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Kinetic studies on oxidations of leucomethylene blue and leucothionine by iron (III) in aqueous solution

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ABSTRACT: The reaction kinetics and mechanism of the oxidations of leucomethylene blue (MBH) and leucothionine (TH) by iron (III) sulfate in aqueous solution were studied spectrophotometrically by the stopped-flow technique. MBH and TH, which were freshly prepared by photoreduction of methylene blue and thionine, respectively, with ascorbic acid were used in the kinetic measurements. The pseudo-first-order rate constants (k_{obsd}) show kinetic saturation at high initial concentrations of iron (III) sulfate for MBH and TH. It was found that the reciprocal of k_{obsd} increases linearly with increase in the reciprocal of $[Fe^{3+}]_0$. A broad absorption band was observed on mixing MBH and Fe^{3+} solutions at low temperatures, and this was attributed to a charge-transfer complex between MBH and Fe^{3+}. The effects of Fe^{2+} ion and L-(+)-ascorbic acid on the rates of oxidation were also investigated. A small kinetic isotope effect on the oxidation rate for MBH was observed. The results can be explained by a general mechanism with stepwise electron–proton–electron transfers with the formation of a complex between reactants. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: hydride transfer; kinetics and mechanism; leucomethylene blue; leucothionine; iron oxidation

INTRODUCTION

There has been considerable interest in the reaction mechanism of hydride transfer from various substrates to π-acceptors.[1–14] Since leucomethylene blue (MBH) and leucothionine (TH) are very unstable and easily oxidized by co-existing oxygen in solution, few kinetic studies on the reactions of these compounds with π-acceptors have been reported. Recently, we have studied the kinetics of the reactions of TH and MBH with two-electron oxidants by producing TH and MBH in a closed system by photoreductions of thionine (T^+) and methylene blue (MB^+) with triethylamine.[15] Kinetics, isotope effects and other evidence have proved that the reactions proceed through stepwise electron–proton–electron (EPE) transfer pathway.

Thionine and methylene blue exist as monovalent cations in the ordinary pH region and their redox reactions are reversible. These dyes are hardly reduced by Fe^{2+} ion in the dark, but the reduction of the dyes occurs easily on irradiation with visible light. It has been reported[16–20] that since the intermediates and products of the photoreductions are re-oxidized to T^+ and MB^+ by Fe^{3+} ion produced during the photoreductions of the dyes by Fe^{2+}, certain photostationary states exist. Hatchad and Parker[19] and Schlag[20] investigated the kinetics of the reoxidatioin of bleached thionine with Fe^{3+} by following the reappearance of thionine absorption after flashing. In these system, however, the starting conditions of oxidation were ambiguous, because the photostationary state depends on the light intensity and the concentrations of Fe^{2+} and Fe^{3+}. It seems that thereafter there has been no report of the reaction of TH or MBH with one-electron oxidants. A detailed kinetic study of the oxidations of TH and MBH with Fe^{3+} is important for elucidating the reaction mechanisms for the photoreduction of T^+ and MB^+ with Fe^{2+}.

In this study, we followed the reactions of TH and MBH with Fe^{3+} by producing TH and MBH by means of photoreductions of T^+ and MB^+ with ascorbic acid in a closed system and by mixing a solution of TH (or MBH) with a solution of Fe^{3+}. This paper reports detailed kinetics and mechanisms of the reactions of TH and MBH with Fe^{3+}.

EXPERIMENTAL

Materials. Thionine ($T^+ Cl^-$) and methylene blue ($MB^+ Cl^-$) were purchased from Tokyo Chemical Industry and Wako Pure Chemical Industries, respectively. L-(+)-Ascorbic acid (AA), iron (III) sulfate [$Fe_2 (SO_4)_3 \cdot nH_2O$] and iron (II) sulfate ($FeSO_2 \cdot 7H_2O$) were obtained from Wako Pure Chemicals Industries. The compounds were used as received. Aqueous solutions were deaerated by

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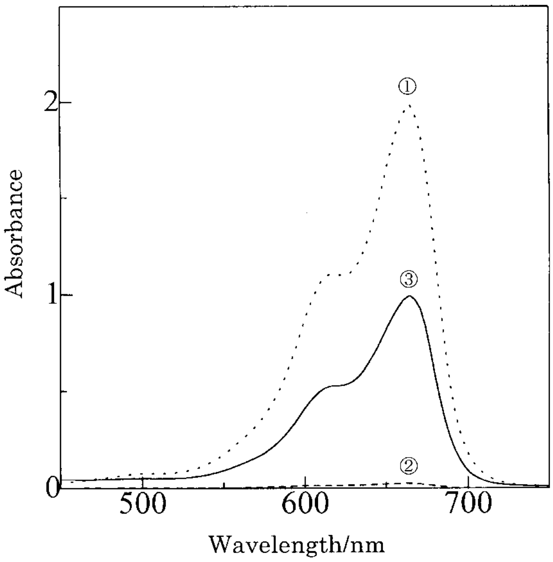

Figure 1. Absorption spectra of MB^+ taken (1) before and (2) after photoreduction and (3) absorption spectrum of a equivolume mixture of MBH and Fe^{3+}

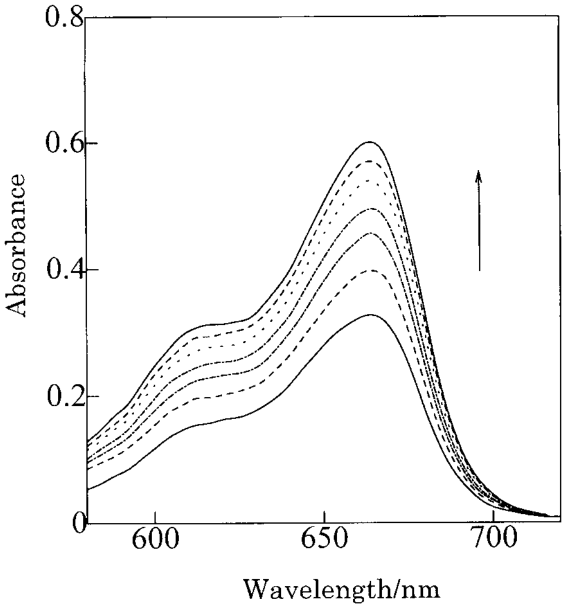

Figure 2. Rapid-scan spectra for the formation of MB^+ in the reaction of MBH with Fe^{3+} at 25 °C in aqueous solution. Cycle time, 40 ms

bubbling 99.99% nitrogen gas for more than 30 min just before use. The concentration of Fe^{3+} was determined by EDTA titration.

Kinetic measurements. MBH (or TH) solution was prepared by irradiating MB^+ (or T^+) and AA aqueous solution (concentration ratio 1:15), deaerated by bubbling with nitrogen gas, with visible light supplied by a 650 W projector lamp in a bath whose temperature was thermostated at the reaction temperature. On irradiation, the solution changed from blue to colorless immediately. This indicates that the leuco dyes (TH and MBH) were formed. Then, the solutions of TH (or MBH) and Fe^{3+} were separately charged in drive syringes of a stopped-flow apparatus (Otsuka Electronics stopped-flow spectrophotometer, RA-401). Mixing was performed within 1 ms by means of nitrogen gas pressure. After mixing, the change in the absorbance at 655 nm for MB^+ (at 599 nm for T^+) was monitored. The runs were repeated 20–30 times. All the runs were performed with excess Fe^{3+} concentrations. During the measurements, the solution of MBH (or TH) was being irradiated continuously to prevent reoxidation of the lueco dyes by oxygen remained in the solution.

Spectroscopic measurements. Rapid-scan spectra were taken every 40 ms after mixing the MBH (or TH) solution with Fe^{3+} solution at 298 K. When EPA (diethyl ether–pentane–ethanol) solutions of MBH and Fe^{3+} were mixed below −70 °C, a colored solution was obtained immediately. The absorption spectra of this solution were obtained at various temperatures with a Union SM-401 spectrophotometer using a cryostat with optical windows. An absorption spectrum different from that of MB^+ was obtained at −63 °C and the spectrum changed to that of MB^+ as the temperature increased.

RESULTS

We produced TH and MBH by photoreductions of thionine and methylene blue with AA. Figure 1 shows the absorption spectra of MB^+ taken before and after the photoreduction [(1) and (2)] and the spectrum of a equivolume mixture of MBH and Fe^{3+} solutions (3).

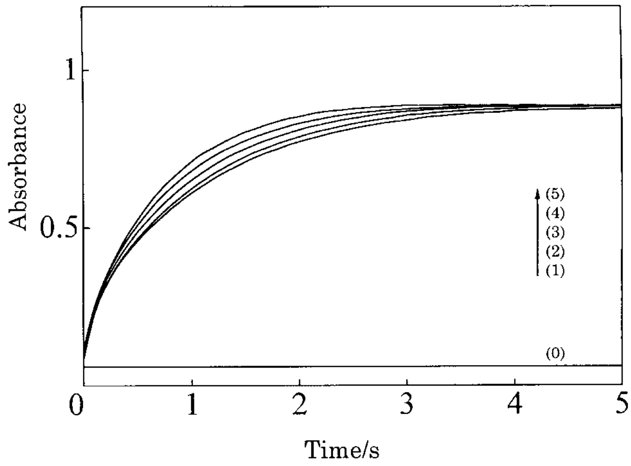

Figure 3. Time dependences of absorption of MB^+ at 655 nm after mixing an MBH solution with Fe^{3+} solutions. Initial concentrations; $[MBH]_0 = 1.20 \times 10^{-5}$ M; $[Fe^{3+}]_0 = 0$ (0); 2.31×10^{-3} M; (1); 2.75×10^{-3} M (2); 3.37×10^{-3} M (3); 4.37×10^{-3} M (4) and 6.24×10^{-3} M (5)

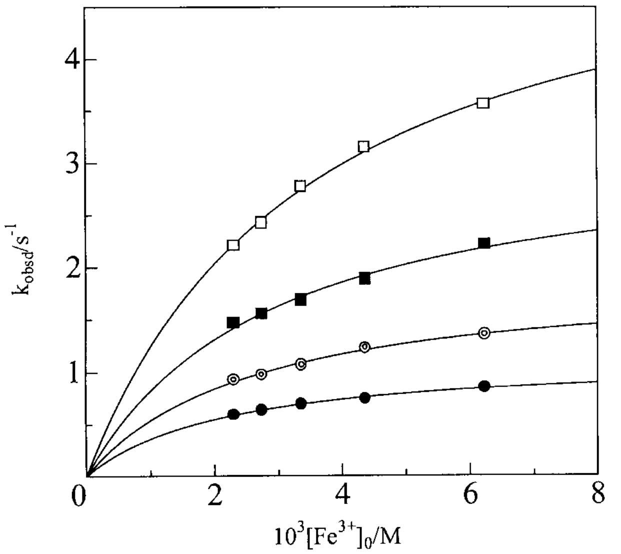

Figure 4. Plots of the observed rate constant (k_{obsd}) vs Fe^{3+} concentration for the oxidation of MBH by Fe^{3+} at 25.4 (●), 30.0 (◎), 34.7 (■) and 39.8 °C (□)

Figure 1 can be explained by the formation of MBH by photoreduction and re-production of MB^+ by oxidation with Fe^{3+}. Inspection of Fig. 1 shows that more than 98% of MB^+ was re-produced. Figure 2 shows the rapid scan spectra for the formation of MB^+.

Time-dependent curves of the absorption at 665 nm after averaging the repeated runs are shown in Fig. 3. The absorbances at 665 nm increased rapidly and reached a constant value after mixing of the MBH solution with Fe^{3+} solutions of several concentrations, whereas it did not increase when MBH solution was mixed with the deaerated solvent. This shows that under these experimental conditions, the reactions with Fe^{3+} proceed nearly to completion, and that the oxidation of MBH by oxygen remaining in the solvent after deaeration and oxygen which was dissolved on mixing and during the reaction can be neglected.

The rates of formation of MB^+ in the presence of a large excess of Fe^{3+} obeyed pseudo-first-order kinetics. The apparent first-order rate constants (k_{obsd}) were estimated for several concentrations of Fe^{3+} at different temperatures. The rate constant (k_{obsd}) increases with increasing Fe^{3+} concentration. Saturation curves were obtained on plotting the k_{obsd} values against $[Fe^{3+}]_0$ at each temperature (Fig. 4). The rate constants (k_{obsd}) for the reaction of TH with Fe^{3+} were also obtained in a similar manner. Similar saturation curves between the k_{obsd} value and $[Fe^{3+}]_0$ were obtained.

Since we used a large excess of AA as a reducing agent for photoreductions of MB^+ and T^+, we examined the influence of AA on the rate of oxidation of MBH (or TH) with Fe^{3+} and found that k_{obsd} is independent of the concentration of AA in the concentration range used here (Table 1).

We produced leucomethylene blue-*d* (MBD) by photoreduction of MB^+ using D_2O instead of H_2O as solvent and measured the rate of the reaction between MBD and Fe^{3+}.

DISCUSSION

As mentioned above, saturation curves were obtained between the k_{obsd} values and $[Fe^{3+}]_0$ for MBH and TH. The dependence of the k_{obsd} values on $[Fe^{3+}]_0$ can be described by

$$k_{obsd} = \frac{a[Fe^{3+}]_0}{1 + b[Fe^{3+}]_0} \qquad (1)$$

where *a* and *b* are parameters discussed later. Equation (1) can be rewritten as

$$\frac{1}{k_{obsd}} = \frac{b}{a} + \frac{1}{a[Fe^{3+}]_0} \qquad (2)$$

This equation is verified by plots of $1/k_{obsd}$ versus $1/[Fe^{3+}]_0$, which are straight lines as shown in Fig. 5. The linearity of $1/k_{obsd}$ versus $1/[Fe^{3+}]_0$ is characteristic of 1:1 complex formation between MBH (or TH) and Fe^{3+}, which equilibrates much more rapidly than the hydride transfer between these species. Indeed, Fukuzumi *et al.*[21] observed the absorption band from a charge-transfer (CT) complex formed between 9,10-dihydro-10-methylacridine (DHMA) and Fe^{3+} and discussed the kinetics of the formation and decay of this complex and its role in the electron-transfer reaction from DHMA to Fe^{3+} according to the above equations. We expected the formation of a CT complex in the present reaction system. At room temperature, however, there was no indication of the formation of a CT complex (only the spectrum for MB^+ was obtained between 400 and 700 nm at 13 ms after mixing of solutions of MBH and Fe^{3+}). When the EPA

Table 1. Effect of the concentration of L-(+)-ascorbic acid on k_{obsd} for the leucomethylene blue–iron(III) sulfate reaction at 25.4 °C[a]

$10^4[AA]_0$ (M)	1.44	1.69	2.05	2.53	3.01
$[AA]/[MB^+]$	12	14	17	21	25
k_{obsd} (s^{-1})	0.860	0.855	0.866	0.858	0.871

[a] $[Fe^{3+}]_0 = 6.65 \times 10^{-3}$ M, $[MBH]_0 = 1.20 \times 10^{-5}$ M.

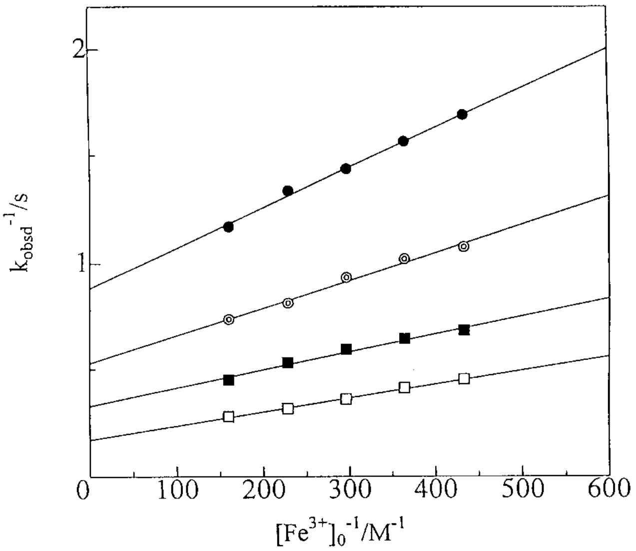

Figure 5. (a) Plots of $1/k_{obsd}$ vs $1/[Fe^{3+}]_0$ for the oxidation of MBH by Fe^{3+} at 25.4 (●), 30.0 (◎), 34.7 (■) and 39.8 °C (□)

solutions of MBH and Fe^{3+} were mixed at low temperatures below −63 °C, a broad absorption band with $\lambda_{max} = 590$ nm was obtained, and on increasing the temperature the spectrum changed to that of MB^+ (Fig. 6). The broad band is characteristic of an intermolecular CT complex. These findings show that a CT complex formed between MBH and Fe^{3+} at low temperatures below −63 °C, and that the hydride transfer reaction occurred and MB^+ was formed at higher temperatures. At room temperature, the formation of the CT complex was not detected, because of its low concentration compared with that at low temperatures or the rapid formation of MB^+ (even during the dead-time of the stopped flow apparatus appreciable amounts of MB^+ were formed).

Such a complex may be productive (Scheme 1) or non-productive (Scheme 2) and these two possibilities are kinetically indistinguishable.

$$MBH + Fe^{3+} \overset{K}{\rightleftharpoons} CTC \xrightarrow{k_1} MBH^{+\cdot} + Fe^{2+} \quad (3)$$

$$MBH^{+\cdot} + H_2O \rightarrow MB^{\cdot} + H_3O^+ \quad (\text{fast}) \quad (4)$$

$$MB^{\cdot} + Fe^{3+} \rightarrow MB^+ + Fe^{2+} \quad (\text{fast}) \quad (5)$$

Scheme 1

$$CTC \overset{K^{-1}}{\rightleftharpoons} MBH + Fe^{3+} \xrightarrow{k_2} MBH^{+\cdot} + Fe^{2+} \quad (6)$$

$$MBH^{+\cdot} + H_2O \rightarrow MB^{\cdot} + H_3O^+ \quad (\text{fast}) \quad (7)$$

$$MB^{\cdot} + Fe^{3+} \rightarrow MB^+ + Fe^{2+} \quad (\text{fast}) \quad (8)$$

Scheme 2

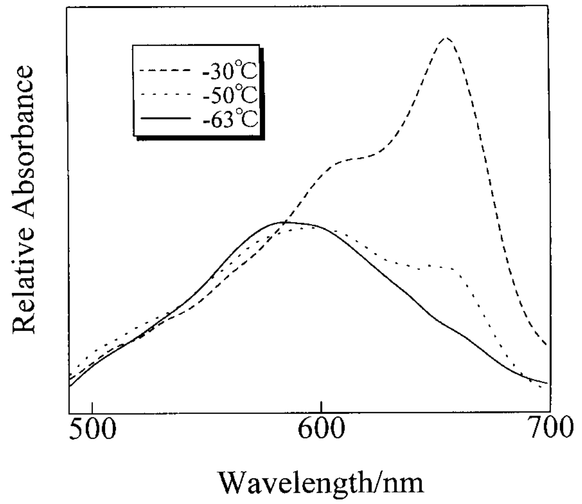

Figure 6. Spectral change as a function of temperature for the MBH–Fe^{3+} system in EPA at low temperatures. $[MBH]_0 \approx 10^{-5}$ M and $[Fe^{3+}]_0 \approx 10^{-4}$ M

In Scheme 1, it is assumed that there is a rapid equilibrium between MBH, Fe^{3+} and the CT complex (CTC). The rate-controlling step is the slow electron transfer from TH to Fe^{3+} giving $MBH^{+\cdot}$ and Fe^{2+} [Eqn 3]. Subsequently, $MBH^{+\cdot}$ is deprotonated by solvent water to provide $MB^{\cdot}$ radical [Eqn 4]. Further, the second electron transfers from $MB^{\cdot}$ to the other Fe^{3+} [Eqn 5]. The overall stoichiometry can be written as

$$MBH + 2Fe^{3+} \rightarrow MB^+ + 2Fe^{2+} + H^+ \quad (9)$$

According to equilibrium hypothesis, if $[Fe^{3+}]_0$ is in very large excess, the pseudo-first-order rate constant (k_{obsd}) for the formation of MB^+ is given by Eqn 10

$$k_{obsd} = \frac{Kk_1[Fe^{3+}]_0}{1 + K[Fe^{3+}]_0} \quad (10)$$

which can be rewritten as Eqn 11

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{1}{Kk_1[Fe^{3+}]_0} \quad (11)$$

In Scheme 2, the CTC is considered to be a 'bystander.' Equation 6 can be described as a rapid equilibrium with a slow electron transfer. From Scheme 2, k_{obsd} is given by Eqn 12

$$k_{obsd} = \frac{k_2[Fe^{3+}]_0}{1 + K[Fe^{3+}]_0} \quad (12)$$

which can be rewritten as Eqn 13

Table 2. Influence of added Fe^{2+} on k_{obsd} for the reaction of MBH and Fe^{3+} at constant $[Fe^{3+}]_0$ and 40.6 °C[a]

$10^4[Fe^{2+}]_0$ (M)	0	0.48	1.92	3.84	6.05
k_{obsd} (s^{-1})	2.30	2.26	2.32	2.38	2.41

[a] $[Fe^{3+}]_0 = 2.46 \times 10^{-3}$ M, $[MBH]_0 = 1.20 \times 10^{-5}$ M.

Table 3. Summary of rate data for the reaction of TH and MBH with Fe^{3+} at various temperatures in aqueous solution[a]

Compound	*T* (°C)	*a* ($l\ mol^{-1}\ s^{-1}$)	*b* ($l\ mol^{-1}$)	*a*/*b* (s^{-1})
TH	19.8	945	361	2.62
	24.7	1470	331	4.44
	29.8	2137	275	7.77
	35.1	3039	259	11.73
MBH	25.4	526	460	1.14
	30.3	749	390	1.92
	34.7	1105	346	3.19
	39.8	1591	283	5.62

[a] For Scheme 1, $a = k_1K$, $b = K$ and $a/b = k_1$; for Scheme 2, $a = k_2$, $b = K$ and $a/b = k_2/K$.

$$\frac{1}{k_{obsd}} = \frac{K}{k_2} + \frac{1}{k_2[Fe^{3+}]_0} \qquad (13)$$

Equations 10 and 11 are kinetically indistinguishable from Eqns 12 and 13, and Eqns 11 and 13 predict a linear correlation between $1/k_{obsd}$ and $1/[Fe^{3+}]_0$. This agrees fairly well with the results obtained (Fig. 5).

Hatchard and Parker[19] studied briefly the kinetics of the re-oxidation of bleached thionine with Fe^{3+} by following the reappearance of thionine absorption after flash photolysis of thionine and iron (II) sulfate. They observed that the apparent first-order rate constant increased linearly with increasing Fe^{3+} concentration for low concentrations of Fe^{3+} and leveled off at high concentrations of Fe^{3+}. They explained these findings by two independent reaction mechanisms: (a) by direct oxidation of leucothionine with Fe^{3+} to give semithionine, followed by oxidation of the latter, or (b) by oxidation of the equilibrium concentration of semithionine by Fe^{3+}. Scheme 1 corresponds to mechanism (a), but the Scheme I includes more detailed reaction steps involving the proton-transfer step.

In both schemes, the rate-determining step is the electron transfer from MBH to Fe^{3+}. If this reaction is reversible, retardation of the Fe^{3+} oxidation of MBH by Fe^{2+} must be observed. Powell et al.[22] studied the kinetics of hexacyanoferrate (III) oxidations of dihydropyridines (PyH_2). They observed that the reactions were inhibited by added $Fe(CN)_6^{4-}$. and proposed a reaction scheme which involves a reversible electron-transfer step between PyH_2 and $Fe(CN)_6^{3-}$. If a similar reaction scheme holds for the present reactions, inhibition of the reaction by added Fe^{2+} could be observed. As is shown in Table 2, the k_{obsd} values are independent of the concentration of Fe^{2+}. This shows that the electron-transfer step is not reversible in the present reactions. Okamoto et al.[23] and Fukuzumi et al.[24] also proposed reaction mechanisms with irreversible electron-transfer steps for the reaction of 1-propyl-1, 4-hydronicotinamide with $Fe(CN)_6^{3-}$ and the oxidation of 1-benzyl-1,4-dihydronicotinamide by iron(III) complexes, respectively.

The parameters *a* and *b* in Eqns 1 and 2 were obtained from the slopes and intercepts of straight lines shown in Fig. 5. Since $a = k_1K$ (Scheme 1) or k_2 (Scheme 2) and $b = K$ (Schemes 1 and 2), the values of k_1 or k_2 and *K* can be obtained from the slopes and intercepts of straight lines at several temperatures and are listed in Table 3.

Figure 7 shows plots of $1/k_{obsd}$ versus $1/[Fe^{3+}]_0$ for MBH and MBD. From the slopes and intercepts of the straight lines, ratios k_1^H/k_1^D (or $(k_2^H K^D/k_2^D K^H)$) = 1.9 ± 0.2 and $K^H/K^D = 1.2 \pm 0.1$ were obtained. The reaction

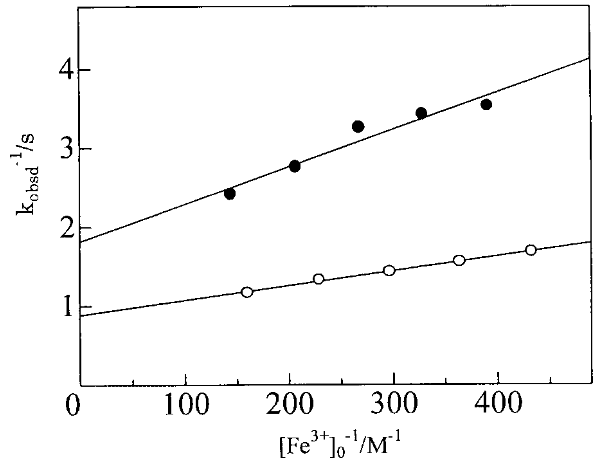

Figure 7. Plots of $1/k_{obsd}$ vs $1/[Fe^{3+}]_0$ for the oxidations of MBH (○) and MBD (●) by Fe^{3+} at 25.4 °C

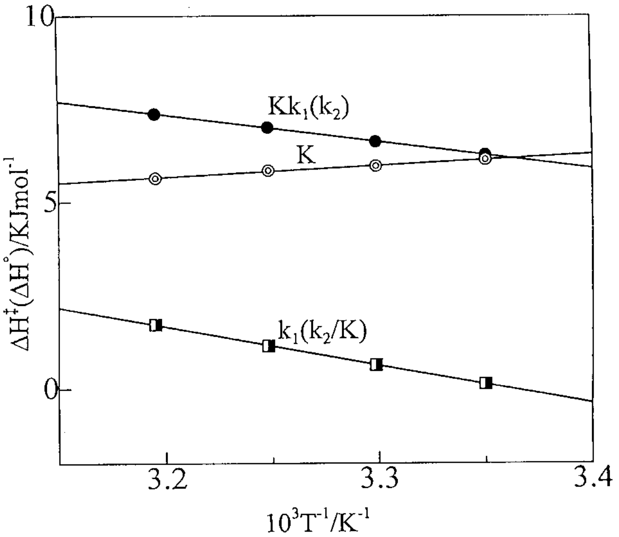

Figure 8. Arrhenius and Van't Hoff plots of Kk_1 (or k_2), k_1 (or k_2/K) and K for the reaction of MBH with Fe^{3+}

sequences in Scheme 1 or 2 predict the secondary isotope effect on the rate. The observed value of k_1^H/k_1^D is too large to be accounted for by the normal secondary isotope effect, and small for the rate-determining deprotonation. Okamoto *et al.*[23] obtained similar results for the reaction of 1-propyl-1,4-hydronicotinamide with $Fe(CN)_6^{3-}$. They pointed out that this reaction under weakly basic conditions proceeds through a mechanism with an electron transfer followed by a proton transfer and that the transfer of a proton participates in the rate-determining electron-transfer step. The results obtained in this study indicate that the reaction of MBH with Fe^{3+} proceeds through a similar mechanism.

Figure 8 shows the Arrhenius and the Van't Hoff plots of k_1 (or k_2/K), k_1K (or k_2) and K. The heat of formation of CTC and the activation enthalpy and entropy for electron-transfer reaction were obtained and are listed in Table 4. These values for the reaction between TH and Fe^{3+} are also listed in Table 4.

It has been reported[21] that the blue transient complex formed between Fe^{3+} and DHMA is a π-complex between Fe^{3+} and the acridine ring and that this π-complex is stabilized by a ligand-to-metal charge-transfer interaction. The degree of charge transfer was estimated to be close 100%, because the absorption maximum of the complex is the same as that of the free radical cation ($C_{13}H_{10}NMe^{+\cdot}$). Although the only kinetic evidence for the formation of the complex for the present cases was obtained at room temperature, the nature of the complex is thought to be similar to that of the complex between DHMA and Fe^{3+}, since the π-electron structures of TH and MBH are similar to that of an acridine ring and the kinetic behaviour for the reaction of TH and MBH with Fe^{3+} is similar to that for the reaction of DHMA with Fe^{3+}.

The mechanistic involvement of CT complexes in a variety of reactions of electron donors and acceptors has been always questioned by an alternative mechanism in which the CT complex is merely an 'innocent bystander' in an otherwise dead-end equilibrium. Recently, we observed a negative activation enthalpy for the reaction between bis[4-(dimethylamino)phenyl]methane (MH_2) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in trichloroethane and pointed out that the hydride transfer from MH_2 to DDQ occurs via electron transfer in the CT complex formed between MH_2 and DDQ.[25] As has been pointed out in many cases, however, Schemes 1 and 2 could not be distinguished in the reactions of TH and MBH with Fe^{3+}.

CONCLUSIONS

We obtained the rate constants (k_{obsd}) for the oxidation of MBH and TH by Fe^{3+} by means of a combination of the formation of MBH and TH by photoreductions of MB^+ and T^+ by ascorbic acid and the stopped-flow technique. We observed that k_{obsd} increased with increasing Fe^{3+} concentration and saturation curves were obtained between k_{obsd} and $[Fe^{3+}]_0$. We have demonstrated that the reaction schemes with the formation of a complex between MBH (or TH) and Fe^{3+} hold in the present reactions. Scheme 1 corresponds to one of the reaction mechanisms proposed by Hatchard and Parker[19] for the re-oxidation of bleached thioine with Fe^{3+}. This study could give a more quantitative relationship between k_{obsd} and $[Fe^{3+}]_0$. The method using a combination of the formation of unstable species by photoreduction and the stopped-flow technique proved to be useful for kinetic studies of rapid reactions of unstable species.

Table 4. Summary of activation parameters for the reactions of TH and MBH with Fe^{3+} in aqueous solution

Compound		E_a (kJmol^{-1})	$\Delta H\neq$ (kJ mol^{-1})	$\Delta S\neq$ (J K^{-1} mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})
TH	$Kk_1(k_2)$	56.9 ± 2.2	54.4 ± 2.2	−1.8 ± 0.05		
	K				−17.3 ± 2.5	−10.2 ± 1.4
	$k_1(k_2/K)$	74.2 ± 3.3	71.7 ± 3.3	8.4 ± 0.4		
MBH	$Kk_1(k_2)$	59.8 ± 0.9	57.3 ± 0.9	−0.9 ± 0.01		
	K				−25.4 ± 3.8	−34.3 ± 2.1
	$k_1(k_2/K)$	85.2 ± 0.9	82.7 ± 0.9	33.4 ± 0.3		

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