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Kinetics and Mechanism of Formation of Monothiocyanato and Mononitrilotriacetato Complexes of Iron(III)

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Kinetics of the formation of monothiocyanato and mononitrilotriacetato complexes of iron(III) in aqueous solution have been studed by using a stopped-flow technique:

$$Fe^{3+} + SCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeNCS^{2+}$$

$$FeOH^{2+} + SCN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeNCS^{2+} + OH^-$$

$$FeOH^{2+} + H_2nta^- \xrightarrow{k} Fe(nta) + H^+$$

Rate constants at 25°C and $\mu=0.5$ ($NaClO_4$) are as follows: $k_1=90\ M^{-1}\ sec^{-1}$, $k_{-1}=1.6\ sec^{-1}$, $k_2=5.1\times 10^3\ M^{-1}\ sec^{-1}$, $k_{-2}=10\times 10^{13}\ M^{-1}\ sec^{-1}$, $k=1.0\times 10^5\ M^{-1}\ sec^{-1}$. Some discussions are made on the effect of hydroxide ion on the complex formation reactions.

The complex formation reactions of iron(III) have been extensively studied for various ligands: F^-[1], Cl^-[2–4], Br^-[4,5], azide[6–8], SCN^-[3,9], aliphatic acids[10–12], SO_4^{2-}[3,13,14], substituted phenols[15], acetylacetone[16], oxalic acid[17], substituted malonic acids[18], salicylic acid[19], sulfosalicylic acid[19], 8-hydroxyquinoline[19], salicylaldehyde[19].

According to the earlier kinetic studies, the reaction

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rate constants for all the $Fe^{3+}+L$ reactions lie in the range 1—10^2 M^{-1} sec^{-1}, and those for the $FeOH^{2+}+L$ reactions in the range 10^2—10^5 $M^{-1}sec^{-1}$ at 25°C. These results indicate that the substitution of a water molecule in the inner coordination sphere of the metal ion is the rate-determining process of the complex formation reaction.[20]

Since there is very little information on the kinetics of complex formation of iron(III) ion with multidentate ligands, we have studied the kinetics of iron(III) ion with nitrilotriacetate (tetradentate) to compare the results with the kinetic properties of monodentate ligands. Our primary intention was to determine whether the rate of the complex formation of iron(III) is controlled by the release of a water molecule in the inner coordination sphere or by the chelate ring closure (sterically controlled substitution) as found for some complexes,[21—23] and to elucidate the effect of hydroxide ion on the complex formation reactions.

Experimental

Reagents. *Iron(III) Perchlorate*: The reagent grade iron(III) chloride was dissolved in perchloric acid and chloride was expelled by evaporation. The absence of chloride ion was checked by silver nitrate. The iron(III) perchlorate was recrystallized twice from 60% perchloric acid solution. Its concentration was determined by a standard EDTA solution with Variamine Blue B as an indicator.[24]

Sodium Thiocyanate: The reagent grade sodium thiocyanate was recrystallized twice from distilled water. The thiocyanate solution was standardized by the method of Volhard.

Nitrilotriacetic Acid: The acid form of NTA obtained from Dojindo Co., Ltd., was recrystallized twice from distilled water. The purified NTA was dissolved in 1 equivalent of sodium hydroxide.

Methods of preparation of sodium perchlorate and sodium hydroxide have been described previously.[25]

Measurements. Supplementary spectra were taken on a JASCO Model ORD/UV-5 optical rotatory dispersion recorder and a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer.

Hydrogen ion concentration was determined by a Radiometer PHM-4d (Copenhagen) with a Type G202 B glass electrode and a Type K 401 calomel. A 1.00×10^{-2} M perchloric acid at an ionic strength of 0.5 M ($[HClO_4]+[NaClO_4]=0.5$ M) was used as a standard solution. The liquid junction potential was taken into consideration.

The acidities of solutions were adjusted by addition of a solution of sodium hydroxide prepared by electrolysis of a sodium perchlorate solution. Ionic strengths were adjusted by addition of sodium perchlorate.

The kinetics of formation of complexes of iron(III) was studied spectrophotometrically by means of a stopped-flow technique using a Rapid Scan Spectrophotometer Type RSP-2 (Hitachi, Ltd., Tokyo). The reactant syringes thermostated at 25±0.1°C were connected to the two-stage mixing chamber with eight jets, with which was aligned a quartz observation tube 10-mm long and 2-mm in diameter. The runs of reactions at a fixed wavelength (460 nm for $FeNCS^{2+}$ and 262.5 nm for Fe(nta)) in the absorption spectrum of the complex were memorized on an oscilloscope (Hitachi V-OL-Memoriscope). The screen of the oscilloscope was photographed. The traces of absorbance against reaction time were analyzed.

Results

Kinetics of Formation of the Monothiocyanato Complex of Iron(III).[26] The kinetic data are consistent with the assumption that the formation of $FeNCS^{2+}$ proceeds *via* two paths, one involving the reaction of Fe^{3+} with SCN^- and the other involving the reaction of $FeOH^{2+}$ with SCN^-, and that the equilibrium between Fe^{3+} and $FeOH^{2+}$ ($Fe^{3+}+H_2O\rightleftharpoons FeOH^{2+}+H^+$) is established throughout the course of the reaction. The rate of formation of $FeNCS^{2+}$ is then given by

$$\frac{d[FeNCS^{2+}]}{dt} = k_1[Fe^{3+}][SCN^-] + k_2[FeOH^{2+}][SCN^-] - k_{-1}[FeNCS^{2+}] - k_{-2}[FeNCS^{2+}][OH^-] \qquad (1)$$

where the rate constants are defined by the following:

$$Fe^{3+} + SCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeNCS^{2+} \qquad (2)$$

$$FeOH^{2+} + SCN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeNCS^{2+} + OH^- \qquad (3)$$

Since $C_{Fe}\gg C_{SCN}$, it follows that

$$[Fe^{3+}] = \frac{C_{Fe}}{1+\dfrac{K^{-H}_{FeOH}}{[H^+]}}$$

where C_{Fe} is the total concentration of iron(III) and $K^{-H}_{FeOH}=[FeOH^{2+}][H^+]/[Fe^{3+}]=10^{-2.73}$.[14,27] Moreover, under the conditions used in this investigation $K^{-H}_{FeOH}/[H^+]\ll1$.

Therefore

$$\frac{d[FeNCS^{2+}]}{dt} = \left(k_1+\frac{k_2K^{-H}_{FeOH}}{[H^+]}\right)C_{Fe}[SCN^-] - (k_{-1}+k_{-2}[OH^-])[FeNCS^{2+}] \qquad (4)$$

Integrating Eq. (4) we get

$$\ln\left(1-\frac{[FeNCS^{2+}]}{[FeNCS^{2+}]_{eq}}\right) = -\left(k_1+k_{-1}+\frac{k_2K^{-H}_{FeOH}}{[H^+]}+k_{-2}[OH^-]\right)t \qquad (5)$$

where $[FeNCS^{2+}]_{eq}$ is the concentration of $FeNCS^{2+}$

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under equilibrium conditions. Then

$$\ln\left(1+\frac{A_t}{A_{eq}}\right) = -k_0t \qquad (6)$$

$$k_0 = k_1C_{Fe} + k_{-1} + \frac{k_2K^{-H}_{FeOH}C_{Fe}}{[H^+]} + \frac{k_{-2}K_w}{[H^+]} \qquad (7)$$

where A_t and A_{eq} are the absorbances of the reaction system at t seconds after the start of the reaction and at equilibrium, respectively, k_0 a conditional rate constant obtained by experiments, and $K_w=[H^+][OH^-]$.

Some conditional rate constants under various experimental conditions are given in Table 1. These data indicate clearly a linear relationship between k_0 and the reciprocal concentration of hydrogen ion with a nonzero intercept (Fig. 1). Thus the conditional rate constant k_0 is expressed by

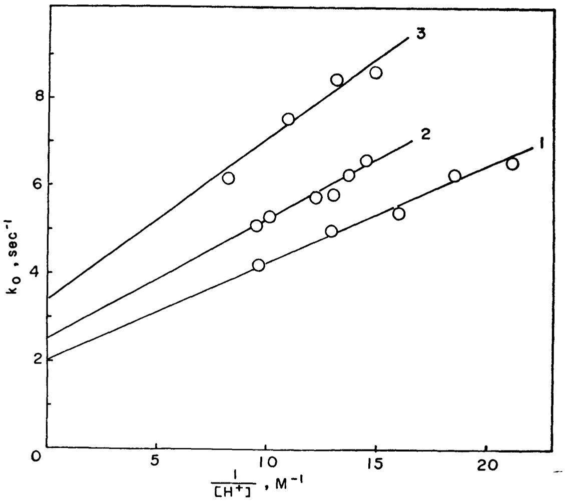

Fig. 1. k_0 as a function of the reciprocal concentration of hydrogen ion. $C_{SCN}=2.00\times10^{-4}$ M, 25°C, $\mu=0.5$ M (NaClO$_4$), 1: $C_{Fe}=3.98\times10^{-3}$ M; 2: $C_{Fe}=9.97\times10^{-3}$ M; 3: $C_{Fe}=2.00\times10^{-2}$ M.

$$k_0 = k_{0(1)} + k_{0(2)}\frac{1}{[H^+]} \qquad (8)$$

Moreover, the values of intercepts ($k_{0(1)}$) are found proportional to the concentration of ferric ion (Fig. 2a). The values of slopes ($k_{0(2)}$) are also linearly related to the concentration of ferric ion (Fig. 2b). These results are consistent with the proposed reaction mechanism, *i. e.*,

$$k_{0(1)} = k_1C_{Fe} + k_{-1} \qquad (9)$$

$$k_{0(2)} = k_2K^{-H}_{FeOH}C_{Fe} + k_{-2}K_w \qquad (10)$$

The values of rate constants k_1, k_{-1}, $k_2K^{-H}_{FeOH}$, and $k_{-2}K_w$ were determined from the intercepts and the slopes of plots by the method of least squares: $k_1=90\pm5$ M^{-1} sec^{-1}, $k_{-1}=1.6\pm0.2$ sec^{-1}, $k_2K^{-H}_{FeOH}=9.5$ M^{-2} sec^{-1}, $k_{-2}K_w=0.19$ M^{-1} sec^{-1}. Using the values $K^{-H}_{FeOH}=1.87\times10^{-3}$ [14,27] and $\log K_w=-13.73$[28] at 25°C and $\mu=0.5$ M, we obtain $k_2=5.1\pm0.5\times10^3$M^{-1} sec^{-1} and $k_{-2}=1.0\pm0.1\times10^{13}$ M^{-1} sec^{-1}.

Kinetics of Formation of the Mononitrilotriacetato Complex of Iron(III). Under the present experimental conditions, the formation reaction of the mononitrilotriacetato complex of iron(III) is expressed as follows:

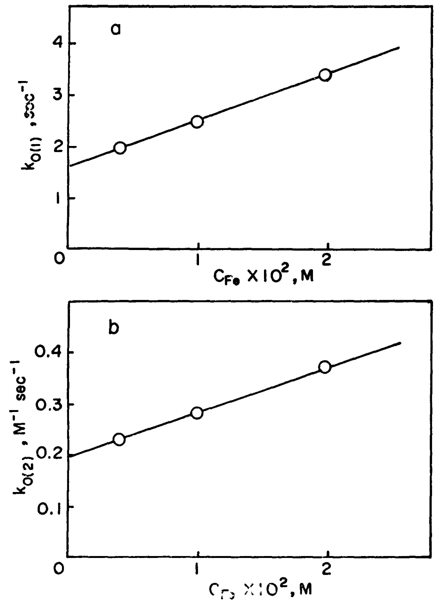

Fig. 2. Rate constants as a function of the total concentration of iron(III) ion.
a: Plot of $k_{0(1)}$ *vs.* C_{Fe}. b: Plot of $k_{0(2)}$ *vs.* C_{Fe}.

TABLE 1. CONDITIONAL RATE CONSTANTS k_0 OF FORMATION OF THE MONOTHIOCYANATO COMPLEX OF IRON(III) AT 25°C AND $\mu=0.5$ (NaClO$_4$)

C_{Fe}, M	[H$^+$], M	k_0, sec^{-1}
3.98×10^{-3}	1.04×10^{-1}	4.20
	7.73×10^{-2}	5.00
	6.25×10^{-2}	5.40
	5.40×10^{-2}	6.25
	4.74×10^{-2}	6.55
9.97×10^{-3}	1.04×10^{-1}	5.10
	9.89×10^{-2}	5.30
	8.20×10^{-2}	5.75
	7.71×10^{-2}	5.80
	7.31×10^{-2}	6.25
	6.92×10^{-2}	6.60
2.00×10^{-2}	1.22×10^{-1}	6.15
	9.14×10^{-2}	7.55
	7.62×10^{-2}	8.45
	6.73×10^{-2}	8.60

$C_{SCN}=2.00\times10^{-4}$ M.

$$Fe' + nta' \xrightarrow{k_{0(H)}} Fe(nta) \qquad (11)$$

where Fe′ and nta′ denote all the species of iron(III) not combined with NTA and those of NTA not combined with iron(III), respectively. The Fe(III)-NTA complex exists as Fe(nta).[29] The rate equation of the formation of the Fe(III)-NTA complex is given by[30]

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[30] The protolytic reactions are sufficiently rapid for these steps to be assumed to be in equilibrium at all times.

$$\frac{\mathrm{d[Fe(nta)]}}{\mathrm{d}t} = k_{0(\mathrm{H})}[\mathrm{Fe'}][\mathrm{nta'}] \tag{12}$$

The linearity of the second-order plot for Eq. (12) is excellent. Thus we can estimate the conditional rate constant $k_{0(\mathrm{H})}$ from the slope of the second-order plot. Some conditional rate constants are given in Table 2.

The rate equation seems to be expressed as follows:

$$\begin{aligned}\frac{\mathrm{d[Fe(nta)]}}{\mathrm{d}t} &= k_1[\mathrm{Fe^{3+}}][\mathrm{H_2nta^-}] + k_2[\mathrm{Fe^{3+}}][\mathrm{H_3nta}] \\ &\quad + k_3[\mathrm{FeOH^{2+}}][\mathrm{H_2nta^-}] + k_4[\mathrm{FeOH^{2+}}][\mathrm{H_3nta}] \\ &= \frac{\dfrac{k_1}{K_{\mathrm{H_3nta}}[\mathrm{H^+}]} + k_2 + \dfrac{k_3K_{\mathrm{FeOH}}^{-\mathrm{H}}}{K_{\mathrm{H_3nta}}[\mathrm{H^+}]^2} + \dfrac{k_4K_{\mathrm{FeOH}}^{-\mathrm{H}}}{[\mathrm{H^+}]}}{\left(1+\dfrac{K_{\mathrm{FeOH}}^{-\mathrm{H}}}{[\mathrm{H^+}]}\right)\left(1+\dfrac{1}{K_{\mathrm{H_3nta}}[\mathrm{H^+}]}\right)}[\mathrm{Fe'}][\mathrm{nta'}]\end{aligned} \tag{13}$$

where

$$[\mathrm{Fe'}] = [\mathrm{Fe^{3+}}] + [\mathrm{FeOH^{2+}}] = [\mathrm{Fe^{3+}}]\left(1+\frac{K_{\mathrm{FeOH}}^{-\mathrm{H}}}{[\mathrm{H^+}]}\right)$$

$$[\mathrm{nta'}] = [\mathrm{H_3nta}] + [\mathrm{H_2nta^-}] = [\mathrm{H_3nta}]\left(1+\frac{1}{K_{\mathrm{H_3nta}}[\mathrm{H^+}]}\right)$$

with $K_{\mathrm{H_3nta}}=[\mathrm{H_3nta}]/[\mathrm{H_2nta^-}][\mathrm{H^+}]=10^{1.9}$.[31] Therefore the conditional second-order rate constant $k_{0(\mathrm{H})}$ has the following relationship.

$$\begin{aligned}&k_{0(\mathrm{H})}\left(1+\frac{K_{\mathrm{FeOH}}^{-\mathrm{H}}}{[\mathrm{H^+}]}\right)\left(1+\frac{1}{K_{\mathrm{H_3nta}}[\mathrm{H^+}]}\right) \\ &\quad = k_2 + \left(\frac{k_1}{K_{\mathrm{H_3nta}}} + k_4K_{\mathrm{FeOH}}^{-\mathrm{H}}\right)\frac{1}{[\mathrm{H^+}]} + \frac{k_3K_{\mathrm{FeOH}}^{-\mathrm{H}}}{K_{\mathrm{H_3nta}}}\frac{1}{[\mathrm{H^+}]^2}\end{aligned} \tag{14}$$

Logarithm of the value of the left side of Eq. (14) is plotted against $-\log\,[\mathrm{H^+}]$ in Fig. 3. The plot gives a straight line with a slope of two. This means that under the present experimental conditions the formation of the Fe(III)-NTA complex proceeds through the reaction of $\mathrm{FeOH^{2+}}$ and $\mathrm{H_2nta^-}$. We estimated the value of k_3 from the intercept of the straight line: $k_3=1.0\pm0.2\times10^5\ \mathrm{M^{-1}sec^{-1}}$ at 25°C and 0.5 M ionic strength.

Discussion

The kinetic behavior of the reactions in the present study is compared with the behavior predicted by the current general mechanism for metal-ligand complex formation as formulated by Eigen (Eigen mechanism),[32,33] which accounts for most kinetic data on the formation of complexes.

Values of k_1 and k_2 are given in Table 3 together with the corresponding values reported by other authors. The rate constants are in reasonable agreement with some previous kinetic results, the difference in conditions being taken into consideration.

TABLE 2. CONDITIONAL RATE CONSTANTS $k_{0(\mathrm{H})}$ OF FORMATION OF THE MONONITRILOTRIACETATO COMPLEX OF IRON(III) AT 25°C AND $\mu=0.5$ ($\mathrm{NaClO_4}$)

C_{Fe}, M	C_{NTA}, M	$-\log\,[\mathrm{H^+}]$	$k_{0(\mathrm{H})}$, $\mathrm{M^{-1}sec^{-1}}$
1.09×10^{-2}	5.00×10^{-3}	0.907	116
		0.940	123
		0.957	136
		0.994	148
	4.00×10^{-3}	0.796	64.5
		0.848	77.0
		0.891	103
		0·941	138
		0.995	187
	2.00×10^{-3}	0.909	101
		0.930	111
		0.948	120
		0.971	131
		0.993	146
5.00×10^{-3}	1.25×10^{-3}	0.820	98.5
		0.919	138
		1.006	206
		1.040	316
		1.228	396
		1.317	591
		1.408	815
		1.523	1.13×10^3
		1.600	1.67×10^3
		1.704	2.30×10^3
		1.801	2.86×10^3

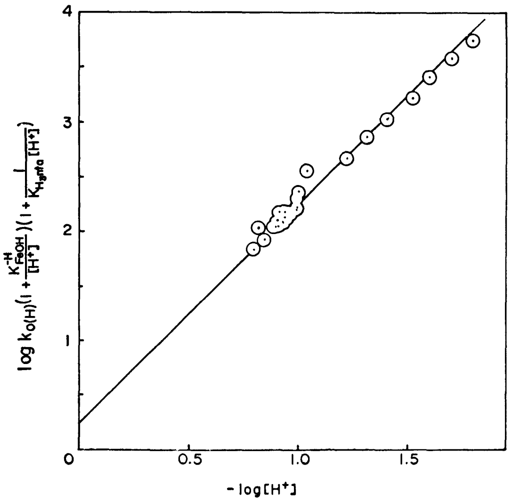

Fig. 3. Hydrogen ion dependence of the rate constants at 25°C and $\mu=0.5\,\mathrm{M}$ ($\mathrm{NaClO_4}$).
The straight line represents the theoretical straight line with a slope of two.

According to the Eigen mechanism, the complex formation reaction involves the fast formation of an outer-sphere complex followed by the substitution of a water molecule coordinated to the metal ion. Therefore the iron(III) complex formation can be depicted as follows:

$$\begin{aligned}&\mathrm{Fe(H_2O)_6}^{3+} + \mathrm{X}^- \overset{K_{\mathrm{os}}}{\rightleftharpoons} \mathrm{Fe(H_2O)_6}^{3+}\cdots\mathrm{X}^- \\ &\qquad \xrightarrow{k_{\mathrm{w}}} \mathrm{FeX(H_2O)_5}^{2+} + \mathrm{H_2O}\end{aligned} \tag{15}$$

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[31] G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **34**, 1589 (1956).

[32] M. Eigen and R. W. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, Amercian Chemical Society, Washington, D. C., (1965).

[33] M. Eigen and K. Tamm, *Z. Elektrochem.*, **64**, 115 (1960).

TABLE 3. VALUES OF RATE CONSTANTS AT 25°C FOR THE REACTIONS OF Fe^{3+} AND $Fe(OH)^{2+}$ WITH SCN^-

k_1, $M^{-1}\,sec^{-1}$	k_2, $M^{-1}\,sec^{-1}$	Reference
127 ± 10	$1.0\pm0.1\times10^4$	Ref. 9[a]
150 ± 50		Ref. 3
90 ± 5	$5.1\pm0.5\times10^3$	This work

a) $\mu=0.4\,M$

$$FeOH(H_2O)_5{}^{2+} + X^- \overset{K_{OS(OH)}}{\rightleftharpoons} FeOH(H_2O)_5{}^{2+}\cdots X^- \xrightarrow{k_{W(OH)}} FeX(H_2O)_5{}^{2+} + OH^- \tag{16}$$

where K_{OS} is the equilibrium constant for outer-sphere association and k_w is the first-order rate constant for the rate-determining water substitution. According to the above mechanism, the second-order rate constant obtained is equal to $K_{OS}k_w$. The rate for the reaction of $FeOH(H_2O)_5{}^{2+}$ is higher than that of $Fe(H_2O)_6{}^{3+}$. As pointed out in the formation of nickel(II) complexes,[34] it is understandable that the electron donation from hydroxide ion makes the dissociation of coordinated water molecules from $FeOH(H_2O)_5{}^{2+}$ faster than from the aquo ferric ion.

The combination of H^+ and OH^- is the fastest reaction possible in aqueous solution. The rate constant has been measured as $1.4\times10^{11}\,M^{-1}\,sec^{-1}$ at 25°C, a value corresponding to the theoretical limit for the rate of a chemical reaction (diffusion-controlled processes).[35] The value of the rate constant k_{-2} of the reaction of $FeNCS^{2+}$ with OH^- is $1.0\times10^{13}\,M^{-1}\,sec^{-1}$ which is greater by more than one order of magnitude than the rate constants for diffusion-controlled reactions.[36] This seems to suggest that the reaction proceeds through the mixed-ligand complex $Fe(OH)(NCS)^+$ involving OH^- and SCN^-, that is,

$$FeNCS(H_2O)_5{}^{2+} + H_2O \xrightleftharpoons{K^{-H}_{Fe(OH)(NCS)}} Fe(OH)(NCS)(H_2O)_4{}^+ + H_3O^+ \tag{17}$$

$$Fe(OH)(NCS)(H_2O)_4{}^+ \xrightarrow{k'_{-2}} FeOH(H_2O)_5{}^{2+} + SCN^- \tag{18}$$

Thus we have the relationship

$$k_{-2} = K^{-H}_{Fe(OH)(NCS)}k'_{-2}/K_W \tag{19}$$

The hydrolysis constant of $FeNCS^{2+}$ was measured by Lister and Rivington: $[Fe(OH)(NCS)^+][H^+]/[FeNCS^{2+}]=6.5\pm1\times10^{-5}$ at 25°C and $\mu=1.2$.[37] Assuming that the value of $K^{-H}_{Fe(OH)(NCS)}$ is $10^{-4.2}$, we have estimated $k'_{-2}=10^{3.5}$, which is about 1000 times larger than the value of the rate constant k_{-1} for the dissociation of $FeNCS^{2+}$. The dissociation of SCN^- from $Fe(OH)(NCS)(H_2O)_4{}^+$ seems to be facilitated by the electron donation from OH^- to a greater extent than that from H_2O in $FeNCS(H_2O)_5{}^{2+}$. This is understood in the same way as in the complex formation where k_2 is greater than k_1.

From the results of the iron(III) complex formation (Eigen mechanism), it is expected that the rate constant for the reaction of $FeOH^{2+}$ with SCN^- is the same as for the reaction of $FeOH^{2+}$ with H_2nta^-, as the charge of reacting ligands is the same. In effect the value of the rate constant for H_2nta^- is 20 times greater than that for SCN^- which is approximately equal to the theoretical value expected from the Eigen mechanism. The enhanced rate for H_2nta^- can be accounted for in terms of the internal conjugate base mechanism proposed by Rorabacher.[38] To account for abnormality of the reaction of nickel ion with polyamines, he proposed a modification of the Eigen mechanism wherein a basic donor atom of a reacting multidentate ligand forms a hydrogen-bond to a coordinated water molecule, thereby stabilizing the outer-sphere complex and labilizing subsequent water loss.

Hydroxo group of $FeOH^{2+}$ is basic and H_2nta^- is acid. Thus the hydrogen-bond would be formed between $FeOH^{2+}$ and H_2nta^- thereby stabilizing more effectively the $FeOH^{2+}\cdots H_2nta^-$ outer-sphere complex than the $FeOH^{2+}\cdots SCN^-$ outer-sphere complex.

A similar enhancement of rate constants for the formation of iron(III) complexes has been observed in the formation of iron(III) complexes with some substituted malonic acids (HL). The rate constants for the reaction ($FeOH^{2+}+HL^-$) are 1.3×10^5, 1.2×10^5, 1.0×10^5, 1.0×10^5, $1.1\times10^5\,M^{-1}\,sec^{-1}$ at 25°C and $\mu=0.5\,M$ for malonic, methylmalonic, *n*-butylmalonic, benzylmalonic, and cyclobutane-1,1-dicarboxylic acids, respectively.[18] It is understandable that larger values of rate constants in these reactions are due to the formation of hydrogen-bond between $FeOH^{2+}$ and HL^-.

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