Figure 2, Raman spectra of successive fractions[20-22] of Limulus oxyhemocyanin, eluted from DEAE cellulose with a three-bottle concave gradient of 0-0.5 M NaCl in 0.05 M HN_4HCO_3, 2 mM $MgCl_2$, then concentrated by vacuum dialysis in the cold and dialyzed against distilled water. Their molecular weights (SDS gel electrophoresis) ranged from 70 000 to 78 000 daltons: (a)-(e) Fractions 1-5, C_{Cu} = 0.4, 1.0, 1.0, 1.1, and 0.35 mM, respectively, pH 7.8. Spectrometer conditions as in Figure 1, sensitivity 1.1-2.4 × 10³ Hz.

2-5, This coalescence is accompanied by a shift in the visible absorption maximum from 560 to 590 nm. Subtle changes in copper coordination geometry might be responsible for the spectral changes which are observed in the five Limulus fractions.

On the other hand, the chromophore structure is independent of the state of protein aggregation. The same spectra are observed at pH 9.8, 8,7 and 7.0 for both Busycon and Limulus hemocyanin, although aggregation is known to increase with decreasing pH over this interval.[18,19]

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Photochemical Generation of Ru(bpy)₃⁺ and O₂⁻

Sir:

From low temperature emission measurements Crosby and his co-workers have concluded that there is considerable charge separation in the luminescent excited state of $Ru(bpy)_3^{2+}$ (bpy is 2,2'-bipyridine) and that the absorption of visible light by the ion leads to the transition:

$$Ru(bpy)_3^{2+} (d^6) \rightarrow [Ru^{III}[(bpy)_3^{-\cdot}]]^{2+} (d^5\pi^*)^{1-3}$$
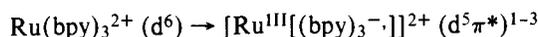
The excited state has simultaneously both oxidizing (Ru(III)) and reducing [(bpy)₃⁻·] sites. Experimental studies based on the electron transfer quenching of $Ru(bpy)_3^{2+*}$ have allowed formal reduction potentials for the excited state acting as either oxidant or reductant to be estimated.[4-6]

$$Ru(bpy)_3^{3+} + e \rightarrow Ru(bpy)_3^{2+*} \qquad E = -0.81 \pm 0.02 \text{ V}$$

$$Ru(bpy)_3^{2+*} + e \rightarrow Ru(bpy)_3^{+} \qquad E = 0.77 \pm 0.02 \text{ V}$$
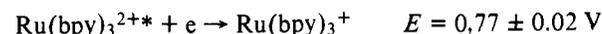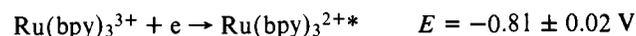
(in 0.1 M [NEt₄]ClO₄-CH₃CN vs. the SSCE)

Oxidative quenching of $Ru(bpy)_3^{2+*}$, which has been demonstrated using flash photolysis,[7,8] gives $Ru(bpy)_3^{3+}$ which is a strong oxidant $(Ru(bpy)_3^{3+} + e \rightarrow Ru(bpy)_3^{2+} E = 1.29$ V) capable of oxidizing water to O_2,[9] Reduction of the excited state, which is suggested by the results of emisson quenching experiments[5] and more recently shown by Creutz and Sutin using flash photolysis,[10] gives $Ru(bpy)_3^+$ which is a powerful reductant $(Ru(bpy)_3^{2+} + e \rightarrow Ru(bpy)_3^+ E = -1.33$ V), thermodynamically capable of reducing water to H_2,[11]

Sprintschnik, Sprintschnik, Kirsch, and Whitten have reported that monolayers formed from long-chain derivatives of $Ru(bpy)_3^{2+}$ act as catalysts for the photodissociation of water.[12] The operation of the photocatalytic system may depend on the electron transfer properties of the excited state or

Table I, Quenching and Back-Electron-Transfer Rate Data in CH_3CN at 22 ± 2 °C

Quencher	$E_{1/2}$, V($D^{+/0}$)[a]	k_q, M^{-1} s^{-1}	k_b, M^{-1} s^{-1} [c]
TMPD	0.15	1.2×10^{10}	5.2×10^9
DMA	0.85	7.1×10^7	4.1×10^9
α-$NH_2C_{10}H_7$	$E_p = 0.63$[b]	1.2×10^8	1.2×10^{10}
p-$NH_2C_6H_4O$-CH_3	$E_p = 0.71$[b]	6.4×10^8	5.6×10^9
10-MPTH	0.83	1.6×10^9	3.8×10^9

[a] In 0.1 M $[N(C_4H_9)_4]PF_6$-CH_3CN vs. the SSCE at 22 ± 2 °C. [b] The E_p values are peak potentials for anodic waves. The $D^{+/0}$ couple is irreversible even at scan rates as high as 5 V/s. [c] k_b values (reaction 3) were calculated from the slopes of plots of $1/\Delta A$ vs. t where slope $= k_b/b\Delta\epsilon$ and ΔA is the observed absorbance change at time t, b is the cell path length, and $\Delta\epsilon$ is the extinction coefficient difference between products and reactants.[19] The calculations of $\Delta\epsilon$ are mentioned in ref 15. Plots of $1/\Delta A$ vs. t were linear for two or more half-lives.

of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^+$ in the monolayers. We report here the generation of $Ru(bpy)_3^+$ by electrochemical reduction, the photochemical generation of $Ru(bpy)_3^+$ by reductive quenching in nonaqueous solvents, and the use of the $Ru(bpy)_3^{2+*/+}$ couple in the photocatalytic production of O_2^-.

In acetonitrile solution, emission from $Ru(bpy)_3^{2+*}$ is quenched in the presence of the mild reductants N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), dimethylaniline (DMA), p-anisidine (p-$NH_2C_6H_4OCH_3$), α-napthylamine (α-$NH_2C_{10}H_7$), or 10-methylphenothiazine (10-MPTH). The quenching was studied as a function of quencher concentration and quenching constants (k_q in Table I) were obtained from plots of I_0/I vs. [quencher] using the Stern–Volmer relation and the lifetime of $Ru(bpy)_3^{2+*}$ in the medium (850 ns).[13] Also given in Table I are electrochemical data for the organic quenchers as reductants.

For each of the five quenchers direct evidence for net electron transfer quenching has been obtained since the redox products expected from reductive quenching are observed following flash photolysis. Simultaneous energy transfer quenching may occur in some cases but we have no definitive experimental evidence that such processes occur. If energy transfer is competitive, k_q values in Table I reflect both the electron transfer and energy transfer processes. For flash photolysis studies, solutions containing quencher (2.5×10^{-4} to 5×10^{-2} M) and $Ru(bpy)_3^{2+}$ (5×10^{-6} to 1×10^{-5} M) in acetonitrile were subjected to five freeze-thaw degassing cycles and sealed at 10^{-4} Torr or less. Following visible ($\lambda > 400$ nm using Corning 3-73 glass filters) flash photolysis using an apparatus described elsewhere,[14] transient spectral changes were observed. There were no or only slight permanent spectral changes after a series of flashes. For TMPD and 10-MPTH as quenchers, the cations $TMPD^+$ (λ_{max} 612 nm, ϵ 1.3×10^4; λ_{max} 564 nm, ϵ 1.3×10^4)[15] and 10-$MPTH^+$ (λ_{max} 753 nm, ϵ 1.3×10^3; λ_{max} 514 nm, ϵ 7.8×10^3)[15] were observed following flash photolysis. The cations disappeared as shown by loss of absorbance at λ_{max}, in processes which followed second-order, equal concentration kinetics.[18] Transient spectral changes at other wavelengths were consistent with the production of a strongly absorbing Ru–bpy intermediate during the flash, followed by reappearance of $Ru(bpy)_3^{2+}$ at the same rate at which the radical cations disappeared.

The transient spectral changes observed are consistent with reactions 1–3 where reductive quenching of $Ru(bpy)_3^{2+*}$ occurs during the flash followed by slower back-electron-transfer.[19] The back-electron-transfer reactions were the processes followed directly by flash photolysis. Since they follow sec-
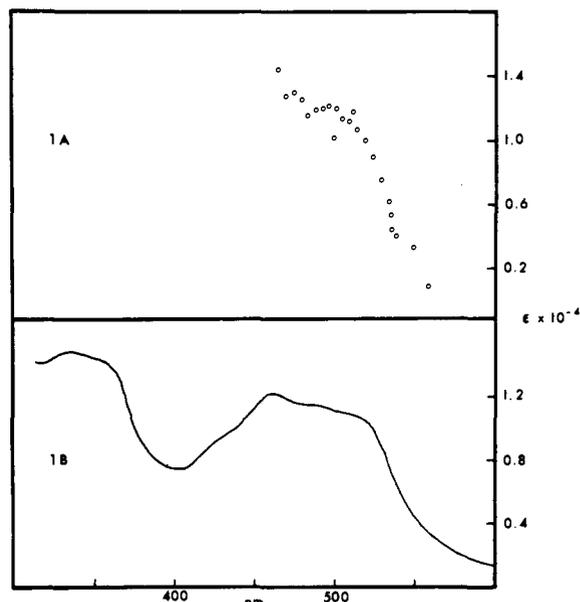
Figure 1, (A) Absorption spectrum of $Ru(bpy)_3^+$ calculated from results obtained by flash photolysis of an acetonitrile solution containing $Ru(bpy)_3^{2+}$ (1×10^{-5} M) and TMPD (2.0×10^{-3} M) at 22 ± 2 °C. (B) Spectrum obtained by electrochemical reduction of $Ru(bpy)_3^{2+}$ in 0.1 M $[NEt_4](PF_6)$-acetonitrile at 22 ± 2 °C.

ond-order, equal concentration kinetics, reactions 2 and 3 are stoichiometric as written.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \quad (1)$$

$$Ru(bpy)_3^{2+*} + D \xrightarrow{k'_q} Ru(bpy)_3^+ + D^+ \quad (2)$$

$$Ru(bpy)_3^+ + D^+ \xrightarrow{k_b} Ru(bpy)_3^{2+} + D \quad (3)$$
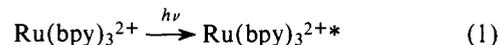
The difference spectra between reactants and products for reaction 3 were obtained by flash photolysis, Using TMPD as quencher, the concentration of $TMPD^+$ following the flash could be estimated by the change in absorbance at 612 nm where $TMPD^+$ is the only strongly absorbing species in solution. From the concentration of $TMPD^+$, the reaction stoichiometry for eq 3, and known extinction coefficients for $Ru(bpy)_3^{2+}$, D^+ ($TMPD^+$),[16] and $D(TMPD)$[16] in the visible, the absorption spectrum for the Ru–bpy intermediate can be calculated and is shown in Figure 1A.

We have prepared solutions of $Ru(bpy)_3^+$ in 0.1 M $[NEt_4]$-(PF_6)-acetonitrile by electrochemical reduction of $Ru(bpy)_3^{2+}$. Exhaustive electrolysis at -0.94 V vs. the Ag wire electrode gave $Ru(bpy)_3^+$ [11] (eq 4, $n = 0.98$) which could be reoxidized quantitatively ($n = 1.0$) to $Ru(bpy)_3^{2+}$.[20]
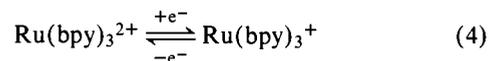
$$Ru(bpy)_3^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Ru(bpy)_3^+ \quad (4)$$

There is good agreement between the spectrum of $Ru(bpy)_3^+$ obtained in the electrochemical experiment (Figure 1B) and the spectrum obtained by flash photolysis (Figure 1A) showing that the Ru–bpy intermediate generated by electron transfer quenching is $Ru(bpy)_3^+$.

The spectrum of $Ru(bpy)_3^+$ in acetonitrile agrees well with the results obtained in aqueous solution by Creutz and Sutin.[10] The complex nature of the absorption spectrum is consistent with the expected $[d^6\pi^*(bpy)]$ electron configuration for $Ru(bpy)_3^+$ and it probably consists of a series of charge transfer, $\pi^*(bpy) \leftarrow d(Ru)$,[1-3,21] and ligand localized, $\pi^* \leftarrow \pi$,[22] transitions. The chemical and spectral properties of $Ru(bpy)_3^+$ and of $Ru(bpy)_3^0$, prepared by the two-electron

reduction of $Ru(bpy)_3^{2+}$, will be discussed in detail in a later publication.

In acetonitrile a rapid reaction occurs between $Ru(bpy)_3^+$ and O_2 to give $Ru(bpy)_3^{2+}$ quantitatively[23] and presumably superoxide ion (eq 5).

$$Ru(bpy)_3^+ + O_2 \rightarrow Ru(bpy)_3^{2+} + O_2^- \qquad (5)$$
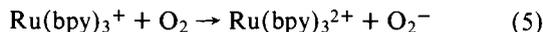
We have obtained evidence for eq 5 by flash photolysis of an acetonitrile solution containing DMA (5.8×10^{-2} M), O_2 (1.4×10^{-3} M),[24] and $Ru(bpy)_3^{2+}$ (1.1×10^{-5} M). Following flash photolysis, the absorbance due to a transient (λ_{max} 470 nm) produced during the flash decreased by a process which followed second-order, equal concentration kinetics. The difference spectrum showed that the transient was DMA^+[15] and that it was the only spectrally observable intermediate.[15,25] No evidence for $Ru(bpy)_3^+$ was found on this time scale.

In the experiment, reactions 1 and 2 (D = DMA) occur during the flash, followed by rapid oxidation of $Ru(bpy)_3^+$ by O_2 (eq 5). The reaction observed by flash photolysis must be eq 6 ($k(22 \pm 2\ ^\circ C) = 8.5 \times 10^8$ M^{-1} s^{-1}).

$$O_2^- + DMA^+ \rightarrow O_2 + DMA \qquad (6)$$
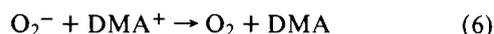
The observation of second-order, equal concentration kinetics for reactions 3 and 6 shows that eq 3, 5, and 6 are stoichiometric as written.[27] The superoxide ion is an activated form of O_2[29] and it may be possible to develop photocatalytic schemes for carrying out useful chemical reactions based on the chemistry of O_2^- or HO_2 where the reactions are driven by visible light.

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Room Temperature Generation of Radicals from Dimethylaminomalononitrile, Probably via Dimethylaminocyanocarbene

Sir:

Under basic or thermal conditions, *tert*-octylaminomalononitrile decomposes with generation of radicals and of hydrogen cyanide; α-elimination of the latter was postulated to give initially an aminocyanocarbene intermediate, but β-elimination could not be entirely ruled out.[1] It is now found that both dimethylaminomalononitrile (**1**)[2] and its monodeutero analogue decompose at ambient temperature to give the dimethylaminodicyanomethyl radical (**3**). The ESR spectrum of a neat degassed sample—taken 4 h after reaching room temperature—and its computer simulation are shown (Figure 1). Generation of the radical **3** in dilute solution requires prior heating to 140 °C for 30 min but is also achieved in the cold by UV irradiation (30 s) of a 5% solution of **1** in benzene/di-*tert*-butyl peroxide (95:5).

In the decomposition of **1**, hydrogen cyanide and the dimethylaminocyanomethyl radical (**4**) are also produced. The formation of hydrogen cyanide is shown by mass spectroscopy and by the isolation of 1-dimethylamino-2-aminomaleonitrile[3] (**7**) from the thermolysis (60 °C) product of **1**. Compound **7** results from addition of hydrogen cyanide to **1** (reaction h).[3]

Direct evidence for the generation of the less stable (see below) radical **4** is lacking since it is not detected by ESR spectroscopy; however, its generation is inferred from the isolation of dimethylglycinonitrile (**5**) from the thermolysis (60 °C) product of **1**. Compound **5** results from hydrogen abstraction by **4** according to reaction f,[3] which additionally leads to the accumulation of radical **3**.

Generation of the radicals **3** and **4** and of hydrogen cyanide also accounts for the formation of the crystalline thermolysis