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Stoichiometry and Kinetics of Base-Promoted Disproportionation with Concomitant Ligand Oxidation of Tetracyano(1,2-diamine)ferrate(III)

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Stoichiometry and kinetics were examined to probe the mechanism of the disproportionation of tetracyano(1,2-diamine)ferrate(III) with ethylenediamine (en), (*R*)-1,2-diaminopropane (*R*-pn), (*R*,*R*)-1,2-diaminocyclopentane (*R*-cptn), (*R*,*R*)-1,2-diaminocyclohexane (*R*-chxn), *N*,*N*′-dimethylethylenediamine (*s*-Me_2en), and 2-(aminomethyl)pyridine (pica) as diamines. The disproportionation leads to the formation of the corresponding iron(II) chelates of intact diamine and 1,2-diimine in the ratio of 3:1 for the *R*-chxn chelates. The rate was expressed in a third-order rate equation, $-\mathrm{d}[[\mathrm{Fe(CN)_4(diamine)}]^-]/\mathrm{d}t = k[[\mathrm{Fe(CN)_4(diamine)}]^-]^2[\mathrm{OH}^-]$, where the values of k are 3.2×10^4, 2.06×10^4, 1.64×10^3, 2.82×10^3, 5.74×10^7, and 1.71×10^8 M^{-2} s^{-1} for en, *R*-pn, *R*-cptn, *R*-chxn, pica, and *s*-Me_2en chelates, respectively. Substitution of methyl groups at the amine nitrogens enhanced the disproportionation by a factor of 3.2×10^3, while substitution at carbon atoms of ethylenediamine with alkyl groups retarded the reaction slightly. The dehydrogenation of the coordinated diamines in the presence of hexacyanoferrate(III) also took a third-order rate expression, $\mathrm{d}[[\mathrm{Fe(CN)_4(diimine)}]^{2-}]/\mathrm{d}t = k_1[[\mathrm{Fe(CN)_4(diamine)}]^-]^2[\mathrm{OH}^-] + k_2[[\mathrm{Fe(CN)_4(diamine)}]^-][[\mathrm{Fe(CN)_6}]^{3-}][\mathrm{OH}^-]$. The rate constants, k_2, have the values of 1.7×10^4, 2.8×10^4, 1.3×10^3, 4.4×10^8, and 1.7×10^7 M^{-2} s^{-1} for en, *R*-pn, *R*-chxn, *s*-Me_2en, and pica chelates, respectively. The kinetic effect of selective amine deuteration on the dehydrogenation was determined with use of pica and 2-(aminodideuteriomethyl)pyridine (pica-d_2) chelates. The observation of a large solvent isotope effect (7.2 for H_2O to D_2O) indicates that deprotonation from the N–H bond is necessary to initiate the dehydrogenation of coordinated diamines. These results together with electrochemical results support a mechanism that includes a base-assisted intramolecular electron transfer mediated by rapid electron exchange between low-spin Fe(II) and low-spin Fe(III) species as the essential step in this reaction.

Introduction

Oxidative dehydrogenation of amines coordinated to transition-metal ions has been reported with Ru(II),[2-8] Fe(II),[9-11] Ni(II),[12-17] Cu(II),[18] and Co(II).[19] The reaction may serve as a useful model for oxidation catalysts of metal-bound organic substrates. These reactions have been recognized to proceed via higher oxidation states, such as Ni(III) and Ru(III),[20] and several metal complexes with higher oxidation states have been isolated.[10,16]

The introduction of one double bond into the ligand requires a two-electron oxidation. The oxidation state of the higher valence metal chelate that undergoes the ligand oxidation is higher by one unit in Ni(III), Fe(III), and Ru(III). This situation requires further redox processes to cause the ligand oxidation. Two mechanisms have been proposed for these processes: (i) Mocella and Barefield have proposed successive oxidation via radical species for Ni(III) macrocyclic amine chelates.[17] But the reaction products from this reaction are complicated, and a detailed mechanism of the dehydrogenation is still unclear for the later stage. (ii) The disproportionation of Ru(III) to Ru(II) and Ru(IV) was earlier proposed for $Ru(NH_3)_5(BzNH_2)$ by Taube[8] and recently modified by Ridd and Keene as the disproportionation involves a Ru(III) complex with deprotonated amines in order to overcome the unfavorable redox potential of Ru(IV).[21] Kinetic studies with isolated compounds with higher valence have not been reported yet.

Tetracyano(1,2-diamine)ferrate(II) is easily oxidized to the corresponding tetracyano(1,2-diimine)ferrate(II) with various oxidants. This system is the simplest structure to undergo dehydrogenation because it has only one diamine ligand and four nondissociable CN^- groups. It is one of the most suitable candidates to be examined, because a series of tetracyano(diamine)ferrate(II), tetracyano(diimine)ferrate(II), and tetracyano(diamine)ferrate(III) complexes have been prepared and characterized.[22-25] Costa Ferreira and Toma have recently reported a detailed study with tetracyano(ethylenediamine)ferrate(II) and have proposed a mechanism in which the Fe(III) complex is involved as the intermediate.[26] We herein report the results of a stoichiometry and kinetics study of the base-promoted ligand oxidation of a series of Fe(III) complexes and propose a mechanism involving an intramolecular electron transfer from a metal-bound organic anion to Fe(III).

Experimental Section

Materials. Sodium tetracyano(diamine)ferrate(II), where diamine = ethylenediamine (en),[22] *N*,*N*′-dimethylethylenediamine (*s*-Me_2en),[22] 2-(aminomethyl)pyridine (pica),[22] (*R*)-1,2-diaminopropane (*R*-pn),[23] (*R*,*R*)-*trans*-1,2-diaminocyclohexane (*R*-chxn),[23] and (*R*,*R*)-*trans*-1,2-diaminocyclopentane (*R*-cptn),[24] were prepared as reported previously. Sodium tetracyano(diamine)ferrate(III) complexes, where diamine = en,[22] *s*-Me_2en,[22] *R*-pn,[25] *R*-cptn,[25] and *R*-chxn,[25] were also prepared as previously reported from the corresponding Fe(II) complexes. A list of the ligands used in this report as well as of their formulas and abbrevi-

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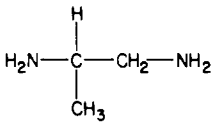
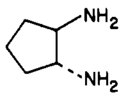
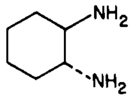
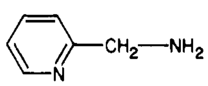
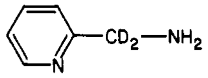
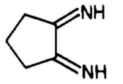
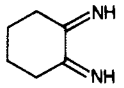
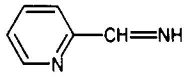
Table I. Abbreviations and Chemical Formulas for Amine and Imine Ligands

ligand	formula	abbrev
ethylenediamine	$H_2N—CH_2—CH_2—NH_2$	en
(*R*)-1,2-diaminopropane	 $H_2N—C(H)(CH_3)—CH_2—NH_2$	*R*-pn
(*R*,*R*)-1,2-diaminocyclopentane		*R*-cptn
(*R*,*R*)-1,2-diaminocyclohexane		*R*-chxn
N,*N*′-dimethylethylenediamine	$CH_3—NH—CH_2—CH_2—NH—CH_3$	*s*-Me$_2$en
2-(aminomethyl)pyridine		pica
2-(aminodideuteriomethyl)pyridine		pica-*d*$_2$
1,2-diiminoethane	$HN{=}CH—CH{=}NH$	o-en
1,2-diiminopropane	$HN{=}C(CH_3)—CH{=}NH$	o-pn
1,2-diiminocyclopentane		o-cptn
1,2-diiminocyclohexane		o-chxn
glyoxal bis(methylimine)	$CH_3—N{=}CH—CH{=}N—CH_3$	o-Me$_2$en
2-(iminomethyl)pyridine		o-pica

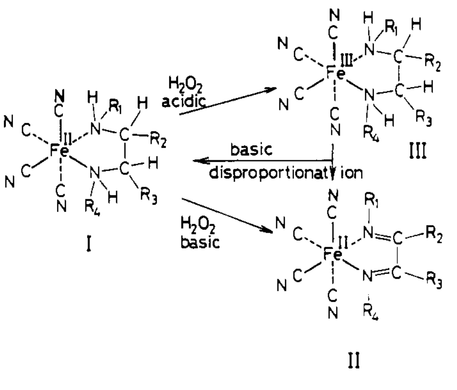
ations is given in Table I, where the dehydrogenated ligands, diimines, are denoted by the prefix of o-. Commercially available potassium hexacyanoferrate(III) (Katayama Kagaku) was used without further purification.

Preparation of Deuterated pica Chelates. 2-(Aminodideuteriomethyl)pyridine (pica-*d*$_2$). This was prepared from 2-cyanopyridine by a method similar to that of Boyer et al.[27] using $LiAlD_4$ (10 g) and D_2O instead of $LiAlH_4$ and H_2O; bp 81.5–82.0 °C (10 mmHg).

Sodium Tetracyano(2-(aminodideuteriomethyl)pyridine)ferrate(II) Trihydrate, $Na_2[Fe(CN)_4(pica\text{-}d_2)]\cdot 3H_2O$. To a 200-mL three-necked round-bottomed flask equipped with a mechanical stirrer and a dropping funnel was placed ferrous perchlorate hexahydrate (13.07 g, 0.036 mol) under nitrogen, and then 20 mL of methanol flushed with nitrogen was added through a serum cap with a syringe. The flask was immersed in an ice–water bath. pica-*d*$_2$ (4.00 g, 0.036 mol) was added with stirring, followed by addition of a solution of NaCN (7.05 g, 0.144 mol) in 60 mL of water from the dropping funnel with vigorous stirring. The reaction mixture was filtered under nitrogen after 30 min. To the filtrate were added 60 mL of ethanol and 60 mL of water, and the mixture was filtered under nitrogen to remove a small amount of blue precipitate. To the brown filtrate was added ethanol until the solution became turbid, and the mixture was allowed to stand in a refrigerator overnight. Separated yellow crystals were collected on a filter and were washed with ethanol and ether, sequentially; yield 4.0 g (33%). Anal. Calcd for $Na_2[Fe(CN)_4(pica\text{-}d_2)]\cdot 3H_2O$: C, 32.45; H, 4.12; N, 22.71. Found: C, 30.29; H, 4.35; N, 21.09.

Sodium Tetracyano(2-(aminodideuteriomethyl)pyridine)ferrate(III) Dihydrate, $Na[Fe(CN)_4(pica\text{-}d_2)]\cdot 2H_2O$. A mixture of 30% hydrogen peroxide (0.6 mL) and methanol (5 mL) was added to $Na_2[Fe(CN)_4(pica\text{-}d_2)]\cdot 3H_2O$ (1.9 g, 5.1 mmol) dispersed in a mixture of ethanol (20 mL) and 1 M HCl (6 mL) at 5 °C. After 5 min, the mixture was filtered. Methanol (10 mL) and then ether was added until the yellow crystals began to separate at 0 °C, and the mixture was allowed to stand in a refrigerator overnight. Separated yellow crystals were collected on a filter, washed with ethanol and ether sequentially, and dried in vacuo. Anal. Calcd for $Na[Fe(CN)_4(pica\text{-}d_2)]\cdot 2H_2O$: C, 36.50; H, 4.28; N, 25.54. Found: C, 36.34; H, 4.38; N, 25.94.

Scheme I



Physical Measurements. Electronic spectra were recorded with a Shimadzu UV-210A spectrophotometer. Infrared spectra were obtained on a Jasco IRA-2 spectrophotometer using Nujol mulls. ^1H NMR spectra were obtained on a JEOL JNM-MH-100 spectrometer using sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) as an internal reference. CD spectra were measured on a Jasco J-40 recording polarimeter. pHs of aqueous solutions were measured on a Toa HM-5A pH meter.

Determination of Product Distribution. Stock solutions of Fe(III) chelates (13.1 and 1.31 mmol/L) were prepared by adding weighed amounts of the chelates to 50 mL of 1×10^{-4} M hydrochloric acid. The reaction was initiated by addition of an aliquot of the solution (3 or 5 mL) to a borate or a phosphate buffer (4 or 10 mL, respectively). At suitable time intervals, visible spectra were recorded until no further change was observed and the concentration of the tetracyano(diimine)ferrate(II) chelate was determined from the absorbance on the basis of their molar absorption coefficients at 515 nm.[22,25] The concentration of the optically active diamine Fe(II) chelates was obtained on CD spectra at 450 nm.[23]

Kinetics of Disproportionation of Fe(III) Chelates under Basic Conditions. A solution of Fe(III) chelate, $Na[Fe(CN)_4(diamine)]\cdot nH_2O$, in 10^{-3} M HCl and a buffer solution were equilibrated at 25 °C and were mixed. The stock solution (borate for pH 6.0–9.2 and phosphate for pH 9.2–10.0) contained sodium chloride to maintain an ionic strength of $\mu = 0.3$ M. Formation of tetracyano(1,2-diimine)ferrate(II) from tetracyano(diamine)ferrate(III) was followed spectrophotometrically at 515 nm, λ_{max} for the diimine chelates, at 25 °C. Slow reactions (half-life > 2 min) were followed by the spectrophotometer, and faster reactions (half-life <30 s) were followed with a Union Giken RA-1100 stopped-flow spectrophotometer. For the measurements of isotope effect, the ionic strength was adjusted to 0.1 M. The kinetic measurements in D_2O were carried out with the same procedure as described above using D_2O and DCl in place of H_2O and HCl. The pD was determined by the equation pD = pH + 0.4 on the pH meter.[28]

Kinetics of Ligand Oxidation of the Fe(III) Chelates with Hexacyanoferrate(III). An aqueous solution of $[Fe(CN)_6]^{3-}$, 1.36×10^{-2} M, was diluted either to 10 or 20 times with borate and phosphate buffers. An aliquot (3.0 mL) of this solution was placed in a photometric cell and thermostated at 25 ± 0.1 °C for 20 min. A stock solution of $[Fe(CN)_4(diamine)]^-$ in 10^{-3} M HCl was added to the $[Fe(CN)_6]^{3-}$ solution, and the increase in absorbance at 515 nm was monitored at 25 ± 0.1 °C. The product, $[Fe(CN)_4(diimine)]^{2-}$, was not stable in the presence of excess $[Fe(CN)_6]^{3-}$, and the initial velocity for the formation of $[Fe(CN)_4(diimine)]^{2-}$ was obtained from the tangent of a slope at time 0 for the plots of absorbances against reaction periods by dividing by the molar absorption coefficients of the diimine chelates.

Electrochemistry of $[Fe(CN)_4(diamine)]^{2-}$. Cyclic voltammetry measurements were made with an instrument composed of a NF circuit Block FG-121B function generator, a Riken Denshi F-3EH XY recorder, and a handmade potentiostat, originally designed by Dr. Kato of Tohoku University, using a saturated KCl–AgCl electrode as a reference electrode and platinum-plate and platinum-spiral working and auxiliary electrodes, respectively. Measurements were made on solutions con-

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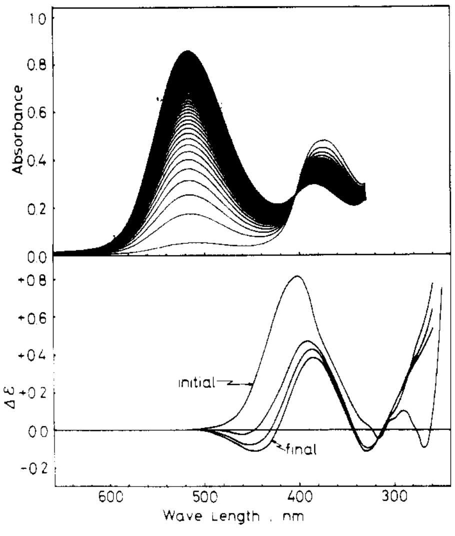

Figure 1. Electronic and circular dichroism spectral changes of Na[Fe(CN)$_4$(R-chxn)]·3H$_2$O on addition to pH 10.9 phosphate buffer at 25 °C: (top) electronic spectral changes, [Fe^{III}]$_0$ = 6.18 × 10^{-4} M, repetition period 2 min; (bottom) CD spectral changes, [Fe^{III}]$_0$ = 4.74 × 10^{-3} M, scanning speed 10 nm min^{-1}. Δε was calculated on the concentration of [Fe^{III}]$_0$.

taining 10^{-3} M [Fe(CN)$_4$(diamine)]$^{2-}$ with use of 0.1 M NaClO$_4$ as supporting electrolyte; nitrogen was passed for 20 min prior to the measurements.

Results

A general outline of the redox relationship among Fe(II) and Fe(III) complexes is shown in Scheme I.

Tetracyano(1,2-diamine)ferrate(II) (I) undergoes oxidative dehydrogenation with various oxidants such as H$_2$O$_2$, ClO$_2^-$, O$_2$, and [Fe(CN)$_6$]$^{3-}$ under neutral or basic conditions.[22] The product, tetracyano(1,2-diimine)ferrate(II) (II), has been isolated and characterized by several spectral properties and X-ray crystallography.[29] The spectrophotometric quantitative analyses of this class of compounds are easily determined because of the intense metal to ligand charge-transfer absorption at ca. 515 nm. Tetracyano(1,2-diamine)ferrate(III) complexes (III) have been isolated as sodium salts by oxidation of I under acidic conditions.[22,25] The difference in the reaction conditions for preparation of II and III suggests that III is the intermediate of II. This was confirmed by spectral changes of III on addition of alkaline buffer solution.

Base-Induced Disproportionation of Fe(III) Chelates. On addition of the optically active [Fe(CN)$_4$(R-chxn)]$^-$ to basic aqueous solution, spectral changes occurred in electronic and CD spectra in the visible region as shown in Figure 1. The absorption at 515 nm attributable to II with isosbestic points at 398 and 298 nm in the visible spectra and the minor negative component of [Fe(CN)$_4$(R-chxn)]$^{2-}$ developed in CD spectra. These spectral changes are consistent with reduction of the metal ion and ligand oxidation. This disproportionation reaction yields chelate compounds with differing unsaturation: the dehydrogenated amines and intact amines coordinated to Fe(II). Yields for the formation of II with en, R-pn, R-cptn, R-chxn, and s-Me$_2$en as diamines were determined from the absorption at 515 nm. The amounts of II never exceeded 25% (the maximum permissible for the proposed mechanism) of the initial amount of III. The yield of [Fe(CN)$_4$(o-chxn)]$^{2-}$ from [Fe(CN)$_4$(R-chxn)]$^-$ was nearly 25% above pH 10, while the reduced product, [Fe(CN)$_4$(R-chxn)]$^{2-}$, formed in ca. 75% yield as determined by CD spectral measurements. The stoichiometry of the reaction is expressed by eq 1.

$$4[\mathrm{Fe(CN)_4}(R\text{-chxn})]^- + 4\mathrm{OH}^- \rightarrow [\mathrm{Fe(CN)_4(o\text{-}chxn)}]^{2-} + 3[\mathrm{Fe(CN)_4}(R\text{-chxn})]^{2-} + 4\mathrm{H_2O} \quad (1)$$

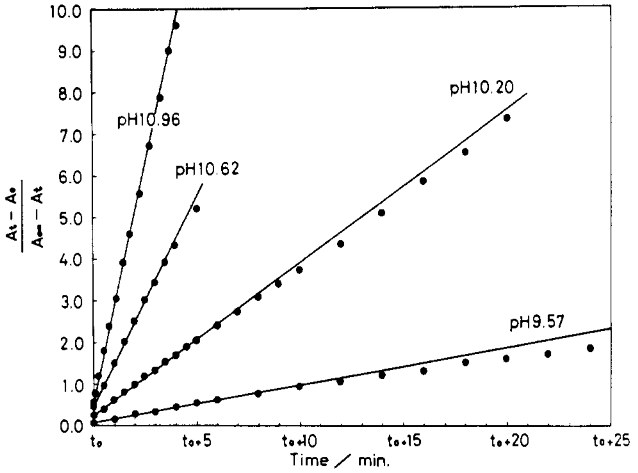

Figure 2. Second-order rate plots of the disproportionation of Na[Fe(CN)$_4$(en)]·3H$_2$O.

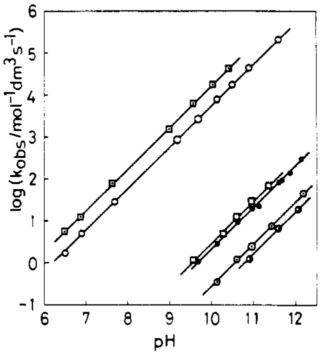

Figure 3. pH profiles of the observed second-order rate constants for the disproportionation of [Fe(CN)$_4$(diamine)]$^-$ for the following diamines: (□) en; (⊡) s-Me$_2$en; (○) pica; (●) R-pn; (⊙) R-chxn; (◑) R-cptn.

For the pica chelate, in which a pyridine ring functions as a monoimine, the stoichiometry is expressed by eq 2.

$$2[\mathrm{Fe(CN)_4(pica)}]^- + 2\mathrm{OH}^- \rightarrow [\mathrm{Fe(CN)_4(pica)}]^{2-} + [\mathrm{Fe(CN)_4(o\text{-}pica)}]^{2-} + 2\mathrm{H_2O} \quad (2)$$

The yield of II increased with substitution of alkyl groups on the carbon atom(s) of ethylenediamine: R-chxn > R-pn > en, with the exception of a small yield for R-cptn, ca. 10%, for which steric hindrance is expected to be responsible.

The increase in the initial concentration of III enhanced the formation of II. This indicates that diimine formation requires intermolecular process(es) between two Fe chelates. Also, the pH of the solution has an effect on the yield of II. This is dependent on the particular diimine used and is due to nucleophilic attack of OH$^-$ on the imine bonds.[30-32]

Kinetics of the Disproportionation. The rate of disproportionation of III was measured by monitoring the increase in absorbance at 515 nm in borate or phosphate buffer solution at constant ionic strength between pH 6.0 and 11.0 at 25 °C. Preliminary measurements showed that the rate was not affected by the presence of air. Therefore, all the manipulations were conducted in the presence of air.

The conversion of III, x, was expressed by the ratio of the absorbance at time t, A_t, to that at infinite time, A_∞, which was measured after at least 20 half-lives. Since the reactants have no absorption at 515 nm, the remaining portion of III is $(A_\infty - A_t)/A_\infty$. In most kinetic runs, the plots of $(A_t - A_0)/(A_\infty - A_t)$ against time gave a straight line for at least 80% of the conversion. The plots for [Fe(CN)$_4$(en)]$^-$ at various pHs are shown as a typical example in Figure 2. From the slope, the second-order rate

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Table II. Third-Order Rate Constants of Disproportionation of $[Fe(CN)_4(diamine)]^-$

	k/mol^{-2} dm^6 s^{-1}		k/mol^{-2} dm^6 s^{-1}
s-Me$_2$en	$(1.71 \pm 0.15) \times 10^8$	*R*-chxn	$(2.82 \pm 0.27) \times 10^3$
en	$(3.19 \pm 0.12) \times 10^4$	*R*-cptn	$(1.64 \pm 0.10) \times 10^3$
R-pn	$(2.06 \pm 0.17) \times 10^4$	pica	$(5.74 \pm 0.26) \times 10^7$

Table III. Isotope Effect on Disproportionation of $[Fe(CN)_4(pica)]^-$

solvent	diamine	k/mol^{-2} dm^6 s^{-1}	comparison	
H_2O	pica	$(5.1 \pm 1.7) \times 10^7$	1.0	
H_2O	pica-d_2	$(3.0 \pm 1.0) \times 10^7$	1/(1.7 ± 0.4)	
D_2O	pica	$(7.2 \pm 2.5) \times 10^6$	1/(7.2 ± 1.7)	1.0
D_2O	pica-d_2	$(4.1 \pm 1.6) \times 10^6$		1/(1.8 ± 0.4)

Table IV. Third-Order Rate Constants for $[Fe(CN)_4(diimine)]^{2-}$ Formation in the Presence of $[Fe(CN)_6]^{3-}$

diamine	k_1/mol^{-2} dm^6 s^{-1}	k_2/mol^{-2} dm^6 s^{-1}	diamine	k_1/mol^{-2} dm^6 s^{-1}	k_2/mol^{-2} dm^6 s^{-1}
s-Me$_2$en	2.0×10^8	4.4×10^8	*R*-chxn	1.3×10^3	1.3×10^3
en	1.9×10^3	1.7×10^4	pica	4.5×10^7	1.7×10^7
R-pn	1.2×10^4	2.8×10^4			

constant, k_{obsd}, was obtained by dividing the slope by the concentration of III at time t_0. The second-order rate constants were dependent on the buffer pH. The pH profiles of the rate constants for the reaction of III with en, *R*-pn, *R*-cptn, *R*-chxn, *s*-Me$_2$en, and pica chelates are shown in Figure 3. The slope of each straight line has the value of 1.0. Thus the rate of the disproportionation is expressed by eq I. The third-order rate constants

$$-d[III]/dt = k_{obsd}[III]^2 = k[III]^2[OH^-] \qquad (I)$$

are tabulated in Table II. The dilution of the buffer did not affect the rate. The rate expression for $[Fe(CN)_4(pica)]^-$ holds for a wide range of pH, between 6.0 and 11.0; thus, the same mechanism operates for the complexes studied here.

Isotope Effects on the Disproportionation. In order to measure the isotope effect on the rate, 2-(aminodideuteriomethyl)pyridine (pica-d_2) was prepared from 2-cyanopyridine by reduction with $LiAlD_4$. ^1H NMR spectra of the Fe(II) chelate revealed the absence of signals of the methylene group at 3.95 ppm.[22] Isotopic purity was estimated from integration of each signal to be more than 95%. The tetracyanoferrate(III) chelate was prepared from the Fe(II) chelate.

The isotope efect on rates was determined with use of $[Fe(CN)_4(pica\text{-}d_2)]^-$ and $[Fe(CN)_4(pica)]^-$ in either H_2O or D_2O medium. The results are tabulated in Table III. The isotope effect of the N-H vs. the N-D bond is large, 7.2, but that of C-H vs. C-D is moderate, 1.7.

Kinetics of Ligand Oxidation with $[Fe(CN)_6]^{3-}$. In the presence of $[Fe(CN)_6]^{3-}$, the Fe(III) chelates, III, are oxidized by a common oxidant, $[Fe(CN)_6]^{3-}$. Therefore, the relative reactivity of III with respect to the particular diamine will be determined from the oxidation with $[Fe(CN)_6]^{3-}$. The product, II, was further oxidized in the presence of excess $[Fe(CN)_6]^{3-}$ to species that have virtually no absorption around 515 nm for en, *R*-pn, and *R*-chxn chelates. Therefore, the ratios of $[[Fe(CN)_6]^{3-}]$ to [III] were kept between 1 and 6. The initial velocities of formation of II were measured by the absorption at 515 nm. The plots of the initial rates against concentrations of $[Fe(CN)_6]^{3-}$ gave a straight line, as shown in Figure 4 for $[Fe(CN)_4(en)]^-$. The intercept varies with increase in the initial concentration of the Fe(III) chelates. The rate of the formation of II is given by eq II. Each observed second-order

$$d[II]/dt = k_{1,obsd}[III]^2 + k_{2,obsd}[III][[Fe(CN)_6]^{3-}] \qquad (II)$$

rate constant was proportional to $[OH^-]$. The third-order rate constants, k_1 and k_2, were derived by dividing the second-order rate constants by $[OH^-]$. The third-order rate constants are listed in Table IV. The rate expression for the formation of the diimine chelate $[Fe(CN)_4(o\text{-}en)]^{2-}$ by oxidation of $[Fe(CN)_4(en)]^-$ with $[Fe(CN)_6]^{3-}$ has been recently reported by Costa Ferreira and Toma.[26] It takes the form of the second term of eq II, and the third-order rate constant is $(1.9 \pm 0.1) \times 10^4$ M^{-2} s^{-1}, which is in good agreement with the present results, 1.7×10^4 M^{-2} s^{-1}. The rate constants for the first term should coincide with those found for the disporportionation. But under the reaction conditions of small concentrations of III, there are considerably more errors in the rate constants than for the disporportionation of the iron(III) chelates listed in Table II.

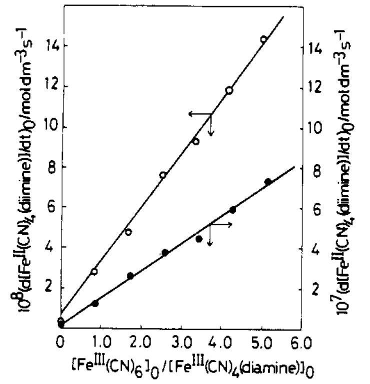


Figure 4. Plots of initial rate of formation of $[Fe(CN)_4(o\text{-}en)]^{2-}$ from $[Fe(CN)_4(en)]^-$ in the presence of $[Fe(CN)_6]^{3-}$. Initial concentration of $[Fe(CN)_4(en)]^-$: (○) 1.97×10^{-4} M; (●) 4.07×10^{-4} M.

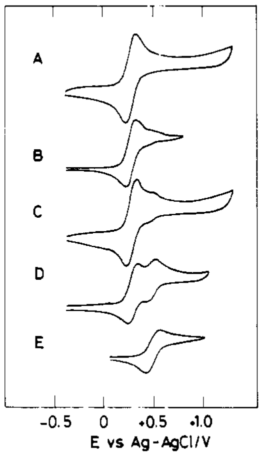


Figure 5. (A-D) Cyclic voltammograms of $[Fe(CN)_4(pica)]^{2-/-}$ with varying pH: (A) pH 10.0; (B) pH 10.5; (C) pH 11.0; (D) pH 11.5. (E) Cyclic voltammogram of $[Fe(CN)_4(o\text{-}pica)]^{2-/-}$ at pH 7.0.

Table V. Half-Wave Potentials of $[Fe(CN)_4(diamine)]^{2-/-}$

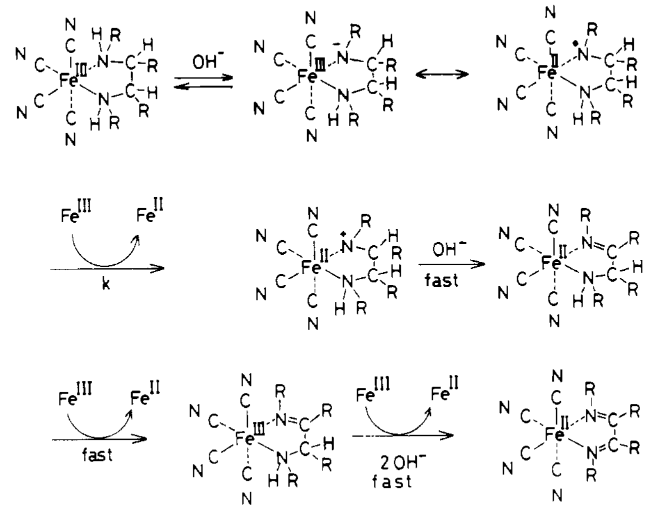
diamine	$E_{1/2}$/V (vs. NHE)	diamine	$E_{1/2}$/V (vs. NHE)
pica	0.45	*R*-pn	0.33
s-Me$_2$en	0.37	en	0.32
R-cptn	0.34	*R*-chxn	0.32

Electrochemical Properties. The half-wave potentials of the $[Fe(CN)_4(diimine)]^{2-/-}$ couples were measured with use of cyclic voltammetry. All the cyclic voltammograms are consistent with reversible processes. The results are listed in Table V. The redox potential of the *s*-Me$_2$en complex is more anodic than that of the en chelate, while alkyl substituents at carbon atom(s) cause the potential to move cathodically. Cyclic voltammograms of $[Fe(CN)_4(pica)]^{2-/-}$ were measured in NaOH solutions with varying pH. At pH 10.0 only a reversible peak was observed at the potential of $[Fe(CN)_4(pica)]^{2-/-}$. But when the pH was increased, a second reversible peak appeared at the potential of $[Fe(CN)_4(o\text{-}pica)]^{2-/-}$.[22] The voltammogram is shown at the bottom of Figure 5.

Discussion

Disproportionation of $[Fe(CN)_4(diamine)]^-$ (III) yields Fe(II) chelates of an intact diamine, I, and a dehydrogenated diimine, II, as shown in Scheme I. This disproportionation confirms the

Scheme II



intermediacy of Fe(III) compounds during the course of oxidative dehydrogenation of Fe(II) chelates with various oxidants. For the *R*-chxn chelate, the yields of II are about 25%, the remainder of the disproportionation product being the Fe(II) diamine complex. The yields of en and *R*-pn chelates are about 20% under the conditions of low pH and initial concentrations between 7 and 8 mM. Successive visible spectra taken during a reaction exhibited isosbestic points, and the product distribution is assumed to be unchanged during a reaction. The stoichiometry of the disproportionation can be postulated for $[Fe(CN)_4(diamine)]^-$ as shown in eq 3.

$$4\mathrm{III} + 4\mathrm{OH}^- \rightarrow \mathrm{II} + 3\mathrm{I} + 4\mathrm{H_2O} \qquad (3)$$

The formation of II requires four deprotonation steps from the coordinated diamine. The participation of the intermediates tetracyano(iminoamine)ferrates(II) and their iron(III) counterparts is expected, although the amounts of these species are always small, based on spectrophotometric determination. This observation shows that the monoimine complex is dehydrogenated in preference to III due to the increased acidity of the allylic type CH_2 of the monoimine. The presence of small amounts of the Fe(II) chelate of the monoimine has been confirmed with the products of the *s*-Me_2en chelates with use of ^{1}H NMR[22] and has been observed for the oxidation of Ru chelates of 1,2-diamino-2-methylpropane.[7] The observation of negligible monoimine chelates indicates that the rate-determining step corresponds to the formation of this species and the following reactions are fast.

On the basis of the discussions described above, a mechanism that involves two consecutive one-electron transfers is proposed and is shown in Scheme II.

As shown in Figure 2, the rate expression of eq I for the disproportionation holds for all the chelates examined over a wide range of pH. Kinetic results of oxidation of III with $[Fe(CN)_6]^{3-}$ are expressed by eq II. The first term represents the disproportionation of III. The second term is first order in [III], $[[Fe(CN)_6]^{3-}]$, and $[OH^-]$. The rate of oxidation of III is first-order in $[[Fe(CN)_6]^{3-}]$ and confirms that $[Fe(CN)_6]^{3-}$ acts as the oxidant. A significant result is that the third-order rate constants do not markedly differ from those for the disproportionation. The order of reactivity is governed by the type of Fe(III) chelate to be oxidized.

The disproportionation consists of electron transfer followed by deprotonation from either C–H or N–H bonds. The large primary isotope effect on k_{N-H}/k_{N-D} for the disproportionation of the pica chelates indicates that the deprotonation which affects the rate is that from the N–H bond.

Deprotonation from coordinated amines has been extensively studied by Buckingham and Sargeson[33-39] in conjunction with the structure of asymmetric nitrogen centers. The rate of H–D exchange and racemization of asymmetric nitrogen centers are first order in $[OH^-]$, and an amide ion is suggested for the intermediate. The isotope solvent effects of H_2O and D_2O are 7[33] and 3[34] for H–D exchange of sarcosinato (sar) and *N*-methylethylenediamine (Meen) in $[Co(sar)(NH_3)_4]^{2+}$ and $[Co(Meen)(NH_3)_4]^{3+}$, respectively. The isotope effects due to the change of solvents for the present disproportionation are almost the same as for the former.

The rate of deprotonation does not necessarily correspond to the rate of the disproportionation. If deprotonation is rate-determining, the acidity constants of diamines should correlate with the rate. For the equilibria $H^+ + L \rightleftharpoons HL^+$ (K_1) and $H^+ + HL^+ \rightleftharpoons HL^{2+}$ (K_2), log K_1 and log K_2 for diamines have been reported to be as follows: en, 10.18, 7.47;[40] pn, 10.18, 7.13;[41] *trans*-chxn, 9.77, 6.34;[42] *s*-Me_2en, 10.03, 6.04.[43] log K_1 of pica is 8.62.[44] The effect of varying diamines on the rate constants for the disproportionation has no correlation with these log K values. Furthermore, if the reaction sequence requires the species deprotonated at the coordinated amine as a preequilibrium, the isotope effect is expected to be smaller.

Deprotonated amine will facilitate intramolecular electron tranfer from deprotonated nitrogen to the Fe(III) center and will yield the Fe(II)–radical species, which is a canonical structure of the amide–Fe(III) species. The presence of such radicals based on nitrogen has been detected by ESR for the base-promoted dehydrogenation of macrocyclic Ni(III) chelates[17] and of an *N*-hydroxypiperidine coordinated to (tetraphenylporphyrinato)iron(II).[45] We have not been able to detect any transient absorption during the reaction course with optical measurements.

The dependency on hydroxide ion concentration is accounted for by eq 4.

$$[Fe(CN)_4(diamine)]^- + OH^- \overset{K_p}{\rightleftharpoons} [Fe(CN)_4(diamine\text{-}H)]^{2-} + H_2O \qquad (4)$$

The analogous rate equations for the disproportionation and the oxidation with $[Fe(CN)_6]^{3-}$ suggests the rate-determining step is an intermolecular electron transfer between the Fe(III) complex which serves as an oxidant and Fe(III) chelates bearing the deprotonated diamine. Alternatively the latter may be an Fe(II) chelate bearing a species with an amine radical.

In both the disproportionation and $[Fe(CN)_6]^{3-}$ oxidation, the intermolecular electron transfer is assumed to be fast. Electron exchanges between low-spin Fe(II) and Fe(III) compounds are known to be fast (10^3–10^6 M^{-1} s^{-1}).[46-48] ^{1}H NMR spectra of a mixture of I and III with identical sets of ligands have shown a linear dependency of observed chemical shift for each resonance on the mole fraction of Fe(III) chelate, III.[49] Thus electron exchange between I and III is the fast limit on the NMR time scale.

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The Fe(II)–radical species so generated will be oxidized to Fe(III)–radical species, which can undergo further intramolecular electron transfer from the nitrogen radical to Fe(III) and generate an Fe(II) cation species. From this species, proton release is enhanced, a process analogous to deprotonation from carbocations. Though the cation–Fe(II) species is speculative, the secondary isotope effect found for the pica and pica-d_2 chelates (1.7 ± 0.4) is rather large for a secondary effect. The order in reactivity of diamines, especially the greatly enhanced reactivity of *s*-Me_2en, has shown that the nitrogen center should be positively charged for the reaction.

These steps make up the rate-determining step expressed by eq 5.

$$[Fe(CN)_4(diamine)]^- + [Fe(CN)_4(diamine\text{-}H)]^{2-} \xrightarrow{k_d} [Fe(CN)_4(diamine)]^{2-} + [Fe(CN)_4(imine\text{-}amine)]^{2-} + H^+ \quad (5)$$

Then, the rate is expressed as eq III, where Ox represents the oxidizing agent (III for the disproportionation and $[Fe(CN)_6]^{3-}$ for the oxidation reactions), K_p is the equilibrium constant for eq 4, and k_d is the rate constant for the intermolecular electron transfer (eq 5).

$$-d[Fe^{III}]/dt = 4K_pk_d[Fe^{III}][Ox][OH^-]/(1 + K_p[OH^-]) \quad (III)$$

As shown in Figure 3, the third-order rate constant did not indicate saturation with increase in $[OH^-]$. For the reaction conditions (pH <12), the term of $K_p[OH^-]$ is far less than unity. Thus, the pK_a of the coordinated pica is greater than 12, and the k_d has a value greater than 1.0×10^5 M^{-1} s^{-1}, which is in good agreement with the results from the NMR measurement.[49]

The half-wave potentials correspond to reversible Fe(II)/Fe(III) redox couples and correlate with the order of reactivity. The more anodic the potential, the faster disproportionation or ligand oxidation proceeds. The rather large anodic potential of the pica chelates, 0.45 V vs. NHE, is due to back-donation from the pyridine ring but is smaller compared to that of tetracyano(diimine)ferrate(II/III) couples.[25] N-methylation produces an anodic shift of the potentials. This is consistent with the energies, −13.540 and −9.582 eV, of the highest occupied orbitals of en and *s*-Me_2en in CNDO/2 calculations.[50] These orbitals essentially correspond to the lone pairs residing on nitrogen atoms. The higher energy is favorable to transfer an electron to the Fe(III) center. The difference in the order of reactivity is expected to correlate with intramolecular electron transfer. The substitution at nitrogen with alkyl groups raises the energy of the HOMO. Thus, oxidative dehydrogenation has also been often found for 2,2′-bipiperidyl and macrocyclic ligands, which naturally have secondary amines coordinated to transition-metal ions.[9,11–19]

The correlation between the half-wave potentials and the rate constants does not hold for the *R*-cptn chelate. This chelate has to overcome steric hindrance to form II because the change from a C—N to a C═N bond exerts internal energy due to the fused cyclopentane ring.

The half-wave potentials of the imine–amine complex are expected at values between those of diamine and of diimine chelates. The monoimine chelate bis(bipyridyl)(2-amino-2-methylpropanal imine)ruthenium(2+/3+) showed a half-wave potential of 1.06 V, whereas half-wave potentials of its diamine and diimine counterparts fall in the region between 0.92 and 0.99 V and 1.29 and 1.20 V,[7] respectively. The stoichiometry of the disproportionation shows that the monoimine–Fe(II) chelates are preferentially oxidized to diimine–Fe(II) chelates. The oxidation of the Fe(II) monoimine proceeds easily, but the half-wave potentials of diimine chelates are far too anodic to be involved in the redox reaction. Cyclic voltammetry measurements of $[Fe(CN)_4(pica)]^{2-}$ were carried out in the pH range 8–11.5. At lower pHs, a single reversible wave was noted, which corresponds to the $Fe^{II/III}$ couple. At higher pHs, a second wave was observed, which corresponded to $[Fe^{II/III}(CN)_4(o\text{-}pica)]^{2-/-}$. The peak increased with higher pH. This behavior is consistent with the three successive processes

$$[Fe(CN)_4(pica)]^{2-} \rightarrow [Fe(CN)_4(pica)]^- + e^- \quad (6)$$

$$2[Fe(CN)_4(pica)]^- + 2OH^- \rightarrow [Fe(CN)_4(pica)]^{2-} + [Fe(CN)_4(o\text{-}pica)]^{2-} + 2H_2O \quad (7)$$

$$[Fe(CN)_4(o\text{-}pica)]^{2-} \rightarrow [Fe(CN)_4(o\text{-}pica)]^- + e^- \quad (8)$$

No further peaks were found up to +1.5 V vs. SCE as shown in Figure 5A. The participation of Fe(IV) is not plausible. The important role of deprotonation at the nitrogen center is thus verified.

Another possible mechanism is the intermolecular hydrogen abstraction of the generated radical–Fe(II) species from a C–H bond of another diamine molecule:

$$Fe^{II}\text{–}\dot{N}H\text{–}R + Fe^{III}\text{–}NH_2\text{–}CH_2R \rightarrow Fe^{II}\text{–}NH_2R + Fe^{III}\text{–}NH_2\text{–}\dot{C}H\text{–}R \quad (9)$$

The disproportionation of a mixture of the *s*-Me_2en and *R*-chxn chelate (1:1) leads to products that are comprised of o-Me_2en and *R*-chxn. The hydrogen abstraction by a radical is not expected to be selective. The observed result is consistent with the postulation that the diamine deprotonated at nitrogen is also oxidized at the carbon atom.

Conclusion. The discussion described in the preceding sections leads to the mechanism depicted in Scheme II. The oxidation of coordinated diamines is initiated by OH^-. The deprotonated coordinated diamines are able to surpass the oxidation barrier with the participation of transition-metal ions. Electron transfer occurs from the resultant amine anions to metal centers which have empty orbitals lying at relatively low energy levels, such as low-spin d^5 and d^9. The overall reaction is governed by this intramolecular electron transfer. The two-electron-oxidation process is accomplished by the participation of the second oxidant: the reactant itself for the disproportionation and $[Fe(CN)_6]^{3-}$ for the oxidation reaction.

The resultant monoimine chelates in Scheme II will be further oxidized to diimine chelates as shown by facile dehydrogenation of the pica chelate.

In the oxidation of substrates by an enzyme that contains transition-metal ion(s), an essential role is expected to be played by peptide side chains in promoting substrates to be susceptible to intramolecular electron transfer and initiate the successive steps of oxidation.

Acknowledgment. We are grateful to the Ministry of Education of the Japanese government for a Grant-in-Aid (Grant No. 454200).

Registry No. en, 107-15-3; *R*-pn, 6852-78-4; *R*-cptn, 40535-44-2; *R*-chxn, 20439-47-8; *s*-Me_2en, 110-70-3; pica, 3731-51-9; $[Fe(CN)_4(en)]^-$, 84330-11-0; $[Fe(CN)_4(o\text{-}en)]^{2-}$, 94250-26-7; $[Fe(CN)_4(R\text{-}pn)]^-$, 94250-21-2; $[Fe(CN)_4(o\text{-}pn)]^{2-}$, 79372-23-9; $[Fe(CN)_4(R\text{-}cptn)]^-$, 94345-86-5; $[Fe(CN)_4(o\text{-}cptn)]^{2-}$, 79372-25-1; $[Fe(CN)_4(R\text{-}chxn)]^-$, 94345-87-6; $[Fe(CN)_4(o\text{-}chxn)]^{2-}$, 79372-27-3; $[Fe(CN)_4(s\text{-}Me_2en)]^-$, 94250-22-3; $[Fe(CN)_4(o\text{-}Me_2en)]^{2-}$, 94250-27-8; $[Fe(CN)_4(pica)]^-$, 94250-23-4; $[Fe(CN)_4(o\text{-}pica)]^{2-}$, 91730-48-2; $Na_2[Fe(CN)_4(pica\text{-}d_2)]$, 94250-24-5; $Na[Fe(CN)_4(pica\text{-}d_2)]$, 94250-25-6; $Fe(CN)_6^{3-}$, 13408-62-3; D_2, 7782-39-0.

Supplementary Material Available: Tables of observed yields of II, observed rate constants for the disproportionation reaction of III, and initial velocities of formation of II from oxidation of III by $[Fe(CN)_6]^{3-}$ (10 pages). Ordering information is given on any current masthead page.

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(50) The calculation was carried out with use of a local CNDO/2 program at the Nagoya City University Computation Center. The atomic coordinates are calculated on the basis of X-ray crystallographic data of *trans*-$[CoCl_2(en)_2]Cl\cdot HCl\cdot 2H_2O$ (Saito, Y.; Nakahara, Y.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 331) and $[Pt(Meen)(R\text{-}pn)][Sb_2((+)\text{-}C_4H_2O_6)_2]\cdot 2H_2O$ (Matsumoto, K.; Ooi, S.; Sakuma, M.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2129) on assuming bond lengths of 1.09 and 0.91 Å for C–H and N–H respectively, and tetrahedral bonding for each carbon and nitrogen center.