

Temperature Dependence of Quenching Rates and Efficiencies of Net Forward and Reverse Electron Transfer in the Quenching of Protonated Triplet Methylene Blue by Complexes of Iron(II)

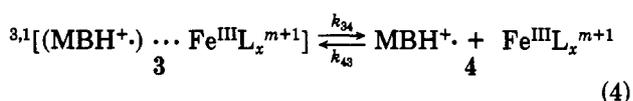
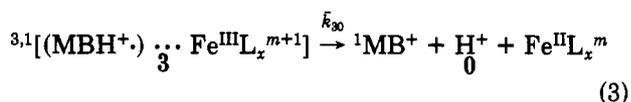
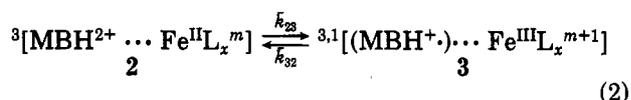
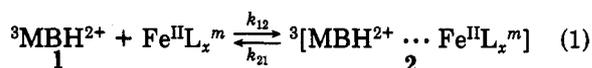
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The temperature dependence of k_q , the specific rate of quenching of protonated triplet methylene blue, ${}^3\text{MBH}^+$, and of k_{et} and k_{ret} , the specific rates of net forward and reverse electron transfer, respectively, have been measured by laser flash photolysis-kinetic spectrometry using 1.0-J, 694.3-nm flashes from a Q-switched ruby laser. The sum of the efficiencies of net forward and reverse electron transfer, F_1 and F_2 , respectively, in the quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ in 30 vol % CH_3CN -70 vol % H_2O has been found to be indistinguishable from unity at 291.0, 298.0, 305.5, 313.0, and 321.0 K. This result supports the prior conclusion that the only significant mechanism of this quenching reaction is reversible electron transfer. In contrast, for quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ in water over the same temperature range, $F_1 + F_2 < 1$, confirming that at least one other mechanism contributes significantly in this case. Thermodynamic quantities of activation, ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger , have been determined for these processes and their implications for mechanism are discussed.

Introduction

We have previously presented and documented a detailed mechanism¹ for quenching of protonated triplet methylene blue, ${}^3\text{MBH}^{2+}$, by low-spin complexes of Fe(II) which are incapable of undergoing energy transfer with ${}^3\text{MBH}^{2+}$. This mechanism, eq 1-4, involves reversible



electron transfer in the quenching encounter complex and implies that the efficiency of net electron transfer is governed by the competition between the dissociation of the caged products of forward electron transfer, process 3 \rightarrow 4, and exergic reverse electron transfer in the encounter pair followed by dissociation, process 3 \rightarrow 0. It follows from this model¹ that the efficiency of net electron transfer, $F_1 \equiv k_{et}/k_q$, where k_{et} and k_q are respectively the specific rates of net forward electron transfer and quenching, is given by eq 5. Similarly, the efficiency of net reverse

$$F_1 = k_{34}/(\bar{k}_{32} + \bar{k}_{30} + k_{34}) \simeq k_{34}/(\bar{k}_{30} + \bar{k}_{34}) \quad (5)$$

electron transfer, $F_2 \equiv k_{ret}/k_D$, where k_{ret} and k_D are respectively the specific rates of net reverse electron transfer and diffusion-controlled encounter between the products of the net forward reaction, is given by eq 6. Equation

$$F_2 = \bar{k}_{30}/(\bar{k}_{32} + \bar{k}_{30} + k_{34}) \simeq \bar{k}_{30}/(\bar{k}_{30} + k_{34}) \quad (6)$$

$$F_1 + F_2 = 1 \quad (7)$$

7 follows from eq 5 and 6 and constitutes a convenient diagnostic characteristic of quenching via reversible electron transfer. With the aid of this criterion, it has been

shown that the mechanism of quenching of ${}^3\text{MBH}^{2+}$ and ${}^3\text{MB}^+$ by several organic compounds is reversible electron transfer.² It has also been shown that, in quenching by high-spin complexes of Fe(II) and Co(II), where quenching via spin-induced intersystem crossing and/or energy transfer is possible, $F_1 + F_2$ is significantly less than unity, indicating that at least two mechanisms of quenching are operating in parallel.³

We now report information concerning the temperature dependence of k_q , k_{et} , k_{ret} , k_D , F_1 , and F_2 for the quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ derived from 694.3-nm laser flash photolysis-kinetic spectrometry.

Experimental Section

Apparatus. A Holobeam Series 630 laser system providing a Q-switched ruby laser pulse at 694.3 nm with a nominal pulse width of 19 ns was used. Flash energy was 1.0 J. Details of the laser and monitoring apparatus are reported elsewhere.⁴ Temperature in the cell compartment was controlled to ± 0.1 °C by circulating water.

Materials. Methylene blue chloride was Fluka puriss grade, purified further on a neutral Al_2O_3 chromatography column to give $\text{MB}^+\text{Cl} \cdot 2\text{H}_2\text{O}$, mol wt 356.⁵ The sample of $\text{K}_2[\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}] \cdot 3\text{H}_2\text{O}$ was from material the preparation of which is reported in ref 1. $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4\text{bpy}]$ was prepared by Cl_2 oxidation of $\text{K}_2[\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}]$ in aqueous solution. Its concentration and purity were verified by UV-vis spectrometry.⁶ All other chemicals were analytical reagent grade. Test solutions were 10^{-5} M in MB^+ and 0.01 M in acid, prepared with acetonitrile and laboratory distilled water which had been further purified by passage through a Millipore deionizer and filter. Samples were deaerated by purging for 15-20 min with N_2 which had been deoxygenated by passage through chromous perchlorate.

Measurements. Pseudo-first-order decay of ${}^3\text{MBH}^{2+}$ was monitored at 370 and 710 nm.⁴ Semireduced methylene blue (mostly as MBH^+) was monitored at 880 nm, taking ϵ_{880} as $24\,000 \text{ M}^{-1} \text{ cm}^{-1}$ in water⁷ and $30\,000 \text{ M}^{-1} \text{ cm}^{-1}$

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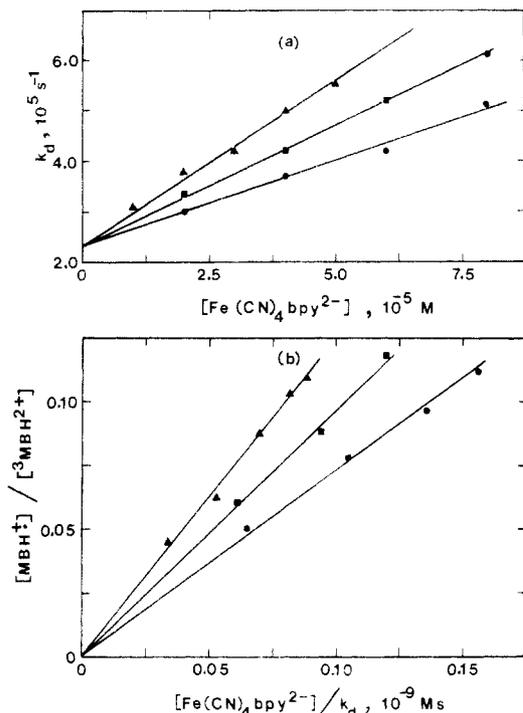


Figure 1. (a) Dependence of pseudo-first-order decay of ${}^3\text{MBH}^{2+}$ on $[\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}]$ in 30% v/v aqueous acetonitrile at (●) 291, (■) 298, and (▲) 313 K; 10^{-5} M MB^+ , 0.01 M HCl, $\mu = 1.2$ M (MgCl_2). (b) Determination of k_{et} in quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ under the same conditions as data of part a.

in 30 vol % CH_3CN –70 vol % H_2O . In order to evaluate k_{ret} , MBH^+ was prepared in the presence of added ferric complex by reduction of ${}^3\text{MBH}^{2+}$ with 0.3–1 mM diphenylamine. The reaction of MBH^+ with ferric complex was monitored by following the regeneration of MB^+ at 635–650 nm as well as by disappearance of “ MBH^+ ”.

Data and Discussion

Values of k_{d} and k_{et} were determined from plots of eq 8 and 9, where k_{d} is the pseudo-first-order rate of decay

$$k_{\text{d}} = k_0 + k_{\text{q}}[\text{Q}] \quad (8)$$

$$[\text{“MBH}^+.”] / [{}^3\text{MBH}^{2+}] = k_{\text{et}}[\text{Q}] / k_{\text{d}} \quad (9)$$

of ${}^3\text{MBH}^{2+}$, $[{}^3\text{MBH}^{2+}] = [\text{MB}_0^+]$, and [“ $\text{MBH}^+.$ ”] is the maximum yield of semimethylene blue under the conditions of observation. Plots of eq 8 and 9 are presented in Figure 1. Values of k_{ret} were determined from the linear dependence of pseudo-first-order rates of decay of “ $\text{MBH}^+.$ ” or of regeneration of MB^+ on concentration of ferric complex, as illustrated in Figure 2. Values of F_1 were determined from the defining relationship, $F_1 = k_{\text{et}}/k_{\text{q}}$. Values of F_2 were determined for quenching by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ from the defining relationship, $F_2 = k_{\text{ret}}/k_{\text{D}}$, by assuming that $k_{\text{D}} = k_{\text{q}}$ at the high ionic strength ($\mu = 1.2$ M)^{1,9} employed in these experiments.

As shown in Table I, F_1 varies inversely with temperature when ${}^3\text{MBH}^{2+}$ is quenched by either $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ or $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$. With $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$, $F_1 + F_2$ is indistinguishable from unity over the temperature range investigated. Because the reaction of semireduced methylene blue with $\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6^{3+}$ is too slow to compete with its

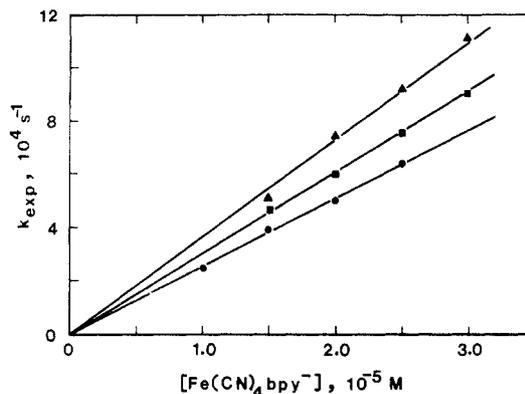


Figure 2. Determination of k_{ret} for oxidation of semimethylene blue by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ in 30% v/v aqueous acetonitrile at (●) 291, (■) 298, and (▲) 313 K; 10^{-5} M MB^+ , 10^{-4} M diphenylamine, 0.01 M HCl, $\mu = 1.2$ M (MgCl_2).

TABLE I: Temperature Dependence of k_{q} , k_{et} , k_{ret} , F_1 , and F_2

T , K	$10^{-9}k_{\text{q}}$, $\text{M}^{-1}\text{s}^{-1}$	$10^{-9}k_{\text{et}}$, $\text{M}^{-1}\text{s}^{-1}$	$10^{-9}k_{\text{ret}}$, $\text{M}^{-1}\text{s}^{-1}$	F_1^a	F_2^c	$F_1 + F_2$
$\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ in 30 vol % CH_3CN –70 vol % H_2O^b						
291.0	3.3	0.92	2.3	0.28	0.70	0.96
298.0	4.6	1.19	3.2	0.26	0.70	0.95
305.5	5.2	1.28	3.7	0.25	0.71	0.95
313.0	6.5	1.56	4.7	0.24	0.72	0.96
321.0	8.6	1.98	6.2	0.22	0.72	0.96
$\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ in H_2O^d						
290.0	0.0027	0.0019 ⁵		0.72		0.72 ^e
299.0	0.0041	0.0024		0.59		0.59 ^e
309.0	0.0064	0.0033		0.52		0.52 ^e
318.0	0.0088	0.0044		0.50		0.50 ^e
328.0	0.0107	0.0052		0.49		0.49 ^e

^a $k_{\text{et}}/k_{\text{q}}$. ^b 0.01 M HCl; ionic strength made up to 1.2 M with MgCl_2 . ^c $k_{\text{ret}}/k_{\text{q}}$. k_{D} taken equal to k_{q} ; see ref 1 for justification. ^d 0.01 M HCl; ionic strength made up to 0.4 M with KCl. ^e F_2 assumed to be negligible. See text for explanation.

back-reaction with $(\text{C}_6\text{H}_5)_2\text{NH}^+$ and in view of the relatively low values of k_{ret} for $\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6^{3+}$ and MBH^+ at $\sim 23^\circ\text{C}$ in several media ($k_{\text{ret}} < 10^6 \text{ M}^{-1}\text{s}^{-1}$),⁸ it is assumed that F_2 is negligible for hexaquoiron under the present conditions. Thus, $F_1 + F_2$ for the latter species is indistinguishable from F_1 and is substantially less than unity over the measured temperature range. These results support the prior conclusion^{1,3} that reversible electron transfer is the only significant mechanism of quenching by the low-spin $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ complex while at least one other mechanism, e.g., catalysis of intersystem crossing, contributes substantially to quenching by high-spin $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$. From the observed decreases in F_1 with increasing temperature, it follows that the maximum efficiency for photogalvanic conversion using these photoredox systems also decreases with increasing temperature. A possibly related decrease of the sunlight engineering efficiency of the iron–thionine photogalvanic cell with increasing temperature has been observed by Kamat et al.¹⁰

Implications of the low values of k_{q} for quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ are discussed elsewhere.

The temperature dependences of the various quantities presented in Table I are conveniently analyzed in terms of two quantities, F_1/F_2 and k_{q} . From eq 5 and 6, it is apparent that $F_1/F_2 = k_{34}/k_{30}$. The slope of a plot of $\ln(F_1/F_2)$ vs. $1/T$ is readily shown to be equal to $(\Delta H^\ddagger_{30} -$

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TABLE II: Thermodynamic Quantities of Activation

quantity (X)	ΔG^\ddagger , kJ mol ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ deg ⁻¹
$X_{30} - X_{34}$ for $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$, ^{a, b}	-2.45	+6.7	+30.7
X_{q} for $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$, ^b	+17.9	+22.0	+13.9
X_{q} for $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$, ^c	+35.2	+27.8	-24.8

^a Derived from temperature dependence of F_1/F_2 .
^b In 30 vol % CH_3CN -70 vol % H_2O . ^c In water.

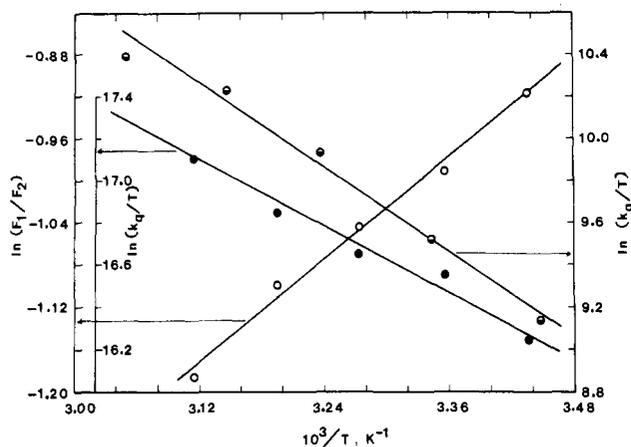


Figure 3. Plots of $\ln(F_1/F_2) = \ln(\bar{k}_{30}/k_{34})$, O, and $\ln(k_q/T)$, ●, for quenching by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ in 30% CH_3CN and $\ln(k_q/T)$ for quenching by $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ in water, ●, vs. $10^3/T$.

$\Delta H^\ddagger_{34}/R$ (and also to $(E_{a,30} - E_{a,34})/R$) when quenching takes place essentially only via reversible electron transfer, as it does for quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$. It also follows that $\Delta H^\ddagger_{30} - \Delta H^\ddagger_{34} = H_{x,3\rightarrow 0} - H_{x,3\rightarrow 4}$, where $H_{x,3\rightarrow n}$ is the activated complex for the process $3 \rightarrow n$. From data summarized in Table II and plotted in Figure 3, $H_{x,3\rightarrow 0} - H_{x,3\rightarrow 4} = 6.7 \text{ kJ mol}^{-1}$. The enthalpy of the activated complex for reverse electron transfer, a process which is overall exergic, is thus greater than the enthalpy of the activated complex for dissociation of the caged pair, $[(\text{MBH}^+) \cdots \text{Fe}^{\text{III}}\text{bpy}^-]$.

Plots of $\ln(k_q/T)$ vs. $10^3/T$ which are incorporated in Figure 3 yield $\Delta H^\ddagger_{\text{q}} = 22.0 \text{ kJ mol}^{-1}$ for quenching by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ and $\Delta H^\ddagger_{\text{q}} = 27.8 \text{ kJ mol}^{-1}$ for quenching by $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$. The former value, according to our model, is the average enthalpy of activation for diffusion of ${}^3\text{MBH}^{2+}$ and $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$. The latter value is the weighted average of $\Delta H^\ddagger_{\text{q}}$ for two or more parallel mechanisms of quenching, all of which are slower than diffusion controlled. For that portion of quenching by $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ which proceeds via reversible electron transfer, as seen in eq 10, k_{q} is related to the rate constants of at least three

$$k_{\text{q}} = k_{12}/\{1 + (k_{21}/\bar{k}_{23})[1 + \bar{k}_{32}/(\bar{k}_{30} + k_{34})]\} \quad (10)$$

elementary steps so that it is difficult to identify a priori the maximum on the potential energy surface for this process.

The values of ΔS^\ddagger at 298 K presented in Table II are conveniently interpreted with the aid of the mechanism represented by eq 1-4. The value of $\Delta S^\ddagger_{30} - \Delta S^\ddagger_{34} (=S_{x,3\rightarrow 0} - S_{x,3\rightarrow 4})$ for quenching by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$, $+30.7 \text{ J mol}^{-1} \text{ deg}^{-1}$, is large and positive. Since the process $3 \rightarrow 4$, $[(\text{MBH}^+) \cdots \text{Fe}^{\text{III}}(\text{CN})_4\text{bpy}]^0 \rightarrow \text{MBH}^+ + \text{Fe}^{\text{III}}(\text{CN})_4\text{bpy}^-$, involves separation of charge, associated electrostriction of solvent may result in ΔS^\ddagger_{34} being negative. The overall process $3 \rightarrow 0$, where 0 is ${}^1\text{MB}^+ + \text{H}^+ + \text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$, involves greater charge separation than does $3 \rightarrow 4$. Presumably, $X_{3\rightarrow 0}$, including the contiguous solvent region, resembles 3 more than does $X_{3\rightarrow 4}$ so that $S_{x,3\rightarrow 0}$ is less negative or more positive than $S_{x,3\rightarrow 4}$. This interpretation of the difference between $S_{x,3\rightarrow 0}$ and $S_{x,3\rightarrow 4}$ is also applicable to the observed difference, $H_{x,3\rightarrow 0} > H_{x,3\rightarrow 4}$. Presumably, solvation contributes less to stabilizing $X_{3\rightarrow 0}$ than to stabilizing $X_{3\rightarrow 4}$.

The observed values of $H_{x,3\rightarrow 0} - H_{x,3\rightarrow 4}$ and $S_{x,3\rightarrow 0} - S_{x,3\rightarrow 4}$ and their interpretation can be used to refine the interpretation of our previous findings¹ on the solvent dependence (at constant temperature) of F_1 for quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$. It was found that $RT \ln[(1/F_1) - 1]$, which according to our model = $-RT \ln(F_1/F_2) = G^\circ_{x,3\rightarrow 4} - G^\circ_{x,3\rightarrow 0}$, varies linearly with Kosower's solvent parameter, Z . From the linearity and the small positive slope, $+0.16$, it was inferred that $G^\circ_{x,3\rightarrow 0}$ is more sensitive to stabilization of charge separation by solvent than is $G^\circ_{x,3\rightarrow 4}$ and that $X_{3\rightarrow 0}$ is more polar than $X_{3\rightarrow 4}$. This inference ignored the entropy term in the free energy. At least in 30% CH_3CN , $|\Delta S^\ddagger_{30} - \Delta S^\ddagger_{34}| > |\Delta H^\ddagger_{30} - \Delta H^\ddagger_{34}|$. If changes in $\Delta G^\ddagger_{30} - \Delta G^\ddagger_{34}$ for the reaction of ${}^3\text{MBH}^{2+}$ with $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$ are also dominated by entropy effects in the previously studied media,¹ then, in general, X_{34} is more "polar" than X_{30} , not less, as we had previously concluded.

The value of $\Delta S^\ddagger_{\text{q}}$ for quenching of ${}^3\text{MBH}^{2+}$ by $\text{Fe}^{\text{II}}(\text{CN})_4\text{bpy}^{2-}$, $+13.9 \text{ J mol}^{-1} \text{ deg}^{-1}$, is small and positive and presumably reflects the average net disordering of solvent at the transition states for diffusion of the two kinds of ion. Interpretation of the relatively large and negative value of $\Delta S^\ddagger_{\text{q}}$ for quenching by $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$, $-24.8 \text{ J mol}^{-1} \text{ deg}^{-1}$, must, as indicated above in discussing ΔH^\ddagger for this process, take into account the occurrence of parallel quenching mechanisms and the multistep nature of the electron-transfer mechanism. The large negative value of $\Delta S^\ddagger_{\text{q}}$ is consistent with transition states for the parallel mechanisms which resemble the collision complex 2, ${}^3[\text{MBH}^{2+} \cdots \text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}]^{4+}$, with intensification of charge resulting in enhanced electrostriction of solvent.

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