

Pyridinium Quenchers of Ru(bpy)₃²⁺. Charge Effects of the Yield of Electron Transfer

Guilford Jones, II* and Vincent Malba

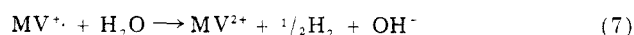
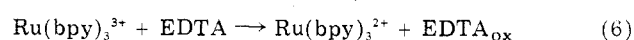
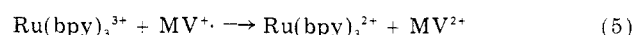
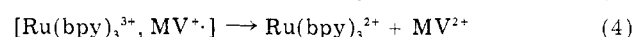
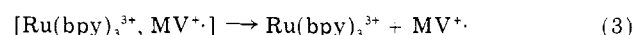
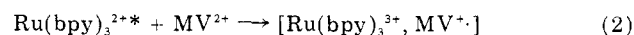
Department of Chemistry, Boston University, Boston, Massachusetts 02215

Received July 9, 1985

The quenching of the luminescent state of tris(2,2'-bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) by a series of pyridinium ions has been studied. 4-Acetyl-, 4-cyano-, 4-carbomethoxy-, or 4-carboxy-1-methylpyridinium, along with the well-known electron-transfer agent methyl viologen (MV²⁺), were employed as electron-acceptor quenchers in order to reveal the effects of charge type on the yield of photoinduced electron transfer involving the Ru(II) luminescent state as electron donor. Rates of quenching by the pyridinium ions were measured by using steady irradiation techniques and compared with expectations based on the calculated energetics of electron transfer. Electron transfer yields were obtained by measurement of the transient absorbances of photogenerated radicals (e.g., pyridinyls) using conventional flash photolysis (broad band visible excitation, pH 5, μ = 0.5). The pyridiniums were less effective electron relays for photocleavage of water in terms of the rate of hydrogen production using the Ru(II) complex as sensitizer, the selected acceptor quenchers, the sacrificial relay, EDTA, and a colloidal platinum catalyst at pH = 5.0. The reduced yield of electron transfer (and photoformation of hydrogen) for quenching by pyridinium ions was consistent with an effect of electrostatic charge in the nascent radical pair produced on electron transfer quenching of Ru(bpy)₃²⁺ by viologens/pyridiniums. The transient photobleaching of Ru(bpy)₃²⁺ by 4-carboxy-1-methylpyridinium was studied by using a Nd:YAG laser with results showing pH control of the charge type and yield of net electron transfer due to in-cage protonation of photogenerated geminate radical pairs. The electrochemical properties of the pyridinium ions were also examined by cyclic voltammetry and a Hammett correlation was made of the reduction potentials.

Tris(2,2'-bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) is a sensitizer whose photophysical and photochemical properties have been extensively studied.¹⁻⁸ The lifetime of Ru(bpy)₃²⁺ is long (0.62 μs in the absence of oxygen), constant as a function of pH and ionic strength, and only moderately influenced by the nature of the solvent.² The excited state of Ru(bpy)₃²⁺ can be quenched either in an oxidative or reductive process, because of suitable redox properties and a sufficiently energetic excited state ($E_{1/2}(\text{Ru}(\text{bpy})_3^{3+/2+}) = 1.26 \text{ V vs. NHE}$; $E_{1/2}(\text{Ru}(\text{bpy})_3^{2+/+}) = -1.28 \text{ vs. NHE}$; $E_{0-0} = 2.12 \text{ eV}$).^{1,8} The constancy of the excited state deactivation in the absence of quenchers over a wide range of conditions and the favorable redox properties make Ru(bpy)₃²⁺ an ideal choice for the study of photochemical electron transfer, including investigations of varied quenchers,⁹ electron relays,¹⁰ catalysts,¹¹ and heterogeneous media.¹²

Scheme I



The suitability of Ru(bpy)₃²⁺ as a light-harvesting agent in a variety of solar energy storage schemes involving the production of useful fuels from common chemicals (e.g., hydrogen and oxygen formation from water) has received considerable attention.¹⁰ A model system for reducing H₂O to H₂ has utilized Ru(bpy)₃²⁺ as a sensitizer, together with methyl viologen as an oxidative quencher, EDTA as an electron donor which is consumed, and colloidal platinum as a catalyst for H₂ production (Scheme I). The quenching of Ru(bpy)₃²⁺ with methyl viologen has been shown¹³ to be an electron-transfer process that proceeds with a respectable yield of charge carriers (between 5% and 35% under a variety of conditions)¹⁴ but that results in virtually no overall chemistry because of bulk recombination of the photoproducts Ru(bpy)₃³⁺ and MV^{·+}. The addition of a moderate concentration of EDTA results in reduction of Ru(bpy)₃³⁺ to Ru(bpy)₃²⁺ leaving the unattended stable radical cation, MV^{·+}, which can linger in solution in the absence of a catalyst. Reaction of MV^{·+} with the colloidal Pt particles results in the oxidation of MV^{·+} to MV²⁺ and reduction of H₂O to H₂. Understanding the factors affecting the yield of the reduced quencher in bulk solution is a necessary prelude to any practical application of such systems.

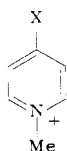
- (1) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, 159.
 (2) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, 101, 4815.
 (3) Sutin, N.; Creutz, C. *Pure. Appl. Chem.* **1980**, 52, 2339.
 (4) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, 75, 1.
 (5) DeGraff, B. A.; Demas, J. N. *J. Am. Chem. Soc.* **1980**, 102, 6169.
 (6) Whitten, D. G. *Acc. Chem. Res.* **1980**, 13, 83.
 (7) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, 98, 4853.
 (8) (a) Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, 98, 6536. (b) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, 104, 3618.
 (9) (a) Amouyal, E.; Zidler, B. *Isr. J. Chem.* **1982**, 22, 117. (b) Takuma, K.; Kajiwara, M.; Matsuo, T. *Chem. Lett.* **1977**, 1199. (c) Takuma, K.; Shuto, Y.; Matsuo, T. *Chem. Lett.* **1978**, 983. (d) Takagi, K.; Ogata, Y. *J. Org. Chem.* **1982**, 47, 1409. (e) Calvin, M. *Acc. Chem. Res.* **1978**, 10, 369.
 (10) (a) Harriman, A.; West, M. A., Eds. "Photogeneration of Hydrogen"; Academic Press: London, 1982. (b) Grätzel, M.; Kalyanasundaram, K.; Kiwi, J. In "Structure and Bonding"; Springer Verlag: New York, 1982; Vol. 49, p 37. (c) Grätzel, M. *Acc. Chem. Res.* **1981**, 14, 376.
 (11) (a) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, 101, 7214. (b) Brugger, P.; Cuendet, P.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, 103, 2923. (c) Dounghong, D.; Borgarello, E.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, 103, 4685. (d) Harriman, A.; Porter, G.; Richoux, M.-C. *J. Chem. Soc., Faraday Trans. 2* **1982**, 78, 1955. (e) Matheson, M. S.; Lee, P. C.; Meisel, D.; Pelizzetti, E. *J. Phys. Chem.* **1983**, 87, 394.
 (12) (a) Tunuli, M.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, 103, 2507. (b) Kopple, K.; Meyerstein, D.; Meisel, D. *J. Phys. Chem.* **1980**, 84, 870. (c) Meisel, D.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1981**, 85, 179. (d) Henglein, A. *J. Phys. Chem.* **1979**, 83, 2209. (e) Spiro, M. J. *Chem. Soc., Faraday Trans. 1* **1979**, 75, 1507.

- (13) (a) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, 61, 2720. (b) Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978**, 2, 547. (c) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1978**, 62, 1345.
 (14) (a) Mandal, K.; Hoffman, M. Z. *J. Phys. Chem.* **1984**, 88, 5632. (b) Kalyanasundaram, K.; Neuman-Spallart, M. *Chem. Phys. Lett.* **1982**, 88, 7.

Correlation of electron-transfer yield with various factors has been an important endeavor in fostering an understanding of photoinduced electron transfer. Quantum yield relationships have been established for dielectric constant and the free energy of excited-state electron transfer, ΔG_{et} .¹⁵ Several studies¹⁶ have shown that, given a common sensitizer, the yield of radical ions that escape the solvent cage increases as ΔG_{et} increases. In other cases (e.g., the quenching of Ru(bpy)₃²⁺ with aromatic amines¹⁷), the yield of net electron transfer can be surprisingly independent of the free-energy change (as long as it is not too positive).

Other potentially important variables governing ion-(radical)-pair dissociation¹⁸ include ionic strength, viscosity, ion-pair radius, temperature, dielectric constant of the medium, and the charges associated with the geminate products of photoinduced electron transfer. Several studies have suggested moderate but significant roles for ionic strength and solvent polarity (among solvents of generally high polarity, e.g., acetonitrile, ethanol, and water).^{14b,19,20} Other investigations²¹ have focused on the charge type of radical pairs for redox systems in homogeneous solution or those involving electron transfer at an interface (colloids, bilayers) with the general conclusion that charge repulsion or attraction can be decisive in dictating electron-transfer yield.

In several related studies, the classic Ru(bpy)₃³⁺/MV²⁺ system has been altered subtly by substitution of methyl viologen with other viologen or pyridinium species⁹ with some emphasis on the structural dependence of electron-transfer energetics. For the present study, a group of pyridinium quenchers was selected for comparison with methyl viologen on the basis of systematic modification of the charge type of the photogenerated radical pairs.



compd	abrev	X
methyl viologen	MV ²⁺	4-Py ⁺ -1-Me
4-acetyl-1-methylpyridinium	AMP ⁺	COCH ₃
4-cyano-1-methylpyridinium	CNMP ⁺	CN
4-carbomethoxy-1-methylpyridinium	CMMP ⁺	COOCH ₃
4-carboxy-1-methylpyridinium	CMP ⁺	COOH
4-carboxy-1-methylpyridinium betaine	CMPB	COO ⁻

(15) (a) Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312. (b) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2. (c) Hino, T.; Akazawa, H.; Masuhara, H.; Mataga, N. *J. Phys. Chem.* **1976**, *80*, 33.

(16) (a) Masuhara, H.; Hino, T.; Mataga, N. *J. Phys. Chem.* **1975**, *79*, 994. (b) Masuhara, H.; Saito, T.; Maeda, Y.; Mataga, N. *J. Mol. Struct.* **1978**, *47*, 243.

(17) Shioyama, H.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1982**, *88*, 161.

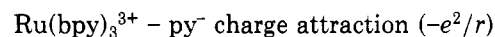
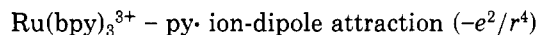
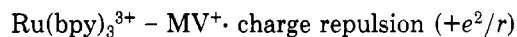
(18) (a) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059. (b) Fuoss, R. M.; Accascina, F. "Electrolytic Conductance"; Interscience: New York, 1959. (c) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanisms"; Wiley: New York, 1981; Chapter 7.

(19) (a) Hino, T.; Masuhara, H.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 394. (b) Gore, B. L.; Harriman, A.; Richoux, M.-C. *J. Photochem.* **1982**, *19*, 209. (c) Houlding, V. H.; Kalyanasundaram, K.; Grätzel, M.; Milgrom, L. R. *J. Phys. Chem.* **1983**, *87*, 3175.

(20) Miedlar, K.; Das, P. K. *J. Am. Chem. Soc.* **1982**, *104*, 7462.

(21) (a) Richoux, M.-C. *Int. J. Sol. Energy* **1982**, *1*, 161. (b) Willner, I.; Yang, J.-M.; Laane, C.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1981**, *85*, 3277. (c) Scaiano, J. C.; Lounnot, D. *J. Phys. Chem.* **1984**, *88*, 3379. (d) Matsuo, T. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 1129. (e) Brugger, P. A.; Grätzel, M.; Guarr, T.; McLendon, G. *J. Phys. Chem.* **1982**, *86*, 944. (f) Oishi, S.; Tajime, K.; Shiojima, I. *J. Mol. Catal.* **1982**, *14*, 383. (g) Fang, Y.; Tollin, G. *Photochem. Photobiol.* **1983**, *38*, 429. (h) Fang, Y.; Tollin, G. *Photochem. Photobiol.* **1984**, *39*, 685. (i) Ohno, T.; Lichtin, N. *N. J. Am. Chem. Soc.* **1980**, *102*, 4636.

Thus, it appeared possible to examine yields of net electron transfer for radical pairs of the following charge type and expected Coulombic effect (in terms of an estimated energy of stabilization (destabilization) for the radical pair):²²



Independently, the effectiveness of the pyridinium radicals which are freed from geminate recombination as charge carriers in the formation of hydrogen from water (Pt catalyst) could be assessed. The study of the fundamental electron-transfer characteristics of the pyridinium series served also as a useful complement to recent work on the photochemical properties of ground-state complexes or ion-pairs of viologen and pyridinium ions.²³

Experimental Section

Materials. Methyl viologen (MV²⁺) was synthesized according to a procedure by Michaelis and Hill²⁴ and was recrystallized three times from methanol. 4-Acetyl-1-methylpyridinium iodide (AMP⁺), 4-carbomethoxy-1-methylpyridinium iodide (CMMP⁺), 4-cyano-1-methylpyridinium iodide (CNMP⁺), and 4-carboxy-1-methylpyridinium iodide (CMP⁺) were synthesized from the corresponding pyridine by refluxing with methyl iodide in acetone, absolute ethanol, or *N,N*-dimethylformamide for 2 h after allowing the solution to stand overnight according to a procedure by Kowower.²⁵ The salts were recrystallized from methanol or ethanol. The chloride salt of CMMP⁺ was prepared from the iodide by passing an aqueous solution through an anionic (chloride-type) ion-exchange resin (Bio-Rad AG1-X8), followed by removal of the water by evaporation in vacuo. 4-Carboxy-1-methylpyridinium betaine (CMPB) was not isolated but was prepared by adjusting the pH of a solution of CMP⁺ above 3.0 [$\text{p}K_a(\text{CMP}^+) = 1.72$]. Tris-2,2'-bipyridine ruthenous dichloride hexahydrate, Ru(bpy)₃²⁺ (G. F. Smith Chemical Co.), 4-carboxy-1-methylpyridinium chloride, CMP⁺ (Aldrich Chemical Co.), and EDTA (Baker, reagent grade) were used as received. Deionized water was used as solvent. Buffers were prepared from Fisher reagent sodium acetate and glacial acetic acid or from various mixtures of Fisher reagent mono-, di-, and trisodium phosphates. Colloidal Pt was prepared by the sodium citrate reduction of hexachloroplatinic acid according to a procedure by Kiwi and Grätzel,^{11a} and was protected with Carbowax 200M (polyethylene glycol).

Luminescence Quenching. Rates of quenching were determined in aqueous solution by the steady state Stern-Volmer method with a Perkin-Elmer MPF-44A fluorescence spectrophotometer. Plots of I_0/I vs. [quencher] were linear with an intercept close to unity in all cases. The quenching experiments were performed in air, and the previously reported lifetime in air, $\tau(\text{Ru(bpy)}_3^{2+}) = 0.40 \mu\text{s}$, was confirmed by nanosecond flash photolysis.^{29b} The ionic strength was held constant throughout by using high buffer concentrations (0.03 M acetate or 0.5 M phosphate at pH = 5; 0.5 M phosphate at pH = 0.5). For the quenching experiments, $[\text{Ru(bpy)}_3^{2+}] = 10^{-5} \text{ M}$, with $\lambda_{exc} = 450 \text{ nm}$ and $\lambda_{mon} = 610 \text{ nm}$.

(22) (a) Shin, H. In "Ion-Molecule Reactions in the Gas Phase"; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1966; p 44. (b) Degani, Y.; Willner, I. *J. Am. Chem. Soc.* **1983**, *105*, 6228.

(23) (a) Hoffman, M. Z.; Prasad, D. R.; Jones, G., II; Malba, V. *J. Am. Chem. Soc.* **1983**, *105*, 6360. (b) Jones, G., II; Malba, V. *Chem. Phys. Lett.*, **1985**, *119*, 105. (c) Jones, G., II; Zisk, M. B. *J. Org. Chem.*, in press.

(24) Michaelis, L.; Hill, E. *J. Gen. Physiol.* **1933**, *16*, 859.

(25) (a) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253. (b) Kosower, E. M. *J. Am. Chem. Soc.* **1955**, *77*, 3883.

(26) Neta, P.; Patterson, L. K. *J. Phys. Chem.* **1974**, *78*, 2211.

(27) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(28) Hermolin, J.; Levin, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4814.

(29) (a) Caspairi, G.; Hughes, R. G.; Endicott, J. F.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1970**, *92*, 6801. (b) Malba, V.; Jones, G., II; Poliakov, E. D. *Photochem. Photobiol.* **1985**, *42*, 451.

Table I. Pyridinium Reduction Potentials, Ion Pair Energies, Free Energies of Electron Transfer for Oxidative Quenching of Ru(bpy)₃²⁺, and σ_p Constants

pyridinium	pH	$E_{1/2}^b$	E_{ip}^c	ΔG_{et}^d	σ_p^e
MV ²⁺	5	-0.45	1.72	-0.40	
AMP ⁺	5	-0.51	1.78	-0.27	0.52
CNMP ⁺	5	-0.62	1.89	-0.23	0.66
CMMP ⁺	5	-0.72	1.99	-0.13	0.44
CMP ⁺ ^{e,f}	0.5	-0.80	2.07	-0.05	0.21
CMPB ^g	5	-0.92	2.19	+0.07	0.0

^a Counterions: Cl⁻ for MV²⁺; I⁻ for AMP⁺, CNMP⁺, CMMP⁺, and CMP⁺; both I⁻ and Cl⁻ for CMMP⁺ and CMP⁺ (without noticeable difference). Conditions: H₂O solvent with 6–8 mM py salt in 0.1 M KCl supporting electrolyte. Working electrodes included Pt, carbon paste, glassy carbon. ^b $E_{1/2} = (E_{pc} + E_{pa})/2$, except for CMP⁺ and CMPB, where $E_{1/2} = E_{pc/2}$ at 200 mV/s (irreversible cathodic current). Reference electrode was Ag/AgCl. $E_{1/2}$ values were converted to volts vs. NHE. ^c Ion pair energy. $E_{ip} = nF[E(D^+/D) + E(A/A^+)]$, where $E(D^+/D) = 1.26$ V for Ru(bpy)₃²⁺ (ref 1). ^d In eV. From ref 41. $E_{0-0}(\text{Ru}(\text{bpy})_3^{2+}) = 2.12$ eV (ref 1). Coulombic interaction term not included. ^e $pK_a(\text{CMP}) = 1.72$ (ref 42). ^f HCl used to adjust pH. $\mu = 0.5$ M. ^g From ref 35b, p 46.

Cyclic Voltammetry. A CV-1A cyclic voltammetry unit from Bio-Analytical Systems was used to measure the potential vs. current curves for the pyridiniums. The cell consisted of a Ag/(0.1 M AgCl) reference electrode, a Pt auxiliary electrode, and one of several working electrodes (platinum (PTE), glassy carbon (GCE), and carbon paste (CPE)) immersed in an aqueous 0.1 M KCl solution containing 6–8 mM pyridinium salt. Measurements were performed both in aerated and deaerated solution, without noticeable difference. MV²⁺, CMMP⁺, and AMP⁺ displayed completely reversible behavior, while CMP⁺ and CMPB were irreversible over the scan rate range of 50–500 mV s⁻¹. CNMP⁺ showed nearly reversible behavior for one or two scans at a fast scan speed, but a new cathodic peak and a new anodic peak grew in at a potential less negative than the original peaks. The two new peaks corresponded to the cyclic voltammogram of MV²⁺, which is known to form from the chemical reduction of CNMP⁺. The potentials listed in Table I are $E_{1/2} = (E_{pc} + E_{pa})/2$, except for CMP⁺ and CMPB, for which $E_{1/2} = E_{pc/2}$ at 200 mV s⁻¹. All potentials are reported vs. NHE, which is -0.222 V vs. Ag/AgCl.

The cyclic voltammetry apparatus was also used with a gold mesh OTE (optically transparent electrode from Bio-Analytical Systems) in a Perkin-Elmer 552 UV-vis spectrophotometer in order to identify the radicals produced during the reduction process, and to obtain to confirm extinction coefficients for these radicals. The OTE consisted of a 1 × 1/2 in. piece of gold mesh (% T ≈ 50% for wavelengths between 320 and 700 nm) sandwiched between two glass microscope slides. The OTE was enclosed in a glass cell with valves which allowed argon to be bubbled through the cell prior to the experiment, and which allowed a pressure of argon to be exerted over the top of the solution during the experiment. Solution was added to the cell in a quantity such that the bottom of the OTE was immersed, but the gold mesh was not. Capillary action caused the solution to rise between the slides, covering the gold mesh. Cyclic voltammograms were taken with the OTE to determine the voltage required for complete reduction on that electrode, and then the CV-1A was set at a potential sufficiently negative to insure reduction. CMP⁺ and CMPB were completely irreversible on reduction at the gold electrode, and no changes in the UV-vis spectra were discernible when reduction was carried out at potentials sufficiently negative to reduce both species. The cyclic voltammograms for the other salts showed quasi-reversible behavior on the gold electrode, as opposed to the reversible behavior observed with the PTE, GCE, and CPE electrodes. Definite changes in the absorption spectra for each of the salts were observed during reduction. The new absorbances correlated well with the literature values for the λ_{max} of the pyridinyl radicals (Table III).

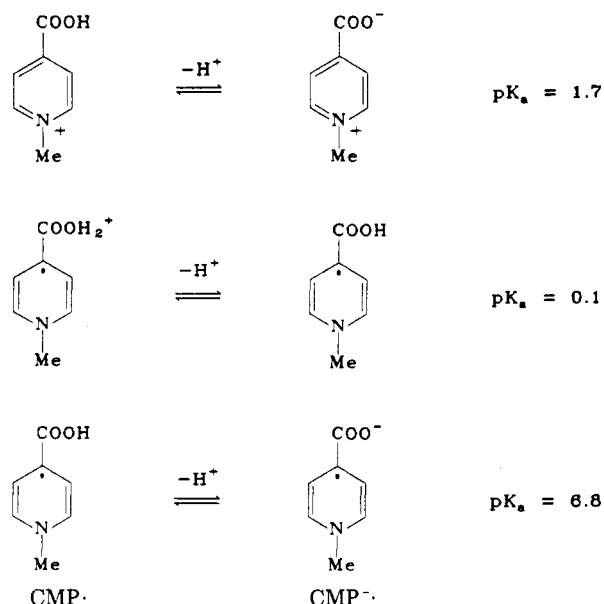
Determination of the extinction coefficients of the pyridinyl radicals was problematic. It was necessary to assume that all of the pyridinium ions within the path length of the electrode were reduced to the corresponding pyridinyl radicals and that the reduced species were stable for a long enough time so that substantial decay had not taken place before or during the observation

time. For AMP⁺ and CMMP⁺, decay of the radical to half the maximum absorbance occurred within a few minutes, while for MV²⁺ decay took a considerably longer time (>30 min). MV²⁺ was examined as a control, since a recent reliable value of ϵ (1.37×10^4 M⁻¹ cm⁻¹) was determined by a similar method.²⁷ The value we obtained for MV⁺ at 605 nm was 9.6×10^3 M⁻¹ cm⁻¹, which is only 70% of the accepted value. The value obtained for CMMP⁺ (3.1×10^3 M⁻¹ cm⁻¹) was only 47% of the best known value²⁸ (see Table III). For AMP⁺ a value of 2.5×10^3 M⁻¹ cm⁻¹ was obtained. Assuming that the same factors responsible for the low value of ϵ for CMMP⁺ were causing a similarly low value for AMP⁺, the ϵ for the AMP⁺ was increased by 53%. Justification for this procedure comes from the similar electrochemical behavior of CMMP⁺ and AMP⁺ and from the similar size and chemical structure, which should result in a similar oscillator strength. Because of the difficulty in determining ϵ for AMP⁺ a significant error may reside in the electron-transfer yield calculated from it. Other ϵ values used for the photochemical study of the pyridiniums were those previously reported.

Flash Photolysis. A conventional flash photolysis apparatus^{29a} consisting of a Xenon Corp. 10-kV high-voltage power supply and xenon flash lamps (FWHM = 35 μ s), a Hilger-Engis monochromator (Model 600), an RCA 4832 PMT, and a Tektronix 564 storage oscilloscope was used to measure relative yields of reduced pyridiniums. ΔOD 's were determined at appropriate wavelengths (see Table III) 200 μ s after the xenon flash lamp discharge, a time during which there was virtually no decay for any of the radical species (with EDTA present to scavenge Ru(bpy)₃²⁺), and a time long enough to be certain that the radicals had reached bulk solution. The λ_{max} (see Table III) for each of the species examined was confirmed by examining several λ_{mon} (see Figure 3). Transient absorbances were recorded at the λ_{max} . Solutions were flashed in a jacketed 22-cm path length cell which was purged with argon prior to irradiation. The cell jacket contained a filter solution (KCrO₄ and 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate in water) which only transmitted light above 400 nm, so that the incident light was absorbed only by Ru(bpy)₃²⁺. [Ru(bpy)₃²⁺] = 4.4×10^{-6} M, [EDTA] = 10 mM, and [pyridinium] was calculated to quench 80% of Ru(bpy)₃²⁺ luminescence by using the values for k_q determined by Stern-Volmer quenching. In order to monitor the various pyridinyl radicals which absorb between 390 and 440 nm, and in order to assure uniform excitation throughout the flash cell, the absorbance of Ru(bpy)₃²⁺ was kept low ($OD_{450}^{1\text{cm}} = 0.06$). 0.5 M acetate buffer ($\mu = 0.5$ M) was used to maintain the pH at 5. The absorbance of MV⁺ persisted for minutes following flash excitation, whereas the other pyridinyls were true transients.

A laser flash photolysis apparatus^{29b} consisting of a 10-Hz Quantel YG-581 Nd:YAG laser, an SI monochromator, an RCA 4840 PMT, and a Lecroy 100-MHz transient recorder interfaced via a Kinetic Systems CAMAC Crate to a PDP-11 microcomputer was used to examine the yield of Ru(bpy)₃²⁺ bleaching as a function of pH in the presence of CMP⁺ but without EDTA (Figure 2). The sample was excited by 60-mJ pulses of the 355-nm laser beam, and Ru(bpy)₃²⁺ was monitored at $\lambda_{max} = 450$ nm ($OD = 0.20$). ΔOD 's were determined 1–4 μ s after the flash, a time during which no recovery back to the base line had occurred. The pyridinyl species was not monitored directly because its extinction coefficient at 395–400 nm is similar to ϵ_{395} for Ru(bpy)₃²⁺ and, consequently, was only barely distinguishable in the absence of EDTA. EDTA was not used in order to prevent the buildup of radical absorbances which would have hampered signal averaging. Each data point was the result of 2–4 separate determinations, each of which consisted of 25–100 laser shots. Samples showed no sign of photodegradation under these conditions. Corrections were made for the percentage of quenching, which ranged from 40% to 85%. Correction was also made for the percentage of light absorbed by Ru(bpy)₃²⁺, which changed slightly as a function of pH, because of the competitive absorption from the CMP⁺/Cl⁻ complex, which is stronger at lower pH's (see reaction 1, Scheme II). [Ru(bpy)₃²⁺] = 3.5×10^{-5} M; [CMP⁺] = 5–60 mM. The pH was adjusted with HCl, and the ionic strength was held constant at $\mu = 2$ M in the pH range from -1 to +2 by the addition of NaCl. For the data points at pH 5 and 8.4, $\mu = 0.06$ M. The pH values above 1.4 were measured with Fisher Accumet pH meter, while the pH values below 1.4 are actually H_0 (Hammett acidity

Scheme II



function) values determined by addition of known amounts of HCl.⁴⁰

Hydrogen Generation. Hydrogen production experiments were performed in an elliptical photoreaction chamber designed by Becker.³⁰ At one focus of an elliptical cylinder constructed of Milar coated cardboard was placed a 450-W high-pressure mercury lamp enclosed in a Hanovia immersion well through which a filter solution (see Flash Photolysis above) was pumped using a thermostated bath to dissipate heat. The sample cell containing 25 mL of solution was positioned at the other focus and was connected through a septum to the top of a buret which was filled with water and closed with a septum. A leveling bulb attached to the bottom of the buret allowed volume readings to be taken at atmospheric pressure. A cold finger, through which thermostated water was continually pumped, was immersed in the reaction solution to control the temperature. Argon was bubbled through the solution and over the top of the water in the buret for 30 min prior to irradiation by inserting a foot-long, flexible, degassing needle through the reaction vessel septum and inserting a vent needle into the buret septum. The buret valve was kept closed during degassing. Solutions contained [Ru(bpy)₃²⁺] = 2.2 × 10⁻⁴ M, [EDTA] = 15 mM, [Pt] = 7.5 × 10⁻⁵ M, 0.36 M phosphate buffer in deionized water, and sufficient pyridinium to quench >95% of Ru(bpy)₃²⁺ luminescence. A solution of pH 5.0 was selected, which is near the optimum value for hydrogen production, determined in several studies.^{10,31}

The volume of gas was monitored at 10-min intervals for 2 h. No actinometry was used to measure photon flux; yields in Table III assume a constant number of photons per 2-h period. The change in the volume was assumed to result entirely from H₂, since no other light gases were detected in the gas chromatographic (GC) analysis, so that the reported yields are actually relative volume changes (CO₂ is retained by a 5-Å molecular sieve so that its presence may have been undetected). GC analysis was performed on a Varian aerograph 90-P GC with a 2.0-m aluminum column containing a 200-mesh 5-Å molecular sieve stationary phase (argon carrier gas). The column, injector, and detector were held at ambient temperature. Pure gases were used to determine retention times: H₂, 0.5 min; O₂, 1.0 min; N₂, 2.4 min.

Results

Table I contains the results of a series of cyclic voltammetry experiments which were conducted in order to obtain $E(A/A^-)$ values for the pyridiniums. The decrease in the reduction potential as the substituent in the 4-position becomes less electron withdrawing was an expected result.

(30) Becker, W. G. Ph.D. Thesis, Boston University, 1982.

(31) (a) Miller, D.; McLendon, G. *Inorg. Chem.* **1981**, *20*, 950. (b) Miller, D. S.; McLendon, G. *J. Am. Chem. Soc.* **1981**, *103*, 6791.

Table II. Quenching of Ru(bpy)₃²⁺ by Pyridinium Ions in Aqueous Solution

quencher ^a	0.5 M phosphate		0.03 M acetate	
	K_{SV}^b/M^{-1}	$10^9 k_q/M^{-1} s^{-1}$	K_{SV}^b/M^{-1}	$10^9 k_q/M^{-1} s^{-1}$
MV ²⁺	510	1.3	400	1.0
AMP ⁺	730	1.8	700	1.8
CNMP ⁺	830	2.1	760	1.9
CMMP ⁺	740	1.9	560	1.4
CMP ⁺	870	2.2		
CMPB	21	0.053	22	0.055

^a Conditions: [Ru(bpy)₃²⁺] = 0.1 mM; pH = 5 except for CMP⁺, for which pH = 0.5. λ_{exc} = 450 nm; λ_{mon} = 610 nm. ^b Determined in aerated solutions. $K_{SV} = k_q \tau_0$. τ_0 = 0.40 μ s, measured by laser flash photolysis.

The reversibility of the voltammograms for MV²⁺, AMP⁺, and CMMP⁺ is also expected because of the known stability of the radical species³² formed upon reduction. The reduction of CNMP⁺, which led to the eventual formation of MV²⁺, is a result foreshadowed by Kosower's finding³³ of similar behavior in homogeneous media when CNMP⁺ is reduced with the chemical reductant, sodium dithionite. The irreversible behavior of CMP⁺ and CMPB is less obvious since CMP⁺ is known to be reversibly reduced in CV experiments in 95% ethanol with 0.2 M KOH ($E_{1/2}$ = -0.79).³⁴ Both CMP[•] and CMP^{-•} are known from pulse radiolysis experiments²⁶ (note ϵ data, Table III). CMP[•] should be the dominant species between pH 0.1 and 6.8 (Scheme II)^{26,42} while CMP^{-•} is not important for the pH ranges in this study. CMP[•] is known to dimerize in water with $k = 10^6 M^{-1} s^{-1}$,²⁶ which is much faster than the rate constants for decay for other pyridinyl radical species; dimerization is the most probable explanation for the irreversible reduction of both CMP⁺ and CMPB.

The results of quenching Ru(bpy)₃²⁺ with the pyridiniums are presented in Table II for two different buffers. Quenching rate constants (k_q) for all of the compounds except CMPB are near the diffusion controlled limit for ions in solution. This is the expected result for electron-transfer quenching, based on the generally exoergic values for ΔG_{et} which were computed from the redox potentials for all quenchers except CMPB. The unusually low k_q value for CMPB can be attributed to the borderline exothermicity of electron transfer as calculated from the Rehm-Weller⁴¹ equation. Although quenching Ru(bpy)₃²⁺ luminescence with MV²⁺ is highly favored based on ΔG_{et} values, in fact $k_q(\text{MV}^{2+})$ is smaller than k_q for the other pyridiniums. This somewhat lower k_q value for methyl viologen results from its greater positive charge, reflecting a diminished rate of encounter by diffusion between ions of higher like charge (i.e., 2+,2+ vs. 2+,1+). The quenching rates under different ionic strengths show minor qualitative trends consistent with Debye-Hückel theory.³⁶ For ions of like charge, the rate of encounter increases with increases in ionic strength. The quenching patterns are consistent with an electron transfer mechanism for the pyridiniums such as the one shown to be applicable for Ru(bpy)₃²⁺ and MV²⁺.¹⁰

Pyridinium quenching of Ru(bpy)₃²⁺ in the presence of 10 mM EDTA in conventional flash photolysis resulted in the unequivocal detection of the pyridinyl radicals based

(32) (a) Kosower, E. M.; Poziomek, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5515. (b) Frangopol, M.; Frangopol, P. T.; Trichilo, C. L.; Geiger, F. E.; Filipescu, N. *J. Org. Chem.* **1973**, *38*, 2355. (c) Grossi, L.; Minisci, F.; Pedulli, G. F. *J. Chem. Soc., Perkin Trans. 2* **1977**, 943. (d) Grossi, L.; Minisci, F.; Pedulli, G. F. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 948.

(33) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524.

(34) Volkeova, V.; Klima, J.; Volke, J. *Electrochimica Acta* **1978**, *23*, 1215.

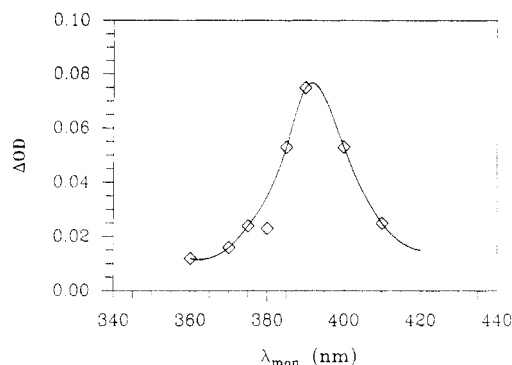


Figure 1. Transient spectrum of $\text{CMP}\cdot$ produced by conventional flash photolysis of 4.4×10^{-6} M $\text{Ru}(\text{bpy})_3^{2+}$; $[\text{CMP}^+] = 0.15$ M, $[\text{EDTA}] = 0.010$ M in aqueous solution at pH = 5.0 (0.5 M acetate buffer). $\lambda_{\text{exc}} > 400$ nm. Transient OD was measured 200 μs after the flash.

Table III. Radical Yields Resulting from Electron Transfer in the Presence of EDTA

pyridinyl	rel ϕ_{radical}^a	rel H_2^b	$\lambda_{\text{mon}}/\text{nm}$	ϵ_{py}	ref (ϵ , λ)
MV^+	1.0	1.0	600	13700	27
$\text{AMP}\cdot$	0.18	<0.01	430	5300	43 ^d
$\text{CNMP}\cdot$		0.27	410		43
$\text{CMMP}\cdot$	0.27	0.17	395	6500	28
$\text{CMP}\cdot$	0.26	<0.01	400	6300	26
$\text{CMP}^{\cdot-}$			395	7000	26

^a Conventional flash photolysis. ΔOD at 100 μs after flash. $[\text{Ru}(\text{bpy})_3^{2+}] = 4.4 \times 10^{-6}$ M; $[\text{EDTA}] = 10$ mM; $[\text{py}]$ sufficient to quench %80 of $\text{Ru}(\text{bpy})_3^{2+}$ luminescence. 0.5 M acetate buffer at pH 5. Filter solution (see Experimental Section) transmitted only above 400 nm. ^b Hanovia 450-W lamp in elliptical photoreaction chamber. $\lambda_{\text{exc}} > 400$ nm. $[\text{Ru}(\text{bpy})_3^{2+}] = 0.2$ mM; $[\text{Pt}] = 0.075$ mM; $[\text{EDTA}] = 15$ mM; 0.4 M phosphate buffer; pH 5. ^c $pK_a = 6.8$ (ref 26). ^d No literature value for ϵ available; ϵ determined with an optically transparent electrode relative to $\text{CMMP}\cdot$ (see Experimental Section).

on the reported absorption data (see Figure 1). In the absence of the secondary electron donor and scavenger, EDTA (Scheme I, reaction 6), transient pyridinyl radicals were not observed because ϵ_{395} of $\text{Ru}(\text{bpy})_3^{2+}$ is similar to ϵ_{395} for the radicals, so that decay of the radical and recovery of $\text{Ru}(\text{bpy})_3^{2+}$ were coincident. The relative yields and other data are presented in Table III. The pyridinium quenchers are only about 25% as effective as MV^{2+} at producing bulk radicals, even though the percentage of quenching of the excited state of $\text{Ru}(\text{bpy})_3^{2+}$ is the same in all cases. The yield of $\text{AMP}\cdot$ is somewhat lower than the yield of radicals from the other pyridinium quenchers, but the extinction coefficient of $\text{AMP}\cdot$ which was determined by an electrochemical method (see Experimental Section) is not known with a high degree of certainty.

During the course of our investigation, a pulsed Nd:YAG flash photolysis system became available.^{29b} Using this alternative technique, we studied the potentially more complicated CMP^+ system in detail by inspecting the transient behavior in a somewhat shorter time regime (~ 1 μs). With laser flash conditions, CMP^+ quenching of $\text{Ru}(\text{bpy})_3^{2+}$ in the absence of EDTA produced bulk radicals with an efficiency of 0.50 ± 0.10 compared with MV^{2+} quenching under similar conditions ($\mu = 0.06$ M; pH = 5.0). For both CMP^+ and MV^{2+} , the transient photobleaching of $\text{Ru}(\text{bpy})_3^{2+}$ was monitored at $\lambda_{\text{mon}} = 450$ nm (instead of monitoring the respective radical absorptions). Figure 2 shows the effect of pH on the transient photobleaching of $\text{Ru}(\text{bpy})_3^{2+}$ on quenching with CMP^+ (or CMPB). Photobleaching increases as pH decreases, corresponding to a titration curve for $pK_a = 0.1$. The latter can be associated with the pK_a of the protonated pyridinyl car-

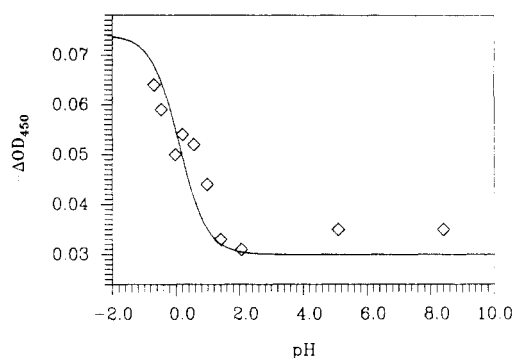


Figure 2. Transient photobleaching of $\text{Ru}(\text{bpy})_3^{2+}$ produced by quenching $\text{Ru}(\text{bpy})_3^{2+}$ with CMP^+ as a function of pH. $[\text{Ru}(\text{bpy})_3^{2+}] = 3.5 \times 10^{-5}$ M; $[\text{CMP}^+] = 5\text{--}60$ mM. $\lambda_{\text{exc}} = 355$ nm; $\lambda_{\text{mon}} = 450$ nm. $\mu = 2.0$ M, except at pH 5.0 and 8.4, for which $\mu = 0.06$ M. The "pH" (H_0) below 1.4 was determined from the concentration of HCl used according to ref 40. The solid titration curve was calculated with $pK_a = 0.1$. Transients were recorded 1 μs following pulse from Nd:YAG laser ($\lambda/3$).

boxylic acid (reaction 2, Scheme II). The data points at pH 5.0 and 8.4 were obtained at $\mu = 0.06$ M, whereas other data were obtained at $\mu = 2$ M. The somewhat higher yield values for pH 5.0 and 8.4 compared with the titration curve are probably due to the lower ionic strength used. High ionic strength has been shown to reduce the yield of cage escape.^{14b}

The hydrogen yields, also presented in Table III, show a pattern of reactivity which differs from expectations based on the yield of free radicals determined by flash photolysis. The system containing methyl viologen was by far the most efficient producer of H_2 , and the relative yield measurements for the MV^{2+} system are in fact probably underestimated because some dark blue color associated with MV^+ persists during the irradiation period and presumably is indicative of some competitive absorption near 400 nm (not observed for the pyridiniums). The effectiveness of CNMP^+ as a relay for water reduction may be due in part to its tendency to produce MV^{2+} , which in turn acts as a quencher and relay. The profile of hydrogen yield in the other cases appears to follow the trend of second order decay of the radicals (presumed tendency to dimerize) in the absence of a Pt catalyst. Thus, the $\text{AMP}\cdot$ and $\text{CMP}\cdot$ radicals decayed in the 10-ms and 0.1-s time regimes, respectively (lowest H_2 yields), whereas $\text{CMMP}\cdot$ persisted for ca. 1.0 s following flash excitation.

Discussion

The electron-accepting properties of the pyridiniums are readily understood in terms of classical substituent influences. A plot of reduction potentials vs. the Hammett substituent constant, σ_p , is shown in Figure 3. The correlation is only fair ($r = 0.88$), but keeping in mind the uncertainties concerning the electrochemical behavior of several of the pyridiniums, a value for the reaction constant, $\rho = 0.53$ V can nevertheless be estimated. For comparison, $\rho = 0.23$ V for substituent influences on the reduction of N-substituted aryl pyridinium,³⁵ also reflecting a modest relative stabilization by electron-withdrawing groups of pyridinium species.

The suppression in the rate of quenching of $\text{Ru}(\text{bpy})_3^{2+}$ as a function of pyridinium reduction potential is qualitatively in line with electron-transfer theory,^{3b,15b,41} i.e.,

(35) (a) Schwabe, K. *Chem. Tech. (Leipzig)* 1957, 9, 129. (b) Zuman, P. "Substituent Effects in Organic Polarography"; Plenum Press: New York, 1967.

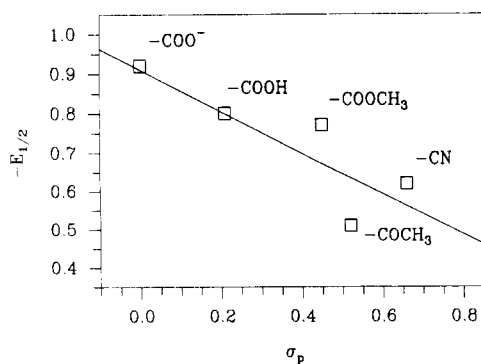


Figure 3. Hammett correlation of $E_{1/2}$ values (NHE) for the 4-substituted 1-methylpyridinium salts vs. σ_p for substitution by functional groups in the para position. $E_{1/2} = (E_{pc} + E_{pa})/2$, except for COOH and COO⁻, for which $E_{1/2} = E_{pc/2}$ at 200 mV/s.

bimolecular quenching will proceed under diffusion control until the electron transfer for the excited state-quencher pair nears thermoneutrality (usually ΔG_{et} ca. -5 kcal/mol or -0.2 eV) at which point k_q is reduced significantly. For the present series, the data for the "slow" regime are insufficient to permit a more quantitative comparison.

The quantum yield of free radicals from pyridinium photoreduction under conditions of virtually complete quenching of the Ru(II) complex will be given by $k_3/(k_3 + k_4)$ (Scheme I), defining the competition between back-electron-transfer and cage-release rates. The absolute values of ϕ_{et} for the viologen/pyridinium series can be reliably calculated based on recently refined data for Ru(bpy)₃²⁺ quenching by MV²⁺.¹⁴ Based on proper comparison with respect to concentrations, ionic strength, and extent of Ru(II) quenching, $\phi_{et} = 0.10$ and 0.050 for quenching by MV²⁺ and CMP⁺, respectively. Although several uncertainties preclude a more quantitative dissection of k_3 and k_4 (their absolute magnitudes are in fact not experimentally defined), an assignment of the observed trend can be qualitatively made. Back electron transfer within the radical pair which resides near 2.0 eV (46 kcal/mol) above the ground state will be fast and subtly dependent on structure and geometry of the pair ($k_4 = 10^{10}$ s⁻¹ or more).³⁷ The rate of back transfer may in fact be slowed as the ion-pair energy is increased (pyridinium quencher is less oxidizing, Table I) due to poor Franck-Condon factors for geminate recombination.³⁸ The observed trend is therefore most consistent with a reduced rate of cage escape, k_3 , associated with the substituent alteration of the charge type for radical pairs. The data for the pyridinium quenchers suggests that alteration of the Coulomb force which potentially binds or repels the radical pair results in an alteration in electron transfer yield by a factor of 2-5 for each unit of charge.

The yield of electron transfer presents some interesting complexities in terms of the state of protonation of various species. The photoreduction of CMP⁺ upon laser flash photolysis is decidedly pH dependent (Figure 2); i.e., an increase in pH leads to a decrease in yield. This pH effect can be ascribed most readily again to a change in the charge type of the radical species formed upon quenching. However, the rate of proton transfer is an unknown factor in attempting to identify the charge type of radicals (ions) in the solvent cage. If the rate of proton transfer is very rapid, then the pK_a of the radical will determine the charge type in the cage, but if the rate of protonation is so slow that it does not successfully compete with cage release, then the pK_a of importance in determining the charge type within the solvent is the pyridinium and not the pyridinyl. The acid-base reactions of importance are shown in

Scheme II, along with the corresponding pK_a values.^{26,42} A titration curve calculated from $pH = pK_a + \log C_B/C_{BH}$ with $pK_a = 0.1$ (Figure 2) closely corresponds to the yield data obtained, suggesting that the acid-base equilibrium which determines the nature of the charge on the cage pair prior to release is the second reaction in Scheme II (i.e., repulsion of the radical conjugate acid becomes important below $pH \sim 1.5$). This result strongly suggests that proton transfer occurs within the cage³⁹ and that the resulting charge of the ion is an important factor in the cage-release rate.

Given the apparent importance of the state of protonation and consequent charge type of the radicals in the solvent cage, the pK_a of CMP[•] (reaction 3 in Scheme II) is not, surprisingly, a factor in determining the relative yield of photobleaching. The answer may be that the attraction between an ion and a molecule, given nominally by $U(r) = -e^2/r^4$,²² may reduce the rate of cage release about as effectively as attraction between oppositely charged ions when specific intermolecular interactions and solvent forces are taken into account. Although this comparison reveals an added complexity for the present analysis, the data from Figure 3 and the fundamental trend of electron-transfer efficiency for the pyridiniums (Table III) remain consistent with an overriding factor of charge repulsion within the solvent cage.

In the presence of EDTA (conventional flash) the relative yield of photoreduction of the pyridiniums (and CMP⁺ in particular) compared with MV²⁺ is only 50% of the yield in the absence of EDTA (laser flash). The rate of production of the pyridinyl radicals (ions) in the presence of EDTA (0.2-ms time regime) depends not only upon the competition between reactions 3 and 4 (Scheme I) which determines the cage-escape yield, $\phi_{cr} = k_3/(k_3 + k_4)$, but also depends upon the competition between reactions 5 and 6. While k_6 will be the same regardless of the pyridinium quencher used, k_5 will depend upon the charge type of the bulk radical species present, because the rate of bimolecular recombination for particles in solution is a function of the charge type (vide supra). Reactions between oppositely charged ions (Ru(bpy)₃³⁺, CMP⁻) are generally faster than reactions between similarly charged ions (Ru(bpy)₃²⁺, MV^{•+})³⁶ (vide supra). Therefore, an "early" loss (before 200 μ s) of pyridinyl species before Ru(bpy)₃³⁺ is completely scavenged may be important and contribute to the apparently low yield of photoreduction of the pyridinium is conventional flash photolysis.

In summary, the supposition that the yield of net photochemical electron transfer for the Ru(bpy)₃²⁺/MV²⁺ system is assisted by charge repulsion in the nascent radical pair is confirmed on comparison of MV²⁺ with a series of monovalent pyridinium quenchers in which geminate photoproducts are expected to have no electrostatic repulsion.¹ Yields of photoformation of hydrogen from water with the Ru(II) complex acting as photosensitizer and the pyridiniums acting as electron relays (in the presence of Pt colloids) are not parallel with this trend of

(36) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

(37) (a) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047 and references therein.

(38) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

(39) A number of picosecond time-resolved studies have documented a fast H⁺ transfer following electron-transfer quenching; see, for example: Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 5708.

(40) Rochester, C. H. "Acidity Functions"; Academic Press: New York, 1970.

(41) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(42) Black, M. L. *J. Phys. Chem.* **1955**, *59*, 670.

(43) Itoh, M.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 369.

efficiency in charge carrier production (Table III), showing that the structure of the electron relay (not just the electrochemical driving force) is important in determining the rate of colloid-catalyzed water splitting.⁴⁴

(44) Whitten has reported that CMMP⁺ is less effective than MV²⁺ as a relay for photocurrent generation (at a Pt electrode) sensitized by benzophenone in isopropyl alcohol.⁴⁵ Launikonis et al. have shown the H₂ yields are a function of pH, E_{1/2} (between -0.5 and -0.7 V), and the structure of diquatery pyridiniums (hydrogenation susceptibility).⁴⁶

Acknowledgment. This research was supported by the Department of Energy, Office of Basic Energy Sciences. We also acknowledge the advice and assistance of Professor Morton Z. Hoffman and Dr. D. R. Prasad.

(45) Chandrasekaran, K.; Whitten, D. G. *J. Am. Chem. Soc.* 1981, 103, 2770.

(46) Launikonis, A.; Loder, J. W.; Mau, A. W.-H.; Sasse, W. H. F.; Summers, L. A.; Wells, D. *Aust. J. Chem.* 1982, 35, 1341.

Inverse Electron Demand Diels–Alder Reactions of Heterocyclic Aza Dienes. Studies on the Total Synthesis of Lavendamycin: Investigative Studies on the Preparation of the CDE β -Carboline Ring System and AB Quinoline-5,8-quinone Ring System

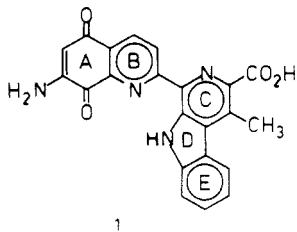
Dale L. Boger,*¹ Steven R. Duff, James S. Panek, and Masami Yasuda

Department of Medicinal Chemistry, The University of Kansas, Lawrence, Kansas 66045-2500

Received September 10, 1985

The investigation and utilization of the inverse electron demand [4 + 2] cycloaddition of 3,5,6-tris(ethoxycarbonyl)-1,2,4-triazine with electron-rich olefins and the subsequent implementation of a palladium(0)-mediated β -carboline synthesis for the preparation of the CDE ring system of lavendamycin are detailed. Studies on the introduction and preparation of the 7-aminoquinoline-5,8-quinone AB ring system of lavendamycin are described.

Lavendamycin (1)², an antitumor antibiotic³ recently isolated from *Streptomyces lavendulae* and structurally related to streptonigrin, has been the focus of synthetic efforts⁴ since its initial structural identification.² A recent,



reported total synthesis of lavendamycin methyl ester, which proved identical with material derived from natural lavendamycin, has verified the proposed structure 1.^{4a} Herein we describe full details⁵ of initial efforts designed

to construct the β -carboline CDE ring system and the 7-aminoquinoline-5,8-quinone AB ring system of lavendamycin which have been conducted in the development of a total synthesis of lavendamycin⁶ and concurrent with our efforts to define the structural features responsible for or potentiating the antimicrobial and cytotoxic properties of quinoline-5,8-quinone antitumor antibiotics.

Studies on the Preparation of the CDE Ring System of Lavendamycin: Inverse Electron Demand Diels–Alder Reaction of 1,2,4-Triazines and Palladium(0)-Mediated β -Carboline Preparation. In recent reports we have detailed the utility of the inverse electron demand Diels–Alder reaction of electron-deficient, substituted 1,2,4-triazines with electron-rich olefins in the preparation of 4-arylpyridines and further demonstrated the potential of this process in a formal total synthesis of streptonigrin.^{7,8} In a continued exploration of the factors governing the reactivity and regioselectivity of the [4 + 2] cycloaddition reactions of 1,2,4-triazines, we describe here full details of a short, effective approach to the preparation of the lavendamycin CDE ring system based on a regioselective inverse electron demand Diels–Alder reaction of 3,5,6-tris(ethoxycarbonyl)-1,2,4-triazine and the implementation of a newly developed palladium(0)-mediated β -carboline synthesis (eq 1).⁵

Thermal cycloaddition of the pyrrolidine enamine of *o*-bromopropiophenone (5a) with 3,5,6-tris(ethoxy-

(1) Searle scholar recipient, 1981–1985. National Institutes of Health research career development award recipient, 1983–1988 (CA 00898/01134). Correspondence regarding this work should be addressed to this author at: Department of Chemistry, Purdue University, West Lafayette, IN 47907.

(2) Doyle, T. W.; Balitz, D. M.; Grulich, R. E.; Nettleton, D. E.; Gould, S. J.; Tann, C.-H.; Meows, A. E. *Tetrahedron Lett.* 1981, 22, 4595. For a recent review, see: Gould, S. J.; Weinreb, S. M. *Fortschr. Chem. Org. Naturst.* 1982, 41, 77.

(3) Balitz, D. M.; Bush, J. A.; Bradner, W. T.; Doyle, T. W.; O'Herron, F. A.; Nettleton, D. E. *J. Antibiot.* 1982, 35, 259.

(4) For the total synthesis of lavendamycin methyl ester and comparison with that derived from natural material, see: (a) Kende, A. S.; Ebetino, F. H. *Tetrahedron Lett.* 1984, 25, 923. Kende, A. S.; Ebetino, F. H.; Battista, R.; Boatman, R. J. Lorah, D. P.; Lodge, E. *Heterocycles* 1984, 21, 91. Hibino, S.; Okazaki, M.; Ichikawa, M.; Sato, K.; Ishizu, T. *Heterocycles* 1985, 23, 261. For the preparation of desmethyl-lavendamycin and related studies, see: (b) Hibino, S.; Okazaki, M.; Sato, K.; Morita, I. *Heterocycles* 1983, 20, 1957. (c) Rao, A. V. R.; Chavan, S.; Sivadasan, L. *Indian J. Chem.* 1984, 23B, 496.

(5) Boger, D. L.; Panek, J. S. *Tetrahedron Lett.* 1984, 25, 3175.

(6) Boger, D. L.; Duff, S. R.; Panek, J. S.; Yasuda, M. *J. Org. Chem.*, following paper in this issue.

(7) (a) Boger, D. L.; Panek, J. S. *J. Org. Chem.* 1983, 48, 621. (b) Boger, D. L.; Panek, J. S. *J. Am. Chem. Soc.* 1985, 107, 5745.

(8) Boger, D. L.; Panek, J. S. *J. Org. Chem.* 1982, 47, 3763; *Idem Ibid.* 1981, 46, 2179. Boger, D. L.; Panek, J. S.; Meier, M. M. *Ibid.* 1982, 47, 895. Boger, D. L. *Tetrahedron* 1983, 39, 2869.