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

\[ \frac{-d[Fe^{II}]}{dt} = k_{1H}[H^{+}] [HCrO_{4}^{-}] [Fe^{II}] + k_{2H}[H^{+}][HCrO_{4}^{-}] [Fe^{II}]^2/[Fe^{III}], \]

with \( k_{1H} = 234 \, \text{mol}^{-1} \, \text{s}^{-1} \) and \( 10^{-9}k_{2H} = 6.92 \times 10^{-4} \, \text{mol}^{-1} \, \text{s}^{-1} \) at 20 °C and ionic strength 1.00 mol l\(^{-1}\) in sodium perchlorate medium with 0.025–0.065 M perchloric acid.

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The iron(II)–chromium(VI) reaction, studied titrimetrically and spectrophotometrically,\(^2\) has hitherto been considered\(^1\) 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\(^2\) find that,

\[ \text{Cr}^{III} + \text{Fe}^{II} \rightleftharpoons \text{Cr}^{V} + \text{Fe}^{III}; \, \text{Cr}^{V} + \text{Fe}^{II} \rightleftharpoons \text{Cr}^{IV} + \text{Fe}^{III}, \]

and finally \( \text{Cr}^{IV} + \text{Fe}^{II} \rightarrow \text{Cr}^{III} + \text{Fe}^{III} \) (rapid).\(^2\)

The additional complexing equilibrium [equation (3)]

\[ \text{Fe}^{III} + \text{HCrO}_{4}^{-} \rightleftharpoons \text{FeCrO}_{4}^{+} + \text{H}^{+} \]

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\(^{II}\), \( >10^{-4} \, \text{M} \) Cr\(^{V}\), and ca. 10^{-3} \, \text{M} \) Fe\(^{III}\), 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) down by employing the rotating platinum-electrode technique successfully used for the FeII-V and FeII-MnIII reactions,4,5 where, for half-lives of seconds the iron(II) diffusion current (proportional to [FeII]) 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 HCrO4⁻ but finally it will be shown to be probably H₂CrO₄.

The Iron(II) First-order Path.—A typical current-time recording is shown in Figure 1. With initial iron(II) at 3.78 x 10⁻⁶ mol l⁻¹ and all other reactants in excess, the simple second-order plot (Figure 2A) shows some curvature. Here (i₀) is the initial diffusion current, iₙ, that at time t, and iₐ, the infinite-time ("residual") current, so that integration of the rate law \( -d[Fe]^{III}/dt = k'[Fe]^{III} \), with [FeIII] \( \propto (i_t - i_\infty) \), gives

\[
(i_0 - i_\infty)/(i_t - i_\infty) - 1 = k'[Fe]^{III} \tag{3}
\]

While linearity—or nonlinearity—is not a conclusive mechanistic test, the rate constants from such plots 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 with [FeIII]₀. This obvious trend indicates an additional necessarily lower-order term in [FeIII]. Hence, most simply,

\[
d[Fe]^{III}/dt = k_1'[Fe]^{III} + k_2'[Fe]^{III} \tag{4}
\]

which yields on integration,

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

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 \( k_2'[Fe]^{III}_0/k_1' = R \) (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 [FeIII], values of \( k_1' \) and \( k_2' \) (Table 2) are reasonably 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.2

**Table 1**

<table>
<thead>
<tr>
<th>Variation of second-order rate constant with [FeIII]₀</th>
<th>(0.0260 M H⁺; 1.0 × 10⁻⁵ M FeIII; 1.02 × 10⁻⁵ M CrVI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^6[Fe]^{III}_0 )</td>
<td>( 10^6 k_1'/s^{-1} )</td>
</tr>
<tr>
<td>3.78</td>
<td>0.52</td>
</tr>
<tr>
<td>5.95</td>
<td>0.46</td>
</tr>
<tr>
<td>5.95</td>
<td>0.44</td>
</tr>
<tr>
<td>11.10</td>
<td>0.52</td>
</tr>
<tr>
<td>17.85</td>
<td>0.39</td>
</tr>
<tr>
<td>25.8</td>
<td>*</td>
</tr>
<tr>
<td>Average: 0.47 ± 0.04</td>
<td>0.73 ± 0.03</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>First- and second-order rate constants</th>
<th>(0.0255 M H⁺; 1.02 × 10⁻⁵ M CrVI; 1.0 × 10⁻⁵ M FeIII)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^6[Fe]^{III}_0 )</td>
<td>( 10^6 k_1'/s^{-1} )</td>
</tr>
<tr>
<td>0.41</td>
<td>0.55</td>
</tr>
<tr>
<td>1.28</td>
<td>0.77</td>
</tr>
<tr>
<td>2.72</td>
<td>0.71</td>
</tr>
<tr>
<td>2.72</td>
<td>0.85</td>
</tr>
<tr>
<td>4.16</td>
<td>0.64</td>
</tr>
<tr>
<td>5.60</td>
<td>1.09</td>
</tr>
<tr>
<td>9.51</td>
<td>(1.24)</td>
</tr>
<tr>
<td>20.7</td>
<td>0.78</td>
</tr>
<tr>
<td>31.8</td>
<td>*</td>
</tr>
<tr>
<td>Average: 0.77 ± 0.12</td>
<td>2.4 ± 0.3</td>
</tr>
</tbody>
</table>

* No value quoted because \( k_2' \) path accounts for only ca. 10% of observed rate.


**Variation of Rate with Iron(III) and Chromium(VI) Concentrations.**—In Table 3A are given values of $k_1'$ and $k_3$ when [Fe(III)] and [Cr(VI)] are varied. If we accept the first term on the right of equation (1), i.e. that $k_1' = k_2' [\text{HCrO}_4^-]/[\text{Fe}^{3+}]$, then values for $k_2$ so obtained show satisfactory constancy (Table 3B). We obtain

$$[\text{Cr(VI)}] = [\text{HCrO}_4^-] + 98[\text{HCrO}_4^-]^2$$

$$\times 2 + 0.6[\text{Fe}^{II}] [\text{HCrO}_4^-]/[\text{H}^+]$$

(6)

dimerisation constant in 1 mol $^{-1}$ for Cr(VI), and $K_3$ for FeCrO$_4^-$ formation in the reaction conditions, respectively. The $[\text{Fe}^{II}]$ is given by $[\text{Fe}^{II}] = [\text{Fe}^{II}] - 0.6[\text{Fe}^{II}] [\text{HCrO}_4^-]/[\text{H}^+]$.

No regular variation of $k_1'$ with [Fe(III)] is discernible, and assumption of simple reaction of Fe$^{II}$ + CrO$_4^{2-}$ gives the values of $k_1 = k_1' [\text{HCrO}_4^-]$/[Fe(III)] 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 majority group the ratios $k_1/k_2$ are far more constant ($10^2 k_1/k_2 = 3.7 \pm 0.5$) than in the other runs ($10^2 k_1/k_2 = 5.1 \pm 2.2$), 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 [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 [H$^+$]-dependence of $k_2$ (Figure 3A), as in equation (1), and an approximately first-order [H$^+$]-dependence of $k_1$ (Figure 3B). Thus our results give the rate law shown in equation (7) with $k_{\text{HH}} = 234 \pm 51$ 1$^{-1}$ mol$^{-2}$ s$^{-1}$ and

$$-d[\text{Fe}^{II}]/dt = k_{1\text{H}} [\text{Fe}^{II}][\text{HCrO}_4^-][\text{H}^+]$$

$$+ k_{3\text{H}} [\text{Fe}^{II}]^2 [\text{HCrO}_4^-][\text{H}^+] [\text{Fe}^{III}]$$

(7)

10$^{-4}$ $k_{\text{HH}} = 0.92 \pm 0.55$ 1$^{-1}$ mol$^{-1}$ s$^{-1}$ at 20 $^\circ$C and ionic strength 1.0 mol$^{-1}$.

**Discussion.**—We do not find the variation of $k_2$ with [HCrO$_4^-$] reported by Espenson and King and interpreted by them to indicate a minor path second order in [HCrO$_4^-$]. However, the [HCrO$_4^-$] dependence claimed is scarcely greater than the unexplained residual trends with [H$^+$] or [Fe$^{III}$]. These authors have, nevertheless, drawn a straight line, in their Figure 2 depicting $k_2$ vs. [HCrO$_4^-$], through points which appear actually to show a much stronger dependence at low (10$^{-5}$ mol $^{-1}$) than at high (2 to 3 $\times$ 10$^{-4}$ mol $^{-1}$) HCrO$_4^-$ concentration. If this decrease of dependence on [HCrO$_4^-$] continues to 8 $\times$ 10$^{-4}$ mol $^{-1}$ 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).

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Our values of $k_{\text{eff}}$ agrees closely with these authors' value at 0 °C for ionic strength 0.2, $1.0 \times 10^4 \text{ mol}^{-1}\text{ s}^{-1}$.

A higher ionic strength will according to Bjerrum-Bronsted considerations 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 Fe(II)-HCrO$_4^-$ pair (complex?) with a proton, or as direct reaction with Fe(II) of H$_2$CrO$_4$, which is present as a few percent in our solutions. In that Cr(VI) must gain yet six more protons as well as two further water molecules in forming ultimately the product Cr$^{3+}$aq, there seems little argument to be made against H$_2$CrO$_4$ as oxidant here. That Fe(II) + Cr(VI) is the slow step for the path first order in H$^+$, while Fe(II) + Cr$^+$ is rate determining for [H$^+$]$^3$, is clearly to be attributed to the differing reactivities of the relevant Cr species with different extents of protonation.

Fe(phen)$_2^{2+}$ and Cr(VI) also react by one pathway which is first order in iron(II). Assuming the [H$^+$] and [Cr(VI)] dependences to be the same as in our work, one finds the aquo-ion reaction to have a rate constant $k_{\text{eff}}$ more than 10 times greater than that for the complex.

This could be accounted for, if both reactions are outer-sphere, by the greater $E^*$ 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, and AnalR potassium dichromate and perchloric acid were used. Reactions were conducted in ionic strength 1.00 M at 20 °C. The polarographic apparatus was that used previously.

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 1.00 M, the method of Espenson and King was closely followed. Data for Fe(III) and Cr(VI) equilibria were again taken from Milburn and Tong and King, and in our conditions $K_3$ was obtained as 0.60 ± 0.2.

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