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MASTER

ELECTRON TRANSFER REACTIONS OF EXCITED DYES WITH METAL COMPLEXES

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DISCLAIMER

ABSTRACT

An apparatus for laser-flash photolysis-kinetic spectrophotometry was completed and put into service. With this apparatus, a previously unreported intense absorption band of $^3MBH^{2+}$, $\lambda_{max} \sim 700nm$, $\varepsilon_{max} \sim 2 \times 10^4$ $\underline{M}^{-1}$ cm^{-1}, was characterized in several media and the pK_A of $^3MBH^{2+}$ was measured by two independent methods to be 7.17±.1 in water solution.

Measurements using conventional flash photolysis have established that semimethylene blue, $MBH^{+}\cdot$, formed by quenching $^3MBH^{2+}$ with $Fe^{II}(H_2O)_6^{2+}$, decays in a number of media entirely by disproportionation and at a diffusion-controlled rate. Rates of decay of the photostationary state of solutions of MB^+ and $Fe^{II}(H_2O)_6^{2+}$ in a number of acidic media have been measured by a crossed-beam technique and the data have been analyzed to yield specific rates of oxidation of leucomethylene blue (MBH_3^{2+}) by MB^+ (synproportionation) and by Fe(III). Combination of rate constants for synproportionation and disproportionation gives equilibrium constants for disproportionation . Laser flash-photolytic measurements have confirmed that quenching of $MB^+(S_1)$ by $Fe(H_2O)_6^{2+}$ can result in electron transfer to give $MBH^{+}\cdot$.

Profound differences between processes initiated by quenching triplet methylene blue with $Fe(H_2O)_6^{2+}$ and with stable coordination complexes of Fe(II) have been established using our new laser-flash photolysis apparatus. Quenchers have included $[Fe^{II}(CN)_6]^{4-}$, $[Fe^{II}(CN)_4(bpy)_2]^{2-}$, $[Fe^{II}(CN)_2(bpy)]^0$ and $[Fe^{II}(bpy)_3]^{2+}$. Measurements have been performed in aqueous and aqueous-alcoholic solutions at pH 2, 4.4 and 8.2. In every case, quenching of $^3MBH^{2+}$ or $^3MB^+$ by a stable complex of Fe(II) proceeds at a diffusion-controlled rate, 10^2 to 10^3 times the rate at which $Fe(H_2O)_6^{2+}$ quenches $^3MBH^{2+}$. In every case, net electron transfer accounts for less than one third of total quenching by complexed Fe(II) and in some cases no net chemical change is detectable. In contrast, quenching by $Fe(H_2O)_6^{2+}$ goes essentially entirely with net electron transfer. We conclude that quenching of triplet methylene blue by the complexes of Fe(II) proceeds <u>via</u> electron transfer which is reversible in the encounter complex. The $MBH^{+}\cdot$ which results from net electron transfer from complexes of Fe(II) decays essentially entirely to MB^+ <u>via</u> oxidation by complexed Fe(III); no disproportionation has been observed. Kinetic order of this oxidative decay depends on the charge type of the oxidant.

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I. COMPLETION OF AN APPARATUS FOR LASER-FLASH PHOTOLYSIS

(Work by T. L. Osif)

An apparatus for laser-flash photolysis-kinetic spectrophotometry was assembled and put into service. A Holobeam Series 630 Laser System with a Q-switched ruby laser capable of providing up to 3.6 joules per flash at 694.3 nm with a nominal pulse width of 19 nsec was used. Measured values of the flash width at half-height were ∿ 28 nsec at 1.8J and ∿ 50 nsec at 1.2J. The cross-section of the laser beam was expanded by two cylindrical lenses to illuminate all of the 2.2 cm-long cell. Variations in the intensity of the incident laser pulses were monitored by reflecting a sample of the beam with a microscopy slide onto a Hewlett-Packard hp 2 4203 808 PIN photodiode and measuring the integrated photocurrent using sample and hold electronics similar to those described by Davies and Hodgkinson (1972). This monitoring system was calibrated against a Quantronix 504 Energy-Power Meter.

Samples were monitored optically by a probe-beam oriented perpendicular to the laser beam. The probe-beam was provided by a 100W, 12V Oriel quartz halogen lamp with a 2.3 x 4.2 mm filament in series with a power-dropping resistor and an NJE Corp. model RSE 18 regulated constant-voltage DC power supply. The lamp was operated at 10V and, to increase the light intensity, could be pulsed to 16V by shorting the resistor (Claesson, Finnström and Hunt, 1975). A series of fused-silica lenses was used to collimate the probe-beam, focus it through the cell, recollimate it and focus it on the entrance slit of an Oriel 7240 grating monochromator. One or more cut-off filters were placed between the sample cell and the monochromator to minimize 694.3 nm light and/or between the monitoring lamp and the cell to minimize photolysis. A rotating-sector shutter placed in the probe-beam minimized illumination of the sample. Three micro-switches activated by cams attached to the shutter shaft were used. One assured that the shutter never stopped in a position which would keep the lamp operating at 16V. Another controlled the timing and width of the probe lamp pulse. The third provided a timing signal, when the probe lamp reached maximum intensity, which initiated the time sequence of firing the laser flash lamp, starting the oscilloscope sweep and firing the Pockels cell Q-switch.

Intensity of the monitoring light was measured by a Hamamatsu R955 photomultiplier tube and a Tektronix 466 storage oscilloscope. In some cases, a fast preamplifier incorporationg an Analog Devices 50J FET amplifier was used. Photographs of oscilloscope traces were enlarged by projecting them onto coordinate paper and tracing the image.

II. RESEARCH COMPLETED DURING THE REPORT PERIOD: A PREVIOUSLY UNREPORTED INTENSE ABSORPTION BAND AND THE pK_A OF PROTONATED TRIPLET METHYLENE BLUE (Work by T. Ohno and T. L. Osif)

The first project completed with our new apparatus involved characterization of a previously unreported intense absorption band of protonated triplet methylene blue, $^3MBH^{2+}$, and a careful redetermination of the pK_A of $^3MBH^{2+}$ in aqueous solution. The newly-discovered T-T band absorbs in the same wavelength region as the intense S-S band of the dye ($\lambda_{max} \sim 665$ nm). Because of the high efficiency of intersystem crossing of $MB^+(S_1)$ and the relatively long lifetime of its T_1 state, 4.5 μsec for $^3MBH^{2+}$ and $\sim$ 100 μsec for $^3MB^+$, two-photon excitation of the dye to an upper triplet state must be a common occurence under intense illumination in the wavelength region of its λ_{max}.

The abstract of the paper describing these results follows and a single copy of the complete text of the paper, COO-2889-6, is transmitted along with this report.

ABSTRACT OF COO-2889-6

Excitation by a Q-switched giant ruby laser (1.2 joule output at 694 nm, ∿ 50 nsec flash) of 2-10 μM solutions of methylene blue in water, 30% ethanol in water or 50 v/v% water - CH_3CN at pH values in the range 2.0 - 9.3 converted the dye essentially completely to its T_1 state. The absorption spectrum of T_1 dye was measured in different media at pH 2.0 and 8.2 by kinetic spectrophotometry. Previously reported T-T absorption in the violet in acidic and alkaline solutions and in the near infrared in alkaline solution was confirmed. Values found for these absorptions in the present work with 30% ethanol in water as solvent are λ_{max} ∿ 370 nm, ε_{max} ∿ 13,200 $\underline{M}^{-1}$ cm^{-1} at pH 2 and λ_{max} ∿ 420 nm, ε_{max} ∿ 9,000 $\underline{M}^{-1}$ cm^{-1}, λ_{max} ∿ 840 nm, ε_{max} ∿ 20,000 $\underline{M}^{-1}$ cm^{-1} at pH 8.2. Long-wavelength T-T absorption in acidic solution is reported here for the first time: λ_{max} ∿ 680 nm, ε_{max} ∿ 19,000 $\underline{M}^{-1}$ cm^{-1} in 30% ethanol in water at pH 2. Observation of a pH-independent isobestic point ∿ 720 nm confirms that the long-wavelength absorptions are due to different protonated states of the same species, $MB^+(T_1)$ and $MBH^{2+}(T_1)$. The pK_A of $MBH^{2+}(T_1)$ in water was determined from the dependence on pH of absorption at 700 and 825 nm to be $7.1_4 \pm .1$ and from the kinetics of decay of triplet absorption to be 7.2. The specific rate of protonation of $MB^+(T_1)$ by $H_2PO_4^-$ in water at pH 4.4 was found to be $4.5 \pm .4 \times 10^8$ $\underline{M}^{-1}$ sec^{-1}.

III. OTHER PUBLICATIONS SUBMITTED WITH THIS REPORT

Transmitted herewith are 6 reprints of COO-2889-3, T. L. Osif, N. N. Lichtin and M. Z. Hoffman, "Kinetics of Dark-Back-Reactions of Products of the Photoreduction of Triplet Thionine by Fe(II): Evidence for Association of Leucothionine and Semithionine with Fe(III)", J. Phys. Chem., 82, 1778-1784 (1978). Also transmitted is a single copy of COO-2889-5, M. Z. Hoffman and N. N. Lichtin, "Photochemical Determinants of the Efficiency of Photogalvanic Conversion of Solar Energy", in "The Chemical Conversion and Storage of Solar Energy", R. B. King, C. Kutal, and R. R. Hautala, eds., The Humana Press, N.J., 1979, in press.

IV. RESEARCH ON PHOTOINITIATED PROCESSES IN THE HEXAAQUO IRON-METHYLENE BLUE SYSTEM DURING THE REPORT PERIOD

Three studies are near completion and will probably be written up for publication by the end of the current contract period.

1. Dependence of the Kinetics of Disproportionation of Semimethylene Blue upon Medium (Work by S. Ray)

Conventional flash photolysis-kinetic spectrophotometry (flash-width at half-height ∿ 45 μsec) was used to study yields of semimethylene blue, $MBH^{\dot{+}}$, produced by the reaction of $^3MBH^{2+}$ with $Fe(H_2O)_6^{2+}$ in acidic solution, the fraction of $MBH^{\dot{+}}$ decaying by disproportionation:

$$2MBH^{\dot{+}} + H^+ \xrightarrow{k_6} MB^+ + MBH_3^{2+},$$

and the dependence of k_6 on solvent, nature of anions, pH and salt concentration. Techniques were similar to those which we employed in our earlier study of the disproportionation of semithionine.[1] The decay of $MBH^{\dot{+}}$ was

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[1] P. D. Wildes, N. N. Lichtin and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 2288 (1975).

found to be second order and to proceed essentially quantitatively *via* disproportionation under the conditions employed. This result is characteristic of the use of $Fe(H_2O)_6^{2+}$ to quench $^3MBH^+$. Very different results are obtained when CN^- and/or α,α'-bipyridyl is coordinated with Fe(II), as reported in section V below. Stoichiometry and kinetics were monitored at 665 nm, λ_{max} of MB^+. Data summarized in Table 1 establish that the rate of disproportionation of semimethylene blue does not display the great sensitivity to solvent (linear correlation with Kosower's Z function) which is shown by the disproportionation of semithionine at pH 2 with $CF_3SO_3^-$ as anion and μ = .1 M. The disproportionation of $MBH^{+\cdot}$ is diffusion controlled or nearly so under all the conditions we have investigated.

TABLE 1

Specific Rates of Disproportionation of
Semimethylene Blue in Various Media
$[MB^+Cl^-]_0$ = 2 μM; $[Fe(II)]_0^a$ = .01 M

Solvent	[Acid] M	[Added Salt] M	$2k_6$ $10^9 M^{-1} sec^{-1}$
Water	.01 H_2SO_4	None	1.9±.3
Water	.001 H_2SO_4	None	2.1±.2
Water	.01 H_2SO_4	.115 K_2SO_4	4.6±.3
Water	.001 H_2SO_4	.12 $KHSO_4$	1.07±.01
Water	.01 HCl	.36 KCl	3.1±.1
50 v/v% aq. CH_3CN	.01 H_2SO_4	None	1.02±.11
50 v/v% aq. CH_3CN	.01 HCl	.36 KCl	3.5±.3
50 v/v% aq. EtOH	.01 H_2SO_4	None	0.51±.02
50 v/v% aq. EtOH	.01 HCl	.36 KCl	1.7±.3

a. Impurity level of Fe(III) in Fe(II) ∿ 0.4% in sulfate solutions, ≤0.1% in chloride solutions. Anion same as that of acid.

Further work is in progress to separate salt effects on the disproportionatin of $MBH^{+\cdot}$ from the dependence of its rate on pH. Synthesis of Azure A (N,N-dimethyl thionine), thionine-4-sulfonic acid and thionine-4,8-disulfonic acid is in progress with the objective of comparing the disproportionation reactions of $TH_2^{+\cdot}$, $MBH^{+\cdot}$ and the half-reduced forms of these dyes under identical conditions.

2. Dependence of the Rates of Synproportionation of Methylene Blue with Leucomethylene Blue and of Oxidation of Leucomethylene Blue by Ferric upon Medium (Work by D. W. Hay)

The crossed beam apparatus which we have described previously[2] was thermostatted and measurements at 25° of the kinetics of decay of the photostationary state were performed and analyzed by methods which we have reported.[3] These measurements yield values of k_{-6}, the synproportionation constant, and of k_{10}, the gross second order rate constant for oxidation of leucothionine by ferric ion:

$$MBH_3^{2+} + MB^{+} \xrightarrow{k_{-6}} 2MBH^{+\cdot} + H^{+}$$

$$MBH_3^{2+} + Fe(III) \xrightarrow{k_{10}} MBH^{+\cdot} + 2H^{+} + Fe(II).$$

Data are summarized in Table 2. We have found that the oxidation of leucotionine by ferric proceeds via a 1:1 complex,[4] but the method used in the

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[2] P. D. Wildes, K. T. Brown, M. Z. Hoffman, D. E. Hall and N. N. Lichtin, "The Dependence of Current Output of the TI-TL SnO_2/Pt Iron-Thionine Photogalvanic Cell on Photostationary State Composition", "Solar Energy" 19, 579-582 (1977).

[3] P. D. Wildes and N. N. Lichtin, "Indirect Measurement of the Thionine-Leucothionine Synproportionation Rate Constant by a Photochemical Perturbation Technique", J. Phys. Chem., 82, 981-984 (1978).

[4] T. L. Osif, N. N. Lichtin and M. Z. Hoffman, "Kinetics of Dark Back-Reactions of Products of the Photoreduction of Triplet Thionine by Fe(II):

Evidence for Association of Leucothionine and Semithionine with Fe(III)", J. Phys. Chem., 82, 1778-1784 (1978).

TABLE 2

Specific Rates[a] of Synproportionation of Leucomethylene Blue with Methylene Blue and of Oxidation of Leucomethylene Blue by Ferric[b] in Various Media at 25°C

Solvent	[Acid] M	[Added Salt] M	μ M	k_{-6} $10^3 M^{-1} sec^{-1}$	k_{10} $M^{-1} sec^{-1}$
Water	.010 H_2SO_4	None	.05	4.1-8.6	20-40
50 v/v% Aq.CH_3CN	.010 H_2SO_4	None	.05	1.1-2.2	800-1600
50 v/v% Aq.CH_3CN	.010 H_2SO_4	.0793 $NaHSO_4$ .0896 Na_2SO_4	.40	.45-.90	180-360
50 v/v% Aq.CH_3CN	.010 HCl	None	.04	1.8-3.6	4000-8000
50 v/v% Aq.CH_3CN	.010 HCl	.360 KCl	.40	12.2-24.4	27,600-55,200
50 v/v% Aq.CH_3CN	.0010 HCl	.369 KCl	.40	18.6-37.2	1,200-2,400
50 v/v% Aq.CH_3CN	.100 HCl	.270 KCl	.40	4.0-8.0	3,300-6,600
50 v/v% Aq. EtOH	.010 H_2SO_4	None	.05	4.9-9.8	2100-4200

a. Twofold uncertainties in tabulated rate constants are a consequence of the method of analysis of raw data.[3] In the case of leucothionine in water with .01M sulfuric acid, measurements by a totally independent method[4] agree well with the lower value of k_{10}.

b. $[Fe(II)]_0$ = .01M in all cases; $FeSO_4$ with H_2SO_4 and $FeCl_2$ with HCl. $[MB^+]_0$ was varied systematically in the range 1-10 μM.

work reported here cannot distinguish between electron transfer in an encounter complex and in a reversibly-formed, relatively long-lived, complex.

The data of Table 2 show that k_{-6} and, particularly, k_{10} are more sensitive to medium than is $2k_6$. Both reactions, unlike $2k_6$, are many orders of magnitude slower than diffusion controlled. The solvent dependence of k_{10} in sulfate media may, possibly, reflect a dependence on Z associated with electron transfer concerted with dissociation of protons, so that charge is dispersed:

$$MBH_3^{2+} + Fe(H_2O)_6^{3+} \longrightarrow MBH^{\overset{+}{\cdot}} + Fe(H_2O)_6^{2+} + 2H^+,$$

since pK_A of $MBH^{+\cdot}$ appears to be between 8 and 10.[5] Possibly, the inverse dependence of k_{10} on salt concentration in sulfate media is another consequence of charge dispersal in the transition state. The dependence of k_{10} on pH and salt concentration in solutions of chloride in 50 v/v% aq. CH_3CN appears to be related to inner sphere complexation of Fe(III) by chloride, as reflected in changes of the absorption spectrum of the iron salt around 340 nm with changing $[Cl^-]$. Apparently, inner-sphere association of Fe(III) with Cl^- greatly accelerates the reaction, perhaps because chloride serves as a bridging ligand. The sharp maximum in k_{10} at pH 2 with $\mu = 0.4$ suggests that at least two proton transfer processes, characterized by different pK_A values, must be involved. Increase in k_{-6} with increasing $[Cl^-]$ and ionic strength, effects opposite to those observed with sulfate, suggests a bridging role for chloride in synproportionation also. The monotonic increase of k_{-6} with pH (with $\mu = 0.4\underline{M}$) may result from increase in $[MBH_2^+]/\{[MBH_2^+] + [MBH_3^{2+}]\}$ with increasing pH.

Combination of data from Tables 1 and 2 makes possible the evaluation of $K_{eq} = k_{-6}/2k_6$, the equilibrium constant for the disproportionation-synproportionation process:

$$H^+ + 2MBH^{+\cdot} \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} MB^+ + MBH_3^{2+}$$

$$K_{eq} = k_{-6}/2k_6 = [MB^+][MBH_3^{2+}]/[MBH^{+\cdot}]^2 \text{ and } [H^+] \text{ is included in } K_{eq}.$$

Values of K_{eq} are summarized in Table 3 along with comparable values for thionine which we have reported previously.[3]

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[5] G. P. Roitman and A. K. Chibisov, Theor. Exp. Chem., $\underline{7}$. 44 (1971).

TABLE 3

Values of $K_{eq} = k_{-6}/2k_6$ for Methylene Blue and Thionine in .01M Acid around 25°C

Solvent	Acid	μ M	$10^6 x K_{eq}$ Meth. Blue	Thionine[a]
Water	H_2SO_4	.05	2.2-4.4	0.4-0.8
50 v/v% aq. CH_3CN	H_2SO_4	.05	1.1-2.2	0.9-1.8
50 v/v% aq. CH_3CN	CF_3SO_3H	.05		0.5-1.0
50 v/v% aq. CH_3CN	HCl	.40	3.5-7.0	
50 v/v% aq. EtOH	H_2SO_4	.05	9.6-19.2	

a. From reference 3.

3. Quenching of Singlet and Triplet Excited Methylene Blue by $Fe(H_2O)_6^{2+}$ in Acid Solution (Work by T. L. Osif)

We previously reported that the pseudo-first order quenching of $^3MBH^{2+}$ in 50 v/v% aq. CH_3CN in .01M HCl is less than first order in $Fe^{II}(H_2O)_6^{2+}$ at high concentrations of ferrous.[6] Careful repetition of this work at constant ionic strength and chloride concentration using our new laser flash-photolysis apparatus established that the reaction is clearly first order in ferrous. Our observation[7] that quenching of $MB^+(S_1)$ by $Fe(H_2O)_6^{2+}$ in .01M aqueous HCl appears to result in reduction of the dye to $MBH^{\dot{+}}$ was reexamined by following the kinetics of generation of absorption by the latter species at 880 nm after laser-flash excitation. It was found that in the presence of, e.g., .05M quencher, extrapolation of the pseudo-first order reaction of $^3MBH^{2+}$ to zero time indicated substantial generation of $MBH^{\dot{+}}$ by a process much faster

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[6] T. L. Osif, S. Ray, N. N. Lichtin and M. Z. Hoffman, "Reductive Quenching of Triplet and Singlet Methylene Blue by Fe^{2+}," Extended Abstracts of the 2nd Internat'l Conference on the Photochemical Conversion & Storage of Solar Energy, 8/10-12/78, Dept. of Physical Chemistry, University of Cambridge, England, ABST. 2.3, p. 17.

than the quenching of the triplet. Presumably this process is diffusion-controlled quenching of the singlet.

V. RESEARCH ON PHOTOINITIATED PROCESSES INVOLVING STABLE COORDINATION COMPLEXES OF Fe(II) AND EXCITED METHYLENE BLUE (Work by T. Ohno)

Rate constants for quenching of $^3MB^+$ and $^3MBH^{2+}$, efficiencies of electron transfer in the quenching process, and kinetics and products of decay of $MBH^{\dot{+}}$ have been examined for systems in which MB^+ was first excited by 694.3 nm, ∿ 50 nsec laser flashes (∿ 1.2J) and quenching was by coordination complexes of Fe(II) which were stable under the conditions employed. Our new laser flash-photolysis apparatus was used in this work. Coordination complexes which have been studied include $Fe^{II}(CN)_6^{4-}$, $Fe^{II}(CN)_4(bpy)^{2-}$, $Fe^{II}(CN)_2(bpy)_2^o$, and $Fe^{II}(bpy)_3^{2+}$, where bpy = α,α'-bipyridyl. The behavior of these systems differs greatly from that of $Fe(H_2O)_6^{2+}$ - methylene blue. We expect that this work will be ready for publication by the end of the present contract period or soon thereafter.

1. Some Preliminary Aspects

Solvents were identified in which dye and complexes were sufficiently soluble and stable. Negatively charged coordination complexes, e.g., $Fe^{II}(CN)_6^{4-}$ or $Fe^{II}(CN)_4(bpy)^{2-}$, perturbed the absorption spectrum of the dye in a way consistent with enhanced dimerization of the dye. Such enhancement could be a consequence of electrostatic association of positively charged ionsof MB^+ with the di- or tetranegatively charged ions of complex. Association of both $Fe^{II}(CN)_6^{4-}$and $Fe^{II}(CN)_4(bpy)^{2-}$ with MB^+ was verified by measurement of the dependence of fluorescence quenching upon concentration of complex. Analysis of Stern-Volmer data on the basis of 1:1 association of the anion with the dye gave association constants in different media which are summarized in Table 4.

TABLE 4

Equilibrium Constants[a] for 1:1 Association of MB^+ with $Fe^{II}(CN)_4(bpy)^{2-}$ in Various Media

Solvent	H_2O	H_2O-EtOH 1:1	H_2O	H_2O-EtOH 2:1	H_2O-CH_3CN 2:1	H_2O-DMA 3:2
pH	2	2	6.1	6.1	6.1	6.1
$[Na_2SO_4]$, $\underline{M}$	.04	.032	.08	.02	.02	.04
K, $\underline{M}^{-1}$	283	194	260	92	425	72

a. Calculated from Stern-Vollmer data.

2. Kinetics of Quenching of Triplet Methylene Blue and the Efficiency of Electron Transfer in the Quenching Process

Kinetics of quenching of triplet methylene blue was measured by monitoring regeneration of ground state dye through its absorbtion at 645 or 665 nm, by monitoring decay of $^3MBH^{2+}$ through its absorbtion at 710 nm and by monitoring decay of $^3MB^+$ through its absorption at 825 nm. With $Fe^{II}(H_2O)_6^{2+}$ or $Fe^{II}(CN)_6^{4-}$ as quencher, decay of $^3MBH^+$ was also monitored at 370 nm. With only one exception, the rate of decay of T-T absorption agreed with the rate of recovery of S-S absorption. In the single exception, $Fe^{II}(CN)_2(bpy)_2^0$ in acidic 20% ethanol in water, recovery of S-S absorption was ∿ 13% slower than decay of the T-T band. In all cases, pseudo-first order rate constants for decay of the triplet (or recovery of the singlet), k_d, varied linearly with concentration of quencher. Second order quenching constants, k_q, evaluated from the sloptes of plots of k_d vs [quencher], are summarized in Table 5.

TABLE 5

Rate Constants, k_q, and Electron Transfer Efficiencies, f, of the Quenching of 10 $\mu\underline{M}$ Triplet Methylene Blue[a] by Complexes of Fe(II)

Quencher	pH	Dye Species	k_q 10^9 $\underline{M}^{-1}sec^{-1}$	f
		H_2O		
$K_4[Fe^{II}(CN)_6]$	4.4[b]	$^3MBH^{2+}$	14.3	.16
$K_2[Fe^{II}(CN)_4(bpy)]$	4.4	$^3MBH^{2+}$	8.0	.09
$K_2[Fe^{II}(CN)_4(bpy)]$[c]	4.4	MBH^{2+}	11.0	.11
$K_2[Fe^{II}(CN)_4(bpy)]$	8.2[d]	$^3MB^+$	4.0	<.01
$[Fe^{II}(bpy)_3][ClO_4]_2$	4.4[b]	$^3MBH^{2+}$	.42	.00
$[Fe^{II}(H_2O)_6][SO_4]$[c]	2.0[e]	$^3MBH^{2+}$	.0055[f]	∿1[f]
		20% EtOH in H_2O		
$Fe^{II}(CN)_2(bpy)_2$	4.4[b]	$^3MBH^{2+}$	3.3[g]	.08
		30% EtOH in H_2O		
$K_2[Fe^{II}(CN)_4(bpy)]$	2.0[e]	$^3MBH^{2+}$	3.8	.24
$K_2[Fe^{II}(CN)_4(bpy)]$	4.4[b]	$^3MBH^{2+}$	4.1	.22
$K_2[Fe^{II}(CN)_4(bpy)]$	8.2[d]	$^3MB^+$	3.0	.07
$K_2[Fe^{II}(CN)_4(bpy)]$[c]	8.2[d]	$^3MB^+$	2.8	.06
		60% EtOH in H_2O		
$K_2[Fe^{II}(CN)_4(bpy)]$	4.4[b]	$^3MBH^{2+}$	4.2	.31
$Fe^{II}(CN)_2(bpy)_2$	4.4[b]	$^3MBH^{2+}$	1.7	.08

a. Concentration of triplet equal to total concentration of dye.

b. .04$\underline{M}$ KH_2PO_4 buffer.

c. 2 $\mu\underline{M}$ dye.

d. .02$\underline{M}$ $Na_2B_2O_7$ and .02$\underline{M}$ Na_2SO_4.

e. .01$\underline{N}$ H_2SO_4.

f. From ref. 7, $\mu = 0.2\underline{M}$, adjusted with Na_2SO_4.

7. P. D. Wildes, N. N. Lichtin, M. Z. Hoffman, L. Andrews and H. Linschitz, "Anion and Solvent Effects on the Rate of Reduction of Triplet Excited Thiazine Dyes by Ferrous Ions", Photochem. Photobiol., 25, 21-25 (1977).

The extent of electron transfer in the triplet-quenching process was calculated routinely from decrease in absorbance at three wavelengths in the S-S band of MB^+, 645, 665 and 685 nm, after quenching was complete but before decay of the product of quenching was significant. This method assumes that absorbance of the product, semimethylene blue, $\mathrm{MBH}^{\dot{+}}$, is negligible in this wavelength region. This assumption was supported by observing that the difference spectrum after quenching of a selected solution was complete coincided exactly with the S-S absorption spectrum of MB^+ at a concentration corresponding to a fixed fraction of the initial concentration of the dye. It was further supported by excellent agreement among the values of $\Delta[\mathrm{MB}^+]$ calculated from ΔO.D. data at the three wavelengths under a given set of conditions. Data were analyzed in terms of the equation,

$$[\mathrm{MBH}^{\dot{+}}]/[\mathrm{Triplet}] = k_q f[\mathrm{Fe(II)}]/k_d,$$

by plotting $[\mathrm{MBH}^{\dot{+}}]/[\mathrm{Triplet}]$ vs $[\mathrm{Fe(II)}]/k_d$, where $[\mathrm{Triplet}] = [\mathrm{MB}^+]_0$. In all cases, except for quenching by $\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_2(\mathrm{bpy})_2^0$ in acidic 60% EtOH in water, the resulting plots were linear with an intercept at the origin. In the latter case, a correction had to be applied for reductive quenching by the solvent. Values of f are presented in Table 5.

The data of Table 5 make clear that k_q for labile $\mathrm{Fe(H_2O)_6^{2+}}$ is much smaller, 1/2600 - 1/76, than it is for any of the four stable complexes of Fe(II) which were studied. The values of k_q for the stable complexes appear to be at or near the diffusion-controlled limit. Comparison of variation of the rate constants in water solution with the variation calculated from the Debye equation,

$$k = k_o z_a z_b e^2/\varepsilon k_b T[\exp(z_a z_b e^2/\varepsilon k_b T) - 1],$$

confirms that quenching is indeed diffusion-controlled, as shown in Table 6.

TABLE 6

Comparison of Observed Variation of k_q in H_2O Solution with Variation Calculated by Means of the Debye Equation

Reactants	Relative k_q Observed	Relative k_q Calculated
$^3MBH^{2+}$ - $[Fe^{II}(CN)_6]^{4-}$	1.00	1.00
$^3MBH^{2+}$ - $[Fe^{II}(CN)_4(bpy)]^{2-}$	.56	.53
$^3MB^{+}$ - $[Fe^{II}(CN)_4(bpy)]^{2-}$	.28	.33
$^3MBH^{2+}$ - $[Fe^{II}(bpy)_3]^{2+}$	.029	.031

Changes in k_q with solvent for the stable complexes are also consistent with diffusion-controlled processes in which k_o decreases with increasing proportion of EtOH due to increased viscosity while decreasing dielectric constant affects the dielectric work term.

The possibility that these diffusion-controlled quenching reactions involve energy transfer from triplet dye to quencher is excluded in most or all of the cases by the absence of a sufficiently low-lying triplet state of the quencher. We propose that diffusion-controlled quenching proceeds via a reversible electron-transfer process in the encounter complex similar to that proposed by Rehm and Weller.[8] The data of Table 5 show that nature of the ligands coordinated with iron, solvent, and state of protonation of the triplet dye can all influence the efficiency of electron transfer, f.

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[8] D. Rehm and A. Weller, Ber. Bunsen. Elect. Chem., 73, 834 (1969).

It is beyond the scope of this report to show at length how these effects can be related to the assumed quenching mechaism. However, it is worthwhile pointing out that the degree of net electron transfer can be correlated with relative solvation energies of reactants and products, redox potentials, and rates of self-exchange electron transfer reactions.

3. Decay of Semimethylene Blue After its Production by the Quenching of Triplet Methylene Blue with Stable Coordination Complexes of Fe(II)

Spectra of products produced by reductive quenching of triplet methylene blue resembled reported spectra of semimethylene blue, $MBH^{\dot{+}}$, but varied somewhat with the nature of the iron complex and the pH. In all cases, bands were observed with peaks around 400 and 880 nm. Presumably, association of $MBH^{\dot{+}}$ with negatively charged complex ions affects the spectrum of $MBH^{\dot{+}}$.

In no case did the decay of $MBH^{\dot{+}}$ proceed via disproportionation. Instead, reoxidation to MB^+ was either complex or accompanied (when $[Fe^{II}(CN)_4(bpy)]^{2-}$ was used in acidic 60% ethanol in water) with a very small amount of permanent bleaching. This behavior stands in contrast to the complete, diffusion-controlled disproportionation which takes place in the presence of hexaaquo iron (see section IV.1, above).

The kinetic order of decay of $MBH^{\dot{+}}$ and its rate depended on the nature of the iron complex and the composition of the medium. With $[Fe^{II}(CN)_6]^{4-}$ as quencher in acid aqueous solution, decay was first order, independent of the concentration of the ferrous complex, with $k \sim 1.7 \times 10^4$ sec^{-1}. This behavior is consistent with back reaction in an $MBH^{\dot{+}} - [Fe^{III}(CN)_6]^{3-}$ ion pair. Similar behavior was observed with $[Fe^{II}(CN)_4(bpy)]^{2-}$ as quencher in 30% EtOH in water at pH 2 and 8.2, with $k_{decay} \sim 2 \times 10^3$ sec^{-1}. At pH 8.2

under the latter conditions, unlike all other cases which were observed, the first order rate of regeneration of MB^+ was slower ($\sim 7 \times 10^2$ sec^{-1}) than the rate of decay of $MBH^{\dot{+}}$. When $Fe^{II}(CN)_2(bpy)_2^0$ was used as quencher in acidic aqueous ethanol, decay of $MBH^{\dot{+}}$ was second order with a rate constant, measured by following recovery of MB^+, which was $\sim 2.5 \times 10^9$ $\underline{M}^{-1}$ sec^{-1}. The decay of $MBH^{\dot{+}}$ formed by quenching with $Fe^{II}(CN)_4(bpy)^{2-}$ in 30, 50 or 60% aqueous ethanolic solution at pH 4.4 did not follow either clean first or second order kinetics.

VI. PREPARATION OF A REVIEW OF THE PHOTOCHEMISTRY OF METHYLENE BLUE
(Work by S. Ray)

During the report period, the first draft of a review article on the photochemistry, spectroscopy, photophysics and redox chemistry of methylene blue was completed.

VII. BIBLIOGRAPHY OF PUBLICATIONS SUPPORTED BY CONTRACT EY-76-S-02-2889

1. COO-2889-3: T. L. Osif, N.N. Lichtin and M. Z. Hoffman, "Kinetics of Dark Back-Reactions of Products of the Photoreduction of Triplet Thionine by Fe(II): Evidence for Association of Leucothionine and Semithionine with Fe(III)", J. Phys. Chem., <u>82</u>, 1778-1784 (1978). Reported in COO-2889-2 as "submitted".

2. COO-2889-4: N. N. Lichtin, P. D. Wildes, T. L. Osif and D. E. Hall, "The Sunlight Engineering Efficiency of Totally Illuminated-Thin Layer Iron-Thiazine Photogalvanic Cells: Evidence Supporting the Speculation that Surface-Induced Back Reaction is a Key Limiting Factor", Advances in Chemistry Series, R. F. Gould, Editor, American Chemical Society, Washington, D.C., No. 173, 1979, pp 296-306. Reported in COO-2889-2 as "submitted".

3. COO-2889-5: M. Z. Hoffman and N. N. Lichtin, "Photochemical Determinants of the Efficiency of Photogalvanic Conversion of Solar Energy",

in "The Chemical Conversion and Storage of Solar Energy", R. B. King, C. Kutal, and R. R. Hautala, eds., The Humana Press, N.J., 1979, in press.

4. COO-2889-6: T. Ohno, T. L. Osif and N. N. Lichtin, "A Previously Unreported Intense Absorption Band and the pK_A of Protonated Triplet Methylene Blue", Photochem. Photobiol., submitted 3/9/79

5. T. L. Osif, S. Ray, N. N. Lichtin and M. Z. HOffman, "Reductive Quenching of Triplet and Singlet Methylene Blue by Fe^{2+}," Extended Abstracts of the 2nd International Conference on the Photochemical Conversion and Storage of Solar Energy, August 10-12, 1978, Dept. of Physical Chemistry, University of Cambridge, England, ABST. 2.3, p.17.

6. N. N. Lichtin, T. L. Osif, S. Ray, and M. Z. Hoffman, "Comparison of Dynamics of Elementary Steps in the Photoredox Reactions of Fe(II) with Thionine and Its N-Methylated Derivatives," Abstracts of the 176th ACS National Meeting, September 10-15, 1978, Miami Beach, Florida, Abst. PHYS 022.

VIII. TIME AND EFFORT DEVOTED TO CONTRACT EY-76-S-02-2889 BY ITS PERSONNEL

Individual	July 1 - August 31, 1978	September 1, 1978 - June 30, 1979
Princ. Inv. N. N. Lichtin	1 man mo.	1.5 man mo.
Co-Princ. Inv. M. Z. Hoffman	1 man mo.	0.5 man mo.
Sr. Res. Assoc. T. Ohno	---	10 man mos.
Res. Assoc. T. L. Osif	2 man mos.	7 man mos.
Grad. Student S. Ray	2 man mos.	5 man mos.
Undergrad. Student D. Hay	2 man mos.	1.5 man mos.