

Photochemically Induced Charge Separation at the Molecular Level. A Chromophore Quencher Complex Containing Both an Electron Transfer Donor and an Acceptor

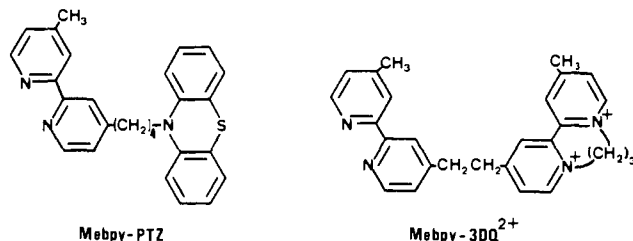
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Examples are known of chromophore-quencher complexes where following optical excitation of a metal-to-ligand charge transfer (MLCT) or a porphyrin $\pi \rightarrow \pi^*$ chromophore, oxidative or reductive intramolecular electron-transfer quenching occurs.¹⁻¹⁰ In a recent example, photolysis of a porphyrin-based system containing both an electron-transfer donor and an acceptor led to a relatively long-lived (3 μ s) photoinduced charge separation onto peripheral donor and acceptor redox sites where in terms of the redox potential stored, $\Delta G^\circ > 1.0$ eV.⁸ One value of such systems is that they begin to reveal how oxidative and reductive equivalents can be generated photochemically and stored within the same molecule. We report here that MLCT-based excitation of the complex $[\text{Ru}(\text{Me}(\text{bpy})\text{-3DQ}^{2+})(\text{Me}(\text{bpy})\text{-PTZ})_2]^{4+}$ is



followed by a sequence of intramolecular events which lead with relatively high efficiency to a charge-separated state based on the -PTZ and -DQ²⁺ redox sites for which the transiently stored free energy is $\Delta G^\circ \sim 1.29$ eV.

The mixed-ligand complex was prepared from $[\text{Ru}(\text{Me}(\text{bpy})\text{-PTZ})_2\text{Cl}_2]^{11a}$ (86 mg) and $[\text{Me}(\text{bpy})\text{-3DQ}](\text{PF}_6)_2^{11b,c}$ (60

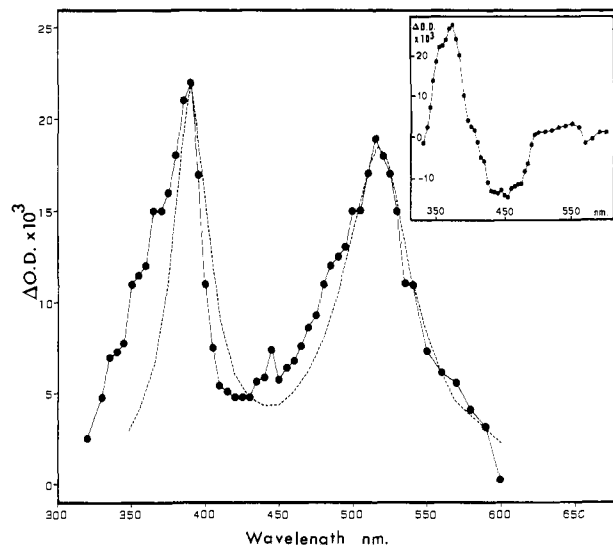
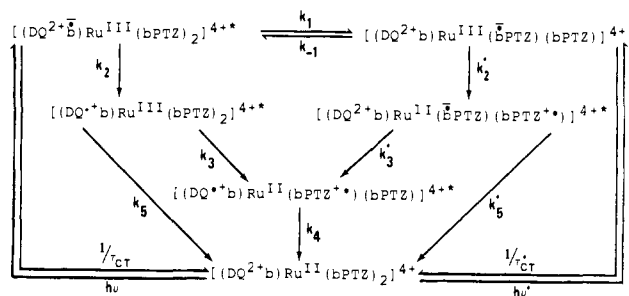


Figure 1. Transient absorbance difference spectrum of $[\text{Ru}(\text{Me}(\text{bpy})\text{-PTZ})_2(\text{Me}(\text{bpy})\text{-3DQ})](\text{PF}_6)_4$ in methylene chloride at room temperature; excitation wavelength 458 nm at 5 mJ/pulse. (—●—) 50 ns after laser pulse and (---) calculated. Insert shows the transient absorbance spectrum for $[\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3](\text{PF}_6)_2$ obtained under the same conditions but 200 ns after the laser pulse.

Scheme I



mg) by heating in ethylene glycol in the dark at 120 °C for 20 min followed by isolation of the PF_6^- salt by the addition of an aqueous solution of NH_4PF_6 . The crude product was chromatographed in the dark on silica gel by using 1:4:5 saturated $\text{KNO}_3/\text{H}_2\text{O}/\text{CH}_3\text{Cl}$, reprecipitated by the addition of $[\text{NH}_4]\text{PF}_6$, and washed with H_2O and finally 4:1 ether/ethanol. Anal. Calcd for $\text{RuC}_{81}\text{H}_{76}\text{N}_{10}\text{S}_2\text{P}_4\text{F}_{24}$: C, 50.24%, H, 4.06%, N, 7.23%. Found: C, 49.86%; H, 3.98%, N, 7.04%. Cyclic voltammetry of the complex in 0.1 M $[\text{N}(\text{n}(\text{C}_4\text{H}_9)_4)(\text{PF}_6)\text{-CH}_3\text{CN}]$ showed reversible or quasi-reversible waves vs. SCE at $E_{1/2} = 1.11$ V ($\text{Ru}^{\text{III/II}}$), 0.67 V ($\text{PTZ}^{+/0}$), -0.62 V ($\text{DQ}^{2+/+}$), -0.88 V ($\text{DQ}^{+/0}$), and -1.38 V ($\text{RuL}_3/\text{RuL}_2$).¹²

At 90 K in 4:1 (v/v) ethanol/methanol, MLCT emission from the chromophore quencher (CQ) complex ($\lambda_{\text{max}} = 620 \pm 2$ nm, $\tau_{\text{obsd}} = 4233 \pm 68$ ns) and its properties are nearly superimposable with those of the model complex $[\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3]^{2+}$ ($4,4'\text{-Me}_2\text{bpy}$ is 4,4'-dimethyl-2,2'-bipyridine) ($\lambda_{\text{max}} = 618 \pm 2$ nm, $\tau_{\text{obsd}} = 4116 \pm 36$ ns). For the CQ complex the emission intensity and lifetime of the emitting state decrease as the temperature increases with complete quenching occurring by 180 K. Kinetic analysis of the emission decay curves shows nonexponential behavior,

(12) There are several possible positional isomers of the complex based on variations in the relative positions of the substituents at the 4 and 4' positions on the bpy ligands. Although there is no evidence for more than one isomer in the electrochemical experiments, broadening in the transient absorption spectrum of the charge separated state (Figure 1) and the possible existence of more than one component in its decay, as evidenced by a slight nonexponentiality, may have their origins in more than one isomer. Although the ground-state properties of the positional isomers might be expected to be nearly equivalent, the charge separated states, note below, could have distinctly different decay characteristics because of differences in the relative spatial orientations of the PTZ^+ and DQ^+ groups.

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(1) (a) Sullivan, B. P.; Abruna, H. D.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Sprintschnik, H.; Meyer, T. J. *Chem. Phys. Lett.* **1978**, *58*, 389. (b) Westmoreland, T. D.; Le Bozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952.

(2) Westmoreland, T. D.; Schanze, K. S.; Neveux, P. E.; Danielson, E.; Sullivan, B. P.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2596.

(3) (a) Wasilewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043. (b) Wasilewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *Ibid.* **1985**, *107*, 5562. (c) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571.

(4) (a) Overfield, R. E.; Scherz, A.; Kaufmann, K. J.; Wasilewski, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 5747. (b) McIntosh, A. R.; Siemiarczuk, A.; Bolton, J. R.; Stillman, M. J.; Ho, T.; Weedon, A. C. *Ibid.* **1984**, *105*, 7215. (c) Siemiarczuk, A.; McIntosh, A. R.; Ho, T.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *Ibid.* **1984**, *105*, 7224.

(5) Miller, J. R.; Calcatera, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

(6) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090.

(7) (a) Schmidt, J. A.; Siemiarczuk, A.; Weedon, A. C.; Bolton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 6112. (b) Pasman, P.; Mes, G. f.; Koper, N. W.; Verhoeven, J. W. *Ibid.* **1985**, *107*, 5839.

(8) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J. C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Lidell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. *Nature (London)* **1984**, *307*, 630.

(9) Calcatera, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670.

(10) Heitle, H.; Michel-Beyerle, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 8286.

(11) (a) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J., manuscript in preparation. (b) Elliott, C. M.; Freitag, R. A.; Blaney, D. B. *J. Am. Chem. Soc.* **1985**, *107*, 4647. (c) Elliott, C. M.; Hershenthart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5588. (d) Wachtoltz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227.

suggesting the existence of a series of competing processes.

Transient absorbance measurements¹³ were conducted at room temperature in methylene chloride and the results of a typical experiment are shown in Figure 1 for both the model and the CQ complex. The difference spectrum for the model complex is characteristic of that expected for an MLCT based excited state with a strong increase in absorbance at $\lambda_{\max} = 375$ nm due to the bipyridyl anion and a decrease in absorbance at $\lambda_{\max} = 455$ nm arising from bleaching of the ground state $\text{Ru}^{\text{II}} \rightarrow \text{bpy}$ MLCT absorption band. For the CQ complex the difference spectrum is that expected for a charge-separated or interligand-charge-transfer (ILCT)¹⁴ excited state with absorbance features appearing for the radical cations 10-MePTZ⁺ ($\lambda_{\max} = 516$ nm)¹⁵ and Me-(bpy)-3DQ⁺ ($\lambda_{\max} = 395, 514$ nm)^{11b} and no bleaching at 455 nm. A calculated difference spectrum based on the known spectra of 10-MePTZ⁺ and Me-(bpy)-3DQ⁺ is shown as an overlay in Figure 1.¹⁶ That the site of reduction following excitation is DQ²⁺ and not bpy is supported by the red shift of ~ 20 nm in the feature at 395 nm and by the appearance of the feature at 515 nm which is a DQ⁺-based absorption that overlaps with an absorption due to PTZ⁺. The absence of bleaching at ~ 455 nm shows that the Ru^{II} -bpy chromophore is present in the charge-separated state. At room temperature in methylene chloride the ILCT state appears during the laser pulse (6 ns), suggesting that the intramolecular quenching events leading to the state are rapid ($k > 10^8$ s⁻¹). Once formed, the ILCT state decays via first-order kinetics with $k_{\text{obsd}} = 6.3 \times 10^6$ s⁻¹, independent of excitation intensity from 2 to 20 mJ/pulse. On the basis of the absorbance changes observed in the figure and using $\epsilon^*(375 \text{ nm}) = 2.9 \times 10^4$ M⁻¹ cm⁻¹ for $\text{Ru}(\text{bpy})_3^{2+}$ ¹⁴ and $\epsilon(514 \text{ nm}) = 4.4 \times 10^3$ M⁻¹ cm⁻¹ for Me-(bpy)-3DQ⁺,^{11b} we estimate that the quantum yield of formation of the ILCT state is $\phi_{\text{sep}} = 0.26 \pm 0.04$.

Our observations and the known redox properties of related systems lead to the quenching scheme in Scheme I where the simplified abbreviations DQ²⁺b and bPTZ have been adopted for the ligands Me-(bpy)-3DQ²⁺ and Me-(bpy)-PTZ. In this scheme MLCT sensitization of the ILCT state could occur by either of two branches depending on whether the initial quenching act is oxidative (k_2) or reductive (k'_2) in nature.

Although emission is observed at low temperature, by room temperature it is completely quenched, $k_2(k'_2) \gg 1/\tau_{\text{CT}}(1/\tau'_{\text{CT}})$. The fact that $\phi_{\text{sep}} < 1.0$ suggests the importance of intramolecular recombination events like k_5 or k'_5 . Factors that may contribute to the lifetime of the charge-separated ILCT state include a possible rate inhibition arising from the fact that both the reduced acceptor and oxidized donor site are positively charged and the fact that space-filling molecular models indicate that direct π overlap between the redox sites is possible.

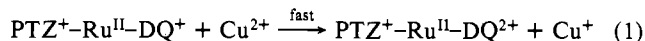
From the potential differences between the -PTZ^{+/0} and -DQ^{2+/+} couples, it can be estimated that the energy of the ILCT state above the ground state is $\Delta G^{\circ'} \sim 1.29$ eV. The excited state is sufficiently long lived to carry out net redox chemistry. In the presence of 4.0×10^{-2} M Cu^{II} in acetonitrile, quenching of the ILCT state occurs via

(13) Transient absorbance experiments were conducted with a Quanta-Ray DCR-2(20) Nd:YAG laser pumping Coumarin 460 dye in a Quanta-Ray PDL-1 dye laser producing an excitation pulse of 6 ns at 5 mJ/pulse. The probe beam, at right angle to the excitation beam, was provided by a pulsed Osram XBO 150-W xenon lamp. Electronic synchronization of the laser and probe was provided by electronics of our own design. The absorption signals were collected with quartz optics ($f3.5$) and imaged onto the slit of a 0.5 m ($f3.4$) monochromator and detected with a R446 5 stage PMT coupled to a Tektronix 7912AD transient digitizer interfaced to a DEC PDP-11/34 microcomputer.

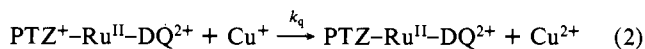
(14) Truesdell, K. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 1787.

(15) The absorbance maximum and extinction coefficient for 10-MePTZ⁺ were determined by chemically oxidizing 10-MePTZ with Br₂. The 10-MePTZ was recrystallized twice and checked for purity by liquid chromatography. For the radical cation in CH_2Cl_2 in the visible region of the spectrum, $\lambda_{\max} = 514 \pm 2$ nm, $\epsilon_{514} = 8050 \pm 72$ M⁻¹ cm⁻¹.

(16) The calculated transient absorbance spectrum was obtained by superposition of the individual maxima for 10-MePTZ⁺ and Me-(bpy)-3DQ⁺ having Lorentzian band shapes with their bandwidths adjusted, linearly in energy units, to agree with those observed spectroelectrochemically for the individual radical cations.



and, as monitored by conventional flash photolysis,¹⁷ the subsequent recombination reaction follows equal-concentration, second-order kinetics with $k_q = 4.3 \times 10^8$ M⁻¹ s⁻¹:



In the sequence of reactions, (1) followed by (2), the $\text{Cu}^{\text{II/I}}$ couple has been used to "discharge" the ILCT state by consecutive outer-sphere electron transfer steps. The experiment also serves to verify that MLCT excitation at room temperature does indeed lead to a PTZ⁺ site since the difference spectrum after Cu^{II} quenching of the ILCT state (eq 1) shows only the band expected for PTZ⁺ with absorption features for DQ⁺ not present, as expected.

Our experiments demonstrate the existence of a MLCT-sensitized charge-separation process that yields separated redox equivalents and that the ILCT state reached can undergo chemical reactions. The charge storage time of $\tau_{\text{sep}} = 165 \pm 14$ ns is not overly long, but it may be possible to extend it considerably by eliminating the structural flexibility associated with the tetramethylene links to the phenothiazine group.

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Registry No. [Ru(Me(bpy)-3DQ²⁺)(Me(bpy)-PTZ₂)₂]⁴⁺, 106763-61-5; [Ru(Me(bpy)-PTZ₂)₂Cl₂], 106763-62-6; [Me(bpy)-3DQ](PF₆)₂, 96897-08-4.

(17) (a) Details of the flash photolysis apparatus have been reported in ref 17b. Samples were freeze-pump-thaw degassed and appropriate filters employed to prevent irradiation higher in energy than 400 nm to prevent photoejection from PTZ. The apparatus was modified to provide optical triggering of the oscilloscope. (b) Young, R. C.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468.

(18) Chambron, J. C.; Sauvage, J. P. *Nouv. J. Chim.* **1985**, *9*, 527.

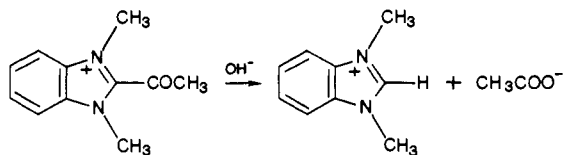
The Unusual Deacylation of the 2-Acetyl-1,3-dimethylbenzimidazolium Cation

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We report the unusual deacylation of the 2-acetyl-1,3-dimethylbenzimidazolium cation in aqueous solution. The cation is deacylated very rapidly by hydroxide ion even at pH 7-8, yet does not react with primary amines unless water is absent.



In the course of studies designed to prepare ketimines derived from the condensation of primary aliphatic and aromatic amines with 2-acylbenzimidazoles and perhaps to demonstrate a facilitated decarboxylation of α -amino acids in the presence of these ketones,¹ we had occasion to mix solutions of benzylamine and aniline in

(1) Owen, T. C.; Young, P. R., Jr. *FEBS Lett.* **1974**, *43*, 308. Young, P. R., Jr.; Howell, L. G.; Owen, T. C. *J. Am. Chem. Soc.* **1975**, *97*, 6544. Lopatin, W.; Young, P. R. Jr.; Owen, T. C. *J. Am. Chem. Soc.* **1979**, *101*, 960.