TABLE I
X-RAY POWDER DATA

Na_3AlH_6		Na_3AlF_6	
d value	Rel intensity	*d* value	Rel intensity
11.2	w	...	...
8.7	w	...	...
7.8	vw	...	...
4.45	w	4.51	mw
3.83	w	3.88	mw
3.44	mw	3.49	vw
3.03	mw	3.33	vw
2.72	vs	2.75	s
2.58	w	...	...
2.42	m–mw	2.42	w
2.32	vvw	2.33	ms
	mw	2.22	vw
2.13	mw	2.15	m–mw
...	...	2.18	mw
1.93	s	1.94	vs
1.865	mw	1.89	w
1.72	mw	1.72	mw
1.68	mw	1.68	mw–w
1.58	s–ms	1.60	m
1.555	s–ms	1.57	ms
...	...	1.49	w–vw
1.46	vw	1.454	vw
1.435	vw	1.425	vw
...	...	1.388	vvw
1.362	m	1.375	w
1.340	w	1.350	w
1.220	m	1.229	w

[a] w, weak; v, very; m, medium; s, strong.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MARSHALL UNIVERSITY, HUNTINGTON, WEST VIRGINIA

Kinetics of Exchange of Iron(II) and Iron(III) 8-Quinolinol Complexes[1,2]

BY M. R. CHAKRABARTY, J. F. STEPHENS, AND E. S. HANRAHAN

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The electron exchange reactions between Fe(II) and Fe(III) have received considerable attention from many investigators.[3] Although a considerable amount of reliable data is available for the Fe(II)–Fe(III) system where the latter is complexed with various 1,10-phenanthrolines,[4,5] reactions involving other complicated organic ligands coordinated to Fe(III) have not been extensively studied. The stability constants of the 1:1 and 1:2 Fe(III) complexes of 8-quinolinol have been measured at 25° and an ionic strength of 0.5 *M*.[6] It was, therefore, decided to study the influence of 8-quinolinol as a ligand on the rate of the electron exchange between Fe(II) and Fe(III).

Experimental Section

Reagents.—Fe^{59} was obtained from the Abbott Laboratories, and Fe^{55} was supplied by the Nuclear Science and Engineering Co. Both of the tracer solutions were received as ferric chloride dissolved in hydrochloric acid and were converted to ferric perchlorate by evaporating to dryness with perchloric acid. Hydrogen peroxide (30%) was added to the tracer solutions before evaporation in order to convert any Fe(II) to Fe(III). None of the tracer solutions showed any positive tests of the probable impurities, such as Co and Mn. Inactive ferric perchlorate and ferrous perchlorate were obtained from the G. F. Smith Chemical Co. and were recrystallized twice from 8 *F* perchloric acid.

Iron(II) was determined by titrating the original solution with the standard ceric sulfate solution. Iron(III) in the stock solutions was determined by reducing it in a Jones reductor and titrating it with a standard ceric sulfate solution. The analytical concentrations of perchloric acid in Fe(II) and Fe(III) stock solutions were determined by passing aliquots of the iron solutions through a column of Dowex 50 cation-exchange resin and titrating the resulting metal ion free acid solutions with a standard sodium hydroxide solution. Knowing the concentrations of Fe(III) and Fe(II) in these solutions, the concentrations of perchloric acid were calculated.

Sodium perchlorate solutions were prepared by neutralizing Baker and Adamson reagent grade sodium carbonate with Baker Analyzed Reagent perchloric acid.

8-Quinolinol (mp 73–74°) was supplied by Eastman Organic Chemicals Co.

All of the solutions were made by using freshly boiled, double-distilled, deionized water and were kept under a nitrogen atmosphere.

The hydrogen ion concentrations were measured by using a Leeds and Northrup No. 7405 pH meter, which was standardized against a potassium acid phthalate buffer. The meter was then calibrated by titrating a 0.5 *M* sodium perchlorate solution with a standard perchloric acid solution (ionic strength 0.5 *M*).

Electron-Exchange Measurements.—An exchange apparatus similar to that described by Sheppard and Wahl[7] was used. The electronic timers employed in this study have been described in a previous paper.[8] The reaction mixtures were quenched with bipyridine obtained from Matheson Coleman and Bell Chemical Co. Iron(III) was precipitated from the quenched solutions by adding a saturated solution of 8-quinolinol. The specific activity of the precipitate was determined by using a Baird Atomic X-ray counter tube for Fe^{55} and a Picker scintillation counter for Fe^{59}. A Picker solid-state scaler was used in all the measurements.

Results and Discussion

The rate, *R*, of the electron-exchange reaction was calculated using the McKay equation. Figure 1 shows representative plots of $\log\,[(y_0 - y_\infty)/y - y_\infty)]$ *vs.* t, where y_0, y, and y_∞ are the specific activities of the initially active species at zero time, at time t, and at infinite time, respectively. Using the following relationship, the apparent second-order rate constant k was calculated

$$R = kab \tag{1}$$

where a and b are the analytical concentrations of ferrous and ferric iron, respectively.

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(1) Presented at the Southeast–Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965.

(2) Taken in part from the M.S. Thesis of J. F. Stephens, Marshall University, Huntington, W. Va., 1965.

(3) For a review of this topic see: (a) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962); (b) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961); (c) B. J. Zwolinski, R. J. Marcus, and H. Eyring, *Chem. Rev.*, **55**, 157 (1955); (d) H. Strehlow, *Ann. Rev. Phys. Chem.*, **16**, 167 (1965).

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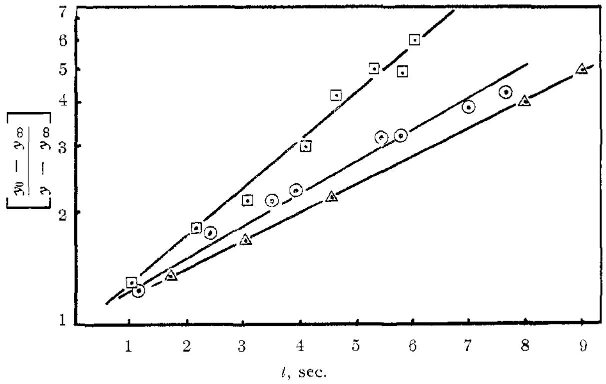

Figure 1.—Plot of log $[(y_0 - y_\infty)/(y - y_\infty)]$ *vs.* time in seconds. Ionic strength 0.50 M, $[Fe^{2+}] = 5.00 \times 10^{-4}\ M$, $[Fe^{3+}] = 5.00 \times 10^{-4}\ F$: ⊡, $[H^+] = 0.025\ M$, $[L^-] = 1.56 \times 10^{-14}\ M$; ⊙, $[H^+] = 0.500\ M$, $[L^-] = 0$; ◬, $[H^+] = 0.029\ M$, $[L^-] = 0$.

At high hydrogen ion concentration (pH <2) and low concentration of Fe^{3+}, the species $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$ may be neglected. Under the experimental conditions, the calculated concentration of unprotonated ligand species $[L^-]$ was $\simeq 10^{-14}\ M$, which corresponds to the value of $[FeL^{2+}]/[FeL_2^+] = \beta_1[L^-]/\beta_2[L^-]^2 \simeq 1/(5 \times 10^{-3})$. Hence, only the following electron-exchange reactions need be considered

$$Fe^{2+} + {}^*Fe^{3+} \xrightarrow{k_1} {}^*Fe^{2+} + Fe^{3+} \qquad (2)$$

$$Fe^{2+} + {}^*FeOH^{2+} \xrightarrow{k_2} {}^*Fe^{2+} + FeOH^{2+} \qquad (3)$$

$$Fe^{2+} + {}^*FeL^{2+} \xrightarrow{k_3} {}^*Fe^{2+} + FeL^{2+} \qquad (4)$$

where L^- represents an 8-quinolinolate ion. The over-all rate of the reaction may then be expressed

$$R = k_1[Fe^{2+}][Fe^{3+}] + k_2[Fe^{2+}][FeOH^{2+}] + k_3[Fe^{2+}][FeL^{2+}] \qquad (5)$$

The above equation may be rewritten

$$R = k_1[Fe^{2+}][Fe^{3-}] + k_2[Fe^{2+}][Fe^{3+}]\frac{K_h}{[H^+]} + k_3[Fe^{2+}][Fe^{3+}]\beta_1[L^-] = ab\left[\frac{k_1 + k_2K_h[H^+]^{-1} + k_3\beta_1[L^-]}{1 + K_h[H^+]^{-1} + \beta_1[L^-]}\right] \qquad (6)$$

where $K_h = 1.82 \times 10^{-3}\ M$,[9] and β, the over-all formation constant of the complex ML^{2+}, is $2.76 \times 10^{13}\ M^{-1}$.[6]

The concentration of unprotonated ligand species L^- may be calculated from

$$H_T = L_T + C \qquad (7)$$

$$H_T = 2[H_2L]^+ + [HL] + [H^+]$$

where H_T is the analytical concentration of titratable hydrogen, L_T the analytical concentration of total ligand, and C the concentration of $HClO_4$ added. Equation 7 may be rewritten in terms of the acid dissociation constants

$$H_T = [L^-]\left\{\frac{2[H^+]^2}{K^H{}_1K^H{}_2} + \frac{[H^+]}{K^H{}_2}\right\} + [H^+] \qquad (8)$$

where $K^H{}_1$ and $K^H{}_2$ are the stoichiometric dissociation constants of 8-quinolinol. The apparent rate constant k may be recognized as the factor in brackets in eq 6. In order to use 6 for the calculation of k_1, k_2, and k_3, it was necessary to carry out exchange reactions at various pH values with and without the ligand species. In the absence of ligand, $[FeL^{2+}] = 0$, and at moderately high pH ($\cong 2$) the concentration of $FeOH^{2+}$ is relatively high. Previous work[10] has shown that $k_2 \gg k_1$; under these conditions $R = k_2[Fe^{2+}][Fe^{3+}] \cdot K_h[H^+]^{-1}$, and k_2 can be evaluated. Once k_2 is evaluated, k_1 may be calculated from the data obtained at a higher hydrogen ion concentration, correcting for the small contribution due to the presence of $FeOH^{2+}$. The values of k_1 and k_2 were obtained at several hydrogen ion concentrations ranging from 0.500 to 0.02 M. The results of this investigation are given in Table I. The values of these two rate constants agree reasonably well with those reported by Fukushima and Reynolds.[11]

TABLE I

ANALYTICAL AND KINETIC DATA ON IRON(II)–IRON(III) EXCHANGE REACTIONS AT 25° ($\mu = 0.50\ M$)

10^4a, M	10^4b, M	$[H^+]$, M	10^3L_T, M	$10^{14}[L^-]$, M	$t_{1/2}$, sec	k, M^{-1} sec^{-1}
4.00	5.00	0.500	0.00	0.00	35.5	19.5
5.00	5.00	0.0295	0.00	0.00	3.77	181.4
4.00	5.00	0.355	0.00	0.00	5.44	151.1
4.00	5.00	0.0201	4.02	2.32	2.31	334.0
5.00	5.00	0.0251	4.02	1.51	2.56	276.0

$k_1 = 8.35\ M^{-1}\ sec^{-1}$, $k_2 = 3020\ M^{-1}\ sec^{-1}$, $k_3 = 450\ M^{-1}\ sec^{-1}$

The rate constant k_3 was obtained by similar measurements in the presence of ligand, using the values of k_1 and k_2 to solve eq 6.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN

On the Rapid Electron Exchange between Ruthenate and Perruthenate Ions in Basic Solutions

BY E. V. LUOMA AND C. H. BRUBAKER, JR.

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Sheppard and Wahl[1] and others[2,3] have studied the rate of electron exchange between manganate and permanganate ions in aqueous solutions, and the present work was undertaken in an effort to extend the information available on outer-sphere electron-transfer processes and to attempt to test further the theory of

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