

## The Iron(II)–Chromium(VI) Reaction: An Additional Pathway First Order in Iron(II)

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The iron(II)–chromium(VI) reaction has been studied by platinum-electrode polarography at low (micromolar) iron(II) concentrations. Here an additional term first order in iron(II) appears in the rate equation, which is found to be  $-d[\text{Fe}^{\text{II}}]/dt = k_{\text{IH}}[\text{H}^+][\text{HCrO}_4^-][\text{Fe}^{\text{II}}] + k_{2\text{H}}[\text{H}^+]^3[\text{HCrO}_4^-][\text{Fe}^{\text{II}}]^2/[\text{Fe}^{3+}]$ , with  $k_{\text{IH}} = 234 \text{ l}^2 \text{ mol}^{-4} \text{ s}^{-1}$  and  $10^{-8}k_{2\text{H}} = 6.92 \text{ l}^4 \text{ mol}^{-4} \text{ s}^{-1}$  at 20 °C and ionic strength 1.00 mol l<sup>-1</sup> in sodium perchlorate medium with 0.025–0.065M perchloric acid.

THE iron(II)–chromium(VI) reaction, studied titrimetrically<sup>1,2</sup> and spectrophotometrically,<sup>2</sup> has hitherto been considered<sup>1–3</sup> to proceed exclusively by a mechanism second order in iron(II), inverse first order in iron(III), and between first and second order in chromium(VI). Espenson and King<sup>2</sup> find that,

$$-\frac{d[\text{Fe}^{\text{II}}]}{dt} = \frac{[\text{H}^+]^3[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]} (k'[\text{HCrO}_4^-] + k''[\text{HCrO}_4^-]^2) \quad (1)$$

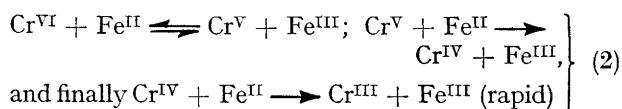
where the  $k''$  term presumably indicates reaction of

<sup>1</sup> C. Benson, *J. Phys. Chem.*, 1903, **7**, 1 and 356.

<sup>2</sup> J. Espenson and E. L. King, *J. Amer. Chem. Soc.*, 1963, **85**, 3328.

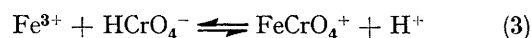
<sup>3</sup> F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419.

dimeric chromium(VI), and the remainder the following sequence:



and finally  $\text{Cr}^{\text{IV}} + \text{Fe}^{\text{II}} \longrightarrow \text{Cr}^{\text{III}} + \text{Fe}^{\text{III}}$  (rapid)

The additional complexing equilibrium [equation (3)]



with an equilibrium constant  $K_3$  of 1.4, had to be recognised in calculating reactant concentrations. Their work at ionic strength 0.086M and 0° was performed with  $>10^{-5}\text{M Fe}^{\text{II}}$ ,  $>10^{-5}\text{M Cr}^{\text{VI}}$ , and *ca.*  $10^{-3}\text{M Fe}^{\text{III}}$ , and

the predominance of the second-order iron(II) term is a consequence of the relatively high iron(II) concentrations taken. We have now been able to extend the usable [iron(II)] downwards, by employing the rotating platinum-electrode technique successfully used for the  $\text{Fe}^{\text{II}}\text{-V}^{\text{V}}$  and  $\text{Fe}^{\text{II}}\text{-Mn}^{\text{III}}$  reactions,<sup>4,5</sup> where, for half-lives of seconds the iron(II) diffusion current (proportional to [iron(II)]) can be traced on a recorder. At these lower iron(II) concentrations a term, first order in both iron(II) and chromium(vi), becomes important. We originally interpreted this chromium(vi) species as being  $\text{HCrO}_4^-$  but finally it will be shown to be probably  $\text{H}_2\text{CrO}_4$ .

*The Iron(II) First-order Path.*—A typical current-time recording is shown in Figure 1. With initial iron(II) at

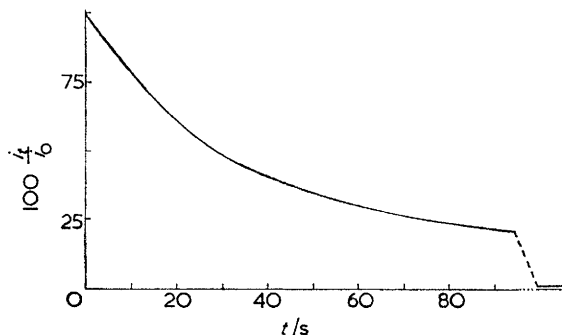


FIGURE 1 Typical recording of current  $i$  against time  $t$ :  $3.78 \times 10^{-6}\text{M Fe}^{\text{II}}$ ,  $1.0 \times 10^{-3}\text{M Fe}^{\text{III}}$ ,  $1.02 \times 10^{-3}\text{M Cr}^{\text{VI}}$ ,  $0.026\text{M H}^+$

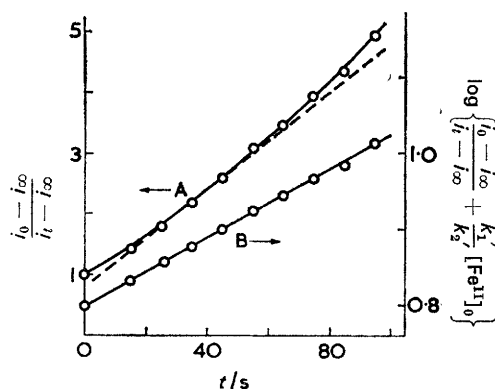


FIGURE 2 A: Unsatisfactory second-order plot (left ordinate). B: First- and second-order rate law (right ordinate) (readings from Figure 1)

$3.78 \times 10^{-6}\text{ mol l}^{-1}$  and all other reactants in excess, the simple second-order plot (Figure 2A) shows some curvature. Here  $i_0$  is the initial diffusion current,  $i_t$  that at time  $t$ , and  $i_\infty$  the infinite-time ('residual') current, so that integration of the rate law  $-d[\text{Fe}^{\text{II}}]/dt = k[\text{Fe}^{\text{II}}]$ , with  $[\text{Fe}^{\text{II}}] \propto (i_t - i_\infty)$ , gives

$$(i_0 - i_\infty)/(i_t - i_\infty) - 1 = k[\text{Fe}^{\text{II}}]_0 t \quad (3)$$

While linearity—or nonlinearity—is not a conclusive mechanistic test, the rate constants from such plots

<sup>4</sup> D. R. Rosseinsky and M. J. Nicol, *Electrochim. Acta*, 1966, **11**, 1069.

should indeed be constant, but the second-order values from  $(i_0 - i_\infty)/(i_t - i_\infty)$  vs.  $t$  are shown in Table 1 to vary

TABLE 1  
Variation of second-order rate constant with  $[\text{Fe}^{\text{II}}]_0$   
( $0.026\text{M H}^+$ ;  $1.0 \times 10^{-3}\text{M Fe}^{\text{III}}$ ;  $1.02 \times 10^{-3}\text{M Cr}^{\text{VI}}$ )

$10^6[\text{Fe}^{\text{II}}]_0$ *	$10^{-4}k/l\text{ mol}^{-1}\text{ s}^{-1}$
3.78	1.10
5.95	0.96
11.10	0.84
17.85	0.77
25.75	0.74

\* Square brackets indicate concentration in  $\text{mol l}^{-1} \equiv \text{M}$ .

with  $[\text{Fe}^{\text{II}}]_0$ . This obvious trend indicates an additional necessarily lower-order term in  $[\text{Fe}^{\text{II}}]$ . Hence, most simply,

$$d[\text{Fe}^{\text{II}}]/dt = k_1'[\text{Fe}^{\text{II}}] + k_2'[\text{Fe}^{\text{II}}]^2 \quad (4)$$

which yields on integration,

$$\ln \left( \frac{i_0 - i_\infty}{i_t - i_\infty} + \frac{k_2'}{k_1'} [\text{Fe}^{\text{II}}]_0 \right) - \ln \left( 1 + \frac{k_2'}{k_1'} [\text{Fe}^{\text{II}}]_0 \right) = k_1' t \quad (5)$$

The values of  $k_1'$  and  $k_2'$  were obtained from a least-squares calculation on a computer. Equally satisfactory is a manual calculation involving firstly the choice of that ratio  $k_2'[\text{Fe}^{\text{II}}]_0/k_1' = R$  (say) which gives the best linearity, and secondly reading  $k_1'$  from the slope, of  $\log \{(i_0 - i_\infty)/(i_t - i_\infty) + R\}$  vs.  $t$ . Figure 2B shows a typical plot of this function demonstrating the satisfactory linearity. With over a hundred-fold variation of  $[\text{Fe}^{\text{II}}]$ , values of  $k_1'$  and  $k_2'$  (Table 2) are reasonably

TABLE 2  
First- and second-order rate constants  
( $0.025\text{M H}^+$ ;  $1.02 \times 10^{-3}\text{M Cr}^{\text{VI}}$ ;  $1.00 \times 10^{-3}\text{M Fe}^{\text{III}}$ )

$10^6[\text{Fe}^{\text{II}}]_0$	$10^2 k_1'/\text{s}^{-1}$	$10^{-4} k_2'/l\text{ mol}^{-1}\text{ s}^{-1}$
3.78	0.52	0.73
5.95	0.46	0.68
5.95	0.44	0.80
11.10	0.52	0.70
17.85	0.39	0.75
25.8	*	0.74
Average: $0.47 \pm 0.04$		$0.73 \pm 0.03$

$10^6[\text{Fe}^{\text{II}}]_0$	$10^2 k_1'/\text{s}^{-1}$	$10^{-4} k_2'/l\text{ mol}^{-1}\text{ s}^{-1}$
0.41	0.55	1.99
1.28	0.77	2.30
2.72	0.71	2.98
2.72	0.85	2.59
4.16	0.64	2.65
5.60	1.09	2.70
9.51	(1.24)	(1.88)
20.7	0.78	1.96
31.8	*	1.90
Average: $0.77 \pm 0.12$		$2.4 \pm 0.3$

\* No value quoted because  $k_1'$  path accounts here for only ca. 10% of observed rate.

constant, with fixed concentrations of other reactants. The scatter, attributable to random errors in the micromolar concentration measurements, appears to be no worse than in Espenson and King's results.<sup>2</sup>

<sup>5</sup> D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, 1968, **64**, 2410.

*Variation of Rate with Iron(III) and Chromium(VI) Concentrations.*—In Table 3A are given values of  $k_1'$  and  $k_2'$  when  $[\text{Fe}^{\text{III}}]$  and  $[\text{Cr}^{\text{VI}}]$  are varied. If we accept the first term on the right of equation (1), *i.e.* that  $k_2' = k_2[\text{HCrO}_4^-]/[\text{Fe}^{2+}]^2/[\text{Fe}^{3+}]$ , then values for  $k_2$  so obtained

TABLE 3

(A) Experimental and (B) derived rate constants  
(0.026M  $\text{H}^+$ ;  $5.6\text{--}7.1 \times 10^{-6}\text{M}$   $\text{Fe}^{\text{II}}$ )

				(A) Experimental	(B) Derived		
$10^3$ [Cr <sup>VI</sup> ]	$10^3$ [HCrO <sub>4</sub> <sup>-</sup> ]	$10^3$ [Fe <sup>III</sup> ]	$10^3$ [Fe <sup>3+</sup> ]	$10^2 k_1'/$ s <sup>-1</sup>	$10^{-4} k_2'/$ l mol <sup>-1</sup> s <sup>-1</sup>	$k_1/$ l mol <sup>-1</sup> s <sup>-1</sup>	$10^{-4} k_2/$ l mol <sup>-1</sup> s <sup>-1</sup>
0.50	0.446	1.09	1.07	0.13	0.56	3.0	1.37
0.51	0.45	1.00	0.99	0.30	0.435	6.7	0.96
1.00	0.83	1.09	1.06	0.26	1.04	3.1	1.33
1.02	0.86	0.26	0.254	0.66	3.60	7.7	1.06
1.02	0.86	0.40	0.39	0.72	2.04	8.5	0.93
1.02	0.86	0.49	0.48	0.25	1.94	2.9	1.06
1.02	0.85	0.64	0.625	0.30	1.12	3.5	0.83
1.02	0.85	0.74	0.72	0.46	1.18	5.4	1.01
1.02	0.85	1.00	0.98	0.27	0.74	3.0	0.85
1.02	0.85	1.00	0.98	0.67	0.88	7.8	1.02
1.53	1.21	1.00	0.97	0.71	1.43	5.9	1.15
2.04	1.52	1.00	0.96	0.74	2.11	4.9	1.33
2.51	1.70	2.17	2.04	0.58	1.10	3.4	1.32
2.51	1.77	1.09	1.02	1.14	2.60	6.4	1.50
2.51	1.77	1.09	1.02	0.98	2.51	5.2	1.44
2.51	1.80	0.54	0.51	0.64	10.2	3.6	(2.90)
5.02	2.99	1.09	0.96	1.49	2.69	5.0	0.86
10.04	4.77	1.09	0.83	2.86	4.86	5.6	0.85
				Average:	5.1	1.17	
					$\pm 1.7$	$\pm 0.21$	

show satisfactory constancy (Table 3B). We obtain  $[\text{HCrO}_4^-]$  from equation (6) where the numerals are the

$$[\text{Cr}^{\text{VI}}] = [\text{HCrO}_4^-] + 98[\text{HCrO}_4^-]^2 \times 2 + 0.60[\text{Fe}^{\text{III}}][\text{HCrO}_4^-]/[\text{H}^+] \quad (6)$$

dimerisation constant <sup>6</sup> in l mol<sup>-1</sup> for Cr<sup>VI</sup>, and  $K_3$  for  $\text{FeCrO}_4^+$  formation in the reaction conditions, respectively. The  $[\text{Fe}^{3+}]/[\sim[\text{Fe}^{\text{III}}]]$  is given by  $[\text{Fe}^{3+}] = [\text{Fe}^{\text{III}}] - 0.60[\text{Fe}^{\text{III}}][\text{HCrO}_4^-]/[\text{H}^+]$ .

No regular variation of  $k_1'$  with  $[\text{Fe}^{\text{III}}]$  is discernible, and assumption of simple reaction of  $\text{Fe}^{2+}$  with  $\text{HCrO}_4^-$  gives the values of  $k_1 = k_1'/[\text{HCrO}_4^-]$  in Table 3B which we deem to be satisfactory support for our assumption.

Since the scatter (though not much greater than in Table 2) is appreciable it is worthwhile to examine the origins and to seek trends. Two thirds of the results show that if  $k_1 >$  average then its concomitant  $k_2$  is  $<$  average, and *vice versa*. Thus for these, while the overall rates as measured are mutually commensurate, division into the  $k_1$  and  $k_2$  paths has some error impressed into the fitting procedure by experimental scatter. The remainder have *both*  $k_1$  and  $k_2$  greater or less (in equal number) than the averages. Here the experimental error has taken the grosser form of indicating an overall rate 'too fast' or 'too slow' relative to average overall rates. Happily the occurrence of both errors together can be discounted. Thus in this minority group the ratios  $k_1/k_2$  are far more constant ( $10^4 k_1/k_2 = 3.7 \pm 0.5$ ) than in the other runs ( $10^4 k_1/k_2 = 5.1 \pm 2.2$ ), indicating that here, despite the overall error, the fitting error is

much reduced. The ratios are in satisfactory agreement, and no trends are discernible. This discussion started by presupposing the correct choice of mechanism, but the conclusions on the distribution and randomness of error support the choice. Throughout, values  $\pm$  average deviations are given.

*Dependence of Rate on Hydrogen-ion Concentration.*—Measurement of  $k_1$  and  $k_2$  over an approximately three-fold  $[\text{H}^+]$  range yields an approximately three-fold increase of  $k_1$  and a seventeen-fold increase in  $k_2$ . The logarithmic plots show a clear third-order  $[\text{H}^+]$ -dependence of  $k_2$  (Figure 3A), as in equation (1),<sup>2</sup> and an

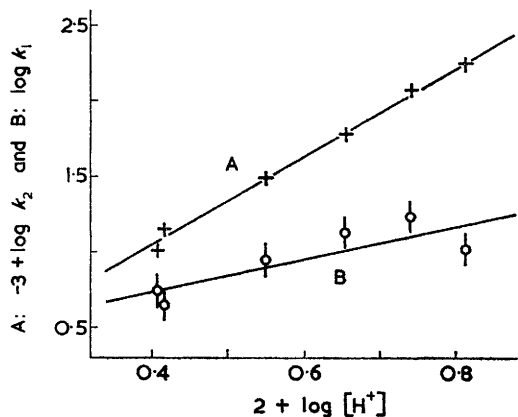


FIGURE 3 Hydrogen-ion dependences.  $2.7$  to  $6 \times 10^{-6}\text{M}$   $\text{Fe}^{\text{II}}$ ,  $1.0\text{--}1.09 \times 10^{-3}\text{M}$   $\text{Fe}^{\text{III}}$ ,  $1.02\text{--}2.51 \times 10^{-3}\text{M}$   $\text{Cr}^{\text{VI}}$ . A:  $\log k_2$  vs.  $\log [\text{H}^+]$ . B:  $\log k_1$  vs.  $\log [\text{H}^+]$ . Least-squares slopes are 2.9 and 1.08 respectively

approximately first-order  $[\text{H}^+]$ -dependence of  $k_1$  (Figure 3B). Thus our results give the rate law shown in equation (7) with  $k_{1\text{H}} = 234 \pm 51$  l<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup> and

$$-\text{d}[\text{Fe}^{\text{II}}]/\text{d}t = k_{1\text{H}}[\text{Fe}^{\text{II}}][\text{HCrO}_4^-][\text{H}^+] + k_{2\text{H}}[\text{Fe}^{\text{II}}]^2[\text{HCrO}_4^-][\text{H}^+]^3/[\text{Fe}^{3+}] \quad (7)$$

$10^{-8} k_{2\text{H}} = 6.92 \pm 0.55$  l<sup>4</sup> mol<sup>-4</sup> s<sup>-1</sup> at 20 °C and ionic strength 1.00 mol l<sup>-1</sup>.

#### DISCUSSION

We do not find the variation of  $k_2$  with  $[\text{HCrO}_4^-]$  reported by Espenson and King<sup>2</sup> and interpreted by them to indicate a minor path second order in  $[\text{HCrO}_4^-]$ . However, the  $[\text{HCrO}_4^-]$  dependence claimed is scarcely greater than the unexplained<sup>2</sup> residual trends with  $[\text{H}^+]$  or  $[\text{Fe}^{3+}]$ . These authors have, nevertheless, drawn a straight line, in their Figure 2 depicting  $k_2$  vs.  $[\text{HCrO}_4^-]$ , through points which appear actually to show a much stronger dependence at low ( $10^{-5}$  mol l<sup>-1</sup>) than at high ( $2$  to  $3 \times 10^{-4}$  mol l<sup>-1</sup>)  $\text{HCrO}_4^-$  concentration. If this decrease of dependence on  $[\text{HCrO}_4^-]$  continues to  $8 \times 10^{-4}$  mol l<sup>-1</sup> and greater, *i.e.* to the range which we have studied, then the independence which we note is not inconsistent with Espenson and King's actual results (rather than with their interpretation).

<sup>6</sup> J. Y. P. Tong and E. L. King, *J. Amer. Chem. Soc.*, 1953, 75, 6180.

Our values of  $k_{2H}$  agrees closely with these authors' value at 0 °C for ionic strength 0.2,  $1.0 \times 10^3 \text{ l}^4 \text{ mol}^{-4} \text{ s}^{-1}$ . A higher ionic strength will according to Bjerrum-Brønsted considerations<sup>7</sup> reduce the rate of reaction of oppositely charged ions, and thus here it counters the effect of the temperature difference (0 and 20 °C).

We might regard the  $k_1$  path as proceeding by reaction of an  $\text{Fe}^{\text{II}}\text{-HCrO}_4^-$  pair (complex?) with a proton, or as direct reaction with  $\text{Fe}^{\text{II}}$  of  $\text{H}_2\text{CrO}_4$ , which is present as a few percent in our solutions. In that  $\text{Cr}^{\text{VI}}$  must gain yet six more protons as well as two further water molecules in forming ultimately the product  $\text{Cr}^{3+}_{\text{aq}}$ , there seems little argument to be made against  $\text{H}_2\text{CrO}_4$  as oxidant here. That  $\text{Fe}^{\text{II}} + \text{Cr}^{\text{VI}}$  is the slow step for the path first order in  $\text{H}^+$ , while  $\text{Fe}^{\text{II}} + \text{Cr}^{\text{V}}$  is rate determining<sup>2</sup> for  $[\text{H}^+]^3$ , is clearly to be attributed to the differing reactivities of the relevant Cr species with different extents of protonation.

$\text{Fe}(\text{phen})_3^{2+}$  and  $\text{Cr}^{\text{VI}}$  also react<sup>2</sup> by one pathway which is first order in iron(II). Assuming the  $[\text{H}^+]$  and  $[\text{Cr}^{\text{VI}}]$  dependences to be the same as in our work, one finds the aquo-ion reaction to have a rate constant  $k_{\text{IH}}$  more than 10 times greater than that for the complex.

<sup>7</sup> D. R. Rosseinsky, *J. Chem. Phys.*, 1968, **48**, 4806.

<sup>8</sup> R. M. Milburn, *J. Amer. Chem. Soc.*, 1955, **77**, 1352; 1957, **79**, 537.

This could be accounted for, if both reactions are outer-sphere, by the greater  $E^\circ$  of the aquo-ion couple, or by the aquo-ion facility denied the complex, of making an oxygen bridge to the chromium(VI).

#### EXPERIMENTAL

Iron(II), iron(III) and the ionic-strength medium sodium perchlorate were prepared as before,<sup>4,5</sup> and AnalaR potassium dichromate and perchloric acid were used. Reactions were conducted in ionic strength 1.00M at 20 °C. The polarographic apparatus was that used previously.<sup>4,5</sup> To start the reaction, suitably acidified chromium(VI) solution was run into the thermostatted polarograph cell containing the iron(II) together with the remainder of the reaction-solution constituents; the decrease of the iron(II) diffusion current was recorded.

In estimating  $K_3$  at 20 °C for reaction (3) in ionic strength 1.00M, the method of Espenson and King<sup>2</sup> was closely followed. Data for  $\text{Fe}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  equilibria were again taken from Milburn<sup>8</sup> and Tong and King,<sup>6</sup> and in our conditions  $K_3$  was obtained as  $0.60 \pm 0.2$ .

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