770 *J. Phys. Chem.* **1984**, *88*, 770–772

Kinetics of the Permanganate–Iron(II) Reaction in Aqueous Acid Medium

John R. Sutter* and Kee B. Park

*Department of Chemistry, Howard University, Washington, D.C. 20059 (Received: April 15, 1983;
In Final Form: July 6, 1983)*

The kinetics of the permanganate–iron(II) redox reaction has been studied in aqueous perchloric acid at 20 °C by using stopped-flow techniques. The disappearance of permanganate was followed at 525 nm, with use of excess iron, and consisted of two consecutive first-order decays. A mechanism consistent with the data is $MnO_4^- + Fe^{2+} \rightleftharpoons O_3MnOFe^+$ (k_1, k_{-1}), $O_3MnOFe^+ \rightarrow Mn(VI) + Fe(III)$ (k_2). The rate constants are $k_1 = 9.97 \times 10^4$ M^{-1} s^{-1}, $k_{-1} = 16.4$ s^{-1}, and $k_2 = 12.9$ s^{-1}. No dependence on H^+ or salt was observed in either step.

Introduction

Although the analysis of iron by permanganate titration has been performed for decades, the kinetics of this important reaction have not been reported. In addition, this reaction allows further study of another permanganate system in which a permanganate–manganate, Fe^{2+}–Fe^{3+} transformation is thermodynamically forbidden. The reaction is extremely fast and, surprisingly, involves no proton dependence.

Experimental Section

A stock solution of recrystallized Baker Analyzed Reagent Grade potassium permanganate was standardized by As_2O_3 titration. The extinction coefficient, determined at 525 nm with use of a Beckman DK-2 spectrophotometer, was 2511 ± 13 M^{-1} cm^{-1}. The $Fe(ClO_4)_2$ solutions were made by dissolving weighed lengths of Baker and Adamson iron wire in a known volume of 0.2726 M $HClO_4$. The solution was flushed with N_2, gently warmed until the Fe dissolved completely, cooled, diluted to mark, and stored under N_2 in the cold. Prepared in this fashion, the solutions have been shown to be stable for a month or so. Fe^{2+} is formed quantitatively as shown by permanganate titration. No reduction products of $HClO_4$ were detected. The $[H^+]$ was calculated by using the stoichiometry of the solution process.

Each Fe^{2+} solution was used for one kinetic measurement, done in replicate. No dilution of a stock was used, so that each kinetic result was an independent measurement.

G. Frederick Smith $NaClO_4$ was shown to be free of reducing agents and was used without further purification. When used in kinetic runs, it was added only to the permanganate solution to ensure that, if present, all contaminants would have been oxidized and would not interfere with the subsequent MnO_4^-–Fe^{2+} kinetics. Distilled water was used throughout.

In one experiment, tank oxygen was slowly bubbled through a solution of Fe^{2+}, prepared as before, held at 60 °C until the Fe^{2+} was oxidized to Fe^{3+}. A portion of this solution was used when preparing fresh Fe^{2+} solutions for use in kinetic runs where both reactants Fe^{2+} and product Fe^{3+} were present initially. With 1.04×10^{-5} M MnO_4^-, 0.0261 M $HClO_4$, 5.73×10^{-4} M Fe^{2+}, and 8.63×10^{-4} M Fe^{3+}, no difference in the rate constants could be observed with or without the added Fe^{3+}.

The stoichiometry of the reaction, in part,

$$MnO_4^- + 5Fe^{2+} = 5Fe^{3+} + Mn^{2+}$$

was determined under run conditions, spectrophotometrically and by titration. The ratio of Fe^{2+} oxidized to MnO_4^- reduced was shown to be 4.8–4.9 at concentrations of Fe^{2+} and MnO_4^- in the 10^{-4} range.

The kinetics of the reaction were studied on both a Durrum-Gibson and an Aminco-Morrow stopped-flow apparatus, each thermostated at 20 °C. The photomultiplier signal was digitized by an Aminco DASAR, stored on magnetic tape cassettes, and analyzed by using a PDP/8E computer and nonlinear least-squares-fitting techniques.

TABLE I: Experimental Rate Constants and Their Concentration Dependence

λ_2,[a] s^{-1}	λ_3,[a] s^{-1}	$10^4 \times$ $[Fe^{2+}]$, M	$10^5 \times$ $[MnO_4^-]$, M	$10^2 \times$ $[HClO_4]$,[h] M
35.0		0.781	*b*	0.391
45.8		2.10	*b*	0.367
46.1		2.42	*c*	10.2
49.4		2.33	*c*	4.04
67.8		4.21	*c*	0.597
86.0	2.38	5.73	*c*	2.61
96.7		4.84	*c*	3.99
128	3.51	9.58	*c*	2.53
122		10.0	*d*	3.21
135		9.57	*e*	3.90
157	4.20	14.2	*c*	2.44
181		13.7	*f*	3.82
196	5.70	17.5	*g*	6.46
217	5.61	17.8	*f*	10.6
238	6.65	19.8	*c*	2.33
472	8.15	44.7	*g*	5.92
	9.36	62.2	*g*	5.57

[a] Typical errors for λ_2 are 8–10%, while for λ_3 they are 3–4%. [b] 0.519. [c] 1.04. [d] 10.4. [e] 2.08. [f] 4.14. [g] 3.63. [h] Ionic strength is the same as $HClO_4$ concentration.

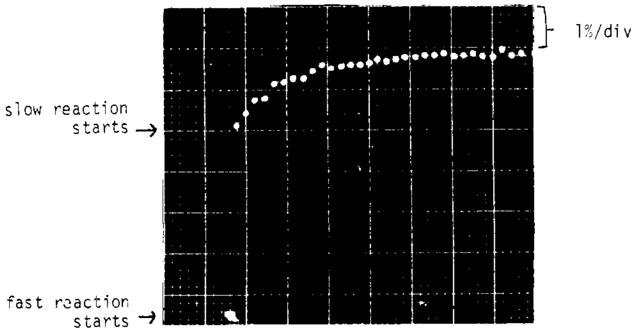
Results and Discussion

The kinetic experiments were performed principally at 525 nm, where the monitor scope traces were distinctly biphasic under certain experimental conditions. At the lower Fe^{2+} excesses (isolation technique), a single kinetic curve was observed, which was analyzed both graphically and by computer as being simple first order in absorbance decrease. As the excess Fe^{2+} was increased, two regions of kinetic interest appeared: the first, the fast first-order decay, followed by a second, much slower, first-order process.

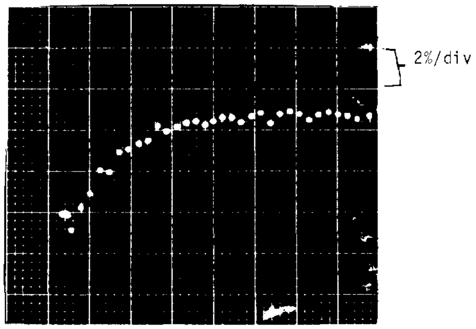
The kinetics were complicated in several ways. From 30% to a half-life or two was lost in instrument dead time because of the speed of the first reaction, whereas the second, slower reaction had a comparatively tiny amplitude. However, as can be seen in Table I, the observed rate constants are quite well separated. The two infinity values could be established simply by changing the dwell time of the A/D converter. This allowed the two steps to be analyzed separately without having to resort to determining the observed rate constants by a difference plot or by a computer fit to a sum of exponentials. A graphical treatment on some selected runs verified this.

The two reactions are shown in Figure 1. The lower trace is the fast reaction. The dots (addresses) are separated horizontally by 1 ms, with 2% change in transmittance/large division vertical. The transmittance increases upward. The upper scan is the second,

0022-3654/84/2088-0770$01.50/0 © 1984 American Chemical Society



slow reaction
50 msec/address



fast reaction
1.0msec/address

Figure 1. Kinetics of the MnO_4^-–Fe^{2+} reaction showing the two consecutive steps ($[MnO_4^-] = 3.63 \times 10^{-5}$ M, $[Fe^{2+}] = 1.65 \times 10^{-3}$ M, $[H^+] = 6.49 \times 10^{-3}$ M; 20 °C).

slower reaction captured at 50 ms/address and a vertical gain of 1%/large division. Observe that in the upper photograph, the reaction(s) begins with the large dot at the lower left of the trace. The gap between this first dot and the kinetics of the slow reaction is the fast reaction, which is not recorded in the first 50 ms of data collection.

Equation 1 shows the simplest two-step mechanism consistent with the data. A discussion of step 2 will follow later.

$$MnO_4^- + Fe^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_3MnOFe^+ \xrightarrow{k_2} Mn(VI) + Fe(III) \xrightarrow{\text{fast}} \tag{1}$$

Since $[Fe^{2+}]$ and $[H^+]$ are held constant, the form becomes simply

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

where the observed rate constants λ_2 and λ_3 are the eigenvalue solutions to a set of coupled differential equations. Because of the isolation technique used, these eigenvalues contain concentration terms. A plot of λ_2 vs. $[Fe^{2+}]$ is linear with intercept for all data points in Table I, whereas λ_3 vs. $[Fe^{2+}]$ exhibits curvature; that is, at higher Fe^{2+} concentrations, λ_3 levels off and exhibits only a small increase with increasing Fe^{2+}.

The coupled differential equations were solved by using Laplace transforms, the solutions, the λ's, being a pair of roots to a quadratic equation. Normally, the individual rate constants could be obtained from plots of $\lambda_2 + \lambda_3$ and $\lambda_2\lambda_3$. In the present case, this information was obtained from the λ's themselves without having to multiply them, thus avoiding the concurrent loss of precision.

The secular equation that results from the mechanism is

$$\begin{vmatrix} \lambda - k_1' & k_{-1} & 0 \\ k_1' & \lambda - k_{-1} - k_2 & 0 \\ 0 & k_2 & \lambda \end{vmatrix} = 0 \qquad k_1' = k_1[Fe^{2+}]$$

which leads to the quadratic expression for λ_2 and λ_3:

$$2\lambda_{2,3} = k_1' + k_2 + k_{-1} \pm [(k_1' + k_2 + k_{-1})^2 - 4k_1'k_2]^{1/2} = p \pm (p^2 - 4b)^{1/2}$$

By expanding the square root term[1] and neglecting $b/p << p$, one arrives at the following equations for λ_2 and λ_3:

$$\lambda_2 = k_1[Fe^{2+}] + k_2 + k_{-1}$$

$$\lambda_3 = \frac{\dfrac{k_1k_2}{k_2 + k_{-1}}[Fe^{2+}]}{1.0 + \dfrac{k_1}{k_2 + k_{-1}}[Fe^{2+}]} = \frac{A_1[Fe^{2+}]}{1.0 + A_2[Fe^{2+}]}$$

A linear and a nonlinear program were used to evaluate the slope and intercept of λ_2 and the two parameters of λ_3.

From λ_2, $k_1 = (9.97 \pm 0.25) \times 10^4$ M^{-1} s^{-1} and $k_2 + k_{-1} = 29.3 \pm 4.0$ s^{-1}. A_1 and A_2 are $(5.4 \pm 0.6) \times 10^3$ and $(4.2 \pm 0.8) \times 10^2$, respectively; their ratio yields $k_2 = 12.9 \pm 2.8$ s^{-1} and hence $k_{-1} = 16.4 \pm 4.9$ s^{-1}. It is apparent that with four experimental parameters and only three rate constants, the system is over determined. Using these values of the k's, one calculates $A_1 = 4.4 \times 10^4$ and $A_2 = 3.4 \times 10^3$. Any other method of handling the data such as plotting $\lambda_2\lambda_3$ vs. $[Fe^{2+}]$ yields similar values for the k's, but when these k's are used to calculate A_1 and A_2, the agreement between experimental and calculated A_1 and A_2 is worse.

As can be seen from the table, neither λ_2 nor λ_3 is H^+ dependent. The presence of an intercept in the λ_2 vs. $[Fe^{2+}]$ must be interpreted as a consecutive mechanism, rather than parallel paths, since MnO_4^- does not decompose spontaneously in acid with a rate constant approaching anywhere near 29 s^{-1}. Further, the $\Delta G°$ for a mechanistic step involving

$$MnO_4^- + Fe^{2+} = MnO_4^{2-} + Fe^{3+} \tag{2}$$

is thermodynamically unfavorable to an extent of +20 kJ/mol. The postulation of an intermediate complex, as we have done before in other permanganate systems,[2] is then both reasonable and in accord with the data. Further, the H^+ dependence that seemed necessary in previous studies is absent. In the present study, an inner-sphere Fe(II)–MnO_4^- complex is possible, whereas in the MnO_4^-–$Fe(phen)_3^{2+}$ reaction[3] the complex is forced outer sphere, and a proton seemed to be required to overcome the thermodynamics of the first step.

Performing the simple Marcus calculation on reaction 2 yields an electron-transfer rate constant of 1.7 M^{-1} s^{-1} for k_2.[4] This value is in reasonable agreement with the experimental value obtained for k_2 and suggests that this is the electron-transfer step. The alternative possibility that step 1, k_1, is actually the electron-transfer step with very bad agreement with the Marcus calculation would have the electron transferred before the complex is formed. In this case step 2 would be the dissociation of the complex or some rearrangement of it. If k_2 does govern the electron-transfer step, this would also indicate that the activation processes for the species involved are indepdendent of each other and that their respective transition states are the same in the exchange reactions as in the cross-reaction.[5]

---

(1) R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970).

(2) S. A. Lawani and J. R. sutter, *J. Phys. Chem.*, **77**, 1547 (1973).

(3) K. W. Hicks and J. R. Sutter, *J. Phys. Chem.*, **75**, 1107 (1971).

(4) An outline of the method and the Fe^{2+}–Fe^{3+} exchange rates may be found in W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer Reactions", Ronald Press, New York, 1966, pp 134, 34. The MnO_4^-–MnO_4^{2-} exchange rate is given by J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957). A value of 10^{11} was taken for Z, the solution collision number.

(5) M. A. Ratner and R. D. Levine, *J. Am. Chem. Soc.*, **102**, 4898 (1980).

TABLE II: Effect of Added Salt on the Rate Constants

λ_2, s^{-1}	λ_3, s^{-1}	$10^4[Fe^{2+}]$, M	$10^5[MnO_4^-]$, M	$[HClO_4]$, M	$[NaClO_4]$, M	μ
86.0 ± 8	2.38 ± 0.08	5.73	1.04	0.0261		0.026
				0.0261	0.078	0.10
				0.0261	0.124	0.150
196.0 ± 17	5.70 ± 0.19	17.5	3.63	0.0646		0.065
				0.0646	0.085	0.150

The actual fate of the complex (step 2) is kinetically uncertain: however, three possibilities warrant discussion.

$$\underset{\text{Mn(VII)–Fe(II)}}{O_3MnOFe^+} \xrightarrow{k_2} MnO_4^{2-} + Fe^{3+} \qquad (3)$$

$$\xrightarrow[H_2O]{k_2} HMnO_4^- + FeOH^{2+} \qquad (4)$$

$$\xrightarrow{k_2} \underset{\text{Mn(VI)–Fe(III)}}{O_3MnOFe^+} \qquad (5)$$

Equations 3 and 4 involve the formation of species, either MnO_4^{2-} [6] or $FeOH^{2+}$,[7] that do not exist in acid solution, yet either reaction should be expected to be facilitated by acid. No effect on the kinetics is seen in step 2 on varying the H^+ concentration. In addition, no indication of a Mn(VI) disproportionation step was observed at 610 nm.[8] Equation 5, an intramolecular electron transfer, is an interesting alternative, which leaves the question of proton involvement unanswered but postpones the need for an answer.

If one attempts to obtain a spectrum of the intermediate by recording the absorbance at the instant-flow stops, a monotonous increase in absorbance is seen from 700 to 350 nm; no special features that could be attributed to Mn(VI) or Mn(V) are observed. However, if one mixes MnO_4^- and Fe^{2+} in a beaker, one sees the rapid disappearance of the purple color, followed by the slower disappearance of a pale yellow-brown solution to the final clear solution. This observation would agree best with eq 5. A few kinetic runs were made at 425 nm. The values of λ_2 and λ_3 were the same as those obtained at 525 nm.

Lastly, as can be seen from Table II, the experimental rate constants, λ_2 and λ_3, appear to have no ionic strength dependence. This results because λ_2 and λ_3 are composite complex functions of the mechanistic rate constants and, in addition, are not concentration independent. As such, the equations for the ionic strength dependence are altered by the inclusion of the concentration term. For example, $\lambda_2 = k_1[Fe^{2+}] + k_{-1} + k_2$ and adopting the Debye–Hückel limiting law $\gamma_i = e^{-AZ_i^2\mu^{1/2}}$ and transition-state formalism $k = (kT/h)K^\ddagger(\gamma_A\gamma_B)/\gamma^\ddagger)$, we seek

$$\frac{\partial \lambda_2}{\partial \mu^{1/2}} = [Fe^{2+}]\frac{\partial k_1}{\partial \mu^{1/2}} + \frac{\partial k_2}{\partial \mu^{1/2}} + \frac{\partial k_{-1}}{\partial \mu^{1/2}}$$

Since the activated complex and the reactant for both steps k_{-1} and k_2 have the same charge, 1+, these terms in λ_2 will not contribute to an ionic strength dependence. Substituting and performing the indicated differentiation, one obtains

$$\frac{\partial \lambda_2}{\partial \mu^{1/2}} = \frac{kT}{h}K_1^\ddagger[Fe^{2+}]A\Delta Z_1^2 e^{A\mu^{1/2}}\Delta Z_1^2$$

where ΔZ_1^2 is the difference in the square of the charge, −4 in this case, of the activated complex and the reactants MnO_4^- and Fe^{2+} in step 1. A related equation would be obtained for $\partial \ln \lambda_2/\partial \mu^{1/2}$. The above equation is similar to the usual ionic strength equation except for the $[Fe^{2+}]$ term. The expected appearance of an ionic strength dependence would, however, be obscured by the presence of this concentration term; that is, the expected slope of a plot of λ_2 vs. $\mu^{1/2}$ would be smaller by a factor of the $[Fe^{2+}]$, about 10^{-3} in this case. A similar, but more complicated, result applies to λ_3:

$$\frac{\partial \lambda_3}{\partial \mu^{1/2}} = \left(\frac{k_2 - \lambda_3}{\lambda_2}\right)\frac{\partial \lambda_2}{\partial \mu^{1/2}}$$

The additional term would render a μ dependence even more difficult to observe, except from observations on the individual rate constants themselves.

Acknowledgment. We acknowledge Tirdad Fattahi, who assisted in the very early experiments. Both K.B.P. and T.F. were undergraduate research participants.

Registry No. Permanganate, 14333-13-2; iron, 7439-89-6.

---

[6] M. W. Lister and Y. Yoshino, *Can. J. Chem.*, **38**, 2341 (1960). $K_a(HMnO_4^-) = 7 \times 10^{-11}$.

[7] "Stability Constants of Metal-Ion Complexes", L. G. Sillén and A. E. Martell, Eds., The Chemical Society, London, 1964, Special Publication 17, p 53.

[8] J. H. Sutter, K. Colquitt, and J. R. Sutter, *Inorg. Chem.*, **13**, 1444 (1974).