Electron Transfer in the Quenching of Triplet Methylene Blue by Complexes of Iron(II)

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Abstract: A Q-switched pulsed ruby laser emitting 1.0-J flashes at 693.4 nm was used in an investigation by means of flash photolysis–kinetic spectrophotometry of the mechanism of quenching of 2–10 μM triplet methylene blue by substitution-inert complexes of Fe(II). Complexes included $Fe(H_2O)_6^{2+}$, $H_2Fe^{II}(CN)_6^{2-}$, $HFe^{II}(CN)_6^{3-}$, $Fe^{II}(CN)_6^{4-}$, $Fe^{II}(CN)_4bpy^{2-}$, $Fe^{II}(CN)_2(bpy)_2^0$, ferrocene^0, and $Fe^{II}(bpy)_3^{2+}$. System variables included solvent (H_2O, aqueous EtOH, aqueous CH_3CN, and aqueous DMF), pH (2.1–8.2) and ionic strength (0.01–1.6 M). Energy transfer from triplet methylene blue to quencher is not possible in any of the cases investigated, and quenching proceeds via partial or complete electron transfer. Rate constants for quenching, k_q, were diffusion-controlled with all quenchers except $Fe^{II}(H_2O)_6^{2+}$ and, possibly, $Fe^{II}(bpy)_3^{2+}$. Efficiency of net electron transfer in the quenching process, $F_1 = k_{et}/k_q$, was measured directly and found to vary with quencher, solvent, and state of protonation of triplet methylene blue and quencher. Values of F_1 from 0.00 to 0.86 were observed. F_1 does not vary systematically with k_q. It was found that $RT \ln [(1/F_1) - 1]$ for the diffusion-controlled quenching of $^3MBH^{2+}$ by $Fe^{II}(CN)_4bpy^{2-}$ varies linearly, with slope $\sim +0.16$, with Kosower's solvent polarity parameter Z in water, aqueous EtOH, aqueous CH_3CN, and aqueous DMF with Z values ranging from 81.5 to 94.6 kcal/mol. The kinetics of the reverse electron-transfer reaction between complexes of Fe(III) and semimethylene blue, $MBH^{+}\cdot$, was studied independently by generating $MBH^{+}\cdot$ by quenching triplet methylene blue with diphenylamine in the presence of a complex of Fe(III). Values of k_{ret}, the second-order specific rate of reverse electron transfer, were measured directly. Values of F_2, the efficiency of net electron transfer in an encounter between $MBH^{+}\cdot$ and a complex of Fe(III), were taken as equal to k_{ret}/k_D, where k_D is the diffusion-controlled specific rate of encounter of the reactants. Values of k_D were obtained by assuming equality between k_D for a given complex of Fe(III) and k_q for quenching of $^3MBH^{2+}$ by the corresponding complex of Fe(II), an assumption which is accurate only at high ionic strength. For the four quenchers and five solvents for which both F_1 and F_2 were determined, $F_1 + F_2 \approx 1$. For the two quenchers and three solvents in which k_D (and, therefore, F_2) was determined accurately, $F_1 + F_2 = 0.99 \pm 0.06$. The data reported in this study are consistent with the following mechanistic features of diffusion-controlled quenching of $^3MBH^{2+}$ by complexes of Fe(II), $Fe^{II}L_x^{m}$: (1) All quenching encounters produce a geminate pair, $[(MBH^{+}\cdot)\cdots Fe^{III}L_x^{m+1}]$, made up of semimethylene blue and the ferric complex. This pair can dissociate before or after undergoing reverse electron transfer. Quenching to the ground state proceeds via dissociation of this geminate pair subsequent to reverse electron transfer. (2) The geminate pair, $[(MBH^{+}\cdot)\cdots Fe^{III}L_x^{m+1}]$, is common to quenching of $^3MBH^{2+}$ by complexes of Fe(II) and to reverse electron transfer between $MBH^{+}\cdot$ and complexes of Fe(III). (3) Intersystem crossing is rapid in both quenching of the triplet and in the reverse reaction of $MBH^{+}\cdot$ with ferric complexes. (4) Solvent effects on F_1, the efficiency of net electron transfer during quenching, are determined primarily by solvation effects upon the return from $[(MBH^{+}\cdot)\cdots Fe^{III}L_x^{m+1}]$ to $^1MB^+$ and $Fe^{II}L_x^{m}$. The kinetic order, rate, and products of decay of $MBH^{+}\cdot$ and ferric complex resulting from quenching of $^3MBH^{2+}$ by ferrous complexes depend on the identity of the quencher and on the medium. Generally, decay was first order, and only MB^+ was formed when the ferric complex was negatively charged. With positively charged ferric complexes, decay was second order and involved both reverse electron transfer to give MB^+ and disproportionation to MB^+ and leucomethylene blue. Disproportionation predominated only in the case of $Fe^{III}(H_2O)_6^{3+}$.

Introduction

Net electron transfer between an excited molecule and a quencher to produce charge carriers is a necessary step in photogalvanic conversion of light into electricity:[1,2]

$$G \xrightarrow{h\nu} {}^*E \rightarrow {}^*R \qquad (1)$$

$$Q + {}^*R \rightarrow Q^+ + R^- \text{ or } Q^- + R^+ \qquad (2)$$

*E is the excited state produced directly by absorption of light while *R is an excited state which is sufficiently long-lived to engage in collisions with quencher. A more detailed picture would delineate production of a Franck–Condon state by the absorption event followed by one or more rapid vibronic relaxation steps and, possibly, a slower change in multiplicity. Such a more detailed picture would also explicitly recognize that, depending on the concentration of Q, more than one energy state might play the role of *R so that eq 2 would represent a family of reactions; e.g., it has recently been shown[3] that 0.05 M $Fe^{II}(H_2O)_6^{2+}$ significantly reduces both the S_1 and T_1 states of methylene blue in 0.01 M solutions of HCl in 50% v/v aqueous CH_3CN. Alternatively, *R may be produced indirectly by sensitization. Regardless of whether or not sensitization is involved in production of *R, or whether *R represents one or more than one excited states, quenching via processes represented by eq 2 must dominate over other quenching mechanisms if production of charge carriers is to be efficient.

Quenching processes which are alternative to net electron transfer include energy transfer to quencher, collisionally induced intersystem crossing to the ground state if the multiplicities of *R and G differ, and collisionally induced internal conversion of the ground state if the multiplicities of *R and G are identical. Energy transfer to the quencher may provide a pathway to production of charge carriers through reaction of the excited quencher with G, eq 3 and 4. Conversely, collisionally induced intersystem crossing or internal conversion may proceed via partial electron transfer (i.e., formation of a charge-transfer complex) or by complete electron transfer followed by complete reversal of electron transfer, both within the lifetime of the encounter complex, as well as by other mechanisms.

$$Q + {}^*R \rightarrow {}^*Q + G \qquad (3)$$

$${}^*Q + G \rightarrow Q^+ + R^- \text{ or } Q^- + R^+ \qquad (4)$$

This paper describes a study by means of laser flash photolysis–kinetic spectrometry of the dependence of quenching rates and the extent of net electron transfer in the quenching of triplet methylene blue by substitution-inert coordination complexes of Fe(II) upon the nature of ligands and medium. In all the cases reported here the quencher has no known excited state with an energy low enough to allow significant energy transfer from the

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[1] N. N. Lichtin in "Solar Power and Fuels", J. R. Bolton, Ed., Academic Press, New York, 1977, pp 119–142.

[2] M. Z. Hoffman and N. N. Lichtin in "Solar Energy: Chemical Conversion and Storage", R. R. Hautala, R. B. King, and C. Kutal, Eds., The Humana Press, Clifton, N.J., 1979, pp 153–187.

[3] T. L. Osif, N. N. Lichtin, M. Z. Hoffman, and S. Ray, *J. Phys. Chem.*, **84**, 410 (1980).

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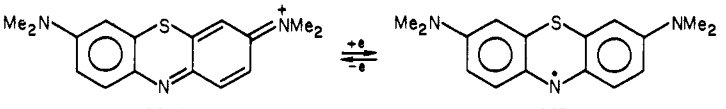
Table I. Relevant Properties of Methylene Blue and Quenchers



MB^+ $MB\cdot$

	$E_{triplet}$, cm^{-1}	$E_{ox}°$,[a] V	$E_{red}°$,[a] V	$10^{-6}\tau$, s	pK_a
MB^+	11 640[b]		−0.23 ($MB^+/MB\cdot$)[d]		
MBH^{2+}	8 220[c]		+0.31 ($MBH^{2+}/MBH^{+}\cdot$)[d]		0.0[e]
MBH_2^{3+}					−5.1[e]
$^3MB^+$			+1.21 ($^3MB^+/MB\cdot$)[g]	85[f]	
$^3MBH^{2+}$			+1.33 ($^3MBH^{2+}/MBH^{+}\cdot$)[g]	4.2[h]	7.2[h]
$MBH^{+}\cdot$			0.51 (pH 2)[i]		~9[j]
$MBH_2^{2+}\cdot$					1.9 (5% aqueous EtOH)[k]
					1.2 (50% v/v aqueous AN)[k]
$Fe^{II}(H_2O)_6^{2+}$	19 800[l]	−0.770[m]			
$HFe^{II}(CN)_6^{3-}$	23 700[n]	−0.56 (μ = 0.1M)[o]			4.2 (pK_4 of $H_4Fe(CN)_6$)[o]
					2.2 (pK_3 of $H_4Fe(CN)_6$)[o]
$Fe^{II}(CN)_4bpy^{2-}$	*p*	−0.56[q]			1.7 (pK_2 of $H_2Fe(CN)_4bpy$)[q]
					~0.3 (pK_1 of $H_2Fe(CN)_4bpy$)[q]
$Fe^{II}(CN)_2(bpy)_2°$	~12 500[r]	−0.78[s]			
ferrocene(0)	~15 000[t]	−0.54 (95% EtOH, pH 0.65)[u]			
$Fe^{II}(bpy)_3^{2+}$	11 500[v]	−1.07[s]			

[a] Vs. std hydrogen electrode. [b] Reference 38. [c] Calculated from $\Delta E_{^3MBH^{2+}} - \Delta E_{^3MB^+} = 2.3RT[pK_a(\text{ground}) - pK_a(\text{excited})]$. [d] Calculated from $E_{red}°'$ at pH 2 = +0.19 V (ref 42) with $E_{red}° = E_{red}°'$ (pH 2) + 0.06(2) $\equiv E_{MBH^{2+}}°$. $E_{MB^+}°$ calculated from $E_{MB^+}° + (2.3RT/F)pK_a^{MBH^{+}\cdot} = E_{MBH^{2+}}° + (2.3RT/F)pK_a^{MBH^{2+}}$. [e] Reference 40. [f] Reference 41. [g] $E_{red}°$ of $^3MB^+ = E_{red}°$ of $MB^+ + E(^3MB^+)$; $E_{red}°$ of $^3MBH^{2+} = E_{red}°$ of $MBH^{2+} + E(^3MBH^{2+})$. [h] Reference 4. [i] Reference 42. [j] References 9 and 43. [k] Reference 8. [l] Reference 44. [m] Reference 45. [n] Reference 46. [o] Reference 35. [p] Assumed to be between 23 700 and 12 500 cm^{-1}. [q] Reference 36. [r] Estimated from the triplet energy of $^3Fe(CN)_2(phen)_2°$, ref 47. [s] Reference 48. [t] Reference 49. [u] Reference 50. [v] Reference 51.

triplet dye. Energies of the T_1 states of methylene blue and quenchers and redox potentials of the S_0 and T_1 states of methylene blue and of the S_0 state of quenchers are summarized in Table I along with pK_a values and intrinsic lifetimes of a number of species involved in this study.

The kinetics of the reaction of semimethylene blue with complexes of Fe(III) has been studied under two circumstances. In one, the back-reaction of the products of photoreduction of triplet methylene blue was followed directly. In the other, semimethylene blue was generated in situ by reduction of triplet dye by diphenylamine and its reaction with excess complex of Fe(III) was followed.

Results appear to be fully accommodated by a mechanism involving complete electron transfer from quencher to dye in the quenching encounter complex and control of efficiency of net electron transfer by competition between dissociation of the products of this transfer to semimethylene blue and the ferric complex and reversal of electron transfer to give the ground-state dye and the ferrous complex.

Experimental Section

Apparatus. A Holobeam Series 630 Laser System with a Q-switched ruby laser capable of providing up to 3.6 J per flash at 694.3 nm with a nominal pulse width of 19 ns was used. Details of the laser and monitoring apparatus are reported elsewhere.[4] Flash intensity of the laser was 1.0 J per pulse in the work reported here and a preamplifier was not employed in the monitoring circuit.

Materials. Methylene blue chloride trihydrate (mol. wt. 374) was Fluka *puriss* grade. Aldrich diphenylamine was recrystallized twice from aqueous methanol and then once from methanol. $K_2[Fe^{II}(CN)_4bpy]\cdot 3H_2O$, $Fe^{II}(CN)_2(bpy)_2\cdot 3H_2O$ and $[Fe^{II}(bpy)_3](ClO_4)_2$ were prepared by the method of Schilt,[5] and their purity was verified by UV–vis spectrometry. $H[Fe^{III}(CN)_4bpy]\cdot 2H_2O$ was prepared by oxidation of $K_2[Fe^{II}(CN)_4bpy]$ in aqueous solution followed by addition of hydrochloric acid. The product was recrystallized from water and its purity verified by UV–vis spectrophotometry.[5] Alfa ferrocene was recrystallized from cyclohexane. Ferrocinium perchlorate, which is unstable[6] both as pure solid and in solution, was prepared immediately before use by oxidation of ferrocene with $Fe(ClO_4)_3$ in 0.01 M aqueous $HClO_4$. Purity was verified by UV–vis spectrophotometry.[6] $K_4[Fe^{II}(CN)_6]$ and $K_3[Fe^{III}(CN)_6]$ were Baker Analyzed Reagent grade. KH_2PO_4, HCl, and H_2SO_4 were Baker Analyzed grade. $HClO_4$ and $Na_2B_4O_7\cdot 10H_2O$ were Fisher Certified ACS grade. Potassium hydrogen phthalate was Mallinckrodt Analytical grade. $MgCl_2$ was Matheson Coleman and Bell ACS Reagent grade. Laboratory distilled water was purified by passage through a Millipore deionizer and filter. Aldrich dimethylformamide was distilled in vacuo. Acetonitrile was Burdick and Jackson UV grade. Ethanol was USI Reagent grade.

Test solutions were deaerated by purging for 15–20 min with deoxygenated nitrogen which had first been bubbled through the same solvent used in the test solution. The nitrogen was deoxygenated by bubbling through chromous solution which was stored over zinc amalgam.

Measurements. Decay of protonated triplet methylene blue ($^3MBH^{2+}$) was monitored at 370 and 710 nm.[4] Measured rates of recovery of ground-state methylene blue (MB^+), monitored at 635–650 nm, and of decay of $^3MBH^{2+}$ were in good agreement in the absence of added quencher. Decay of $^3MB^+$ was monitored at 415 and 825 nm.[4] Yields of semimethylene blue, $MBH^{+}\cdot$, were measured by decrease of absorbance of MB^+ at 635–650 nm immediately after decay of absorbance by $^3MBH^{2+}$ or $^3MB^+$. Decay of $MBH^{+}\cdot$ was monitored directly at 840 or 880 nm[7] and indirectly by increase in absorbance due to MB^+. It was verified that $MBH^{+}\cdot$ does not absorb significantly at 570–700 nm, where MB^+ absorbs strongly, by observing that the decrease in absorbance in this region (difference spectrum) caused by conversion of MB^+ to $MBH^{+}\cdot$ agreed very well with the spectrum of MB^+. In studies of the kinetics of oxidation by the ferric complex of $MBH^{+}\cdot$ which had been generated by reduction of $^3MBH^{2+}$ or $^3MB^+$ by 0.3–1 mM diphenylamine (DPA) both MB^+ and $MBH^{+}\cdot$ were monitored. The rate constant for quenching of triplet methylene blue by DPA was ~1 × 10^9 M^{-1} s^{-1} in all the media investigated. Concentrations of ferric complexes were less than 0.08 mM in all cases.

Data

Quenching Constants, k_q. Specific rates of quenching of triplet methylene blue, $^3MBH^{2+}$ or $^3MB^+$ depending on pH (pK_a = 7.2 in aqueous solution),[4] by ferrous complexes were determined from the slopes of plots of pseudo-first-order specific rates of its decay vs. concentration of quencher, eq 5. Quenchers included $Fe^{II}(H_2O)_6^{2+}$, $Fe^{II}(bpy)_3^{2+}$ (where bpy = 2,2′-bipyridyl), ferrocene(0),

$$k_d = k_0 + k_q[Fe^{II}] \qquad (5)$$

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[4] T. Ohno, T. L. Osif, and N. N. Lichtin, *Photochem. Photobiol.*, **30**, 541–546 (1979).

[5] A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000–3005 (1960).

[6] J. R. Pladziewicz and J. H. Espenson, *J. Am. Chem. Soc.*, **95**, 56–63 (1973).

[7] J. Faure, R. Bonneau, and J. Joussot-Dubien, *J. Chim. Phys.*, **65**, 369–370 (1968).

Table II. Values of k_q and $F_1(\equiv k_{et}/k_q)$ in Quenching of Triplet Methylene Blue[a] by Complexes of Fe(II)

quencher	solvent[b]	buffer	μ, M	$10^9 k_q$, $M^{-1}\ s^{-1}$	F_1
$Fe^{II}(H_2O)_6{}^{2+}$	H_2O	0.01 M H_2SO_4[d]	0.2[j]	0.0055[l]	
	50% v/v AN	0.01 M H_2SO_4[d]	0.2[j]	0.085	0.84
$Fe^{II}(CN)_6{}^{4-}$	H_2O	0.04 M KH_2PO_4[e]	~0.08	14.3	0.16
$H_2Fe^{II}(CN)_6{}^{2-}$	5% EtOH	0.01 N H_2SO_4[f]	~0.02	11.4	0.23
$Fe^{II}(CN)_6{}^{4-}$	5% EtOH	0.04 M potassium hydrogen phthalate[g]	~0.08	9.0	0.36
	5% EtOH	0.006 M Na_2HPO_4, 0.04 M KH_2PO_4[h]	1.6[k]	4.0	0.27
$H_2Fe^{II}(CN)_6{}^{2-}$	45% EtOH	0.01 N H_2SO_4	~0.02	5.6	0.52
$Fe^{II}(CN)_6{}^{4-}$	55% EtOH	0.04 M KH_2PO_4	~0.08	4.3	0.58
$H_2Fe^{II}(CN)_6{}^{2-}$	75% EtOH	0.01 N H_2SO_4	~0.02	4.2	0.53
	60% DMF	0.01 N H_2SO_4	~0.02	2.8	0.70
$Fe^{II}(CN)_4bpy^{2-}$	H_2O[c]	0.04 M KH_2PO_4[e]	~0.08	11.0	0.088
	H_2O[c]	0.04 M KH_2PO_4[e]	~0.14[j]	7.7	0.095
	H_2O[c]	0.025 M $Na_2B_4O_7$[i]	~0.06	4.0	0.00
	5% EtOH	0.01 N H_2SO_4[f]	~0.02	8.5	0.10
	5% EtOH	0.008 M HCl	1.5[k]	3.1	0.095
	30% EtOH	0.01 N H_2SO_4	~0.02	3.8	0.24
	30% EtOH	0.04 M KH_2PO_4	~0.14[j]	4.1	0.22
	30% EtOH	0.025 M $Na_2B_4O_7$	~0.06	2.8	0.07
	60% EtOH	0.01 N H_2SO_4	~0.02	2.8	0.32
	60% EtOH	0.04 M KH_2PO_4	~0.08	4.2	0.31
	78% EtOH	0.01 N H_2SO_4	~0.02	2.7	0.58
	88% EtOH	0.01 N H_2SO_4	~0.02	2.2	0.69
	30% DMF	0.01 N H_2SO_4	~0.02	4.3	0.28
	70% DMF	0.01 N H_2SO_4	~0.02	2.5	0.86
	30% v/v AN	0.01 N H_2SO_4	1.2[k]	3.6	0.30
	50% v/v AN	0.01 N H_2SO_4	0.5[k]	4.4	0.47
	75% v/v AN	0.01 N H_2SO_4	0.1[k]	7.1	0.66
$Fe^{II}(CN)_2(bpy)_2{}^0$	20% EtOH	0.04 M KH_2PO_4	~0.08	3.3	0.078
	60% EtOH	0.04 M KH_2PO_4[m]	~0.08	1.7	0.076
ferrocene(0)	78% EtOH	0.01 M $HClO_4$	~0.01	3.4	0.68
	95% EtOH	0.01 M $HClO_4$	~0.01	4.9	0.68
$Fe^{II}(bpy)_3{}^{2+}$	5% EtOH	0.008 M HCl	1.5[k]	1.12	0.00
	H_2O	0.04 M KH_2PO_4[e]	~0.08	0.42	0.00

[a] $[^3MBH^{2+}]$ at pH $\leqslant$ 5.5, $[^3MB^+]$ at pH 8.8. [Triplet] = $[MB^+]_0$ = 10 μM unless otherwise indicated. [b] All binary solvents have H_2O as second component. Compositions designated as *n*% EtOH or DMF signify *n* volume of solvent made up to a 100 volume with water. Compositions designated as *n*% v/v AN signify *n* volume of AN mixed with 100 − *n* volume of water. Principal states of protonation of quenchers are shown as they would be in water at the indicated concentrations of buffers. [c] $[MB^+]_0$ = 2 μM. [d] pH 2.0. [e] pH 4.4. [f] pH 2.1. [g] pH 5.5. [h] pH 6.0. [i] pH 8.2. [j] Made up with Na_2SO_4. [k] Made up with $MgCl_2$. [l] Taken from ref 10. [m] Buffering of triplet dye incomplete.

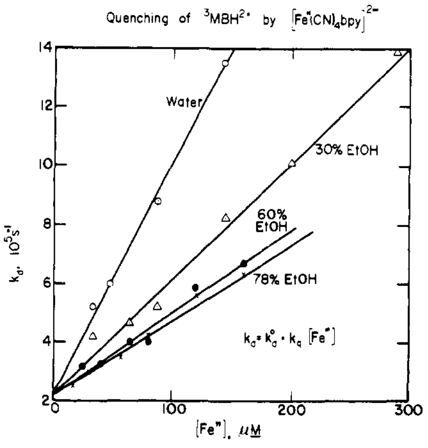

Figure 1. Dependence of pseudo-first-order specific rate of decay of $^3MBH^{2+}$ on $[Fe^{II}(CN)_4bpy]^{2-}$ in water and aqueous ethanol: 10 μM MB^+; 0.01N H_2SO_4 in 60% and 78% aqueous EtOH; 0.04 M KH_2PO_4 and 0.02 M Na_2SO_4 in 30% aqueous EtOH and water.

$Fe^{II}(CN)_2(bpy)_2{}^0$, $Fe^{II}(CN)_4(bpy)^{2-}$, and $Fe^{II}(CN)_6{}^{4-}$. Typical data are illustrated in Figure 1. The resulting values of k_q are total specific rates of quenching summed over whatever quenching mechanisms are operative.

Dependence of k_q on nature of quencher, solvent, and anions as well as on pH and ionic strength was explored. Values of k_q are presented in Table II along with values of F_1, the fraction of quenching events resulting in net reduction to semimethylene blue, $MBH_2{}^{2+}\cdot$, $MBH^+\cdot$, or MB^0 depending on pH (pK_{a_1} = 1.9 and pK_{a_2} = 9.0 in aqueous solution[8,9]). The determination of F_1 values is described in the next section.

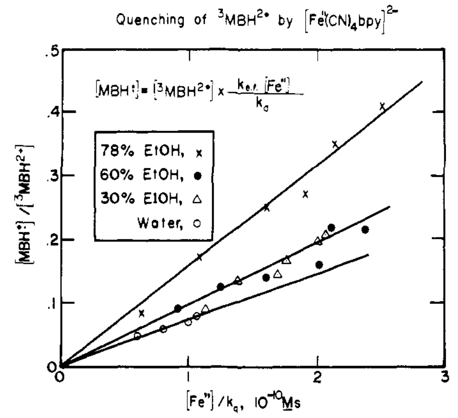

Figure 2. Determination of k_{et} in quenching of $^3MBH^{2+}$ by $Fe^{II}(CN)_4bpy^{2-}$ under the same conditions as data of Figure 1.

Quenching by $Fe^{II}(H_2O)_6{}^{2+}$ is at least two orders of magnitude slower than the diffusion-controlled rate. All the other complexes quench at or near the diffusion-controlled limit.

Rate Constants for Net Electron Transfer from Ferrous Complexes Acting as Quenchers to Triplet Methylene Blue, k_{et}, and Values of $F_1 = k_{et}/k_q$. Values of k_{et} were determined with the aid of eq 6 where $[^3Dye] = [^3MBH^{2+}]$ or $[^3MB^+]$, depending upon

$$[MBH^+\cdot]/[^3Dye] = k_{et}[Fe^{II}]/k_d \qquad (6)$$

the pH, was shown to be equal under the conditions employed

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(8) P. V. Kamat and N. N. Lichtin, *Photochem. Photobiol.*, **31**, in press.

(9) R. Bonneau, J. Faure, and J. Joussot-Dubien, *Ber. Bunsenges. Phys. Chem.*, **72**, 263-266 (1968).

Table III. Values of k_{ret} and F_2 ($=k_{ret}/k_D$)[a] in Oxidation of Semimethylene Blue by Complexes of Fe(III)

oxidant	solvent[b]	buffer	μ, M	$10^4 k_{ret}$, $M^{-1}\ s^{-1}$	F_2	$F_1 + F_2$
$Fe^{III}(CN)_6^{3-}$	5% EtOH	0.01 N H_2SO_4[c]	~0.02	4.7	0.41	0.64
	5% EtOH	0.04 M potassium hydrogen phthalate[d]	~0.08	3.9	0.43	0.79
	5% EtOH	0.04 M KH_2PO_4, 0.006 M Na_2HPO_4[e]	1.6[f]	2.8	0.70	0.97
	75% EtOH	0.01 N H_2SO_4	~0.02	0.73	0.17	0.70
$Fe^{III}(CN)_4bpy^-$	5% EtOH	0.01 N H_2SO_4[c]	~0.02	4.4	0.52	0.62
	5% EtOH	0.008 M HCl[c]	1.5[f]	2.4	0.79	0.89
	30% v/v AN	0.01 N H_2SO_4	1.2[f]	2.9	0.80	1.10
	50% v/v AN	0.01 N H_2SO_4	0.5[f]	2.3	0.52	0.99
	75% v/v AN	0.01 N H_2SO_4	0.1[f]	1.46	0.21	0.87
ferrocenium(1+)	75% EtOH	0.01 M $HClO_4$	0.01	0.40	0.12	0.80
$Fe^{III}(H_2O)_6^{3+}$	50% v/v AN	0.01 M H_2SO_4	~0.05[g]	0.00002[h]	0.00001[i]	0.84

[a] k_D taken as equal to k_q for the corresponding ferrous complex under the indicated conditions. [b] See footnote *b* of Table II for explanation of compositions. [c] pH 2.1 in aqueous solution. [d] pH 5.5 in aqueous solution. [e] pH ~6.0. [f] Made up with $MgCl_2$. [g] Made up with Na_2SO_4. [h] From ref 13. [i] Estimated by assuming $k_D = 2.0 \times 10^9$.

to the total initial concentration of methylene blue and k_d is defined in eq 5 above. Typical data for quenching by $Fe^{II}(CN)_4bpy^{2-}$ in 0.01 N aqueous and aqueous alcoholic solution are shown in Figure 2. Values of $F_1 = k_{et}/k_q$ are summarized in Table II. Values of k_{et} can be obtained by multiplying F_1 values by corresponding values of k_q given in Table II. Casual perusal of Table II reveals that F_1 varies systematically with medium in a way which is different from the dependence of k_q on medium. This systematic variation is part of the evidence for a quenching mechanism which is presented at length in the Discussion below.

Rate Constants for Electron Transfer to Ferric Complexes from Semimethylene Blue, k_{ret}, and Values of $F_2 = k_{ret}/k_{encounter}$. An important aspect of the quenching mechanism which is presented below in the Discussion is the partitioning of a caged pair consisting of a molecule of semimethylene blue and a molecule of ferric complex between, on the one hand, free ground state methylene blue and ferrous complex and, on the other, free semimethylene blue and ferric complex. Equation 7 illustrates the process. In

$$[(MBH^{+}\cdot)\cdots Fe^{III}(CN)_4bpy^{-}] \begin{cases} \xrightarrow{k_{34}} MBH^{+}\cdot + Fe^{III}(CN)_4bpy^{-} \\ \xrightarrow{\bar{k}_{30}} MB^{+} + H^{+} + Fe^{II}(CN)_4bpy^{2-} \end{cases} \qquad (7)$$

this connection, there is a requirement for knowledge of the ratio $\bar{k}_{30}[k_{34} + \bar{k}_{30}] \equiv F_2$. Second-order rate constants for oxidation of semimethylene blue by ferric complexes, k_{ret}, are equal to F_2 multiplied by k_D, the diffusion-controlled specific rate of formation of the geminate encounter pair in the latter reaction. Values of k_{ret} have been measured directly. We have chosen to estimate values of k_D by equating them to values of k_q, the specific rate of quenching of triplet methylene blue by ferrous complexes, under identical conditions. The validity of our conclusion that most values of k_q are diffusion-controlled is taken up in the Discussion below. Quenching of triplet methylene blue by the *ferric* complexes is slower than diffusion-controlled for all the cases we investigated.[10a,b]

The assumption that $k_q = k_D$ cannot be rigorously correct for all cases because of differences in ionic charge; e.g., at $1.9 < pH < 9$ in aqueous solution,[8,9] the principal species of semimethylene blue is $MBH^{+}\cdot$ while, at $pH < 7.2$ in aqueous solution,[4] the principal species of triplet dye is $^3MBH^{2+}$. If the ferrous complex bore a 1+ charge and the ferric complex bore a 2+ charge the ideal situation shown in eq 8 could result. However, the quenchers

$$^3MBH^{2+} + Fe^{II}L_x^{+} \rightarrow MBH^{+}\cdot + Fe^{III}L_x^{2+} \qquad (8)$$

which were actually used bore the charges 4–, 2–, 0, or 2+. The error inherent in our method of estimating k_D for oxidation of $MBH^{+}\cdot$ by ferric complexes decreases with increasing ionic strength. Thus, Holzwarth and Jürgensen have shown that the specific rates of a group of eight diffusion-controlled electron-transfer reactions of coordination complexes ranging in charge type from $A^{3+} + B^{4-}$ through $A^0 + B^0$ to $A^{3+} + B^{2+}$ approach each other with increasing ionic strength in aqueous solution and have a common value of $(3.2 \pm 0.1) \times 10^{-9}\ M^{-1}\ s^{-1}$ at 23 °C with $\mu \geq 1$ M.[11] With $\mu = 0.1$ M the rate constants vary from 2.0×10^9 to 6.3×10^9 over the same range of charge types while with $\mu = 0.01$ M the range of variation of rate constants is a factor of ~16.[11]

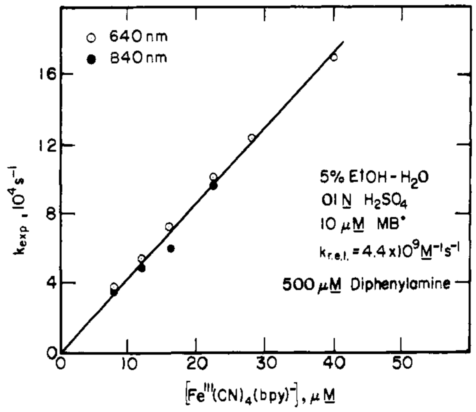

Figure 3. Determination of k_{ret} for oxidation of semimethylene blue by $Fe^{III}(CN)_4bpy^-$ in 5% EtOH.

Semimethylene blue was prepared in the presence of complexes of Fe(III) through photoreduction of methylene blue by an excess of unprotonated diphenylamine.[12] Values of k_{ret} were derived from the dependence of pseudo-first-order specific rates of conversion of semimethylene blue to methylene blue upon concentration of ferric complex as illustrated in Figure 3. Table III summarizes values of k_{ret} and $F_2 = k_{ret}/k_q$, where k_q is the specific rate of quenching of triplet methylene blue by the corresponding *ferrous* complex in the same medium, as given in Table II. Also included in Table III are values of $F_1 + F_2$ which are compared in the Discussion below with predictions of the mechanistic model.

Kinetics of Decay of Semimethylene Blue after Its Formation by Quenching Triplet Methylene Blue with Complexes of Fe^{II}. As has been pointed out,[2] the attractiveness of the $Fe^{II}(H_2O)_6^{2+}$–thionine photoredox reaction for photogalvanic conversion of light to electricity is to a large measure the result of efficient disproportionation of semithionine to give leucothionine which is sufficiently long-lived under cell conditions to carry reducing equivalents to an anode over distances of the order of 100 μm.[14,15]

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Under conditions where disproportionation is the dominant fate of the half-reduced dye it is difficult to investigate the reaction of the half-reduced dye with the product of photooxidation of quencher, ferric complexes in the present study. Conversely, a system in which back-reaction of the initial products of electron transfer which occurs during the quenching process is very rapid is not attractive for photogalvanic conversion. Such rapid back-reaction occurs with all the complexes of iron used in this study except the hexaaquo. In some cases, the kinetic order of decay of semimethylene blue was first order or mixed, as detailed below, and determination of k_{ret} from kinetics of decay of the products of quenching of triplet methylene blue by ferrous complexes was either impossible or inconvenient.

The kinetics of decay of semimethylene blue is dependent on the nature of the reductant used in the photoreduction of triplet methylene blue as well as on pH and nature of the medium. We have used the latter dependences to determine the pK_a of $MBH_2^{2+}\cdot$ in water and 50% v/v aqueous CH_3CN by using diphenylamine as the reductant.[8]

In the present study, it was observed that semimethylene blue decayed via a first-order process when it had been produced by quenching of $^3MBH^{2+}$ by $Fe^{II}(CN)_6^{4-}$ and $HFe^{II}(CN)_6^{3-}$ in aqueous solution at pH 4.4 (0.04 M KH_2PO_4) or by $Fe^{II}(CN)_4bpy^{2-}$ in neutral 30% aqueous EtOH or acidic (0.01 N H_2SO_4) 30% aqueous EtOH. Presumably, in these cases $MBH^{+}\cdot$ and, in acid solution, some $MBH_2^{2+}\cdot$, remains associated with its counterproduct, $Fe^{III}(CN)_6^{3-}$ or $Fe^{III}(CN)_4bpy^-$, during the decay process. This presumption is supported by the fact that these first-order decays of semimethylene blue resulted in complete regeneration of methylene blue.

Semimethylene blue which had been produced by reduction of $^3MBH^{2+}$ by ferrocene(0) in acidic (0.01 M $HClO_4$) 78% aqueous ethanol or by $Fe^{II}(CN)_2bpy_2^0$ in weakly acidic (0.04 M KH_2PO_4) 20% or 60% aqueous EtOH decayed via second-order processes, presumably involving both the reaction of dissociated $MBH^{+}\cdot$ with ferrocinium(1+) or $Fe^{III}(CN)_2bpy_2^+$ and disproportionation. The second-order specific rate of decay of the products of quenching by ferrocene was 5.0×10^8 M^{-1} s^{-1}, 25% larger than k_{ret} measured in the same medium (see Table III). The rate constant for disproportionation of $MBH^{+}\cdot$ in this medium was independently determined to be 1.0×10^8 M^{-1} s^{-1}. The second-order specific rate of decay of the products of quenching by $Fe^{II}(CN)_2(bpy)_2^0$ was $(2-3) \times 10^9$ M^{-1} s^{-1}, close to the diffusion-controlled limit. The second-order decays of semimethylene blue did not result in complete regeneration of methylene blue, as expected where disproportionation contributes to the decay of $MBH^{+}\cdot$.

In weakly acidic (0.04 M KH_2PO_4) 60% aqueous EtOH the decay of semimethylene blue which had been formed by reduction with $Fe^{II}(CN)_4bpy^{2-}$ followed kinetics intermediate between first and second order.

Discussion

Diffusion Control of Most Quenching Rates. It is pointed out above that all the coordination complexes of Fe(II) which were used as quenchers, except for $Fe^{II}(H_2O)_6^{2+}$, quench "at or near" the diffusion-controlled rate. We assume here that values of k_q for all the quenchers except $Fe^{II}(H_2O)_6^{2+}$ and, possibly, $Fe^{II}(bpy)_3^{2+}$, are, in fact, diffusion-limited. Whether quenching by $Fe^{II}(bpy)_3^{2+}$ is diffusion-limited can be questioned because $E°$ for the reduction of $^3MBH^{2+}$ to $MB^{+}\cdot$ by $Fe^{II}(bpy)_3^{2+}$ is only +0.27 V ($\Delta G° = -6.2$ kcal/mol), significantly below the limit, $\Delta G° < -10$ kcal/mol, for diffusion-controlled quenching of triplet states of dyes by reducing agents observed by Vogelmann et al.[16] The values of k_q for $Fe^{II}(bpy)_3^{2+}$ are, in fact, smaller than were observed for any quencher other than $Fe^{II}(H_2O)_6^{2+}$ under comparable conditions, including measurements in solutions with $\mu = 1.5$ M where the effect of charge on diffusion-controlled encounter rates is negligible.[11] $\Delta G°$ is −9.9 kcal/mol or more negative for all the other quenchers employed.

To rigorously prove that k_q is diffusion-controlled for all quenchers except $Fe^{II}(H_2O)_6^{2+}$ and $Fe^{II}(bpy)_3^{2+}$ would be difficult. The reasonableness of this assumption is, however, supported by the overall pattern of the data; e.g., for uncharged quenchers, k_q is expected to vary inversely with solvent viscosity and this is observed approximately with $Fe^{II}(CN)_2(bpy)_2^0$ and nearly exactly with ferrocene (η of 60% EtOH $\sim 1.4 \times \eta$ of 20% EtOH and η of 78% EtOH $\sim 0.67 \times \eta$ of 95% EtOH at 25 °C)[17].

Detailed Mechanism of Quenching. Background. The dependence of efficiency of net electron transfer in quenching of an organic triplet upon characteristics of quenchers including charge type and on the medium when quenching is diffusion-controlled does not appear to have been systematically investigated. The observed patterns of behavior observed in the present work provide evidence for a mechanistic model for quenching when energy transfer is not possible which is applicable to other systems in addition to the quenching of triplet methylene blue by stable coordination complexes of Fe^{II}.

Complete or partial electron transfer has been implicated in a substantial number of examples of quenching of molecules in their lowest triplet states. The following list of examples is illustrative: quenching of triplet methylene blue by ferrocene in ethanol,[18] quenching of triplet methylene blue by alkyl- and arylamines in methanol,[12] quenching of triplet thionine and lumiflavin by aromatic hydrocarbons and methoxy- or dimethylamino-substituted benzenes in methanol,[16] quenching of triplet methylene blue by aromatic amines and hydrocarbons in acetonitrile,[19] quenching of triplet states of aromatic hydrocarbons and organic carbonyl compounds by a number of inorganic ions,[20] quenching of triplet duroquinone by inorganic ions, arylamines, and methoxybenzenes in homogeneous or micellar solution in various solvents,[21] quenching of triplet thionine by organic quenchers in methanol solution,[22] quenching of the triplet states of several aromatic hydrocarbons by quinones in benzene,[23] quenching of triplet 2,6-diphenyl-1,4-benzoquinine by aromatic amines in organic solvents of low polarity,[24a] and quenching of triplet fluorenone by diazabicyclooctane in propylene carbonate.[24b] Closely related is a study of the quenching of charge-transfer to ligand excited states of polypyridine and phenanthroline complexes of Ru^{II} by Cu^{II} in aqueous solutions.[25] Several of these papers examine dependence of the efficiency of net electron transfer in the quenching event upon various factors.[17,18,22,24b,25]

Hoselton, Lin, Schwarz, and Sutin analyzed the quantum yields for net electron transfer in the quenching of charge-transfer-to-ligand excited states of $Ru^{II}L_3^{2+}$ complexes by Cu^{II} in terms of electron-transfer rates within primary cages and rates of thermal back-reaction.[25] These quenching processes are slower than diffusion-controlled and take place with reactants for which energy transfer is energetically allowed. Nevertheless, the mechanistic model which Hoselton et al. conclude is best supported by their data is similar in its main features to the model which we believe accounts well for the very different quenching systems which are reported here. Of particular importance is control of net electron transfer in the quenching process by competition between *disso-*

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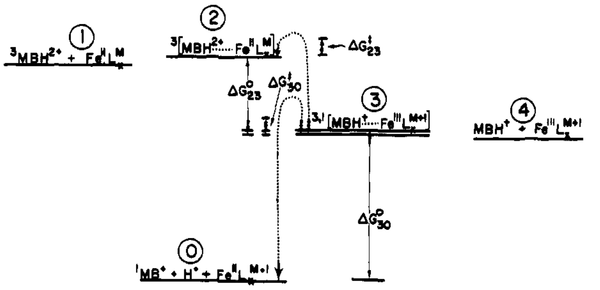

Figure 4. Schematic representation of relative energies of reactants, intermediates, and products in the quenching of triplet methylene blue by complexes of Fe(II) and in the oxidation of semimethylene blue by complexes of Fe(III).

ciation of the components of the caged encounter pair produced by electron transfer between excited molecule and quencher and thermodynamically favored *reverse electron transfer* in the encounter pair prior to dissociation.

The Model. Equations 9–12 represent the steps in the quenching

$$\overset{\textcircled{1}}{{}^3\mathrm{MBH}^{2+} + \mathrm{Fe^{II}L}_x{}^m} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \overset{\textcircled{2}}{{}^3[\mathrm{MBH}^{2+}\cdots\mathrm{Fe^{II}L}_x{}^m]} \qquad (9)$$

$$\overset{\textcircled{2}}{{}^3[\mathrm{MBH}^{2+}\cdots\mathrm{Fe^{II}L}_x{}^m]} \underset{\bar{k}_{32}}{\overset{\bar{k}_{23}}{\rightleftarrows}} \overset{\textcircled{3}}{{}^{3,1}[(\mathrm{MBH}^{+}\cdot)\cdots\mathrm{Fe^{III}L}_x{}^{m+1}]} \qquad (10)$$

$$\overset{\textcircled{3}}{{}^{3,1}[(\mathrm{MBH}^{+}\cdot)\cdots\mathrm{Fe^{III}L}_x{}^{m+1}]} \xrightarrow{\bar{k}_{30}} \overset{\textcircled{0}}{{}^1\mathrm{MB}^+ + \mathrm{H}^+ + \mathrm{Fe^{II}L}_x{}^m} \qquad (11)$$

$$\underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} \overset{\textcircled{4}}{\mathrm{MBH}^{+}\cdot + \mathrm{Fe^{III}L}_x{}^{m+1}} \qquad (12)$$

of triplet methylene blue (arbitrarily shown in its monoprotonated state) by the generalized ferrous complex $\mathrm{Fe^{II}L}_x{}^m$, where m may be positive or negative and caged pairs are designated by brackets. The rate constant of a process involving electron transfer is designated by $\bar{k}_{ij}$. The multiplicity of the caged pair $[(\mathrm{MBH}^{+}\cdot)\cdots\mathrm{Fe^{III}L}_x{}^{m+1}]$ is designated as 3,1 to indicate that changes between triplet and singlet states of this species are rapid compared to its lifetime and/or during the process 2 → 3 and/or 3 → 0. The evidence for this conclusion is presented below. The energetics of reactions 9–12 is presented schematically in Figure 4.

Evidence for Rapid Intersystem Crossing in the Geminate Pair $^{3,1}[(\mathrm{MBH}^{+}\cdot)\cdots\mathrm{Fe^{III}L}_x{}^{m+1}]$. The values of F_1 assembled in Table II vary from 0.00 to 0.86 with most values less than 0.5. If intersystem crossing were slow in the caged pair $[(\mathrm{MBH}^{+}\cdot)\cdots\mathrm{Fe^{III}L}_x{}^{m+1}]$, species 3, compared to the lifetime of the encounter and during the process 2 → 3 and 3 → 0, the caged pair, when generated by quenching of $^3\mathrm{MBH}^+$, could only decay by dissociation to free $\mathrm{MBH}^{+}\cdot$ and $\mathrm{Fe^{III}L}_x{}^{m+1}$, giving $F_1 = 1.00$ in disagreement with the observed range of values of F_1. In contrast, species 3, when generated by the reverse process, 4 → 3, would be formed in a 3:1 ratio of triplet to singlet. Only the singlet state of 3 could decay directly to $^1\mathrm{MB}^+ + \mathrm{H}^+ + \mathrm{Fe^{II}L}_x{}^m$. Thus, the maximum possible values of F_2 would be 0.25. The most reliable values of F_2 presented in Table III are those measured at high ionic strength, e.g., $\mu \geq 0.5$ M. The four values of F_2 measured with $\mu \geq 0.5$ M are greater than 0.5. Three additional values of F_2 obtained with negatively charged complexes and $\mu = 0.02$ or 0.08 M fall in the range 0.41–0.52. The error in estimating F_2 at low ionic strength for negatively charged complexes is a consequence of assuming $k_\mathrm{q} = k_\mathrm{D}$ when, in fact, $k_\mathrm{q} > k_\mathrm{D}$. The estimated values of F_2 are accordingly smaller than the correct ones. It is clear that the observed values of both F_1 and F_2 are incompatible with a rate of intersystem crossing in 3 which is slow compared to the lifetime of species 3.

Rapid intersystem crossing in the exciplex assumed as the activated complex for the electron-transfer process 2 → 3 is consistent with the presence in it of two relatively heavy atoms, S and Fe.[23,24] A different mechanism of intersystem crossing can be expected in intermediate 3. Intersystem crossing within the lifetime of initially singlet geminate pairs of organic ion radicals has been directly observed in polar solvents in the absence of heavy atoms, and the process has been accounted for in terms of hyperfine interaction of nuclear and electron spins.[26,27] The components of the geminate pairs were of charge type [1+,1−] in these cases, and their lifetimes are relevant to the majority of our cases in which species 3 was of charge type [1+,1−] or [1+,3−].

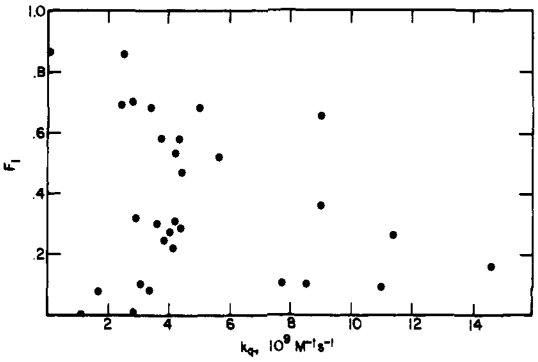

Figure 5. Plot of k_q vs. F_1 for the quenching of triplet methylene blue by complexes of Fe(II).

Theoretical Limitations on k_q. Equation 13 follows from the

$$k_\mathrm{q} = \frac{k_{12}}{1 + \dfrac{k_{21}}{\bar{k}_{23}} + \left(\dfrac{k_{21}}{\bar{k}_{23}}\right)\dfrac{\bar{k}_{32}}{\bar{k}_{30} + k_{34}}} \qquad (13)$$

mechanism summarized in eq 9–12 and Figure 4. Since k_{12} is a diffusion-limited specific rate of encounter, k_q will be diffusion-limited if $k_{21}/k_{23} \ll 1$ and $\bar{k}_{32}/(\bar{k}_{30} + k_{34}) \leq 1$. These conditions are apparently met for all the quenchers investigated in this study except $\mathrm{Fe^{II}(H_2O)_6}^{2+}$ and, possibly, $\mathrm{Fe^{II}(bpy)_3}^{2+}$, the only positively charged quenchers which were studied. Because electrostatic repulsion between Q^{2+} and $^3\mathrm{MBH}^{2+}$ (or $^3\mathrm{MB}^+$) will increase k_{21}, possibly sufficiently to lead to significant deviation from $k_{21}/\bar{k}_{23} \ll 1$, only in low ionic strength media, the fact that k_q for $\mathrm{Fe^{II}(bpy)_3}^{2+}$ in 5% EtOH with $\mu = 1.5$ M is 1.1×10^9, only one-third of k_D, may be explained in terms of a relatively small value of $\bar{k}_{23}$. Values of $\bar{k}_{23}$ can be estimated by means of the Rehm–Weller[28,29] or Marcus[30,31] equations provided that requisite values of $\Delta G_{ij}{}^\circ$, $\Delta G_{ii}{}^\ddagger$ and $\Delta G_{jj}{}^\ddagger$ are available. In the present case no information is available on the rate of self-exchange of $^3\mathrm{MBH}^{2+}$ with $\mathrm{MBH}^{+}\cdot$, so that calculation is limited to relative values of $\bar{k}_{23}$ or, alternatively, to use of an estimated value of $\Delta G_{ii}{}^\ddagger$. Reported self-exchange rate constants (in $\mathrm{M^{-1}\ s^{-1}}$) are 4 for $\mathrm{Fe(H_2O)_6}^{2+/3+}$,[32] 7×10^9 for $\mathrm{Fe(bpy)_3}^{2+/3+}$,[11] 5×10^3 for $\mathrm{Fe(CN)_6}^{4-/3-}$,[33] and 6×10^6 for ferrocene(0)/ferrocinium(1+).[34] Self-exchange constants are not available for $\mathrm{Fe(CN)_4bpy}^{2-/-}$ and $\mathrm{Fe(CN)_2(bpy)_2}^{0/+}$, but it is not unreasonable to assume that they are intermediate between the values for $\mathrm{Fe(bpy)_3}^{2+/3+}$ and $\mathrm{Fe(CN)_6}^{4-/3-}$, i.e., 7×10^9 and 5×10^3 $\mathrm{M^{-1}\ s^{-1}}$. Thus, the self-exchange constant for $\mathrm{Fe(H_2O)_6}^{2+/3+}$ is smaller by a factor of at least 10^3 than it is for the other quenchers, and $\bar{k}_{23}$ is expected to be substantially smaller for $\mathrm{Fe(H_2O)_6}^{2+/3+}$ than for the other quenchers. A reduced value of $\bar{k}_{23}$ for $\mathrm{Fe^{II}(bpy)_3}^{2+}$ can be associated with the fact that $\Delta G_{23}{}^\circ$, though negative, is small, as discussed above. Since the process 3 → 2 is endergic and 3 →

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0 is exergic in all cases studied, it is reasonable to expect $\bar{k}_{32}/\bar{k}_{30} \ll 1$ for all of them and, accordingly, $\bar{k}_{32}/(\bar{k}_{30} + \bar{k}_{34}) \ll 1$.

Correlation of Values of F_1 and F_2 with Mechanistic Model and Properties of Media. Relationship of F_1 to k_q and $\Delta G°$ for Electron Transfer. A plot of values of F_1 and k_q, for individual quenchers, Figure 5, documents the absence of any simple relationship between these quantities. Comparison of redox potentials assembled in Table I with values of F_1 presented in Table II clearly shows that, except for quenching by $Fe^{II}(H_2O)_6^{2+}$, in the same or very similar media F_1 decreases with increasing $E_{red}°$ of the oxidized quencher. F_1 for $Fe^{II}(H_2O)_6^{2+}$ appears to be anomalously high.

Relationship of F_1 and F_2 to the Mechanistic Model. F_1 is defined above as k_{et}/k_q. According to the mechanism summarized in eq 9–12 and Figure 4, k_{et} is given by eq 14 and F_1 is given by eq 15. F_2 is defined in the data section as equal to $\bar{k}_{30}/(\bar{k}_{30} + k_{34})$. This relationship is in fact an approximation which is accurate for the case where $\bar{k}_{32}$ is small. For the more general case, $F_2 = \bar{k}_{30}/(\bar{k}_{32} + \bar{k}_{30} + k_{34})$. For all cases to which the model of eq 9–12 and Figure 4 is applicable, eq 16 holds. For those cases where $\bar{k}_{32}$ is negligible, eq 17 maintains. This approximation is applicable to all the quenchers reported here with the possible exception of $Fe^{II}(bpy)_3^{2+}$.

$$k_{et} = k_q k_{34}/(\bar{k}_{32} + \bar{k}_{30} + k_{34}) \quad (14)$$

$$F_1 = k_{et}/k_q = k_{34}/(\bar{k}_{32} + \bar{k}_{30} + k_{34}) \simeq k_{34}/(\bar{k}_{30} + k_{34}) \quad (15)$$

$$F_1 + F_2 = \frac{k_{34} + \bar{k}_{30}}{\bar{k}_{32} + k_{34} + \bar{k}_{30}} \quad (16)$$

$$F_1 + F_2 = 1 \quad (17)$$

The data of Table III are in reasonable agreement with eq 17. The four cases measured with $\mu \geq 0.5$ M, so that the error in F_2 was small, have an average value of $F_1 + F_2$ equal to 0.99 ± 0.06 (mean deviation). The six cases measured with $\mu = 0.02$–0.1 M for negatively charged or uncharged quenchers give an average value of 0.74 ± 0.08. As pointed out above, F_2 is somewhat underestimated in these cases because k_q is expected to be somewhat larger than the encounter rate for reactants in the process 4 → 3. Since F_2 is negligible when $Fe^{II}(H_2O)_6^{2+}$ is the quencher, this source of error cannot account for the small but probably significant difference between the measured value of $F_1 + F_2$, i.e., 0.84, and unity.

The agreement of the data with eq 17, $F_1 + F_2 = 1$, clearly indicates that all quenching encounters involving quenchers which give this result produce a geminate pair, $[(MBH^{+}\cdot)\cdots Fe^{III}L_x^{m+1}]$, made up of semimethylene blue and the ferric complex which can dissociate before or after undergoing reverse electron transfer. This suggests that the extent of net electron transfer with such quenchers should depend upon the reduction potential of the oxidized quencher and upon the solvent.

As has been pointed out above, with the exception of the data for $Fe^{II}(H_2O)_6^{2+}$, values of F_1 measured in the same or very similar media decrease with increasing $E_{red}°$ of the oxidized quencher. The value of F_1 for $Fe^{II}(H_2O)_6^{2+}$ is much higher than would be expected from comparison with other quenchers. This apparent anomaly is consistent with the uniquely low self-exchange rate for the $Fe^{III}(H_2O)_6^{3+}/Fe^{II}(H_2O)_6^{2+}$ couple[32] which is referred to above in our discussion of k_q values. Thus, $\bar{k}_{30}$ can be expected to be "abnormally" small for $Fe^{II}(H_2O)_6^{2+}$ while k_{34} should be unaffected by this factor.

The high sensitivity of F_1 and F_2 to solvent is apparent in the data of Tables II and III and is analyzed in the following section.

Correlation of ln $[(1/F_1) - 1]$ with Kosower's Z. The data show that, on the whole, for a given quencher in a given solvent, F_1 varies little with change in ionic strength or nature of anions or pH so long as the protonated state of the triplet dye and the quencher are constant. In the two cases observed, F_1 for quenching of $^3MB^+$ by $Fe^{II}(CN)_4bpy^{2-}$ is smaller than it is for quenching of $^3MBH^{2+}$: 0.00 in water and 0.07 in 30% EtOH for quenching of $^3MB^+$ vs., respectively, 0.09 and 0.23 for quenching of $^3MBH^{2+}$. The smaller values of F_1 may be related to the fact that $E_{red}°$ is lower for the $MB^+/MB\cdot$ couple than for the $MBH^{2+}/MBH^{+}\cdot$ couple, −0.23 vs. + 0.31 V, respectively (see Table I). At pH 8.2, where the reaction of $^3MB^+$ was observed, protonation of the MB· component of species 3, generated as $^{3,1}[(MB\cdot)\cdots Fe^{III}L_x^{m+1}]$, is very slow compared to $\bar{k}_{30}$ and k_{34}. The higher oxidation potential of MB· then leads to enhancement of $\bar{k}_{30}$ relative to k_{34}.

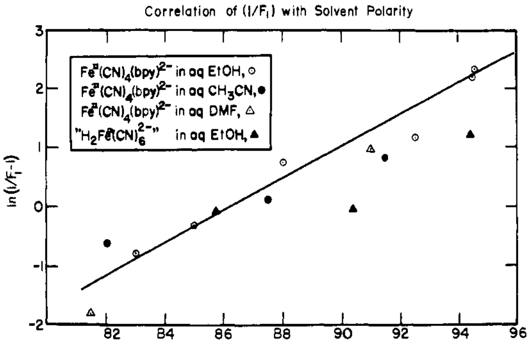

Figure 6. Correlation of ln $[(1/F_1) - 1]$ for the quenching of $^3MBH^{2+}$ by complexes of Fe(II) in various solvents with Kosower's solvent polarity parameter, Z. Line based only on data for $Fe^{II}(CN)_4bpy^{2-}$ in aqueous EtOH.

For some, but not all, of the quenchers the much more abundant data for quenching of $^3MBH^{2+}$ shows a strong dependence of F_1 on the nature of the solvent. Analysis of this dependence must make proper allowance for possible variation of the state of protonation of a given quencher. This variation is especially important in the case of relatively basic $Fe^{II}(CN)_6^{4-}$. The pK_a values of its fully protonated conjugate acid in aqueous solution at 25 °C are,[35] respectively, p$K_1 < 1$, p$K_2 < 1$, p$K_3 = 2.22$, and p$K_4 = 4.17$. These values can be expected to be solvent dependent and also to vary with ionic strength. Nevertheless, values of F_1 for this quencher (acting on $^3MBH^{2+}$) tend to increase with increasing relative proportion of ethanol in aqueous ethanolic solvents. The situation is simpler with $Fe^{II}(CN)_4bpy^{2-}$ for which the pK_a values of the fully protonated conjugate acid in aqueous solution at 20 °C with $\mu = 0.89$ M are p$K_1 \approx 0.3$ and p$K_2 \approx 1.7$.[36] In the present work, the spectrum of this quencher was observed to be the same in 5% aqueous EtOH containing 0.01 N H_2SO_4, $\mu \approx 0.02$ M, or 0.008 M HCl, $\mu = 1.5$ M (added $MgCl_2$). The estimated value of pK_2 under the latter conditions is ~1.1. It is assumed that the fully deprotonated anion was the principal form of $Fe^{II}(CN)_4bpy^{2-}$ in all the work reported here. It is ap-

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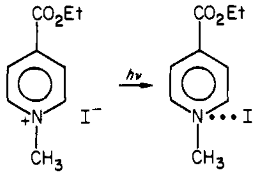
parent from Table II that F_1 for quenching of $^3\mathrm{MBH}^{2+}$ by this species increases with increasing proportion of the organic component of aqueous ethanol, DMF, or acetonitrile. The data of Table III show that, as required by eq 17, F_2 for $\mathrm{Fe^{III}(CN)_6}^{3-}$ and $\mathrm{Fe^{III}(CN)_4bpy^-}$ decreases with increasing proportion of organic cosolutes. In contrast, F_1 for quenching of $^3\mathrm{MBH}^{2+}$ by the uncharged quenchers, ferrocene(0) and $\mathrm{Fe^{II}(CN)_2(bpy)_2}^0$ (which do not participate in protonic equilibria in the pH range of these measurements), does not vary with the proportion of EtOH in aqueous ethanol although Kikuchi et al. report a value of F_1 of 0.09 for the quenching of triplet methylene blue by ferrocene in unbuffered EtOH.[18]

It is apparent from eq 15 that $(1/F_1) - 1 = (\bar{k}_{30} + \bar{k}_{32})/k_{34}$, or, by taking $\bar{k}_{32}$ as negligible, $(1/F_1) - 1 = \bar{k}_{30}/k_{34}$. From this relationship, $\ln[(1/F_1) - 1] = (\Delta G_{34}{}^{\ddagger} - \Delta G_{30}{}^{\ddagger})/RT$. Figure 6 shows that for the quencher $\mathrm{Fe^{II}(CN)_4bpy^{2-}}$ in three sets of solvents $\ln[(1/F_1) - 1]$ varies in a similar fashion with Kosower's solvent polarity parameter Z. This parameter is defined as the Franck–Condon energy in kcal/mol of the charge-transfer transition:



It can be readily shown that $\Delta G_{34}{}^{\ddagger} - \Delta G_{30}{}^{\ddagger} = G_{\mathrm{X3\to4}}{}^{\circ} - G_{\mathrm{X3\to0}}{}^{\circ}$, where $G_{\mathrm{X3\to4}}{}^{\circ}$ and $G_{\mathrm{X3\to0}}{}^{\circ}$ are the standard free energies of the activated complexes for reactions 3 → 4 and 3 → 0, respectively. From the positive slopes in Figure 6 it is apparent that increased stabilization of the polar ground state of *N*-methylpyridinium-4-carbethoxy iodide by solvent (increase in *Z*) correlates with increased stabilization of the activated complex for the 3 → 0 process relative to that for the 3 → 4 process. It can therefore be concluded that X3 → 0 is more polar than X3 → 4. Presumably reverse electron transfer has proceeded far enough at the transition state for the 3 → 0 process that X3 → 0 can be approximated as $[\mathrm{Fe^{II}(CN)_4bpy^{2-}\cdots MBH^{2+}}]$ or $[\mathrm{Fe^{II}(CN)_4bpy^{2-}\cdots{}^1MB^+\cdots H^+}]$. The transition state for the 3 → 4 process occurs at some point where solvation of the $\mathrm{Fe^{III}(CN)_4bpy^-}$ and $\mathrm{MBH^{+\cdot}}$ ions is intermediate between that characteristic of the geminate pair and the free ions in bulk solution. The difference between solvation of the two activated complexes parallels the difference between solvation of ground and excited states of Kosower's diagnostic compound but is more subtle. Values of $\ln[(1/F_1) - 1]$ and Z in aqueous ethanol and aqueous $\mathrm{CH_3CN}$ indeed correlate linearly with $RT \times \text{slope} \approx 0.16$. The two points measured in aqueous DMF suggest a sensitivity which is ~50% greater but still only about a fourth of the sensitivity to solvent polarity of the excitation energy of Kosower's compound.

The observed negligible dependence on solvent of F_1 for quenching of $^3\mathrm{MBH}^{2+}$ by the two uncharged quenchers, ferrocene(0) and $\mathrm{Fe^{II}(CN)_2(bpy)_2}^0$, is consistent with the analysis of solvent effect on quenching by $\mathrm{Fe^{II}(CN)_4bpy^{2-}}$. Charge distributions in X3 → 0 and X3 → 4 involving the uncharged quenchers can be represented by $[\mathrm{Fe^{II}L_x{}^0\cdots{}^1MBH^{2+}}]$ or $[\mathrm{Fe^{II}L_x{}^0\cdots{}^1MB^+\cdots H^+}]$ and respectively $\mathrm{Fe^{III}L_x{}^{1+}\cdots MBH^{1+}}$. Any difference in energy of solvation of these species must be very small. The small value of F_1, 0.09, reported by Kikuchi et al. for the quenching of triplet methylene blue by ferrocene in unbuffered EtOH[18] is presumably due to the preponderance of $^3\mathrm{MB}^+$ over $^3\mathrm{MBH}^{2+}$ in this medium.

With hexacyanoferrous as quencher of $^3\mathrm{MBH}^{2+}$ in 0.01 N $\mathrm{H_2SO_4}$ solutions in aqueous ethanol, $\ln[(1/F_1) - 1]$ does not appear to vary linearly with Z but does increase with increasing Z. Analysis of the data is complicated by the probability that the state of protonation of the quencher varies significantly with change of solvent composition, particularly since $\mathrm{p}K_2$ is 2.22 in water.[35] However, explanation of the solvent dependence of F_1 for this quencher in terms of differences in the solvation energies of X3 → 0 and X3 → 4 is still appropriate.

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