

and borohydride are accessible. The small observed catalysis has literature precedent and can be ascribed to a favorable accumulation of borohydride at the cationic Stern region. This is confirmed by a 4- and 2--fold rate decrease with steroids A and F, respectively, when the 0.020 M HTAB is replaced with an anionic surfactant, 0.010 M laurate.

Reduction rates for the micellar steroids in Figure 1 vary only slightly when the D-ring substituent is changed from ionic to polar (compare A with F). These trivial kinetic variations imply that even extremely water-insoluble steroids bind where water and borohydride are available. The obvious preference for surface adsorption over internal dissolution has two explanations. (1) Surface binding is far less disruptive to the micelle structure than solubilization in an already crowded core. (2) Water surrounds those chain segments that happen to reside outside the core, because water must fill the spaces that necessarily exist between the chains. When a hydrophobic guest encounters a micelle, the guest enters and displaces micellar water (an entropically favorable process). Thus, suggestions not to the contrary, micelle-guest association takes place in pores and on "fatty patches" where water meets a disorganized assembly of surfactant tails.

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Homogeneous Catalysis of the Photoreduction of Water by Visible Light. 2. Mediation by a Tris(2,2'-bipyridine)ruthenium(II)-Cobalt(II) Bipyridine System¹

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The visible-light-induced formation of hydrogen from water is a subject of much current interest.² Many of the systems that have been studied are based on the use of tris(2,2'-bipyridine)ruthenium(II) [Ru(bpy)₃²⁺] as a photosensitizer and require the presence of heterogeneous catalysts such as Pt or Au.²⁻⁹ Very few homogeneous systems have been reported.^{1,7,9} Our approach to the homogeneous generation of hydrogen is to convert the luminescent excited state of tris(2,2'-bipyridine)ruthenium(II) [*Ru(bpy)₃²⁺] to the more strongly reducing (and longer lived) ion Ru(bpy)₃⁺.¹ The Ru(bpy)₃⁺ reduces a metal complex which reacts with H₃O⁺ or H₂O to form an unstable hydride. The hydride in turn decomposes to yield hydrogen. The blue cobalt(I) bipyridine complexes produced by Na(Hg)¹⁰ or electrochemical¹¹

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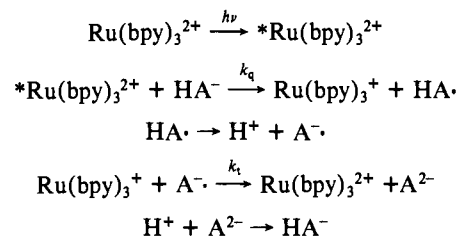
Table I. Quantum Yields for Hydrogen Formation at 450 ± 20 nm and 25 °C^{a,b}

pH	10 ³ [bpy], M	10 ³ [Co(II)], M	Φ _{H₂} , ^c mol einstein ⁻¹
3.5			3 × 10 ^{-4 d}
4.1			2 × 10 ^{-4 d}
5.0			0.7 × 10 ^{-4 d}
6.0			0.4 × 10 ^{-4 d}
3.5	4.0		~0.4 × 10 ⁻⁶
5.0	4.0		~0.4 × 10 ⁻⁶
5.0	0.0	2.0	0.5 × 10 ^{-2 e}
5.0	0.2	2.0	1.0 × 10 ⁻²
5.0	0.4	2.0	1.8 × 10 ⁻²
5.0	0.7	2.0	1.5 × 10 ⁻²
5.0	2.0	2.0	0.6 × 10 ⁻²
5.0	0.0	10.0	0.6 × 10 ^{-2 e}
5.0	0.2	10.0	1.3 × 10 ⁻²
5.0	0.4	10.0	2.4 × 10 ⁻²
5.0	0.7	10.0	2.7 × 10 ⁻²
5.0	2.0	10.0	2.0 × 10 ⁻²
5.0	2.2 ^f	10.0	13 × 10 ⁻²

^a The Ru(bpy)₃²⁺ and total ascorbate concentrations were 5 × 10⁻⁴ and 0.7 M, respectively, and the light intensity was (3-5) × 10⁻⁷ einstein s⁻¹. Photolysis times were typically 1-3 h. ^b The observed quantum yields were corrected for the fraction of *Ru(bpy)₃²⁺ quenched by HA⁻ (K_{SV} = 12 M⁻¹) and the fraction of light absorbed by Ru(bpy)₃²⁺. The hydrogen was determined by gas chromatography and also volumetrically.⁹ ^c Unless otherwise noted, the quantum yields were calculated from the rates of hydrogen evolution immediately after the end of an induction period which was 2-5 min in the presence of added bpy and Co²⁺. ^d These quantum yields were calculated by dividing the total number of moles of H₂ produced by the number of photons absorbed during the photolysis time (~2.5 h) minus the induction period (~0.5 h). ^e In contrast to the solutions that contained both added bpy and Co²⁺, the induction period for these systems was ~45 min. ^f In this case 4,4'-(CH₃)₂bpy was added instead of bpy. When the photolysis was performed in D₂O the gas formed was more than 90% D₂.

reduction of cobalt(II) bipyridine complexes are very powerful reducing agents (E⁰ ~ -1 V vs. NHE) and are not likely to form stable hydrides in solution. Cobalt(I) bipyridine complexes are thus excellent candidates for mediating the homogeneous formation of hydrogen.¹² This expectation has been confirmed: visible-light irradiation of solutions containing Ru(bpy)₃²⁺, ascorbate, Co²⁺, and bpy or substituted bpy and phen derivatives produces hydrogen with a quantum yield of up to 0.13 mol einstein⁻¹. Low yields of H₂ are also produced in the absence of Co²⁺. The latter system is discussed first.

Previous studies^{13,14} have shown that the main reactions occurring in the Ru(bpy)₃²⁺-ascorbate system under flash-photolysis conditions are



where HA⁻ is the ascorbate ion, HA· is the protonated ascorbate

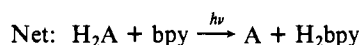
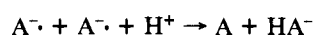
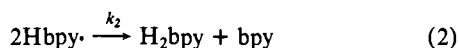
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(12) Kirch, Lehn, and Sauvage have reported⁷ that some hydrogen is produced when solutions containing Ru(bpy)₃²⁺, CoCl₂, bpy, and triethanolamine are photolyzed at pH 8.5-12.5 in the presence of K₂PtCl₄ and have invoked cobalt(I) complexes as intermediates. The generation of H₂ by cobalt(I) complexes has also been reported by: Schrauzer, G. N.; Deutsch, E.; Windgassen, R. *J. Am. Chem. Soc.* **1968**, *90*, 2441. Chao, T.-H.; Espenson, J. H. *Ibid.* **1978**, *100*, 129.

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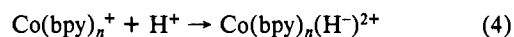
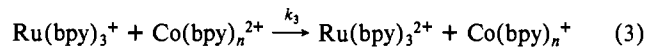
radical, and k_q and k_t are 2.0×10^7 and $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at 25 °C and 0.5 M ionic strength. The cage escape yield of the primary quenching products $[\text{Ru}(\text{bpy})_3^+]$ and $\text{HA}\cdot$ is ~ 0.5 . Upon continuous photolysis $\text{Ru}(\text{bpy})_3^{2+}$ is gradually consumed, and some H_2 (Table I) and dihydrobipyridine (H_2bpy) are produced.^{15,16} The H_2 yield increases with decreasing pH, and its formation may involve the reaction of H_3O^+ with $\text{Ru}(\text{bpy})_3^+$ (or with some other ruthenium species) or with $\text{Ru}(\text{bpy})_3^0$ produced in the disproportionation of $\text{Ru}(\text{bpy})_3^+$.^{17,18} The H_2bpy could arise either from the acid-assisted reduction of a co-ordinated bpy in $\text{Ru}(\text{bpy})_3^+$ or $\text{Ru}(\text{bpy})_3^0$ or from the reduction of Hbpy^+ formed upon ligand loss from $\text{Ru}(\text{bpy})_3^+$ or $\text{Ru}(\text{bpy})_3^0$. In order to further examine these possibilities continuous photolyses were carried out in the presence of added bpy. It was found that much less H_2 is produced under these conditions ($\Phi_{\text{H}_2} = 0.5 \times 10^{-6}$ mol einstein⁻¹ in the presence of 4×10^{-3} M bpy compared with 2×10^{-4} mol einstein⁻¹ in the absence of added bpy) and that the added bpy was completely consumed and converted to H_2bpy in more than 50% yield.^{15,16} The conversion of bpy into H_2bpy can be accounted for in terms of reactions 1 and 2.¹⁹



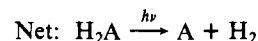
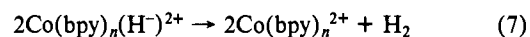
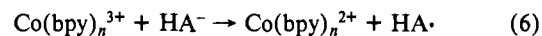
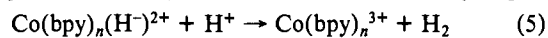
The rate constant for the reaction of $\text{Ru}(\text{bpy})_3^+$ with Hbpy^+ (k_1), determined in laser-flash-photolysis studies^{1,8,20} of pH 4 solutions containing $\text{Ru}(\text{bpy})_3^{2+}$, ascorbate, and bpy, is $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, while the rate constant for the disproportionation of $\text{Hbpy}\cdot$ ($2k_2$), determined in pulse radiolysis studies,¹⁶ is $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7–13.

The H_2bpy yield is decreased and the yield of H_2 is dramatically increased (Table I) when Co^{2+} is added to the $\text{Ru}(\text{bpy})_3^{2+}$, ascorbate, bpy solutions. The principal cobalt(II) bipyridine complexes present under the conditions used ($[\text{bpy}] = (0.2\text{--}2.0) \times 10^{-3} \text{ M}$, $[\text{Co}(\text{II})] = (2\text{--}10) \times 10^{-3} \text{ M}$) are the mono and bis species.²¹ Laser-flash photolysis of solutions containing $\text{Ru}(\text{bpy})_3^{2+}$, ascorbate, bpy, and excess $\text{Co}(\text{II})$ at pH 7.5 showed that $\text{Ru}(\text{bpy})_3^+$ is rapidly oxidized ($k_3 \geq 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and that an intermediate with an absorbance maximum in the 650–675-nm region is formed. This intermediate is identified as a cobalt(I) bipyridine complex.^{22,23} Although appreciable amounts of H_2

are also produced in the cobalt-mediated system in the absence of added bpy, the induction period is relatively long under these conditions and some free bpy could be produced during this period. Since Co^{2+} , bpy, and Hbpy^+ do not significantly quench $^*\text{Ru}(\text{bpy})_3^{2+}$, the following mechanism is proposed for the formation of H_2 in the continuous photolysis²⁴



followed either by the first-order (eq 5, 6) or second-order (eq 7) decomposition of the hydride intermediate to form hydrogen.



The overall reaction shown above, the light-induced oxidation of ascorbic acid to dehydroascorbic acid, involves net energy storage.¹ The optimum pH for hydrogen formation is 5.0. This optimum probably reflects a compromise between the competition of $\text{Co}(\text{bpy})_n^{2+}$ and Hbpy^+ for $\text{Ru}(\text{bpy})_3^+$ (eq 3 vs. eq 1), which is favored by high pH, and the formation of the cobalt hydride (eq 4), which is favored by low pH. The rate of H_2 evolution is linear in light intensity and decreases upon prolonged photolysis. This decrease may be due to the parallel formation of dihydrobipyridine, as well as to reactions involving the dehydroascorbic acid produced in the photolysis. The formation of hydrogen appears unique to Co^{2+} ; the hydrogen yield is much lower when the Co^{2+} is replaced by Fe^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , or Mn^{2+} at comparable concentrations. As is evident from the data in Table I, the quantum yield for H_2 formation is considerably higher when bpy is replaced by 4,4'-(CH_3)₂bpy.

The above results are of considerable interest since they show that $\text{Ru}(\text{bpy})_3^+$ can function both as a homogeneous hydrogenation catalyst and as a mediator in the homogeneous formation of hydrogen. The fact that the latter function is promoted by Co^{2+} is of particular interest, since recent studies have shown that Co^{2+} is also an effective catalyst for the homogeneous oxidation of water to O_2 by $\text{Ru}(\text{bpy})_3^{3+}$.^{25,26} Additional studies aimed at the further characterization of these systems are in progress.^{27,28}

Acknowledgment. We thank Dr. C. Creutz for performing the flash-photolysis experiments and for helpful discussions. We are also grateful to Dr. B. S. Brunshwig for performing the equilibrium calculations. This research was performed under the auspices of the U.S. Department of Energy and supported by its Division of Basic Energy Sciences.

(15) In common with previous work,¹⁶ we find that the dihydrobipyridine is not stable but undergoes further reactions, possibly polymerization.

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(17) Hydrogen is produced when water is added to acetonitrile solutions of $\text{Ru}(\text{bpy})_3^0$.¹⁵

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(21) The concentrations of the bipyridine complexes were calculated on the assumptions that the stability constant of $\text{Co}(\text{HA})^+$ is 4 M ("Critical Stability Constants"; Martell, A. E., Smith, R. M., Eds.; Plenum Press: New York, 1977; Vol. 3) and that the concentrations of mixed bipyridine/ascorbate complexes are negligible.

(22) The absorbance maximum of the intermediate is at somewhat longer wavelengths than that of the cobalt(I) complex produced in the pulse radiolysis of 3:1 mixtures of bpy and Co^{2+} at pH 7.²³

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(27) Some of the electron-transfer reactions induced by $\text{Ru}(\text{bpy})_3^+$ may be similar to those proposed to account for the formation of H_2 , CH_4 , and hydrogenated phenanthroline derivatives in the thermal reactions of methyl-substituted 1,10-phenanthroline complexes of bis(η^5 -cyclopentadienyl)titanium.²⁸ However, although H_2 and hydrogenated phenanthroline derivatives are produced, we do not detect any CH_4 when solutions containing tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)ruthenium(II) and ascorbate are photolyzed.

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