Article

Effect of Oxygen on Linked Ru(bpy)−Viologen Species and Methylviologen: A Reinterpretation of the Electrogenerated Chemiluminescence

Catherine D. Clark, Jeff D. Debad, Edward H. Yonemoto, Thomas E. Mallouk, and Allen J. Bard

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Effect of Oxygen on Linked Ru(bpy)$_3$$^{2+}$−Viologen Species and Methylviologen: A Reinterpretation of the Electrogenerated Chemiluminescence

Catherine D. Clark,[†] Jeff D. Debad,[†] Edward H. Yonemoto,[‡]
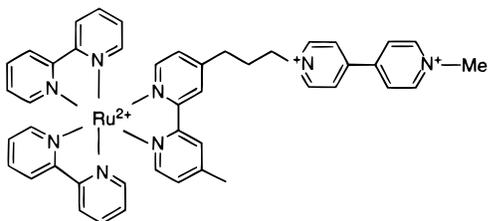**Thomas E. Mallouk,[‡] and Allen J. Bard*,[†]**

Contribution from the Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, and Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received June 5, 1997$^{\otimes}$

Abstract: The effect of oxygen on the electrogenerated chemiluminescence (ECL) of the ruthenium trisbipyridyl−viologen complexes (4,4′-R$_2$-2,2′-bipyridine)$_2$Ru(1-(4-methyl-2,2′-bipyridin-4′-yl-(CH$_2$)$_n$-4,4′-bipyridindiium-1′-methyl)$^{4+}$ (n = 1, 2, 3, 5, or 8; R = H or Me) has been investigated. This light emission is shown to occur not from a MLCT excited state localized on an unsubstituted bipyridine ligand as had been previously proposed, but from decomposition products formed during the ECL experiments when trace amounts of oxygen are present. These ECL-active species are generated when oxygen reduction products react with the pendant viologen to alter or remove this ligand, thereby disabling the electron-transfer quenching of the excited state by the intact viologen. Electrolysis and extended ECL experiments with methylviologen and the ruthenium-linked viologen compounds verify that a number of products are formed under ECL conditions when oxygen is present in solution. Some of these products have been identified.

Introduction

A previous report from this laboratory[1] dealt with the electrochemical oxidation of Ru^{II}(bpy)$_2$(bpy-(CH$_2$)$_3$-MV^{2+})$^{4+}$ (bpy = 2,2′-bipyridine, MV^{2+} = methylviologen, and bpy-(CH$_2$)$_3$-MV^{2+} = 4′-methylbipyridine attached to a substituted viologen via a propyl chain at the 4 position) and the reaction

of the oxidized species with different strong reducing agents, e.g., the reduced form of the complex (1+ species) in MeCN, to produce light (electrogenerated chemiluminescence, ECL). Since light was observed with this complex under very different conditions, i.e., in MeCN with the above 5+/3+ annihilation reaction as well as by production of the 5+ species in aqueous solutions in the presence of coreactants C$_2$O$_4$$^{2-}$ or tri-*n*-propylamine (TPrA), and the emission was near that of the familiar luminescence of Ru(bpy)$_3$$^{2+}$, we proposed that emission was from the excited-state species Ru^{III}(bpy$^{\bullet-}$)(bpy)(bpy-(CH$_2$)$_3$-MV^{2+})$^{4+*}$ generated upon electron transfer between the 5+ species and the strong reductant, as is found with many other ECL reactions. However, emission from this species was surprising because the electron of the bpy$^{\bullet-}$ ligand should rapidly transfer to the MV^{2+} moiety to form Ru^{III}(bpy)$_2$(bpy-(CH$_2$)$_3$-

MV$^{\bullet+}$)$^{4+}$, which would not emit. This quenching occurs during photoexcitation of Ru^{II}(bpy)$_2$(bpy-(CH$_2$)$_3$-MV^{2+})$^{4+}$ and related species, so that photoluminescence is not observed.[2,3] Thus it was necessary to invoke special characteristics of the species formed via electron transfer and slower electron transfer among the ligands than appeared reasonable from photophysical studies of related complexes.[4]

To probe this proposed reaction sequence further, we have now carried out similar studies with other molecules of the same general class with different lengths of linking chains and with methyl substitutions on the bipyridines (Figure 1) to see if trends in the ECL emission intensity followed expectations about electron-transfer rates. For example, more efficient electron-transfer quenching would be expected with an eight-carbon linker, which might allow the group better access to the bpy$^{\bullet-}$, while intercalation of the MV^{2+} group with β-cyclodextrin would decrease the quenching, as observed in previous photoluminescence studies.[2] The lack of correspondence of these results, outlined below, led us to examine the reactions under more rigorous conditions, with greater care in oxygen removal and more quantitative (relative to Ru(bpy)$_3$$^{2+}$) determination of ECL emission intensities. We found that the appearance of ECL emission depends upon dissolved oxygen levels and the reaction of the pendant viologen with oxygen reduction products. This effect was probed in greater detail by bulk electrolysis experiments of the complexes and of MV^{2+} itself, with observation of an array of reaction products. Details of these experiments, described below, demonstrate that in the rigorous absence of oxygen only negligible levels of ECL are found with these systems.

† University of Texas.
‡ Pennsylvania State University.
$^{\otimes}$ Abstract published in *Advance ACS Abstracts,* October 1, 1997.
(1) Xu, X.; Shreder, K.; Iverson, B. L.; Bard, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3656.

(2) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786.
(3) Yonemoto, E. H.; Riley, R. L.; Kim, Y. I.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081.
(4) Cooley, L. F.; Headford, C. E. L.; Elliot, C. M.; Kelley, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 6673.

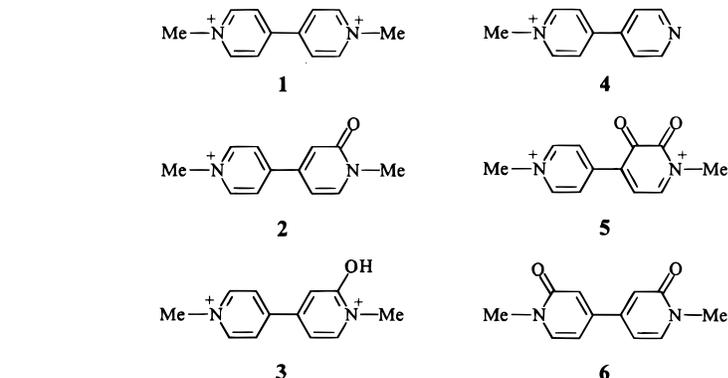| Compound	R	n	X
H1M	H	1	(N,N'-dimethyl-4,4'-bipyridinium)
H2M	H	2	"
H3M	H	3	"
H5M	H	5	"
M1M	Me	1	"
M2M	Me	2	"
M8M	Me	8	"
H5Mon	H	5	(N-methyl-4,4'-bipyridinium)
H7OH	H	7	−OH

Figure 1.

Experimental Section

All $Ru(bpy)_2(bpy-(CH_2)_n-MV)(PF_6)_4$ complexes were synthesized as previously described or using similar methodology.[2,3] $Ru(bpy)_3Cl_2$·$6H_2O$ (Strem), tri-*n*-propylamine (TPrA), methylviologen dichloride hydrate, and β-cyclodextrin (Aldrich) were used as received. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF_6, SACHEM, Austin, TX) was recrystallized three times from ethanol/water (4:1) and dried under vacuum at 100 °C for 4 h. $Ru(bpy)_3(PF_6)_2$, $MV(NO_3)_2$, and $MV(PF_6)_2$ were prepared from their chloride salts by ion metathesis followed by recrystallization. Deionized water from a Millipore Milli-Q system was used to prepare all aqueous solutions. MeCN (UV grade, Baxter) was used as received but was opened and stored in an inert atmosphere (He) glovebox (Vacuum Atmospheres Corp.).

Aqueous ECL measurements were performed either with an Origen I analyzer (IGEN, Inc., Rockville, MD) controlled by an IBM PS/2 computer, as previously described,[1] or in a sealable glass cell. The latter electrochemical cell possessed rigidly fixed electrodes and could be reproducibly positioned in front of a charge-coupled device (CCD) camera (Photometrics, Inc., Tucson, AZ) for integration of the ECL emission. The working electrode consisted of platinum foil (6 mm × 6 mm) and was positioned 8 mm behind the counter electrode (9 × 10 mm, platinum foil) which contained a round hole (4 mm diameter) though which the light from the working electrode was directed toward the CCD camera. A silver wire served as a quasi-reference electrode (AgQRE). This cell design ensured reproducible measurements and allowed the relative ECL intensities of different compounds to be compared. Each measurement performed on the Origen I analyzer consisted of the average of three to six separate analyses on air-equilibrated 3 μM solutions of the ruthenium complex in 0.12 M phosphate buffer (pH 7.2) containing 0.12 M TPrA. Stock solutions of $Ru(bpy)_3(PF_6)_2$ and $Ru(bpy)_3Cl_2$ were used as standards for MeCN and aqueous measurements, respectively, and good reproducibility was obtained (~1% variation in relative ECL intensities vs $Ru(bpy)_3^{2+}$). Buffer solutions (0.12 M phosphate, pH 7.2) for the aqueous ECL and electrolysis experiments were prepared as described previously.[1]

ECL experiments in MeCN were performed in the same glass cell described above for the aqueous experiments. ECL spectra were obtained as described previously.[5] MeCN solutions for ECL and cyclic voltammetry were prepared with 0.2 M TBAPF_6 in a glovebox. The concentration of ruthenium complex was calculated from absorbance spectra, using $\epsilon_{450} = 1.4 \times 10^4$ M^{-1} cm^{-1} for $Ru(bpy)_3^{2+}$ and $\epsilon_{450} = 1.49 \times 10^4$ M^{-1} cm^{-1} for all the other compounds (this value is for $Ru(4,4'-Me_2bpy)_3^{2+}$).[6]

A Model 175 universal programmer and a Model 173 potentiostat (Princeton Applied Research, Princeton, NJ) were used for the ECL experiments in MeCN and electrolysis experiments, and cyclic voltammograms were recorded on a Model 660 electrochemical workstation (CH Instruments, Inc.). Potentials are reported versus AgQRE. The electrochemical potentials of this series of compounds in MeCN have been reported previously.[3]

Bulk electrolyses in both aqueous and MeCN solutions were carried out in a two-compartment cell using a platinum mesh working electrode (area ~ 2 cm²), a platinum mesh counter electrode, and a AgQRE that was contained in a small fritted tube in the working electrode compartment. The general procedure for electrolysis and isolation of products is exemplified by the experiment described below. In each case, the progress of the reaction was monitored by thin-layer chromatography (TLC). For electrolyses in acetonitrile, the reactions were halted when all of the starting material was consumed. Aqueous electrolyses were run only until a small fraction of the starting material had reacted to avoid large pH changes in the buffer system.

Luminescence and absorbance data were collected as previously described.[1]

Bulk Electrolysis of H5M in MeCN. H5M (25 mg) was placed in the working compartment of the electrolysis cell and MeCN containing electrolyte (0.2 M TBAPF_6) was added to both working and counter electrode compartments (~5 mL in each). While bubbling oxygen into the working compartment, electrolysis was performed at −0.9 V vs AgQRE until the starting material was completely consumed. The resulting solution was placed onto a small silica (Baxter, 60 Å) column, and the column was then washed with MeCN. The product was washed off of the column using $CH_3CN/H_2O/KNO_3$(sat.) (5:4:1; solvent system

(5) McCord, P.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *318*, 91.
(6) Nakamaru, K. *Bull. Chem. Soc.* **1982**, *55*, 2697.

Table 1. Relative Photoluminescence (PL) and ECL in Air-Equilibrated TPrA/Phosphate Solutions[a]

compd	% PL	% ECL[b]
Ru(bpy)$_3^{2+}$	100	100
Ru(4,4′-Me$_2$bpy)$_3^{2+}$	46	39
Ru(4,4′-Me$_2$bpy)(bpy)$_2^{2+}$	68	54
H7OH	75	180
M1M	0	34
M2M	0	6.7
M8M	2	8.6
M8M/β-CD[c]	20	12 (7.4[e])
H1M	0	35
H2M	2[d]	28
H3M	0	10 (20[f])
H5M	2	7.8

[a] 3 μM complex in 0.12 M phosphate buffer, pH 7.2; [TPrA] = 0.12 M. [b] Measured on a commercial ECL analyzer: scanned from 500 to 1500 mV vs AgCl, average of three to six analyses. [c] 20 mM β-cyclodextrin (β-CD). [d] PL is likely due to impurity. [e] Measured vs Ru(bpy)$_3^{2+}$/β-CD. [f] From ref 1.

A). This orange eluate was evaporated and redissolved in water, and a small amount of concentrated aqueous KPF$_6$ solution was added. Methylene chloride was then used to extract the products from the water layer as PF$_6^-$ salts. This extract was then chromatographed on preparative TLC plates (silica gel, 2−25 μM) using solvent system A to elute. Three major bands developed, as well as at least seven minor bands, and all were fluorescent orange under a hand-held UV lamp. The compounds forming the three major bands (R_f = 0.50, 0.63, and 0.68) were isolated from the silica and converted to their PF$_6^-$ salts. For the R_f = 0.63 and 0.68 products, a second chromatographic separation was necessary using KCl instead of KNO$_3$ as the eluant salt to remove TBA$^+$ impurity. Characterization data for the three products are listed below. Only the R_f = 0.50 product was confidently identified.

R_f = 0.50 Product. Ru(bpy)$_2$(4-(5-(4,4′-bipyridinium)pentyl)-4′-methyl-2,2′-bipyridine)$^{3+}$ (H5Mon): 300 MHz ^{1}H NMR (CD$_3$CN) δ 1.45 (2H, m, CH$_2$), 1.72 (2H, m, CH$_2$), 2.0 (m, CH$_2$, partially obscured by solvent peak), 2.51 (3H, s, *Me*-bpy), 2.78 (2H, m, CH$_2$), 4.52 (2H, m, CH$_2$), 7.21 (2H, m, bpy′), 7.36 (4H, m, bpy), 7.52 (2H, m, bpy′), 7.69 (4H, m, bpy), 7.75 (2H, m, viologen), 8.02 (4H, m, bpy), 8.30 (2H, m, bpy), 8.32 (2H, s, viologen), 8.37 (2H, s, viologen), 8.46 (4H, m, bpy′), 8.76 (2H, m, bpy′), 8.83 (2H, m, bpy); electrospray mass spectrometry, *m/z* 477 (H5Mon^{3+} + PF$_6^-$). As further confirmation of the identity of this compound, H5Mon was reacted with an excess of methyl iodide in dichloromethane at 50 °C for 1 h. H5M was formed quantitiatively and was identified by comparison of the ^{1}H NMR spectrum of the product to that of an authentic sample.

R_f = 0.63 Product: 300 MHz ^{1}H NMR (CD$_3$CN) δ 1.41 (2H, m, CH$_2$), 1.70 (2H, m, CH$_2$), 2.55 (3H, s, *Me*-bpy), 2.78 (2H, m, CH$_2$), 2.93 (2H, m, CH$_2$), 7.20 (2H, m, bpy′), 7.37 (4H, m, bpy), 7.52 (2H, m, bpy′), 7.70 (4H, m, bpy), 8.02 (4H, m, bpy), 8.37 (1H, s, bpy′), 8.43 (1H, s, bpy′), 8.46 (4H, m, bpy); electrospray mass spectrometry, *m/z* 408, 335.

R_f = 0.68 Product: 300 MHz ^{1}H NMR (CD$_3$CN) δ 1.50 (2H, m, CH$_2$), 1.69 (2H, m, CH$_2$), 2.52 (3H, s, *Me*-bpy), 2.78 (2H, m, CH$_2$), 3.14 (2H, m, CH$_2$), 7.21 (2H, m, bpy′), 7.38 (4H, m, bpy), 7.52 (2H, m, bpy′), 7.70 (4H, m, bpy), 8.02 (4H, m, bpy), 8.33 (1H, s, bpy′), 8.39 (1H, s, bpy′), 8.47 (4H, m, bpy); electrospray mass spectrometry, *m/z* 348.

Results

Photoluminescence and ECL in Aqueous Solutions. The compounds and naming scheme used in this study are shown in Figure 1. Photoluminescence intensities for these species are reported relative to Ru(bpy)$_3^{2+}$ (100%) and range from 0% for the short chain compounds to 2% for H5M and M8M (Table 1). H2M would be expected to have ∼0% photoluminescence (PL); however, the observed PL (2%) may indicate low levels of a luminescent impurity in this sample.

ECL emission was readily observed for all of the HnM/MnM complexes in air-equilibrated buffered aqueous solutions con-

taining TPrA. In general, apparent ECL efficiencies range between 10% and 35% that of Ru(bpy)$_3^{2+}$ (Table 1). A value of ∼20% ECL was previously reported for H3M[1] under similar conditions, whereas the same compound here gives 10%, indicating some variability in these measurements.

The PL and ECL of various model compounds were also measured: Ru(4,4′-Me$_2$bpy)$_3^{2+}$, a model for the MnM series; Ru(bpy)$_2$(4,4′-Me$_2$bpy)$^{2+}$, a model for the HnM series; and H7OH, similar to the HnM compounds but containing a hydroxyl group in place of the viologen ligand. These complexes have smaller ECL and photoluminescence intensities than Ru(bpy)$_3^{2+}$, but the values of the electro- and photogenerated intensities are comparable (Table 1). The addition of 20 mM β-cyclodextrin (β-CD) to a solution of M8M increased PL from 2% to 20%, as also previously described.[2] There was, however, no associated increase in ECL, which remained at ∼10%.

The ECL of H3M in air-equilibrated TPrA/phosphate buffer solution was also measured using the CCD camera apparatus described in the Experimental Section. This setup allowed the possibility of degassing the solution, an option that was not available with the commercial ECL analyzer. Upon sweeping the working electrode to +1.5 V vs AgQRE, a substantial amount of light was produced at the electrode surface. When the solution was then purged with argon for 15 min, the ECL emission decreased to ∼0.7% of the value measured in air and increased again when air or pure oxygen was bubbled through the solution. An identical experiment using Ru(bpy)$_3^{2+}$ resulted in an emission increase upon argon purging because oxygen is known to quench partially the excited state of this molecule.[7]

A similar experiment was performed using 0.2 mM M2M in TPrA/phosphate buffer; however, in this case, the solution was first subjected to five freeze−pump−thaw degassing cycles. ECL was still produced by sweeping the electrode potential to +1.5 V, although the emission was less than 1% of a typical level in aerated solution. The solution did not exhibit any measurable luminescence after these measurements; however, after extended ECL experiments in the presence of air, the solution exhibited a bright photoluminescence (λ_{max} = 630 nm). A solution of M2M in aerated TPrA/phosphate buffer does not become luminescent upon standing, indicating that the application of a potential is required for the production of the solution luminescence.

ECL in MeCN Solutions. HnM/MnM MeCN solutions prepared in a glovebox were tested for ECL by alternately generating the reduced and oxidized form of the compounds at an electrode surface. Cyclic voltammograms for each of the complexes (see Figure 2a for a typical example) do not change significantly during these experiments if the cell is sealed. No ECL emission was observed by pulsing the electrode potential between wave I (Ru$^{III/II}$) and wave II (MV$^{2+/1+}$) because the free-energy difference of the electron-transfer reaction, about 1.7 eV in this case, is too small to populate the emitting state at about 2.1 eV.[8] However, emission was observed for pulsing between wave I and any of the more negative waves (III for MV$^{+1/0}$ or IV for bpy$^{0/-1}$), with efficiencies less than 1% that of Ru(bpy)$_3^{2+}$. No emission was observed at any of these pulsing potentials for a MeCN solvent blank containing only electrolyte.

To determine if this low-level ECL was due to trace oxygen in the solutions prepared in the glovebox, an experiment was performed to remove as much dissolved gases as possible. A

(7) Mulazzani, Q. G.; Sun, H.; Hoffman, M. Z.; Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 5139.
(8) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.
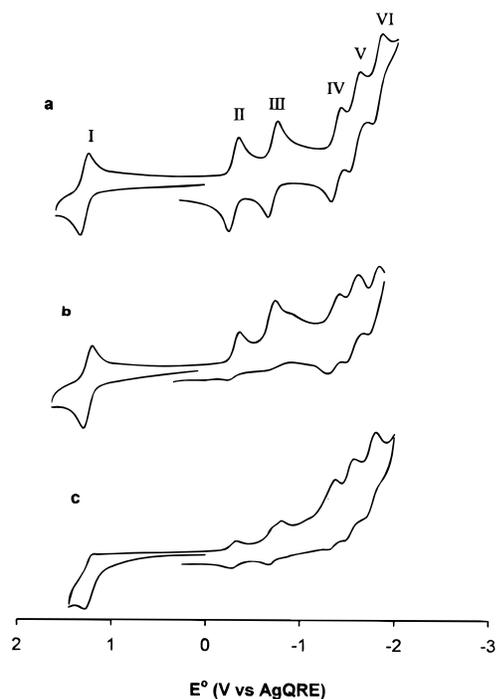
Figure 2. Cyclic voltammograms of a 0.7 mM solution of M2M in MeCN at a glassy carbon electrode (0.2 M TBAPF$_6$; scan rate 200 mV/s) (a) before ECL, (b) with added oxygen, and (c) after extended ECL in the presence of air. Solutions in a and c are oxygen-free.

solution of M2M in MeCN was subjected to five freeze−pump−thaw degassing cycles and then tested for ECL. The initial cyclic voltammogram of this solution is shown in Figure 2a, and the solution at this point exhibited no detectable photoluminescence. Upon pulsing the electrode potential between the ruthenium oxidation (wave I) and the first bipyridyl reduction (wave IV), very low levels of ECL were observed,[9] approximately 10^{-4}% as intense as Ru(bpy)$_3$$^{2+}$. When the solution was allowed to equilibrate with air, the M2M ECL emission increased dramatically. A cyclic voltammogram of the solution containing a small amount of air is shown in Figure 2b. The viologen waves become irreversible under these conditions, and the oxygen reduction peak is clearly visible at a slightly more negative potential than the second viologen reduction. The first viologen wave is reversible in the presence of oxygen, although both waves become irreversible if the potential is swept low enough to reduce oxygen. After the ECL measurements were made in the presence of oxygen, the M2M solution was freeze−pump−thaw degassed once again. ECL from this solution was observed, although the intensity was greater than that from the original solution, indicating that some ECL-active species was generated during the previous ECL experiment. The cyclic voltammogram of a degassed M2M solution after extended ECL in air-equilibrated MeCN solution (Figure 2c) indicated that some decomposition had occurred. This solution was highly luminescent, with an emission spectrum ($\lambda_{max} = 626$ nm) similar to the ECL spectrum of the solution.

The behavior discussed above for M2M was common to the other HnM/MnM complexes, where all exhibited ECL in MeCN solutions containing air or oxygen. The measured photoluminescence of these solutions, which were similar to aqueous values reported in Table 1, increased during the ECL experiments performed under these conditions.

Bulk Electrolyses in Aqueous Solution. Bulk electrolysis of H3M was performed in aqueous solution in the presence of air to simulate extended ECL experiments and to test for the formation of photoluminescent products. A 0.066 mM solution of H3M in the same TPrA/phosphate buffer used in the ECL experiments was electrolyzed at +1.5 V vs AgQRE while bubbling air through the solution. No luminescence was detectable in the initial solution, but some was present ($\lambda_{max} \sim$ 620 nm) after electrolysis. The experiment was repeated using H5M with a higher concentration of compound, and TLC of the final reaction mixture showed the presence of many fluorescent orange species. The major product of the reaction displayed an R_f value of 0.52 (solvent system A) and was not further characterized. However, it was shown that this product was not Ru(2,2′-bipyridine)$_2$(4-(5-(4,4′-bipyridinium)pentyl)-4′-methyl-2,2′-bipyridine)$^{3+}$ (H5Mon, see Figure 1 for structure) by TLC against an authentic sample of this demethylated compound.

An electrolysis was performed on an aerated 0.5 mM solution of H5M in phosphate buffer without TPrA, with the potential held at −0.9 V vs AgQRE (i.e., at the first viologen reduction wave) to simulate the reducing conditions that are presumably present during aqueous ECL experiments.[10] The resulting luminescent solution was evaporated and dried under vacuum. Extraction with MeCN and subsequent TLC using solvent system A showed the presence of at least four luminescent products. The major product of the reaction had an R_f value identical to that of H5Mon, and when co-spotted with an authentic sample, no new bands were eluted.

To determine the stability of the pendant viologen on the HnM/MnM compounds under ECL conditions, a solution of methylviologen in aerated TPrA/phosphate buffer was also electrolyzed at +1.4 V. TLC of the resulting solution revealed the production of a fluorescent yellow compound ($R_f = 0.51$ using CH$_3$CN/H$_2$O/KNO$_3$(sat.), 7:2:1, solvent system B). This species displayed an absorbance spectrum ($\lambda_{max} = 355$ nm, solvent system A) and R_f value identical to those of the monopyridone, *N*-methyl-(4-(*N*-methyl-4′-pyridinium))-2-pyridone (**2**).[11] No other products were observed in this experiment.

When electrolysis of methylviologen was performed in the presence of oxygen using a potential corresponding to the first viologen reduction (−0.9 V), at least 10 products formed, as shown by TLC. The three major products of the reaction were identified by either isolation or by TLC against standards as *N*-methyl-(4-(*N*-methyl-4′-pyridinium))-2-hydroxypyridinium[12] (**3**), the monopyridone **2**, and *N*-methyl-4-(4′-pyridinyl)-pyridinium (**4**, Figure 1). The latter compound, also known in the literature as monoquat, quenches the fluorescence of the TLC plates. The other products were not identified. When the same electrolysis was performed at a potential capable of reducing only oxygen and not the viologen (−0.4 V vs AgQRE), only two products were observed; the monopyridone **2** and the hydroxypyridinium compound **3**.

---

(9) This extremely weak ECL is presumably due to an ECL-active impurity present in very low concentration. Similar experiments with other HnM/MnM compounds reveal no detectable ECL under these conditions.

(10) Upon oxidation, TPrA is thought to undergo a fast deprotonation to form a strong reducing agent. In typical ECL reactions using this coreactant, the reducing agent then reacts with the oxidized form of the luminescent compound (e.g., Ru(bpy)$_3$$^{3+}$) to form an excited state capable of emission (Ru(bpy)$_3$$^{2+*}$): Leland, J. K.; Powell, M. J. *J. Electrochem. Soc.* **1990**, *137*, 3127.

(11) Calderbank, A.; Charlton, D. F.; Farrington, J. A.; James, R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 139.

(12) Characterization data for compound **3**: absorption $\lambda_{max} = 426$ nm (ethanol); fluorescence, $\lambda_{max} = 542$ nm (ethanol); ^{1}H NMR (CD$_3$OD) δ 4.19 (3H, s, Me), 4.39 (3H, s, Me), 7.67 (1H, dd, $J = 6.3$, 1.5 Hz), 7.92 (1H, d, $J = 1.5$ Hz), 7.94 (1H, d, $J = 6.3$ Hz), 8.71 (2H, d, $J = 6.9$ Hz), 8.87 (2H, d, $J = 6.9$ Hz); high-resolution chemical ionization mass spectrum $m/z = 203.1170$ [(M + H)$^+$], calcd for C$_{12}$H$_{15}$N$_2$O 203.1184.

Bulk Electrolyses in MeCN Solutions. Electrolysis of H5M at a potential corresponding to the second reduction of the pendant viologen (wave III, Figure 2a) in air-saturated MeCN was performed to simulate the conditions in an extended annihilation-mode ECL experiment. Complete loss of starting material is observed in this reaction to form three major and at least 10 minor fluorescent products, as judged by TLC. One product was formed in great excess over the others and was isolated using preparative TLC. The compound was identified by electrospray mass spectrometry and ^{1}H NMR spectroscopy as H5Mon (Figure 1). This product is similar to the starting material but has undergone loss of Me$^+$ from the viologen ring, leaving a monoquat moiety in place of the viologen. H5Mon has a luminescence efficiency 80% that of Ru(bpy)$_3$$^{2+}$ and an emission maximum at 615 nm and is capable of ECL. Further confirmation of the identity of this complex was obtained by its reaction with methyl iodide to quantitatively form H5M.

Two other luminescent products were isolated from the above reaction mixture, although exact determination of their structures was hampered by the small amounts isolated. The ^{1}H NMR spectra of both compounds exhibit methylene signals of the pentyl chain but lack viologen aromatic signals, indicating loss of the pendant viologen ligand. By comparison of the methylene proton shifts to those in H7OH, it is clear that neither of the unidentified products contain a terminal alcohol group.

A similar electrolysis of methylviologen in aerated MeCN at a potential corresponding to the second reduction wave (-1.0 V vs AgQRE) also resulted in decomposition to at least five products, of which two were isolated by preparative TLC techniques. One product quenched the fluorescence of the TLC plates ($R_f = 0.53$, solvent system B) and was identified as monoquat (**4**) by comparison of its ^{1}H NMR spectrum to that of an authentic sample.[3] The other isolated product was the hydroxypyridinium compound **3**. The other minor products were not isolated or identified.

Reactivity of TPrA with HnM/MnM and Methylviologen in MeCN. An attempt was made to generate ECL in MeCN using TPrA as a coreactant as is done in aqueous media. However, it was noticed that the HnM/MnM compounds spontaneously decomposed under these conditions in the presence of air, even in the dark. If a solution of H5M in MeCN containing approximately 100 M excess of TPrA is stirred in air, the starting material decomposes to a complex mixture similar to that formed during electrochemical reduction in MeCN as discussed above. TLC shows that similar products are formed in both reactions, although the relative amounts have changed. By chromatographing against an authentic sample, the major product was again identified as H5Mon.

Spontaneous decomposition of methylviologen in aerated MeCN containing excess TPrA was also observed. If oxygen is initially excluded from the system, the solution becomes blue, indicating a reaction between methylviologen and TPrA leading to the formation of reduced viologen (MV$^{\bullet+}$).[13] Addition of air or oxygen gives rise to a yellow solution and complete decomposition of the viologen. TLC using solvent system B separated at least eight products from the reaction mixture. One of these products quenched the TLC plate fluorescence and had an R_f value identical to that of monoquat (**4**). The remaining products all appeared fluorescent, the major species being the hydroxypyridinium compound **3**. Another product was identified by chromatography against an authentic sample as monopyridone **2**. A fluorescent blue product was also observed ($R_f = 0.85$) and was not identified, although chromatography

revealed that this product was not 4,4′-(N,N'-dimethyl)-2,2′-bipyridone (**6**), a product known to form upon oxidation of **2**.[11]

Discussion

Photoluminescence and ECL of HnM/MnM Compounds. The ruthenium trisbipyridine−viologen compounds exhibit little or no photoluminescence due to quenching of the MLCT excited state by the attached viologen (Table 1). The quenching mechanism involves an electron transfer from the bipyridine ligand to the pendant viologen, the rate of which has been shown to decrease with increasing chain length up to $n = 4$.[2,3] Longer chains ($n = 5, 8$) are thought to allow the viologen to interact with the bpy ligands directly, allowing through-space electron transfer, whereas the compounds with smaller chains rely on a through-bond electron-transfer mechanism.

Despite the low photoluminescence of the HnM/MnM compounds, ECL is clearly observed in aqueous solutions of these species, although the apparent ECL efficiencies are much lower than that of Ru(bpy)$_3$$^{2+}$ (Table 1). The efficiencies decrease with increasing chain length as was expected from the proposed theory of an ECL-generated excited state localized on an unsubstituted bpy;[1] however, other observations lead to the conclusion that the HnM/MnM compounds were not responsible for the observed ECL.

One such observation is that, although β-CD addition increases photoluminescence for M8M by encapsulating the viologen and preventing it from interacting with the bipyridine ligands, ECL is not affected by the presence of β-CD. This suggests that the ECL is not due to an excited state that is quenched by an attached viologen ligand, no matter which bipyridine ligand is involved in the ECL-generated MLCT excited state. Another trend that does not fit the proposed theory is the dependence of the apparent ECL efficiency on the presence of dissolved oxygen. Purging aqueous solutions of the HnM/MnM compounds with argon leads to a dramatic decrease in emission, and careful degassing of acetonitrile solutions leads to complete elimination of the ECL signal. These experiments suggest that dissolved oxygen somehow triggers the production of ECL in these systems.

Ru(bpy)$_3$$^{2+}$ is stable under the conditions used to produce HnM/MnM ECL,[14] and therefore, decomposition of the ruthenium trisbipyridyl core in these complexes is not expected in the experiments discussed here. It is also clear that the viologen ligand is stable under ECL conditions in carefully degassed acetonitrile solutions. However, when oxygen is present in solution, decomposition occurs to form ECL-active products. As shown here, this reactivity is centered on the pendant viologen, leading to deactivation of the quenching mechanism and allowing emission from the electrogenerated excited state. Thus, it is instructive to first discuss the behavior of methylviologen itself under the conditions used to promote ECL to understand the type and extent of decomposition expected for the pendant viologen attached to the ruthenium compounds.
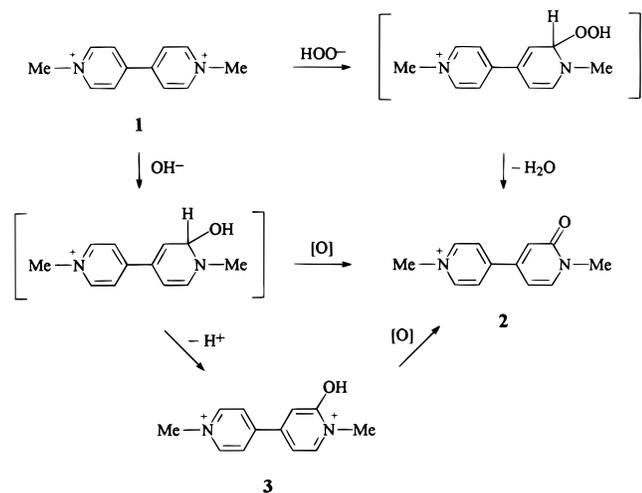
Methylviologen Reactivity Under ECL Conditions. Electron-transfer reactions between methylviologen and oxygen in aqueous solutions have been studied extensively in an attempt to explain the toxic effects of this compound.[15] In vivo, MV^{2+} is readily reduced to MV$^{\bullet+}$ by photosynthetic or respiratory electron-transfer proteins. The exact mechanism of viologen

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

(14) Knight, A. W.; Greenway, G. M. *Analyst* **1994**, *119*, 879 and references therein.

(15) (a) Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372. (b) Thorneley, R. N. F. *Biochim. Biophys. Acta* **1974**, *333*, 487. (c) Fridovich, I.; Hassan, M. *Trends Biochem. Sci.* **1979**, *4*, 113.

Scheme 1

Me—N⁺=⟨⟩—⟨⟩=N⁺—Me   —HOO⁻→   [Me—N⁺=⟨⟩—⟨ H, OOH ⟩—N—Me]

1

↓ OH⁻   &   ↓ −H₂O

[Me—N⁺=⟨⟩—⟨ H, OH ⟩—N—Me]   —[O]→   Me—N⁺=⟨⟩—⟨ O ⟩—N—Me

2

↓ −H⁺   &   ↗ [O]

Me—N⁺=⟨⟩—⟨ OH ⟩—N—Me

3

toxicity is still controversial, but it has been suggested that products of oxygen reduction by $MV^{\bullet+}$ are responsible for cell damage.[16]

Although stable at neutral pH, methylviologen is not stable under basic conditions and reacts with hydroxide to form monoquat (**4**) and methanol in degassed aqueous solutions (eq 1).[17] Multiple products are formed when oxidizing agents are

Me—⁺N=⟨⟩—⟨⟩=N⁺—Me   —OH⁻→

1

Me—⁺N=⟨⟩—⟨⟩=N   +   MeOH   (1)

4
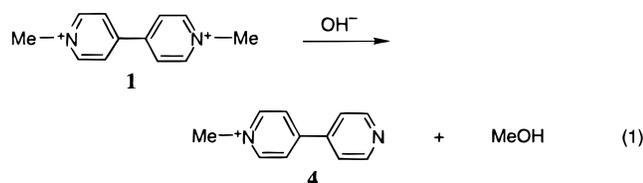
also present in the solution. The identified products of such reactions using oxygen, $Fe(CN)_6{}^{3-}$ or hydrogen peroxide as oxidizing agents include the mono- and bipyridones, complexes **2**, **5**, and **6** (Figure 1). These species are presumed to form by hydroxide attack on the pyridine ring followed by oxidation and deprotonation, as demonstrated in Scheme 1 for the monopyridone. Hydrogen peroxide has also been shown to attack the pyridine ring as the hydroperoxide ion (HOO^-) under basic conditions to yield the monopyridone **2** (Scheme 1) and to react with the reduced form of the viologen, $MV^{\bullet+}$, to cause decomposition.[18] *N*-Alkylated pyridinium species such as methylviologen are susceptible to nucleophilic attack at the ring carbons adjacent to the nitrogen and undergo a variety of oxidation, substitution, and ring-opening reactions following initial attack of a nucleophile at these positions.[19]

Only one nonaqueous study relevant to the present work has been reported on the reactivity of methylviologen. In this work, superoxide ($O_2{}^{\bullet-}$) was reacted directly with methylviologen radical cation in dimethylformamide.[20] At least nine products were observed to form, of which the monopyridone **2**, the dipyridones **5** and **6**, and 1-methyl-2-pyridone were identified. The first three compounds are presumed to form via direct superoxide attack on the pyridine rings, while the latter arises from photochemical decomposition of the pyridone products.

(16) Fridovich, I.; Hassan, M. *Trends Biochem. Sci.* **1979**, 113.

(17) Farrington, J. A.; Ledwith, A.; Stam, M. F. *Chem. Commun.* **1969**, 259.

(18) Bellin, J. S.; Alexander, R.; Mahoney, R. D. *Photochem. Photobiol.* **1973**, *17*, 17.

(19) Schofield, K. *Hetero-Aromatic Nitrogen Compounds. Pyrroles and Pyridines*; Plenum Press: New York, 1967.

(20) Nanni, E. J., Jr.; Angelis, C. T.; Dickson, J.; Sawyer, D. T. *J. Am. Chem. Soc.* **1981**, *103*, 4268.

Polymeric materials were also observed and were presumed to form by polymerization of ring-opened products.

To determine if similar chemistry could occur during our ECL experiments, methylviologen solutions were placed under ECL conditions and analyzed for decomposition. Oxidation of TPrA in an oxygenated aqueous solution of methylviologen does indeed demonstrate that the viologen is unstable in this environment. The product of this reaction is the monopyridone **2**, which likely results from reaction of the viologen with hydrogen peroxide (or OOH^-) produced via oxygen reduction by the strong reducing agent formed upon TPrA oxidation (Scheme 1).[10] Another plausible mechanism would involve reaction of methylviologen with $^{\bullet}OH$ (formed at the electrode by solvent oxidation) and subsequent deprotonation and oxidation to form the pyridone.

By reducing oxygen directly at an electrode in aqueous solutions of methylviologen, the monopyridone can again be produced, demonstrating that this species forms in the presence of oxygen reduction products. The other compound formed under these conditions is the hydroxypyridinium species, **3**, which is presumably a result of OH^- reaction with the viologen followed by deprotonation (Scheme 1). This compound is not observed in the coreactant oxidation reactions because it would be converted into **2** via oxidation at the electrode.

Methylviologen is also not stable in aerated MeCN when exposed to a potential great enough to reduce oxygen. The formation of the two major products in the complex reaction mixture, the hydroxypyridinium **3** and monoquat (**4**), can most easily be explained by the action of base on methylviologen. Superoxide ($O_2{}^{\bullet-}$) or, more likely, OH^- formed by deprotonation of residual water could lead to either product as shown in eq 1 and Scheme 1. The large number of products observed in this reaction are presumably formed via similar pathways or reactions of the reduced forms of the viologen.

Attempts to simulate coreactant ECL using TPrA in MeCN revealed that TPrA spontaneously reduces methylviologen to form the blue radical $MV^{\bullet+}$. This reduction is presumably driven by the highly favored reactions that occur after TPrA oxidation and is assisted by the well-documented ability of *N*-alkylpyridinium compounds to interact strongly with nucleophiles.[19] Once TPrA is initially oxidized by the viologen, it deprotonates to produce a strong reducing agent[10] that can produce more $MV^{\bullet+}$. Addition of oxygen to such MeCN solutions of TPrA and methylviologen leads to complete decomposition of the viologen and formation of monoquat (**4**), the monopyridone **2**, and the hydroxypyridinium compound **3**, among many other unidentified products. Superoxide and hydroxide formation upon oxygen reduction by the TPrA-derived reducing agent and their reaction with the MV^{2+} and $MV^{\bullet+}$ could explain the formation of the observed products, as discussed above. The analogous reaction in buffered aqueous solution does not occur, doubtless because TPrA is protonated under these conditions and is harder to oxidize.

Decomposition of HnM/MnM Complexes During ECL. The instability of methylviologen under ECL conditions implies that the pendant viologen in the HnM/MnM compounds will also decompose during ECL generation if trace amounts of oxygen are present. Damage to the viologen ligand would deactivate the excited-state quenching mechanism and lead to species that are capable of producing ECL, explaining the unexpected emission from these complexes.

All of the HnM/MnM compounds tested exhibit ECL in both air-equilibrated and degassed aqueous solutions and produce luminescent products. In previous work,[1] luminescence was not detected in such solutions, probably due to the short scan

times utilized in the commercial ECL analyzer and the low concentrations of compound required by this instrument. However, electrolysis experiments that simulate extended ECL generate enough of these products to be observed by photoluminescence and by TLC.

Oxidation of TPrA and H5M in aerated aqueous solution produces a number of luminescent products that are responsible for the observed ECL emission. Direct electrode reduction of oxygenated H5M solutions, which models the reducing conditions formed near the electrode by the TPrA-derived reducing agent, also leads to a number of luminescent species. These products are presumably produced when peroxide or other oxygen reduction products damage or remove the viologen ligand from the linking chain in reactions analogous to those discussed above for methylviologen. Carefully degassed TPrA/phosphate buffer solutions also exhibit ECL, although much weaker than aerated solutions, probably because oxygen is formed via water oxidation upon application of the +1.5 V potential used to generate ECL. A previous electrolysis of H3M in a TPrA/phosphate buffer solution did not produce a luminescent solution.[1] Unfortunately, this experiment was performed in a dry bag purged with argon so that undetectable levels of photoluminescent products were formed.

The relative amount of light emitted by H1M and M1M is approximately three times that of the longer chain analogues and suggests that more decomposition is occurring with these two compounds. This presumably arises from H1M and M1M being slightly easier to reduce than the other complexes, indicating that they are more prone to nucleophilic attack by the oxygen reduction products.

ECL emission from HnM/MnM compounds in MeCN is observed only if oxygen is present in solution. The earlier report of ECL for H3M in argon-purged MeCN[1] and the ECL observed for the HnM/MnM compounds tested here are explained by trace amounts of O_2. When the solutions are freeze−pump−thaw degassed, little or no light is produced. Electrolysis of these complexes in oxygenated MeCN solution to simulate extended ECL experiments leads to the formation of a number of luminescent products which, as in the aqueous system, are responsible for the observed ECL. The major product of these experiments is the demethylated species, e.g., H5Mon from H5M, formed by the action of base, in analogy to the production of monoquat from methylviologen. Base-induced dealkylation of the pentyl-substituted end of the viologen in H5M is probably kinetically disfavored, since the other major products were not identified as the hydroxy-terminated species that would arise from such a reaction. H5Mon is luminescent and capable of

ECL because the pendant monoquat ligand is unable to quench the electrogenerated excited state. Thus, the formation of this product alone explains the observation of ECL from MeCN solutions of the HnM/MnM compounds when trace amounts of oxygen are present, although from the TLC data it is obvious that many other luminescent products are also produced that would add to this ECL emission.

The spontaneous decomposition of the HnM/MnM compounds to a number of luminescent products was observed in aerated MeCN containing TPrA when these compounds were mixed in preparation for coreactant ECL in MeCN. Many of the products of this reaction are the same as those produced during the reduction of H5M and oxygen in MeCN, indicating that reducing conditions present in both reactions are responsible for at least some of the products. As in the methylviologen case, the pendant viologen in the HnM/MnM compounds can be reduced by TPrA. This generates a strong reducing agent (from the oxidized TPrA) capable of forming superoxide, which leads to ligand decomposition. The major product, again in analogy to the methylviologen case, is the dealkylated species that forms when superoxide or hydroxide acts as a base to dealkylate the pendant viologen.

Summary

The ruthenium trisbipyridine−viologen compounds used in this and a previous study[1] do not show ECL due to quenching of the electrochemically generated excited state by the attached viologen. ECL is observed, however, if trace amounts of oxygen are present in these systems. This emission results not from the starting materials, but from decomposition products that have undergone damage or removal of the pendant viologen, which deactivates the quenching mechanism and allows ECL to be seen. Experiments with methylviologen and the HnM/MnM compounds under conditions that mimic extended ECL experiments permit the isolation and identification of some of these reaction products, whose formation have been explained by the attack of oxygen reduction products on the viologens.