

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

Goro WADA* and Aiko KAWAUCHI

Department of Chemistry, Nara Women's University, Nara 630

(Received February 9, 1980)

Synopsis. When pyridine is added to the reaction system of the electron transfer between Fe(II) and Fe(III) in aqueous solution at constant $[\text{HClO}_4]_0$, the apparent rate constant k grows rapidly with $[\text{Py}]_0$ at $[\text{Py}]_0 < [\text{HClO}_4]_0$, while k suddenly diminishes to a small and constant value at $[\text{Py}]_0 > [\text{HClO}_4]_0$. 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 $\text{Fe(II)} + * \text{Fe(III)} \rightarrow \text{Fe(III)} + * \text{Fe(II)}$ 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 $[\text{Py}]_0$ is increased in aqueous solutions of iron(II) and iron(III) at a constant concentration of perchloric acid $[\text{HClO}_4]_0$, the apparent rate constant of the electron transfer reaction k grows rapidly at first, and becomes almost infinitely large until $[\text{Py}]_0$ reaches to values closely equal to $[\text{HClO}_4]_0$. After that, nevertheless, it suddenly diminishes to a constant value as small as $k = 4.5 \pm 1.6 \text{ M}^{-1} \text{ s}^{-1}$ ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) indifferent to both $[\text{Py}]_0$ and $[\text{HClO}_4]_0$. A few cases of the phenomenon are shown in Fig. 1, in which k is plotted against $[\text{Py}]_0$ when $[\text{HClO}_4]_0$ is kept at 0.05, 0.10, and 0.20 M respectively, at $\mu = 0.2 \text{ M}$ and 25°C .

The apparent rate constant k was determined by the method using radioactive tracer Fe-59, as described elsewhere.^{2,3)}

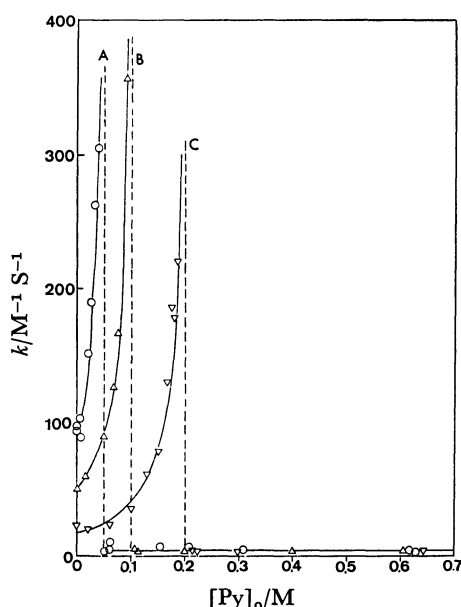


Fig. 1. The variation of k with $[\text{Py}]_0$ at $[\text{HClO}_4]_0 = 0.05 \text{ M}$ (a), 0.10 M (b), and 0.20 M (c).

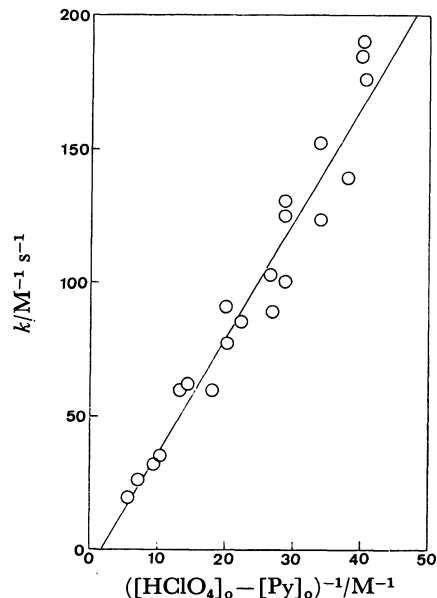


Fig. 2. The linear relationship of k with $([\text{HClO}_4]_0 - [\text{Py}])^{-1}$ at $[\text{Py}]_0 < [\text{HClO}_4]_0$.

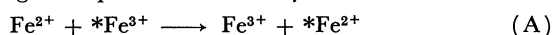
The observed fact that k varies peculiarly with the increase in $[\text{Py}]_0$ at a constant $[\text{HClO}_4]_0$ should be reasonably understood by the following consideration. At the concentration range of $[\text{Py}]_0 < [\text{HClO}_4]_0$, the concentration of hydrogen ion $[\text{H}^+]$ becomes smaller by as much as $[\text{Py}]_0$ than $[\text{HClO}_4]_0$, because pyridine is a considerably strong base with a basicity constant $K_b = 2.8 \times 10^5 \text{ M}^{-1}$ at $\mu = 0.5 \text{ M}$ and 25°C where $K_b = [\text{PyH}^+]/[\text{Py}][\text{H}^+]$.^{4,5)} Therefore, the actual value of the hydrogen ion concentration in the reaction system is approximately equal to $[\text{HClO}_4]_0 - [\text{Py}]_0$. Consequently, when k is plotted against $([\text{HClO}_4]_0 - [\text{Py}])^{-1}$ instead of plotting against $[\text{HClO}_4]_0^{-1}$, a single straight line is obtained as is shown in Fig. 2. This indicates that k can be expressed by the following equation:

$$k = k_0 + \frac{k_H K_H}{[\text{HClO}_4]_0 - [\text{Py}]_0}$$

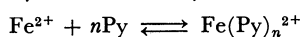
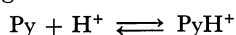
where k_0 and k_H denote the reaction rate constants of the electron transfer $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{2+}/\text{FeOH}^{2+}$ respectively, and K_H the hydrolysis constant of Fe^{3+} , $K_H = [\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}]$.

The slope of the straight line is found to be 4.4 s^{-1} which is fairly close to the value $k_H K_H = 6.0 \text{ s}^{-1}$ observed in aqueous solutions, using the value $K_H = 2.2 \times 10^{-3} \text{ M}^{-1}$.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

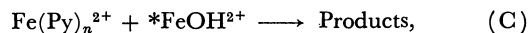
reaction in the present system, the asterisked iron $^*\text{Fe}$ expressing the species labelled by radiotracer.



When $[\text{Py}]_0$ becomes larger than $[\text{HClO}_4]_0$, the apparent rate constant k suddenly diminishes and keeps almost constant value, as shown in Fig. 1. In this concentration range of $[\text{Py}]_0 > [\text{HClO}_4]_0$, a part of pyridine is protonated with H^+ to be pyridinium ion and the rest of pyridine coordinates to Fe^{2+} to be $\text{Fe}(\text{Py})_n^{2+}$.⁷⁾ Since $[\text{H}^+]$ decreases to a considerable extent due to the protonation of pyridine, Fe^{3+} is forced to be hydrolyzed to give FeOH^{2+} . Consequently, each of the equilibria of the following three reactions declines towards the right-hand side.



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



the rate constant of which may be approximately equal to the apparent rate constant observed after $[\text{Py}]_0$ surpasses $[\text{HClO}_4]_0$. Although pyridine may be supposed to coordinate to 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. Bruchlman, 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).