analysis. Note that reaction 14 is expected to decrease the Br_3^- yield.

$$HO_2 + Br_2(Br_3) \rightarrow H^+ + Br_2 \rightarrow + O_2$$
(14)

We have no evidence that reaction 14 indeed takes place under our experimental conditions. If reaction 14 is important, it is expected to be pseudo first order, after some Br_3^- has accumulated. The other reactions that would compete with (14) are (12) and (13). Such a competition is expected to depend on the light intensity, in contradiction with our results which give the same yields of Br_3^- at different light intensities. The decrease of the quantum yield of Br_3^- (and Br_2) with irradiation time can be explained by the competition between reactions 11 and 15. This

$$[\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]^+ + \operatorname{Br}_3^- \rightarrow [\operatorname{Ir}(C^3, N'\operatorname{bpy})(\operatorname{bpy})_2]^{2+} + \operatorname{Br}^- + \operatorname{Br}_2^- \cdot (15)$$

suggestion is supported by the oxygen effect on the Br_3^- yield. Figure 1 shows that in oxygenated solutions Br_3^- is better protected from the back reactions than in aerated solutions.

At relatively low doses of light, the yield of Br_3^- in air roughly equals that in oxygen-saturated solutions (Figure 1). This is expected because the initial Br_3^- yield, before reaction 15 becomes significant, is not affected by the rate of reaction 11. Luminescence measurements confirmed the quenching of both [Ir- $(C^3, N'$ -bpy)(bpy)₂]^{2+*} and ([Ir(C^3, N' -bpy)(bpy)₂] Br_2^-)* by O₂ with rate constants (5±1) × 10⁸ and ~7 × 10⁸ M⁻¹ s⁻¹, respectively. At high (Br⁻] O₂ has two opposing effects on the yield of Br₃⁻. Via reaction 11, it contributes to increase the yield of Br₃⁻, while by the quenching of the "Br₂⁻ exciplex" it decreases the Br₃⁻ yield. Note that quenching of the initial triplet iridium complex by O₂ cannot compete with reaction 2. Also, the short lifetime of the "Br exciplex" makes it unlikely to react with O₂.

In fact, the limiting yield of Br_3^- at doses approaching zero is expected to be higher in aerated, as compared to oxygenated, solutions. The accuracy of the analytical method did not enable us to measure under such conditions.

The effect of pH on the yield of Br_3^- (Figure 3) indicates that the acid form of the iridium complex is considerably more active as compared to the basic form. The change of the Br_3^- yield with pH seems to be related to the pK of the ground state of [Ir-(C^3 ,N'-bpy)(bpy)₂]²⁺ which has been reported to be 3.0.³ HO₂. has a pK at 4.75,¹⁹ and Figure 3 clearly shows a strong pH dependency far below this pH, indicating that the acid dissociation of the Ir complex, and not the HO₂. is responsible for the pH effect.

Energy Storage. The net effect of the photolysis of the Br^- oxygen system is the formation of Br_3^- (in equilibrium with bromine) and H_2O_2 according to equation 16. This reaction,

$$3Br^{-} + O_2 + 2H^+ \rightarrow H_2O_2 + Br_3^{-}$$
 (16)

under standard conditions, is uphill by 32 kcal/mol, based on the standard redox potentials of the systems involved. Our experiments have not been carried out under standard conditions, as H_2O_2 and Br_3^- are at activities considerably lower than 1 M. Under our conditions of a typical experiment, e.g., when 10^{-3} M of the H_2O_2 and Br_3^- have been accumulated at pH 1.5, temporary storage of 12.9 kcal/mol is obtained.

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Registry No. $[Ir(C^3, N'-bpy)(bpy)_2]^{2+}$, 87137-18-6; Br⁻, 24959-67-9; H₂O₂, 7722-84-1; Br₃⁻, 14522-80-6; Br₂, 7726-95-6; O₂, 7782-44-7.

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