Kinetics of the Aqueous Manganese(III)+Iron(II) Reaction by Platinum-Electrode Polarography

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The rate equation $-d[Fe^{II}]/dt = k_{obs}[Fe^{II}][Mn^{III}]$ was established by measurements of the iron(II) diffusion current. For 0·3-15°C in 0·54-3 M $HClO_4$ the variation of k_{obs} was consistent with the relation $k_{obs} = (k_0[H^+] + k_1 K_h)/([H^+] + K_h)$, where K_h is the manganese(III) hydrolysis constant. Values of k_0 are just less than k_1 as in the comparable oxidation of vanadium(IV). It is concluded from further comparisons of rates that the activated complexes are outer-sphere.

Kinetic studies of oxidations by manganese(III) [1] include two brief reports on the reaction with iron(II),[2,3] each dealing only sketchily with the acidity dependence of rate. Here a wider study again reveals the extensive hydrolysis of manganese(III), and allows comparisons in detail with the oxidation of vanadium(IV).[1] Rates were measured from the change with time of the diffusion current due to iron(II) at a rotating platinum electrode immersed in the reaction solution.

EXPERIMENTAL

Preparations of reactants have been described.[1] The polarographic apparatus was that [4] used for the $Fe^{II} + V^V$ reaction; there the results agreed satisfactorily with independent e.m.f.[5] and spectrophotometric [6] measurements. The reactions were conducted in aqueous sodium+hydrogen perchlorate solutions of total concentration 3·04 M except where otherwise stated. Reactions were initiated by addition of manganese(III) to iron(II) solutions. Half-lives of 10-30 sec were found at tractable reactant concentrations ($\sim 10^{-5}$ M); a recorder for tracing the diffusion current was necessary. The possibility of catalysis by the platinum electrode was tested for by increasing the electrode area threefold, addition of 20 cm² of Pt foil, and change of the applied potential from 0·8 to 1·0 V.

For a second-order reaction at constant $[H^+]$, $-d[Fe^{II}]/dt = k_{obs}[Fe^{II}][Mn^{III}] = k_{obs}(a-x)(b-x)$. Taking the observed diffusion current $(i_t - i_\infty)$ as being proportional to $[Fe^{II}]$, with i_0, i_t and i_∞ representing the currents observed initially, at time t, and after completion of reaction respectively, we have

$a = g(i_0 - i_\infty)$ where g is the proportionality factor,

$a - x = g(i_t - i_\infty) = a(i_t - i_\infty)/(i_0 - i_\infty)$,

and $\qquad b - x = (a - x) + (b - a)$.

Hence the integrated equation

$$k_{obs}t = (b-a)^{-1} \ln\left(\frac{b(i_0 - i_\infty) - a(i_0 - i_t)}{a(i_t - i_\infty)}\right) + \text{constant}.$$

With $[Fe^{II}] \ll [Mn^{III}]$, $k_{obs}tb = -\ln(i_t - i_\infty) + $ second constant. Values of k_{obs} were obtained from plots of the r.h.s. function against t.

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RESULTS

Linearity of graphs of the second-order function (fig. 1A) and of the first-order function (fig. 1B) indicates the bimolecularity of the reaction. The reproducibility for second-order conditions over a range of reactant concentrations is shown in table 1 (± 3-4 %); first-order measurements were rejected for quantitative purposes
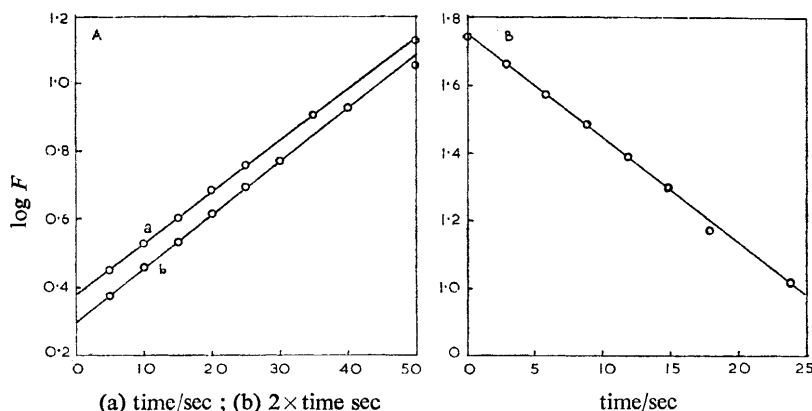

(a) time/sec ; (b) $2 \times$ time sec   time/sec

FIG. 1.—A: Typical second-order plots. For these, F is $\{b(i_0-i_\infty)-a(i_0-i_t)\}/a(i_t-i_\infty)$. (a) 3·04 M H$^+$, 0·3°C; (b) 2·04 M H$^+$, 15°C. B: first-order plot. Here F is (i_t-i_∞). 1·64 M H$^+$, $-13\cdot4$°C.

TABLE 1.—RATE CONSTANTS AT 0·3°C IN 3·04 M HClO$_4$ SOLUTION

Solutions with 2×10^{-3} M Mn^{II}:

10^5[Fe^{II}] mole $l.^{-1}$	10^5[Mn^{III}] mole $l.^{-1}$	$10^{-5}k_{obs}$ $l.$ mole^{-1} min^{-1}
0·62	6·4	1·05
0·73	1·56	1·07
1·28	1·56	0·98
1·41	3·20	1·14
1·35	6·4	1·07
2·79	3·20	1·10
		mean 1·07 $\pm$0·04

Solutions with (1·32 to 1·44)$\times 10^{-5}$ M Fe^{II} and $3\cdot2\times10^{-5}$ M Mn^{III}:

	$10^{-5}k_{obs}$ $l.$ mole^{-1} min^{-1}
6·4$\times 10^{-3}$ M Fe^{III} added initially	1·04
2·1$\times 10^{-2}$ M Mn^{II} added initially	1·12
electrode area increased threefold	1·10
potential increased to 1·0 V	1·05
20 cm^2 Pt foil inserted	1·09
	mean 1·08 $\pm$0·03

because of errors arising from their short duration and the smallness of current at the necessarily low [Fe^{II}], $\lesssim 10^{-6}$ M. No heterogeneous catalysis was observed, and the absence of any effect of high initial concentrations of product is clear. Variation of [ClO$_4^-$] at constant formal ionic strength, by substitution of Zn and Al for Na as medium cation, left k_{obs} unaltered (table 2), suggesting that ClO$_4^-$ is not involved. The change in rate with ionic strength is in the expected direction.

Rate constants k_{obs} (most the mean of two measurements) were shown to decrease with increasing $[HClO_4]$ at constant formal ionic strength (table 3).

TABLE 2.—VARIATION OF k_{obs} WITH $[ClO_4^-]$ AND IONIC STRENGTH I IN 1.00 M $HClO_4$ AT $10.0\,°C$

$(0.93$ to $1.11) \times 10^{-5}$ M Fe^{II}; $(2.88$ to $2.96) \times 10^{-5}$ M Mn^{III}; 2×10^{-3} M Mn^{II}

added salt	$[ClO_4^-]$ mole $l.^{-1}$	I mole $l.^{-1}$	$10^{-5}k_{obs}$ $l.$ mole^{-1} min^{-1}
$Al(ClO_4)_3$	2.00	3.00	2.99
$Zn(ClO_4)_2$	2.33	3.00	2.98
$NaClO_4$	3.00	3.00	2.97
$NaClO_4$	2.00	2.00	2.74
$NaClO_4$	1.50	1.50	2.56
$NaClO_4$	1.00	1.00	2.41

TABLE 3.—VARIATION OF k_{obs} WITH $[H^+]$ AND TEMPERATURE

$(0.76$ to $1.50) \times 10^{-5}$ M Fe^{II}; $(2.45$ to $4.20) \times 10^{-5}$ M Mn^{III}; 2×10^{-3} M Mn^{II}; ionic strength 3.04 M with $NaClO_4$

$[HClO_4]$ mole $l.^{-1}$	$10^{-5}(k_{obs}/l.$ mole^{-1} min^{-1})			
	$0.3°C$	$5.0°C$	$10.0°C$	$15.0°C$
3.04	1.06	1.53	2.38	3.26
2.04	1.14	1.68	2.52	3.58
1.54	1.24	1.79	2.72	3.82
1.04	1.40	2.01	2.99	4.22
0.64	1.59	2.30	3.46	5.10
0.54	1.65	2.40	3.74	5.20

DISCUSSION

The k_{obs} values are of the same order of magnitude as found for the $Ce^{IV} + Fe^{II}$ reaction.[7]   The variation of k_{obs} with $[H^+]$ closely resembles that in the $Mn^{III} + V^{IV}$ reaction,[1] being most simply interpreted as indicating the following steps.

$$Mn^{3+} + Fe^{2+} \xrightarrow{k_0} Mn^{2+} + Fe^{3+}$$

$$Mn^{3+} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} MnOH^{2+} + H^+ \qquad \text{(rapid)}$$

$$MnOH^{2+} + Fe^{2+} \xrightarrow{k_1} Mn^{2+} + Fe^{3+} + OH^-.$$
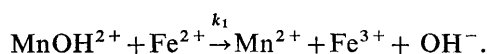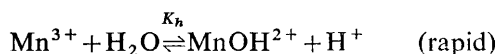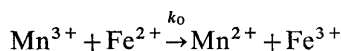
Hence

$$k_{obs}([H^+] + K_h) = k_0[H^+] + k_1 K_h.$$

Though the precision of the present results greatly exceeds that for the $Mn^{III} + V^{IV}$ reaction, again it is not good enough to establish all three parameters k_0, k_1 and K_h from the measurements.   Thus, as before,[1] we assume the value $K_h = 0.88$ M at $25°C$ with $\Delta H_h = 4.8$ kcal mole^{-1}, measured at ionic strength 4,[8] and fit corresponding values of k_0 and k_1 from a plot of the l.h.s. of the preceding equation against $[H^+]$ (fig. 2).   As with the V^{IV} data, an equally good fit is got assuming $K_h = 0.63$ M at $12.5°$ and $\Delta H_h = 10$ kcal mole^{-1}, only the k_1 values being appreciably altered thereby.   Both sets of hydrolysis parameters give extrapolated overall rate constants agreeing to within $\sim 17\,\%$ of Sutin's k_{obs} values from spectrophotometric stopped-flow measurements at $25°$, which is reasonable.   The values of k_0 and k_1 in table 4

give the activation parameters of table 5, where a comparison is made with the corresponding quantities for V^{IV} as reductant. (The Fe^{II} values differ slightly from the original [2] because of the present wider and better-analysed $[H^+]$ variation.)
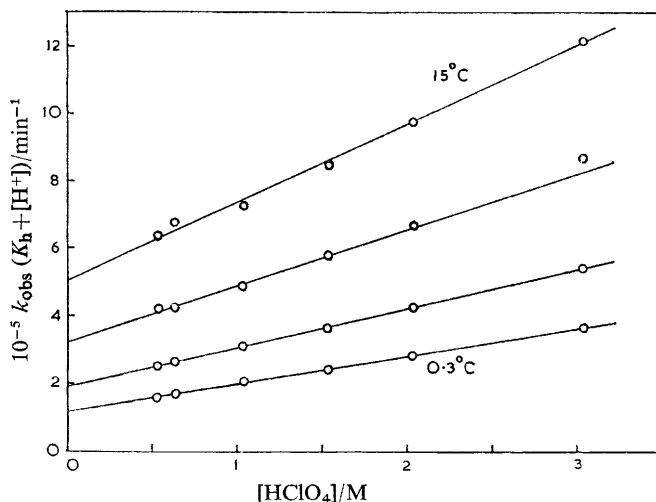

FIG. 2.—$[HClO_4]$ dependence of k_{obs} with assumed K_h (10°C) = 0·59 M and ΔH_h = 4·8 kcal mole^{-1}.

TABLE 4.—VARIATION OF k_0 AND k_1 (IN l mole^{-1} min^{-1}) WITH TEMP. AND WITH CHOICE OF K_h

temp. °C	K_h (10°C) = 0·59 M, ΔH_h = 4·8 kcal mole^{-1}		K_h (10°C) = 0·55 M, ΔH_h = 10 kcal mole^{-1}	
	$10^{-5}k_0$	$10^{-5}k_1$	$10^{-5}k_0$	$10^{-5}k_1$
0·3	0·82	2·67	0·84	3·21
5·0	1·17	3·72	1·17	4·17
10·0	1·65	5·40	1·67	5·65
15·0	2·33	7·41	2·24	7·23

TABLE 5.—ACTIVATION PARAMETERS FOR OXIDATIONS BY MANGANESE(III)

	assumed ΔH_h kcal mole^{-1}	ΔH_0^* kcal mole^{-1}	ΔS_0^* cal mole^{-1} deg.$^{-1}$	ΔH_1^* kcal mole^{-1}	ΔS_1^* cal mole^{-1} deg.$^{-1}$
Fe^{II} reaction	4·8	10·6	−5·2	10·3	−4·2
V^{IV} reaction	4·8	11·1	−11·5	9·6	−13·9
Fe^{II} reaction	10	10·0	−7·5	8·3	−11·0
V^{IV} reaction	10	11·2	−11·5	6·4	−24·9

(For Fe^{II} reactions, fitting errors in ΔH^* are $\pm 0·2$ kcal mole^{-1}, and in ΔS^* $\pm 0·7$ cal mole^{-1} deg^{-1}.)

From a comparison of rate constants some conclusions can be reached concerning the mode of electron transfer. As with $Mn^{III} + V^{IV}$, here the k_1 values are just $> k_0$, and the activation parameters for the k_0 and k_1 paths are related to each other in a similar manner for both systems. Furthermore,[1] the rates of the reactions $Fe^{II} +$ oxidant show a remarkable parallelism with those of $V^{IV} +$ oxidant for the oxidants (in order of increasing rate) $Tl^{III} < Fe^{III} < Co^{III} < Mn^{III} < V^V$; the reactions of vanadium(IV) are constantly slower. The two reductants have some similarities, but greater differences. Besides being bipositive, both, in a simplified view of the electron arrangements, have one electron in excess of a spherically symmetrical distribution. However, the numbers of $3d$ electrons do differ, the molecular dissymmetry

of VO^{2+} is marked, and its electric dipole must be appreciable. The close juxtaposition involved in bridged mechanisms would involve specific oxidant-reductant interactions which are unlikely to allow the parallelism of rate actually observed, and we now believe the activated complexes to be of the outer-sphere type. While the relative rapidity of the iron(II) reactions might arise from the more negative ΔG° values, a greater radial extension of the iron(II) transfer orbital, achieving sufficient overlap at wider transition-state separations, could ensue from the lower core charge (as indicated by the lower oxidation state).

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