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Excited-State Photochemistry in the Tris(2,2′-bipyridine)ruthenium(II)–Sulfite System

Sir:

We have previously noted that, in many respects, the chemistry of the luminescent excited state of tris(2,2′-bipyridine)ruthenium(II) ($^*Ru(bpy)_3^{2+}$) is as well characterized as that of many ground-state metal complexes:[1] $^*Ru(bpy)_3^{2+}$ is relatively inert to substitution,[2] but, being both a strong reductant[3-5] and oxidant,[6] readily undergoes outer-sphere electron-transfer reactions with redox quenchers to produce $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$. In this communication the analogy between this excited molecule and ground-state metal complexes is further extended to include charge-transfer photochemistry; in the presence of sulfite ion the use of high intensity visible light[7] effects the sequential two-photon photolysis of $Ru(bpy)_3^{2+}$ to yield $Ru(bpy)_3^{+}$.

Laser flash photolysis (λ 530 nm, pulse length Δt = 20 ns, photons in at least tenfold excess over $Ru(bpy)_3^{2+}$)[8] provides a convenient technique for the production of $^*Ru(bpy)_3^{2+}$. When solutions containing $Ru(bpy)_3^{2+}$ (5×10^{-5} M) and a reductant (0.01–1.0 M) such as Eu_{aq}^{2+} or sodium ascorbate (HA^-) are subjected to laser flash photolysis, the product $Ru(bpy)_3^{+}$ (monitored by absorbance changes at 500 nm where $Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_3^{2+}$ have the same molar absorptivity) is seen to form predominantly in the second of three well-resolved stages. (1) During the laser pulse, ground-state $Ru(bpy)_3^{2+}$ is excited (eq 1, $^*k_1 = 2.3 \times 10^3 I_0\epsilon_1\phi_1$, where I_0 is the laser intensity in einstein $cm^{-1}\ s^{-1}$, ϵ_1 = 850 $M^{-1}\ cm^{-1}$, the molar absorptivity of $Ru(bpy)_3^{2+}$ at 530 nm, and ϕ_1 is the quantum yield for $^*Ru(bpy)_3^{2+}$ formation at 530 nm[9]). (2) On the 0.1–1-μs time scale $Ru(bpy)_3^{+}$ formation by reaction of $^*Ru(bpy)_3^{2+}$ with Eu_{aq}^{2+} or HA^- (eq 2, $k_q = 2.8 \times 10^7\ M^{-1}\ s^{-1}$ [10] and $2 \times 10^7\ M^{-1}\ s^{-1}$, respectively) parallels $^*Ru(bpy)_3^{2+}$ disappearance via eq 1 ($k_{-1} = 1.7 \times 10^6\ s^{-1}$) and eq 2. (3) On a much longer time scale ($t_{1/2} \geq 20$ μs for Q = Eu_{aq}^{2+} and HA^-) back-reaction of the photoproducts (eq 3) regenerates $Ru(bpy)_3^{2+}$ and Q ($k_t = 2.7 \times 10^7$ and $1 \times 10^9\ M^{-1}\ s^{-1}$ for Eu_{aq}^{3+} [10] and HA^-, respectively). The above description applies over the range of light intensities investigated (10^0–10^2 einstein $cm^{-2}\ s^{-1}$ or $^*k_1 = 2 \times 10^6\ s^{-1}$ to $2 \times 10^8\ s^{-1}$).

$$Ru(bpy)_3^{2+} \underset{k_{-1}}{\overset{*k_1}{\rightleftharpoons}} {}^*Ru(bpy)_3^{2+} \qquad (1)$$

$$^*Ru(bpy)_3^{2+} + Q \xrightarrow{k_q} Ru(bpy)_3^{+} + Q^+ \qquad (2)$$

$$Ru(bpy)_3^{+} + Q^+ \xrightarrow{k_t} Ru(bpy)_3^{2+} + Q \qquad (3)$$

By contrast, when solutions containing $Ru(bpy)_3^{2+}$ (5×10^{-5} M) and Na_2SO_3 (0.1–1.0 M, 25 °C) are flash photolyzed at moderate to high light intensities (10^1–10^2 einstein $cm^{-2}\ s^{-1}$), $Ru(bpy)_3^{+}$ is seen to form in *both* of the first two stages—that is both during and after the laser pulse. The relative amount formed during the pulse rises steeply with laser intensity. Formation of $Ru(bpy)_3^{+}$ in the second ("slow") stage is observed at all intensities and its rate of formation is, within experimental error, the same as that for $^*Ru(bpy)_3^{2+}$ disappearance. Thus the "slow" contribution may be attributed to dynamic quenching according to eq 2 with $k_q \sim 3 \times 10^5\ M^{-1}\ s^{-1}$.[11] (Back-reaction is very slow, with $k_t \leq 10^6\ M^{-1}\ s^{-1}$.) The additional $Ru(bpy)_3^{+}$ is produced during the laser pulse in yields which are a sensitive function of laser intensity.

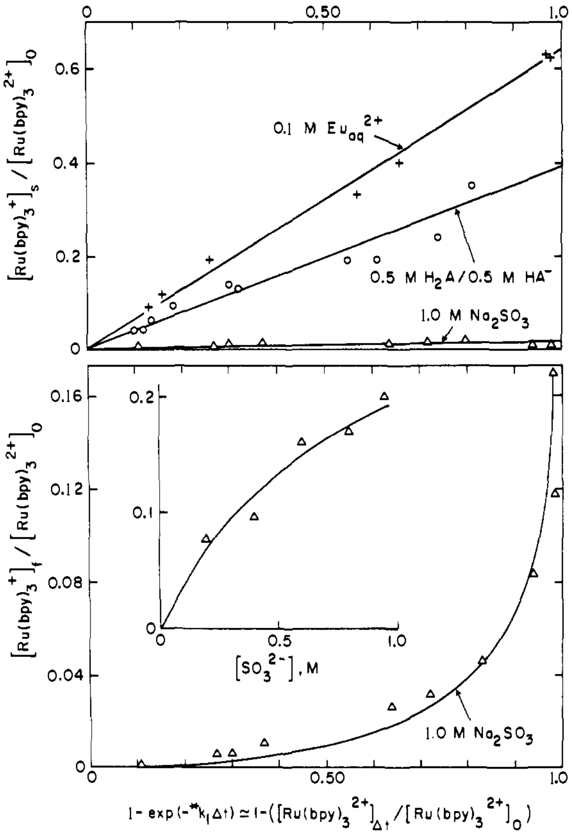

Figure 1. Plot of the yield of $Ru(bpy)_3^{+}$ produced after (top) and during (bottom) the 20-ns laser pulse as a function of the quantity ($1 - \exp(-^*k_1\Delta t)$). The solutions are 5×10^{-5} M in $Ru(bpy)_3^{2+}$ with concentrations of reducing agent as given in the figure. In the lower major figure the curve drawn is for κ = 0.05. The insert in the lower figure gives the sulfite ion dependence of the yield of $Ru(bpy)_3^{+}$ produced during the laser pulse. Error bars on the sulfite data are ±15% of the values shown. The error bars on the other data are ±7%.

The formation of $Ru(bpy)_3^{+}$ during the pulse may be explained in terms of a model involving photolysis of an excited state/sulfite ion pair (eq 4) according to eq 5.

$$^*Ru(bpy)_3^{2+} + SO_3^{2-} \overset{*K}{\rightleftharpoons} {}^*Ru(bpy)_3^{2+}/SO_3^{2-} \qquad (4)$$

$$^*Ru(bpy)_3^{2+}/SO_3^{2-} \xrightarrow{*k_2} Ru(bpy)_3^{+} + SO_3^{-} \qquad (5)$$

(Here $^*k_2 = 2.3 \times 10^3 I_0\epsilon_2\phi_2$ (ϵ_2 is the molar absorptivity of the $^*Ru(bpy)_3^{2+}/SO_3^{2-}$ ion pair at 530 nm and ϕ_2 is the quantum yield for production of $Ru(bpy)_3^{+}$ from the ion pair.)

This model is supported by the data presented in Figure 1. For both upper and lower major figures the abscissa is the fraction of $Ru(bpy)_3^{2+}$ depleted after the laser pulse as calculated from $1 - \exp(-^*k_1\Delta t)$ assuming a 20-ns rectangular pulse and the excess photon limit. In the absence of multiphoton processes and/or very rapid disappearance of $^*Ru(bpy)_3^{2+}$, this expression gives the fraction of $Ru(bpy)_3^{2+}$ converted to $^*Ru(bpy)_3^{2+}$. In the presence of Eu_{aq}^{2+} and HA^- (upper portion of figure) this quantity of $^*Ru(bpy)_3^{2+}$ may subsequently be converted to $Ru(bpy)_3^{+}$ via eq 2 with a yield (Y) determined by the product of the quenching yield ($Y_Q = k_q[Q]/(k_{-1} + k_q[Q])$ and the cage escape yield[12] ($Y_t = 1 -$

k_t/k_d where k_d is the diffusion-controlled rate constant for eq 3[12]). In the upper figure the yield of $Ru(bpy)_3^+$ is seen to be a linear function of the amount of $*Ru(bpy)_3^{2+}$ produced at a given light intensity; the extrapolated value of Y with 0.1 M Eu_{aq}^{2+}, 0.63, is determined by the fraction of $*Ru(bpy)_3^{2+}$ undergoing reaction 2 (Y_Q) at this Eu(II) level ($Y_t = 1$). By contrast, with 0.5 M HA^-, Y_Q is larger (0.86) but k_t is much greater (Y_t smaller) so that the total yield of $Ru(bpy)_3^+$ produced is smaller. Finally, data for "slow" $Ru(bpy)_3^+$ production in the presence of 1 M SO_3^{2-} (triangles, upper figure) may be understood in terms of a small Y_Q with a large Y_t.

In the lower portion of the figure are presented data for "fast" $Ru(bpy)_3^+$ production in the presence of SO_3^{2-}. Both ordinate and abscissa are the same as for the upper figure. Obviously $Ru(bpy)_3^+$ formation is not determined simply by $*Ru(bpy)_3^{2+}$ production as above. Instead these data may be treated semiquantitatively in terms of the scheme $A \rightarrow B \rightarrow C$[13,14] (eq 1, eq 4 + eq 5); the lower figure is then a plot of $[C]/[A]_0$ vs. $1 - [A]/[A]_0$. (The assumption that $1 - \exp(-*k_1\Delta t) = 1 - [A]/[A]_0$ is valid only when $*k_2' = *K*k_2[SO_3^{2-}]/(1 + *K[SO_3^{2-}]) > k_{-1}$ or for $I_0 > 30$ einstein $cm^{-2}\ s^{-1}$, vide infra.) In this scheme, the fraction of C present for a given extent of total reaction $(1 - [A]/[A]_0)$ is determined by the ratio of the two rate constants, here $*k_2'/*k_1 = \kappa$. The smooth curve is drawn for $\kappa = 0.05$. It is apparent that the calculated curve provides a good fit for the experimental data for $1 - \exp(-*k_1\Delta t) > 0.8$ or $I_0 > 30$ einstein $cm^{-2}\ s^{-1}$. At lower light intensities the observed points fall above the calculated curve—probably because the "slow" stage has not been completely subtracted from the fast. The insert in the lower figure gives the sulfite concentration dependence of the ion-pair photolysis.

The biphotonic production of $Ru(bpy)_3^+$ could result from either of two pathways: ion-paired sulfite may simply act as an efficient scavenger for the short-lived second excited state; alternatively, the association of $*Ru(bpy)_3^{2+}$ with SO_3^{2-} may give rise to visible charge-transfer absorption within the outer-sphere complex. The estimated λ_{max} for charge-transfer absorption of the $*Ru(bpy)_3^{2+}/SO_3^{2-}$ ion pair lends tentative support to the latter interpretation. From the spectrum of the $Ru(NH_3)_6^{3+}/SO_3^{2-}$ ion pair (λ_{max} 405 nm), λ_{max} for the $*Ru(bpy)_3^{2+}/SO_3^{2-}$ ion pair is estimated to be ~550 nm.

In this report three efficient photochemical methods for the generation of $Ru(bpy)_3^+$ in aqueous solution have been described. Both $*Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^+$ are excellent reducing agents and so may be of value as mediators in photoproduction of secondary species capable of bringing about the rapid reduction of water to dihydrogen. In this context, $Ru(bpy)_3^+$ could be of greater practical value than $*Ru(bpy)_3^{2+}$, not only because of its greater reducing power and longer lifetime, but also because the back-reaction (reverse of eq 6) is much less favorable and so likely to be slower. With these properties of $Ru(bpy)_3^+$ as motivation, the photolysis of $Ru(bpy)_3^{2+}/Q$ solutions ($Q = Eu_{aq}^{2+}, SO_3^{2-}, HA^-$) in the presence of possible dihydrogen production mediators is currently being carried out.[15]

$$Ru(bpy)_3^+ + Ox \rightleftharpoons Ru(bpy)_3^{2+} + Red \qquad (6)$$

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Homogeneous Catalysis of the Photoreduction of Water by Visible Light. Mediation by a Tris(2,2′-bipyridine)ruthenium(II)–Cobalt(II) Macrocycle System

Sir:

In recent years the luminescent excited state of tris(2,2′-bipyridine)ruthenium(II) ($*Ru(bpy)_3^{2+}$) has attracted considerable attention because of its promise as a mediator in solar energy conversion schemes.[1-3] This excited state, a very strong reductant, rapidly reduces even mild oxidants[4-6] and is thermodynamically capable of reducing water to hydrogen. However there is no evidence that the latter reaction occurs rapidly in homogeneous solution. In the strategy employed here, the short-lived reductant $*Ru(bpy)_3^{2+}$ is transformed into the longer-lived, more strongly reducing ion, $Ru(bpy)_3^+$. The $Ru(bpy)_3^+$ reduces a metal complex which in turn reacts rapidly with H_3O^+ or H_2O to form an unstable hydride. As has been previously noted, metal hydrides can be useful intermediates in the catalyzed photodissociation of water.[7] Here we report the success of two such systems for the photochemically initiated evolution of H_2 from aqueous solution.

Europium(II)[8,9] and ascorbate ion[10] react with $*Ru(bpy)_3^{2+}$ in aqueous solution to form high transient concentrations of $Ru(bpy)_3^+$. Macrocyclic cobalt(I) complexes such as $Co^I(Me_6[14]dieneN_4)^+$ have been shown by pulse-radiolysis studies[11] to react rapidly with H_3O^+. The related cobalt(I) complex, $Co^I(Me_4[14]tetraeneN_4)^+$, reacts with H_2O and other protic solvents with the evolution of H_2.[12] From electrochemical data in CH_3CN,[13,14] the $Ru(bpy)_3^+$ ion is thermodynamically capable of reducing $Co^{II}(Me_6[14]dieneN_4)(H_2O)_2^{2+}$ ($Co^{II}L$) to the corresponding Co(I) complex. A