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Kinetic Studies of the Electron Transfer Reaction in Iron(II) and Iron(III) Systems. IV. The Reaction in Mixed Solvents of Dimethyl Sulfoxide and Water[1]

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The rate constants, k_{app}, of the electron transfer reaction between iron(II) and iron(III) in mixed solvents of DMSO and water were measured at various acid and DMSO concentrations at $\mu=0.50$M and 25°C. The k_{app} decreased linearly with the increase in [DMSO] at a constant [H$^+$] and increased linearly with the increase in 1/[H$^+$] at a constant [DMSO]. The reaction is considered to proceed through two paths: $Fe^{2+}+{}^*Fe^{3+} \rightarrow Fe^{3+}+{}^*Fe^{2+}$ and $Fe^{2+}+{}^*FeOH^{2+} \rightarrow FeOH^{2+}+{}^*Fe^{2+}$, with the rate constants of k_0 and k_H respectively. Both k_0 and k_H were suppressed by the addition of DMSO to water because of the occurrence of molecular association between DMSO and water. The hydration number of DMSO in a very dilute aqueous solution was approximately six, as revealed by the cryoscopic measurements. The suppression of k_0 and k_H was proportional to [DMSO], with a common proportional constant. Consequently, DMSO was deduced to destroy the chains of water molecules connected by hydrogen bondings and to interfere with the ease of hydrogen atom transfer between the reducing and oxidizing iron species. DMSO itself did not serve as a ligand to catalyze the reaction as *N*-methylacetamide, *N,N*-dimethylacetamide, and various other anions do.

In aqueous media, the electron transfer reaction between iron(II) and iron(III), $Fe(II)+{}^*Fe(III) \rightarrow Fe(III)+{}^*Fe(II)$, has been concluded to proceed generally *via* the hydrogen atom transfer mechanism[2] except when the iron species were complexed with some catalytic ligands with a bridging nature or with conjugate double bond systems, in which cases the reaction occurred predominantly *via* the inner- or outer-sphere mechanism respectively instead.[3]

In pure dimethyl sulfoxide (DMSO), however, the reaction between the simply solvated iron species was found to occur faster than in water in the absence of any complexing ligands, although DMSO had no exchangeable hydrogen atoms which might have promoted the reaction to proceed *via* the hydrogen atom transfer mechanism;[4] therefore, the electron transfer reaction between the solvated iron species may occur not only at a different rate, but also through a different path, as the reaction medium changes.

When either *N*-methylacetamide or *N,N*-dimethylacetamide was added to water, the reaction was slightly accelerated in quite a similar way. This can be accounted for by the fact that the coordination of one of these substances to the iron ion favored the transfer of hydrogen atoms of water molecules, as a non-bridging ligand attaching to the central ions at the opposite side of the reactive site.[5]

The reaction in mixed solvents of DMSO and water was first observed by Menashi and others,[4] who recognized that the reaction rate exhibited a broad minimum at a certain mole fraction range of DMSO when the hydrogen ion concentration was not very low. In the present paper, the effect of the addition of a small amount of DMSO on the reaction mechanism was investigated in more detail in order to clarify the cause of the decrease in the reaction rate. This phenomenon seems to be related to the strong associative nature of DMSO with water molecules.

Experimental

The methods of preparing the chemical materials used and of the kinetic measurements were quite the same as have been described previously.[1,4] The temperature and the ionic strength of the reaction systems were kept at 25°C and $\mu=0.50$M respectively, unless otherwise noted.

Since the iron(III) species was initially labelled with ^{59}Fe, the iron(II) species gradually became radioactive as time passed after the initiation of the reaction. If the total concentrations of the iron(II) and iron(III) species in the reaction system are represented as [Fe(II)] and [Fe(III)] respectively, and the radioactivities of the iron(II) species at time, t, and infinite time, t_∞, as x and x_∞ respectively, the McKay relation will hold as follows:

$$\ln\left(1-\frac{x}{x_\infty}\right) = -\frac{[Fe(II)]+[Fe(III)]}{[Fe(II)][Fe(III)]}Rt \qquad (1)$$

where R is the total rate of the electron transfer reaction.[6]

The freezing-point depression of water by the addition of DMSO was measured by the usual method in order to determine the hydration number of DMSO in their mixtures.

Results and Discussion

A typical plotting of the linear relation of $\log(x_\infty-x)$ against t is shown in Fig. 1. The slope of the straight line gives the half-life period of the reaction, $t_{1/2}$; thus, the total rate of the electron transfer reaction, R, is obtained:

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

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[1] Part III: G. Wada, N. Yoshizawa, and Y. Sakamoto, This Bulletin, **44**, 1018 (1971).

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

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y. (1967), p. 454.

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

[5] G. Wada and R. Yoshihara, *Kogyo Kagaku Zasshi*, **73**, 2309 (1970).

[6] H. A. C. McKay, *Nature*, **42**, 997 (1938).

Table 1. Variation of the rate with [DMSO] and $[H^+]$ at μ=0.50M and 25°C

$[H^+]$ M	[DMSO] M	[Fe(II)] $\times 10^4$ M	[Fe(III)] $\times 10^5$ M	$t_{1/2}$ sec	k_{app} (obsd) M^{-1} sec^{-1}	k_{app} (calcd) M^{-1} sec^{-1}
0.45	0.601	3.439	2.88	126	14.7	15.7
0.30	0	1.999	2.50	134	22.9	23.6
	0.188	2.635	2.11	108	22.7	22.9
	0.395	1.809	2.23	169	20.2	20.7
	0.601	1.445	1.95	233	18.0	19.4
	0.940	1.630	1.74	228	16.9	17.7
	1.22	2.749	2.55	166	13.9	15.0
	1.35	1.206	2.12	363	13.5	14.5
	1.50	1.358	2.01	345	12.9	13.4
	1.75	2.211	2.83	252	11.0	12.0
	2.00	2.205	2.17	287	9.9	9.7
	2.00	2.064	2.61	321	9.3	9.7
0.20	0	2.053	2.34	108	28.4	31.8
	0	1.825	1.58	111	31.5	31.8
	0	1.439	1.85	134	31.9	31.8
	0.094	2.488	1.36	87	30.2	31.0
	0.188	1.146	1.96	163	31.7	30.0
	0.188	1.206	1.41	182	28.3	30.0
	0.188	1.434	1.74	136	31.8	30.0
	0.188	2.450	1.25	81	33.7	30.0
	0.301	2.140	1.85	97	30.4	28.9
	0.507	1.499	2.50	169	23.9	26.9
	0.507	1.608	1.96	149	25.8	26.9
	0.940	1.250	2.55	132	22.1	23.0
	0.940	1.782	1.90	148	23.7	23.0
	1.22	3.085	0.76	98	22.2	20.2
	1.22	1.738	1.63	168	20.9	20.2
	1.50	2.499	2.06	141	17.9	17.6
	1.75	4.346	1.63	86	17.8	15.6
	2.00	2.559	1.47	194	13.2	12.7
	2.00	2.401	1.68	202	13.4	12.7
0.15	0.601	2.401	2.61	76	34.5	32.2
	0.940	1.711	2.23	131	27.3	28.2
0.10	0	0.380	1.96	227	53.2	54.3
	0	0.527	2.06	174	54.2	54.3
	0	1.124	2.17	90	56.7	54.3
	0	1.450	2.07	68	60.9	54.3
	0.188	1.228	1.96	96	52.8	51.2
	0.395	0.511	1.96	198	49.7	47.7
	0.601	0.951	1.96	129	46.6	44.5
	0.940	0.983	2.17	146	39.5	39.2
	1.22	1.070	2.17	143	36.9	34.4
	1.35	1.032	2.34	174	31.6	32.3
	1.50	1.331	2.06	155	29.2	29.9
	1.75	1.059	1.96	213	25.8	26.3
	2.00	1.032	2.06	234	23.8	21.7
0.07	0.601	1.423	2.28	70	60.0	60.1
	0.940	1.380	2.17	82	53.0	52.6
	1.22	2.272	2.60	58	47.7	46.7
	1.50	0.999	2.28	137	41.2	40.4
0.05	0.601	0.462	2.28	126	79.8	80.4
	0.601	0.652	2.45	93	83.6	80.4
	0.940	1.179	2.01	69	72.8	70.5
	1.22	0.842	2.66	100	62.3	62.1
	1.50	1.776	2.28	60	57.5	54.0
	2.00	1.619	2.61	83	43.8	39.4

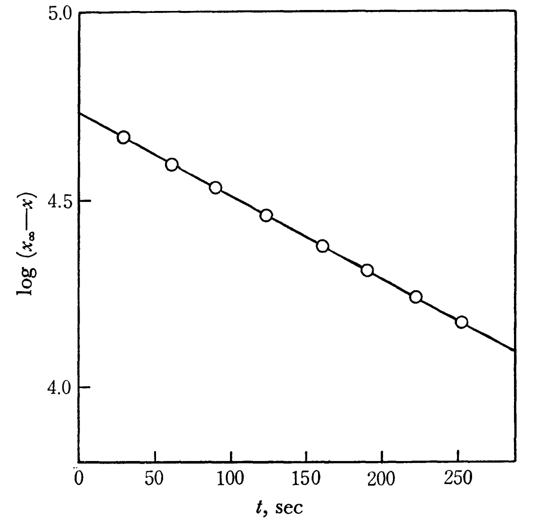

Fig. 1. Plot of log (x_∞—x) vs. time at μ=0.50M and 25°C.
[Fe(II)]=9.99$\times 10^{-5}$M [Fe(III)]=2.28$\times 10^{-5}$M
[DMSO]=1.50M $[H^+]$=0.07M

The results of the measurements are listed in Table 1. In the table, there are some groups of data on the cases in which both the $[H^+]$ and [DMSO] used were kept constant; for example, there is a set of data for four kinetic runs performed at $[H^+]$=0.20M and [DMSO]= 0 188M, with the half-lives of the respective runs being different from one another. If the rate is proportional to both [Fe(II)] and [Fe(III)], the second-order rate

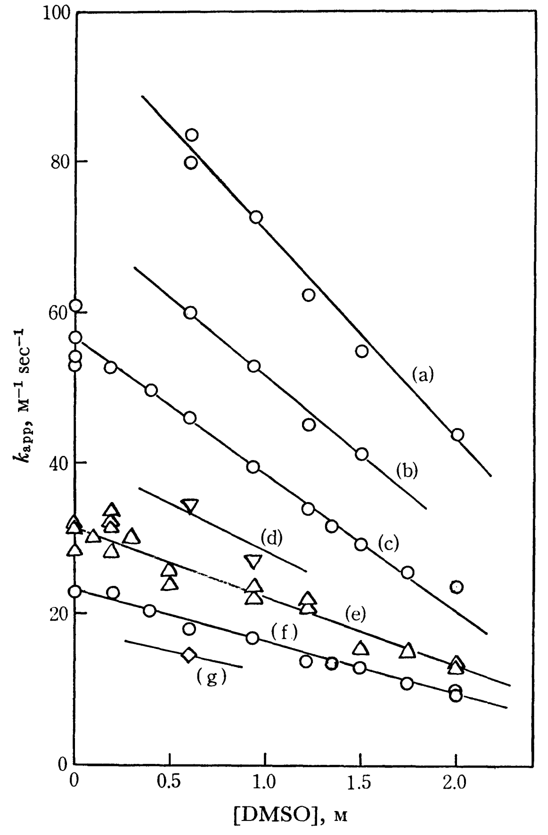

Fig. 2. Plot of k_{app} vs. [DMSO] at various $[H^+]$ at μ=0.50M and 25°C.

(a) $[H^+]$=0.05M (b) $[H^+]$=0.07M (c) $[H^+]$=0.10M
(d) $[H^+]$=0.15M (e) $[H^+]$=0.20M (f) $[H^+]$=0.30M
(g) $[H^+]$=0.45M

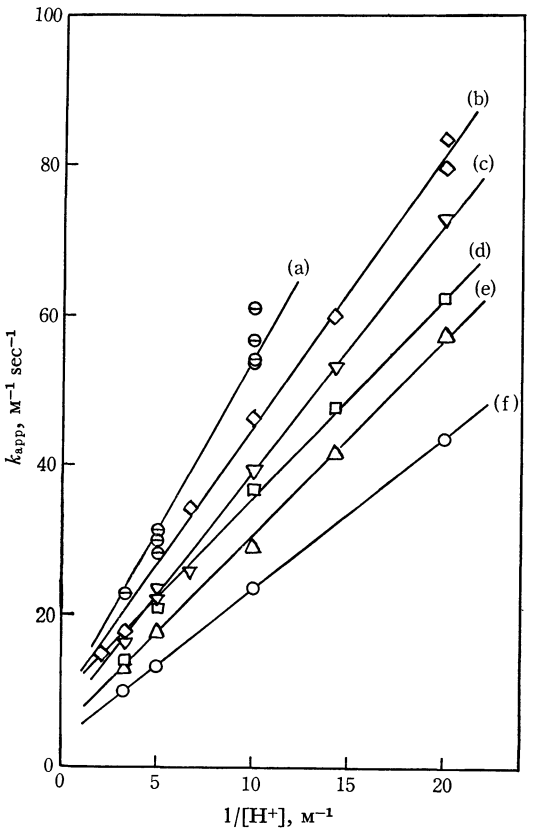

Fig. 3. Plot of k_{app} *vs.* 1/[H$^+$] at various [DMSO] at μ= 0.50M and 25°C.
(a) [DMSO]=0M (b) [DMSO]=0.601M
(c) [DMSO]=0.940M (d) [DMSO]=1.22M
(e) [DMSO]=1.50M (f) [DMSO]=2.00M

constant, k_{app}, is obtained by the following equations:

$$R = k_{app}[\mathrm{Fe(II)}][\mathrm{Fe(III)}] \tag{3}$$

$$k_{app} = \frac{0.693}{([\mathrm{Fe(II)}]+[\mathrm{Fe(III)}])t_{1/2}} \tag{4}$$

The values of k_{app} obtained in this way at fixed [H$^+$] and [DMSO] values show a good constant value within the range of experimental error. Therefore, this fact indicates that the reaction can be considered to be of the first order with respect to both [Fe(II)] and [Fe(III)]. In Table 1, the k_{app}'s derived by means of Eq. (4) are shown as the observed values.

It is noticeable that the values of k_{app} in Table 1 vary as the concentration of the hydrogen ion or of DMSO varies. Fig. 2 shows that the k_{app} decreases linearly as the DMSO concentration increases at a constant [H$^+$], and Fig. 3, that the k_{app} is also linear with respect to the reciprocal hydrogen-ion concentration at a constant [DMSO].

When *N*-methylacetamide or *N,N*-dimethylacetamide was added to water instead of DMSO, the matter was quite different from the case of DMSO, with the result that the k_{app} grew larger as the concentration of *N*-methylacetamide or *N,N*-dimethylacetamide became higher.[5] In other words, *N*-methylacetamide and *N,N*-dimethylacetamide are accelerators, while DMSO acts as an inhibitor, of the present reaction.

In aqueous solvents, the main paths of the electron transfer between iron(II) and iron(III) species are the following two reactions:

$$\mathrm{Fe}^{2+} + {}^*\mathrm{Fe}^{3+} \xrightarrow{k_0} \mathrm{Fe}^{3+} + {}^*\mathrm{Fe}^{2+} \tag{5}$$

$$\mathrm{Fe}^{2+} + {}^*\mathrm{FeOH}^{2+} \xrightarrow{k_H} \mathrm{FeOH}^{2+} + {}^*\mathrm{Fe}^{2+} \tag{6}$$

The respective rate constants are represented as k_0 and k_H. Fe^{2+} and Fe^{3+} represent solvated species, and FeOH^{2+}, an iron(III) one of whose solvating water molecules has been hydrolyzed to lose a proton.

When a foreign substance is added to the reaction system, the possibility of the occurrence of an electron transfer between the species coordinated with the substance as a ligand must be taken into account in addition to the paths of (5) and (6). This consideration has been successful in the cases of various anions and mono- and di-methylacetamide, where these substances promote the reaction, while in the present case of DMSO, this kind of procedure can not interpret the decrease in k_{app} at all. The decrease in k_{app} due to the addition of DMSO seems to be attributable to the depression of the activity of water in the mixed solvent.

It is well known that the electron transfer processes expressed by (5) and (6) occur predominantly *via* the hydrogen atom transfer mechanism, in which water molecules used as the solvent play an important role through the chains connected by hydrogen bondings.[2] When DMSO is added to water, it strongly interacts with water, depressing the water activity, as will be described below. If the rate constants, k_0 and k_H, are assumed to be lowered in proportion to the concentration of DMSO, these constants in the mixed solvent may be expressed in the following forms where k_0^0 and k_H^0 represent the constants in the absence of DMSO and where a and b are proportional constants:

$$k_0 = k_0^0\,(1-a[\mathrm{DMSO}]) \tag{7}$$

$$k_H = k_H^0\,(1-b[\mathrm{DMSO}]) \tag{8}$$

Then, according to the usual method of calculation, the k_{app} can be expressed as a function of [H$^+$] and [DMSO]:

$$k_{app} = \frac{k_0^0(1-a[\mathrm{DMSO}])+k_H^0K_H(1-b[\mathrm{DMSO}])/[\mathrm{H}^+]}{1+K_H/[\mathrm{H}^+]} \tag{9}$$

in which K_H is an equilibrium constant for the hydrolysis, $\mathrm{Fe}^{3+} \rightleftharpoons \mathrm{FeOH}^{2+} + \mathrm{H}^+$, being equal to 1.59×10^{-3}M.[7] Even at the lowest value of [H$^+$]=0.05M used in the present experiment, the denominator on the right-hand side of Eq. (9) may reasonably be regarded as unity. Thus, the rearrangement of Eq. (9) leads us to the following:

$$k_{app} = \left(k_0^0+\frac{k_H^0K_H}{[\mathrm{H}^+]}\right)-\left(ak_0^0+\frac{bk_H^0K_H}{[\mathrm{H}^+]}\right)[\mathrm{DMSO}] \tag{10}$$

$$= k_0^0(1-a[\mathrm{DMSO}]) + \frac{k_H^0K_H(1-b[\mathrm{DMSO}])}{[\mathrm{H}^+]} \tag{11}$$

Eq. (10) demonstrates the linear relationship between the k_{app} and [DMSO] as is pictured in Fig. 2, and Eq. (11), that between the k_{app} and 1/[H$^+$], as is pictured in Fig. 3. If the slope of a straight line in Fig. 2 is

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7) A. S. Wilson and H. Taube, *J. Amer. Chem. Soc.*, **74**, 3509 (1952).

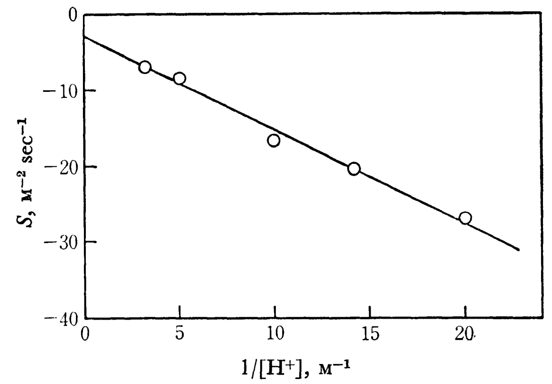

Fig. 4. Plot of slopes of straight lines in Fig. 2 *vs.* 1/[H⁺].

denoted by S, S is expressed by this equation:

$$S = -ak_0{}^0 - \frac{bk_H{}^0K_H}{[H^+]} \qquad (12)$$

which also indicates the linear relationship between the S and $1/[H^+]$, as is shown in Fig. 4, with an intercept of $-ak^0_0 = -3$M^{-2}sec^{-1} and with a slope of $-bk^0_H K_H = -1.4$M^{-1}sec^{-1}. Since k^0_0 and $k^0_H K_H$ are known from the intercept and the slope of the straight line at [DMSO]=0 in Fig. 3 as $k^0_0 = 9$M^{-1}sec^{-1} and $k^0_H K_H = 4.6$ sec^{-1} respectively,[8] a and b can be approximately calculated as follows:

$$a \doteqdot 0.3\,\mathrm{M}^{-1}$$
$$b \doteqdot 0.3\,\mathrm{M}^{-1}$$

These numerical results for a and b suggest that the addition of DMSO to water equally depresses the rates of both reactions, (5) and (6). Thus, the calculated values of k_{app} using the various constants obtained above are listed in the last column in Table 1. The agreement between the observed and the calculated results is pretty good.

The characteristic interactions between DMSO and water have been recognized from several points of view; the viscosities and local liquid structures in DMSO-water mixtures[9] and the heat of solution of DMSO in water[10] were especially investigated, indicating that a molecular association occurs between DMSO and water.

If there were no molecular association between them, the ideal freezing-point depression of water, ΔT_f^0, would be expected to be given by the following equation:

$$\Delta T_f{}^0 = \frac{1000gK_f}{GM} \qquad (13)$$

in which G and g are the weights of water and DMSO contained in the system respectively, M, the molecular weight of DMSO, and K_f, the molar depression of freezing point of water. However, the actually observed depression of the freezing point of water, ΔT_f, was always much larger than the expected value by Eq. (13). This is because DMSO associates with water; therefore, there occurs a decrease in the amount of water as the solvent, by as much as p:

$$\Delta T_f = \frac{1000gK_f}{(G-p)M} \qquad (14)$$

Consequently, the hydration number of DMSO, h, can be defined from Eq. (14) as follows:

$$h = \frac{p}{18m_{\mathrm{DMSO}}}$$
$$= \frac{m_{\mathrm{W}}}{m_{\mathrm{DMSO}}} - \frac{55.5K_f}{\Delta T_f} \qquad (15)$$

where m_w and m_{DMSO} represent the numbers of the moles of water and DMSO contained in the system, being equal to $G/18$ and g/M respectively. The observed h is plotted against the mole fraction of DMSO in Fig. 5. Although the hydration numbers are slightly scattered, they seem to decrease gradually with the increase in the concentration of DMSO. At a very dilute concentration, a DMSO molecule associates with approximately five or six molecules of water, the structure of the associate being not known yet. This kind of interaction of DMSO with water seems to be quite characteristic, because a similar experiment done with dimethylformamide in place of DMSO exhibited only a small number of hydration, about 0.7. Thus, the strong formation of molecular associates may depress the activity of water and suppress the ease of the hydrogen atom transfer along the chains of hydrogen bondings.

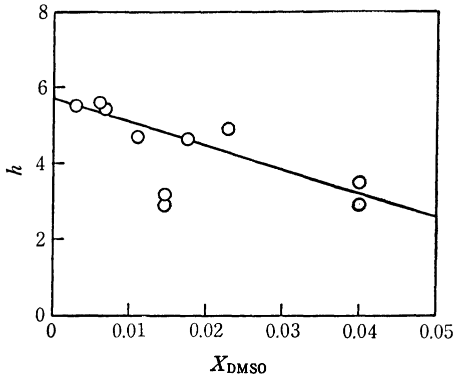

Fig. 5. Plot of hydration number of DMSO *vs.* X_{DMSO}.

Depending upon the NMR investigation concerned with the ionic solvation,[11] Al^{3+} was found to be preferentially solvated with water when water is present in a larger amount than DMSO and with DMSO when DMSO is present in a larger amount than water, in the mixed solvents of DMSO and water. A similar phenomenon may be supposed to occur in the case of Fe^{3+}; it may be solvated overwhelmingly with water in a dilute aqueous solution of DMSO. According to our unpublished data on the optical densities of the systems containing Fe^{3+}, H^+, and DMSO in water, iron(III) was observed to be solvated with DMSO in no noticeable amount, at least not by the optical method.

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[8] Values appearing in the literature[7] are $k^0_0 = 4.0$M^{-1} sec^{-1}, $k^0_H = 3.0\times10^3$M^{-1} sec^{-1}, $K_H = 1.59\times10^{-3}$M and therefore $k^0_H K_H = 4.8$ sec^{-1}.

[9] S. A. Schichman and R. L. Amey, *J. Phys. Chem.*, **75**, 98 (1971).

[10] J. M. Corkill, J. F. Goodman, and J. R. Tate, *Trans. Faraday Soc.*, **65**, 1742 (1969).

[11] S. Thomas and W. L. Reynolds, *Inorg. Chem.*, **9**, 78 (1970).

This is the reason why any reaction paths in which the solvated iron species with DMSO take part have been ignored in the present case, only the (5) and (6) reactions being paid much attention to.

Summarizing the above-mentioned considerations, the electron transfer reaction between iron(II) and iron(III) in mixed solvents of DMSO and water when the DMSO concentration is less than 2M proceeds predominantly through the hydrogen atom transfer mechanism, which is retarded by the addition of DMSO to the reaction system because of the strong formation of molecular associates between DMSO and water and, consequently, because of the depression of the activity of water, the depression being proportional to the concentration of DMSO.

At higher DMSO concentrations, DMSO begins to coordinate with iron and to participate in the electron transfer as a catalytic ligand through the inner- or outer-sphere mechanism. In pure DMSO,4) the latter path only is of importance, with a higher reaction rate than that through the hydrogen atom transfer mechanism in pure water.