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Kinetic Studies of the Electron Transfer Reaction in Iron(II) and Iron(III) Systems. VI. Reaction in *N*,*N*-Dimethylformamide[1]

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The electron transfer reaction between Fe(II) and Fe(III) in *N*,*N*-dimethylformamide (DMF) was found to be influenced by the presence of perchloric acid, chloride ion, and water in the reaction system. This suggests that the reaction involves chemical species such as partially hydrated iron, its deprotonated iron, and $FeCl^{2+}$ and $FeCl_2^+$. The individual rate constants in DMF, containing a small amount of water, are $k_0=33.6\ M^{-1}s^{-1}$ for Fe^{2+}–Fe^{3+}, $k_1=1.2\times10^2\ M^{-1}s^{-1}$ for Fe^{2+}–$FeCl^{2+}$, and $k_2=\sim10^3\ M^{-1}\ s^{-1}$ for Fe^{2+}–$FeCl_2^+$ at $\mu=0.20$ M and 25 °C. The formation constant for $FeCl^{2+}$ was determined to be $K_1=(2.0\pm0.3)\times10^4\ M^{-1}$ at $\mu=0.20$ M and 25 °C. In the mixed solvents of DMF and water, the apparent rate constant exhibited a minimum at a certain water concentration. The activation parameters for the reactions Fe^{2+}–Fe^{3+} and Fe^{2+}–$FeCl^{2+}$ are $\Delta H_0^{\ne}=8.3$ kcal/mol, $\Delta S_0^{\ne}=-24$ cal/deg·mol, $\Delta H_1^{\ne}=4.5$ kcal/mol, and $\Delta S_1^{\ne}=-34$ cal/deg·mol, respectively. The results are compared with those in H_2O, D_2O, and DMSO.

The electron transfer reaction between iron(II) and iron(III) has been investigated in various solvents. In protic solvents such as water[2,3] and mixed solvents of water with some alcohols,[1,4,5] the predominant reaction path in the absence of catalytical bridging ligand was deduced to be one *via* a hydrogen-atom-transfer mechanism, first proposed by Reynolds and Lumry.[6] On the other hand, in dimethyl sulfoxide (DMSO)[7] as an aprotic solvent, the reaction was found to proceed faster than in water, although the hydrogen-atom-transfer mechanism does not seem to occur in aprotic solvents. In such a medium, therefore, an inner-sphere mechanism should be more favorable.

In this study, *N*,*N*-dimethylformamide(DMF), another aprotic solvent, of a little larger basicity than DMSO,[8,9] was adopted in order to see how its properties reflect on the reaction mechanism. Dependence upon the concentrations of acid, chloride ion, and water was investigated.

Experimental

Materials. Commercial DMF of E. P. grade (Nakarai Chemicals, Ltd.) was dried over potassium carbonate and sodium sulfate, and distilled twice under reduced pressure of nitrogen at about 40 °C. DMF solution of perchloric acid, prepared by mixing 70% perchloric acid of reagent grade and pure DMF, was used soon after preparation. The water content introduced by this method was about twice in molarity of the acid concentration in DMF. The concentration of water was kept constant at 0.3 M, unless otherwise stated.

An extremely anhydrous acid solution could be made up either by dissolving an anhydrous solid acid such as crystal of toluenesulfonic acid in DMF, or by passing a DMF solution of ammonium perchlorate through a column of cation-exchange resin of H-form. However, the former method was not free from the anion effect upon the reaction and the latter was accompanied by a small degree of decomposition of DMF during the treatment, deteriorating the reproducibility of the rate measurements considerably. Thus neither method was employed in the present preparation.

Other materials used were prepared by the procedure described elsewhere.[7,10] The ionic strength of the solution was controlled with sodium perchlorate at $\mu=0.20$ M. Radioactive iron-59 was used as a tracer.

Apparatus and Procedure. The methods for determining the formation constants and the rate constants were similar to those described previously.[7,10,11]

Results and Discussion

Reaction Order with Respect to Iron Concentrations. The reaction rate R of the electron transfer reaction, Fe(II)+*Fe(III)→Fe(III)+*Fe(II), is expressed by the following McKay's relation,[12]

$$R=\frac{0.693[\mathrm{Fe(II)}][\mathrm{Fe(III)}]}{\{[\mathrm{Fe(II)}]+[\mathrm{Fe(III)}]\}t_{1/2}} \tag{1}$$

where [Fe(II)] and [Fe(III)] represent the total concentrations of iron(II) and iron(III) species, respectively, and $t_{1/2}$ the half-life period of the reaction. If the reaction is of the first order with respect to each of [Fe(II)] and [Fe(III)], the apparent second-order rate constant k_{app} of the reaction can be obtained by the following equation, which should give a constant value at different iron concentrations under a fixed condition, this being proved in Table 1.

$$k_{app}=\frac{0.693}{\{[\mathrm{Fe(II)}]+[\mathrm{Fe(III)}]\}t_{1/2}} \tag{2}$$

Acid Dependence. The reaction rate was influenced by the concentration of perchloric acid in the concentration range 0.03—0.15 M; the higher the acid concentration the slower the reaction. When k_{app} was plotted against the reciprocal acid concentra-

Table 1. Constancy of second-order rate constants at fixed acid and water concentrations at $\mu=0.20$ M and 25 °C

$[HClO_4]$ M	$[H_2O]$ M	[Fe(II)] 10^{-4} M	[Fe(III)] 10^{-4} M	$t_{1/2}$ s	k_{app} $M^{-1}s^{-1}$
0.15	0.3	1.55	0.10	112	37.5
		1.26	0.34	120	36.9
		0.972	0.12	172	36.9
0.05	1.80	1.61	0.12	155	25.9
		1.22	0.20	161	30.6
		0.73	0.23	272	26.5
		0.59	0.21	305	28.7

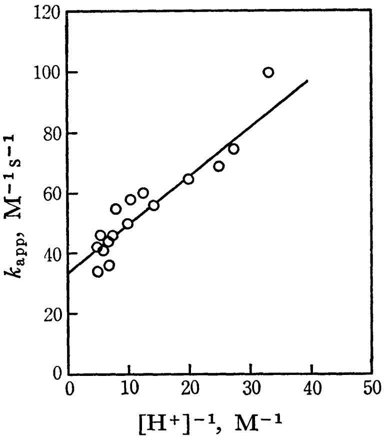

Fig. 1. Dependence of k_{app} upon $[H^+]^{-1}$ at $[H_2O] = 0.3$ M, $\mu = 0.20$ M, and 25 °C in DMF.

tion, a straight line was obtained with an intercept 33.6 $M^{-1}s^{-1}$ and a slope 1.71 s^{-1} at 25 °C, as is shown in Fig. 1. This implies that the reaction involves a path with a deprotonated species of the reactant. Thus, the acid-dependent reaction scheme in the presence of water in DMF is deduced as follows:

$$Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+} \quad (k_o) \tag{3}$$

$$Fe^{2+} + {}^*Fe(-H)^{2+} \rightarrow Fe(-H)^{2+} + {}^*Fe^{2+} \quad (k_H) \tag{4}$$

where $Fe(-H)^{2+}$ stands for an iron(III) species, of which one coordinated solvent molecule is deprotonated, keeping an equilibrium with acid concentration in the medium, and Fe^{2+} and Fe^{3+} stand for normally solvated ones.

Since DMF is more basic than DMSO,[8,9] it is not likely that the solvating DMF dissociates to lose a proton as an acid. The deprotonated species $Fe(-H)^{2+}$ might be one attributed to a coordinating water molecule which is present in the solvent. Thus, k_{app} can be expressed by the following equation, in which K_H is defined as the dissociation constant of the equilibrium $Fe^{3+} \rightleftarrows Fe(-H)^{2+} + H^+$.

$$k_{app} = \frac{k_o + k_H K_H/[H^+]}{1 + K_H/[H^+]} \tag{5}$$

Accordingly, $k_{app}(1 + K_H/[H^+])$ should have a linear relationship with $[H^+]^{-1}$. The value of K_H is not known here but since $K_H/[H^+]$ seems to be negligibly small as compared with unity, k_{app} would also exhibit an approximate linearity with $[H^+]^{-1}$, as is evident from Fig. 1. Thus, k_0 and $k_H K_H$ are found to be $k_0 = 33.6\ M^{-1}s^{-1}$ and $k_H K_H = 1.71\ s^{-1}$, respectively.

The value of k_0 is very close to that of the corresponding reaction in DMSO, 34.4 $M^{-1}s^{-1}$.[10] On the other hand, the value of $k_H K_H$ is difficult to be quantitatively analyzed. However, when *N*-methylacetamide or *N,N*-dimethylacetamide partially coordinates with iron(III) in aqueous solution, the electron transfer reaction is known still to occur *via* path 4.[13] It is not absurd to consider that the reaction can occur in a similar way in water-containing DMF.

Formation Constants of Fe(III)-Cl⁻ Complex. When sodium chloride is added to iron(III) perchlorate solution at $[Cl] = 3.53 \times 10^{-4}$ M, $[Fe(III)] = 4.92 \times 10^{-5}$ M, $[H^+] = 0.15$ M in DMF, the optical absorbance in the wavelength range 280—400 nm diminishes as a whole with a peak at *ca.* 340 nm and a minimum at *ca.* 290 nm. In Fig. 2, Job's curves are given at different total concentrations of iron(III) and chloride ion at $[H_2O] = 0.3$ M, $\mu = 0.2$ M, and $[H^+] = 0.15$ M, where the acid concentration is so high that the influence of the deprotonation of iron(III) species is removed. Curves (a) and (b) indicate that a 1 : 1 complex is formed between iron(III) and chloride ion at lower total concentrations and curve (c) that, at a higher concentration, a higher complex, probably of a composition of $FeCl_2^+$, is formed. The formaiton constant, $K_1 = [FeCl^{2+}]/[Fe^{3+}][Cl^-]$, and the molar absorptivity ε_1^{290} for $FeCl^{2+}$ are calculated[11] from the curves (a) and (b) at 25 °C and 16 °C as follows.

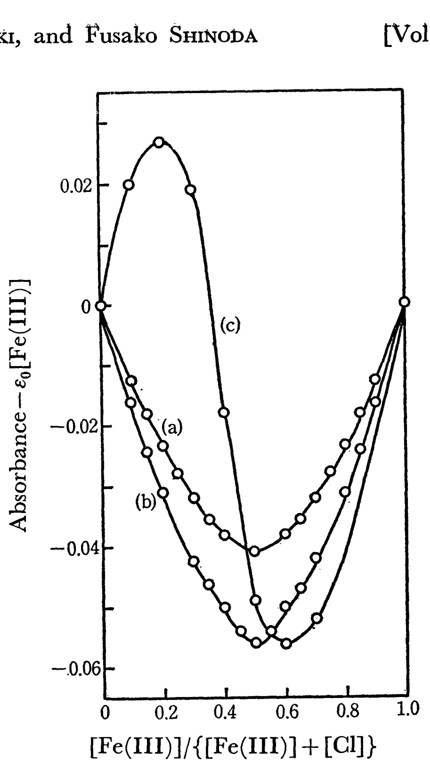

Fig. 2. Job's continuous variation curves for Fe(III) and Cl^- at $[H^+] = 0.15$ M, $[H_2O] = 0.3$ M, $\mu = 0.20$ M, and 25 °C in DMF.

(a) $[Fe(III)] + [Cl] = 1.4 \times 10^{-4}$ M at 290 nm
(b) $[Fe(III)] + [Cl] = 1.8 \times 10^{-4}$ M at 290 nm
(c) $[Fe(III)] + [Cl] = 2.0 \times 10^{-3}$ M at 440 nm

$$\left.\begin{aligned} K_1 &= (2.0 \pm 0.3) \times 10^4\ M^{-1} \\ \varepsilon_1^{290} &= (5.35 \pm 0.06) \times 10^3\ M^{-1}\,cm^{-1} \end{aligned}\right\}\ 25\ °C$$

$$\left.\begin{aligned} K_1 &= (1.9 \pm 0.4) \times 10^4\ M^{-1} \\ \varepsilon_1^{290} &= (5.20 \pm 0.05) \times 10^3\ M^{-1}\,cm^{-1} \end{aligned}\right\}\ 16\ °C$$

Both K_1 and ε_1^{290} seem to be independent of temperature. The K_1 value at 25 °C is about five times greater than that in DMSO, $K_1 = 3.7 \times 10^3\ M^{-1}$.[11]

Catalysis by Chloride Ion. The electron transfer reaction is accelerated by the presence of chloride ion; its apparent rate constant grows higher as the concentration of chloride ion increases at a constant acid concentration, $[H^+] = 0.15$ M. If chloroiron(III) complexes such as $FeCl^{2+}$ and $FeCl_2^+$ are involved in the reaction, the following two paths may occur in addition to 3 and 4:

$$Fe^{2+} + {}^*FeCl^{2+} \rightarrow FeCl^{2+} + {}^*Fe^{2+} \quad (k_1) \tag{6}$$

$$\mathrm{Fe^{2+} + {}^*FeCl_2{}^+ \rightarrow FeCl_2{}^+ + {}^*Fe^{2+}} \quad (k_2) \tag{7}$$

The apparent rate constant k_{app} is expressed by

$$k_{\mathrm{app}} = \frac{k_0 + k_{\mathrm{H}}K_{\mathrm{H}}/[\mathrm{H^+}] + k_1K_1[\mathrm{Cl^-}] + k_2K_1K_2[\mathrm{Cl^-}]^2}{1 + K_{\mathrm{H}}/[\mathrm{H^+}] + K_1[\mathrm{Cl^-}] + K_1K_2[\mathrm{Cl^-}]^2} \tag{8}$$

where K_2 represents the second stepwise formation constant of $\mathrm{FeCl_2{}^+}$, which is roughly estimated to be about $10^3\ \mathrm{M^{-1}}$ from a simple comparison with that of DMSO. According to Eq. 8, the following linearity between Y and $[\mathrm{Cl^-}]$ should be established, where D is the denominator in Eq. 8.

$$\begin{aligned} Y &= \frac{k_{\mathrm{app}}\cdot D - (k_0 + k_{\mathrm{H}}K_{\mathrm{H}}/[\mathrm{H^+}])}{[\mathrm{Cl^-}]} \\ &= k_1K_1 + k_2K_1K_2[\mathrm{Cl^-}] \end{aligned} \tag{9}$$

The linearity is proved in Fig. 3. The intercept and slope of the straight line give the values $k_1K_1 = 2.37 \times 10^6\mathrm{M^{-2}s^{-1}}$ and $k_2K_1K_2 = 4.64 \times 10^{10}\mathrm{M^{-3}s^{-1}}$, respectively. By using the values of K_1 and K_2, the individual rate constants are obtained as follows.

$$k_1 = 1.2 \times 10^2\ \mathrm{M^{-1}\,s^{-1}}$$
$$k_2 = \sim 10^3\ \mathrm{M^{-1}\,s^{-1}}$$

Dependence upon Water Concentrations. Since the DMF we used inevitably contained a small amount of water, it was necessary to examine the influence of water upon the rate constants. When the water concentration was changed in DMF as mixed solvents, the value of k_{app} decreases with the increase in water concentration and reaches a broad minimum, beyond which it increases at a constant acid concentration. The minimum points of k_{app} appear at about 2 and 4 M of water concentration when the fixed acid concentrations are 0.01 M and 0.05 M, respectively. Such behaviors of water are reproduced in Fig. 4. The value of k_{app} is always smaller at higher acid concentrations within the water concentration range studied.

In aqueous DMF, the partially-hydrated iron species such as $\mathrm{Fe(III)(H_2O)}_x\mathrm{(DMF)}_{6-x}$ should be considered to be involved in the electron transfer reaction. Judging from the fact that k_{app} is dependent upon the acid concentration, the deprotonated species of the hydrated iron, $\mathrm{Fe(III)(OH^-)(H_2O)}_{x-1}\mathrm{(DMF)}_{6-x}$, seems also to take part in the reaction with a larger rate constant than that due to the unhydrolyzed one. Since the formation constants and hydrolysis constants for the iron species hydrated to various extents are not known, the individual rate constants cannot be estimated.

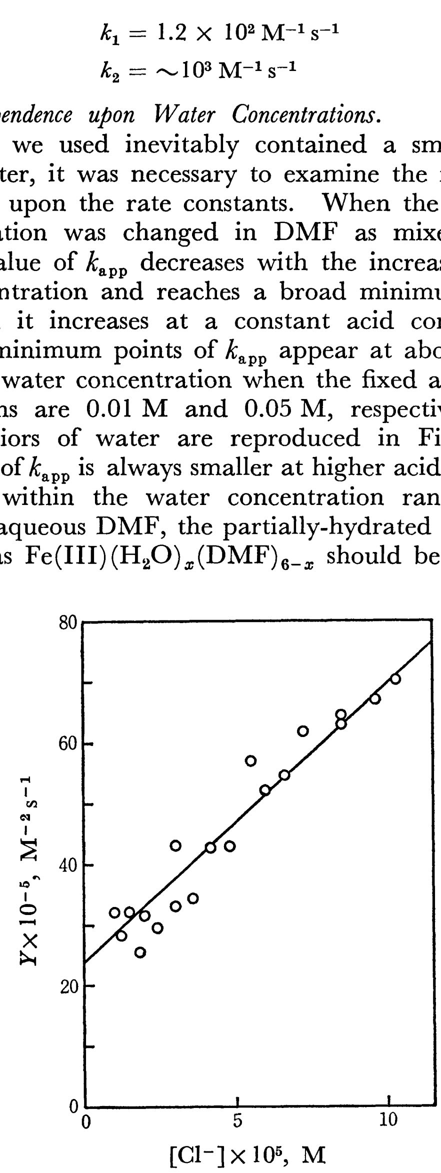

Fig. 3. Linear relationship between Y and $[\mathrm{Cl^-}]$ at $[\mathrm{H^+}] = 0.15\ \mathrm{M}$, $[\mathrm{H_2O}] = 0.3\ \mathrm{M}$, $\mu = 0.20\ \mathrm{M}$, and 25 °C in DMF.

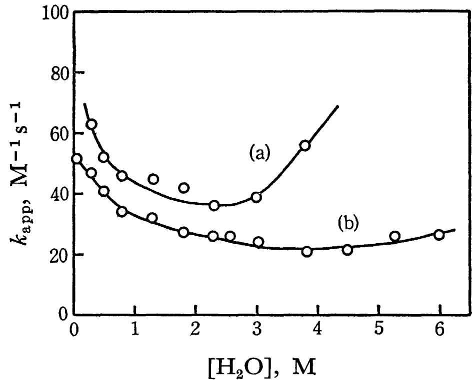

Fig. 4. Dependence of k_{app} upon $[\mathrm{H_2O}]$ at $\mu = 0.20$ M and 25 °C in DMF.
(a) $[\mathrm{H^+}] = 0.01\ \mathrm{M}$, (b) $[\mathrm{H^+}] = 0.05\ \mathrm{M}$

The phenomenon that k_{app} exhibits a minimum at a certain water concentration when the acid concentration is constant, has been also observed in the cases of mixed solvents of DMSO and water.⁷⁾ As the water content varies from zero to 100%, the predominant mechanism of the reaction may also turn from an inner-sphere type to a hydrogen-atom-transfer one in DMF as in DMSO.

The DMSO used for the first investigation on the electron transfer reaction between iron(II) and iron(III) contained water at as high as $[\mathrm{H_2O}] = 0.015\ \mathrm{M}$.⁷⁾ The water concentration was much higher than those of reactants $10^{-5}-10^{-4}$ M. However, since DMSO is very hydrophilic¹⁴⁾ and water is likely to be preferentially excluded from the coordination sphere of metal ions in DMSO-rich mixed solvents of DMSO and water,¹⁵⁾ the occurrence of partially hydrated iron species was not so great as expected. This might be the case with DMF, although the water concentration is larger.

An important difference between DMSO and DMF is as follows. In the former, the acid dependence of k_{app} tends to disappear⁷⁾ or become smaller at least¹⁰⁾ as the water concentration is lowered. In the latter, it tends to remain according to the extrapolation of water concentration to zero. The reason for this is not clear at present.

Activation Parameters and General Discussion. Kinetic measurements were carried out at 10 °C—35 °C at intervals of five degrees. The activation parameters, $\Delta H_0^{\neq}$, $\Delta S_0^{\neq}$, $\Delta H_1^{\neq}$, and $\Delta S_1^{\neq}$ were calculated from the linearity between $\log(k_0/T)$ and $\log(k_1/T)$ *vs.* T^{-1}, respectively. The results are listed in Table 2, along with various related data in other solvents in literature. The data related to DMF may be approximately regarded as those in pure DMF.

TABLE 2. SUMMARY OF RATE CONSTANTS AND ACTIVATION PARAMETERS IN VARIOUS SOLVENTS

Solvent	Dielectric constants	Condition μ, temp. °C	k_0 $M^{-1} s^{-1}$	k_1 $M^{-1} s^{-1}$	k_2 $M^{-1} s^{-1}$	$\Delta H_0^{\neq}$ kcal/mol	$\Delta S_0^{\neq}$ cal/deg·mol	$\Delta H_1^{\neq}$ kcal/mol	$\Delta S_1^{\neq}$ cal/deg·mol	log K_1 (M^{-1})
H_2O[3,16]	80	0.5, 25°	4.0	22.8(20°)	53(20°)	10.5	−20.6	11.0	−15	1.48
D_2O[3,16]	79	0.5, 25°	1.0	9.1(20°)	—	—	—	13.2	−10	—
DMSO[7,10,17]	46.7	0.2, 20°	34.4(25°)	1.3×10^2 $(\mu=0.1)$	1.02×10^3 $(\mu=0.1)$	9.7	−19	5.2	−27	3.62
DMF	36.1	0.2, 25°	33.6	1.2×10^2	$\sim10^3$	8.3	−24	4.5	−34	4.30

The rate constants and activation parameters for DMSO and DMF are very close. This suggests that the solvent effects on the reaction are similar to each other, and accordingly the reaction scheme is the same. DMF, as well as DMSO, is a unique aportic solvent in which the value of k_0 is larger than that in water.

A DMF molecule coordinates with an iron ion on the oxygen atom,[18] and has a tendency to be hydrolyzed to give formate ion and dimethylamine in the presence of hydroxide ion in DMF–water mixture.[19] Thus, it is probable that hydroxide ion reacts with DMF intramolecularly in the coordination sphere of an $Fe(OH^-)(DMF)$-type complex in the case of DMF–water mixed solvents, making the electron transfer reaction somewhat more complicated.

The value of the formation constant of $FeCl^{2+}$, log K_1 in Table 2, varies in the sequence H_2O <DMSO <DMF, being in line with what is expected from the dielectric constants of the solvents.

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