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Spectroscopic Evidence of a Net Formation of MV$^+$ via Photolysis of Ru(bpy)$_3^{2+}$ and MV^{2+} Adsorbed on Porous Vycor Glass

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The capture of photonic energy in the form of the radical cation of MV$^+$ has received considerable attention during the past decade.[1] When generated via oxidative quenching of *Ru(bpy)$_3^{2+}$, the redox products are transistory, and an external electron donor is required for the net formation of MV$^+$.[2-4] Recent studies suggest that it is possible to significantly curtail or prevent the exergonic back reaction in heterogeneous media.[5-9] However, direct evidence of a net formation of Ru(bpy)$_3^{3+}$ and MV$^+$ in the absence of an external electron donor has yet to be reported. In this paper, we describe spectroscopic evidence that MV$^+$ formation occurs in porous Vycor glass, PVG, in the absence of an electron donor.

Ru(bpy)$_3^{2+}$ uniformly impregnates the first 0.5 ± 0.1 mm of calcined 25- × 25- × 4-mm PVG samples leaving the interior of the support (ca. 80% of the total volume) vacant.[10-12] Immersing samples containing 1.5×10^{-7} mol of Ru(bpy)$_3^{2+}$/g of PVG in aqueous solutions 10^{-2} M in MV^{2+} for 80 min leads to the adsorption of $1.0 \pm 0.1 \times 10^{-4}$ mol of MV^{2+}/g. MV^{2+} cation exchanges onto PVG without desorption of or any change in the Ru(bpy)$_3^{2+}$ distribution.

Placing a PVG sample containing 1.5×10^{-7} mol of Ru(bpy)$_3^{2+}$/g in aqueous solutions of MV^{2+} leads to emission quenching, $k = 2.2 \pm 0.2 \times 10^8$ M^{-1} s^{-1}. However, dry samples containing 1.0×10^{-4} mol of MV^{2+}/g, which corresponds to a MV^{2+}:Ru(bpy)$_3^{2+}$ ratio of 700:1, fail to exhibit intensity quenching beyond experimental error. Since the surface coverage by Ru(bpy)$_3^{2+}$ is ≤2% within the impregnated regions, it was assumed that MV^{2+} impregnates the same regions. In fact, spectroscopic analysis of the cross sectional distribution[10-12] reveals that these reagents partition within PVG. Ru(bpy)$_3^{2+}$ remains on the outer surfaces whereas MV^{2+} (determined spectrally by spraying the ground surface with a basic solution of $N_2S_2O_4$) penetrates into the glass and impregnates the unoccupied regions.[13]

A 450-nm irradiation of a partitioned sample containing 1.0×10^{-4} mol of MV^{2+}/g and 1.5×10^{-7} mol of Ru(bpy)$_3^{2+}$/g in vacuo results in the appearance (Figure 1) of a weak absorption at 510 nm and more intense absorptions at 395 and 610 nm. The latter agree exactly with the spectrum of adsorbed MV$^+$ generated by $Na_2S_2O_6$ reduction. In vacuo, the spectrum of MV$^+$ does not change for at least 30 min after photolysis, but on exposure to air the 395- and 610-nm bands quickly dissappear. MV$^+$ is visually apparent only in those boundary regions impregnated with both MV^{2+} and Ru(bpy)$_3^{2+}$. The net formation of MV$^+$ is limited to a narrow range of samples containing $9.0 \pm 0.1 \times 10^{-5}$ mol of MV^{2+}/g and $1.7 \pm 0.3 \times 10^{-7}$ mol of Ru(bpy)$_3^{2+}$/g. The quantum yield of MV$^+$ formation during 450-nm photolysis of a sample containing 10^{-4} mol of MV^{2+}/g and 1.5×10^{-7} mol of Ru(bpy)$_3^{2+}$/g is 10^{-4}. The latter, which is based on the total light absorbed, must be regarded as an estimate since a significant amount of the excitation is absorbed by Ru(bpy)$_3^{2+}$ on the outer surfaces where there is no MV^{2+}.

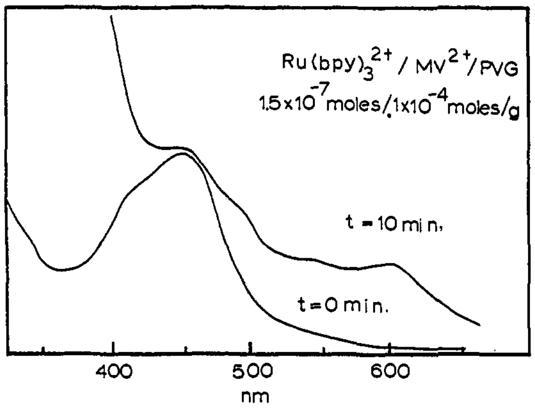

Figure 1. Spectra recorded before and after a 457.9-nm photolysis (0.50 W/cm^2) of a PVG sample in vacuo containing 4.5×10^{-4} mol of MV^{2+} (1.0×10^{-4} mol/g) and 6.75×10^{-7} mol of Ru(bpy)$_3^{2+}$ (1.5×10^{-7} mol/g).

The molar extinction coefficient of Ru(bpy)$_3^{3+}$, 476 M^{-1} cm^{-1} at 675 nm, precludes optical detection.[9] However, EPR spectra establish that Ru(bpy)$_3^{3+}$ is stable in PVG.[10] Product stability cannot be attributed to chemical changes in the adsorbates or an impurity effect. Spectra of the adsorbed complex and its photophysical properties closely resemble those in deareated, aqueous solution.[12] Similarly, the absorption spectrum of adsorbed MV^{2+}, a strong band at 275 nm, and its facile reduction by $Na_2S_2O_4$ resemble fluid solution properties. The absence of MV$^+$ formation during a 450-nm photolysis of a sample, in vacuo, containing only 10^{-4} mol of MV^{2+}/g, and the increase in the Ru(bpy)$_3^{2+}$ emission quantum yield when adsorbed on PVG preclude an impurity effect or impurity quenching which yields MV$^+$.

Photoexcitation of Ru(bpy)$_3^{2+}$ initiates the reaction, but the absence of MV^{2+} quenching in the dry samples, i.e., the conditions under which MV$^+$ formation occurs, precludes direct oxidative quenching. The emission polarization ratio for the adsorbed complex, 0.16 ± 0.02 at 22 ± 1 °C, is within experimental error of that in 77 K, hydrocarbon glasses.[12] The absence of rotational motion implies that the translational mobility of Ru(bpy)$_3^{2+}$ is severly curtailed or nonexistent. The diffusion coefficients of MV^{2+} in Nafion and clays are slightly larger than those of Ru(bpy)$_3^{2+}$, but both are considerably smaller than those in water.[14,15] These data as well as the absence of intensity quenching suggest a reaction within a fixed array of immobilized ions.[10]

MV$^+$ formation is attributed to the photoionization of Ru(bpy)$_3^{2+}$ [10,16-18] where the photodetached electron, which is mobile on the PVG surface, reduces MV^{2+} within the electron-transfer distance, 50 ± 10 Å.[10,19] The thermal reactions between Ru(bpy)$_3^{3+}$ and various viologen radical cations, having driving forces of 0.1–0.6 eV, require a mean separation ranging from a contact distance to 10 Å in glycerol at 0 °C.[20,21] Since the electron

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migration distance exceeds that for the back reaction, the redox products are stable.[10]

The weak absorbance at 510 nm (Figure 1) is attributed to $[Ru(bpy)_2(bpy^-)]^+$ that arises from the photoinduced disproportionation of the complex.[10,18] Since the oxidation potential of $[Ru(bpy)_2(bpy^-)]^+$, 1.3 V, exceeds the reduction potential of MV^{2+}, −0.44 V, MV^+ formation may also arise from the secondary reaction

$$[Ru(bpy)_2(bpy^-)]^+ + MV^{2+} \rightarrow Ru(bpy)_3^{2+} + MV^+ \quad (1)$$

when the reactants are within the thermal-electron-transfer distance. Electron transfer between $^*Ru(bpy)_3^{2+}$ and MV^{2+}, which has a driving force of 0.4 eV, occurs in cellulose when the separation is ≤14 Å.[22] Reaction 1 is not burdened by an exergonic thermal back reaction, and its occurrence promotes product stability by reducing the driving force for the back reaction from 2.5 eV for the disproportionation products to 1.6 eV for the $Ru(bpy)_3^{3+}$–MV^+ reaction.

In both reaction sequences, product stability occurs provided the mean separation between the immobilized redox products exceeds that for the thermal back reaction.[10] Our experiments indicate that this spatial separation occurs within the boundary region between these partitioned reagents. Further experiments are in progress, but the current data illustrate that a net formation of MV^+ occurs in PVG in the absence of an external electron donor.

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Supplementary Material Available: A plot of the optical densities of adsorbed $Ru(bpy)_3^{2+}$ at 450 nm and chemically generated MV^+ at 610 nm as a function of relative thickness of an impregnated 25- × 25- × 4-mm PVG sample (1 page). Ordering information is given on any current masthead page.

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Mechanistic Investigation of the Photoinitiated Autocatalytic Chain Decomposition (PACD) Reaction of Phenyl Azide and Derivatives

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Investigations of the photochemistry of phenyl azide[1–7] have led to documentation of an autocatalytic (branching[8]) chain reaction. This molecular explosion in solution is characterized by quantum yields for the disappearance of phenyl azide that greatly exceed unity[1,5,7] and which increase exponentially with increasing concentration.[5,7] Cryogenic[4] and transient absorption[3,6] spectral methods have been used in attempts to identify the branching chain propagator. Tetraaza species, i.e., 1,4-diphenyl tetraazadiene, have been eliminated since irradiation of phenyl azide and of phenyl isocyanate afforded essentially identical cryogenic and transient absorption spectra. Thus, a C_6H_5N species is thought to be the chain propagator. Four species are possibilities:[9] singlet phenylnitrene, triplet phenylnitrene, and the singlet species benzazirine[12–16] and azacycloheptatetraene.[10,11,16,17] We report here the use of substituted phenyl azides[18] and triplet-sensitized photochemical methods to identify which C_6H_5N species is the branching chain propagator.

Table I. Quantum Yields of Disappearance of Phenyl Azide and Derivatives[a]

[azide], M[b]	Φ phenyl azide[c]	 4-bromo phenyl azide[c]	 2,4,6-tribromo phenyl azide[c]	 4-nitrophenyl azide[d]
10^{-4}	0.56	0.80	0.16	0.54
10^{-3}	4.7	1.6	0.46	1.7
10^{-2}	93	6.6	15	6.4
10^{-1}	1800	81	143[e]	434

[a] Acetonitrile solutions deoxygenated by bubbling with nitrogen gas for 3 min at 0 °C. [b] Concentrations range was (0.868–2.06) × 10^{-Y}, Y = 1–4. [c] 254-nm excitation. [d] 313-nm excitation. [e] Concentration = 5.05 × 10^{-2} M.

Table II. Triplet-Sensitized Quantum Yields of Disappearance of 4-Nitrophenyl Azide[a]

sensitizer	λ, nm[b]	[azide], M	[sensitizer], M	Φ
none	313[c]	0.10	0	319
benzophenone	254[d]	0.10	0.073	677
biphenyl	254[d]	0.10	0.093	593
none	313[c]	0.20	0	846
benzophenone	254[e]	0.19	0.15	2500
biphenyl	254[e]	0.19	0.19	937

[a] Acetonitrile solution deoxygenated by nitrogen bubbling. [b] Wavelength of excitation. [c] I(313 nm) = 1.0 × 10^{14} photons/s. [d] I(254 nm) = 2.98 × 10^{13} photons/s. [e] I(254 nm) = 3.26 × 10^{13} photons/s.

Quantum yields of disappearance (Φ) were measured[1,5,7] for phenyl azide, 4-bromophenyl azide, 2,4,6-tribromophenyl azide, and 4-nitrophenyl azide as a function of concentration: values greatly exceed unity, Table I.[21] On the basis of absorption spectral

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