Oxidation of Light and Heavy Water by Peroxydisulphate

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Abstract

Oxidation of light and heavy water by peroxydisulphate was studied at 60-70°C. The acid independent and acid dependent rate constants and respective ΔE values were computed. An attempt is made to explain the kinetic isotopic effect observed. A probable mechanism is proposed.

Results reported on oxidation of light water by peroxydisulphate by several workers1-7 revealed that oxidation proceeds both by (i) acid dependent as well as (ii) acid independent paths. The rate constants and Arrhenius parameters for these paths reported by Kolthoff and Miller1 were in sharp contrast from those of Breuer and Jenkins. All the mechanisms suggested both for acid catalysed and acid independent reactions lead to

$$\text{S}_2\text{O}_8^- + \text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + \frac{1}{2}\text{O}_2$$

as the final stoichiometric equation; (i) was assumed to proceed by homolysis of $\text{S}_2\text{O}_8^-$ to radical ions $\text{SO}_4^-$ which react with water producing $\text{HSO}_4^-$ and OH radicals which dimerise to $\text{H}_2\text{O} + \frac{1}{4}\text{O}_2$. (ii) involved the formation of $\text{HS}_2\text{O}_5^-$ which decomposes to $\text{HSO}_4^-$ and $\text{SO}_4$ radicals, the latter reacting further in $\text{SO}_4 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2$ and $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HSO}_4^-$. OH and $\text{SO}_4$ are therefore the precursors for $\text{O}_2$ from (i) and (ii) respectively. We have studied the oxidation of light water by $\text{S}_2\text{O}_8^-$ in the pH range 0-10 at 60-80°C. Acid dependent and acid independent rate constants and the respective ΔE values are being reported. Similar studies with heavy water were made but confined to the pH range 2-8, $k_{H_2O}/k_{D_2O}$ values have been reported for the ‘overall rate’ constants as well as for ‘acid catalysed’ and ‘acid independent’ reactions. Curiously enough for the overall rate, $k_{D_2O}/k_{H_2O} < 1$ while for the latter reactions $k_{H_2O}/k_{D_2O} > 1$ were observed. The rate was found to be proportional to total acidity and not to Hammett's
H₂O, thus emphasizing participation of both H⁺ and H₂O in the transition state for the catalysed reaction.

**Experimental**

K₂S₂O₈ (E Merck; G.R.); H₂SO₄ (A.R. 36 N Basynth; India); HClO₄ (A.R., 60%; Mayand Baker); NaOH (G.R., E. Merck); Heavy Water (Atomic Energy, Trombay, India; 99.4% purity) were employed. Distilled water, distilled over alkaline KMnO₄ twice and then passed through Ion exchange resin (Biodeminrolit; Permutit Co., U.K.) was used for preparation of all solutions. Adjustments of ionic strengths were made with H₂SO₄, HClO₄ and NaOH solutions. pHs of solutions were measured in pH meter (Leeds and Northrup Cat. No. 7666) provided with a system of glass and calomel electrodes and standardised by potassium biphthalate (M/20; pH = 4.00 at 35°C). All the experiments were confined to [S₂O₈²⁻] = 0.005 M and ~ 35% conversions of the former and for ~ 90 minutes.

The solution of S₂O₈²⁻ (in light or heavy water) after adjustment of pH (by the addition of H₂SO₄ or NaOH) was thermostated at the required temperature (60-80°C) ± 0.1°C, controlled by a relay and toluene regulator. Aliquots (5 c.c.) were withdrawn at 10 min. intervals; quenched in ice-cold water (25 c.c.) containing KI (2 gm.); set aside for about 45 minutes; acidified with acetic acid (6.0 N, 2 ml.) and titrated against standard sodium thiosulphate (0.025 N). From [S₂O₈²⁻] reacted, rate of S₂O₈²⁻ disappearance, -Rₛ₂o₈²⁻, was computed. Rate measurements by addition of excess standard (Fe⁺²) to aliquots and back titration with standard KMnO₄ or ceric sulphate compared well with those by iodometry and the rates may be considered accurate to within ±1%.

**Results and Discussion**

(i) The orders with respect to [S₂O₈²⁻] were observed to be unity, the log (a− x) vs. t plots being linear in H₂O (Fig. 1, A) as well as D₂O (Fig. 1, B) at various pHs. Perchloric acid in place of H₂SO₄ for adjustments of pH in H₂O did not make any difference. The pseudo first order rate constants in light and heavy water kH₂O and kD₂O respectively at 60° and 70°C at various pHs together with the respective ΔE values, etc., appear in Table I. It is seen from Table I that there is an irregular increase and decrease in ΔE values with variations in pH and the lowest value for ΔE = 10.7 at pH 2.14 in H₂O was noticed. Our values are in better agreement with those of Breuer and Jenkins⁷ (ΔE = 23-35) than those of Kolthoff and Miller¹
### Table I

**Rate constants and $\Delta E$ values at various pHs**

<table>
<thead>
<tr>
<th>pH</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>1.9</th>
<th>2.0</th>
<th>2.14</th>
<th>2.31</th>
<th>2.49</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{H_2O} \times 10^4$</td>
<td>1.33</td>
<td>0.89</td>
<td>0.5</td>
<td>0.77</td>
<td>0.97</td>
<td>1.6</td>
<td>0.8</td>
<td>0.31</td>
<td>0.23</td>
</tr>
<tr>
<td>($H_2SO_4$)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>(0.96)</td>
<td>(1.61)</td>
<td>(0.81)</td>
<td>...</td>
<td>(0.23)</td>
</tr>
<tr>
<td>$k_{D_2O} \times 10^4$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>0.77</td>
<td>0.96</td>
<td>0.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>3.05</th>
<th>3.4</th>
<th>4.4</th>
<th>5.0</th>
<th>6.0</th>
<th>7.0</th>
<th>8.0</th>
<th>9.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{H_2O} \times 10^4$</td>
<td>0.74</td>
<td>1.4</td>
<td>1.9</td>
<td>2.8</td>
<td>3.7</td>
<td>1.7</td>
<td>1.44</td>
<td>0.39</td>
<td>0.58</td>
</tr>
<tr>
<td>($H_2SO_4$)</td>
<td>(0.69)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$k_{D_2O} \times 10^4$</td>
<td>0.74</td>
<td>1.33</td>
<td>0.74</td>
<td>...</td>
<td>...</td>
<td>1.0</td>
<td>0.92</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

**$\Delta E$ in K.cal.—**

<table>
<thead>
<tr>
<th>$H_2O$</th>
<th>20.2</th>
<th>21.4</th>
<th>20.7</th>
<th>20.1</th>
<th>18.7</th>
<th>9.0</th>
<th>10.0</th>
<th>17.0</th>
<th>26.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_2O$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

Values in brackets refer to those in $HClO_4$ in $H_2O$.

All $k_H$ and $k_D$ values have dimensions sec.$^{-1}$.
(\Delta E = 26-33 \text{ K.cal./mole}). All these workers confined their oxidation studies to 40-50°C range while our investigations were carried out in the 60-70°C range.

(ii) Form of H\(^+\) (D\(^+\)) function: It was found that \(\log k_{H_2O}\) (or \(k_{D_2O}\)) was found to be proportional to total acidity [H\(^+\)] and plots of \(\log k_{H_2O}\) vs. \(H_0\) were curves (Fig. 1, F).

![Figure 1](image_url)

**Fig. 1.** Plots A and B, \(\log (a - x)\) vs. time. \([S_2O_8^{2-}] = 0.005 \text{ M in } H_2O (A), D_2O (B) at 60^\circ \text{ C.} \) Plot C, pseudo first order rate constant vs. \([H^+]\) ml.\(^{-1}\) for \(H_2O\) at 60°C. Plot D, Pseudo first order rate constant \(k_{obs}\) vs. \([H^+]\) ml.\(^{-1}\) for \(H_2O\) at 60°C. Plot E, \(k_{obs}\) vs. \([H^+]\) ml.\(^{-1}\) for \(D_2O\) at 60°C. Plot F, \(\log k_{obs}\) vs. \(H_0\) for both \(H_2O\) and \(D_2O\).
Oxidation Studies—V

(iii) Separation of \(k_{H_2O}(k_{D_2O})\) to acid independent \(k_{1H_2O}(k_{1D_2O})\) and acid dependent \(k_{2H_2O}(k_{2D_2O})\) terms: From the intercepts and slopes of the plots \(-R_{S_2O_5^-} w. [H^+]\) (Fig. 1, C, D and E) \(k_{1H_2O}\) and \(k_{2H_2O}\) respectively were evaluated at 60° and 70° C. Similarly \(k_{1D_2O}\) and \(k_{2D_2O}\) were also evaluated (Table II).

**TABLE II**

*Acid dependent and acid independent rate constants and Arrhenius parameters in \(H_2O\) and \(D_2O\)*

<table>
<thead>
<tr>
<th>pH range</th>
<th>Rate constants (60°) and (70°) C.</th>
<th>Isotopic effects (60°) and (70°) C.</th>
<th>Activation parameters in K. cal./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k_H \times 10^5) (k_D \times 10^5) (k_{H_2}) (k_{D_2}) (k_{H_2}/k_{D_2}) (k_{H_2}/k_{D_2}) (\Delta E_{H_2}) (\Delta E_{D_2}) (\Delta E_{H_2O}) (\Delta E_{D_2O})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-13 for light water</td>
<td>2.2</td>
<td>1.65</td>
<td>6.3</td>
</tr>
<tr>
<td>2.2-7.9 for (D_2O)</td>
<td>7.0</td>
<td>5.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

It is seen that \(k_{D_2O}/k_{H_2O}\) are usually greater than unity (1.041, 0.98 and 0.936 at 60° C and 3.4, 3.1 and 2.90 at 70° C. all in the pH range 2-2 to 8). The isotopic effects (\(k_{H_2O}\) and \(k_{D_2O}\) were resolved into \(k_{1H_2O}, k_{2H_2O}, etc.\)): \(k_{1H_2O}/k_{1D_2O} = 2.05\) and 1.41 at 60° and 70° C. respectively and \(k_{2H_2O}/k_{2D_2O} = 1.27\) and 0.82 respectively at 60° and 70° C. all in the pH range 2-2 to 8-0. It may be seen that the kinetic isotopic effect \(k_{D_2O}/k_{H_2O} > 1\) and the ratio increases with increase of temperature. The opposite effects are found in the kinetic isotopic effects with the resolved constants \(k_{1H_2O}/k_{1D_2O} > 1\) and \(k_{2H_2O}/k_{2D_2O} > 1\) and the ratio decreases with increase of temperature. These are rather anomalous. In the case of organic substrates with C–H bonds the \(k_{H_2O}/k_{D_2O} > 1\) is usually understood in terms of a proton transfer being involved in the rate-determining step; on the other hand \(k_{D_2O}/k_{H_2O} > 1\) meant the equilibrium involving the substrate, \(S + H^+ \rightleftharpoons SH^+\) being important. If similar arguments apply for a substrate like \(S_2O_8^-\) (which does not involve a C–H bond) it is rather likely that acid catalysed reaction is

\[
S_2O_8^- + H^+ \rightleftharpoons HS_4O_6^- \quad (1)
\]

slow

\[
HS_2O_6^- + H_2O \rightleftharpoons 2HS_4^- + H^+ + \frac{1}{2}O_2 \quad (2)
\]
This mechanism is also supported by the fact that rate is a function of total acidity and not of Hammetts function $H_0$. An alternative to step (2) may be (2a):

$$\text{HS}_2\text{O}_5^- + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}^+ + \text{SO}_4^{2-} + \text{OH}$$  \hspace{1cm} (2a)

which may be important in substrate oxidations. The kinetic isotopic effects decreasing with increasing temperature are in order. Acid independent path may follow the course not involving any proton transfer:

$$\text{S}_2\text{O}_8^- \rightarrow 2 \text{SO}_4^{2-}$$  \hspace{1cm} (3)

$$2 \text{SO}_4^{2-} + 2 \text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + 2 \text{OH}$$  \hspace{1cm} (4)

$$2 \text{OH} \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$$  \hspace{1cm} (5)

The kinetic isotopic effect $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} > 1$ is probably subject to solvent isotopic effects which are not quite clear.

**ACKNOWLEDGEMENT**

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**REFERENCES**

5. Schum and Rittner \hspace{1cm} *J. Amer. Chem. Soc.*, 1940, 62, 3416.