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Kinetic Studies of the Electron Transfer Reactions in Iron(II) and Iron(III) Systems. XII. The Ratios of the Reaction Rates of the Outer-sphere *vs.* Inner-sphere Electron Transfer Mechanisms in the Presence of X^- ($X^-=Cl^-$, SCN^-, and N_3^-) in Aqueous Solutions, as Judged from the Kinetics of the Dissociation Reactions of FeX^{2+}

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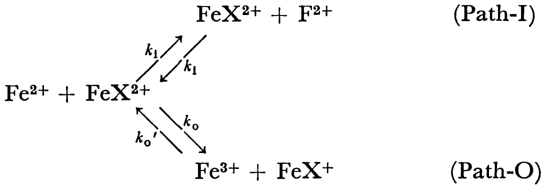
The electron transfer reactions between Fe^{2+} and FeX^{2+} ($X^-=Cl^-$, SCN^-, or N_3^-) may take place through the inner- or outer-sphere mechanism or through both in parallel. The process of the outer-sphere mechanism is just equivalent to the process of dissociation of FeX^{2+} catalyzed by Fe^{2+} in appearance. When the overall rate constant of the electron transfer reaction and the rate constant of Fe^{2+}-assisted dissociation reaction of FeX^{2+} are denoted by k_E and k_o respectively, the fraction r of the outer-sphere mechanism to the total is given in terms of $r=2k_o/k_E$. Thus, the r values were determined with the results that $r(Cl^-)=44\%$ at $I=1.5$ M (1 M=1 mol dm^{-3}) and 25 °C, $r(SCN^-)=100\%$ at $I=0.5$ M and 25 °C, and $r(N_3^-)=0\%$ at $I=0.55$ M and 10 °C. These facts suggest that r depends considerably upon the bridging ability of X^-; formation of binuclear intermediate may be favored by the symmetrical structure and the size of X^-, which make the inner-sphere mechanism easier with the stronger coordinate bond and the weaker electric repulsion between the two reactants beyond the bridging ligand.

The electron transfer reactions between iron(II) and iron(III), $Fe^{II}+Fe^{III}\rightarrow Fe^{II}+Fe^{II}$, have been known to be accelerated by the presence of some anions, X^-, in aqueous perchloric acid media.[1–8] In such catalytic actions, X^- usually coordinates to iron(III) to form a precursor complex, FeX^{2+}, which participates in the electron transfer reaction *via* either of the two paths shown as follows:



The former of the two paths is called the inner-sphere mechanism, in which X^- bridges the two reacting ions and is transferred from Fe(III) to Fe(II) as an atom or radical (X) transfer, leaving an electron of X^- on Fe(III), while the latter path is the outer-sphere mechanism, in which an electron of Fe(II) is directly transferred to Fe(III) without accompanying any ligand substitution in the first coordination spheres of both ions. Generally, the two reaction mechanisms may compete with each other, with a certain ratio, the outer-sphere *vs.* inner-sphere mechanism, depending upon the properties of the bridging anion ligand X^- in aqueous solution.

Since the chemical species appearing as the reactants or products in the Path-I are identical in both sides, the rate constants of the forward and reverse reactions are equally k_I, while the Path-O is not a symmetric reaction with the product species different from the reactant ones, so that the rate constant of the forward reaction k_o should be unequal to that of the reverse reaction k_o'.

Now, let us consider an aqueous solution containing Fe(II), Fe(III), and X^-; all of the probable chemical species being at equilibrium. If the electron transfer reactions, both Path-I and Path-O, are simultaneously occurring in this system, the overall reaction rate, R, can be expressed by the sum of the three individual rates.

$$R = k_I[Fe^{2+}][FeX^{2+}] + k_o[Fe^{2+}][FeX^{2+}] + k_o'[Fe^{3+}][FeX^{+}] \quad (1)$$

Since the reaction system is at equilibrium, the concentrations of all the species in it must be individually kept constant. Although FeX^+ produced is very labile and is going soon to decompose, any probable side-reaction is quite indifferent to the reverse process of Path-O. Generally, the reverse process has the same mechanism as that of the forward process. Therefore, the rate of the forward reaction in Path-O should be equal to that of the reverse one at equilibrium.

$$k_o[Fe^{2+}][FeX^{2+}] = k_o'[Fe^{3+}][FeX^{+}] \quad (2)$$

By using the relationship of Eq. 2, Eq. 1 then becomes[8]

$$R = (k_I+2k_o)[Fe^{2+}][FeX^{2+}] \quad (3)$$

and the apparent overall rate constant k_E of the electron transfer reaction is expressed as follows:

$$k_E = k_I + 2k_o. \quad (4)$$

If both k_E and k_o are separately determined for a reaction system in the presence of X^-, we can define the fraction r of the outer-sphere mechanism to the overall reaction rate.

$$r = \frac{2k_o}{k_E} \quad (5)$$

In order to determine k_E, the radioactive isotope ^{59}Fe has been frequently used as a tracer by several workers since the first investigation by Silverman and Dodson.[1] For the determination of k_o, on the other hand, an idea is useful as described below.

When the dissociation reaction of FeX^{2+}, $FeX^{2+}\rightarrow Fe^{3+}+X^-$, is accelerated by the presence of Fe^{2+}, it looks like that Fe^{2+} acts as a catalyst for the dissociation reaction:

$$FeX^{2+} + Fe^{2+} \xrightarrow{k_d} Fe^{3+} + FeX^{+} \qquad \text{(Path-D)}$$

Reaction Path-D is seemingly a ligand exchange reaction of X^-, but it is just the same reaction with Path-O in appearance. Consequently, the observed k_d is equivalent to k_o of the outer-sphere electron transfer in Path-O.

In the present investigation, the kinetics of the catalytic dissociation of FeX^{2+} was studied, and the values of r were determined in the cases of Cl^-, SCN^-, and N_3^- and were interpreted by virtue of the nature of these anions. For the case of Cl^-, Sutin and his coworkers[8] estimated the r value earlier, which will be compared with the present results.

Experimental

Materials. *$Fe(ClO_4)_2$*: The preparative method was described elsewhere.[9]

$Fe(ClO_4)_3$: Aqueous perchloric acid solution of $Fe(ClO_4)_2$ was oxidized to $Fe(ClO_4)_3$ by adding approximately equivalent amount of H_2O_2. The precipitated crystals of $Fe(ClO_4)_3$ were filtered, washed by chloroform, and dried in vacuum.

NaCl, KSCN, NaN_3, and $NaClO_4$: Commercial reagents of the purest grade were recrystalized from their aqueous solutions, respectively.

Water: Tap water was purified by double distillation after being deionized through ion-exchange resin.

Procedure. Kinetic measurements were carried out by use of a Yanako stopped-flow spectrophotometer Model SPS-1 connected with an Iwatsu memoriscope MS-5019A. The reaction compartment was thermostated at a given reaction temperature. The dissociation reaction of FeX^{2+} in the presence or absence of Fe^{2+} was initiated by mixing two solutions A and B, containing Fe^{3+}, X^-, $HClO_4$, and $NaClO_4$ in A and Fe^{2+} or none, $HClO_4$, and $NaClO_4$ in B, respectively. Sodium perchlorate was used for adjusting the ionic strength of the reaction media. The reaction rate was followed by the decrement in absorbance due to the disappearance of FeX^{2+}, at wavelengths 370 nm for $FeCl^{2+}$, 460 nm for $FeSCN^{2+}$ and FeN_3^{2+}, respectively.

The apparent dissociation rate constant k_{app} was obtained from the linearity of $\ln([FeX^{2+}]-[FeX^{2+}]_e)$ *vs.* time t by the following relationship:

$$\ln\frac{[FeX^{2+}]-[FeX^{2+}]_e}{[FeX^{2+}]_o-[FeX^{2+}]_e} = -k_{app}t. \tag{6}$$

Since FeX^{2+} in solution A was in equilibrium with free Fe^{3+} and X^- before mixing with solution B, the equilibrium was suddenly perturbed and forced to shift towards a new equilibrium by dilution, with the forward (dissociation) rate constant k and the reverse (recombination) one k'. If the formation constant of FeX^{2+} is denoted by K_x $(=[FeX^{2+}]/[Fe^{3+}][X^-])$, K_x is equal to k'/k and, thus, k is given by the following equation:

$$k = \frac{k_{app}}{1+K_x([Fe^{3+}]_e+[X^-]_e)}. \tag{7}$$

The notations $[\ \ ]_o$ and $[\ \ ]_e$ in Eqs. 6 and 7 denote the concentrations at the initial time and at the equilibrium, respectively.

Results and Discussion

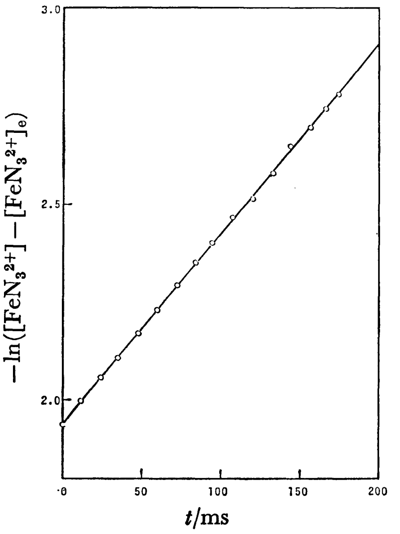


Fig. 1. Linear relationship of $-\ln([FeN_3^{2+}]-[FeN_3^{2+}]_o)$ *vs.* t at $[Fe(ClO_4)_3]_t=[NaN_3]_t=1.96\times10^{-3}$ M, $[Fe(ClO_4)_2]_t=0$, $[HClO_4]_t=0.01$ M, $I=0.55$ M at 10 °C.

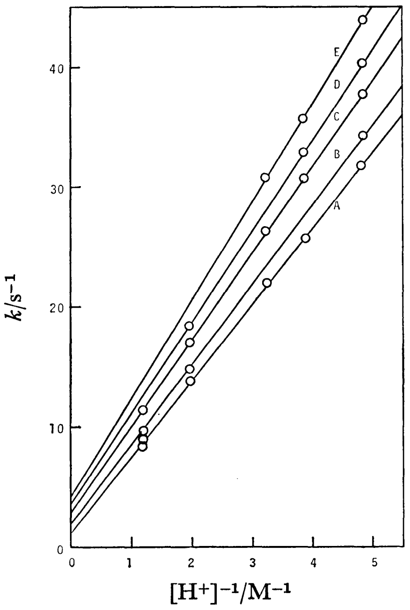


Fig. 2. Linear relationship of k *vs.* $[H^+]^{-1}$, at $[Fe^{3+}]_t=4.63\times10^{-3}$ M, $[Cl^-]_t=4.58\times10^{-3}$ M, $[H^+]=0.2$—0.8 M, $I=1.5$ M at 25 °C.
A: $[Fe^{2+}]_t=0$, B: $[Fe^{2+}]_t=0.05$ M, C: $[Fe^{2+}]_t=0.01$ M, D: $[Fe^{2+}]_t=0.15$ M, E: $[Fe^{2+}]_t=0.20$ M.

An example of a plot of $\ln([FeN_3^{2+}]-[FeN_3^{2+}]_e)$ against reaction time t is shown in Fig. 1. The observed straight line represents Eq. 6 very well, from the slope of which k_{app} can be calculated. On account of the relatively low value of the formation constants, $K_{Cl}=3.0\times10^{10)}$ and $K_{SCN}=4.2\times10^{2}$,[11] both at $I=0$ and 25 °C, k is considered to be approximately equal to k_{app} from Eq. 7 for $X^-=Cl^-$ or SCN^-. In the case of N_3^-, however, the situation is more complicated as will be described below.

Dissociation of $FeCl^{2+}$ and $FeNCS^{2+}$ Catalyzed by Fe^{2+}. The reaction rate was found to be dependent upon the concentration of perchloric acid, either in the absence or presence of Fe^{2+}. Since the rate constant k is in linear relationship with the reciprocal of hydrogen ion concentration at $[Fe^{2+}]_t=0$—0.2 M ($[\ ]_t$ represents the total concentration), as shown in Fig. 2, the reaction scheme and the rate equation are given as follows:

$$\begin{array}{lll} FeX^{2+} \left\{ \begin{array}{l} \xrightarrow{k_1} Fe^{3+} + X^- \\ + Fe^{2+} \xrightarrow{k_3} Fe^{3+} + FeX^+ \end{array} \right. & & \begin{array}{r} \text{(i)} \\ \text{(iii)} \end{array} \\ H^+ \Big\Updownarrow -H^+ & & \\ Fe(OH)X^+ \left\{ \begin{array}{l} \xrightarrow{k_2} Fe(OH)^{2+} + X^- \\ + Fe^{2+} \xrightarrow{k_4} Fe(OH)^{2+} + FeX^+ \end{array} \right. & & \begin{array}{r} \text{(ii)} \\ \text{(iv)} \end{array} \end{array}$$

$$k = k_1 + \frac{k_2K_H}{[H^+]} + \left(k_3 + \frac{k_4K_H}{[H^+]}\right)[Fe^{2+}], \tag{8}$$

where the individual rate constants are denoted by k_1, k_3, k_2, and k_4 respectively, and the hydrolysis constant of FeX^{2+} is expressed as $K_H=[Fe(OH)X^+][H^+]/[FeX^{2+}]$. In the absence of Fe^{2+}, k_1 and k_2K_H are determined from the intercept and the slope of the straight line obtained by plotting the observed k against $[H^+]^{-1}$, respectively. In the presence of Fe^{2+}, the linear relationship of $\{k-(k_1+k_2K_H/[H^+])\}/[Fe^{2+}]$ against $[H^+]^{-1}$ gives k_3 and k_4K_H from the intercept and the slope of the straight line, respectively, the linearity being shown in Fig. 3.

The experimental results thus obtained are listed in Table 1 for both $X^-=Cl^-$ and SCN^-. From the table, it is clear that Fe^{2+} catalyzes the dissociation reaction of FeX^{2+} in both systems, and that the reaction is more accelerated by Fe^{2+} in the $FeNCS^{2+}$ system than in the $FeCl^{2+}$ system, according to the value of k_3/k_1. Further, the unhydrolyzed species, FeX^{2+}, is more easily accelerated to dissociate that the hydrolyzed one, $Fe(OH)X^+$, because k_3/k_1 is larger than k_4/k_2. Anyway, the rate constant k_3 for Reaction iii coincides with the rate constant k_o in the electron transfer reaction through the outer-sphere mechanism, Path-O, which is really the rate constant aimed in the present study.

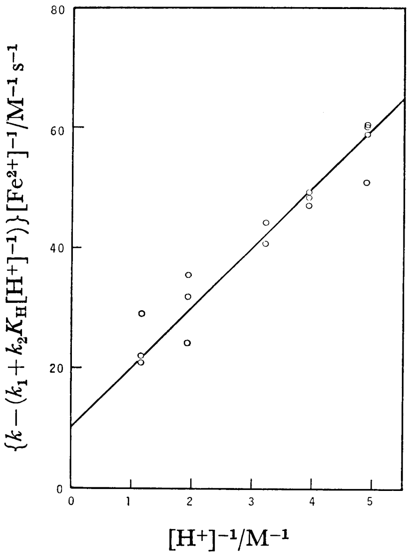


Fig. 3. Linear relationship of $\{k-(k_1+k_2K_H[H^+]^{-1})\}$ $[Fe^{2+}]^{-1}$ *vs.* $[H^+]^{-1}$, the conditions being the same as in Fig. 2.

Dissociation of FeN_3^{2+} Catalyzed by Fe^{2+}. In the reaction system containing N_3^-, the equilibrium, $H^+ + N_3^- \rightleftarrows HN_3$, has to be taken into account, in addition to the equilibria of the complex formation between Fe^{3+} and N_3^-, and of the hydrolysis of Fe^{3+}, in order to calculate the concentrations of free Fe^{3+}, N_3^-, and other relevant species. The equilibrium constants used are as follows: $K_{N_3}=[FeN_3^{2+}]/[Fe^{3+}][N_3^-]=2.7\times10^4$ M^{-1},[5,12)] $K_a=[H^+][N_3^-]/[HN_3]=3.0\times10^{-5}$ M,[5)] and $K_h=[Fe(OH)^{2+}][H^+]/[Fe^{3+}]=6.7\times10^{-3}$ M[6)] at $I=0.55$ M and 10 °C. The reaction temperature chosen was 10 °C, because of the fact that the rate-determining step in the electron transfer reaction between Fe^{2+} and FeN_3^{2+} is the first stage among the successively occurring elementary processes below 13 °C, above which temperature the reaction mechanism would be more complicated.[5)]

The rate measurements were performed at $[Fe(ClO_4)_3]_t=[NaN_3]_t=1.96\times10^{-3}$ M, $[HClO_4]_t=0.01$—0.5 M, $[Fe(ClO_4)_2]_t=0$—0.08 M, $I=0.55$ M and 10 °C. The observed k_{app} was transformed into k according to Eq. 7, since the values of the denominator on the right-hand side in Eq. 7 are no longer regarded to be nearly equal to unity for $X^-=N_3^-$, under the present conditions. When all the observed k's are plotted against $[H^+]$, k first decreases rapidly with the increase in $[H^+]$ in its low concentration range, and then k grows up almost linearly with a mild slope at higher $[H^+]$ range. Moreover, another linear relationship is also seen between k and $[H^+]^{-1}$ only within the lower $[H^+]$ range, $[H^+]=0.01$—0.075 M, namely $[H^+]^{-1}=13$—100 M^{-1}, as is shown in Fig. 4. Many observed points appear within the limited range as shown in the figure, independently of $[Fe^{2+}]$. Accordingly, the rate constant k can be expressed by Eq. 9, in which a term proportional to $[H^+]$ is supplemented to Eq. 8. This supplemented term may correspond to Reaction v, as shown below.

$$k = k_1 + \frac{k_2K_H}{[H^+]} + \left(k_3 + \frac{k_4K_H}{[H^+]}\right)[Fe^{2+}] + k_5[H^+], \tag{9}$$

Table 1. The individual rate constants for the dissociation reactions of $FeCl^{2+}$, $FeNCS^{2+}$, and FeN_3^{2+} catalyzed by Fe^{2+}

X^-	I / M	Temp / °C	k_1 / s^{-1}	k_2K_H / M s^{-1}	k_3 / $M^{-1}\ s^{-1}$	k_4K_H / s^{-1}	k_5 / $M^{-1}\ s^{-1}$	k_3/k_1 / M^{-1}	k_4/k_2 / M^{-1}
Cl^-	1.5	25	1.3	6.3	10.0	9.9	—	7.7	1.6
SCN^-	0.5	25	0.80	0.21	23	1.1	—	29	5.2
SCN^-	1.5	25	0.39	0.16	30	2	—	77	13
N_3^-	0.55	10	5.3×10^{-2}	1.4×10^{-2}	≈0	≈0	8.5×10^{-2}	0	0

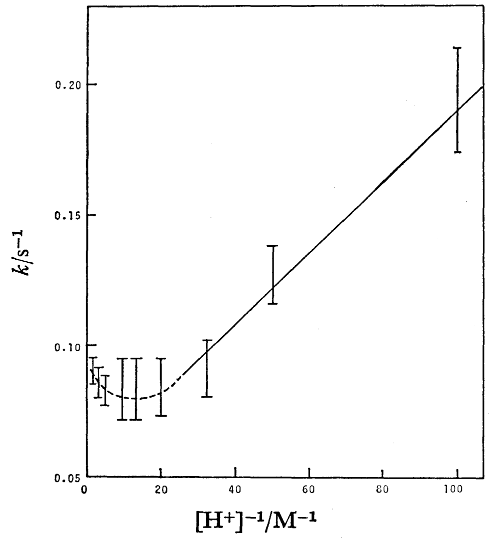


Fig. 4. Linear relationship of k vs. $[\mathrm{H}^+]^{-1}$, at $[\mathrm{Fe}^{3+}]_t = [\mathrm{N}_3^-]_t = 1.96 \times 10^{-3}$ M, $[\mathrm{H}^+] = 0.01$—0.05 M ($[\mathrm{H}^+]^{-1} = 100$—$20$ M^{-1}), $I = 0.55$ M, and 10 °C.
About 20 observed points scattering randomly between the two limiting values indifferent to the concentrations of existing Fe^{2+}, $[\mathrm{Fe}^{2+}]_t = 0.025$, 0.050, or 0.075 M, at each $[\mathrm{H}^+]^{-1}$ values.

$$\mathrm{FeN_3}^{2+} + \mathrm{H}^+ \xrightarrow{k_5} \mathrm{Fe}^{3+} + \mathrm{HN}_3. \qquad (\mathrm{v})$$

Reaction v is a hydrogen ion-assisted dissociation of $\mathrm{FeN_3}^{2+}$, where H^+ acts similarly as a catalyst in place of Fe^{2+} in Reaction iii.

Figure 4 looks like indicating that the rate constant k is probably unaffected by the concentration of Fe^{2+} within the experimental errors. The least squares method based on 128 observations give the most probable individual rate constants as follows:

$$k_1 = (5.34 \pm 0.22) \times 10^{-2}\,\mathrm{s}^{-1}$$
$$k_2K_\mathrm{H} = (1.37 \pm 0.05) \times 10^{-2}\,\mathrm{s}^{-1}$$
$$k_3 = (0.00 \pm 0.43) \times 10^{-1}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$$
$$k_4K_\mathrm{H} = (0.02 \pm 0.09) \times 10^{-2}\,\mathrm{s}^{-1}$$
$$k_5 = (8.52 \pm 0.72) \times 10^{-2}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}.$$

With fairly large errors, k_3 and k_4K_H should be regarded as zero, suggesting that the $\mathrm{FeN_3}^{2+}$ dissociation is not catalyzed by Fe^{2+}. These rate constants are listed in Table 1, along with those for $\mathrm{X}^- = \mathrm{Cl}^-$ and SCN^-.

The Ratio of Outer-sphere Mechanism in the Electron Transfer Reaction. As has been described above, the electron transfer reaction between Fe^{2+} and FeX^{2+} proceeds through either the inner-sphere or the outer-sphere mechanism or through both. The observed k_3 gives directly the rate constant k_o in the outer-sphere path. In Table 2, the overall rate constant k_E reported by previous workers, the outer-sphere rate constants k_o, and their ratios r defined by Eq. 5 are listed. According to the table, the electron transfer between Fe^{2+} and FeNCS^{2+} occurs wholly through the outer-sphere path. On the contrary, the electron transfer between Fe^{2+} and $\mathrm{FeN_3}^{2+}$ occurs wholly through the inner-sphere path, while that between Fe^{2+} and FeCl^{2+} undergoes both paths competitively.

Table 2. The total and the outer-sphere rate constants, k_E and k_o, and their ratio r of the electron transfer reaction

X^-	I / M	Temp / °C	k_o / $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	k_E[a] / $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	r / %
Cl^-	1.5	25	10	45[6,8]	44
SCN^-	0.5	25	23	41.5[3]	≈ 100
$\mathrm{N_3}^-$	0.55	10	≈ 0	4.75×10^3 [5]	≈ 0

a) Corrected to the given temperatures and ionic strengths.

To compare the two redox mechanisms, $\mathrm{N_3}^-$ and SCN^- have been frequently used, on the basis that the former ion is capable of bridging two reactants, resulting in the inner-sphere mechanism, whereas the latter ion is not.[13,14] The assumed intermediate complex in the inner-sphere mechanism bridged by $\mathrm{N_3}^-$ may be $[\mathrm{Fe{-}N{-}N{-}N{-}Fe}]^{4+}$ with a linear and symmetric structure. On the other hand, SCN^- is linear, but not symmetric having a larger S atom on one end than an N atom on the other end. Thus, the coordination of S with Fe^{2+} in the binuclear structure, $[\mathrm{Fe^{III}{-}N{-}C{-}S{-}Fe^{II}}]$, will be sterically unfavorable as a bridging ligand.

An additional condition is required for the inner-sphere mechanism that at least one of the two reactants should be substitution-labile, and this is fully satisfied in Fe^{2+}. Since the rate constant for the solvent water exchange reaction on $\mathrm{Fe}^{3+}{}_\mathrm{aq}$ has been known to be $1.6 \times 10^2\,\mathrm{s}^{-1}$ at 25 °C, that on $\mathrm{Fe}^{2+}{}_\mathrm{aq}$ may be larger than this value.[15] In this connection, the large value of $k_\mathrm{E}(\mathrm{N_3}^-)/k_\mathrm{E}(\mathrm{SCN}^-)$ ratio is usually believed to give a firm indication of the inner-sphere mechanism for $\mathrm{CoX(NH_3)_5}^{2+}/\mathrm{Fe}^{2+}{}_\mathrm{aq}$,[16] $\mathrm{CoX(NH_3)_5}^{2+}/\mathrm{Eu}^{2+}{}_\mathrm{aq}$,[17] *etc.*

For Cl^-, both mechanisms are probable. Chloride ion has more than two lone electron-pairs which may be favorable to bridge the two reactants, leading to the inner-sphere path, so-called "chlorine atom transfer." But in the Cl^--bridged binuclear intermediate, $[\mathrm{Fe{-}Cl{-}Fe}]^{4+}$, the nuclear distance between the two metal ions is too short to overcome the Coulombic repulsion between electric charges of the same sign, as compared with the case of $\mathrm{N_3}^-$ with the longer nuclear distance between the two iron ions, this fact being unfavorable to the inner-sphere mechanism. After all, the two mechanisms compete with each other in the Cl^- system. Sutin and his co-workers[8] carried out similar experiments, and concluded that the electron transfer between Fe^{2+} and FeCl^{2+} proceeded mainly by a chloride-bridged inner-sphere activated intermediate at $I = 3.0$ M and 25 °C, ignoring the process between Fe^{2+} and $\mathrm{Fe(OH)Cl}^+$, namely the fourth term $(k_4K_\mathrm{H}/[\mathrm{H}^+])[\mathrm{Fe}^{2+}]$ in Eq. 8, in the dissociation reaction of FeCl^{2+}. The forward and reverse reactions for the systems $\mathrm{Co^{II}}$(chelate) and $\mathrm{Fe^{III}(CN)_5X}$ are also considered to have trends of taking place through both mechanisms.[18] This is probably due to the fact that the bridging ligand, CN^-, is not only unsymmetric but also still too small to separate the electric charges on two reacting ions in its binuclear intermediate, inspite of its strong coordinating ability.

If the activation energies of the electron transfer reaction differed to a considerable extent between the two mechanisms, the ratio r would vary with temperature, and finally the reaction would go almost 100% *via* one of the two mechanisms at appropriately elevated or lowered temperatures. The systems of SCN^- and N_3^- observed above are just instances of such two limiting cases, respectively, while the Cl^- system may probably be transient between the two.

In conclusion, the symmetry and the length or size of the bridging ligand may be important factors to decide an inner-sphere mechanism or an outer-sphere one, or both in parallel.

Difference between Reaction Mechanisms of Outer-sphere Electron Transfer and Ligand Exchange. In the above descriptions, the electron transfer reaction through the outer-sphere mechanism (Path-O, k_o) and the dissociation reaction catalyzed by Fe^{2+} (Path-iii, k_3) are expressed by an identical equation.

$$Fe^{2+} + FeX^{2+} \longrightarrow Fe^{3+} + FeX^+$$

When one of the iron species is labeled by the isotopic tracer ^{59}Fe (represented by *Fe), however, two distinctly different reactions will become possible. If only one electron is really transferred from Fe^{2+} to FeX^{2+} with no change in chemical bondings (the outer-sphere electron transfer), the reaction is expressed as follows:

$$Fe^{2+} + {}^*FeX^{2+} \longrightarrow Fe^{3+} + {}^*FeX^+. \qquad (E)$$

On the other hand, if X^- is transferred from FeX^{2-} to Fe^{2+} without altering their oxidation states (the ligand exchange), the labeled Fe(III) remains still as Fe(III).

$$Fe^{2+} + {}^*FeX^{2+} \longrightarrow FeX^+ + {}^*Fe^{3+} \qquad (S)$$

These two chemical reactions, E and S, involve quite different elementary processes with each other, but in the present experimental method, we cannot distinguish between them explicitly.

Since the unimolecular dissociation reaction of FeX^{2+}, $FeX^{2+} \rightarrow Fe^{3+} + X^-$ (k_1), has been revealed to be very slow as shown in Table 1,[19] Reaction S might be reasonably supposed to occur in a way that Fe^{2+} encounters directly with FeX^{2+} before the spontaneous decomposition of FeX^{2+}, forming an inner-sphere intermediate. If so, N_3^- may be considered to be most favorable for Reaction S due to its largest bridging ability among three ligand anions. This expectation, however, is denied by the results in Table 1 which informs us that k_3 is almost zero in the case of N_3^-. Therefore, Reaction S may be impossible, and the acceleration of the FeX^{2+} dissociation by Fe^{2+} proceeds probably through the outer-sphere electron transfer due to Path-O, with the rate constant k_3 which is essentially the same with k_o.

When Mg^{2+}, Co^{2+}, Ni^{2+}, or Mn^{2+} was used in place of Fe^{2+} in the $FeCl^{2+}$ dissociation reaction, the reaction was found to be little affected by the presence of these ions.[8] This fact indicates that these metal ions except Fe^{2+} work neither as Cl^- acceptor (Reaction S) nor as electron donor (Reaction E). Only Fe^{2+} can catalyze the dissociation reaction of $FeCl^{2+}$ *via* the electron transfer process of the outer-sphere mechanism.

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