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# Kinetic Studies of the Electron Transfer Reaction in Iron(II) and Iron(III) Systems. X. The Electron Transfer Reaction between Iron(II) and Iron(III) in the Presence of Pyridine in Aqueous Solution

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**Synopsis.** When pyridine is added to the reaction system of the electron transfer between Fe(II) and Fe(III) in aqueous solution at constant $[HClO_4]_0$, the apparent rate constant $k$ grows rapidly with $[Py]_0$ at $[Py]_0 < [HClO_4]_0$, while $k$ suddenly diminishes to a small and constant value at $[Py]_0 > [HClO_4]_0$. The predominant paths of the reaction will be discussed.

We have been investigating the reaction mechanisms of the electron transfer between iron(II) and iron(III) complexes $Fe(II) + {}^*Fe(III) \rightarrow Fe(III) + {}^*Fe(II)$ in various solutions.[1] In this note, we will report on an interesting phenomenon observed in the case that pyridine(Py) is added to the reaction system. Namely, when the total concentration of pyridine $[Py]_0$ is increased in aqueous solutions of iron(II) and iron(III) at a constant concentration of perchloric acid $[HClO_4]_0$, the apparent rate constant of the electron transfer reaction $k$ grows rapidly at first, and becomes almost infinitely large until $[Py]_0$ reaches to values closely equal to $[HClO_4]_0$. After that, nevertheless, it suddenly diminishes to a constant value as small as $k = 4.5 \pm 1.6$ $M^{-1}\,s^{-1}$ ($1\ M = 1\ mol\ dm^{-3}$) indifferent to both $[Py]_0$ and $[HClO_4]_0$. A few cases of the phenomenon are shown in Fig. 1, in which $k$ is plotted against $[Py]_0$ when $[HClO_4]_0$ is kept at 0.05, 0.10, and 0.20 M respectively, at $\mu = 0.2$ M and 25 °C.

The apparent rate constant $k$ was determined by the method using radioactive tracer Fe-59, as described elsewhere.[2,3]

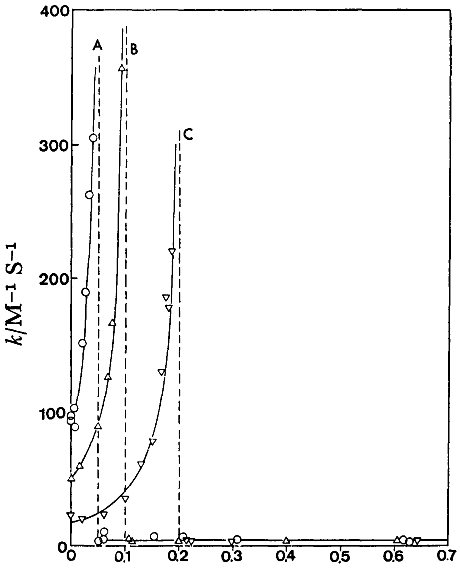

Fig. 1. The variation of $k$ with $[Py]_0$ at $[HClO_4]_0 = 0.05$ M (a), 0.10 M (b), and 0.20 M (c).

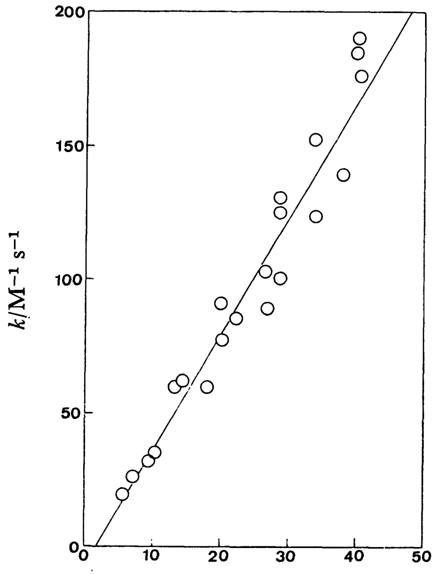

Fig. 2. The linear relationship of $k$ with $([HClO_4]_0 - [Py]_0)^{-1}$ at $[Py]_0 < [HClO_4]_0$.

The observed fact that $k$ varies peculiarly with the increase in $[Py]_0$ at a constant $[HClO_4]_0$ should be reasonably understood by the following consideration. At the concentration range of $[Py]_0 < [HClO_4]_0$, the concentration of hydrogen ion $[H^+]$ becomes smaller by as much as $[Py]_0$ than $[HClO_4]_0$, because pyridine is a considerably strong base with a basicity constant $K_b = 2.8 \times 10^5\ M^{-1}$ at $\mu = 0.5$ M and 25 °C where $K_b = [PyH^+]/[Py][H^+]$.[4,5] Therefore, the actual value of the hydrogen ion concentration in the reaction system is approximately equal to $[HClO_4]_0 - [Py]_0$. Consequently, when $k$ is plotted against $([HClO_4]_0 - [Py]_0)^{-1}$ instead of plotting against $[HClO_4]_0^{-1}$, a single straight line is obtained as is shown in Fig. 2. This indicates that $k$ can be expressed by the following equation:

$$k = k_0 + \frac{k_H K_H}{[HClO_4]_0 - [Py]_0}$$

where $k_0$ and $k_H$ denote the reaction rate constants of the electron transfer $Fe^{2+}/Fe^{3+}$ and $Fe^{2+}/FeOH^{2+}$ respectively, and $K_H$ the hydrolysis constant of $Fe^{3+}$, $K_H = [FeOH^{2+}][H^+]/[Fe^{3+}]$.

The slope of the straight line is found to be 4.4 $s^{-1}$ which is fairly close to the value $k_H K_H = 6.0\ s^{-1}$ observed in aqueous solutions, using the value $K_H = 2.2 \times 10^{-3}$ M.[6] Therefore, the equation suggests that the reaction path between $Fe^{2+}$ and $FeOH^{2+}$ (Path B) takes an important part in parallel with the reaction path between $Fe^{2+}$ and $Fe^{3+}$ (Path A) in the electron transfer reaction in the present system, the asterisked iron *Fe expressing the species labelled by radiotracer.

$$\mathrm{Fe^{2+} + {}^{*}Fe^{3+} \longrightarrow Fe^{3+} + {}^{*}Fe^{2+}} \qquad \text{(A)}$$

$$\mathrm{Fe^{2+} + {}^{*}FeOH^{2+} \longrightarrow FeOH^{2+} + {}^{*}Fe^{2+}} \qquad \text{(B)}$$

When $[\mathrm{Py}]_0$ becomes larger than $[\mathrm{HClO_4}]_0$, the apparent rate constant $k$ suddenly diminishes and keeps almost constant value, as shown in Fig. 1. In this concentration range of $[\mathrm{Py}]_0>[\mathrm{HClO_4}]_0$, a part of pyridine is protonated with $\mathrm{H^+}$ to be pyridinium ion and the rest of pyridine coordinates to $\mathrm{Fe^{2+}}$ to be $\mathrm{Fe(Py)}_n{}^{2+}$.7) Since $[\mathrm{H^+}]$ decreases to a considerable extent due to the protonation of pyridine, $\mathrm{Fe^{3+}}$ is forced to be hydrolyzed to give $\mathrm{FeOH^{2+}}$. Consequently, each of the equilibria of the following three reactions declines towards the right-hand side.

$$\mathrm{Py + H^+ \rightleftharpoons PyH^+}$$

$$\mathrm{Fe^{2+}} + n\mathrm{Py} \rightleftharpoons \mathrm{Fe(Py)}_n{}^{2+}$$

$$\mathrm{Fe^{3+} \rightleftharpoons FeOH^{2+} + H^+}$$

Thus, the main path of the electron transfer reaction should be the reaction between $\mathrm{Fe(Py)}_n{}^{2+}$ and $\mathrm{FeOH^{2+}}$ (Path C),

$$\mathrm{Fe(Py)}_n{}^{2+} + {}^{*}\mathrm{FeOH^{2+}} \longrightarrow \text{Products,} \qquad \text{(C)}$$

the rate constant of which may be approximately equal to the apparent rate constant observed after $[\mathrm{Py}]_0$ surpasses $[\mathrm{HClO_4}]_0$. Although pyridine may be supposed to coordinate to $\mathrm{FeOH^{2+}}$, the occurrence of the coordinated species has not been ascertained yet as far as the spectrophotometric observation was performed.

## References

1) The previous paper of this series: G. Wada, Y. Ohta, S. Hayashida, H. Sugino, T. Mizui, and Y. Aihara, *Bull. Chem. Soc. Jpn.*, **53**, 1278 (1980).

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

3) G. Wada, N. Yoshizawa, and Y. Sakamoto, *Bull. Chem. Soc. Jpn.*, **44**, 1018 (1971).

4) R. J. Bruehlman, and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

5) M. S. Sun, and D. G. Brewer, *Can. J. Chem.*, **45**, 2729 (1967).

6) G. Wada, and A. Endo, *Bull. Chem. Soc. Jpn.*, **45**, 1073 (1972).

7) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950); *Acta Chem. Scand.*, **27**, 970 (1973).