Coordination Selectivity in the Reaction of Iron(II) with 8-Hydroxy-7-(8-quinolyl)azo-5-quinolinesulfonic Acid

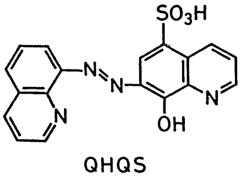
Masaki Noritake, Ken-ichi Okamoto,† Jinsai Hidaka,† and Hisahiko Einaga*
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305
†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

(Received January 20, 1989)

The formation of an iron(II) complex with 8-hydroxy-7-(8-quinolyl)azo-5-quinolinesulfonic acid (QHQS, H_2qhqs) has been investigated on the basis of the electronic absorption spectra, the equilibrium, and the stopped-flow kinetics in a 0.10 mol dm^{-3} aqueous sodium chloride solution at 25 °C with a view to elucidating the coordination selectivity of the ligand. A 1 : 2 (metal : ligand) complex forms in an acidic medium with a selective coordination of QHQS to iron(II), with its 2-(8-quinolylazo)phenol moiety acting as a terdentate ligand. The complex formation reaction proceeds through a single pathway of Fe^{2+} with $Hqhqs^-$, a ligand species singly protonated at the phenolate oxygen, with the rate constant (k_{21}) of $k_{21}=(3.16\pm0.20)\times10^5$ mol^{-1} dm^3 s^{-1}, to form a mono-ligand complex as the rate-determining step. The coordination of the ligand by 8-quinolyl nitrogen, followed by a rate-determining bonding of phenolato oxygen, was suggested as the reaction mechanism.

The coordination selectivity of multidentate ligands having aromatic and/or heterocyclic backbone, which restrict the ligand to one among two or several possible coordination modes, is one of our recent concerns. In our previous papers,[1)] the coordination selectivity has been studied, from thermodynamic and kinetic points of view, on aluminum(III) complexes with 7-substituted 8-hydroxy-5-quinolinesulfonate ligands, in which the substituents have ligating groups. It has been found that these multidentate ligands show a selective coordination to aluminum(III), with either one of two possible coordination modes, depending on the nature of the ligating substituents and that, in special cases, they show a linkage isomerism[1e)] between these two possible coordination modes. Now, a new concern arises as to what this sort of coordination selectivity becomes on going from aluminum(III), a non-transition metal ion of an octahedral coordination, to a transition metal ion of the same coordination structure, and from the multidentate ligands showing *O-N-O* and *O-N* coordination modes[1)] to those showing *N-N-O* and *O-N* modes. As a typical example of a transition metal ion, iron(II) is of much interest because it has a high affinity to nitrogen as well as to oxygen-donor atoms and because it plays a significant role in bioinorganic chemistry.

In the present work, 8-hydroxy-7-(8-quinolyl)azo-5-quinolinesulfonic acid (QHQS, H_2qhqs)—which is capable of taking either one of two possible coordination modes—as the *N-N-O* terdentate (2-(8-quinolylazo)phenol moiety) or the *N-O* bidentate (8-quinolinol moiety), was synthesized for the first time, and its coordination selectivity to iron(II) was studied on the basis of the electronic absorption spectra, the equilibrium, and the kinetics. The coordination reaction mechanism of QHQS to iron(II) will be discussed in detail.


QHQS

Experimental

Reagents. The QHQS ligand was synthesized by the diazotization of 8-aminoquinoline with sodium nitrite in aqueous sulfuric acid, followed by the coupling of the diazonium salt with 8-hydroxy-5-quinolinesulfonic acid (HQS, H_2hqs) in an alkaline aqueous solution of pH 9—10, which had been kept steady by the addition of sodium carbonate. The crude product was isolated from an acidified solution of pH 3—4 by the use of acetic acid and was purified by recrystallization from an aqueous solution, with its acidity changed by the addition of hydrochloric acid. Calcd for $C_{18}H_{11}N_4O_4SNa\cdot2H_2O\cdot0.5HCl$: C, 47.29; H, 3.42; N, 12.26%. Found: C, 47.13; H, 3.61; N, 12.04%.

The related ligands, 4-hydroxy-3-(8-quinolyl)azo-1-naphthalenesulfonic acid (QNS, H_2qns) and 8-hydroxy-7-phenylazo-5-quinolinesulfonic acid (PHQS, H_2phqs), were synthesized in the same way as QHQS, but by using 4-hydroxy-1-naphthalenesulfonic acid in place of HQS in the case of QNS, and aniline in place of 8-aminoquinoline in the case of PHQS, respectively.

An aqueous iron(II) solution was prepared from $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$ supplied by the Kanto Chemical Co., Ltd., Tokyo, and was slightly acidified with sulfuric acid in order to prevent the hydrolysis of iron(II). The absence of traces of iron(III) in the stock solution was checked by studying its reaction with 2-hydroxy-5-sulfobenzoic acid (sufosalicylic acid). The iron(II) stock solution was standardized with an ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA) solution. All the other reagents used were of an analytical or equivalent grade and were used without further purification.

Measurements. The electronic absorption spectral measurements were carried out by using JASCO spectrophotometers, models UVIDEC-1M and -610A. The protonation and stability constants were determined spectrophotometrically at 510 nm and at 500 nm (log β_1) and at 550 nm (log β_2) respectively. Stopped-flow kinetic measurements were made with a JASCO spectrophotometer, model SS-25, to which were attached a stopped-flow apparatus (model SFC-5), a data processor (model DP-500), and a Watanabe Sokki X-Y recorder (model WX-441). Kinetic runs were made at 550 nm under pseudo-first-order kinetic conditions with an excess of the ligand. The observed rate constant, k_{obsd}, was calculated from Eq. 1:

$$\ln\{(A_\infty - A_0)/(A_\infty - A_t)\} = k_{\mathrm{obsd}}\, t \qquad (1)$$

where A_0, A_t, and A_∞ stand for the absorbances at the initial state, at time t, and at equilibrium respectively.

The equilibrium and kinetic measurements were carried out at 25.0±0.1 °C in an aqueous 0.10 mol dm^{-3} sodium chloride solution. The stability and the rate constants were constant within the limits of experimental error when sodium chloride was replaced by sodium perchlorate.

The pH of the solution was measured with an Orion Research pH meter, model 801A, with two electrodes, one glass and one saturated calomel. The hydrogen-ion concentration was calculated from the measured pH value, $\mathrm{pH_{meas}}$, according to Eq. 2:

$$-\log[\mathrm{H^+}] = \mathrm{pH_{meas}} + \log f_{\mathrm{H^+}} \qquad (2)$$

The activity coefficient of the hydrogen ion, $f_{\mathrm{H^+}}$, of 0.83 was taken from the literature;[2)] the value was in good agreement with that obtained when a solution containing 0.010 mol dm^{-3} HCl and 0.090 mol dm^{-3} NaCl at 25 °C is defined as $-\log[\mathrm{H^+}] \equiv 2.00$.[3)] The hydrogen-ion concentration was adjusted with chloroacetic acid-sodium chloroacetate and acetic acid-sodium acetate buffer solutions, the concentrations of which were maintained as low as possible (usually below 10^{-2} mol dm^{-3} for the former and 10^{-3} mol dm^{-3} for the latter in total concentration) in order to confirm that they had no influence on the complex-formation reaction of iron(II) with QHQS.

Results and Discussion

Electronic Absorption Spectra. Figure 1 shows the electronic absorption spectra of QHQS in variously protonated forms. The $\mathrm{qhqs^{2-}}$ species (pH 12.08) gives an intense absorption maximum at 20.5×10^3 cm^{-1}, corresponding to the $\pi^* \leftarrow \pi$ transition of the azo group, and absorption maxima and shoulder at 30.0×10^3, at 33.8×10^3, and around 39×10^3 cm^{-1} respectively, assignable to the $\pi^* \leftarrow \pi$ transitions of the quinoline rings.[1)] The protonations at phenolate oxygen and 8-quinolinol nitrogen cause a bathochromic shift of the $\pi^* \leftarrow \pi$ transition of the azo group; the absorption peak around 20×10^3 cm^{-1} decreases its intensity to show a shoulder attributable to the appearance of an intense absorption maximum at 25.2×10^3 cm^{-1} of $\mathrm{H_3qhqs^+}$. These spectral changes with the protonation, characteristic in the $(15-27)\times10^3$ cm^{-1} region, can be used for the determination of the protonation constants of QHQS.

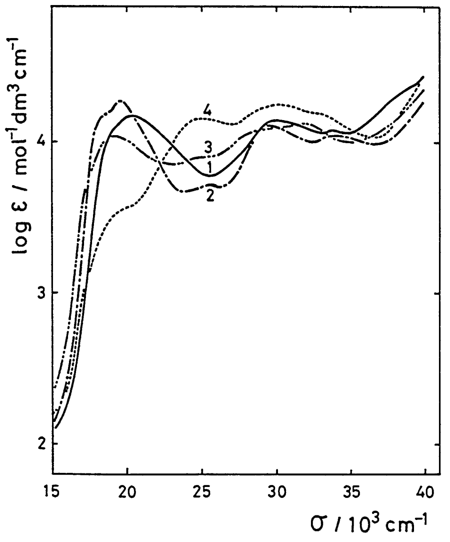


Fig. 1. Absorption spectra of QHQS.
1: pH 12.08 ($\mathrm{qhqs^{2-}}$); 2: pH 4.78 ($\mathrm{Hqhqs^-}$); 3: pH 2.14 (characteristic for $\mathrm{H_2qhqs}$); and 4: pH 1.05 ($\mathrm{H_3qhqs^+}$).

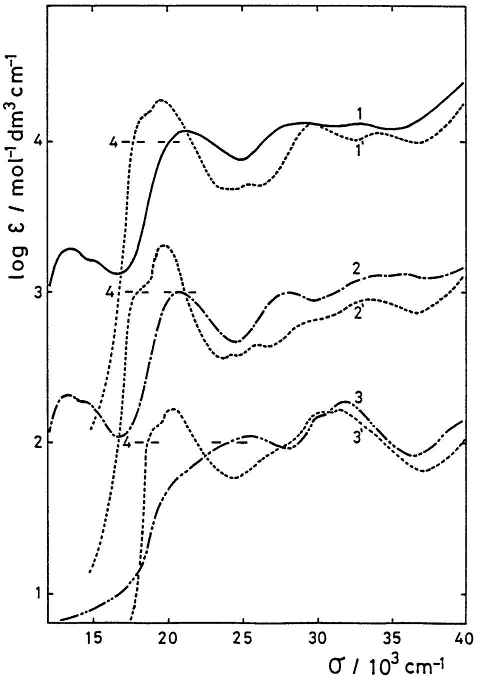


Fig. 2. Absorption spectra of QHQS, QNS, PHQS, and their iron(II) complexes.
1: Fe(qhqs) (pH 4.78); 1′: $\mathrm{Hqhqs^-}$ (pH 4.78); 2: Fe(qns) (pH 4.78); 2′: $\mathrm{Hqns^-}$ (pH 4.78); 3: Fe(phqs) (pH 4.78); and 3′: $\mathrm{Hphqs^-}$ (pH 4.78). Curves 2 and 2′ are shifted downward for 1 unit and those 3 and 3′ for 2 units for clarity.

Absorption spectrum of the iron(II) complex with QHQS is depicted in Fig. 2, together with that of the ligand species $\mathrm{Hqhqs^-}$ (pH 4.78). The coordination of QHQS to iron(II) is especially remarkable in the spectral region of the $(12-25)\times10^3$ cm^{-1} region: The absorption maximum of $\mathrm{Hqhqs^-}$ in the $\pi^* \leftarrow \pi$ transition region of the azo chromophore shifts hypsochromically upon the coordination, and an absorption maximum at 13.4×10^3 cm^{-1}, with a shoulder around 15×10^3 cm^{-1} of a magnitude of the molar-absorption coefficient of the order of 10^3, appears in the lowest-energy region; this maximum can be assigned to the metal-to-ligand charge-transfer (CT) bands. These absorption spectral features can be used to analyze the coordination of the azo group of QHQS to iron(II).

Coordination Selectivity of QHQS to Iron(II). The QHQS ligand has two coordination modes attributable to steric hindrance, either with the *N-N-O* terdentate or with the *N-O* bidentate. Figure 2 also depicts the absorption spectra of iron(II) complexes and the free ligand of QNS, which functions solely as the *N-N-O* terdentate, and of PHQS, which functions solely as the *N-O* bidentate. The change in the spectral features on the coordination of QHQS to iron(II) in the CT and azo-chromophore $\pi^*\leftarrow\pi$ transition regions is in good agreement with that of QNS to iron(II), but is quite different from that of PHQS to iron(II). Specifically, the $\pi^*\leftarrow\pi$ transitions of Hqhqs$^-$ and Hqns$^-$ show, on coordination to iron(II), a hypsochromic shift from 20×10^3 to 21×10^3 cm^{-1}, but the $\pi^*\leftarrow\pi$ transition of Hphqs$^-$ shows a hypsochromic shift from 20×10^3 to 25×10^3 cm^{-1}; moreover, the CT band of the former has a distinct band with a maximum and a shoulder, whereas that of the latter has only a shoulder. These results reflect the fact that the coordinated iron(II) chromophore is different between the former, i.e., the iron(II) complexes with QHQS and QNS, and the latter, i.e., the iron(II) complex with PHQS.

Hence, QHQS may be concluded to show coordination selectivity as the *N-N-O* terdentate. Incidentally, the iron(II) complexes with QHQS and QNS were found to form in an acidic aqueous solution with as low a pH value as 1.5, where the coordination of PHQS to iron(II) was not observed at all; an increase in the pH of the solution to above 3 was necessary for the formation of the iron(II) complex with PHQS.

Stability. The protonation constants, K_{ai} $(i=1-3)$, of QHQS,

$$K_{ai}=[\mathrm{H}_i\mathrm{qhqs}^{(2-i)-}]/[\mathrm{H}^+][\mathrm{H}_{i-1}\mathrm{qhqs}^{(3-i)-}] \qquad (3)$$

were determined spectrophotometrically by using these relations:

$$A^{\mathrm{L}}=A^{\mathrm{L}}_1+(A^{\mathrm{L}}_0-A^{\mathrm{L}}_1)/(1+K_{a1}[\mathrm{H}^+]) \qquad (4)$$

$$A^{\mathrm{L}}=A^{\mathrm{L}}_3+\{(A^{\mathrm{L}}_1-A^{\mathrm{L}}_3)+(A^{\mathrm{L}}_2-A^{\mathrm{L}}_3)K_{a2}[\mathrm{H}^+]\}+(1+K_{a2}[\mathrm{H}^+] + K_{a2}K_{a3}[\mathrm{H}^+]^2) \qquad (5)^{3)}$$

which can be derived by assuming conformity to Beer's law for all the coexisting ligand species. In Eqs. 4 and 5, A^{L}_0, A^{L}_1, A^{L}_2, and A^{L}_3 refer to the absorbance of a solution of the qhqs^{2-}, Hqhqs$^-$, $\mathrm{H_2}$qhqs, and $\mathrm{H_3}$qhqs$^+$ ligand species respectively, while A^{L} refers to the absorbance of a solution in which qhqs^{2-} and Hqhqs$^-$ (Eq. 4) or Hqhqs$^-$, $\mathrm{H_2}$qhqs, and $\mathrm{H_3}$qhqs$^+$ coexist (Eq. 5) at the hydrogen-ion concentration of $[\mathrm{H}^+]$. Equations 4 and 5 were solved by the curve fitting method[3)] to estimate K_{a1} for the former and K_{a2} and K_{a3} for the latter from the experimental data plots of A^{L} vs. $-\log[\mathrm{H}^+]$ ($-\log[\mathrm{H}^+]>7$ for K_{a1} and $-\log$

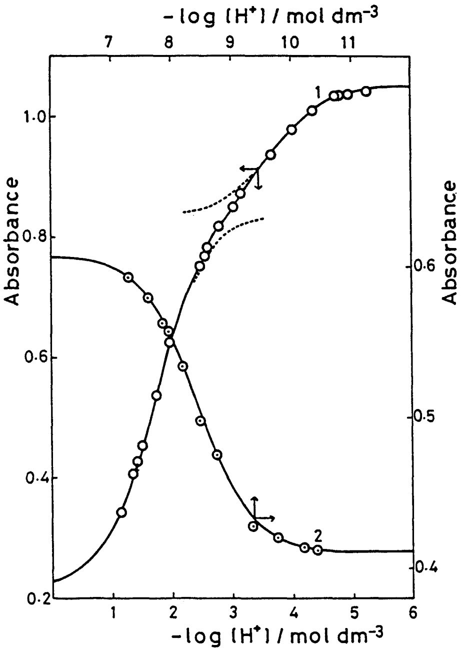


Fig. 3. Relation between absorbance and $-\log[\mathrm{H}^+]$ for QHQS.
[QHQS]: 5.65×10^{-5} (1) and 3.25×10^{-5} mol dm^{-3} (2). λ: 510 nm. 0.10 mol dm^{-3} (NaCl), 25 °C. Curve 1 is a theoretical one drawn by using $\log K_{\mathrm{a(hqNH)}}$ of 3.70 and $\log K_{\mathrm{a(qyNH)}}$ of 1.73 mol^{-1} dm^3. Curve 2 is the one drawn by using $\log K_{\mathrm{a(phOH)}}$ of 8.42 mol^{-1} dm^3.

Table 1. Protonation and Stability Constants

	$\log K_{\mathrm{a(qyNH)}}$ mol^{-1} dm^3	$\log K_{\mathrm{a(hqNH)}}$ mol^{-1} dm^3	$\log K_{\mathrm{a(phOH)}}$ mol^{-1} dm^3	Remarks	References
QHQS	1.73±0.10	3.70±0.10	8.42±0.10	0.10 mol dm^{-3} (NaCl), 25 °C	This work
HQS	—	4.06±0.11	8.97±0.10	0.10 mol dm^{-3} (NaCl), 25 °C	1b
	$\log\beta_1$ mol^{-1} dm^3	$\log\beta_2$ mol^{-2} dm^6			
$[\mathrm{Fe(qhqs)_2}]^{2-}$	11.88±0.20	21.9±0.5		0.10 mol dm^{-3} (NaCl), 25 °C	This work
$[\mathrm{Fe(hqs)_3}]^{4-}$ [a)]	8.4	15.1		0.01 mol dm^{-3} (—), 20 °C	12

a) The value of $\log\beta_3$ has been reported to be 21.75 mol^{-3} dm^9 (0.3 mol dm^{-3} (NaCl), 25 °C).[12)]

$[H^+]<6$ for K_{a2} and K_{a3}).

From the experimental data given in Fig. 3, $\log K_{a1}$, $\log K_{a2}$, and $\log K_{a3}$ were determined to be 8.42±0.10, 3.70±0.10, and 1.73±0.10 $mol^{-1}\,dm^3$ respectively (cf. Table 1). By means of a comparison of these protonation constants with those of ligands with related structures[1] and a consideration of the spectral characteristics (vide supra), K_{a1} was assigned to the protonation at the phenolate oxygen ($K_{a1}\equiv K_{a(phOH)}$); K_{a2}, to that at the 8-quinolinol nitrogen ($K_{a2}\equiv K_{a(hqNH)}$); and K_{a3}, to that at the 8-quinolyl nitrogen ($K_{a3}\equiv K_{a(qyNH)}$).

The molar-ratio and continuous variation methods revealed that the composition of the iron(II) complex with QHQS had 1 : 2 (metal : ligand) ratio at ca. pH 4.8. Additionally, a clear inflection point was noticed on the molar-ratio plot of unity at pH 1.5. On the basis of the hydrolysis constant of iron(II) ($\log K_{FeOH}=-9.5$ $mol\,dm^{-3}$ (1.0 $mol\,dm^{-3}$($NaClO_4$), 25 °C); $K_{FeOH}=[FeOH^+][H^+]/[Fe^{2+}]$[4]) and the protonation constants of QHQS, the following relation can be derived between the absorbance of the iron(II)–QHQS system and the total concentration of iron(II), C_M, under the conditions of $C_M \gg C_L$ below pH 2, where C_L is the total concentration of QHQS:[3]

$$(A-A_{min})/(A_{max}-A)=\beta_1 C_M/(K_{a(qyNH)}[H^+]+1)K_{a(phOH)}[H^+] \quad (6)$$

Here, A_{min}, A_{max}, and A stand for the absorbances of a solution of the ligand, of the mono-ligand complex, and of a solution in which the mono-ligand complex and the free ligand coexist at the hydrogen-ion concentration of $[H^+]$. The experimental plots obtained at 500 nm are given in Fig. 4 (line 1), from which the stability constant of the mono-ligand complex ($\beta_1=[Fe((H)qhqs)^+]/[Fe^{2+}][(H)qhqs^-]$), where $(H)qhqs^-$ specifies the ligand species protonated at the non-coordinating 8-quinolinol nitrogen) was calculated to be $\log \beta_1=11.88\pm0.20$ $mol^{-1}\,dm^3$ (cf. Table 1).

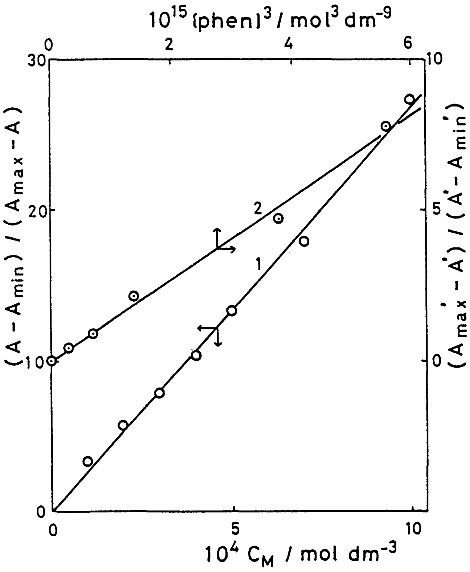


Fig. 4. Dependence of absorbance on total concentration of iron(II) for estimation of β_1 and on concentration of phen for that of β_2.
1: C_L: 1.00×10^{-5} $mol\,dm^{-3}$; $-\log\,[H^+]$: 1.44; and λ: 500 nm. 2: C_L: 4.46×10^{-5} $mol\,dm^{-3}$; C_M: 6.71×10^{-6} $mol\,dm^{-3}$; $-\log[H^+]$: 4.82; and λ: 550 nm. 0.10 $mol\,dm^{-3}$ (NaCl), 25 °C. Curve 1 is a theoretical one drawn by using $\log K_{a(phOH)}$ of 8.42, $\log K_{a(qyNH)}$ of 1.73, and $\log \beta_1$ of 11.88 $mol^{-1}\,dm^3$. Curve 2 is the one drawn by using $\log K_{a(phOH)}$ of 8.42 mol^{-1} dm^3, $\log \beta_{Fe(phen)_3}$ of 21.15 $mol^{-3}\,dm^9$ (0.1 $mol\,dm^{-3}$ (——), 25 °C),[5] and $\log \beta_2$ of 21.9 $mol^{-2}\,dm^6$.

The stability constant of the bis-ligand complex was determined by using a ligand-substitution reaction with 1,10-phenanthroline (phen). It was found that, at the wavelength of 550 nm, the absorbances due to the iron(II) complex with phen as well as those due to the free metal ion and the phen ligand species were negligibly small as compared with those due to the iron(II) complex with QHQS and the free QHQS species. Furthermore, $[Fe(phen)_3]^{2+}$ has as an exceptionally high stability constant as compared with the stability constants of $Fe(phen)^{2+}$ and $Fe(phen)_2{}^{2+}$.[5] Hence, the following relation can be derived between the absorbance of the reaction system and the total concentration of phen, C_{phen}, under the experimental conditions of $C_L \gg C_M$ and $C_{phen} > 3C_M$ at a constant pH of 4.9, where the ligand substitution reaction proceeds to a reasonable degree depending on C_{phen} ($=[phen]+3C_M(A_{max}'-A')/(A_{max}'-A_{min}')$), assuming the conformity to Beer's law and the material balance:

$$(A_{max}'-A')/(A'-A_{min}')=\beta_{Fe(phen)_3}K_{a(phOH)}{}^2[H^+]^2[phen]^3/\beta_2 C_L{}^2 \quad (7)$$

Here, A_{max}', A_{min}', and A' stand for the absorbances of a solution in which the ligand-substitution does not take place, one that takes place quantitatively, and one that takes place in fractions at the hydrogen-ion concentration of $[H^+]$. The experimental plots are given in Fig. 4 (line 2), from which the stability constant, β_2 ($=[[Fe(qhqs)_2]^{2-}]/[Fe^{2+}][qhqs^{2-}]^2$), was calculated to be $\log \beta_2=21.9\pm0.5$ $mol^{-2}\,dm^6$ with the use of $\log \beta_{Fe(phen)_3}$ of 21.15 $mol^{-3}\,dm^9$ (0.1 $mol\,dm^{-3}$(—), 25 °C)[5] (cf. Table 1).

Kinetics and Mechanism. The complex-formation-reaction kinetics were followed spectrophotometrically in the acidity region of pH 2.5—4.5 under the conditions of $C_L \gg C_M$. A single exponential absorbance vs. time curve was obtained; the logarithmic absorbance change-with-time plots were linear for more than 3.5 half-life periods. Furthermore, at a constant $[H^+]$, k_{obsd} increased linearly with an increase of C_L in the range of C_L/C_M of 6.6—26.4 and could be extrapolated to the point of origin within the limits of experimental error. Hence, it is deduced that the complex-formation reaction of iron(II) with QHQS proceeds through the coordination of the first QHQS to iron(II) as the rate-determining step.

Considerations of the hydrolysis constant of iron(II) and the protonation constants of QHQS indicate that, in a weakly acidic aqueous solution in which the complex-formation reaction proceeds, iron(II) and QHQS may be expected to contribute to the reaction in the forms of Fe^{2+} for the former and $Hqhqs^-$ and $qhqs^{2-}$ for the latter.[6] Additionally, the protonation and deprotonation processes can reasonably be assumed to be always in equilibrium when compared with the coordination reaction process.[7] Hence, the following relation can be derived:

$$d[[Fe(qhqs)_2]^{2-}]/dt=k_{obsd}([[Fe(qhqs)_2]^{2-}]_\infty-[[Fe(qhqs)_2]^{2-}]) \tag{8}$$

$$k_{obsd}=(k_{21}K_{a(phOH)}[H^+]+k_{22})C_L/\{(K_{a(qyNH)}[H^+]+1)K_{a(phOH)}[H^+]\} \tag{9}$$

where k_{2j} ($j=1$ and 2) refers to the rate constant for the pathway of Fe^{2+} with $H_{2-j}qhqs^{j-}$ and the suffix ∞, to the equilibrium state. In Fig. 5, k_{obsd}' ($\equiv k_{obsd}(K_{a(qyNH)}[H^+]+1)K_{a(phOH)}[H^+]C_L^{-1}$) is plotted against $[H^+]$ on the basis of the experimental data. The linear relation between k_{obsd}' and $[H^+]$ with a zero intercept indicates that the formation of the iron(II) complex with QHQS proceeds through a unique reaction pathway of Fe^{2+} with $Hqhqs^-$. The rate constant, k_{21}, is given in Table 2.

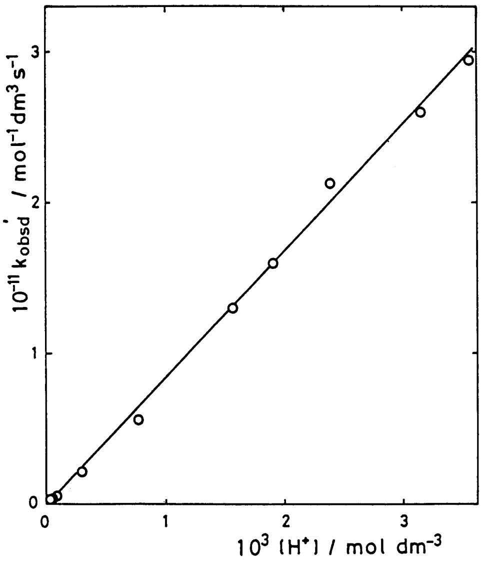


Fig. 5. Dependence of k_{obsd}' on $[H^+]$.
$k_{obsd}'\equiv k_{obsd}(K_{a(qyNH)}[H^+]+1)K_{a(phOH)}[H^+]C_L^{-1}$. C_L: 4.46×10^{-5} mol dm^{-3}; C_M: 6.71×10^{-6} mol dm^{-3}; and λ: 550 nm. 0.10 mol dm^{-3} (NaCl), 25 °C.

Several kinetic data on the iron(II) complex-formation reaction have been reported. Those of special interest to the present investigation are collected in Table 2. All these data relate to the rate constants of the first ligand-coordination to iron(II) as the rate-determining step. The rate constant for the formation pathway of Fe^{2+} with $Hqhqs^-$ is of a reasonable magnitude when compared with those compiled in Table 2, when differences in the formal charges of the ligands are taken into consideration. It can be deduced from Table 2 that the rate constant for the formation of pyridine nitrogen to iron(II) is of the order of 5×10^4—2×10^5 mol^{-1} dm^3 s^{-1} at 25 °C. However, no reliable rate constant can be estimated for the donation of phenolato oxygen to iron(II), because there have been no literature data on the oxygen-donating ligands except for one report on acetohydroxamic acid. In this report, the observed rate constants have been analyzed by assuming only a pathway of Fe^{2+} with a monoprotonated ligand species and with a complete neglect of the contribution of the pathway of Fe^{2+} with a deprotonated ligand species; taking that contribution into account would result in an over-estimation of the rate constant for the formation reaction pathway.

On the basis of this knowledge of the kinetics of the iron(II) complexes, our findings can not simply be attributed to a pathway in which a direct donation of phenolato oxygen to iron(II) is the mechanistic rate-determining step. Preferably, it can be considered reasonable to explain our results on the basis of a rapid donation of 8-quinolyl nitrogen to iron(II), followed by a chelate-ring closure through the donation of phenolato oxygen as the mechanistic rate-determining step. In fact, iron(II) forms a mono-ligand complex with the stability constants (log $\beta_{1(N)}$) of 0.71[8] and 0.6 mol^{-1} dm^3 [9] 0.5 mol dm^{-3} (pyridine+HNO_3), 25 °C; $\beta_{1(N)}=[Fepy^{2+}]/[Fe^{2+}][py]$), but no stability constant data have been reported on the iron(II) complex with phenol and related oxygen-donating ligands. In case this rapid donation of 8-quinolyl nitrogen precedes the rate-determining phenolato-oxygen donation, then k_{21} can be approximated in a

Table 2. Rate Constants for Iron(II) Complexes with QHQS and Related Ligands

Ligand[a]	Pathway	k_{ij}/mol^{-1} dm^3 s^{-1}	Remarks	References
QHQS	$Fe^{2+}+Hqhqs^-$ (k_{21})	$(3.16\pm0.20)\times10^5$	0.10 mol dm^{-3} (NaCl), 25 °C	This work
tpy	Fe^{2+}+tpy (k_{20})	5.6×10^4	Variable (—), 25 °C[d]	13
tpy	Fe^{2+}+tpy (k_{20})	$(8.0\pm0.5)\times10^{4,b)}$ $(2.1\pm0.3)\times10^{4,c)}$	0.10 mol dm^{-3} ($NaClO_4$), 25 °C	14
bpy	Fe^{2+}+bpy (k_{20})	1.6×10^5	Variable (—), 25 °C[d]	15
tptz	Fe^{2+}+tptz (k_{20})	1.3×10^5	0.1 mol dm^{-3} (KCl), 25 °C	16
$CH_3CONHOH$(HL)	Fe^{2+}+HL (k_{20})	$(6.69\pm0.20)\times10^4$	0.10 mol dm^{-3} ($NaNO_3$), 10 °C	17

a) tpy: 2,2′:6′,2″-terpyridine; bpy: 2,2′-bipyridine; tptz: 2,4,6-tri(2-pyridyl)-1,3,5-triazine; and $CH_3CONHOH$: acetohydroxamic acid. b) $C_L \gg C_M$. c) $C_M \gg C_L$. d) No adjustment to a constant ionic strength.

reasonable way by a product of the stability constant of an intermediate, Fe(Hqhqs-N)$^+$, i.e., the stability constant, $\beta_{\mathrm{Fe-N}}$, and the chelate-ring-closure rate constant, $k_{21(\mathrm{crc})}$. By using $\beta_{1(N)}$ as a first approximation to $\beta_{\mathrm{Fe-N}}$, then $k_{21(\mathrm{crc})}$ can be calculated to be (6—8)$\times 10^4\,\mathrm{s}^{-1}$. This value is about 50 times as small as the rate constants for the coordinated water exchange, $3.2\times10^6\,\mathrm{s}^{-1}$ (0.1 mol dm^{-3}(HClO$_4$), 25 °C)$^{10)}$ and $(4.39\pm0.25)\times10^6\,\mathrm{s}^{-1}$ (0.0546—0.378 mol dm^{-3} (HClO$_4$), 25 °C),$^{11)}$ based on the ^{17}O NMR data, but it can be considered of a reasonable magnitude for the kinetic characteristics of iron(II) as a member of the first-row transition-metal divalent cations. Before the general features of the multidentate ligand kinetics of iron(II) can be established, more kinetic data will be required on the formation reaction of iron(II) with phenolato oxygen-containing multidentate ligands; this will be the purpose of our succeeding investigation. However, it can be stated that the complex formation of QHQS as a terdentate N-N-O ligand to iron(II) proceeds with a rapid donation of the first QHQS through its 8-quinolyl nitrogen, followed by a chelate-ring closure, with the coordination of the phenolato oxygen as the mechanistic rate-determining step and that of azo nitrogen to complete a fused chelate-ring structure.

References

1) a) K. Hayashi, K. Okamoto, J. Hidaka, and H. Einaga, *J. Chem. Soc., Dalton Trans.*, **1982**, 1377; b) K. Hayashi, T. Ohsawa, K. Okamoto, J. Hidaka, and H. Einaga, *J. Coord. Chem.*, **12**, 243 (1983); c) H. Iwasaki, K. Okamoto, J. Hidaka, and H. Einaga, *J. Coord. Chem.*, **12**, 219 (1983); d) I. Ohkura, K. Fujiwara, K. Okamoto, J. Hidaka, and H. Einaga, *J. Coord. Chem.*, **13**, 221 (1984); e) Z.-P. Bai, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 1959 (1988).

2) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

3) Y. Hara, K. Okamoto, J. Hidaka, and H. Einaga, *Bull. Chem. Soc. Jpn.*, **57**, 1211 (1984).

4) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Chem. Soc., London (1964), Sp. Pub. No. 17, p. 52.

5) Ref. 4, p. 665.

6) The protonation equilibrium at the non-coordinating 8-quinolinol nitrogen is assumed to make no important contribution to the formation-reaction kinetics of iron(II) with QHQS.

7) Ref. 3 and the references cited therein.

8) Ref. 4, p. 440.

9) D. D. Perrin, "Stability Constants of Metal-Ion Complexes," Part B, Organic Ligands, Pergamon, Oxford (1979), IUPAC Chemical Data Series, No. 22, p. 264.

10) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

11) Y. Ducommun, K. E. Newman, and A. E. Merbach, *Inorg. Chem.*, **19**, 3696 (1980).

12) Ref. 4, p. 610.

13) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

14) R. Mohr and R. van Eldik, *Inorg. Chem.*, **24**, 3396 (1985).

15) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

16) G. K. Pagenkopf and D. W. Margerum, *Inorg. Chem.*, **7**, 2514 (1968).

17) L. A. Dominey and K. Kustin, *Inorg. Chem.*, **23**, 103 (1984).