Oxidation by Fe(VI): Kinetics of Fe(VI) Oxidation of Alcohols

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The kinetics of oxidation of methanol, ethanol, n-propanol, propan-2-ol and n-butanol by Fe(VI) has been studied at pH 10.8 using orthophosphate buffer in the presence of periodate. The self-decomposition of Fe(VI) under these conditions has been found to be the minimum. The order in [Fe(VI)] and [alcohol] is unity each. The rate of oxidation decreases with increase in pH, in the pH range of 9.8 to 11.9. Effect of [buffer] on the rate is negligible. Increase in [periodate] increases the rate slightly. A mechanism involving abstraction of a hydride ion from α-CH of alcohol has been suggested to explain the kinetic data.

Potassium ferrate(VI) is a powerful two-electron oxidant with an oxidation potential of 2.2 V in acid medium and 0.72 V in basic medium. Only sporadic references are available in literature on the mechanistic details of ferrate(VI) oxidation, particularly the oxidation of organic compounds, probably due to its instability and difficulty in the preparation of a stable compound of Fe(VI). Bartzatt et al. studied the kinetics of ferrate(VI) oxidation of some simple alcohols in the pH range of 8.12 to 9.02 in phosphate buffers and reported mixed order dependence of rate on [ferrate(VI)], i.e. first and second order in [Fe(VI)]. However under these conditions the self-decomposition of the oxidant was found to be considerable. Solutions containing Fe(VI) have been reported to be stabilized by periodate. Schreyer and Ockerman using phosphate buffers in the pH range of 7 to 8 reported marked retardation in the self-decomposition of Fe(VI) in water. In view of this the authors have tried to establish the conditions under which periodate and orthophosphate buffer stabilize Fe(VI) solution. Though periodate itself is a good oxidizing agent it is inactive towards monohydric alcohols. In order to fulfil our objectives presently we have studied the kinetics and mechanism of oxidation of methanol, ethanol, n-propanol, propan-2-ol and n-butanol by Fe(VI) in the presence of orthophosphate and periodate mixtures under different conditions.

Materials and Methods
Potassium ferrate(VI) was prepared by the method of Thompson et al. and assayed by both the chromite method as well as by visible spectrophotometry. It was found to be 92% pure. All the chemicals used were of AR (BDH) grade and further purified wherever necessary by standard methods. Doubly distilled water was used throughout. Buffer solutions of required pH were prepared by mixing appropriate quantities of 0.2 mol dm\(^{-3}\) KH\(_2\)PO\(_4\) and 0.2 mol dm\(^{-3}\) KOH.

The reactions were initiated by adding requisite amounts of solid potassium ferrate (K\(_2\)FeO\(_4\)) to a thermally equilibrated solution containing orthophosphate buffer, periodate and alcohol. The addition of potassium ferrate(VI) to the solution produced a purple colour which faded as K\(_2\)FeO\(_4\) was reduced. The absorbance of ferrate(VI) was noted at regular intervals of time using Carl Zeiss spectrophotometer 'SPEKOL' at 505 nm at which the molar absorptivity of Fe(VI) is 1030 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) (ref. 8).

Stoichiometry and product analysis
Under the conditions [Fe(VI)] ≫ [alcohol] in phosphate buffer-periodate medium, the change in absorbance of Fe(VI) was noted after an interval of 24 hr in the presence and absence (blank) of alcohol; one mole of Fe(VI) was found to react with 2 moles of alcohol indicating 1:2 stoichiometry.

The product of oxidation was characterised as corresponding aldehyde or ketone. Here Fe(VI) was reduced to Fe(II) which was then reoxidized to Fe(III) by dissolved oxygen in solution or by Fe(VI). The formation of Fe(II) as an intermediate during the reduction of Fe(VI) was detected by the addition of 1,10-phenanthroline. Polymerisation of the monomer, acrylamide or methyl methacrylate did not occur when added to the reaction mixture even after a long time indicating absence of free radicals.

Results and Discussion
Self decomposition of ferrate(VI)
The self-decomposition of ferrate(VI) in the
absence and presence of periodate at different pH values has been investigated. In the absence of periodate self-decomposition of Fe(VI) was less at pH 9.8, but below and above this pH, decomposition rate markedly increased. However, in the presence of periodate, self-decomposition of Fe(VI) was markedly decreased with increase in pH, and was quite small at pH 10.8, compared to that in the absence of periodate at pH 9.8 (Table 1). The self-decomposition rate was found to be minimum at [periodate] = 2.5 × 10⁻⁴ mol dm⁻³. The effect of varying [buffer] on self-decomposition rate was found to be negligible. Though the order in [Fe(VI)] was one as evidenced by the linear log [Fe(VI)] versus time plot, the rate decreased with the increase in [Fe(VI)]. This could be attributed to formation of unreactive dimerised forms of Fe(VI) as per equilibrium (1).

\[ 2\text{FeO}_4^- + 2\text{H}^+ \rightarrow \text{Fe}_2\text{O}_7^{2-} + \text{H}_2\text{O} \quad \ldots \text{(1)} \]

In the self-decomposition study it was suggested by earlier workers that the kinetic data best fit a rate equation that had a first and second order term in [Fe(VI)] and approximately first order in [H⁺] as shown by Eq. (2)

\[ \text{Rate} = k_1 \text{[FeO}_4^-] + k_2 \text{[FeO}_4^-]^2 \text{[H}^+] \quad \ldots \text{(2)} \]

where x and y are nearly equal to one.

In the present study also we have tried to find out the applicability of Eq. (2) when IO₄⁻ and phosphate buffers were employed as the medium. Equation (2) at constant pH may be rewritten as Eq. (3)

\[ \text{Rate} = k_1 \text{[FeO}_4^-] + k_2 \text{[FeO}_4^-]^2 \]

or

\[ \frac{\text{Rate}}{\text{[FeO}_4^-]^2} = k_1 + k_2 \frac{\text{[FeO}_4^-]}{\text{[FeO}_4^-]^2} \quad \ldots \text{(3)} \]

Rate/[FeO₄²⁻]² versus 1/[FeO₄²⁻] plot was linear with an intercept nearly equal to zero \((k_2 = -0.0025)\) and positive slope \((k_1 = 4.62 \times 10^{-3})\) indicating that the second order term is negligible.

**Oxidation of alcohols**

All the reactions were carried out in the absence and presence of alcohol at pH 10.8 in the presence of periodate under optimum concentration \((2.5 \times 10^{-4} \text{ mol dm}^{-3})\) at which self-decomposition of Fe(VI) was minimum. The rate of oxidation of alcohols was much greater than the rate of self-decomposition of Fe(VI) under the above conditions (Fig. 1A, A). Under the conditions \([\text{alcohol} \gg [\text{Fe}(\text{VI})]_n\), plots of log (absorbance) versus time were linear indicating first order dependence in [Fe(VI)] which was also checked by initial rate method. The rate constants for true oxidation of alcohol was calculated by subtracting the self-decomposition rate. The pseudo-first order rate constants \((k_{obs})\) at different [Fe(VI)] are given in Table 2.

<table>
<thead>
<tr>
<th>pH</th>
<th>(k_{obs} \times 10^3)</th>
<th>(10^4 k = k_{obs}/[S])</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.80</td>
<td>9.72</td>
<td>2.23</td>
</tr>
<tr>
<td>8.40</td>
<td>1.30</td>
<td>2.03</td>
</tr>
<tr>
<td>8.75</td>
<td>0.740</td>
<td>2.39</td>
</tr>
<tr>
<td>9.15</td>
<td>0.280</td>
<td>0.680</td>
</tr>
<tr>
<td>9.40</td>
<td>0.260</td>
<td>0.390</td>
</tr>
<tr>
<td>9.80</td>
<td>0.190</td>
<td>0.130</td>
</tr>
<tr>
<td>10.5</td>
<td>0.240</td>
<td>0.100</td>
</tr>
<tr>
<td>10.8</td>
<td>0.710</td>
<td>0.090</td>
</tr>
<tr>
<td>11.1</td>
<td>1.14</td>
<td>0.110</td>
</tr>
</tbody>
</table>

Table 2—Effect of Varying \([K_2\text{FeO}_4]\) and \([\text{Propan-2-ol}\) on Rate of Oxidation of Propan-2-ol by \(K_2\text{FeO}_4\)

\(\text{[IO}_4^-] = 2.50 \times 10^{-4} \text{ mol dm}^{-3}; \text{[buffer]} = 0.133 \text{ mol dm}^{-3}; \text{temp} = 298 \text{ K}; \text{pH} = 10.8\)

\( [K_2\text{FeO}_4] \times 10^4 \quad \text{[Propan-2-ol]} \quad k_{obs} \times 10^3 \quad 10^4 k = k_{obs}/[S] \quad (\text{mol dm}^{-3}) \quad (\text{mol dm}^{-3}) \quad (\text{s}^{-1}) \quad (\text{cm}^{-2} \text{mol}^{-1} \text{s}^{-1}) \)

<table>
<thead>
<tr>
<th>temp</th>
<th>(\text{[Propan-2-ol]})</th>
<th>(k_{obs})</th>
<th>(10^4 k = k_{obs}/[S])</th>
</tr>
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<tr>
<td>1.80</td>
<td>0.830</td>
<td>4.01</td>
<td>—</td>
</tr>
<tr>
<td>2.96</td>
<td>0.830</td>
<td>3.70</td>
<td>—</td>
</tr>
<tr>
<td>5.15</td>
<td>0.830</td>
<td>3.55</td>
<td>—</td>
</tr>
<tr>
<td>8.50</td>
<td>0.830</td>
<td>3.53</td>
<td>—</td>
</tr>
<tr>
<td>6.30</td>
<td>0.250</td>
<td>1.05</td>
<td>4.19</td>
</tr>
<tr>
<td>6.30</td>
<td>0.500</td>
<td>2.11</td>
<td>4.21</td>
</tr>
<tr>
<td>6.30</td>
<td>1.000</td>
<td>4.16</td>
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<td>6.30</td>
<td>1.500</td>
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<tr>
<td>6.30</td>
<td>2.000</td>
<td>8.46</td>
<td>4.23</td>
</tr>
</tbody>
</table>

The combined rate equation which includes self-decomposition and oxidation of alcohols at a constant pH can be written as Eq. (4) which can be rewritten as Eq. (5)

\[ \text{Rate} = k_1 \text{[FeO}_4^-] + k_2 \text{[FeO}_4^-][S] \quad \ldots \text{(4)} \]

\[ k_{obs} = k_1 + k_2[S] \quad \ldots \text{(5)} \]

From the linear plots of \(k_{obs}\) versus [S], \(k_1\) and \(k_2\) were calculated for different alcohols. The order in [alcohol] was nearly one (Table 2) (varying from 0.8-1.0 for different alcohols) as obtained from the slope of the linear plot of log \((k_{obs} - k_1)\) against log[S]. The rate decreased with increase in pH in the pH range of 9.8-11.9. With propan-2-ol the order in [H⁺] varied from 0.40 in the pH range of 9.8 to 10.5 to 0.12 in the pH range of 10.5 to 11.9. A similar trend was observed by Bartzatt for the same substrate. The rate of oxidation
Fig. 1—(A) Plot of log $a/(a-x)$ versus time in the absence of propan-2-ol ($[K_2FeO_4]=6.30 \times 10^{-4} \text{ mol dm}^{-3}; [IO_4^-]=2.50 \times 10^{-4} \text{ mol dm}^{-3}; [\text{buffer}]=0.133 \text{ mol dm}^{-3}; pH=10.8; \text{temp}=298 \text{ K}$)

(A') Plot of log $a/(a-x)$ versus time for oxidation of propan-2-ol by $K_2FeO_4$ ($[K_2FeO_4]=6.30 \times 10^{-4} \text{ mol dm}^{-3}; [IO_4^-]=2.50 \times 10^{-4} \text{ mol dm}^{-3}; [\text{propan-2-ol}]=0.833 \text{ mol dm}^{-3}; [\text{buffer}]=0.133 \text{ mol dm}^{-3}; pH=10.8; \text{temp}=298 \text{ K}$)

(B) Plot of $1/k^*$ versus $1/[IO_4^-][K_2FeO_4]=6.30 \times 10^{-4} \text{ mol dm}^{-3}; [\text{propan-2-ol}]=0.833 \text{ mol dm}^{-3}; [\text{buffer}]=3.33 \times 10^{-2} \text{ mol dm}^{-3}; pH=10.8; \text{temp}=298 \text{ K}$

(C) Plot of $1/k_{obs}$ versus $1/[\text{propan-2-ol}]$ ($[K_2FeO_4]=6.30 \times 10^{-4} \text{ mol dm}^{-3}; [\text{buffer}]=0.133 \text{ mol dm}^{-3}; [IO_4^-]=2.5 \times 10^{-4} \text{ mol dm}^{-3}; pH=10.8; \text{temp}=298 \text{ K}$)
slightly increased with increase in [IO₇⁻], and change in [buffer] had negligible effect. Also the order in [IO₇⁻] was fractional (0.43) as obtained from the slope of the linear plot of log $k^*$ versus log [IO₇⁻]. Plot of $1/k^*$ versus $1/[IO₇⁻]$ was linear with an intercept (Fig. 1B) indicating formation of a complex between Fe(VI) and IO₇⁻.

Ferrate(VI) is known to exist in three different forms in aqueous solution (see equilibria (6) and (7))

H₂FeO₄ $\rightleftharpoons$ HFeO₄⁺ + H⁺ \hspace{1cm} (6) (K' = 3.16 × 10⁻⁴)

HFeO₄⁻ $\rightleftharpoons$ FeO₄²⁻ + H⁺ \hspace{1cm} (7) (K° = 1.58 × 10⁻⁸)

Under the conditions of the experiment (pH > 7) equilibrium (6) may be assumed to lie far to the right and only equilibrium (7) is more probable as can be seen from $K^*$ value. If HFeO₄⁺ is to be the reactive species, the rate should increase with increase in [H⁺] or decrease with increase in pH. This infact has been observed in the present study suggesting HFeO₄⁺ to be the most likely reactive species.

Alcohols are also known to exist in neutral form or as alkoxides depending upon the pH. But in view of the very low ionization constants of alcohols" (nearly of the order of $10^{-16}$) alkoxide can exist only in strongly basic media (pH > 14). Therefore, it can be safely assumed that neutral form of alcohol is the only predominant species in the pH range of 9.8 to 12.0. Accordingly a mechanism involving reaction between an ion (HFeO₄⁺) and dipole (alcohol) is proposed. This contention receives support from the studies of effect of ionic strength (or buffer concentration) on the rate which was negligible.

In the light of the results and observations recorded above Scheme 1 is suggested to explain the results.

\[
\text{HFeO}_4^- + \text{IO}_7^- \xrightarrow{K_1} \text{C}_1 \text{(Complex)} \quad \ldots (8)
\]

\[
\text{C}_1 + \text{S} \xrightarrow{K_2} \text{C}_2 \text{(Complex)} \quad \ldots (9)
\]

\[
\text{C}_2 \xrightarrow{k} \text{products} \quad \ldots (10)
\]

Scheme 1

Since

[S] = [HFeO₄⁺]_{free} + C₁ + C₂

Rate = $k C₂ \quad \ldots (11)$

The expression for the concentration of $C₂$ can be written as

\[
C₂ = \frac{[\text{HFeO}_4^+], K_1 K_2 S [\text{IO}_4^-]}{1 + K_1 [\text{IO}_7^-] + K_1 K_2 S [\text{IO}_4^-]}
\]

Substituting the value of $C₂$ in rate Eq. (11) we get

\[
\text{Rate} = \frac{k K_1 K_2 [\text{HFeO}_4^+], [S] [\text{IO}_4^-]}{1 + K_1 [\text{IO}_7^-] + K_1 K_2 S [\text{IO}_4^-]} \quad \ldots (12)
\]

Since the order in [alcohol] is nearly one, the term $K_1 K_2 S [\text{IO}_4^-]$ in the denominator of Eq. (2) may be neglected compared to other terms.

Hence,

\[
k_{\text{obs}} = \frac{k K_1 K_2 [S] [\text{IO}_4^-]}{1 + K_1 [\text{IO}_7^-]} \quad \ldots (13)
\]

Taking reciprocal of Eq. (13) we get Eq. (14)

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [S] [\text{IO}_4^-]} + \frac{1}{k K_2 [S]} \quad \ldots (14)
\]

which predicts that the plot of $1/k_{\text{obs}}$ versus $1/[\text{IO}_7^-]$ should be linear. Such plots have been obtained in the present study (see Fig. 1B) supporting the proposed mechanism. At constant [IO₇⁻], $1/k_{\text{obs}}$ versus $1/[S]$ plot as per Eq. (14) was linear with a very small intercept (Fig. 1C). Though this cannot be taken as a clear cut evidence for formation of even an unstable complex, in view of intensification of colour of Fe(VI) on adding alcohol formation of an unstable complex during the reaction has been incorporated in the mechanism.

In view of the general applicability of the rate expressions derived, the mechanism suggested may be assumed to be operative in the present study.

The reactivities of alcohols followed the order: methanol < propan-2-ol < ethanol < n-propanol < n-butanol. Taft's plot was linear with $r^* = -1.05$ ($r = 0.98$). This indicates the formation of an electron-deficient centre in the transition state. In view of the above results it may be assumed that the complex (C₂) undergoes disproportionation with the elimination of a hydride ion from α-carbon of alcohol to give rise to the products. Removal of hydrogen from α-carbon receives further support from the absence of any reaction between Fe(VI) and t-butanol.
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References