December, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54*, *3739—3742 (1981)* 3739

Kinetic Studies of the Electron Transfer Reactions in Iron(II) and Iron(III) Systems. XI. Electron Transfer Reaction between Aquairon(II) and Tris(1,10-phenanthroline)iron(III) in Water Mixed with Methanol, Ethanol, 1-Propanol, and Ethylene Glycol

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(Received January 29, 1981)

The electron transfer reaction $\mathrm{Fe^{2+}{}_{aq}+Fe(phen)_3{}^{3+}\rightarrow Fe^{3+}{}_{aq}+Fe(phen)_3{}^{2+}}$ has been investigated in order to find out the influence of the dielectric nature of media on the reaction rates, by the method of stopped-flow spectrophotometry. As the reaction media, were used aqueous mixtures with various alcohols, such as methanol, ethanol, 1-propanol, and ethylene glycol at their various mole fractions x. The second-order rate constant k grows larger approximately linearly with the increase in x, in a sequence: methanol<ethylene glycol<ethanol<1-propanol. When ln k is plotted against D^{-1} (the reciprocal dielectric constant), all points come together on a single straight line with a positive slope, indifferent to the kinds of the alcohols used. This fact suggests that the reaction proceeds through three successive elementary processes, $\mathrm{Fe^{2+}{}_{aq}+Fe(phen)_3{}^{3+}\xrightarrow{i}[Fe(H_2O)_6{}^{2+}\cdot Fe(phen)_3{}^{3+}]\xrightarrow{ii}[Fe(H_2O)_6{}^{3+}\cdot Fe(phen)_3{}^{2+}]\xrightarrow{iii}Fe^{3+}{}_{aq}+Fe(phen)_3{}^{2+}}$, in which Process i is the formation of an outer-sphere ion-pair between two reacting ions, Process ii the intramolecular electron transfer in the intermediate complex, and Process iii the separation of the ion-pair into the product ions, the last being the rate-determining step. The reaction scheme is compared with that of the reaction $\mathrm{Fe^{2+}{}_{aq}+Fe(OH)^{2+}\rightarrow Fe(OH)^{2+}+Fe^{2+}{}_{aq}}$, where the first step of the ion-pair formation is rate-determining.

The electron transfer reactions between iron(II) and iron(III) species in various media have been investigated extensively since the study of Silverman and Dodson.[1] The kinetics of the electron transfer reactions are now roughly divided into two main categories; the inner-sphere and outer-sphere mechanisms, the latter including the hydrogen-atom transfer mechanism. The oxidation reaction of aquairon(II) by tris(1,10-phenanthroline)-iron(III) was first studied by Sutin and Gordon[2,3] by applying a flow method, and was found to proceed *via* the outer-sphere mechanism, with a rate constant $k=3.7\times10^4\ \mathrm{M^{-1}\,s^{-1}}$ in a 0.5 M perchloric acid media at 25 °C ($\mathrm{M=mol\ dm^{-3}}$).

In the present study, this reaction was again adopted in order to see which of the two processes, the ionic association process between the two reacting ions or the ionic dissociation process of the associated ion-pair into the two leaving ions, is the rate-determining step in the overall outer-sphere electron transfer. For this purpose, aqueous media mixed with a number of alcohols such as methanol, ethanol, 1-propanol, and ethylene glycol were used with diversely different dielectric constants according to the kinds and the mixing ratios of alcohols. A part of the results have been preliminarily reported elsewhere.[4]

The reaction under consideration is as follows:

$$\mathrm{Fe^{2+}_{aq}} + \mathrm{Fe(phen)_3^{3+}} = \mathrm{Fe^{3+}_{aq}} + \mathrm{Fe(phen)_3^{2+}}. \qquad (1)$$

Since the standard redox potentials of $\mathrm{Fe^{3+}{}_{aq}/Fe^{2+}{}_{aq}}$ and $\mathrm{Fe(phen)_3{}^{3+}/Fe(phen)_3{}^{2+}}$ are 0.76 V and 1.14 V respectively, the equilibrium constant of Reaction 1 is calculated to be $K_\mathrm{a}=2.69\times10^6$ at 25 °C. Therefore, the rate of the backward reaction can be ignored in the course of the kinetic measurements. The reaction rate is consequently expressed by an equation

$$v = k[\mathrm{Fe^{2+}_{aq}}][\mathrm{Fe(phen)_3^{3+}}] \qquad (2)$$

with a second-order rate constant k. Under a condition of excess $[\mathrm{Fe^{2+}{}_{aq}}]$ over $[\mathrm{Fe(phen)_3{}^{3+}}]$, the rate can be measured as an apparent pseudo-first-order reaction.

$$v = k'[\mathrm{Fe(phen)_3^{3+}}] \qquad (3)$$
$$k' = k[\mathrm{Fe^{2+}_{aq}}]$$

Experimental

Materials. *Fe(ClO$_4$)$_2$*: Iron wire of 99.99% purity was dissolved in 3 M perchloric acid and the solution was concentrated under a reduced pressure at 60 °C. The precipitated crystals were washed by ether to remove the occluded acid and dried completely in vaccum.

[Fe(phen)$_3$](ClO$_4$)$_3$: Crystals of $\mathrm{[Fe(phen)_3]Cl_2}$ were precipitated by adding an appropriate amount of NaCl crystals to a solution containing iron(II) perchlorate and 1,10-phenanthroline with the concentration of the latter slightly excess over the molar ratio 1 : 3. A solution of $\mathrm{[Fe(phen)_3]Cl_2}$ in 1 M sulfuric acid was gradually added with $\mathrm{PbO_2}$ powder to oxidize $\mathrm{Fe(phen)_3{}^{2+}}$ ion to $\mathrm{Fe(phen)_3{}^{3+}}$ ion, and after filtering the solution to remove the deposited $\mathrm{PbSO_4}$ and the excess $\mathrm{PbO_2}$, crystals of $\mathrm{NaClO_4}$ were added to the solution to precipitate the crystals of $\mathrm{[Fe(phen)_3](ClO_4)_3}$, which were then filtered out, washed by ether, and dried in a vacuum. The crystals of 1,10-phenanthroline were a commercial reagent and were used without further purification.

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

Alcohols: The alcohols used in the present study were methanol, ethanol, 1-propanol, and ethylene glycol. The first three of the above alcohols were distilled under ordinary atmospheric pressure and the last one under reduced one.

Procedure. Kinetic measurements were carried out by use of a Yanagimoto stopped-flow spectrophotometer Model SPS-1 with a thermostated equipment. The reaction was initiated by mixing two solutions containing $\mathrm{Fe^{2+}{}_{aq}}$ and $\mathrm{Fe(phen)_3{}^{3+}}$ ions respectively. The reaction rate was traced by observing the diminution of transmittance due to the production of $\mathrm{Fe(phen)_3{}^{2+}}$ ion at 510 nm, which was recorded on a memoriscope. The temperature was always kept at

25 °C unless otherwise noted and the ionic strength of the reaction solution was adjusted at 1.0 M with $\mathrm{NaClO_4}$.

The apparent pseudo-first-order rate constant k' was evaluated from the slope of a straight line obtained by plotting the values of the left-hand side in the following equation *vs.* reaction time t,

$$\ln([\mathrm{Fe(phen)_3^{3+}}]_0 - [\mathrm{Fe(phen)_3^{2+}}]) = -k't + \ln[\mathrm{Fe(phen)_3^{3+}}]_0 \qquad (4)$$

where $[\mathrm{Fe(phen)_3{}^{3+}}]_0$ is the initial concentration of $\mathrm{Fe(phen)_3{}^{3+}}$ ion at $t=0$. An example of the linearity for a reaction run is shown in Fig. 1. For each mole fraction of alcohols x in water, rate measurements were generally performed about ten times, changing the initial concentrations in ranges of $[\mathrm{Fe^{2+}}]_0$ $(0.6\text{—}5.0)\times10^{-3}$ M and $[\mathrm{Fe(phen)_3{}^{3+}}]_0$ $(0.5\text{—}10.0)\times10^{-5}$ M, the values of k being averaged.

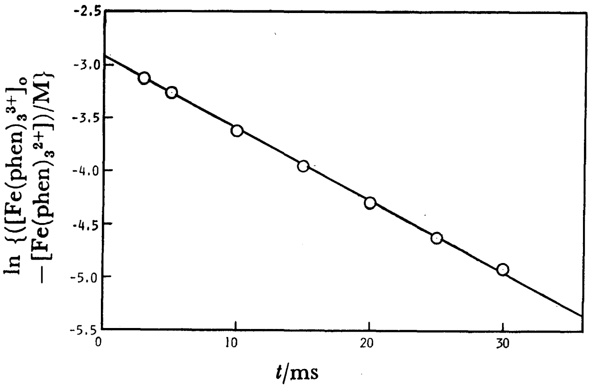

Fig. 1. Plots of $\ln([\mathrm{Fe(phen)_3{}^{3+}}]_0-[\mathrm{Fe(phen)_3{}^{2+}}])$ *vs.* t at $[\mathrm{Fe^{2+}}]_0=8.47\times10^{-4}$ M, $[\mathrm{Fe(phen)_3{}^{3+}}]_0=9.28\times10^{-6}$ M, $[\mathrm{HClO_4}]=0.05$ M, $\mu=0.1$ M, and 25 °C, in a mixed solvent of water and methanol at $x_{\mathrm{MeOH}}=0.225$.

Results and Discussion

Figure 2 shows the variation of k according to the increase in the mole fractions of alcohols. Within the lower mole fractions $x<0.1$, k grows up approximately linearly with the increase in x with steeper slopes in an order, methanol<ethylene glycol<ethanol<1-propanol; namely, it seems that the more the number of the carbon atoms in the monohydric alcohols and the less the number of OH groups in the alcohols with two carbon atoms, the more accelerated is k with the increase in x. In other words, the hydrophobicity of alkyl groups looks like to make the electron transfer reaction occur faster, while the hydrophilicity of OH group shows a trend to behave unfavorably to the reaction.

When the logarithms of k are plotted against the reciprocals of the dielectric constants of the mixed solvents[5] as are depicted in Fig. 3, they come altogether on an approximately single straight line with a positive slope indifferent to the kinds of the alcohols adopted.

$$\frac{\mathrm{d}\ln k}{\mathrm{d}D^{-1}}>0 \qquad (5)$$

This fact indicates that the reaction is largely controlled by the dielectric constants of the media, although the molecular and structural features of alcohols have been seen to partly affect the reaction rates to some extent as mentioned above. Thus, the linearity in Fig. 3 can be interpreted by a hypothesis that an electrostatic interaction between the two reacting species plays an important role in the rate-determining step as shown below.

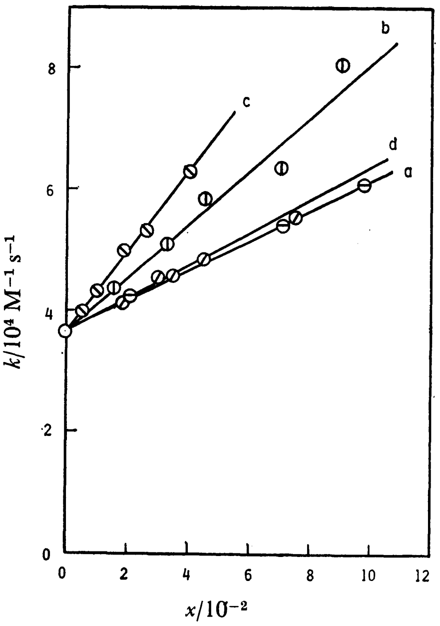

Fig. 2. Variation of k *vs.* mole fraction of alcohol x. a(⊖): Methanol, b(⦶): ethanol, c(⦸): 1-propanol, d(⊘): ethylene glycol.

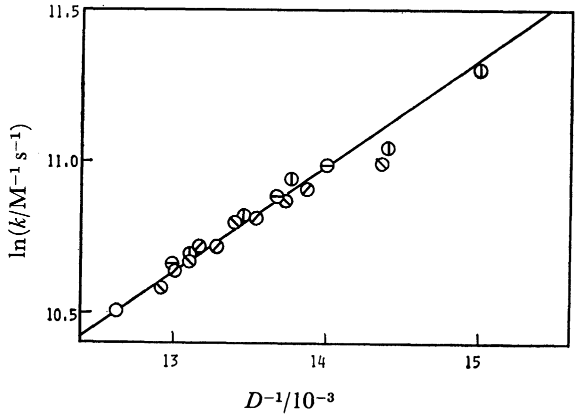

Fig. 3. Plots of ln k *vs.* D^{-1} in mixed solvents of water and alcohols.

○: Pure water, ⊖: water+methanol, ⦶: water+ethanol, ⦸: water+1-propanol, ⊘: water+ethylene glycol.

Now, let us consider the mechanism of Reaction 1 as taking place *via* three successive elementary processes.

$$\mathrm{Fe_{aq}^{2+}} + \mathrm{Fe(phen)_3^{3+}} \rightleftharpoons [\mathrm{Fe(H_2O)_6^{2+}}.\,\mathrm{Fe(phen)_3^{3+}}] \qquad \text{(i)}$$

$$[\mathrm{Fe(H_2O)_6^{2+}}.\,\mathrm{Fe(phen)_3^{3+}}] \rightleftharpoons [\mathrm{Fe(H_2O)_6^{3+}}.\mathrm{Fe(phen)_3^{2+}}] \qquad \text{(ii)}$$

$$[\mathrm{Fe(H_2O)_6^{3+}}.\,\mathrm{Fe(phen)_3^{2+}}] \longrightarrow \mathrm{Fe_{aq}^{3+}} + \mathrm{Fe(phen)_3^{2+}} \qquad \text{(iii)}$$

Process i is a step in which an outer-sphere ion-pair formation occurs with a pre-equilibrium constant K_i, Process ii is an intramolecular electron transfer process with an equilibrium constant K_{ii}, and Process iii is a separation process of the ion-pair into two leaving ions.

When the rate constants of the forward reactions of Processes i, ii, and iii are denoted by k_i, k_{ii}, and k_{iii} and those of the reverse reactions of Processes i and ii by k'_i and k'_{ii} respectively, the apparent second-order rate constant k is expressed by the following relation, derived by virtue of the steady-state method considering both $[Fe(H_2O)_6^{2+}\cdot Fe(phen)_3^{3+}]$ and $[Fe(H_2O)_6^{3+}\cdot Fe(phen)_3^{2+}]$ as reaction intermediates.

$$k = \frac{k_{I}k_{II}k_{III}}{k'_{I}k'_{II}+k'_{I}k_{III}+k_{II}k_{III}} \tag{6}$$

For the three limiting cases, the relation can be simplified as follows:

If $k_{II}k_{III} \gg (k'_{II} + k_{III})k'_{I}$

$$k = k_{I}, \tag{7}$$

if $k'_{I}k_{III} \gg k'_{I}k'_{II} + k_{II}k_{III}$,

$$k = K_{I}k_{II}, \tag{8}$$

and if $k'_{I}k'_{II} \gg (k'_{I} + k_{II})k_{III}$,

$$k = K_{I}K_{II}k_{III}. \tag{9}$$

Each of these three cases corresponds to that in which Process i, ii, or iii is rate-determining, respectively.

If the overall rate of Reaction 1 were actually controlled by Process i, the dielectric dependence of k_i would be shown by the Scatchard relation,[6,7]

$$\ln k_{I} = \ln k_{I}^{\circ} - \frac{z_A z_B e^2}{kTd_{I}D}, \tag{10}$$

where D is the dielectric constant of the mixed solvents, $\boldsymbol{k}$ the Boltzmann constant, d_i the internuclear distance between Fe(II) and Fe(III) in the outer-sphere ion-pair formed in Process i, k_i° the imaginary k_i at $D=\infty$, and Z_A and Z_B the numbers of electric charges on the respective reacting ions, *viz.* $Z_A=2$ and $Z_B=3$ in the present case. According to Eq. 10, the linearity of the plot of ln k *vs.* D^{-1} should have a negative slope, this expectation being against the observed fact shown in Fig. 3. Therefore, the assumption that Process i is the rate-determining step is not probable.

Next, if Process ii were rate-determining, ln k would vary dependently upon D as follows.

$$\frac{\mathrm{d}\ln k}{\mathrm{d}D^{-1}} = \frac{\mathrm{d}\ln K_{I}}{\mathrm{d}D^{-1}} + \frac{\mathrm{d}\ln k_{II}}{\mathrm{d}D^{-1}} \tag{11}$$

Since Process ii is an intramolecular electron transfer, the rate would not be seriously affected by D, and consequently, $\mathrm{d}\ln k_{ii}/\mathrm{d}D^{-1}$ would be approximately equal to zero. But $\mathrm{d}\ln K_i/\mathrm{d}D^{-1}$ would have a negative value with a similar reason to the case in Eq. 10. Therefore, $\mathrm{d}\ln k/\mathrm{d}D^{-1}$ should be negative, this being also contrary to the experimental result.

Finally, the case that Process iii is rate-determining must be considered. By differentiating Eq. 9 with respect to D^{-1}, the following relation is given.

$$\frac{\mathrm{d}\ln k}{\mathrm{d}D^{-1}} = \frac{\mathrm{d}\ln K_{I}}{\mathrm{d}D^{-1}} + \frac{\mathrm{d}\ln K_{II}}{\mathrm{d}D^{-1}} + \frac{\mathrm{d}\ln k_{III}}{\mathrm{d}D^{-1}} \tag{12}$$

Since Processes i and iii are the process of ionic association and ionic separation respectively, the following three relations will be established.

$$\frac{\mathrm{d}\ln K_{I}}{\mathrm{d}D^{-1}} = -\frac{z_A z_B e^2}{\boldsymbol{k}Td_{I}} < 0 \tag{13}$$

$$\frac{\mathrm{d}\ln K_{II}}{\mathrm{d}D^{-1}} \fallingdotseq 0 \tag{14}$$

$$\frac{\mathrm{d}\ln k_{III}}{\mathrm{d}D^{-1}} = \frac{z_C z_D e^2}{\boldsymbol{k}Td_{III}} > 0 \tag{15}$$

The symbols appearing in Eq. 15 are similar to those described above, with $Z_C=3$ and $Z_D=2$ in this case. Since $Z_A Z_B = Z_C Z_D = 6$, Eq. 12 becomes

$$\frac{\mathrm{d}\ln k}{\mathrm{d}D^{-1}} = \frac{6e^2}{\boldsymbol{k}T}\cdot\frac{d_{I}-d_{III}}{d_{I}d_{III}} > 0. \tag{16}$$

The bond lengths $d(Fe^{II}–O)$ and $d(Fe^{III}–O)$ in aquairon complexes to be taken are 2.21 Å and 2.05 Å respectively,[8] and $d(Fe^{II}–N)$ in $Fe(phen)_3^{2+}$ ion would be shorter than $d(Fe^{III}–N)$ in $Fe(phen)_3^{3+}$ ion due to the stronger bonding by back donation in the former complex. Accordingly, $d_i(Fe^{II}–O,\ Fe^{III}–N)$ will be larger than $d_{iii}(Fe^{III}–O,\ Fe^{II}–N)$, resulting in a positive value in Eq. 16, being consistent with the experimental fact in Fig. 3 and Eq. 5.[†] This indicates that the absolute value of the electrostatic repulsive energy required to form an ion-pair between ions with the same sign in Process i is smaller than that liberated to dissociate the ion-pair in Process iii. Therefore, it may be reasonably recognized that the rate-determining step of Reaction 1 must be Process iii. Evidence for an initial association, as an example, has been known also in reactions of plastocyanin with some inorganic complexes.[10]

As far as the mole fractions of alcohols are lower than 0.1, the obvious preferential solvation of alcohol molecules would not occur around iron(III) ion[11] and, therefore, the structure of the intermediate ion-pair may be commonly available throughout this range of mole fractions. Since the second-order rate constant for the water exchange in $Fe(H_2O)_6^{3+}$ ion is $k=2.8\times10^2$ $M^{-1}\,s^{-1}$ [12,13] and $Fe(phen)_3^{2+}$ ion is substitution-inert, the intermediate outer-sphere ion-pair is considered to be probable.

A contrasting instance to Reaction 1 has been found in the electron transfer reaction in mixed solvents of water and alcohols at various mole fractions,[14]

$$Fe_{aq}^{2+} + Fe(OH)^{2+} \longrightarrow Fe(OH)^{2+} + Fe_{aq}^{2+} \tag{17}$$

in which case the plot of logarithms of the rate constants shows a good linear relationship with D^{-1} with a negative slope, instead of having a positive slope as in the case of Reaction 1. This fact suggests that the first step must be rate-determining, where the two reacting ions encounter to each other in Reaction 17 with the rate constant $k=k_i$ as a typical instance as is shown in Eq. 7. On this viewpoint, the trend how the dielectric

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[†] According to the numerical calculation from the slope of the straight line in Eq. 16, the values of d_{I} and d_{III} can not be strictly decided, but only roughly estimated. Although sets of $d_{I}=14.0$ Å and $d_{III}=6.2$ Å, $d_{I}=12.0$ Å and $d_{III}=5.7$ Å, $d_{I}=10.0$ Å and $d_{III}=5.2$ Å, etc. are numerically derived, any of them may not be probable, as compared with the dimension of the complexes.[9] This discrepancy may mostly be caused by the dielectric saturation phenomenon in the direct vicinity aroud ions.

constants of the reaction media exhibit an influence on the reaction rate looks like to offer a nice tool as a method for distinguishing the rate-determining step among some successive elementary processes in the electron transfer reactions.

The activation enthalpy and the activation entropy of Reaction 1 in a mixed solvent $x_{\mathrm{MeOH}}=0.16$ were found to be $\Delta H^{*}=-0.4\pm0.8$ kJ mol^{-1} and $\Delta S^{*}=-160$ J K^{-1} mol^{-1} by measuring the reaction rates at 14, 25, 33, and 40 °C. These values are in good accordance with those $\Delta H^{*}=3.2\pm0.8$ kJ mol^{-1} and $\Delta S^{*}=-155$ J K^{-1} mol^{-1} measured in pure water by Sutin and Gordon.[2] Cramer and Meyer[15] pointed out that the very small or even slightly negative values of ΔH^{*} in the oxidation reactions of $\mathrm{Fe^{2+}}_{\mathrm{aq}}$ by polypyridine complexes of iron(III) and ruthenium(III) suggest the possibility of occurrence of multiple paths in the electron transfer reactions. This idea may also prevail for the reactions in the mixed solvents of alcohols, and may support the reaction mechanism proposed above. They also indicate[15] that the reaction is "non-Marcus" because calculated values for the Fe(II)–Fe(III) polypyridine self-exchange rates are too low approximately by 10^5 [16,17] as expected from the observed rate constant k_{11} for $\mathrm{Fe^{2+}}_{\mathrm{aq}}$–$\mathrm{Fe^{3+}}_{\mathrm{aq}}$ reaction[1,14] and the one k_{12} for the reaction under consideration, according to the Marcus relations which are shown in the followings, the symbols being the same as usual.[18]

$$k_{12}=(k_{11}k_{22}K_{12}f)^{1/2} \tag{18}$$

$$\ln f=\frac{(\ln K_{12})^2}{4\ln(k_{11}k_{22}/z^2)} \tag{19}$$

The reason for the dissatisfaction to the Marcus theory is not only due to the existence of the multiple paths throughout the electron transfer reaction as Cramer and Meyer noticed, but also because of the fact that the reaction $\mathrm{Fe^{2+}}_{\mathrm{aq}}$–$\mathrm{Fe^{3+}}_{\mathrm{aq}}$ does not go through an outer-sphere mechanism in a strictly narrow sense of the word, but through a hydrogen-atom-transfer mechanism.[14] Therefore, k_{11} should not actually satisfy the value expected from the Marcus theory, as a matter of course.

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