ELECTRON TRANSFER IN THE QUENCHING OF PROTONATED TRIPLET THIONINE AND METHYLENE BLUE BY GROUND STATE THIONINE

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Summary

The quenching of the monoprotonated lowest triplet state of thionine ($^3TH_2^{2+}$) by ground state thionine (TH^+) was investigated by laser flash photolysis–kinetic spectrophotometry employing frequency-doubled (347.2 nm) flashes from a Q-switched ruby laser. The quenching of the monoprotonated lowest triplet state of methylene blue ($^3MBH^{2+}$) by TH^+ was similarly investigated using the fundamental (694.3 nm) ruby frequency. In 0.01 M acid the quenching of $^3TH_2^{2+}$ by TH^+ is accompanied by net electron transfer to give the semi-oxidized radical (TH^{2+}) and the semi-reduced radical (TH_2^+) while the quenching of $^3MBH^{2+}$ by TH^+ is accompanied by the net one-electron oxidation of $^3MBH^{2+}$ by TH^+ to give MB^{2+} and TH_2^+. Spectra of TH^{2+} and TH_2^+ in water, 50 vol.% aqueous CH_3CN and 50 vol.% aqueous C_2H_5OH in the presence of 0.01 M acid were characterized. The dependence of the specific rate k_q of quenching and the specific rate k_{et} of net electron transfer for the quenching of $^3TH_2^{2+}$ by TH^+ on the solvent composition, the nature of the anions and the salt concentration was investigated. The efficiency F_1 ($= k_{et}/k_q$) of net electron transfer in the quenching of $^3TH_2^{2+}$ by TH^+ correlates with Kosower's solvent polarity parameter Z as it does in the quenching of $^3MBH^{2+}$ by a reversible electron transfer mechanism, namely $\ln\{(1/F_1) - 1\}$ varies linearly with Z. Values of k_q and k_{et} for the quenching of $^3MBH^{2+}$ by TH^+ are similar to those for the quenching of $^3MBH^{2+}$ by ground state methylene blue (MB^+) and about one-tenth of those for the quenching of $^3TH_2^{2+}$ by TH^+ in the same media. Values of F_1 for the quenching of $^3TH_2^{2+}$ by TH^+ differ little from those for the quenching of $^3MBH^{2+}$ by MB^+ in the same media except that increased salt concentration sharply reduces F_1 in the former case and does not significantly affect it in the latter. Values of F_1 for the quenching of $^3MBH^{2+}$ by TH^+ are substantially lower than for the homogeneous cases. The mechanism of crossed and homogeneous ground state quenching and the implications of ground state quenching for the efficiency of Fe–thiazine photogalvanic cells are discussed.

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1. Introduction

In recent years, photoredox systems employing the thiazine dyes, ground state thionine (TH^+) and/or ground state methylene blue (MB^+), have been of considerable interest in the photogalvanic transduction of light into electricity [1, 2]. Despite continuing efforts to improve the performance of photogalvanic cells [3], the maximum engineering efficiency for photo-galvanic conversion of sunlight into electricity which has been reported is less than 0.1% [4]. It has been concluded that high concentrations, *e.g.* 0.1 M, of the light-absorbing dye are necessary for optimization of the efficiency of photogalvanic conversion [5], but the literature indicates that the use of such high concentrations of dye may lead to wastage of absorbed quantum energy via a variety of processes. Such wastage is reflected in a reduction in the quantum yield for the conversion of light into electrical current by the totally illuminated thin layer (TITL) Fe—thionine photo-galvanic cell when the concentration of dye is increased above 10^{-5} M [6]. One process responsible for such wastage is the ground state dimerization of thionine, which is prominent in aqueous solutions. Light absorbed by the thionine dimer is not significantly transformed into electricity by the TITL cell [7]. Another process which can result in wastage is the quenching of the triplet dye by the monomeric ground state dye. We have reported a study of such ground state quenching of protonated triplet methylene blue ($^3MBH^{2+}$) in which it was shown that, under all conditions of measurement, the efficiency F_1 of the net electron transfer in quenching was less than 0.5 per quenching event [8]. Quenching without net electron transfer degrades the photon energy to heat. Thus, ground state quenching can reduce the conversion efficiency of photogalvanic cells based on methylene blue. Similar losses via both dimerization and ground state quenching have recently been observed in the Fe^{II}—new methylene blue system [9].

We now report results of a laser flash photolysis—kinetic spectrometric study of the kinetics and mechanism of the quenching of protonated triplet thionine ($^3TH_3^{2+}$) and $^3MBH^{2+}$ by TH^+ in water, aqueous CH_3CN and aqueous C_2H_5OH. The data are interpreted in the light of our recent investigation of the quenching of $^3MBH^{2+}$ by a number of coordination complexes of Fe^{II} [10].

2. Experimental details

2.1. 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 in the experiments involving the quenching of $^3MBH^{2+}$ by TH^+ [11]. In the experiments involving the quenching of $^3TH_2^{2+}$ by TH^+, the TH^+ was excited with a 347 nm flash obtained with the aid of a frequency doubler. Flash energies were 1.0 J at 694.3 nm and 30 - 100 mJ at 347 nm.

The absorption spectra of the ground state dyes were recorded with a Cary 118 spectrophotometer. The fluorescence measurements were carried out with a Perkin–Elmer MPF 44A fluorescence spectrophotometer.

2.2. Materials

The methylene blue chloride was Fluka Puriss grade while the thionine was MCB 99+% grade. Both dyes were purified by column chromatography on Fisher Certified ACS grade neutral alumina of Brockman activity 1 using $C_2H_5OH:C_6H_6$ (7:3) containing 0.4 ml glacial acetic acid per 100 ml [8, 12]. Spectrally pure fractions were crystallized by concentration of the eluate under vacuum and the crystals were dried to a constant weight in a vacuum desiccator at room temperature to give $MB^+Cl^- \cdot 2H_2O$ (molecular weight, 356) [8] and $TH^+Cl^- \cdot 1.5H_2O$ (molecular weight, 290.8). The theoretical composition was 49.57% C, 4.51% H, 14.45% N, 11.03% S and 12.19% Cl; the actual composition (determined by Atlantic Microlabs Inc., Atlanta, GA) was 48.85% C, 4.46% H, 14.24% N, 11.66% S and 12.91% Cl. The values of λ_{max} and ϵ_{max} for TH^+ in an aqueous medium were 600 nm and 69 500 M^{-1} cm^{-1} respectively. USI reagent grade C_2H_5OH, Burdick and Jackson UV grade CH_3CN and laboratory distilled water which had been further purified by passage through a Millipore deionizer and filter were used. All other chemicals were Fisher Certified ACS grade. Union Carbide prepurified grade nitrogen was deoxygenated by bubbling through chromous perchlorate solution over zinc amalgam.

Test solutions were deaerated by purging with deoxygenated nitrogen for 15 · 20 min.

2.3. Measurements

The pseudo-first-order decay of $^3TH_2^{2+}$ was monitored at 650 and 380 nm while that of $^3MBH^{2+}$ was monitored at 710 and 370 nm (Table 1). The initial concentrations of $^3TH_2^{2+}$ were calculated with the aid of molar absorptivities (which had been determined under the conditions of the experiments) by extrapolating pseudo-first-order decay data to the time of the flash. In the quenching of $^3MBH^{2+}$ by TH^+, the MB^+ (10^{-5} M) was fully excited to its triplet state. The electron transfer yield in both cases was measured by monitoring semi-reduced thionine ($TH_2^{\cdot}$), taking $\epsilon^{TH_2^{\cdot}}_{770\ nm}$ to be 16 000 M^{-1} cm^{-1} in water, 32 000 M^{-1} cm^{-1} in aqueous CH_3CN and 29 000 M^{-1} cm^{-1} in aqueous C_2H_5OH (Table 1). These values were determined under the conditions of the experiment.

3. Results and discussion

3.1. Spectral and kinetic data

The flashing of solutions of MB^+ which were 0.01 M in acid at 694.3 nm in the presence or absence of TH^+ gave prompt (less than 0.5 μs) spectra

TABLE 1

Spectral characteristics of various energy and redox states of methylene blue and thionine in 0.01 M acid solution

	Aqueous		50 vol.% aqueous CH$_3$CN		50 vol.% aqueous C$_2$H$_5$OH	
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})
MB$^+$(S$_0$)[a]	665	91 000	662.5	95 000	664.5	93 000
^{3}MBH^{2+}(T$_1$)[b]	690	14 500	710	16 200	703	18 700
	370	14 200	370	15 300	370	13 200
MBH$^+$ [c,e]	880	24 000	880	38 000	880	30 000
MB^{2+} [d]	520	60 000	520	58 000	520	42 500
TH$^+$(S$_0$) [a]	600	69 500	600	81 000	603	82 000
^{3}TH$_2^{2+}$(T$_1$) [a]	650	16 000	650	20 000	650	20 500
	380	14 000	380	15 500	380	16 500
TH$_2^+$ [a,e]	770	16 000	770	32 000	770	29 000
TH^{2+} [a,e]	470	16 000	470	46 000	470	30 000

[a]This work.
[b]Ref. 10.
[c]Ref. 13.
[d]Ref. 8.
[e]Significant and solvent-dependent proportions of the conjugate acid (of MBH$^+$ and TH$_2^+$) or the conjugate base (of TH^{2+}) present in 0.01 M acid.

characteristic of ^{3}MBH^{2+}. Similarly, the flashing of solutions of TH$^+$ which were 0.01 M in acid at 347 nm gave prompt spectra characteristic of ^{3}TH$_2^{2+}$. The spectra of the protonated triplets decayed rapidly by pseudo-first-order processes into secondary transient spectra which were relatively long lived and decayed by processes which were second order in the intensity of the secondary spectra. The secondary spectra produced during the quenching of ^{3}TH$_2^{2+}$ and ^{3}MBH^{2+} by TH$^+$ are shown in Figs. 1 and 2 respectively.

Second-order rate constants k_q for the quenching of ^{3}TH$_2^{2+}$ or ^{3}MBH^{2+} by TH$^+$(S$_0$) were evaluated with the aid of the equation

$$k_d = k_0 + k_q[TH^+]_0 \tag{1}$$

from the linear dependence on $[TH^+]_0$ of the observed pseudo-first-order specific rates k_d of decay of the triplet, as illustrated in Fig. 3. Second-order rate constants k_{et} for the net electron transfer in the quenching process were calculated with the aid of the equation

$$\frac{[TH_2^+]_{max}}{[^3TH_2^{2+} \text{ or } ^3MBH^{2+}]_{max}} = \frac{k_{et}[TH^+]_0}{k_d} \tag{2}$$

from the maximum concentrations of ^{3}TH$_2^{2+}$ and TH$_2^+$ [8]. Typical plots are illustrated in Fig. 4. Values of k_q, k_{et} and $F_1 = k_{et}/k_q$ which are given in
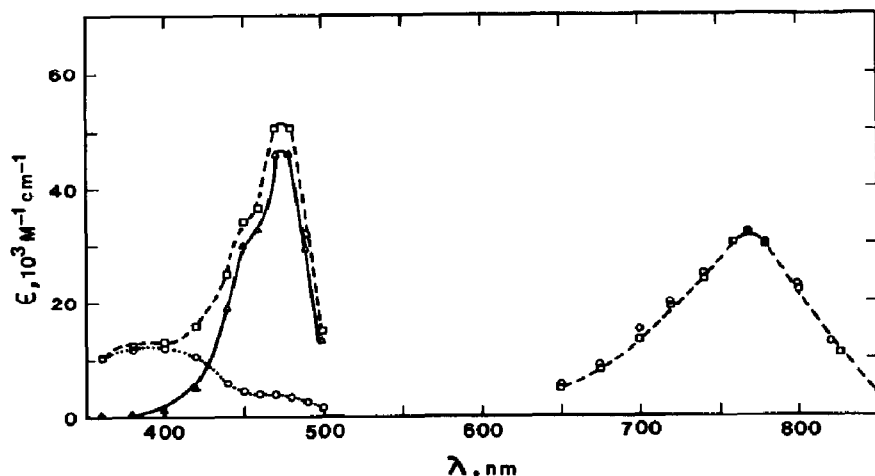
Fig. 1. Absorption spectra of radicals produced by the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$ in 50 vol. % aqueous CH_3CN (0.01 M in HCl; 0.39 M in KCl; 2×10^{-4} M in TH^+): □, $TH^{2+} + TH_2^+$; ○, TH_2^+; △, TH^{2+}.
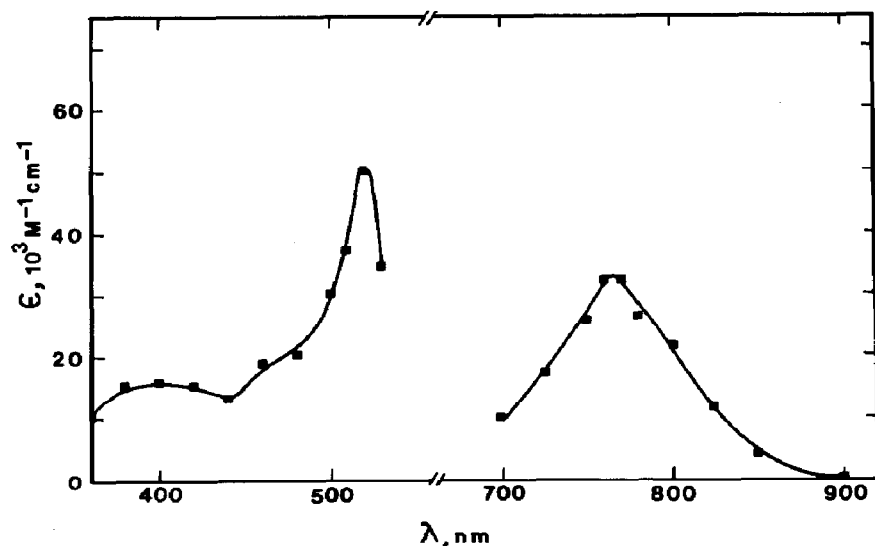
Fig. 2. Absorption spectra (■) of radicals ($MB^{2+} + TH^{2+}$ produced by the quenching of $^3MBH^{2+}$ by $TH^+(S_0)$ in 50 vol.% aqueous CH_3CN (0.01 M in HCl; 0.39 M in KCl; 10^{-5} M in MB^+; 1.5×10^{-4} in TH^+).

Tables 1 and 2 are dependent on the nature of the solvent, the nature of the anions and the ionic strength. In all the observed cases, F_1 is less than 0.5, *i.e.* less than half of all the quenching events resulted in a net electron transfer.

3.1.1. Quenching of $^3TH_2^{2+}$ by $Fe^{II}(H_2O)_6^{2+}$

The absorption spectrum of $^3TH_2^{2+}$ was characterized by monitoring prompt absorbance on excitation of 10^{-4} M solutions of TH^+ in different media. The flash intensity was kept constant and the concentration of
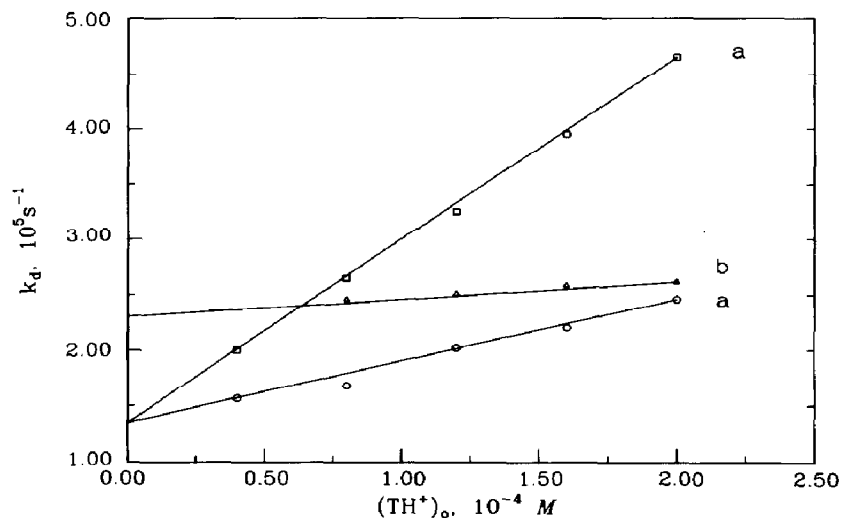
Fig. 3. Dependence of the pseudo-first-order specific rate k_d of decay of the triplet dye on the stoichiometric concentration $[TH^+]_0$ of the dye in 50 vol. % aqueous CH_3CN (0.01 M in HCl): curves a, quenching of $^3TH_2{}^{2+}$ by $TH^+(S_0)$ ($\square$, $\mu = 0.01$; $\bigcirc$, $\mu = 0.4$); curve b, quenching of $^3MBH^{2+}$ by $TH^+(S_0)$ ($\triangle$, $\mu = 0.4$).
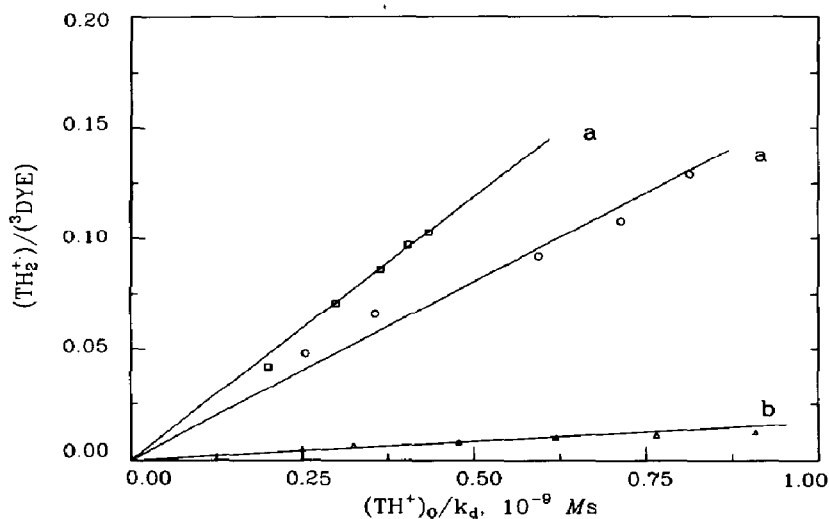

Fig. 4. Determination of k_{et} under the same conditions as given in Fig. 3.

$^3TH_2{}^{2+}$ was determined from the diminution of the ground state absorption at 630 nm, on the assumption that the absorbance of $^3TH_2{}^{2+}$ at 630 nm is negligible. Characteristics of the absorption spectrum of $^3TH_2{}^{2+}$ are recorded in Table 1.

The quenching of $^3TH_2{}^{2+}$ by $Fe^{II}(H_2O)_6{}^{2+}$ was carried out similarly to our previous study [10] of the quenching of $^3MBH^{2+}$ by $Fe^{II}(H_2O)_6{}^{2+}$. Long-lived transient absorption was attributed to $TH_2{}^+$, the product of net

TABLE 2

Rate constants[a] k_q for quenching and k_{et} for net electron transfer and the efficiencies F_1 $(= k_{et}/k_q)$ of the net electron transfer in the quenching of $^3TH_2^{2+}$ by TH^+

Proportion of organic solvent[b] (vol.%)	Anions	μ (M)	k_q ($\times 10^8$ M^{-1} s^{-1})	k_{et} ($\times 10^8$ M^{-1} s^{-1})	F_1	Z^c (kcal mol^{-1})
0	Cl$^-$	0.01	1.2	0.70	0.06	94.6
50 CH$_3$CN	Cl$^-$	0.01	5.6	1.60	0.29	87.5
50 CH$_3$CN	Cl$^-$	0.40[d]	16.0	2.35	0.15	87.5
50 CH$_3$CN	Cl$^-$	0.40[e]	15.0	2.28	0.15	87.5
50 CH$_3$CN	SO$_4^{2-}$–HSO$_4^-$	0.01	5.2	1.43	0.28	87.5
50 CH$_3$CN	SO$_4^{2-}$–HSO$_4^-$	0.2[f]	15.0	1.54	0.10	87.5
75 CH$_3$CN	Cl$^-$	0.01	5.0	2.25	0.45	82.0
90 CH$_3$CN	Cl$^-$	0.01	12.2	6.00	0.49	80.0
50 C$_2$H$_5$OH	Cl$^-$	0.01	2.5	0.43	0.17	89.5
75 C$_2$H$_5$OH	Cl$^-$	0.01	1.5	0.54	0.36	84.0
90 C$_2$H$_5$OH	Cl$^-$	0.01	2.9	1.30	0.45	81.0

[a]T = 23 ± 1 °C; all solutions are 0.01 M in acid.
[b]Other component of the solvent is water.
[c]See ref. 14 for the source of the Z values.
[d]Made up with KCl.
[e]Made up with MgCl$_2$.
[f]Made up with Na$_2$SO$_4$–NaHSO$_4$.

electron transfer in the quenching event. The concentration of $TH_2^{\ddagger}$ was determined from the amount of bleaching at 630 nm. The absorption characteristics of $TH_2^{\ddagger}$ are given in Table 1 and Fig. 1. The electron transfer efficiency F_1 was determined to be 0.82 in 50 vol.% aqueous CH_3CN (0.01 M in acid ($\mu = 0.2$)). This value differs little from the reported value of 0.84 for F_1 in the quenching of $^3MBH^{2+}$ by $Fe^{II}(H_2O)_6^{2+}$ under similar conditions [10].

3.1.2. Quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$

The absorption spectrum of the long-lived transients produced in the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$ exhibits two distinct absorption bands at 770 nm and at 470 nm. Absorption from 650 to 850 nm in a given medium coincides with the known absorption spectrum of the $TH_2^{\ddagger}$ ion radical in that medium, as illustrated in Fig. 1. The band at 470 nm is attributed to the semi-oxidized thionine (TH^{2+}) ion radical. These two absorption bands are similar to the absorption bands with λ_{max} at 880 nm and at 520 nm observed in the ground state quenching of $^3MBH^{2+}$, which have been assigned respectively to semi-reduced methylene blue ($MBH^{\ddagger}$) and semi-oxidized methylene blue (MB^{2+}) [8]. It is accordingly assumed that the only net chemical transformation associated to a significant degree with the observed quenching of $^3TH_2^{2+}$ in the presence of large excesses of $TH^+(S_0)$ is electron transfer to yield equal amounts of $TH_2^{\ddagger}$ and TH^{2+} (in 0.01 M acid).

The absorption spectrum of TH^{2+} was calculated from the differential spectrum obtained at a constant flash intensity, on the assumption that the absorption of MB^{2+} in the vicinity of 770 nm is negligible. Extinction coefficients of TH^{2+} were calculated with the aid of the equation

$$\epsilon^{TH^{2+}}_\lambda = \frac{(\Delta OD)_\lambda}{l[TH^{2+}]_0} + 2\epsilon^{TH^+}_\lambda - \epsilon^{TH_2^{\ddagger}}_\lambda \qquad (3)$$

where $(\Delta OD)_\lambda$ is the measured maximum change in the absorbance at a given wavelength relative to the absorbance of the initial solution, l is the optical path length, $[TH^{2+}]_0$ is the initial, i.e. maximum, concentration of TH^{2+} and $\epsilon^{TH^+}_\lambda$ and $\epsilon^{TH^{2+}}_\lambda$ are respectively the molar absorptivities of $TH^+(S_0)$ and TH^{2+} at a given wavelength. The concentration of TH^{2+} was taken as equal to the concentration of $TH_2^{\ddagger}$ calculated from the maximum absorbance at 770 nm. From the absorption spectrum as recorded in Fig. 1, the extinction coefficient of TH^{2+} at 470 nm is 46 000 M^{-1} cm^{-1} in 50 vol.% aqueous CH_3CN containing 0.01 M HCl. Similarly obtained values of $\epsilon^{TH^{2+}}_{470\ nm}$ in other solvents are 16 000 M^{-1} cm^{-1} in water and 30 000 M^{-1} cm^{-1} in 50 vol.% aqueous C_2H_5OH. Values of $\epsilon_{520\ nm}$ for MB^{2+} have been reported as 58 500 M^{-1} cm^{-1}, 60 000 M^{-1} cm^{-1} and 42 500 M^{-1} cm^{-1} in 50 vol.% aqueous CH_3CN, neat water and 50 vol.% aqueous C_2H_5OH respectively. The much greater variation in $\epsilon_{470\ nm}$ of TH^{2+} with solvent in 0.01 M acid solutions suggests that TH^{2+}, unlike MB^{2+}, has a pK_a value near 2, the exact value of which is solvent dependent. This suggestion is supported by the fact that TH^{2+} has four nitrogen-bound protons while MB^{2+} has none.

These protons are expected to be much more acidic in the semi-oxidized radical than in the parent dye. A similar change in the apparent extinction coefficient is associated with the acid dissociation of the conjugate acid of MBH^+ where pK_a is 1.15 in 50 vol.% aqueous CH_3CN and 1.8 in $5\%C_2H_5OH-95\%H_2O$ [15].

The dimerization of $TH^+(S_0)$ was determined spectrophotometrically to be negligible in solvents containing 50 vol.% organic solvent. Association is significant in neat water (the dimerization constant is $1 \times 10^3 \ M^{-1}$ at 27 °C with $\mu \leqslant 0.001 \ M$ [13]). In a solution of 250 $\mu M \ TH^+$, nearly 73% of the dye is present as monomer. The value of k_q in neat water calculated with the aid of eqn. (1) is not very different from the k_q values in aqueous organic solvents. This rules out the possibility that the dimer is a much more effective quencher than the monomer.

3.1.3. Quenching of $^3MBH^{2+}$ by $TH^+(S_0)$

The absorption spectrum of the long-lived transients formed during the quenching of $^3MBH^{2+}$ by TH^+ in 50 vol.% aqueous CH_3CN (0.01 M in HCl) is illustrated in Fig. 2. The absorption bands at 770 nm and at 520 nm closely match the characteristic absorption maxima of TH_2^+ and MB^{2+} [8]. It can be concluded that the net chemical transformation associated with the quenching of $^3MBH^{2+}$ by TH^+ in 0.01 M acid is an electron transfer to yield equal amounts of MB^{2+} and TH_2^+:

$$^3MBH^{2+} + TH^+ \rightarrow MB^+ + TH^+ + H^+ \tag{4}$$

$$^3MBH^{2+} + TH^+ \rightarrow MB^{2+} + TH_2^+ \tag{5}$$
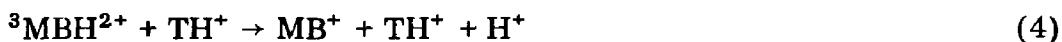
The fact that the fluorescence of $MB^+(S_1)$ was unaffected at all concentrations of TH^+ confirms that this quenching process involves the triplet state of the dye.

The values of k_q, k_{et} and F_1 in aqueous CH_3CN are given in Table 3. The quenching rate constant k_q in 50 vol.% aqueous CH_3CN is $9.0 \times 10^7 \ M^{-1} \ s^{-1}$

TABLE 3

Rate constants[a] k_q for quenching and k_{et} for net electron transfer and the efficiencies $F_1(= k_{et}/k_q)$ of net one-electron oxidation of $^3MBH^{2+}$ in the quenching of $^3MBH^{2+}$ by TH^+

Proportion of CH_3CN in water (vol.%)	Anion	μ (M)	k_q ($\times 10^7 \ M^{-1} \ s^{-1}$)	k_{et} ($\times 10^7 \ M^{-1} \ s^{-1}$)	F_1	Z^b
50	Cl^-	0.01	9.0	1.02	0.11	87.5
50	Cl^-	0.4^c	14.0	1.50	0.11	87.5
75	Cl^-	0.01	8.3	1.05	0.13	82.0

[a]T = 23 ± 1 °C; all solutions are 0.01 M in acid.
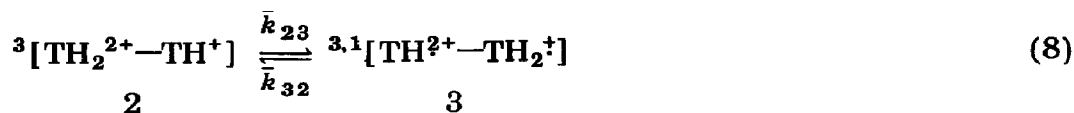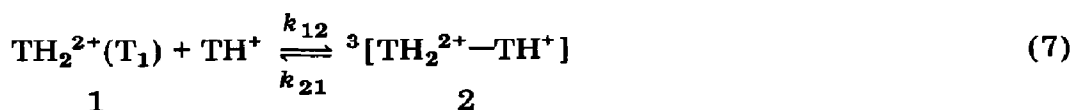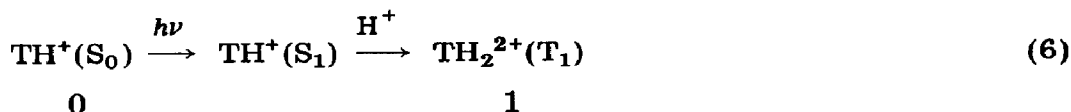[b]See ref. 14 for the source of the Z values.
[c]Made up with KCl.

with $F_1 = 0.11$, *i.e.* 89% of the quenching process does *not* result in net electron transfer. The values of k_q for the quenching of $^3MBH^{2+}$ by $TH^+(S_0)$ are less than one-tenth of the values for the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$ under identical conditions but differ only slightly from comparable values for the quenching of $^3MBH^{2+}$ by $MB^+(S_0)$ [7]. The values of F_1 for the quenching of $^3MBH^{2+}$ by $TH^+(S_0)$ in 50 vol.% aqueous CH_3CN are similar to those for the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$ under the same conditions but are less than half the comparable values of F_1 for the quenching of $^3MBH^{2+}$ by $MB^+(S_0)$. The F_1 values for both homogeneous quenching processes are three or more times greater in 75 vol.% aqueous CH_3CN than for the quenching of $^3MBH^{2+}$ by $TH^+(S_0)$ under the same conditions.
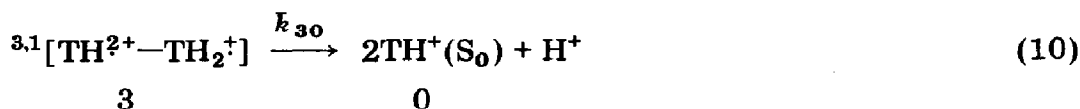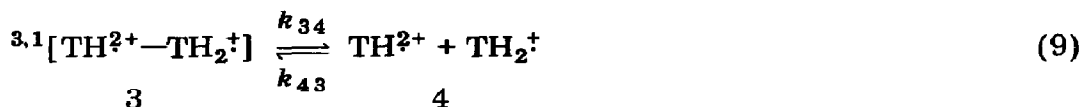
Because of the low values of k_q and F_1 observed in neat water and aqueous C_2H_5OH, it was not possible to carry out precise measurements in these solvents.

3.2. Mechanism of the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$

In our previous work we have shown that the quenching of $^3MBH^{2+}$ by several complexes of iron(II) [10] and organic quenchers [16] proceeds essentially entirely via reversible electron transfer in the encounter complex of the excited dye and quencher. In these cases, $F_1 + F_2 = 1$ where F_1 (= k_{et}/k_q) is the efficiency of the net electron transfer in the quenching events and F_2 (= k_{ret}/k_D) is the efficiency of the net reverse electron transfer in diffusion-controlled encounters (k_D is the rate constant of encounters between the products of forward electron transfer and k_{ret} is the specific rate of net reverse electron transfer).

As for the quenching of $^3MBH^{2+}$ by $MB^+(S_0)$ [8], the values of F_2 are not accessible because the values of k_D for encounters of TH^{2+} and TH_2^+ have not been determined accurately. Thus, it is not possible to apply the condition $F_1 + F_2 = 1$ as a criterion of the quenching mechanism. However, energy transfer in ground state quenching is a degenerate process leading to no net change and there is no basis for assuming the "physical" induction of intersystem crossing. Reversible electron transfer in the encounter complex appears to be the principal mechanism of quenching in the present case. The quenching event can therefore be represented by [8, 10]

$$TH^+(S_0) \xrightarrow{h\nu} TH^+(S_1) \xrightarrow{H^+} TH_2^{2+}(T_1) \qquad (6)$$
$$\quad 0 \qquad\qquad\qquad\qquad 1$$

$$TH_2^{2+}(T_1) + TH^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} {}^3[TH_2^{2+}-TH^+] \qquad (7)$$
$$\quad 1 \qquad\qquad\qquad\qquad 2$$

$$^3[TH_2^{2+}-TH^+] \underset{\bar{k}_{32}}{\overset{\bar{k}_{23}}{\rightleftharpoons}} {}^{3,1}[TH^{2+}-TH_2^+] \qquad (8)$$
$$\quad 2 \qquad\qquad\qquad\qquad 3$$

$$^{3,1}[TH^{2+}-TH_2^{\cdot+}] \; \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \; TH^{2+} + TH_2^{\cdot+} \tag{9}$$
$$\qquad\quad 3 \qquad\qquad\qquad 4$$

$$^{3,1}[TH^{2+}-TH_2^{\cdot+}] \; \overset{\bar{k}_{30}}{\longrightarrow} \; 2TH^+(S_0) + H^+ \tag{10}$$
$$\qquad\quad 3 \qquad\qquad\qquad 0$$

and

$$k_q = \frac{k_{12}}{1 + k_{21}/\bar{k}_{23} + (k_{21}/\bar{k}_{23})\bar{k}_{32}/(\bar{k}_{30} + k_{34})} \tag{11}$$

The quenching rate constant k_q will be diffusion controlled for $k_{21}/\bar{k}_{23} \ll 1$ and $\bar{k}_{32}/(\bar{k}_{30} + k_{34}) \ll 1$. Apparently, these conditions are not met in the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$. The values of k_q which are listed in Table 2 are less than the expected rate constants for diffusion-controlled reactions.

The dependence of F_1 on Kosower's parameter Z as shown in Fig. 5 is consistent with the fact that reversible electron transfer is the principal mechanism of the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$. Such a linear relationship between $\ln\{(1/F_1) - 1\}$ and Kosower's Z parameter was also observed in the quenching of $^3MBH^{2+}$ by $Fe^{II}(CN)_4bpy^{2-}$ which proceeds via reversible electron transfer [10] and in the quenching of $^3MBH^{2+}$ by $MB^+(S_0)$ [8]. This behavior has been explained in terms of competitive paths for the decay of the geminate pair of products formed by forward electron transfer represented in the present case by eqns. (9) and (10). It is apparent that $1/F_1 - 1 = (k_{30} + \bar{k}_{32})/k_{34} \approx \bar{k}_{30}/k_{34}$. From the positive slope in Fig. 5, it
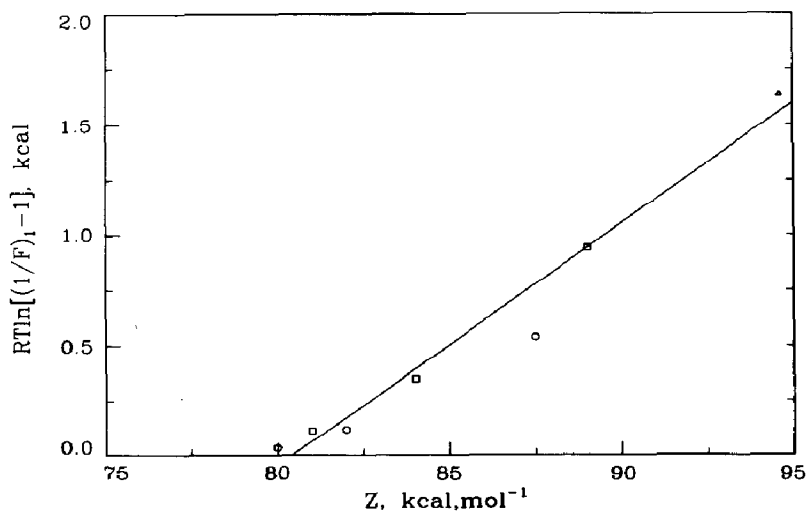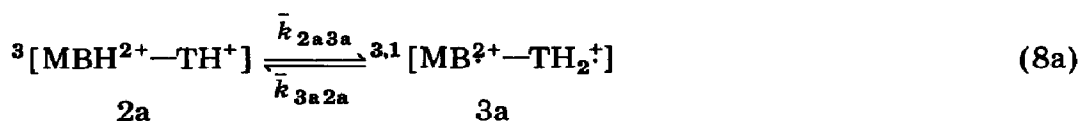

Fig. 5. Dependence of $RT\ln\{(1/F_1) - 1\}$ for the ground state quenching of $^3MBH^{2+}$ on Kosower's solvent polarity parameter Z (slope, 0.11): $\bigcirc$, aqueous CH_3CN; $\square$, aqueous C_2H_5OH; $\triangle$, water.

can be concluded [8, 10] that increasing Z stabilizes the activated complex for the process $3 \rightarrow 0$ (eqn. (10)) relative to that for the process $3 \rightarrow 4$ (eqn. (9)).
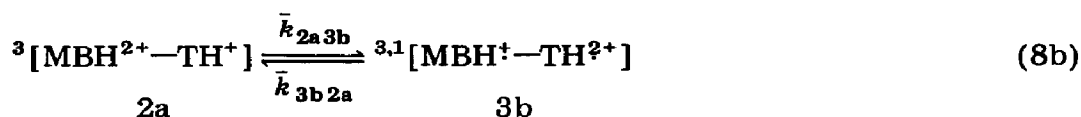
The dependence of F_1 on the nature of the anions is marginal, as was observed for the ground state quenching of $^3MBH^{2+}$. However, increased ionic strength significantly reduces the F_1 values for the quenching of $^3TH_2^{2+}$ by $TH^+(S_0)$, in contrast with the insensitivity of F_1 for the quenching of $^3MBH^{2+}$ by $MB^+(S_0)$ to the ionic strength in the range 0.01 - 0.4 M [8]. The reason for this difference in the sensitivity of F_1 to the ionic strength is not obvious.

3.3. Mechanism of the quenching of $^3MBH^{2+}$ by $TH^+(S_0)$

It is a reasonable extension of the conclusion that the only significant mechanism of quenching of both $^3MBH^{2+}$ and $^3TH_2^{2+}$ by their respective ground states involves reversible electron transfer in encounter complexes that the quenching of $^3MBH^{2+}$ by TH^+ proceeds similarly. The fact that the portion of the quenching process resulting in net electron transfer yields MB^{2+} and TH_2^+ must be interpreted in the light of this inference. The data of Fig. 2 do not reveal the presence of either MBH^+ or TH^{2+}. However, the data do not provide a basis for determining the degree to which this result reflects unidirectional forward electron transfer from $^3MBH^{2+}$ to $TH^+(S_0)$

$$^3[MBH^{2+}-TH^+] \underset{\bar{k}_{3a2a}}{\overset{\bar{k}_{2a3a}}{\rightleftharpoons}} {}^{3,1}[MB^{2+}-TH_2^+] \tag{8a}$$
$$\quad\quad 2a \quad\quad\quad\quad\quad\quad\quad\quad 3a$$

or essentially complete decay of the product of forward electron transfer in the opposite direction, to $MB^+(S_0)$ and $TH^+(S_0)$

$$^3[MBH^{2+}-TH^+] \underset{\bar{k}_{3b2a}}{\overset{\bar{k}_{2a3b}}{\rightleftharpoons}} {}^{3,1}[MBH^+-TH^{2+}] \tag{8b}$$
$$\quad\quad 2a \quad\quad\quad\quad\quad\quad\quad\quad 3b$$

3.4. Implications of ground state quenching for photogalvanic conversion in Fe–thiazine cells

In any Fe–thiazine photogalvanic cell the quenching of triplet thiazine by ground state dye competes with reductive quenching by iron(II). The critical quantity is the ratio of the sum of the $k_qF_1[Q]$ terms for quenching by ground state dye and iron(II) to the sum of the corresponding $k_q[Q]$ terms plus the specific rate of intrinsic decay. This follows from the expectation that the semi-oxidized dye, e.g. TH^{2+}, will rapidly oxidize iron(II) to iron(III). Thus, ground state quenching with net electron transfer followed by oxidation of iron(II) by the semi-oxidized dye radical and quenching of the triplet dye by iron(II) with net electron transfer give the same products, e.g. TH_2^+ and iron(III). For the quenching of $^3MBH^{2+}$ by

$Fe^{II}(H_2O)_6{}^{2+}$ in 50 vol.% aqueous CH_3CN (0.01 M in acid with $SO_4{}^{2-}$–$HSO_4{}^-$ as the anion and μ = 0.2 M), k_q = 8.5 × 10^7 M^{-1} s^{-1} and F_1 = 0.84 [8]. Under identical conditions, the constants for the quenching of $^3MBH^{2+}$ by $MB^+(S_0)$ are k_q = 11.2 × 10^7 and F_1 = 0.25 [8]. With both $Fe^{II}(H_2O)_6{}^{2+}$ and MB^+ 0.01 M and if the intrinsic decay of $^3MBH^{2+}$ (k = 2.3 × 10^5 s^{-1} [10]) is taken into account the calculated fraction of $^3MBH^{2+}$ converted into $MBH^{\dagger}$ is 0.45. Analogous use of the value of F_1 of 0.82 in the quenching of $^3TH_2{}^{2+}$ by $Fe^{II}(H_2O)_6{}^{2+}$ reported in this paper in conjunction with the ground state quenching data of Table 2 and the k_q data for $Fe^{II}(H_2O)_6{}^{2+}$ which had been measured previously [17] gives a calculated fraction of $^3TH_2{}^{2+}$ converted into $TH_2{}^{\dagger}$ equal to 0.52 under the same conditions as those given for MB^+ except that μ was 0.01 M. Clearly, one requirement for efficient photogalvanic conversion in Fe–methylene blue and Fe–thionine cells is a high $[Fe^{II}]_0/[dye]_0$ ratio.

Acknowledgment

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