Ag(I)-catalysed Oxidation of Cr(III) by Peroxodisulphate Ion

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The silver(I)-catalysed oxidation of chromium(III) to chromium(VI) by peroxodisulphate anion in 1M sulphuric acid is a first order reaction in silver(I), zero order in chromium(III) and fractional order in peroxodisulphate anion. There is a temperature dependent induction period. The retardation in the rate with sulphuric acid and bisulphate ion is interpreted in terms of increasing reactivity of the free radicals OH' > HSO₄⁻ > SO₄²⁻.

The kinetics of Ag(I)-catalysed oxidation of chromium(III) to chromium(VI) by peroxodisulphate was first examined by Yost1. The study was limited to the examination of the effect of concentrations of various reactants over a very limited range. Ag(III) was considered to participate in the reaction but no mechanistic details were given. The kinetics and mechanism of the uncatalysed reaction in aqueous perchloric acid was studied by Frennesson and Fronaeus2, who expressed the opinion that it was chemically less plausible that OR reacted much faster than S0₄ in oxidizing Cr(III) to Cr(VI).

Dagliotti and Hayon3, however, showed that the reactivity of HSO₄⁻ was not as strong as that of OH'. The reaction (1) between sulphuric acid and OH' was also studied by Sworski4.

H₂SO₄ + OH' → HSO₄⁻ + H₂O

It is thus clear that in a reaction where OH' has a stronger reactivity over HSO₄⁻, a retardation would be expected with increasing sulphuric acid. The reinvestigation of the title reaction was, therefore planned in the presence of aqueous sulphuric acid.

Materials and Methods

The stock Cr(III) solution was prepared by two methods. In one method5 the solution of potassium dichromate (BDH, AR) in 0.5M sulphuric acid was reduced by hydrogen peroxide (Sarabhai Merck). The unreacted hydrogen peroxide was removed by boiling the solution and the resulting Cr(III) solution standardized by reoxidizing it to Cr(VI) with peroxodisulphate anion in the presence of Ag(I).

In the other method Cr(III) solution was prepared by the electrolytic reduction of chromic acid. The use of either solutions yielded identical results.

Kinetic run — The reaction was studied at constant ionic strength, 1·8M; aluminium sulphate was used for the purpose with the assumption that it is completely dissociated. The progress of the reaction was monitored with Beckman DU-2 spectrophotometer at 350 nm where the principal Cr(VI) species HCrO₄ and H₄CrO₄ absorb strongly. The other experimental details were similar to those described elsewhere6.

Results and Discussion

A temperature dependent induction period was observed (shown by the dotted curve in Fig. 1) on plotting [Cr(VI)] against time. The reaction was found to be zero order with respect to chromium(III) and the rate constant, k₀, were calculated from the slope of the solid part of the curves by the method of least squares. The k₀ values, obtained from the replicate runs, were reproducible within ±5%. The average values are reported in Tables 1-7.

Stoichiometry — An excess of known Cr(III) solution was treated with a deficient known solution of peroxodisulphate in presence of Ag(I) at 40°. The optical density of the resulting Cr(VI) solution was checked from time to time till it reached a stationary value. The results of several such investigations indicated that [Cr(III)]/[S₂O₈²⁻] = 0·67 ± 0·005. Hence the reaction could be expressed by Eq. (2).

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Fig. 1 — Zero-order plots for the reaction with respect to Cr(VI). The plot is drawn between [Cr(VI)] and time with different [S₂O₈²⁻] — ○ 0·025M; — 0·05M; — 0·075M; — △ 0·1M.
TABLE 1 — ZERO-ORDER DEPENDENCE OF THE REACTION WITH RESPECT TO [CHROMIUM(III)]

\[
\begin{align*}
\{\text{S}_2\text{O}_5^{-}\} & = 0.1 \text{M; } \{\text{H}_2\text{SO}_4\} = 1 \text{ M; } \{\text{Ag(I)}\} = 0.0002 \text{ M; } \\
\text{temp.} & = 40^\circ \text{C; } I = 1.8 \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>10^6[Cr(III)] (M)</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^6k_0 (mol dm^{-3} sec^{-1})</td>
<td>6.4</td>
<td>6.39</td>
<td>6.80</td>
<td>6.40</td>
<td>6.42</td>
<td>6.40</td>
</tr>
</tbody>
</table>

TABLE 2 — DEPENDENCE OF THE ZERO-ORDER RATE CONSTANT ON THE INITIAL [Ag(I)]

\[
\begin{align*}
\{\text{S}_2\text{O}_5^{-}\} & = 0.1 \text{ M; } \{\text{H}_2\text{SO}_4\} = 1 \text{ M; } \{\text{Cr(III)}\} = 0.002 \text{ M; } \\
\text{temp.} & = 40^\circ \text{C; } I = 1.8 \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>10^4 [Ag(I)] (M)</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^6k_0 (mol dm^{-3} sec^{-1})</td>
<td>1.3</td>
<td>2.9</td>
<td>6.5</td>
<td>9.8</td>
<td>13.2</td>
<td>16.5</td>
</tr>
</tbody>
</table>

TABLE 3 — DEPENDENCE OF THE ZERO-ORDER RATE CONSTANT ON THE INITIAL [S_2O_5^2-]

\[
\begin{align*}
\{\text{Cr(III)}\} & = 0.002 \text{ M; } \{\text{S}_2\text{O}_5^{-}\} = 0.1 \text{ M; } \{\text{Ag(I)}\} = 0.0002 \text{ M; } \\
\text{temp.} & = 40^\circ \text{C; } I = 1.8 \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>[S_2O_5^2-] (M)</th>
<th>0.025</th>
<th>0.05</th>
<th>0.075</th>
<th>0.10</th>
<th>0.15</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^6k_0 (mol dm^{-3} sec^{-1})</td>
<td>1.9</td>
<td>3.4</td>
<td>4.8</td>
<td>6.4</td>
<td>8.7</td>
<td>12.5</td>
</tr>
</tbody>
</table>

TABLE 4 — DEPENDENCE OF THE ZERO-ORDER RATE CONSTANT ON THE INITIAL [H_2SO_4]

\[
\begin{align*}
\{\text{Cr(III)}\} & = 0.002 \text{ M; } \{\text{S}_2\text{O}_5^{-}\} = 0.1 \text{ M; } \{\text{Ag(I)}\} = 0.0002 \text{ M; } \\
\text{temp.} & = 40^\circ \text{C; } I = 1.8 \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>[H_2SO_4] (M)</th>
<th>0.2</th>
<th>0.5</th>
<th>0.8</th>
<th>1.2</th>
<th>1.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^6k_0 (mol dm^{-3} sec^{-1})</td>
<td>9.2</td>
<td>8.2</td>
<td>7.0</td>
<td>5.7</td>
<td>4.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>

TABLE 5 — DEPENDENCE OF THE ZERO-ORDER RATE CONSTANT ON [H_2SO_4] AT CONSTANT [H^+]

\[
\begin{align*}
\{\text{Cr(III)}\} & = 0.002 \text{ M; } \{\text{S}_2\text{O}_5^{-}\} = 0.1 \text{ M; } \{\text{Ag(I)}\} = 0.0002 \text{ M; } \\
\{\text{H}_2\text{SO}_4\} & = 0.4 \text{ M; } \text{temp.} = 40^\circ \text{C}
\end{align*}
\]

<table>
<thead>
<tr>
<th>[NaHSO_4] (M)</th>
<th>0.0</th>
<th>0.1</th>
<th>0.4</th>
<th>0.8</th>
<th>1.2</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H_2SO_4] (M)</td>
<td>2.0</td>
<td>1.2</td>
<td>1.6</td>
<td>2.0</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>10^6k_0 (mol dm^{-3} sec^{-1})</td>
<td>8.6</td>
<td>8.2</td>
<td>6.8</td>
<td>5.5</td>
<td>4.2</td>
<td>2.9</td>
</tr>
</tbody>
</table>

TABLE 6 — EFFECT OF RADICAL SCAVENGER ON THE ZERO-ORDER RATE CONSTANT

\[
\begin{align*}
\{\text{Cr(III)}\} & = 0.002 \text{ M; } \{\text{Ag(I)}\} = 0.0002 \text{ M; } \{\text{S}_2\text{O}_5^{-}\} = 0.1 \text{ M; } \\
\text{temp.} & = 40^\circ \text{C; } I = 1.8 \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>[Acrylamide] (M)</th>
<th>0.25</th>
<th>0.50</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^6k_0 (mol dm^{-3} sec^{-1})</td>
<td>4.6</td>
<td>4.2</td>
<td>3.4</td>
<td>2.7</td>
<td>2.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

TABLE 7 — EFFECT OF TEMPERATURE ON ZERO-ORDER RATE CONSTANT

\[
\begin{align*}
\{\text{Cr(III)}\} & = 0.002 \text{ M; } \{\text{Ag(I)}\} = 0.0002 \text{ M; } \{\text{S}_2\text{O}_5^{-}\} = 0.1 \text{ M; } \\
\text{temp.} & = 40^\circ \text{C}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>40.0</th>
<th>45.0</th>
<th>50.0</th>
<th>55.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^6k_0 (mol dm^{-3} sec^{-1})</td>
<td>6.4</td>
<td>8.9</td>
<td>12.6</td>
<td>18.0</td>
</tr>
</tbody>
</table>

which establishes the rate relationship expressed in Eq. (3).

\[3\text{S}_2\text{O}_5^{-} + 2\text{Cr}^{3+} \rightarrow 6\text{SO}_4^{2-} + 2\text{Cr}^{6+} \quad \ldots (2)\]

\[\frac{d[\text{Cr(III)}]}{dt} = \frac{d[\text{Cr(VI)}]}{dt} - \frac{2d[\text{S}_2\text{O}_5^{-}]}{dt} \quad \ldots (3)\]

The results in Tables 1 and 2 are respectively consistent with a zero-order dependence in [Cr(III)] and a first order dependence in [Ag(I)] thus confirming the earlier results of Yost. Further, the linear plot between \(k_0\) and [Ag(I)] (Fig. 2) almost passed through the origin indicating the absence of any uncatalysed reaction between peroxydisulphate and Cr(III) at the optimum temperature.

Dependence on peroxydisulphate — The previous authors\(^\text{1-2}\) have reported a first order dependence in peroxydisulphate ion. However, the present results, within the range of \([\text{S}_2\text{O}_5^{-}]\) investigated, indicate a fractional order in peroxydisulphate because the plot between \(1/k_0\) and [Ag(I)] (Fig. 2) is found to be linear with an intercept on the rate axis. It might be added that a similar plot was obtained (plot B in Fig. 3) on plotting the rate-data of Frennesson and Fronaeus\(^\text{3}\). The rate data is reported in Table 3.
rate measurements were carried out in solutions of varying ionic strengths. The results (Table 4) yielded a linear plot between $1/k_0$ and $[\text{H}_2\text{SO}_4]$ as is illustrated in Fig. 4.

**Dependence on bisulphate ion** — These measurements (Table 5) were also carried out in solutions of differing ionic strength. The $k_0$ values decreased with increasing $[\text{HSO}_4^-]$ added as sodium salt. A plot similar to Fig. 4 was obtained in plotting $k_0^{-1}$ against $[\text{HSO}_4^-]^{-1}$.

**Dependence on monomer** — The decrease in the rate constant $k_0$ with the increasing concentration of acrylamide (Table 6) indicated that free radicals are involved in the progress of the reaction.

**Dependence on temperature** — The $k_0$ values at different temperatures are reported in Table 7. The Arrhenius plot was linear and the energy of activation and entropy of activation, both calculated with $k_0$, have a value of $58.5 \pm 4$ kJ mole$^{-1}$ and $-184 \pm 12$ JK$^{-1}$ mole$^{-1}$ respectively.

The presence of the induction period and a linear correlation between $1/k_0$ and $[\text{S}_2\text{O}_8^{2-}]^{-1}$ distinguishes the present study from the previous studies. In view of the latter results the following mechanism (Scheme 1) is proposed and the consideration of the observed induction period is deferred to a later stage.

The further oxidation of Cr$^{4+}$ to Cr$^{6+}$ could be visualized by any of the following fast reactions (9)-(13) where the superscript number refers to the oxidation state and not to the charge carried by the metal atom.

The existence of AgHSO$_4$ is well documented in aqueous solutions of sulphuric acid. Since the progress of the reaction was measured in terms of appearance of Cr(VI), the rate expression is given in Eq. (13).

Again, the correlation between $[\text{Ag}^+]$ and the total $[\text{Ag(I)}]$, as calculated from the reactions (4)
and (5) could be expressed by Eq. (15)

\[ [Ag^+] = \frac{[Ag(I)]}{1 + K_1[H_2SO_4] + K_2[S_2O_8^{2-}]}. \]  

(15)

The rate Eq. (14) takes the form of Eq. (16) after the proper substitution of the value of \([Ag^+]\) from Eq. (15).

\[ \frac{d[Cr(VI)]}{dt} = \frac{2k_2K_1[Ag(I)]S_2O_8^{2-}}{1 + K_1[H_2SO_4] + K_2[S_2O_8^{2-}].} \]  

(16)

The validity of Eq. (16) is supported by the experimental results described with the assumption that sulphuric acid is 1:1 electrolyte because the dissociation constant of bisulphate ion is small enough \((K = 9.76 \times 10^{-3} at 25^\circ}\) to be effective in changing the concentration of bisulphate ion either added from outside or coming from sulphuric acid present in the reaction mixture.

Frennesson and Fronaeus\(^a\) reported that the rate of uncatalysed reaction, in terms of appearance of Cr(VI), approached a constant value for \([H^+] > 0.1M\). However, an entirely opposite inference is to be drawn from the plots shown in Fig. 3. It is to be noted that the plot for the variation of sulphuric acid (both \(H^+\) and \(HSO_4^-\) are varying) runs below the plot belonging to variation of \(HSO_4^-\) \((H^+ kept constant at 0.4M)\) after about 0.4M. This indicated that \(H^+\) catalysed the rate.

The catalysis by \(H^+\) has been generally explained on the assumption that the protonated species of the peroxodisulphate anion decompose to give sulphur tetraoxide molecule as shown in Eq. (17). However, Bawn and Margerison\(^a\) have reported that \(SO_4^{2-}\) did not show active radical characteristics in the \(pH\) range 3-7. As such any inclusion of Eq. (17) in the mechanism is open to question.

\[ H_2SO_4 \rightarrow SO_4 + HSO_4^- \]  

(17)

The retardation effect of \(HSO_4^-\) that of sulphuric acid has been quantitatively explained in terms of Eq. (16). However, there is another explanation that needs consideration. This explanation also helps to explain the catalytic effect of \(H^+\) in addition to the retardation of the rate by bisulphate ion. This explanation takes into account the relative reactivity of \(OH^-\), \(HSO_4^-\) and \(SO_4^{2-}\) radicals. The order of reactivity is \(OH^- > HSO_4^- > SO_4^{2-}\). It might be added that Dagliotti and Hayon\(^a\) have shown that the reactivity of \(SO_4^{2-}\) is not as strong as that of \(OH^-\) radical. The increased reactivity of \(HSO_4^-\) over that of \(SO_4^{2-}\) is understandable in view of the observed catalytic effect of \(H^+\) as shown in the reaction (21).

\[ HSO_4^- + OH^- \rightarrow OH^- + HSO_4^- \]  

(18)

or

\[ H_2SO_4 + OH^- \rightarrow H_2O + HSO_4^- \]  

(19)

\[ S_2O_8^{2-} \rightarrow 2SO_4^{2-} \]  

(20)

\[ H^+ + SO_4^{2-} \rightarrow HSO_4^- \]  

(21)

The reaction (20) is the well known disproportionation reaction of the peroxodisulphate anion in the absence of \(H^+\). The reaction (21), to the extent of formation of \(HSO_4^-\), could also be represented by the reaction (22) which is the alternate representation for reaction (17).

\[ HS_2O_8 \rightarrow HSO_4^- + SO_4^{2-} \]  

(22)

The order of the reactivity of radicals \(OH^+ > HSO_4^- > SO_4^{2-}\), as indicated by the results of the present study, is consistent with the actual rate measurements in the oxidation of Ce(III). Anbar and Neta\(^b\) reported a value of \(2.2 \times 10^{-6}\) litre mol\(^{-1}\) sec\(^{-1}\) for the oxidation of Ce(III) by \(OH^-\) radical. Dagliotti and Hayon\(^a\) have reported a value of \(1.3 \times 10^{-6}\) litre mol\(^{-1}\) sec\(^{-1}\) for the reaction with \(SO_4^{2-}\) radical.

The reactions (18)-(21) were not considered as the regular ones in the mechanism because these are the side reactions in a system which is itself very complex. Beside the reactions (4)-(8), and the side reactions (18)-(21) there are other side reactions also. Frennesson and Fronaeus\(^a\) have expressed the possibility of the formation of complex(es) between peroxodisulphate anion and Cr(III). Chromium(III) can exist either as an aquated ion, \(Cr^{3+}\), or as \(CrSO_4\) complex. If one assumes that \(CrSO_4\) is less reactive than \(Cr^{3+}\), the retarding effect of \(HSO_4^-\) is equally explainable in terms of any of the reactions (4), (18) and (23) and a specific choice becomes difficult. Beside the reaction (19) explaining the retarding effect of sulphuric acid on the rate, there is yet another explanation. Mathews et al.\(^a\) have calculated the quotient of \([SO_4^{2-}]/[OH^-]\) at different concentrations of sulphuric acid and have found that the quotient increased much more rapidly than the increase in sulphuric acid. This observation supports our view regarding reaction (19) that the reaction can not be considered as the basic reaction of the mechanism. It may be added that the consideration of such side reactions is not unusual in peroxodisulphate oxidations where the overall reaction could be expressed by several alternate reactions. As an example the formation of \(OH^-\) in the system could be visualized by the additional reaction (24).

\[ Cr^{3+} + HSO_4^- \rightarrow CrSO_4^- + H^+ \]  

(23)

\[ SO_4^{2-} + H_2O \rightarrow OH^- + HSO_4^- \]  

(24)

**Induction period** — The induction period could be explained as the consequence of the reaction (6) in which a build-up of the actual oxidant species involved in the oxidation of Cr(III) to Cr(IV) is considered.

**Acknowledgement**

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**References**