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 → B → 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

Table I. Quantum Yield for Hydrogen Formation at 450 ± 20 nm and 25 °C[a]

reducing agent, conditions	$[Co^{II}L]$, M	ϕ_{H_2}	
		obsd	cor[b]
1×10^{-4} M $Ru(bpy)_3^{2+}$, 0.1 M Eu(II), 1 M HCl	4×10^{-3}	0.021 ± 0.005	0.042
1×10^{-4} M $Ru(bpy)_3^{2+}$, 0.1 M Eu(II), 0.1 M HCl	4×10^{-3}	0.024 ± 0.004	0.051
1×10^{-4} M $Ru(bpy)_3^{2+}$, 0.1 M Eu(II), 1 M HCl	0	3×10^{-3}	
5×10^{-4} M $Ru(bpy)_3^{2+}$, 0.5 M H_2A, 0.5 M NaHA, pH 4	2×10^{-3}	1.3×10^{-4}	1.6×10^{-4}
1×10^{-4} M $Ru(bpy)_3^{2+}$, 0.9 M H_2A, 0.1 M NaHA, pH 3.1	5×10^{-3}	1.8×10^{-4}	4.6×10^{-4}
1×10^{-4} M $Ru(bpy)_3^{2+}$, 1.0 M H_2A, pH 1.5	5×10^{-3}	1×10^{-5}	
1×10^{-4} M $Ru(bpy)_3^{2+}$, 0.5 M H_2A, 0.5 M HA^-	0	2×10^{-6}	

[a] Irradiation times ranged from 0.5 to 1 h for Eu(II) solutions and from 1 to 7 h for ascorbate solutions. [b] The observed quantum yield was corrected for the fraction of light (A_{Ru}/A_{tot}) absorbed by $Ru(bpy)_3^{2+}$ at 450 nm (ϵ_{Ru} 1.46×10^4, ϵ_{Co} 1.18×10^2, ϵ_{Eu} ~0 M^{-1} cm^{-1}) and for the fraction of $*Ru(bpy)_3^{2+}$ quenched by the reducing agent (fraction quenched = $K_{SV}[Q]/(1 + K_{SV}[Q])$, where K_{SV} = 17 and 12 M^{-1} for Eu(II) and HA^-, respectively).

system consisting of $Ru(bpy)_3^{2+}$, $Co^{II}L$, and either ascorbate ion or Eu(II) is therefore a rationally designed system in which to attempt the catalyzed photoreduction of water using visible light.

The quantum yields for H_2 evolution in solutions containing $Ru(bpy)_3^{2+}$, $Co^{II}L$, and the reducing agent were determined at 450 ± 20 nm.[15] These quantum yields are given in Table I as a function of the concentration of the various reactants. With Eu(II) as the reducing agent (chloride medium), the quantum yield for H_2 evolution is independent of the concentration of H_3O^+ in the range 0.1-1.0 M. The probable steps leading to the hydrogen formation are outlined below.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} *Ru(bpy)_3^{2+} \tag{1}$$

$$*Ru(bpy)_3^{2+} + Eu(II) \rightarrow Ru(bpy)_3^{+} + Eu(III) \tag{2}$$

$$Ru(bpy)_3^{+} + Co^{II}L \rightarrow Ru(bpy)_3^{2+} + Co^{I}L \tag{3}$$

$$Co^{I}L + H^+ \rightarrow Co^{III}LH^- \xrightarrow{H^+} Co^{III}L + H_2 \tag{4}$$

$$Co^{III}L + Eu(II) \rightarrow Co^{II}L + Eu(III) \tag{5}$$

(Here eq 4 has been postulated[11] but its stoichiometry has not been established.) The net light-driven reaction is

$$2Eu(II) + 2H^+ \xrightarrow{h\nu} 2Eu(III) + H_2 \tag{6}$$

Although reaction 6 is thermodynamically favorable by 0.43 V[16] in the absence of light, the thermal reaction is slow unless heterogeneous catalysts are present.[17] An overall quantum yield for H_2 formation of 0.05 is obtained for 450 ± 20 nm irradiation after correction for the fraction of light absorbed by $Ru(bpy)_3^{2+}$ and for the fraction of $*Ru(bpy)_3^{2+}$ quenched by Eu(II). Visible irradiation of $Rh_2[1,3\text{-diisocyanopropane}]_4^{2+}$ in 9 M HBr gives H_2 with a quantum yield of 0.044.[18] The use of visible light to produce hydrogen has also been reported for a system consisting of $Ru(bpy)_3^{2+}$, a rhodium bipyridine complex, triethanolamine, and chloroplatinate.[19] Unfortunately no quantum yield data were reported and we have not been able to reproduce these results using 450 ± 20 nm radiation.[20] Experiments using broad-band irradiation were carried out to demonstrate that the evolution of H_2 in the present system is truly catalytic in $Ru(bpy)_3^{2+}$. Using a 405-nm long-pass filter,[21] ~10 mol of H_2/mol of $Ru(bpy)_3^{2+}$ were produced. This corresponds to ~1 mol of H_2/mol of $Co^{II}L$.[22] (Although blank experiments show evidence for production of H_2 in the absence of $Co^{II}L$, only ~5-10% of the H_2 observed arises from this route.[23]) Qualitative observations indicate that the rate of H_2 evolution decreases as the photolysis proceeds.

The Eu(II) reaction system was also studied by laser flash photolysis.[24] The absorbance of $Ru(bpy)_3^{+}$ (from eq 2) was monitored and the lifetime of this species was followed as a function of the concentration of $Co^{II}L$. (In the absence of Eu_{aq}^{2+} neither $Ru(bpy)_3^{3+}$ nor $Ru(bpy)_3^{+}$ was produced with 8×10^{-3} M $Co^{II}L$.) The rate constant for generation of Co(I) (eq 3) was found to be 1.8×10^8 M^{-1} s^{-1} at 25 °C. The reported rate constant for protonation of Co(I) (eq 4) is 3.1×10^9 M^{-1} s^{-1}.[11] As expected, we see no evidence for the accumulation of $Co^{I}L$ (λ_{max} 630 nm (ϵ 9.1×10^3 M^{-1} cm^{-1})[11]) or any other transient species.

A system in which ascorbate ion (HA^-) is used to reduce the excited state of $Ru(bpy)_3^{2+}$ also evolves H_2 (Table I). The quantum yield is, however, about two orders of magnitude lower than for the system using Eu(II). The quantum yield maximizes around pH 3 where 10% of the ascorbic acid (H_2A) is present as HA^- (pK_a = 4.0 at 25 °C). The anticipated mechanism for H_2 evolution in the ascorbate system is given by eq 1, 7, 3, 4, 8, 9. In the pH range 2.5-4.0, the ascorbate radical HA· disproportionates (eq 8) to ascorbic acid and dehydroascorbic acid (A) with a rate constant of ~8×10^7 M^{-1} s^{-1}.[25] The net reaction being driven photochemically is shown in eq 10. The formation of A and H_2 from H_2A is thermodynamically unfavorable by 0.41 V at $[H^+] \geqslant 10^{-4}$ M.[26]

$$*Ru(bpy)_3^{2+} + HA^- \rightarrow Ru(bpy)_3^{+} + HA\cdot \tag{7}$$

$$2HA\cdot \rightarrow HA^- + H^+ + A \tag{8}$$

$$Co^{III}L + HA^- \text{ (or } H_2A) \rightarrow Co^{II}L + HA\cdot \tag{9}$$

$$H_2A \xrightarrow{h\nu} A + H_2 \tag{10}$$

Laser flash photolysis of a solution of $Ru(bpy)_3^{2+}$, $Co^{II}L$, and ascorbic acid, adjusted to pH 8.1 with NaOH shows the presence of an intermediate which appears with a rate comparable with that for disappearance of $Ru(bpy)_3^{+}$. The spectrum of this intermediate (Figure 1) is, within experimental error, identical with that reported for $Co^{I}L$.[11] Based on the latter and the concentration of $Ru(bpy)_3^{+}$ generated in the absence of $Co^{II}L$, the yield of $Co^{I}L$ for reaction 3 is 1.0 ± 0.2 under these conditions. By contrast, when pH 4 ascorbic acid solutions containing both $Ru(bpy)_3^{2+}$ and $Co^{II}L$ were flash photolyzed as above, no absorbance changes ascribable to $Co^{I}L$ were observed, although the rapid disappearance of $Ru(bpy)_3^{+}$ provided indirect evidence that $Co^{I}L$ was produced. Thus at pH 4 the rate of disappearance of $Co^{I}L$ must exceed its rate of formation. At longer times (50-100 μs after the pulse) a transient with an absorption maximum at 520 nm was observed. Based on 100% reaction of the $Ru(bpy)_3^{+}$ initially formed, ϵ_{520} for this species is ~4×10^3 M^{-1} cm^{-1}. From the time of formation of this transient and its high absorptivity, it seems likely that it is a cobalt-ascorbate adduct. The decay of the transient is quite complicated and follows multiphasic kinetics. Evidently, the $Co^{I}L$ produced with high efficiency in eq 3 (or $Co^{III}LH^-$) undergoes reaction with ascorbic acid. The pH dependence of the quantum yield indicates that this process occurs in competition with the reaction of $Co^{I}L$ (or $Co^{III}LH^-$) with proton donors to give hydrogen. Such side reactions are undoubtedly responsible for the low value of the absolute quantum yield in the ascorbate system. Although photochemical formation of H_2 from the ascorbate solutions is in-

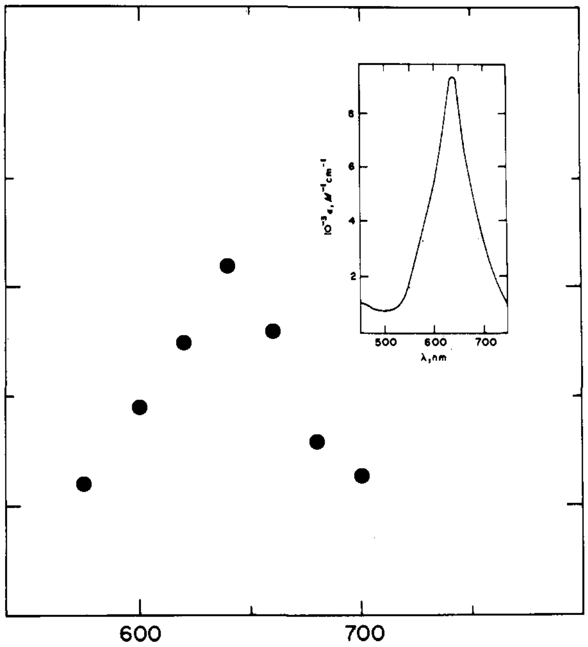

Figure 1. Spectrum of the transient observed 600–800 ns after the 530-nm laser pulse; $[Ru(bpy)_3{}^{2+}] = 5 \times 10^{-5}$ M, $[Co^{II}L] = 8 \times 10^{-3}$ M, $[HA^-] = 0.5$ M, pH 8.1, 25 °C. Shown in the insert is the spectrum of $Co^I[Me_6[14]dieneN_4]$ reported in ref 11.

efficient compared with that of the Eu(II) system, the ascorbate system is important because it represents a photochemically driven upconversion of ~20 kcal mol^{-1}.

The reduction of other substrates may prove of greater value than the photoreduction of water. Here we have demonstrated the photoproduction of a Co(I) species that undergoes oxidative-addition of a hydronium ion. It should be possible to photogenerate catalysts which undergo other oxidative-addition reactions. The feasibility of this alternative is supported by work of Fleischer and Krishnamurthy[27] who report the catalytic reduction of acetylene to ethylene and the stoichiometric reduction of N_2 to NH_3 by a Co(I) porphyrin in aqueous solution. Current efforts in these laboratories are directed toward the identification of systems in which photochemically initiated hydrogenation of such substrates can be carried out.

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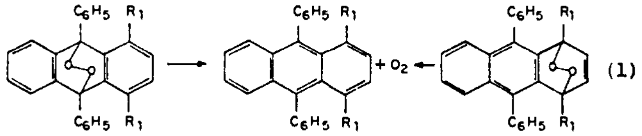
Thermolysis of Anthracene Endoperoxides. Concerted vs. Diradical Mechanisms. Microscopic Reversibility in Endothermic Chemiluminescent Reactions

Sir:

Thermolysis of 9,10-anthracene endoperoxides **1** and **2** and of 1,4-anthracene endoperoxides **3** and **4** results[1-4] in nearly quantitative (>95%) production of molecular oxygen and the parent anthracene (eq 1). For the thermolysis of anthracene endoperoxides **1–4** we have measured (1) the yields of both singlet[5] and triplet molecular oxygen, (2) the activation parameters,[6] and (3) the reaction enthalpies,[7]



1 ($R_1 = H$)
2 ($R_1 = CH_3$)

5 ($R_1 = H$)
6 ($R_1 = CH_3$)
7 ($R_1 = OCH_3$)

3 ($R_1 = CH_3$)
4 ($R_1 = OCH_3$)

From Table I it is noted that each reaction is *endothermic*. Nonetheless, the chemiluminescent process to generate $^1O_2$ reaches efficiencies approaching 100% for **3** and **4**. Thus, the bulk of the energy for formation of $^1O_2$ comes from activation energy and not reaction exothermicity. From Table I it is found that a correlation exists between $\Delta S^{\ddagger}$ for the thermolyses and the yield of $^1O_2$; a high positive value of $\Delta S^{\ddagger}$ (9,10-endoperoxides) correlates with a low yield of $^1O_2$ and a near-zero (or slightly negative) value of $\Delta S^{\ddagger}$ (1,4-endoperoxides) correlates with close to a quantitative yield of $^1O_2$.

Consider Figure 1 which displays a schematic representation of the pertinent energy surfaces corresponding to the reaction coordinate for eq 1. According to theoretical calculations,[4] a singlet-triplet surface crossing is expected along the reaction

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