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Flash-Quench Technique Employed To Study the One-Electron Reduction of Triiodide in Acetonitrile: Evidence for a Diiodide Reaction Product

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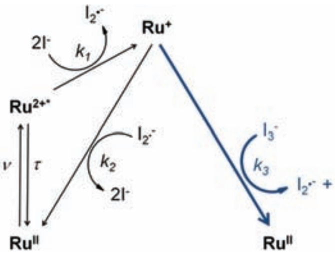
The one-electron reduction of triiodide (I_3^-) by a reduced ruthenium polypyridyl compound was studied in an acetonitrile solution with the flash-quench technique. Reductive quenching of the metal-to-ligand charge-transfer excited state of $[Ru^{II}(deeb)_3]^{2+}$ by iodide generated the reduced ruthenium compound $[Ru^{II}(deeb^-)(deeb)_2]^+$ and diiodide ($I_2^{\bullet-}$). The subsequent reaction of $[Ru^{II}(deeb^-)(deeb)_2]^+$ with I_3^- indicated that $I_2^{\bullet-}$ was a product that appeared with a second-order rate constant of $(5.1 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$. After correction for diffusion and some assumptions, Marcus theory predicted a formal potential of -0.58 V (vs SCE) for the one-electron reduction of I_3^-. The relevance of this reaction to solar energy conversion is discussed.

Iodide and triiodide have emerged as optimal redox mediators for regenerative dye-sensitized solar cells based on mesoporous TiO_2 thin films.[1−3] Mediator solutions are typically prepared with 0.5 M LiI and 0.05 M I_2 in acetonitrile. The relevant equilibrium shown below has $K_{eq} > 10^7\ M^{-1}$, which is much larger than the value in water, ~750 M^{-1}, such that I_3^- is produced in significant quantities.[1]

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (1)$$

The function of this mediator is well understood: (1) iodide reduces the oxidized dye molecule after electron injection into TiO_2, and (2) the eventual oxidized iodide product, I_3^-, diffuses to a platinum counter electrode to complete the circuit. Many alternative mediator donors accomplish the first step quantitatively yet still yield very poor solar conversion efficiencies because of an unwanted recombination between the injected electrons and oxidized donors.[1] What makes the I^-/I_3^- system special is, therefore, the fact that I_3^- is able to avoid recombination as it diffuses through a ~10-μm-thick mesoporous TiO_2 film. Why the injected electrons do not reduce I_3^- efficiently is unknown. This question is difficult to address because such a recombination is generally assumed to involve one electron,[2] limiting the use of conventional electrochemistry techniques where two-electron chemistry dominates.[4,5] Stopped-flow[6,7] and pulse-radiolysis[8] measurements that could provide insight have largely been limited to aqueous solution. Here we report application of the flash-quench technique[9] to characterize the reduction of I_3^- in acetonitrile. The data provide the first direct evidence that diiodide ($I_2^{\bullet-}$) is a reaction product and allow for an estimation of the formal potential for the one-electron reduction of I_3^-.

Scheme 1



The strategy for the flash-quench experiment is shown in Scheme 1, and a typical experiment is described below. Pulsed-laser excitation of $[Ru^{II}(deeb)_3](PF_6)_2$, where bpy is 2,2′-bipyridine and deeb is 4,4′-$(CO_2CH_2CH_3)_2$-2,2′-bipyridine, in argon-saturated acetonitrile yields the metal-to-ligand charge-transfer excited state (Ru^{2+*}) with a lifetime of 2.1 μs. Ru^{2+*} is a potent photooxidant, $E°(Ru^{2+*}/^+) = +1.28$ V (vs SCE), that efficiently oxidizes iodide, $k_1 = 4.8 \times 10^{10}\ M^{-1}\ s^{-1}$. In typical experiments, millimolar concentrations of tetrabutylammonium iodide (TBAI) were used to reductively quench the excited-state lifetime to <50 ns. Transient absorption studies revealed characteristic features expected for $[Ru^{II}(deeb^-)(deeb)_2]^+$ (Ru^+) and $I_2^{\bullet-}$. Recombination between Ru^+ and $I_2^{\bullet-}$ to yield ground-state products is energetically favored; however, the presence of excess I_3^- effectively suppresses this reaction and enables a study of

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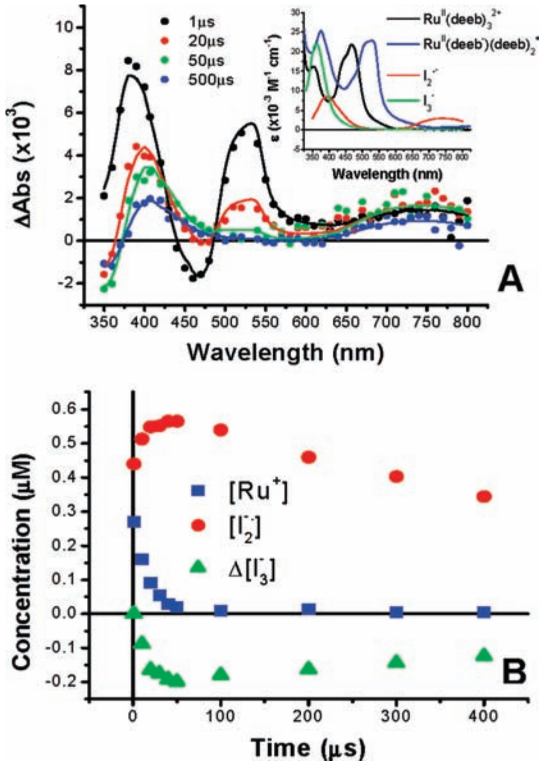

Figure 1. (A) Transient absorbance spectra recorded at the indicated delay times after 532 nm pulsed-laser excitation (8 ns fwhm, 10 mJ/pulse) of an argon-purged acetonitrile solution that contained 30 μM [Ru^{II}(deeb)$_3$]-(PF$_6$)$_2$, 7 mM TBAI, and 9 μM TBAI$_3$. Solid lines are simulated spectra based on the standard addition of Ru^+, $I_2^{\bullet -}$, and I_3^- extinction coefficient spectra (inset) subtracted from the ground-state spectrum. (B) Concentration vs time plot resulting from spectral modeling.

the one-electron reduction of I_3^-. It is worth mentioning that previous studies have shown that the mechanism of $I_2^{\bullet -}$ formation via iodide oxidation can involve iodine atoms and/or iodide ion pairs.[10−14] The detailed mechanism of iodide oxidation was, however, not the focus of this work.

Transient absorption changes measured after 532 nm pulsed-laser excitation of [Ru^{II}(deeb)$_3$]$^{2+}$ dissolved in an acetonitrile solution with 7 mM TBAI and 9 μM TBAI$_3$ are shown in Figure 1A. Standard addition of the known absorption spectra of Ru^+, $I_2^{\bullet -}$, and I_3^- accurately simulated the transient data and enabled their time-dependent concentrations to be calculated (Figure 1B). We note that the $I_2^{\bullet -}$ and Ru^+ spectra were obtained as previously described; however, they are reported here over a broader spectral range.[10] In principle, the concentrations of Ru^+ and $I_2^{\bullet -}$ should have been equal at time zero. However, the calculated Ru^+ concentration was 30−40% lower than the $I_2^{\bullet -}$ concentration. This discrepancy could be the result of an error in the extinction coefficients that arises from weak ground-state ion pairing or a rapid reaction of Ru^+. Regardless of this apparent systematic error, it is evident from Figure 1B that the I_3^- and Ru^+ concentrations decreased concurrently over the first 50 μs with the formation of $I_2^{\bullet -}$. On longer time scales than what is shown, [$I_2^{\bullet -}$] and Δ[I_3^-] returned to the baseline with an equal second-order rate constant, 3×10^9 M^{-1} s^{-1}, in accordance with disproportionation of $I_2^{\bullet -}$ to yield I_3^- and I^-.[10,15] Steady-state absorption spectra recorded before and after laser excitation revealed no evidence for permanent photochemistry.

To quantify the reaction rate constant for I_3^- reduction, k_3 in Scheme 1, the I_3^- concentration was varied and transient absorption changes were monitored at wavelengths based on their principal importance to the transient species: 520, 425, and 360 nm, Figure 1A (inset). Deconvolution of transient data into [Ru^+], [$I_2^{\bullet -}$], and Δ[I_3^-] concentrations was prudent and was accomplished with a simple matrix analysis whose accuracy was verified by comparison to full spectral data.

Figure 2A shows the [Ru^+] concentration as a function of time with added I_3^-. Overlaid on this data are pseudo-first-order kinetic fits. The noise resulted mainly from the need to operate at low concentrations to avoid the direct excitation of I_3^- with the 532 nm pulsed light.[10] Time-dependent data for Δ[I_3^-] decay and [$I_2^{\bullet -}$] growth were also fit to a pseudo-first-order kinetic model. The observed rate constants were related to k_2 and k_3 in Scheme 1 by $k_{obs} = k_2[I_2^{\bullet -}] + k_3[I_3^-]$. A plot of k_{obs} values extracted from [Ru^+], Δ[I_3^-], and [$I_2^{\bullet -}$] data versus the I_3^- concentration is shown in Figure 2B. The data on both axes were divided by the initial $I_2^{\bullet -}$ concentration, $[I_2^{\bullet -}]_0$. This allowed data from multiple experiments to be plotted together provided that [$I_2^{\bullet -}$] changed very little over the fitted time domain; this behavior was verified with data like that shown in Figure 1B, where [$I_2^{\bullet -}$] changed less than 0.2 μM over the first 75 μs. Thus, k_{obs} was dominated by the $k_3[I_3^-]$ term. Second-order rate constants of $k_2 = (2.0 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1} and $k_3 = (5.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1} were abstracted from the data shown in Figure 2B.

The one-electron reduction of $I_2^{\bullet -}$ has previously been studied under similar conditions. For example, a rate constant of 2.1×10^{10} M^{-1} s^{-1} has been reported when Ru^+ was Ru^{II}(bpz$^-$)(bpz)(deeb)$^+$, where bpz is 2,2′-bipyrazine.[10] This value agrees quite well with the data reported here, especially considering that the $E°(Ru^{II/+})$ reduction potentials of Ru^{II}(bpz)$_2$(deeb)$^{2+}$ and Ru^{II}(deeb)$_3$$^{2+}$ are very similar, −0.82 and −0.88 V (vs SCE), respectively.

To our knowledge, the one-electron reduction of I_3^- has not been previously reported in an organic solvent, although aqueous solution experiments have appeared.[6−8] In aqueous studies, the simultaneous reduction of I_2 and I_3^- was invoked, leading to complicated mechanistic interpretations because both reactions were proposed to yield $I_2^{\bullet -}$. For the experiments reported herein, the concentration of I_2 was calculated to be $< 10^{-9}$ M at all concentrations of I_3^- employed, and thus the transient growth of $I_2^{\bullet -}$ can be attributed solely to the one-electron reduction of I_3^-.

In this experiment, the coincident loss of Ru^+ and I_3^- with the growth of $I_2^{\bullet -}$ implies that diiodide was a primary reaction product. However, a short-lived I_3^{2-} intermediate that undergoes a rapid unimolecular dissociation to yield the $I_2^{\bullet -}$ product is likely. A closely related intermediate has been proposed for diiodide reduction by the solvated electron, $I_2^{\bullet -} + e^- \rightarrow I_2^{2-} \rightarrow 2I^-$, and is assumed to be the case with I_3^- as well.[16]

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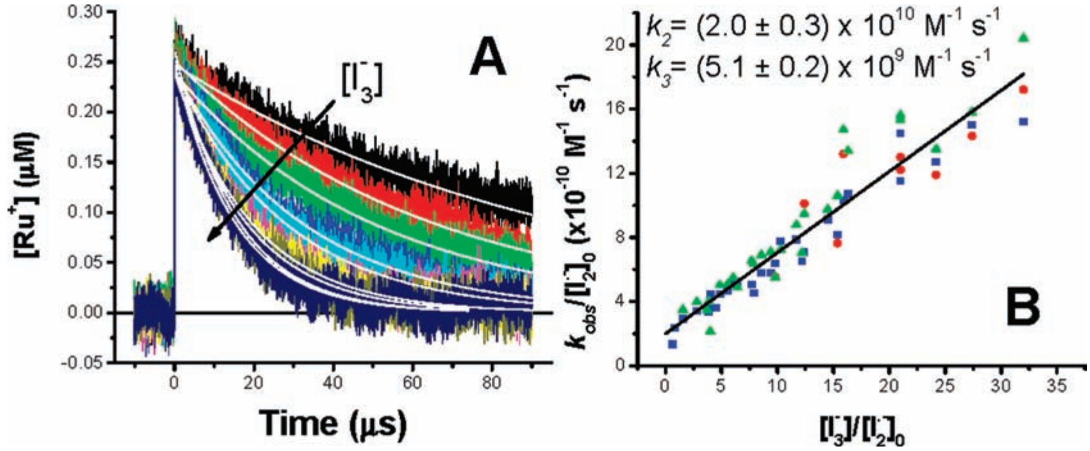

Figure 2. (A) A $[Ru^+]$ vs time plot (10 pt adjacent average smooth) increasing $[I_3^-]$. Overlaid are fits to a pseudo-first-order kinetic model. (B) A $k_{obs}/[I_2^{\bullet-}]_0$ plot vs the $[I_3^-]/[I_2^{\bullet-}]_0$ concentration for $[Ru^+]$ decay (blue ■), $\Delta[I_3^-]$ decay (light-green ▲), and $[I_2^{\bullet-}]$ growth (red ●). All data were collectively fit to the linear equation $k_{obs}/[I_2^{\bullet-}]_0 = k_2 + k_3[I_3^-]/[I_2^{\bullet-}]_0$. Standard error is reported along with extracted k_2 and k_3 terms.

The observed rate constant reported herein for I_3^- reduction includes contributions from diffusion, formation of an encounter complex, and electron transfer as described by Sutin.[17] Within this context, eq 2 may be used to estimate an electron-transfer rate constant if diffusional factors are known.

$$1/k_{obs} = 1/k_{diff} + 1/K_A k_{et} \qquad (2)$$

A rate constant for diffusion, k_{diff}, can be estimated based upon eq 3, where N_A is Avogadro's number and D_{Ru^+} and $D_{I_3^-}$ are the diffusion coefficients for Ru^+ and I_3^-, respectively.[18] The effective reaction radius, β, is defined by eq 4. This term adjusts the sum of the ionic radii, $R = r_{Ru^+} + r_{I_3^-}$, by accounting for ionic interactions through the Onsager radius, $R_c = [z_{I_3^-} z_{Ru^+} e^2/4\pi\varepsilon_r\varepsilon_0 k_B T]$, and the Debye length, $\kappa = [2000 e^2 N_A I/\varepsilon_r\varepsilon_0 k_B T]^{1/2}$. In these two parameters, I is the ionic strength, and all other terms retain their normal meaning.

$$k_{diff} = 4\pi N_A (D_{Ru^+} + D_{I_3^-})\beta \qquad (3)$$

$$\beta = R_c \exp(R_c\kappa)/[\exp(R_c/R) - 1] \qquad (4)$$

The degree to which the encounter complex, $[Ru^+, I_3^-]$, forms can be quantified by estimating an association constant, K_A, using eq 5, where all terms have been previously defined.[19]

$$K_A = 1000(4/3)\pi R^3 \exp(-R_c/R) \exp[R_c\kappa/(1+\kappa R)] \qquad (5)$$

Employing eqs 2−4, we arrive at theoretical estimates for the diffusion rate constant, $k_{diff} = 2.6 \times 10^{10}$ M^{-1} s^{-1}, and the association constant, $K_A = 7.4$ M^{-1}, both calculated for $I = 0.0082$ M. From k_{obs}, k_{diff}, and K_A, an estimate of the electron-transfer rate constant for I_3^- reduction, $k_{et} = 8.6 \times 10^8$ s^{-1}, was calculated.

$$k_{et} = \nu_n \kappa_{el} \exp[-(\Delta G^\circ + \lambda)^2/4\lambda RT] \qquad (6)$$

The Marcus equation can then be applied directly to k_{et} to yield ΔG° for the reaction, eq 6. With some basic assumptions ($\nu_n\kappa_{el} = 10^{11}$ s^{-1} and $\lambda = 1.0$ eV), $\Delta G^\circ = -0.3$ eV was calculated. This resulted in $E^\circ(I_3^-/(I_2^{\bullet-}, I^-)) = -0.58$ V (vs SCE). This value is remarkably close to −0.59 V, estimated by Boschloo and Hagfeldt using a Latimer-type analysis.[2] This experimental estimate should be viewed with some caution because it was determined based on only one rate constant with the assumptions noted. Flash-quench studies of a series of ruthenium(II) polypyridyl compounds with a range of $E^\circ(Ru^{II/+})$ potentials will help to elucidate a more confident value.

In summary, we have reported compelling evidence that $I_2^{\bullet-}$ is a product of the one electron reduction of I_3^- in acetonitrile for the first time. The rate constant for the electron-transfer reaction was determined, $k_{et} = 8.6 \times 10^8$ s^{-1}, and from this value, a formal reduction potential was abstracted, $E^\circ(I_3^-/(I_2^{\bullet-}, I^-)) = -0.58$ V (vs SCE). This value has important implications for dye-sensitized solar cells and is directly relevant to the ability of I_3^- to escape recombination with injected electrons. *Electrons trapped in TiO_2 react slowly with I_3^- because the reaction is endergonic*. Indeed, density of states analyses like those reported by Bisquert et al. show that a large number of trapped TiO_2 electrons are present at potentials more positive than −0.58 V (vs SCE).[20,21] This result, coupled with the low concentrations of other iodine acceptors within dye-sensitized solar cells, appears to account for the low overall recombination and high solar conversion efficiencies confirmed for the I^-/I_3^- redox mediator.

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