

Visible Light Driven Nanosecond Bromide Oxidation by a Ru Complex with Subsequent Br–Br Bond Formation

Guocan Li,[†] William M. Ward,[‡] and Gerald J. Meyer^{*,†}

[†]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States

[‡]Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States

ABSTRACT: Visible light excitation of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ (deeb = 4,4'-diethylester-2,2'-bipyridine; bpz = 2,2'-bipyrazine), in Br^- acetone solutions, led to the formation of Br–Br bonds in the form of dibromide, $\text{Br}_2^{\bullet-}$. This light reactivity stores ~ 1.65 eV of free energy for milliseconds. Combined ^1H NMR, UV–vis and photoluminescence measurements revealed two distinct mechanisms. The first involves diffusional quenching of the excited state by Br^- with a rate constant of $(8.1 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. At high Br^- concentrations, an inner-sphere pathway is dominant that involves the association of Br^- , most likely with the 3,3'-H atoms of a bpz ligand, before electron transfer from Br^- to the excited state, $k_{\text{et}} = (2.5 \pm 0.3) \times 10^7 \text{ s}^{-1}$. In both mechanisms, the direct photoproduct Br^\bullet subsequently reacts with Br^- to yield dibromide, $\text{Br}^\bullet + \text{Br}^- \rightarrow \text{Br}_2^{\bullet-}$. Under pseudo-first-order conditions, this occurs with a rate constant of $(1.1 \pm 0.4) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ that was, within experimental error, the same as that measured when Br^\bullet were generated with ultraviolet light. Application of Marcus theory to the sensitized reaction provided an estimate of the Br^\bullet formal reduction potential $E(\text{Br}^\bullet/\text{Br}^-) = 1.22 \text{ V}$ vs SCE in acetone, which is about 460 mV less positive than the accepted value in H_2O . The results demonstrate that Br^- oxidation by molecular excited states can be rapid and useful for solar energy conversion.

The formation of chemical bonds with visible light is of relevance to solar energy conversion and storage.¹ In particular, the sustained splitting of HBr to yield $\text{H}_2(\text{g})$ and Br–Br bonded products is of both fundamental and practical interest,² yet requires semiconductor electrodes and/or ultraviolet light.³ The use of molecular excited states to drive this chemistry is advantageous, as the reactivity can be understood and optimized on a molecular level. Herein it is reported that visible light excitation of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$, where deeb is 4,4'-diethylester-2,2'-bipyridine and bpz is 2,2'-bipyrazine,⁴ in Br^- acetone solutions generates Br atoms as primary photochemical products that subsequently react with a Br^- to yield Br–Br bonds. Interestingly, two mechanistic pathways were identified for this reaction. Under optimal conditions, excited state electron transfer was fast, $k_{\text{et}} = (2.5 \pm 0.3) \times 10^7 \text{ s}^{-1}$. Application of Marcus theory provided an estimate of the standard Br^\bullet reduction potential. To the best of our knowledge, this report represents the first example of visible light driven bromide oxidation by a molecular excited state.

The $[\text{Ru}(\text{deeb})(\text{bpz})_2](\text{PF}_6)_2$ complex was prepared according to a published procedure.⁵ Figure 1a shows that the visible

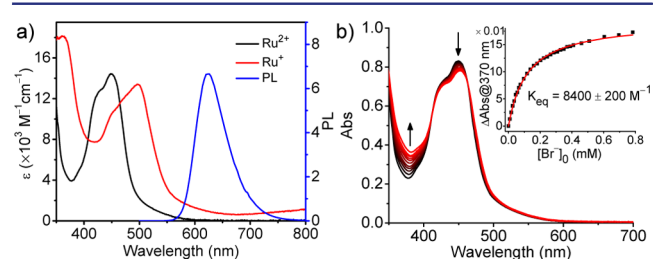
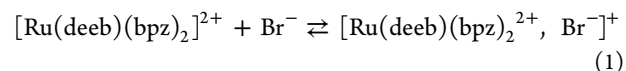


Figure 1. (a) Absorption spectra of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ (black), and the 1-electron reduced form, $[\text{Ru}(\text{deeb})(\text{bpz})(\text{bpz})]^+$ (red), as well as the PL spectrum of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+*}$ (blue) in acetone. (b) Absorption change of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ in acetone with the addition of TBABr. Inset: absorption change at 370 nm as a function of Br^- concentration and an overlaid fit from which the equilibrium constant was abstracted.

absorption spectrum of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ in acetone is dominated by two overlapping metal-to-ligand charge transfer (MLCT) absorption bands centered at about 450 and 425 nm. Addition of tetrabutyl ammonium bromide, TBABr, induced an appreciable change in the absorption spectrum, attributed to ground state adduct formation.⁶ A slight bleach of the MLCT absorption band and a growth at 370 nm were observed. Two isosbestic points at 410 and 460 nm were maintained, indicative of a single equilibrium between $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ and Br^- , eq 1. A previously described Benesi–Hildebrand-type analysis was used to extract the equilibrium constant, K_{eq} , of $8400 \pm 200 \text{ M}^{-1}$ from the titration data, Figure 1b inset.^{6b}

Bromide titrations with $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ in CD_3CN monitored by ^1H NMR spectroscopy revealed that Br^- induced a significant downfield shift in the 3 and 3' hydrogen atoms of the bpz ligands. Resonances from both of the bpz ligands shifted unequally when less than 1 equiv of Br^- was present, indicative of slow Br^- exchange on the NMR time scale.



Visible light excitation into the MLCT absorption bands resulted in room temperature photoluminescence, PL, with a maximum at 630 nm, Figure 1a, and a quantum yield of 9.0%.

Three successive ligand-based reductions were observed by cyclic voltammetry in a 0.1 M TBAPF₆ acetone electrolyte

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solution. By analogy to related complexes,^{5a} the first reduction at -0.73 V vs SCE was bpz based, from which the excited state potential $E(\text{Ru}^{2+*/+})$ was calculated to be 1.45 V vs SCE; $E(\text{Ru}^{2+*/+}) = E(\text{Ru}^{\text{II}/+}) + \Delta G_{\text{es}}$. Thus, the MLCT excited state of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ is a potent photo-oxidant in acetone.

Bromide addition was found to dramatically quench the PL intensity. An ~ 10 nm red shift accompanied a significant decrease in the PL intensity. Stern–Volmer plots of the steady state PL data were nonlinear and displayed upward curvature. To better understand the nature of the nonlinear Stern–Volmer plots, time-resolved PL measurements were made, Figure 2a. In neat acetone, excited state relaxation was first-

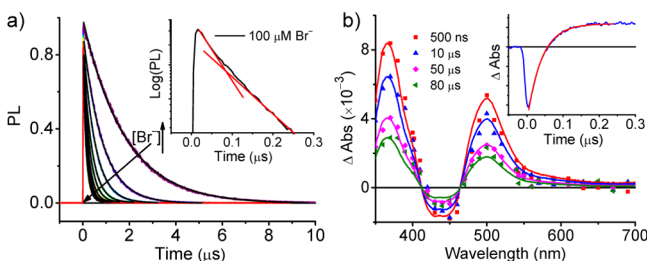


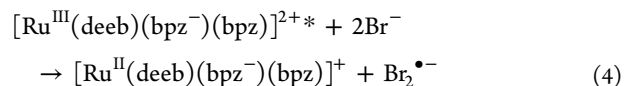
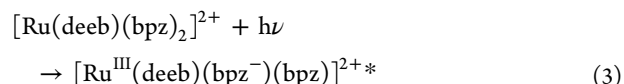
Figure 2. (a) Time-resolved PL of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+*}$ with increasing $[\text{Br}^-]$ in acetone. Inset: log of the PL intensity with $100 \mu\text{M}$ Br^- present and overlaid linear fits (red) to biexponential kinetic model. (b) Absorption change measured after pulsed 532 nm laser excitation of $50 \mu\text{M}$ $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ and $100 \mu\text{M}$ Br^- . The solid lines are simulated absorption spectra based on equivalent amount of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^+$ and $\text{Br}_2^{\bullet-}$. Inset: absorption change of $50 \mu\text{M}$ $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ and 1 mM Br^- in acetone at 500 nm after pulsed laser excitation at 532 nm. Overlaid in red is single exponential fitting with fixed lifetime of 40 ns.

order with a lifetime of $1.75 \mu\text{s}$. The addition of Br^- resulted in the appearance of non-exponential relaxation that was well described by a biexponential kinetic model, eq 2.

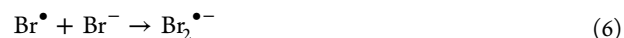
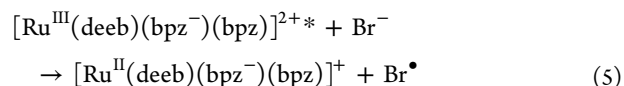
$$\text{PL}(t) = \alpha_s \exp(-t/\tau_s) + \alpha_d \exp(-t/\tau_d) \quad (2)$$

Interestingly, when a large excess (>100 -fold) of Br^- was present, excited state relaxation was again first-order with a 40 ± 5 ns lifetime, τ_s , that was independent of the $[\text{Br}^-]$. In contrast, τ_d was first-order in the free $[\text{Br}^-]$ and a Stern–Volmer analysis yielded $K_{\text{SV}} = (1.4 \pm 0.1) \times 10^5 \text{ M}^{-1}$ corresponding to $k_q = (8.1 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Significantly, the relative amplitudes of the two components, α_s/α_d , were directly correlated with the $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}, \text{Br}^-/[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ concentration ratio abstracted from the ground state absorption spectra. This provides compelling evidence that τ_s was the lifetime of the $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}, \text{Br}^-$ adduct and τ_d was the lifetime of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+*}$.

Pulsed 532 nm light excitation of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ in acetone led to transient absorption spectra consistent with the formation of the MLCT excited state, eq 3. When excess Br^- was present, long-lived absorption features were observed that exhibited two positive bands at 360 and 500 nm. The transient data were well modeled by standard addition of equal concentrations of $\text{Br}_2^{\bullet-}$ and $[\text{Ru}^{\text{II}}(\text{deeb})(\text{bpz})(\text{bpz})]^+$, Figure 2b. Thus, the net photochemistry stoichiometry was well described by eq 4. The reduced Ru complex absorbs light predominantly at 500 nm, whereas both $\text{Br}_2^{\bullet-}$ and the reduced complex absorb at 360 nm.



As written, the stoichiometry of eq 4 implies a termolecular reaction. Two underlying mechanism(s) for $\text{Br}_2^{\bullet-}$ were identified. The first was most relevant at low Br^- concentrations, where the appearance of the reduced Ru complex displayed biphasic kinetics. The dominant slower component displayed a first-order dependence on the Br^- concentration. These data provided a second-order rate constant for the formation of the reduced Ru complex, $(8.1 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, that was, within experimental error, the same as the quenching constant obtained from Stern–Volmer analysis. This identifies $[\text{Ru}(\text{deeb})(\text{bpz})_2]^+$ as a primary photoproduct of the excited state reaction. The rate constant for the formation of $\text{Br}_2^{\bullet-}$ was found to be $(1.1 \pm 0.4) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, about 8 times smaller than excited state relaxation, indicating that $\text{Br}_2^{\bullet-}$ was not a primary photoproduct. These data suggest that the mechanism for Br–Br bond formation first involves electron transfer from Br^- to the Ru^{III} metal center in the excited state, to yield a Br atom and the reduced ruthenium complex, eq 5. The Br atom then reacts with Br^- to yield $\text{Br}_2^{\bullet-}$, eq 6. The Br atom was not directly observed, but its presence was inferred by the subsequent appearance of $\text{Br}_2^{\bullet-}$. Additional evidence for this mechanism comes from studies where Br atoms were generated in Br^- acetone solutions with ultraviolet light; a second-order rate constant of $(9.2 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for reaction 6, that was, within experimental error, the same as that measured for the sensitized reaction.



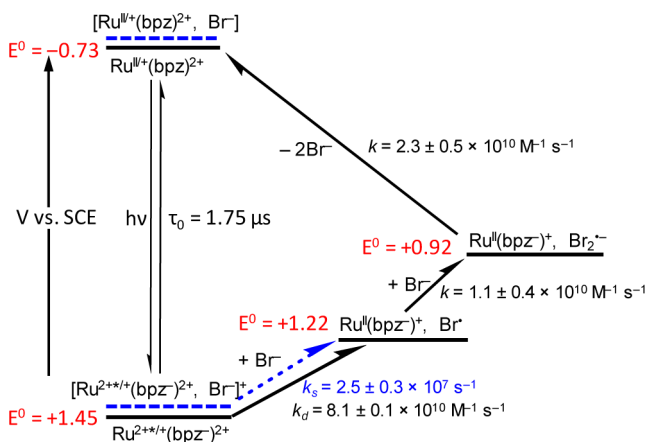
The second mechanism prevails at very high Br^- concentrations where the equilibrium in eq 1 falls far to the right, Figure 2b inset. Excited state electron transfer occurs by an inner-sphere pathway with a rate constant $k_{\text{et}} = (2.5 \pm 0.3) \times 10^7 \text{ s}^{-1}$. The appearance of $\text{Br}_2^{\bullet-}$ again occurred on a much slower time scale indicating that Br^\bullet was the primary product.

Based on the observed dynamic quenching constant, the free energy change for the excited state electron transfer reaction ΔG° was estimated by Marcus theory to be -0.23 eV with the assumptions that $A = 10^{11} \text{ s}^{-1}$ and $\lambda = 1$ eV, equation 7.⁷ Since the excited state reduction potential $E(\text{Ru}^{2+*/+})$ was calculated to be 1.45 V, this affords an $E(\text{Br}^\bullet/\text{Br}^-) = 1.22$ V (vs SCE) in acetone, which is 460 mV less positive than the accepted value in water.⁸

$$k_{\text{et}} = A \exp \left[\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda RT} \right] \quad (7)$$

As shown in Scheme 1, photo-oxidation of bromide by $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+*}$ was 230 mV downhill and yielded Br^\bullet as a direct photoproduct that subsequently reacted with a Br^- to form the Br–Br bond. At high Br^- concentrations excited state electron transfer was rapid and facilitated by an inner-sphere pathway (dashed lines) while at lower Br^- concentrations a

Scheme 1. Jablonski-Type Diagram of the Kinetic and Energetic Information of Bromide Oxidation by $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ *



*Dashed lines and arrow represent the $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}, \text{Br}^-$ adduct and corresponding static quenching pathway, respectively. A bpz and deeb ligand were removed for clarity.

dynamic pathway was also evident. The bond forming reaction of the Br atom results in a free energy loss that was estimated to be ~ 0.3 eV based on data obtained in aqueous solution.⁸ Recombination to yield ground state products occurred with a rate constant of $(2.3 \pm 0.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Thus, $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ was able to convert a visible photon to the free energy stored in the Br–Br bonded $\text{Br}_2^{\bullet-}$ and the reduced Ru complex for milliseconds.

In conclusion, bromide oxidation by the MLCT excited state of $[\text{Ru}(\text{deeb})(\text{bpz})_2]^{2+}$ proceeded by two distinct pathways in acetone. At high Br^- concentrations an inner-sphere mechanism was operative that generated Br atoms with a large first-order rate constant, $(2.5 \pm 0.3) \times 10^7 \text{ s}^{-1}$. Mechanistic studies provided compelling evidence that Br^\bullet was the primary photochemical product and an intermediate in the generation of Br–Br bonds in the form of $\text{Br}_2^{\bullet-}$. Marcus theory provided $E(\text{Br}^\bullet/\text{Br}^-) = 1.22$ V (vs SCE) in acetone. This study provides the first example of visible light driven Br–Br bond formation with a molecular excited state and shows that ion-pair formation can provide an inner-sphere electron transfer pathway that supports nanosecond Br^- oxidation, behavior that can potentially be exploited in dye-sensitized and photoelectrochemical solar cells.⁹

AUTHOR INFORMATION

Corresponding Author

*gjmeier@email.unc.edu

Notes

The authors declare no competing financial interest.

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