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Kinetic Studies of the Electron Transfer Reaction in Iron(II) and Iron(III) Systems. III. Complex Formation and Catalytic Action with Thiocyanate Ion in Dimethyl Sulfoxide[1]

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The formation constants K_1 and K_2 of the complexes $Fe(NCS)^{2+}$ and $Fe(NCS)_2{}^+$ in dimethyl sulfoxide (DMSO) and the rate constants and the activation parameters of the electron transfer reaction between Fe(II) and Fe(III) in DMSO catalyzed by thiocyanate ion were measured. K_1 and K_2 are $(8.4\pm0.9)\times10^2\ \mathrm{M}^{-1}$ and $(0.97\pm0.10)\times10^2\ \mathrm{M}^{-1}$ at $\mu=0.1$ M and 25°C, respectively. The apparent rate constant k_{app} is nearly independent of acid concentrations and increases markedly with total thiocyanate ion concentration. The rate constants k_1 and k_2 of Fe^{2+}-$Fe(NCS)^{2+}$ and Fe^{2+}-$Fe(NCS)_2{}^+$ systems are $(2.24\pm0.35)\times10^2\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$ and $(2.96\pm0.64)\times10^3\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$ at $\mu=0.2$ M and 25°C, respectively. $\Delta H_1^{\ddagger}=8.9\pm1.0$ kcal/mol and $\Delta S_1^{\ddagger}=-17\pm3$ cal/deg·mol are obtained from the temperature dependence of k_{app}. From a comparison with the data of cases catalyzed by Cl^- and SCN^- ions in water and DMSO, the present electron transfer reaction is deduced to proceed probably *via* the inner-sphere mechanism with the SCN^- ion as a bridging ligand, similar to the Cl^- ion-catalyzed reaction in DMSO.

In the electron transfer reaction between iron(II) and iron(III) species in aqueous solutions, the hydrogen atom transfer mechanism seemed to prevail because the hydrogen atoms of water molecules played an important role.[2] This was proved directly and indirectly by further evidence that the reaction still proceeded at a considerable rate even in the solid state[3] or in the very concentrated perchloric acid media[4] and that the reaction rate decreased with the addition of certain substances, such as nitromethane,[5] 2-propanol,[6] and some other alcohols,[7] because no or less exchangeable hydrogen atoms attached to the molecules of these substances. However, dimethyl sulfoxide (DMSO) was found to be not a substance making the reaction proceed slower but rather to be a medium better than water for the reaction, although DMSO seems to have no such exchangeable hydrogen atoms through which long chains of molecules are formed by hydrogen bondings, as water molecules easily do.[8] Moreover, the rate constants of the electron transfer reaction catalyzed by the chloride ion in this solvent are much larger than those in water.[9] Thus, there must be a reaction path other than the path *via* the hydrogen atom transfer mechanism.

According to recent more precise investigations, the electron transfer reactions of both the Fe^{2+}-$FeCl^{2+}$[10] and Fe^{2+}-$FeNCS^{2+}$[11] systems proceed predominantly even in aqueous solutions, *via* the inner-sphere mechanism and not *via* hydrogen atom transfer mechanism.

The present work was undertaken to see what effect thiocyanate ion has on the rate of the electron transfer reaction in DMSO, as compared with the case in which chloride ion was used in the same solvent.[9] In order to obtain the individual rate constants of the elementary reactions, the formation constants for the complexes between the existing species in DMSO had to be determined first. This was performed by the methods used in our previous investigation in the iron(III)-chloride ion-DMSO system.[12]

Experimental

Materials. Commercial DMSO of guaranteed reagent grade was distilled under a reduced nitrogen atmosphere of 3—4 mmHg, dried by shaking with activated alumina, and redistilled under the same condition. Iron(II) perchlorate crystal was prepared by dissolving pure iron wire in dilute perchloric acid and recrystallizing under an atmosphere of nitrogen. Iron(III) perchlorate was, then, easily prepared by oxidation of the iron(II) salt by hydrogen peroxide and the following recrystallization. Both crystals were not anhydrous but contained some lattice water. This did not matter at all, since the crystals were used only at very dilute concentrations and it was confirmed that a small amount of water does not seriously influence the results. Anhydrous sodium perchlorate was obtained by drying monohydrous salt recrystallized from water at 300°C. Anhydrous ammonium thiocyanate was obtained by storing wet crystal in a desiccator at room temperature, after recrystallization twice. The perchloric acid in DMSO was prepared by means of cation exchange resin. Dowex 50 w×8 resin of 50—100 mesh was treated with 6 N hydrochloric acid to transform it into H-type, washed with water to eliminate chloride ion completely, dried in an electric oven at a temperature not over 100°C, allowed to swell in DMSO, filled in a column, and then made to pass through a DMSO solution of 0.7 M ammonium perchlorate, until ammonium ion became detectable by the Nessler reagent in the eluent. The ammonium-free perchloric acid in DMSO obtained

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[1] Previous paper: G. Wada and R. Yoshihara, *Kogyo Kagaku Zasshi*, **73**, 2309 (1970).

[2] W. L. Reynolds and R. W. Lumry, *J. Chem. Phys.*, **23**, 2460 (1955).

[3] R. A. Horne, *J. Inorg. Nucl. Chem.*, **25**, 1139 (1963).

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[5] A. G. Maddock, *ibid.*, **55**, 1268 (1959).

[6] N. Sutin, *J. Phys. Chem.*, **64**, 1766 (1960).

[7] R. A. Horne, "Exchange Reactions," I.A.E.A., Vienna, (1965), p. 67.

[8] J. Menashi, W. L. Reynolds, and G. van Auken, *Inorg. Chem.*, **4**, 299 (1965).

[9] G. Wada and W. L. Reynolds, *ibid.*, **5**, 1354 (1966).

[10] R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Amer. Chem. Soc.*, **86**, 4591 (1964).

[11] T. J. Conocchioli and N. Sutin, *ibid.*, **89**, 282 (1967).

[12] G. Wada, This Bulletin, **41**, 882 (1968).

was titrated with sodium hydroxide.

The stock solution of the radioactive tracer of ^{59}Fe was manufactured as follows: The radioactive $^*FeCl_3$ in hydrochloric aqueous solution was heated in an evaporating dish, and a few drops of perchloric acid were added just before dryness. After repeating the procedure several times, the final perchloric salt was dissolved in DMSO and stored in the cold.

Photometry. For determination of optical densities of sample solutions, a Hitachi-Perkin-Elmer UV-VIS spectrophotometer Model 139 was used with a thermostated cell compartment and 1-cm silica cells.

Rate Measurements of Electron Transfer Reactions. The reaction was started by mixing two solutions, A and B, in a reaction vessel in a thermostat. Contents of solution A were $Fe(ClO_4)_3$ (labeled with ^{59}Fe), NH_4SCN, $HClO_4$, and $NaClO_4$. Those of solution B were the same as solution A except for $Fe(ClO_4)_2$ in place of $Fe(ClO_4)_3$. Nitrogen gas saturated with DMSO vapor was continuously bubbled through the reaction solution before and after the initiation of the reaction. Nitrogen bubbling was carried out not only for stirring but also for preventing oxidation. At certain intervals, an aliquot of the reaction solution was quickly taken out by a syringe or a thermostated pipet, into a quenching solution containing 2,2′-bipyridyl which immediately stopped the reaction because of quick formation of $Fe(bipy)_3^{2+}$. The quenching solution also contained aluminum nitrate. By addition of ammonia, aluminum ion was coprecipitated with iron(III) ion as hydroxide. The precipitate was filtered from the solution and the radioactivity of a definite portion of the filtrate was measured with a well-type scintillation counter. The rest of the filtrate was used for optical determination of the concentration of iron(II) in the form of $Fe(bipy)_3^{2+}$ at 522 nm. The sample of the reaction solution at infinite time was taken at least ten half lives of the reaction after the initiation. In order to determine the total concentration of iron species in the system, the iron(III) was reduced to iron(II) by hydroxylamine. A more detailed procedure of the rate measurement was described previously.8,9)

Results and Discussion

Absorption Spectra and Formation Constants of Fe^{3+}-SCN^- *Complexes in DMSO.* The absorption spectra of $Fe(ClO_4)_3$ and of $Fe(ClO_4)_3$-NH_4SCN in DMSO at $HClO_4$ concentration of 0.02 M are shown in Fig. 1. Curves A and B show respectively the spectrum of the simply solvated Fe^{3+}, and that of a mixture of Fe^{3+} and SCN^-, which partly form monothiocyanato complex. By combining both curves and the value of K_1 which will be obtained later, curve C can be calculated as the true spectrum of $FeNCS^{2+}$ complex, which exhibits a peak at 450 nm. The spectra A and C coincide well with those of Wada *et al.*9,12) and Csiszar *et al.*,13) respectively. The spectra were not influenced by the change in acid concentration.

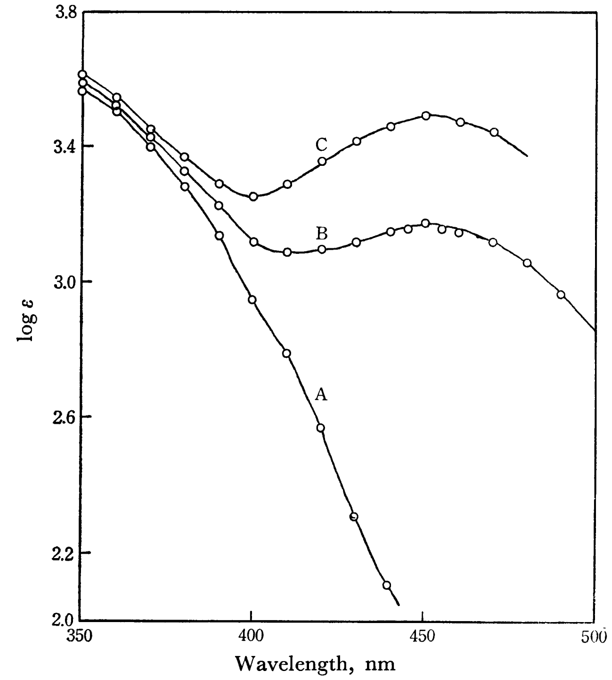

Fig. 1. Absorption spectra of Fe^{3+}, $FeNCS^{2+}$ in DMSO, at $[HClO_4]=0.02$ M, $\mu=0.10$ M and 25°C.
Curve A. $[Fe^{3+}]_0=5.40\times10^{-5}$ M
Curve B. $[Fe^{3+}]_0=5.40\times10^{-5}$ M, $[SCN^-]_0=9.78\times10^{-4}$ M
Curve C. Calculated for $FeNCS^{2+}$

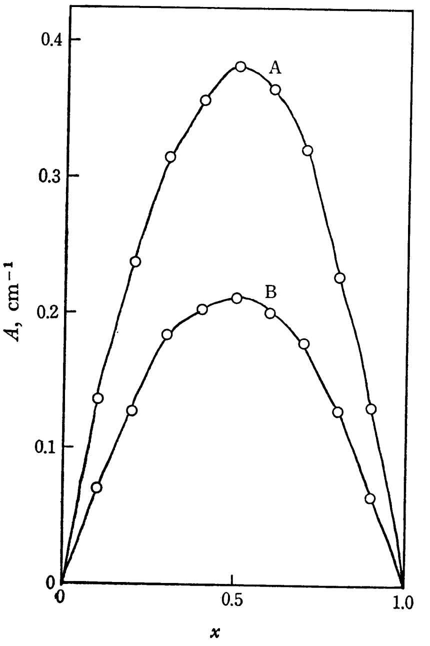

Fig. 2. Job's curves for Fe^{3+}-SCN^- system in DMSO at $[HClO_4]=0.02$ M, $\mu=0.10$ M, 25°C and 450 nm.
Curve A. $C_a=1.00\times10^{-3}$ M
Curve B. $C_b=0.700\times10^{-3}$ M

The formation constant of $FeNCS^{2+}$, $K_1=[FeNCS^{2+}]/[Fe^{3+}][SCN^-]$, was determined by means of Job's continuous variation method.12) Job's curves at $C_a=1.00\times10^{-3}$ and $C_b=0.70\times10^{-3}$ M are depicted in Fig. 2, C_a and C_b being the sum of the total concentrations of iron(III) and thiocyanate ion, $[Fe^{3+}]_0$ and $[SCN^-]_0$. The maximum points appear just at the center of the symmetrical curves indicating that the complex formed at these concentrations is of the composition Fe^{3+} : SCN^- = 1 : 1. The observations were carried out at 440, 450, and 460 nm. K_1 and the

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13) B. Csiszar, V. Gutmann, and E. Wychera, *Monatsh. Chem.*, **98**, 12 (1967).

molar extinction coefficient ε_1 of FeNCS^{2+} are calculated by the following equation.[12]

$$A = \varepsilon_0[\mathrm{Fe}^{3+}] + \varepsilon_1[\mathrm{FeNCS}^{2+}] - \varepsilon_0[\mathrm{Fe}^{3+}]_0 = (\varepsilon_1-\varepsilon_0)[\mathrm{FeNCS}^{2+}] \tag{1}$$

$$[\mathrm{FeNCS}^{2+}] = \frac{x_a(1-x_a)C_a^2-x_b(1-x_b)C_b^2}{C_a-C_b} \tag{2}$$

$$[\mathrm{Fe}^{3+}] = x_aC_a - [\mathrm{FeNCS}^{2+}] \tag{3}$$

$$[\mathrm{SCN}^-] = (1-x_a)C_a - [\mathrm{FeNCS}^{2+}] \tag{4}$$

$$\varepsilon_1 = \frac{A}{[\mathrm{FeNCS}^{2+}]} + \varepsilon_0 \tag{5}$$

The values of $\varepsilon_0[\mathrm{Fe}^{3+}]+\varepsilon_1[\mathrm{FeNCS}^{2+}]$ in Eq. (1) correspond to the observed absorbances of the sample at individual wavelengths. By means of Eqs. (2), (3), and (4), the following value was obtained.

$$K_1 = (8.4\pm0.9) \times 10^2\,\mathrm{M}^{-1} \text{ at } 25^\circ\mathrm{C} \tag{6}$$

Another K_1 value obtained by means of stopped flow method by other authors is $1.18\times10^3\,\mathrm{M}^{-1}$ at $\mu=0.024$ M and 25°C, which is a little larger than ours.[14,15]

At higher concentrations, dithiocyanato complex seems to be formed gradually, because the linearity between $\bar{\varepsilon}$ and $(\bar{\varepsilon}-\varepsilon_0)/[\mathrm{SCN}^-]$ is no longer established.[12,16] However, the linear relationship between $\bar{\varepsilon}$ and $\Delta\bar{\varepsilon}(1+K_1[\mathrm{SCN}^-])/K_1[\mathrm{SCN}^-]^2$ becomes noticeable, according to the equation

$$\bar{\varepsilon} = \varepsilon_2 - \frac{1}{K_2}\,\frac{\Delta\bar{\varepsilon}(1+K_1[\mathrm{SCN}^-])}{K_1[\mathrm{SCN}^-]^2} \tag{7}$$

where $\bar{\varepsilon}$ is the apparent molar extinction coefficient of iron(III), $\Delta\bar{\varepsilon}$ the deviation of the observed $\bar{\varepsilon}$ from hypothetical $\bar{\varepsilon}$ which would have been obtained if no $\mathrm{Fe(NCS)_2}^+$ formation occurred, and K_2 is defined to be the stepwise formation constant $K_2=[\mathrm{Fe(NCS)_2}^+]/[\mathrm{FeNCS}^{2+}][\mathrm{SCN}^-]$. Figure 3 shows the straight line according to Eq. (7), from whose intercept and slope ε_2 and K_2 are obtained at 25°C as follows:

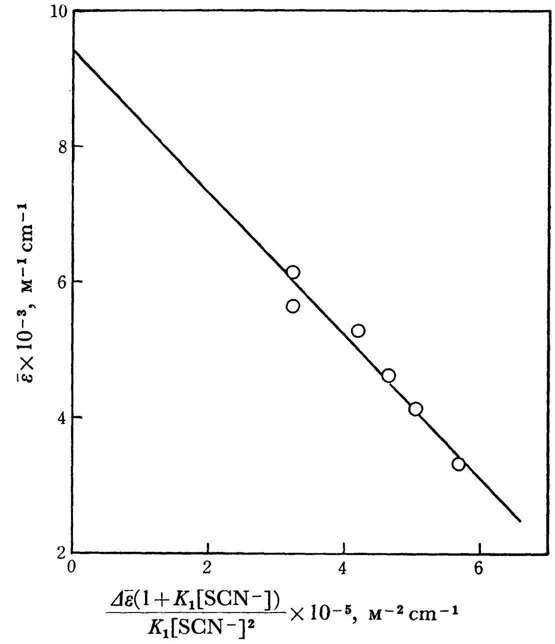

Fig. 3. Linear relation of $\bar{\varepsilon}$ against $\Delta\bar{\varepsilon}(1+K_1[\mathrm{SCN}^-])/K_1[\mathrm{SCN}^-]^2$ at $[\mathrm{HClO_4}]=0.02$ M, $\mu=0.10$ M, 25°C and 450 nm.
$[\mathrm{Fe}^{3+}]_0=1.89\times10^{-4}$ M
$[\mathrm{SCN}^-]_0=(3.14-11.73)\times10^{-3}$ M

$$\varepsilon_2 = (9.4\pm0.5) \times 10^3\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1} \text{ at } 450\,\mathrm{nm} \tag{8}$$

$$K_2 = (0.97\pm0.10) \times 10^2\,\mathrm{M}^{-1} \text{ at } 25^\circ\mathrm{C} \tag{9}$$

The dependence of K_1 and K_2 upon the dielectric constant of the solvents is listed in Table 1, in which the solvents are arranged in the sequence of their dielectric constants. It is seen that the lower the dielectric constant, the larger the stability of the complex, as expected theoretically. The linear relationship of $\log K_1$ *vs.* the reciprocal of the dielectric constant is roughly established.

By similar trials to determine the formation constant

TABLE 1. DEPENDENCE OF K_1 AND K_2 UPON THE DIELECTRIC CONSTANT OF SOLVENTS

Solvent	Temperature °C	Dielectric constant	$\log K_1$	$\log K_2$	Ref.
$\mathrm{H_2O}$ 0.5 M $\mathrm{NaClO_4}$	25	80	2.14	1.31	17)
$\mathrm{H_2O}$ 0.128 M $\mathrm{HClO_4}$	—	80	2.37	—	18)
20% acetone 0.1 H^+	20	71	2.43	—	19)
40% acetone 0.1 H^+	20	58	2.57	—	19)
DMSO $\mu=0.1$	25	46.7	2.92	1.99	Present work
DMSO $\mu=0.024$	25	46.7	3.07	—	14)
80% acetone 0.1 H^+	20	32	3.2	—	19)
90% ether	—	29.8	4.70	—	20)

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14) C. H. Langford and F. M. Chung, *J. Amer. Chem. Soc.*, **90**, 4485 (1968).

15) According to Keiko Ohnishi in our laboratory, the value of K_1 determined by conductivity method is $6\times10^4\,\mathrm{M}^{-1}$, which is much larger than that by spectrophotometry. The discrepancy indicates that iron(III) ion has a widely spread ionic atmosphere around itself with its high electric charges in low dielectric medium. The value determined by the spectrophotometry only measures the complex which coordinates with thiocyanate ion in the first coordination sphere of the central ion.

16) T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).

17) G. S. Laurence, *Trans. Faraday Soc.*, **52**, 236 (1956).

18) H. S. Frank and R. L. Oswalt, *J. Amer. Chem. Soc.*, **69**, 1321 (1947).

19) A. K. Babko and L. V. Markova, *Ukr. Khin. Zh.*, **25**, 363 (1959).

20) A. K. Babko and V. S. Kodenskaya, *Zh. Obshch. Khim.*, **17**, 1080 (1947).

of the Fe^{2+}-SCN^--DMSO system, no formation of complex species was recognized, in spite of the fact that the formation of $FeNCS^+$ has been found with the equilibrium constant 7.0±0.5 M^{-1} by a flow technique in water.[11]

Rate Constants of Electron Transfer Reaction. According to McKay, isotopic exchange reactions including such types as the present electron transfer generally obey the rate equation[21-23]

$$\ln\left(1-\frac{x}{x_\infty}\right) = -\frac{a+b}{ab}Rt \tag{10}$$

in which x and x_∞ represent radioactivity at time t and infinite time t_∞, respectively, and a and b the analytical total concentrations of iron(II) and iron(III), respectively, employed in the reaction system. R is the reaction rate. A typical linear relation of $\log(x_\infty - x)$ *vs.* time is drawn in Fig. 4. If the half life of the reaction is denoted by $t_{1/2}$, and if the reaction is regarded as that of first order with respect to both iron(II) and iron(III) concentrations, the apparent second order rate constant k_{app} is given by

$$k_{app} = \frac{0.693}{(a+b)t_{1/2}} \tag{11}$$

If the reaction is of first order with respect to the individual concentrations of both iron(II) and iron(III), a rate equation $R = k_{app}ab$ is doubtlessly established, since the arbitrary variation in both concentrations gave a good constant k_{app} as long as other conditions of the reaction were kept unchanged, although it was practically impossible to assure the separate concentration dependence of both iron(II) and iron(III) because of experimental difficulty.

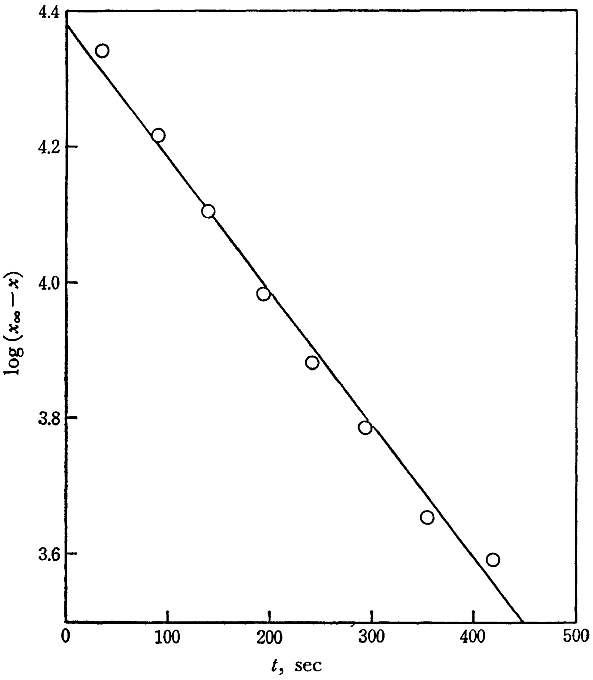

Fig. 4. Typical rate measurement of the reaction at 25°C.
$[Fe(II)]_0 = 3.69 \times 10^{-5}$ M
$[Fe(III)]_0 = 2.61 \times 10^{-5}$ M
$[SCN^-]_0 = 2.32 \times 10^{-4}$ M
$[HClO_4] = 1 \times 10^{-2}$ M
$\mu = 0.2$ M

Calculation of the values of k_{app} was performed by the method of least squares. The probable error was usually less than 5%.

Dependence of k_{app} on Acid Concentrations. Table 2 shows the dependence of k_{app} on the variation of acid concentrations in the range 6.9×10^{-5}—1.01×10^{-1}M. This indicates a slight but regular decrease of k_{app} with the increase of acid concentration. Acid concentration dependence of k_{app} appears to be much less than in the case of chloride ion-catalyzed electron transfer reaction in DMSO.[24] It might be said that k_{app} is nearly independent of the acid concentration except at very high acid concentration.

TABLE 2. DEPENDENCE OF k_{app} UPON ACID CONCENTRATION
$[SCN^-]_0 = 3.07 \times 10^{-4}$ M, $\mu = 0.2$ M, 25°C

$[HClO_4]$ M	$[Fe(II)]_0 \times 10^5$ M	$[Fe(III)]_0 \times 10^5$ M	k_{app} $M^{-1}sec^{-1}$
6.9×10^{-5}	5.27	2.77	84.9
1.4×10^{-4}	9.67	3.36	79.6
3.4×10^{-4}	6.63	3.85	79.5
1.03×10^{-3}	7.28	2.06	79.2
5.15×10^{-3}	10.32	1.68	78.8
1.00×10^{-2}	3.86	1.46	77.3
1.01×10^{-1}	7.77	1.14	58.5

Dependence of k_{app} on SCN^- Ion Concentration. The reaction is markedly catalyzed by thiocyanate ion; its effects on k_{app} are summarized in Table 3. k_{app} is accelerated by the presence of SCN^- ion, similar as to the case of Cl^- ion.[9] Thus, the following three reaction paths can be considered to represent the principal mechanisms.

$$Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+} \qquad k_0 \tag{12}$$

$$Fe^{2+} + {}^*FeNCS^{2+} \rightarrow FeNCS^{2+} + {}^*Fe^{2+} \qquad k_1 \tag{13}$$

$$Fe^{2+} + {}^*Fe(NCS)_2^{+} \rightarrow Fe(NCS)_2^{+} + {}^*Fe^{2+} \qquad k_2 \tag{14}$$

The symbols Fe^{2+}, Fe^{3+}, $FeNCS^{2+}$, and $Fe(NCS)_2^+$ in the equations stand for the individual solvated species $Fe(DMSO)_6^{2+}$, $Fe(DMSO)_6^{3+}$, $Fe(DMSO)_5(NCS)^{2+}$, and $Fe(DMSO)_4(NCS)_2^+$, respectively, and the rate constants for the reactions (12), (13), and (14) are represented by k_0, k_1, and k_2, respectively. The first five values of k_{app} in Table 3 indicate that $k_0 = 34.4$ $M^{-1}sec^{-1}$ as the mean value.

Since the observed rate is the sum of the values through the three paths, and the concentrations of the complexes involved in the reaction are decided by their formation constants, k_{app} is written as follows:

$$k_{app} = \frac{k_0 + k_1K_1[SCN^-] + k_2K_1K_2[SCN^-]^2}{1 + K_1[SCN^-] + K_1K_2[SCN^-]^2} \tag{15}$$

When the denominator in Eq. (15) is substituted into D for simplicity, Eq. (15) can be rearranged to

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[21] H. A. C. Mckay, *Nature*, **42**, 997 (1938).

[22] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

[23] T. Takaishi, This Bulletin, **42**, 1266 (1969).

[24] G. Wada and W. L. Reynolds, "Exchange Reactions," I.A.E.A., Vienna (1965), p. 59.

Table 3. Dependence of k_{app} upon thiocyanate ion concentration
$[HClO_4]=0.01$ M, $\mu=0.2$ M, 25°C

$[SCN^-]_0\times10^4$ M	$[SCN^-]\times10^4$ M	$[Fe(II)]_0\times10^5$ M	$[Fe(III)]_0\times10^5$ M	k_{app} $M^{-1}sec^{-1}$
—	—	11.4	4.35	33.7
—	—	6.68	2.71	37.7
—	—	11.6	3.66	35.3
—	—	12.0	3.91	33.5
—	—	8.15	6.25	32.0
0.77	0.765	5.76	1.30	44.9
1.08	1.06	3.15	2.28	62.7
1.55	1.54	3.75	0.87	51.9
1.55	1.53	2.66	1.84	61.9
2.32	2.28	3.69	2.61	73.4
2.32	2.295	5.32	1.47	71.8
3.07	3.04	3.86	1.46	77.3
3.09	3.06	4.07	1.26	87.1
3.30	3.26	7.01	1.14	94.1
3.87	3.83	3.69	1.63	120.5
3.87	3.83	6.25	1.47	136.3
3.87	3.83	2.01	1.74	99.1
4.64	4.585	4.35	1.95	123.6
5.41	5.36	3.59	1.73	141.2
6.19	6.14	2.44	1.47	178.3
6.96	6.90	7.17	1.74	177.3
7.73	7.565	6.02	4.28	166.2
7.73	7.675	4.40	1.41	176.2
7.73	7.66	2.01	1.79	177.4
9.29	9.19	5.11	2.11	248.2
10.83	10.76	6.08	1.52	256.7

express a linear relationship between Y and $[SCN^-]$:

$$Y = \frac{k_{app}D - k_0}{[SCN^-]} = k_1K_1 + k_2K_1K_2[SCN^-] \tag{16}$$

The plot of Y against $[SCN^-]$ is shown in Fig. 5. The intercept and the slope of the straight line give k_1 and k_2 respectively, by the least squares calculation, using the given values of K_1 and K_2:

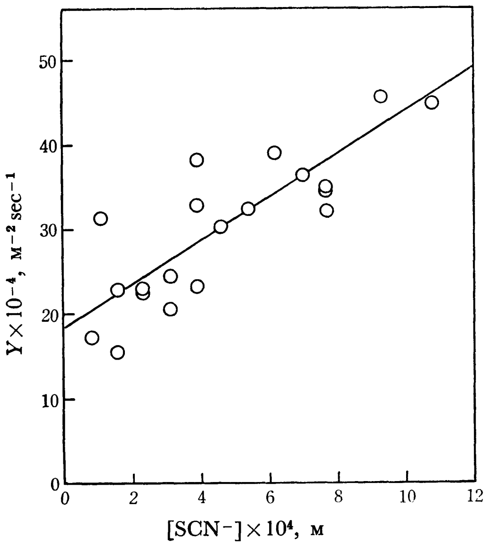

Fig. 5. Linear relation of Y against $[SCN^-]$ at $[HClO_4]=0.01$ M, $\mu=0.2$ M, 25°C.

$$k_1 = (2.24\pm0.35)\times10^2\ M^{-1}sec^{-1} \tag{17}$$

$$k_2 = (2.96\pm0.64)\times10^3\ M^{-1}sec^{-1} \tag{18}$$

Temperature Dependence of k_{app} and Activation Parameters. At constant acid and thiocyanate ion concentrations, the reaction rate was measured at different temperatures; 20, 25, 30, and 35°C. The results are given in Table 4. The plots of $\log k_0$ and $\log k_1$ against $1/T$ correspond to the activation parameters in the following:

$$\Delta H_0^{\ddagger} = 9.7\pm0.7\ \text{kcal/mol} \tag{19}$$

$$\Delta H_1^{\ddagger} = 8.9\pm1.0\ \text{kcal/mol} \tag{20}$$

$$\Delta S_0^{\ddagger} = -19\pm2\ \text{cal/deg}\cdot\text{mol} \tag{21}$$

$$\Delta S_1^{\ddagger} = -17\pm3\ \text{cal/deg}\cdot\text{mol} \tag{22}$$

The values of $\Delta H_0^{\ddagger}$ and $\Delta S_0^{\ddagger}$ agree with those by Menashi *et al.*[8]; $\Delta H_0^{\ddagger}=9.6$ kcal/mol and $\Delta S_0^{\ddagger}=$

Table 4. Temperature dependence of k_0 and k_1
$[HClO_4]=0.01$ M, $\mu=0.2$ M

Temperature °C	$[SCN^-]_0=0$ k_0 $M^{-1}sec^{-1}$	$[SCN^-]_0=3.30\times10^{-4}$ M k_1 $M^{-1}sec^{-1}$
20	26.5	216
25	34.4	310
30	44.1	380
35	60.4	461

−20 cal/deg·mol.

General Discussion. The various elementary rate constants at room temperature and the activation enthalpies and entropies of the electron transfer reactions between iron(II) and iron(III) uncatalyzed and catalyzed by Cl⁻ and SCN⁻ ions in water and DMSO are collected and listed in Table 5. Generally speaking, k_0, k_1, and k_2 in DMSO are much larger than the corresponding ones in water, k_1 catalyzed by SCN⁻ ion is about twice as large as k_1 catalyzed by Cl⁻ ion in both solvents. So is also k_2 catalyzed by SCN⁻ ion compared to k_2 catalyzed by Cl⁻ ion in DMSO, while k_2 catalyzed by SCN⁻ ion is much smaller than k_2 catalyzed by Cl⁻ ion in water.

The exchange rates of DMSO molecules between the molecules coordinated to Co(II) or Ni(II) and the ones in the bulk in DMSO[25] and in mixed solvents of DMSO and nitromethane[26] are known by the NMR method. If the exchange rates in the case of iron ions do not differ very much from those of Co(II) and Ni(II), since the solvated species of these metal ions are considered to be high spin complexes, the exchange rate constant of DMSO may be greater than the rate constants of the electron transfer reaction k_0 and k_1 in DMSO listed in Table 5. Langford and Chung[14] determined the rate constant of the anation reaction $FeS_6^{3+}+SCN^- \rightarrow FeS_5(NCS)^{2+}+S$ in which S stands for DMSO by the stopped-flow method to be 670±10 $M^{-1}sec^{-1}$, which is also greater than k_0 and k_1 in DMSO in Table 5. Considering this with the fact that DMSO has no hydrogen atoms which would play an important role in the hydrogen atom transfer mechanism, it is very probable that the inner-sphere mechanism is the path actually occurring in the electron transfer reaction in DMSO. Thus, the effects of the bridging ligands appear clearly in DMSO, although it is not the case in water, where the role of the anions is indirect and latent when the reaction proceeds through the hydrogen atom transfer mechanism. Recently, however, Cl⁻ and SCN⁻ ions were found to act as bridging anions in the inner-sphere mechanism even in water,[11] as stated before. As a bridging ligand, SCN⁻ ion appears to be better than Cl⁻ ion in both water and DMSO. A detailed discussion on the observed values of the activation parameters is not possible as yet.

Appendix: Incomplete Separation of Radioactive Precipitate. In the rate measurements, we frequently experienced a small fraction of the radioactive iron(III) to penetrate through filter paper into the filtrate liquid containing iron(II), when iron(III) was coprecipitated with aluminum hydroxide by ammonia. Thus, the extent of the electron transfer reaction at time t looked apparently larger than the true rate, because the radioactivity of the filtrate was larger than that purely due to the iron(II) species only. According to preliminary tests, however, the penetration factor of iron(III) through the precipitate layer leaking into the filtrate, α, was independent of the concentrations of iron(II) and iron(III) under the present experimental conditions, as long as the concentrations of aluminum ion and ammonia were kept constant. Consequently, the α can be easily fixed to be constant throughout at least one kinetic run.

When radioactivity at time t of iron(II), iron(III), and total iron is represented by x, y, and c respectively, then $x+y$ is equal to c, where c is time-independent. Since the radioactivity of iron(III) which has leaked into iron(II) is $(c-x)\alpha$, the apparent radioactivity of iron(II) at time t, x', is given by

$$x' = x + (c-x)\alpha \tag{23}$$

In the same way, the apparent radioactivity of iron(II) at time t_∞, x'_∞, is given by

$$x'_\infty = x_\infty + (c-x_\infty)\alpha \tag{24}$$

In the actual plotting of Eq. (10), $1-(x'/x'_\infty)$ is used instead of $1-(x/x_\infty)$. Then, the following ratio β is defined by use of Eqs. (23) and (24).

$$\beta = \frac{1-(x'/x'_\infty)}{1-(x/x_\infty)} = \frac{(1-\alpha)x_\infty}{(1-\alpha)x_\infty+c\alpha} \tag{25}$$

The value of β at any different time is shown to be constant for a kinetic run, because β is independent of x, x', and x'_∞, being smaller than unity ($\beta=1$ only when $\alpha=0$). Thus, the linearity of $\log(x'_\infty-x')$ and $\log(x_\infty-x)$ *vs.* time is given by

TABLE 5. SUMMARIZED DATA OF THE Fe(II)-Fe(III) ELECTRON TRANSFER REACTION CATALYZED BY Cl⁻ AND SCN⁻ IONS IN H_2O AND DMSO AT 25°C

Solvent	Catalyst	k_0 $M^{-1}sec^{-1}$	k_1 $M^{-1}sec^{-1}$	$\Delta H_0^{\ddagger}$ or $\Delta H_1^{\ddagger}$ kcal/mol	$\Delta S_0^{\ddagger}$ or $\Delta S_1^{\ddagger}$ cal/deg·mol	k_2 $M^{-1}sec^{-1}$	Ref.
H_2O	—	4.0	—	10.5	−20.6	—	a)
	Cl⁻	—	22.8[e]	11.0	−15	53[e]	b)
	SCN⁻	—	41.5	7.9	−26	7	c)
DMSO	—	34.4	—	9.7	−19	—	—
	Cl⁻	—	130[e]	5.2	−27	1.02×10^3 [e]	d)
	SCN⁻	—	224	8.9	−17	2.96×10^3	—

a) S. Fukushima and W. L. Reynolds, *Talanta*, **11**, 283 (1964).
b) N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961); Ref. 22.
c) G. S. Laurence, *Trans. Faraday Soc.*, **53**, 1326 (1957).
d) Ref. 9.
e) Observed at 20°C.

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25) S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **46**, 4164 (1967).

26) L. S. Frankel, *Chem. Commun.*, **1969**, 1254.

$$\log(x'_\infty - x') = \log x'_\infty + \log\beta - \frac{(a+b)R}{2.303\,ab}t \tag{26}$$

$$\log(x_\infty - x) = \log x_\infty - \frac{(a+b)R}{2.303\,ab}t \tag{27}$$

The slope of the straight line does not change even if x' and x'_∞ are used instead of x and x_∞ respectively, whereas the intercept of the straight line is lowered by $(\log x'_\infty + \log\beta) - \log x_\infty$, since $x'_\infty\beta/x_\infty$ is equal to $1-\alpha$. As a result of the lowering of the straight line, the reaction seemingly proceeds somewhat faster than the true reaction. Theoretically, x should be zero at time zero, but it frequently happens that x shows an appreciable value when time is extrapolated to zero. This does not affect the rate constant, as long as the leaking of iron(III) occurs by a definite factor α.