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The Oxidation of Iron(II) by Molecular Oxygen Catalyzed by Chloride Ion, Thiocyanate Ion, and Ethylenediamine in Dimethyl Sulfoxide

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The rates of the oxidation reactions of iron(II) to iron(III) by molecular oxygen in DMSO were measured under the catalyses of Cl^-, SCN^-, and en. The rate was proportional to the partial pressure of oxygen and was of the second order to [Fe(II)] in catalyses of Cl^- and SCN^-, while it was of the first order to [Fe(II)] in catalysis of en. The reaction rate was also linear to $[X]^2$ and $[H^+]$, where X represents Cl^- or SCN^-, indicating that the reaction proceeds via both the electron-transfer and hydrogen-atom-transfer mechanisms, side by side. The reaction order of [Fe(II)] depends upon which step is rate-determining among those of the oxygenation of Fe(II), its spontaneous decomposition, and its bimolecular reaction with another Fe(II) and, therefore, may be variable according to the concentrations of the reacting species. The autoxidation rate can be affected by the kinds of the catalyzing ligands. The autoxidation may be slow when an Fe(II) complex with low spin is oxidized to an Fe(III) complex with high spin and may be fast when from high spin type to low spin one. In the present cases of Cl^-, SCN^-, and en in DMSO, it seems to go from high spin type to high spin one with moderately large rates.

The autoxidation of iron(II) proceeds considerably slow in acidic aqueous solutions being catalyzed by a variety of existing anions and molecules as coordinating ligands. The rate equations for the oxidation of iron(II) in aqueous media are expressed in the first order with respect to the concentration of iron(II) when $H_2PO_4^-$,1,2) $H_2P_2O_7^{2-}$,2,3) F^-,4) Cl^-,5) ethylenediaminetetraacetic acid (EDTA),6) or one of other specific chelating ligands7,8) is present in the reaction system, while they are of the second order with respect to that of iron(II) when either of NO_3^-,9) SO_4^{2-},10,11)

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1) M. Cher and N. Davidson, *J. Amer. Chem. Soc.*, **77**, 793 (1955).

2) J. King and N. Davidson, *ibid.*, **80**, 1542 (1958).

3) S. Utsumi and K. Muroshima, *Nippon Kagaku Zasshi*, **86**, 593 (1965).

4) J. Weiss, *Experimentia*, **9**, 61 (1953).

5) A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

6) Y. Kurimura, R. Ochiai, and N. Matsuura, This Bulletin, **41**, 2234 (1968).

7) Th. Kaden, D. Walz, and S. Fallab, *Helv. Chim. Acta*, **43**, 1639 (1960).

8) Th. Kaden and S. Fallab, *ibid.*, **44**, 714 (1961).

9) J. R. Pound, *J. Phys. Chem.*, **43**, 955 (1939).

10) A. B. Lamb and L. W. Elder, *J. Amer. Chem. Soc.*, **53**, 137 (1931).

11) R. E. Huffman and N. Davidson, *ibid.*, **78**, 4836 (1956).

or ClO_4^- [12] is present in the reaction system, although ClO_4^- ion does not necessarily act as a coordinating ligand.

George pointed out[13] that the one-electron-transfer mechanism proposed first by Haber and Weiss[14,15] was not satisfactory to explain the cases in which the reaction took place at a rate of the second order with respect to the iron(II) concentrations. Weiss, then, revised his mechanism and extended it to the so-called two-electron-transfer mechanism. George, on the other hand, showed an idea on another novel mechanism of hydrogen-atom-transfer in which the oxidation occurred via transfer of a hydrogen atom from a water molecule coordinated with an iron(II) ion to FeO_2^{2+}, instead of considering a radical mechanism.[12] Fallab discussed the autoxidation of various transition metal ions by molecular oxygen on the basis of the redox potentials of oxygen.[16]

The autoxidation of iron(II) in alcohols is known to occur much faster than that in aqueous solutions,[17] although those in other non-aqueous solutions than alcohols are not known yet. In the present research, therefore, the reactions in dimethyl sulfoxide (DMSO) as catalyzed by Cl^-, SCN^- ions and ethylenediamine (en) were investigated. As the results, the reaction proceeded at a rate proportional to $[Fe(II)]^2$ when it was catalyzed by Cl^- or SCN^- ion, and at one proportional to [Fe(II)] when catalyzed by en. The reaction schemes in each case in DMSO will be developed below.

Experimental

Materials. Commercial DMSO was distilled in a reduced atmosphere of nitrogen at about 3 mmHg, dried over activated alumina overnight to remove water, distilled again in the same way as before, and stocked for use. Sodium chloride, ammonium thiocyanate, ammonium perchlorate, and sodium perchlorate of the guaranteed reagent grade were recrystallized twice from water. Ethylenediamine of the guaranteed reagent grade was used without further purification. Perchloric acid in DMSO was prepared by passing a DMSO solution of ammonium perchlorate through a column charged with cation-exchange resin Dowex 50 of H-type. Iron(II) perchlorate was prepared by dissolving pure iron wire in perchloric acid and recrystallizing it under an atmosphere of nitrogen to protect it from oxidation.

Procedure. The reaction was initiated by mixing a solution of iron(II) perchlorate in DMSO with that containing one of the catalyzing substances, Cl^-, SCN^- ion or en, and perchloric acid in DMSO. Two methods were adopted for the kinetic measurements. In a flow-method, air or a mixed gas of oxygen and nitrogen at various ratios was let to flow into the reaction solution at a constant flow rate and aliquots were taken out of the solution into quenching solutions for analyses at appropriate time intervals. When Cl^- ion or en was adopted as a catalyst, α,α'-bipyridyl was contained in the quenching solutions, forming $Fe(bipy)_3^{2+}$ at once which not only interupted further progress of the reaction but also was used for the spectrophotometric determination of iron(II) concentration at 522 nm at the individual reaction times. When SCN^- ion was adopted as a catalyst, on the other hand, aliquots of the reaction solution were diluted into a definite amount of water to slow down the reaction velocity and were soon used for the spectrophotometric determination of iron(III) concentration in the form of thiocyanato complex at 470 nm.

As a second method, a Warburg apparatus was used for the volumetric pursuit of oxygen gas consumed by oxidation. The procedure for the initiation of the reaction was the same with that of the flow method.

The ionic strength and the temperature of the reaction systems were always kept constant at 0.2 M and 25 °C respectively.

Photometry. A Hitachi-Perkin-Elmer UV-VIS spectrophotometer Model 139 and a Hitachi Recording spectrophotometer Model EPS-3T were used for the optical determinations of the concentrations of iron species and for the measurements of the absorption spectra of reaction solutions, respectively.

Results and Discussion

Catalyses by Cl^- and SCN^- Ions. Under a constant partial pressure of oxygen, p, the relationship of $(1/[Fe(II)]-1/[Fe(II)]_0)$ *vs.* time, t, was linear for reactions catalyzed by Cl^- or SCN^- ion, as is shown in Fig. 1, as an example at $[Fe(II)]_0=2\times10^{-2}$ M, $p=0.2$ atm, $\mu=0.2$ M, and 25°C, and at various $[Cl^-]$ and $[H^+]_0$. Here, $[Fe(II)]_0$ and $[H^+]_0$ represent the initial concentrations of Fe(II) and H^+. These linearities indicate that the reaction proceeds in the second order of the concentration of iron(II). When the partial pressure of oxygen, p, was varied under a fixed reaction condition except p, another proportionality between the reaction rate and p was recognized,

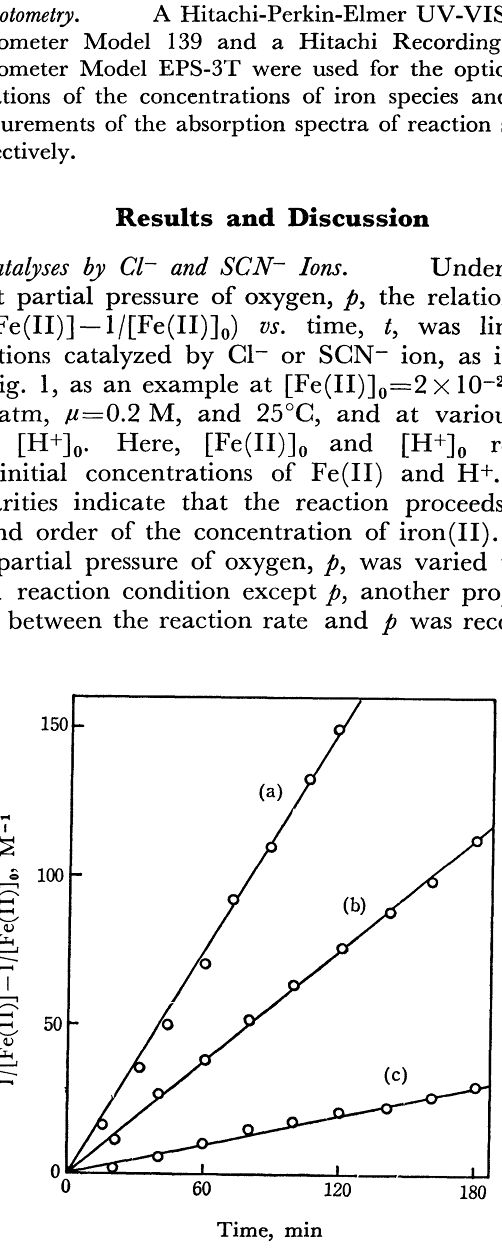

Fig. 1. Plot for a reaction of the second order with respect to [Fe(II)] at $[Fe(II)]_0=2.00\times10^{-2}$ M, $p=0.2$ atm., $\mu=0.2$ M, and 25°C.

(a) $[Cl^-]=3.52\times10^{-2}$ M, $[H^+]_0=3.00\times10^{-2}$ M

(b) $[Cl^-]=2.73\times10^{-2}$ M, $[H^+]_0=5.00\times10^{-2}$ M

(c) $[Cl^-]=1.82\times10^{-2}$ M, $[H^+]_0=1.00\times10^{-2}$ M

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[12] P. George, *J. Chem. Soc.*, **1954**, 4349.

[13] P. George, *Adv. Catalysis*, **4**, 367 (1952).

[14] F. Haber and J. Weiss, *Proc. Roy. Soc. Ser. A*, **147**, 332 (1934).

[15] J. Weiss, *Naturwissenschaften*, **23**, 64 (1935).

[16] S. Fallab, *Angew. Chem.*, **79**, 500 (1967).

[17] J. R. Pound, *J. Phys. Chem.*, **43**, 969 (1939).

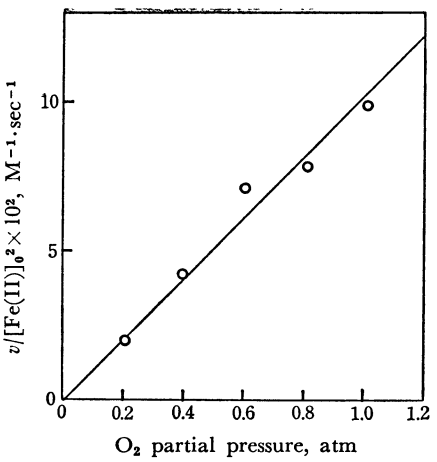

Fig. 2. The proportionality of the reaction rate with the partial pressure of oxygen at $[Fe(II)]_0=2.00\times10^{-2}$ M, $[Cl^-]=3.50\times10^{-2}$ M, $[H^+]_0=3.00\times10^{-2}$ M, $\mu=0.2$ M, and 25°C.

indicating that the reaction is of the first order with respect to p. This is shown in Fig. 2. Similar relationships were also observed in the case of SCN^- catalysis. Thus, the reaction rate equation for the both catalytic reactions is expressed in the form:

$$v=-\frac{d[Fe(II)]}{dt}=kp[Fe(II)]^2 \qquad (1)$$

The mole ratio of the reacting iron(II) to the consumed oxygen was found to be 4 : 1, indicating that one molecule of oxygen oxidizes four ions of iron(II) to iron(III). The spectral changes during the reaction supported this stoichiometric relation. A spectrum of an acidic solution containing iron(II) after the completion of the reaction coincided well with that containing iron(III) at the same concentration, as shown in Fig. 3. Therefore, the overall chemical equation of the reaction is written as follows:

$$4Fe(II) + O_2 + 4H^+ \rightarrow 4Fe(III) + 2H_2O \qquad (2)$$

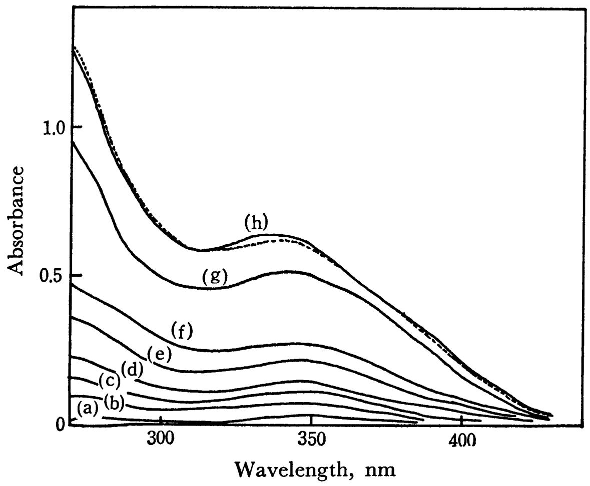

Fig. 3. Spectral changes during the reaction to complete oxidation at $[H^+]_0=1.00\times10^{-2}$ M, $[Cl^-]=2.00\times10^{-2}$ M, and $\mu=0.2$ M.

Solid curves: $[Fe(II)]_0=1.00\times10^{-4}$ M at times after the initiation of the reaction (a) 7 min, (b) 74 min, (c) 135 min, (d) 200 min, (e) 330 min, (f) 460 min, (g) 1400 min, (h) ∞

Dotted curve: $[Fe(III)]=1.00\times10^{-4}$ M

The rate constant, k, defined in Eq. (1) was also observed to be dependent upon the concentrations of both acid and catalyzing ions. Approximate linear relationships of k with $[Cl^-]^2$ at various $[H^+]_0$ and with $[H^+]_0$ at various $[Cl^-]$ are shown in Figs. 4 and 5, respectively, although their linearities look like worse than those revised by theoretical treatment below.

The stoichiometry of the reaction in the case of SCN^- ion and the dependence of k upon $[SCN^-]^2$ and $[H^+]_0$ were quite similar to the case of Cl^- ion, although their plots corresponding to Figs. 1—5 are not shown here.

Reaction Schemes for Cl^- and SCN^- Catalyses. Since the reaction proceeds at rates linearly depending upon $[X]^2$ and $[H^+]_0$, k can be expressed empirically as below, where X stands for Cl^- or SCN^- and A, B, C,

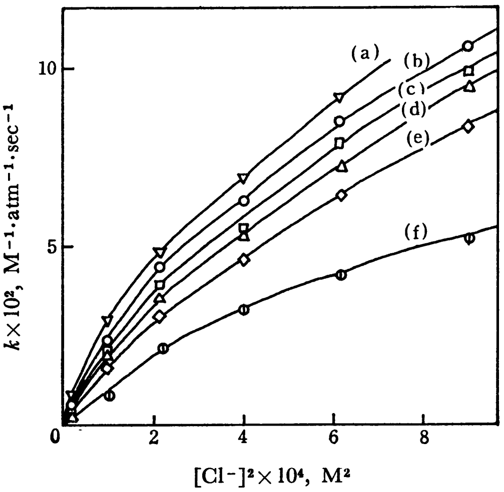

Fig 4. Relations between k and $[Cl^-]^2$ at $[Fe(II)]_0=2.00\times10^{-2}$ M, $\mu=0.2$ M, and 25°C.

(a) $[H^+]_0=1.00\times10^{-1}$ M (b) $[H^+]_0=7.00\times10^{-2}$ M
(c) $[H^+]_0=5.00\times10^{-2}$ M (d) $[H^+]_0=3.00\times10^{-2}$ M
(e) $[H^+]_0=1.00\times10^{-2}$ M (f) $[H^+]_0=1.00\times10^{-3}$ M

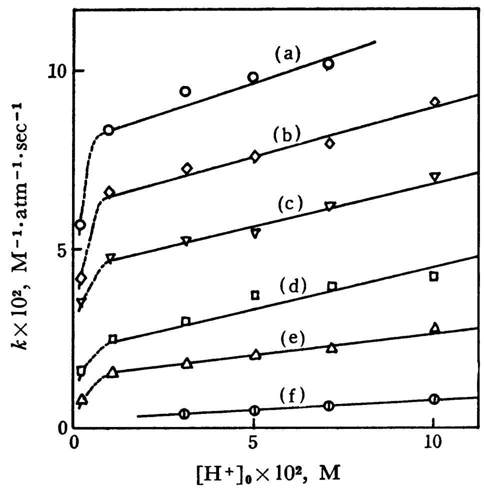

Fig. 5. Relations between k and $[H^+]_0$ at $[Fe(II)]_0=2.00\times10^{-2}$ M, $\mu=0.2$ M, and 25°C.

(a) $[Cl^-]=3.00\times10^{-2}$ M (b) $[Cl^-]=2.50\times10^{-2}$ M
(c) $[Cl^-]=2.00\times10^{-2}$ M (d) $[Cl^-]=1.50\times10^{-2}$ M
(e) $[Cl^-]=1.00\times10^{-2}$ M (f) $[Cl^-]=5.00\times10^{-3}$ M

and D are constants:

$$k = A + B[\mathrm{X}]^2 + C[\mathrm{H}^+] + D[\mathrm{H}^+][\mathrm{X}]^2 \qquad (3)$$

The following four paths from (a) through (d) are reasonably deduced corresponding to the respective four terms on the right-hand side of Eq. (3).

(a) $\mathrm{Fe^{2+} + O_2 \xrightleftharpoons{K_0} FeO_2{}^{2+}}$ (a1)

$\mathrm{FeO_2{}^{2+} + Fe^{2+} \xrightarrow{k_a} [Fe.O_2.Fe]^{4+}}$

$\mathrm{\longrightarrow Fe^{3+} + O_2{}^{2-} + Fe^{3+}}$ (a2)

(b) $\mathrm{Fe^{2+} + X^- \xrightleftharpoons{K_1} FeX^+}$ (b1)

$\mathrm{FeX^+ + O_2 \xrightleftharpoons{K_0'} XFeO_2{}^+}$ (b2)

$\mathrm{XFeO_2{}^+ + FeX^+ \xrightarrow{k_b} [X.Fe.O_2.Fe.X]^{2+}}$

$\mathrm{\longrightarrow FeX^{2+} + O_2{}^{2-} + FeX^{2+}}$

(b3)

(c) $\mathrm{Fe^{2+} + O_2 \xrightleftharpoons{K_0} FeO_2{}^{2+}}$ (c1), (a1)

$\mathrm{Fe^{2+} + H^+ \xrightleftharpoons{K_H} FeSH^{3+}}$ (c2)

$\mathrm{FeO_2{}^{2+} + FeSH^{3+} \xrightarrow{k_c} [Fe.O_2.HS.Fe]^{5+}}$

$\mathrm{\longrightarrow Fe^{3+} + HO_2{}^- + Fe^{3+}}$

(c3)

(d) $\mathrm{Fe^{2+} + X^- \xrightleftharpoons{K_1} FeX^+}$ (d1), (b1)

$\mathrm{FeX^+ + O_2 \xrightleftharpoons{K_0'} XFeO_2{}^+}$ (d2), (b2)

$\mathrm{FeX^+ + H^+ \xrightleftharpoons{K_H'} HSFeX^{2+}}$ (d3)

$\mathrm{XFeO_2{}^+ + HSFeX^{2+} \xrightarrow{k_d} [X.Fe.O_2.HS.Fe.X]^{3+}}$

$\mathrm{\longrightarrow FeX^{2+} + HO_2{}^- + FeX^{2+}}$

(d4)

Equilibrium constants and rate constants appearing in the individual steps are represented by respective symbols in the equations, and S stands for DMSO as solvated with iron ions which functions as a proton acceptor. The bracketed species shown in every path means activated complexes.

In the whole reaction, these four paths may be prevailing in parallel with one another; (a) and (b) involve two electron-transfer processes from two Fe(II) ions to an $\mathrm{O_2}$, and (c) and (d) involve, on the other hand, a hydrogen-atom-transfer process from an Fe(II) to an $\mathrm{O_2}$ as well as an electron-transfer process from another Fe(II) to the same $\mathrm{O_2}$, producing $\mathrm{O_2{}^{2-}}$ and $\mathrm{HO_2{}^-}$ respectively.

The common products of the above reactions, $\mathrm{O_2{}^{2-}}$ and $\mathrm{HO_2{}^-}$, will be followed by further reactions of their own, being finally reduced to $\mathrm{H_2O}$ in order to hold the stoichiometry as shown in the reaction (2).

(t) $\mathrm{O_2{}^{2-} + H^+ \longrightarrow HO_2{}^-}$ (t1)

$\mathrm{HO_2{}^- + H^+ \longrightarrow H_2O_2}$ (t2)

$\mathrm{H_2O_2 + Fe(II) \longrightarrow OH + OH^- + Fe(III)}$ (t3)

$\mathrm{OH + Fe(II) \longrightarrow OH^- + Fe(III)}$ (t4)

$\mathrm{H^+ + OH^- \longrightarrow H_2O}$ (t5)

Thus, the overall rate constant of the reaction is expressed in a following form:

$$k = 4\cdot\frac{k_\mathrm{a}K_0 + k_\mathrm{b}K_0'K_1{}^2[\mathrm{X}]^2 + k_\mathrm{c}K_0K_\mathrm{H}[\mathrm{H}^+] + k_\mathrm{d}K_0'K_\mathrm{H}'K_1{}^2[\mathrm{H}^+][\mathrm{X}]^2}{\{1 + K_1[\mathrm{X}] + K_\mathrm{H}[\mathrm{H}^+] + K_\mathrm{H}'K_1[\mathrm{H}^+][\mathrm{X}] + K_0[\mathrm{O_2}] + K_0'K_1[\mathrm{X}][\mathrm{O_2}]\}^2} \qquad (4)$$

where the last two terms appearing in the denominator of the right-hand side of Eq. (4) are negligibly small as compared to the rest ones in it, because the solubilities of oxygen in the reaction media, $[\mathrm{O_2}]$, are very small.[18]

When the denominator of the right-hand side of Eq. (4) is denoted by d^2 for brevity, kd^2, instead of k itself, should be linearly dependent upon $[\mathrm{X}]^2$ at constant $[\mathrm{H}^+]_0$ and upon $[\mathrm{H}^+]_0$ at constant $[\mathrm{X}]$.

$$kd^2 = 4k_\mathrm{a}K_0 + 4k_\mathrm{b}K_0'K_1{}^2[\mathrm{X}]^2 + 4k_\mathrm{c}K_0K_\mathrm{H}[\mathrm{H}^+] + 4k_\mathrm{d}K_0'K_\mathrm{H}'K_1{}^2[\mathrm{H}^+][\mathrm{X}]^2 \qquad (5)$$

If d does not vary much within the concentration ranges of $[\mathrm{X}]$ and $[\mathrm{H}^+]_0$ employed under the present consideration, k will also show approximately linear relationships with $[\mathrm{X}]^2$ and $[\mathrm{H}^+]$, which are the cases of Eq. (3) and Figs. 4 and 5. In the case of Cl⁻ ion catalyst, the values of $K_1 = 20\ \mathrm{M^{-1}}$ and $K_\mathrm{H} = K_\mathrm{H}' = 5\ \mathrm{M^{-1}}$ give best fits for the linearities of kd^2 with $[\mathrm{Cl^-}]^2$ and $[\mathrm{H}^+]_0$, which are drawn in Figs. 6 and 7. As are clearly recognized in the figures, the linearities in Figs. 4 and 5 are fairly revised to give those in Figs. 6 and 7, respectively. In Fig. 7, the curves fail from the linearities at very low concentrations of hydrogen ion below 1.00×10^{-2} M, where the steps as controlled by $[\mathrm{H}^+]$ might be rate-determining.

The straight lines at various hydrogen ion concentrations in Fig. 6 will give intercepts and slopes, indicating as follows:

$$\text{Intercept} = 4k_\mathrm{a}K_0 + 4k_\mathrm{c}K_0K_\mathrm{H}[\mathrm{H}^+] \qquad (6)$$

$$\text{Slope} = 4k_\mathrm{b}K_0'K_1{}^2 + 4k_\mathrm{d}K_0'K_\mathrm{H}'K_1{}^2[\mathrm{H}^+] \qquad (7)$$

Plotting of those slopes against $[\mathrm{H}^+]$ will also give a

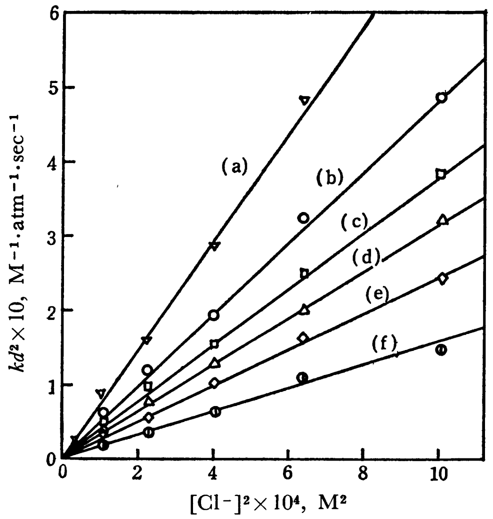

Fig. 6. Relations between kd^2 and $[\mathrm{Cl^-}]^2$ at the same conditions with Fig. 4.

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[18] T. Fujinaga, K. Izutsu, and T. Adachi, This Bulletin, **42**, 140 (1969).

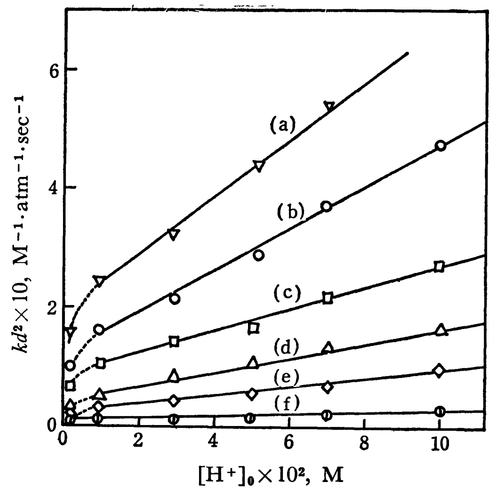

Fig. 7. Relations between kd^2 and $[H^+]_0$ at the same conditions with Fig. 5.

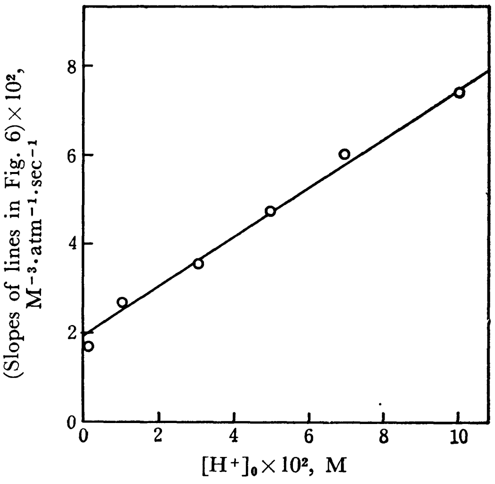

Fig. 8. Linear relationship of the slopes in Fig. 6 *vs.* $[H^+]_0$.

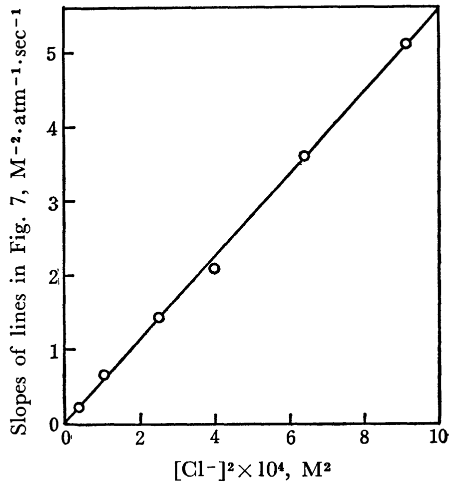

Fig. 9. Linear relationship of the slopes in Fig. 7 *vs.* $[Cl^-]^2$.

straight line having an intercept $4k_bK_0'K_I^2$ and a slope $4k_dK_0'K_H'K_I^2$, as shown in Fig. 8.

In quite a similar way, the straight lines in Fig. 7 give slopes at different Cl^- ion concentrations, and those slopes have also a linear relationship with $[Cl^-]^2$, as shown in Fig. 9. The intercept and the slope in Fig. 9 correspond to $4k_cK_0K_H$ and $4k_dK_0'K_H'K_I^2$, respectively.

Table 1. Various rate and equilibrium constants in the cases of Cl^- and SCN^- ions used as catalysts

Constants $M^{-1}\cdot atm^{-1}\cdot sec^{-1}$	Catalysts	
	Cl^-	SCN^-
k_aK_0	~ 0	~ 0
k_bK_0'	1.3×10^{-1}	7.5×10^{-3}
k_cK_0	1.0×10^{-3}	1.0×10^{-3}
k_dK_0'	6.8×10^{-1}	4.2×10^{-2}

Various linearities are similarly noticed in the case of SCN^- ion as a catalyst, as well as in that of Cl^- ion. Thus, constants obtained directly by means of the least-squares method from Eq. (5) are summarized in Table 1 in both catalysts. In the case of SCN^- ion, the values of $K_I=10\,M^{-1}$ and $K_H=K_H'=5\,M^{-1}$ were adopted for the best linearities.

Since neither K_0 nor K_0' can be estimated at the present stage, we have to compare rate constants multiplied by K_0 or K_0'. Fortunately, nevertheless, the ratios k_d/k_b are found to be almost equal, being 5.2 in Cl^- and 5.6 in SCN^-. It is worth noticing that, although the rate constant at each path seems smaller in SCN^- than in Cl^-, the acceleration ratio, k_d/k_b, of the oxidation due to the participation of the hydrogen-atom-transfer mechanism is approximately the same in both catalysts. Of course, k_a and k_c are indifferent to the kind of catalyzing ions because no catalyst is involved in the reaction scheme (a) and (c), and this is definitely proved by the results in the table, k_aK_0 and k_cK_0 being nearly zero and $1.0\times 10^{-3}\,M^{-1}\cdot atm^{-1}\cdot sec^{-1}$ in both systems.

Catalysis by Ethylenediamine and its Reaction Scheme. When en is added in the reaction system, the oxidation reaction goes much faster than the cases catalyzed by Cl^- and SCN^- ions. Figure 10 indicates that the reaction is of the first order with respect to [Fe(II)] under

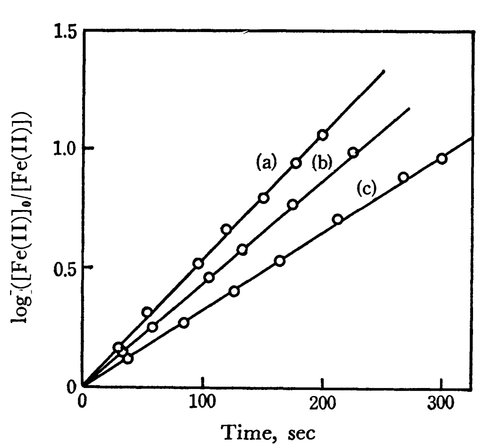

Fig. 10. Plot for a reaction of the first order with respect to [Fe(II)] at $[Fe(II)]_0=2.00\times 10^{-2}\,M$, $p=0.2$ atm, $\mu=0.2\,M$, and 25 °C.
(a) $[en]_0=9.00\times 10^{-2}\,M$, $[H^+]_0=1.00\times 10^{-2}\,M$
(b) $[en]_0=1.20\times 10^{-1}\,M$, $[H^+]_0=3.00\times 10^{-2}\,M$
(c) $[en]_0=1.05\times 10^{-1}\,M$, $[H^+]_0=5.00\times 10^{-2}\,M$

a constant partial pressure of oxygen, because log-[Fe(II)] decreases linearly with the lapse of reaction time, being in contrast with the cases of Cl^- and SCN^- ions. The dependence of the reaction rate upon the partial pressure of oxygen, p, was found to be in a proportional correlation, as equally to the cases of Cl^- and SCN^- ions. Therefore, the rate equation is established as:

$$v = kp[\mathrm{Fe(II)}] \tag{8}$$

The absorption spectra of a reaction solution containing iron(II) and en were observed to vary with time and finally to agree with those of iron(III) at the same concentration with the initial one of iron(II). This observation shows that the reaction only goes by simple oxidation of iron(II) to iron(III) without any further chemical changes of the substances involved. The rate of consumption of oxygen also showed the stoichiometry of the overall reaction to be quite the same with the cases of Cl^- and SCN^- ions, as represented by Eq. (2).

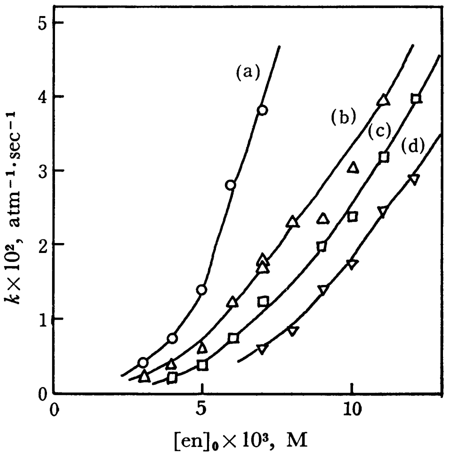

Fig. 11. The dependence of k upon $[\mathrm{en}]_0$ and $[\mathrm{H}^+]_0$ at $p=0.2$ atm, $\mu=0.2$ M, and 25 °C.
(a) $[\mathrm{H}^+]_0=2.00\times10^{-3}$ M (b) $[\mathrm{H}^+]_0=3.00\times10^{-3}$ M
(c) $[\mathrm{H}^+]_0=4.00\times10^{-3}$ M (d) $[\mathrm{H}^+]_0=6.00\times10^{-3}$ M

The apparent rate constant k in Eq. (8) is affected by the concentrations of both en and acid; the higher the concentration of en and the lower that of acid, the larger the rate constant, as is shown in Fig. 11. Judging from these experimental facts, the following reaction scheme (e) can be deduced in addition to those of (a) and (c), although the contribution due to (a) and (c) may be negligibly small.

$$\text{(e)}\quad \mathrm{Fe^{2+} + en \xrightleftharpoons{K_1} Fe.en^{2+}} \qquad \text{(e1), (b1)}$$

$$\mathrm{Fe.en^{2+} + O_2 \xrightleftharpoons{K_0'} en.FeO_2{}^{2+}} \qquad \text{(e2), (b2)}$$

$$\mathrm{en.FeO_2{}^{2+} \xrightarrow{k_e}} \qquad \text{(e3)}$$

$$\mathrm{en.FeO_2{}^{2+} + Fe.en^{2+} \longrightarrow} \qquad \text{(e4)}$$

$$\mathrm{en + H^+ \xrightleftharpoons{K_e} enH^+} \qquad \text{(e5)}$$

Since the reaction is of the first order with respect to [Fe(II)], either the forward reaction of (e2) or (e3) may be rate-determining, with the rate constant k_0' or k_e, respectively. If (e2) is rate-determining, it may be followed by (e3) and/or (e4), and if (e3) is so, (e4) must not occur and (e2) establishes an equilibrium. Whichever the rate-determining step may be, they will produce $O_2{}^{2-}$ and will be succeeded similarly by the reactions as shown in (t). Thus, k is expressed as follows:

$$k = \frac{EK_1[\mathrm{en}]}{1+K_1[\mathrm{en}]} \tag{9}$$

in which E represents $4k_0'$ or $4k_1K_0'$ according to whether the rate-determining step is (e2) or (e3). When the total concentration of en is expressed by $[\mathrm{en}]_0$, the concentration of free en is defined approximately by

$$[\mathrm{en}]_0 = (1+K_e[\mathrm{H}^+]+K_1[\mathrm{Fe}^{2+}])[\mathrm{en}] \tag{10}$$

The values of log K_e in aqueous media is as large as about 10.[19] Although DMSO is more basic than water in nature,[20] log K_e in DMSO can be regarded to be still so large as compared with $(1+K_1[\mathrm{Fe}^{2+}])$ and $K_1[\mathrm{en}]_0$. Then, k is rewritten as:

$$k = \frac{EK_1[\mathrm{en}]_0}{K_e[\mathrm{H}^+]} \tag{11}$$

At constant total acid concentrations, $[\mathrm{H}^+]_0$, the hydrogen ion concentration $[\mathrm{H}^+]$ decreases with increasing $[\mathrm{en}]_0$. This is the reason why k exhibits no rigorous linear relationship with $[\mathrm{en}]_0$ but a trend of abrupt increase with increasing $[\mathrm{en}]_0$ as shown in Fig. 11. From the slope of the curve at very low $[\mathrm{en}]_0$, EK_1/K_e is roughly estimated to be 3.5×10^{-4} atm⁻¹·sec⁻¹.

General Consideration on the Order of the Reaction with Respect to [(Fe(II)]. In a reaction system, $\mathrm{FeL^{2+}}$, $\mathrm{FeSH^{3+}}$, and $\mathrm{HSFeL^{3+}}$ can be considered to exist in individual equilibria with their composing species, where L stands for one of the catalyzing ligands, Cl^-, SCN^-, or en. If any one of these iron(II) complexes is simply denoted by Fe(II), the reaction schemes as have been described above are generalized as follows:

$$\begin{tikzcd} & & {} \\ \mathrm{Fe(II)} + \mathrm{O_2} \arrow[r, "(A)"] & \mathrm{Fe(II).O_2} \arrow[ur, "(B)"] \arrow[dr, "(C)"', "+\mathrm{Fe(II)}"] & \\ & & {} \end{tikzcd}$$

Depending upon the rates of the reaction of passing the steps, (A), (B), and (C), there may possibly come out the following three cases:

(i) (A) < (B), (C)
(ii) (A) > (B), (C), and (B) ≫ (C)
(iii) (A) > (B), (C), and (B) ≪ (C)

The rate-determining step will be (A), (B), or (C) according to the case (i), (ii), or (iii), respectively. In the cases (i) and (ii), the reaction is of the first order with respect to [Fe(II)], while in the case of (iii), it is of the second order with respect to [Fe(II)]. When Cl^- and SCN^- ions are employed as ligands, the case (iii) must actually happen because of the fact that the reaction is of the second order. When en is used, on

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19) "Stability Constants of Metal-Ion Complexes," ed. by L. G. Sillén and A. E. Martell, The Chemical Society Special Publication No. 17 (1964), p. 370.

20) G. Wada, This Bulletin, **42**, 890 (1969).

the other hand, the case must be (i) or (ii) although it is not decided yet which it is, at the present stage.

By taking into account all of the possible elementary reactions of the schemes from (a) through (e), and by using the steady-state method for the species appearing as intermediates, a set of probable elementary reactions and a rate equation can be drawn out as follows:

$$\mathrm{Fe^{2+} + L \rightleftharpoons FeL^{2+}} \qquad (K_1) \qquad \text{(b1, d1, e1)}$$

$$\mathrm{Fe^{2+} + H^+ \rightleftharpoons FeSH^{3+}} \qquad (K_H) \qquad \text{(c2)}$$

$$\mathrm{FeL^{2+} + H^+ \rightleftharpoons HSFeL^{3+}} \qquad (K_H') \qquad \text{(d3)}$$

$$\mathrm{Fe^{2+} + O_2} \overset{k_0}{\rightleftharpoons} \mathrm{FeO_2{}^{2+}} \qquad (K_0) \qquad \text{(a1, c1)}$$

$$\mathrm{FeL^{2+} + O_2} \overset{k_0'}{\rightleftharpoons} \mathrm{LFeO_2{}^{2+}} \qquad (K_0') \qquad \text{(b2, d2, e2)}$$

$$\mathrm{FeO_2{}^{2+}} \xrightarrow{k_1}$$

$$\mathrm{LFeO_2{}^{2+}} \xrightarrow{k_e} \qquad \text{(e3)}$$

$$\mathrm{FeO_2{}^{2+} + Fe^{2+}} \xrightarrow{k_a} \qquad \text{(a2)}$$

$$\mathrm{LFeO_2{}^{2+} + FeL^{2+}} \xrightarrow{k_b} \qquad \text{(b3, e4)}$$

$$\mathrm{FeO_2{}^{2+} + FeSH^{3+}} \xrightarrow{k_c} \qquad \text{(c3)}$$

$$\mathrm{LFeO_2{}^{2+} + HSFeL^{3+}} \xrightarrow{k_d} \qquad \text{(d4)}$$

$$v = \frac{4p\{\alpha + (\beta/\delta)[\mathrm{Fe(II)}]\}\gamma[\mathrm{Fe(II)}]}{\{\alpha + (\beta/\delta)[\mathrm{Fe(II)}] + \gamma\}\delta} \qquad (12)$$

$$\alpha = k_1K_0 + k_eK_0'K_1[\mathrm{L}] \qquad (13)$$

$$\beta = k_aK_0 + k_bK_0'K_1{}^2[\mathrm{L}]^2 + k_cK_HK_0[\mathrm{H^+}] + k_dK_H'K_0'K_1{}^2[\mathrm{H^+}][\mathrm{L}]^2 \qquad (14)$$

$$\gamma = k_0 + k_0'K_1[\mathrm{L}] \qquad (15)$$

$$\delta = 1 + K_H[\mathrm{H^+}] + K_1[\mathrm{L}] + K_H'K_1[\mathrm{H^+}][\mathrm{L}] \qquad (16)$$

Under limiting conditions, the following extreme three cases can be derived, corresponding to the three ones, (i), (ii), and (iii) respectively, as mentioned above and Eq. (12) results in typically simple forms.

(i) If $\alpha + (\beta/\delta)[\mathrm{Fe(II)}] \gg \gamma$,

$$v = \frac{4\gamma}{\delta}p[\mathrm{Fe(II)}] \qquad (17),\ (8)$$

(ii) If $\alpha + (\beta/\delta)[\mathrm{Fe(II)}] \ll \gamma$ and $\alpha \gg (\beta/\delta)[\mathrm{Fe(II)}]$

$$v = \frac{4\alpha}{\delta}p[\mathrm{Fe(II)}] \qquad (18),\ (8)$$

(iii) If $\alpha + (\beta/\delta)[\mathrm{Fe(II)}] \ll \gamma$ and $\alpha \ll (\beta/\delta)[\mathrm{Fe(II)}]$

$$v = \frac{4\beta}{\delta^2}p[\mathrm{Fe(II)}]^2 \qquad (19),\ (1)$$

Equation (19) coincides with the empirical rate equation (1), which was seen in the cases of $\mathrm{Cl^-}$ and $\mathrm{SCN^-}$ catalysts, while Eqs. (17) and (18) coincide with the empirical one (8) under the catalysis of en.

In the cases (i) and (ii), it is possible to distinguish whether Eq. (17) or (18) is actually available, in the following manner. When [Fe(II)] is made larger, Eq. (17) remains unchanged as a function of the first order of [Fe(II)], while Eq. (18) becomes no longer useful and the reaction order with respect to [Fe(II)] gradually grows higher up to the second order, with increasing [Fe(II)]. Even in the case (iii), on the other hand, the reaction order may fall down from the second order to the first at the extremely low value of [Fe(II)] as is easily understood from Eq. (19). Unfortunately, we could not realize these extreme cases at very high and very low [Fe(II)] due to the experimental difficulties. Anyway, it is worth noticing that the reaction order is not definitely specific nor characteristic to the catalyzing ligands but depends upon their reaction conditions; a similar kind of thing to this is also known in the Lindemann mechanism in which a reaction of the first order at a certain concentration may become to be of the second order at a lower concentration than that with respect to a reacting species. Therefore, the order of the reaction itself is not essentially important, unless the reaction conditions are rigorously taken into account.

Ligand and Solvent Effects upon the Reaction Rates of Oxidation. Aquocobalt(II) ion in aqueous solution is thermodynamically stable and is, therefore, impossible to be oxidized to cobalt(III). However, when Co(II) is coordinated with ammonia,[21] en,[22] or histidine,[23] it forms a high spin complex which acts as an oxygen carrier and is rapidly oxidized to a Co(III) complex of low spin. In the cases of iron complexes, it is known that $\mathrm{Fe(bipy)_3{}^{2+}}$ and $\mathrm{Fe(phen)_3{}^{2+}}$ which are of low spin complexes in aqueous solution are very stable and inert against oxidation, whereas another low spin complex of iron(II), $\mathrm{Fe(CN)_6{}^{4-}}$, is easily oxidized to produce $\mathrm{Fe(CN)_6{}^{3-}}$ which is also of a low spin complex. The overall formation constants, $\log\beta$, of $\mathrm{Fe(bipy)_3{}^{2+}}$, $\mathrm{Fe(phen)_3{}^{2+}}$, and $\mathrm{Fe(CN)_6{}^{4-}}$ are 17.6,[24] 21,[25] and 24[26] respectively, and those for their oxidized states are unknown for $\mathrm{Fe(bipy)_3{}^{3+}}$ and 14.1 and 31 for $\mathrm{Fe(phen)_3{}^{3+}}$[25] and $\mathrm{Fe(CN)_6{}^{3-}}$[26], respectively. The oxidation of iron(II), therefore, results in the decrease in stabilities in the cases of bipy and phen complexes, while it results in the increase in stability in the case of cyano complex. This is likely to be the reason why only the cyano complex undergoes a rapid oxidation. Kurimura and others[6] found out that there exists a linear relationship between $\log k$ and $\log[\beta(\mathrm{III})/\beta(\mathrm{II})]$ among many iron complexes coordinated with organic ligands of various polyaminoacetic and other acids, where k, β(III), and β(II) stand for rate constant of oxidation reaction, overall formation constants of iron(III) and iron(II) complexes, respectively. This relationship is, in other words, a linear relation between the activation free energies and the thermodynamical standard free energies of the reaction, similar cases to which are also observed in the electron transfer reactions between iron(II) and iron(III) complexes coordinated with

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[21] J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **91**, 1325 (1969).

[22] F. Miller, J. Simplicio, and R. G. Wilkins, *ibid.*, **91**, 1962 (1969).

[23] M. S. Michailidis and R. B. Martin, *ibid.*, **91**, 4683 (1969).

[24] P. Krumholz, *Anais. Acad. Brasil de Cienco*, **22**, 2484 (1950).

[25] T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Amer. Chem. Soc.*, **70**, 2348, 3596 (1948).

[26] C. C. Stephenson and J. C. Morrow, *ibid.*, **78**, 275 (1956).

Table 2. Types of changes in electronic structures associated with the oxidation Fe(II)→Fe(III)

Types	Electronic configurations Fe(II) → Fe(III)	Examples of ligands
L→H	$t_{2g}{}^6e_g{}^0 \rightarrow t_{2g}{}^3e_g{}^2$	
L→L	$t_{2g}{}^6e_g{}^0 \rightarrow t_{2g}{}^5e_g{}^0$	CN$^-$, phen, bipy
H→H	$t_{2g}{}^4e_g{}^2 \rightarrow t_{2g}{}^3e_g{}^2$	en, Cl$^-$, SCN$^-$, H_2O
H→L	$t_{2g}{}^4e_g{}^2 \rightarrow t_{2g}{}^5e_g{}^0$	

various ligands.[27]

Summarizing the above-described considerations, as long as the linear free energy relation is available, four types of the autoxidation reaction in connection with the electronic structures of the reactants and products can be deduced, as shown in Table 2. On the basis of stability variations involved in the course of oxidation, a change in the electronic configuration from low spin to high spin (L→H) might be most difficult to take place, while a change of the reverse direction (H→L) might occur most easily, although such cases have not been found yet. Examples of L→L type are seen in the cases of bipy, phen, and CN$^-$ ion, among which the former two are slow and the latter is fast.

The formation constants, log K_1, of $FeCl^{2+}$ and $FeSCN^{2+}$ in DMSO have been measured as 3.6[28] and 2.9,[29] although those of iron(II) species with the same ligands were not determined due to their low stabilities. Moreover, those of Fe–en complexes for both oxidation states in DMSO are not known either. In spite of such lacks of data, it may be safely said that the autoxidation catalyzed by these three ligands, en, Cl$^-$, and SCN$^-$ ions, in DMSO proceeds via H→H type, with moderately large reaction rates in the sequence of en$>$Cl$^-$$>SCN^-$, being faster than L→H type and slower than H→L one.

The solvent effect that the reaction proceeds much faster in DMSO than in water can be attributed to the larger differences in the formation constants of the iron complexes between the two oxidation states in DMSO than those in water. The electrostatic repulsion between ions of like signs is clearly larger in DMSO of a lower dielectric constant than in water of a higher one. This effect should contribute toward the reaction disadvantageously and make the reaction proceed slower in DMSO than in water, this being not the case though. Consequently, the latter effect in repulsion must be conquered by the former in stability after all.

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[27] K. Bächmann and K. H. Lieser, "Exchange Reactions," International Atomic Energy Agency, Vienna (1965), p. 29.

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

[29] G. Wada, N. Yoshizawa, and Y. Sakamoto, *ibid.*, **44**, 1018 (1971).