Chromium(III) catalysed cerium(IV) oxidation of DMSO in aqueous perchloric acid

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Chromium(III) catalysis of cerium(IV) oxidation of DMSO in aqueous perchloric acid has been investigated. It is found that the reaction occurs with the intervention of chromium(IV) and formation of free radicals of DMSO.

Kinetics of oxidation of DMSO by a number of oxidants has been extensively studied, though catalysis by different metal ions does not seem to have received much attention. Catalysis by silver(I) is modest but our preliminary studies indicated that Cr(III) catalysis is more pronounced. In this study, the results of the title reaction are given.

Experimental
The reagents and the kinetic procedure employed were similar to those adopted earlier. Duplicate runs agreed within ±5%. The reagents were found to be Ce(III) and dimethyl sulphone (m.p. 108°, lit. m.p. 109°), the latter being identified by spot tests for sulphone. No change in [Cr(III)] was found during the reaction as indicated by the absorption maximum at 583 nm.

Results and discussion
The order in oxidant is unity as shown by linear plots of log [Ce(IV)] versus time over a range of 70% or more and the order in DMSO is ≈ 0.8 as revealed by the log-log plots of initial rates versus [DMSO]. The effect of varying [Cr(III)] on the reaction was studied in the Cr(III) concentration range of 0.5 × 10⁻⁵ to 4.0 × 10⁻³ mol dm⁻³ under pseudo-first order conditions ([DMSO] ≫ [oxidant]) keeping all other concentrations fixed. The order in Cr(III), as derived from log-log plots of rate constant versus [Cr(III)] is around 0.9. In the presence of added Ce(III), kcat substantially decreases (by about 40%) with increase in [Ce(III)] from 0 to 2.0 × 10⁻² mol dm⁻³.

The results of the studies on the effect of increasing acidity ([HClO₄]) on the catalysed reaction are shown in Table 1. The results may be ascribed to the formation of different sulphate complexes of cerium(IV). With increase in acidity, the concentrations of different forms of cerium(IV) that can exist in the presence of sulphate such as Ce⁴⁺, Ce(OH)₃⁺, Ce(SO₄)₂⁺, Ce(SO₄)₂, HCe(SO₄)₃⁻ and H₂Ce(SO₄)₄ vary. Such concentrations, calculated from the competing equilibria and the known equilibrium constants as in earlier work are given in Table 1. It is found that a parallelism with rate constant and increasing acidity occurs only in the case of concentrations of Ce⁺⁺ and H₃Ce(SO₄)₄ and not others. Again, to distinguish between Ce⁺⁺ and H₃Ce(SO₄)₄, experiments with added sulphate at ionic strength of 1= 2.0 mol dm⁻³ and in the absence of sulphate were performed, the results of which clearly showed that Ce⁺⁺ was chiefly responsible for increase in rate with increase in acidity. Hence Ce⁺⁺ is likely to be the major active species although the other Ce(IV)-species may also be active. The plots of log kcat and [Ce⁺⁺], each versus log[H⁺] were similar. Analogous results leading to Ce⁺⁺ as the major active species in acid sulphate media have been found in the uncatalysed reaction also. Thus the role of acidity (H⁺ ions) is to prevent hydrolysis of Ce(IV) to the comparatively inactive Ce(OH)₃⁺ and to contribute to a corresponding increase in the Ce⁺⁺ concentration. This also accounts for the order of 0.9 in [H⁺]².

As the Ce(IV) oxidation of DMSO in aqueous perchloric acid proceeds with measurable rate in the absence of Cr(III), the catalysed oxidation is understood to occur in parallel paths with contributions from both the uncatalysed and catalysed paths. Thus the catalysed reaction follows the rate law (1), the first and second terms on the right hand side accounting for

\[
\frac{d[Ce(IV)]}{dt} = \frac{k_a[k_1ag[Ce(IV)][Cr(III)]//\text{DMSO}]}{k_{-1}[Ce(III)] + k_2[DMSO]} \quad \ldots (1)
\]

de the uncatalysed and catalysed paths respectively. The data of the catalysed path are in agreement with Scheme 1 in which the equilibrium step of formation of reactive Cr(IV) species is followed by oxidation of DMSO by Cr(IV) and the two steps together determine the rate. Experiments
Table 1 – Effect of increasing acidity on the uncatalysed and chromium(III) catalysed cerium(IV)-DMSO reaction at 40°C

<table>
<thead>
<tr>
<th>[HClO₄]⁺ (mol dm⁻³)</th>
<th>[H⁺] (mol dm⁻³)</th>
<th>[Ce⁺]x10⁴ (mol dm⁻³)</th>
<th>[H₂Ce(SO₄)₃]x10⁷ (mol dm⁻³)</th>
<th>kₑ × 10⁴ (s⁻¹)</th>
<th>kₑ × 10⁴ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>0.71</td>
<td>3.4</td>
<td>0.90</td>
<td>3.7</td>
<td>1.2</td>
</tr>
<tr>
<td>0.80</td>
<td>0.91</td>
<td>4.4</td>
<td>0.97</td>
<td>4.7</td>
<td>1.5</td>
</tr>
<tr>
<td>1.0</td>
<td>1.1</td>
<td>5.2</td>
<td>1.1</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td>1.2</td>
<td>1.3</td>
<td>5.9</td>
<td>1.2</td>
<td>6.6</td>
<td>2.6</td>
</tr>
<tr>
<td>1.4</td>
<td>1.5</td>
<td>6.9</td>
<td>1.4</td>
<td>7.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

*A constant amount, 9.2 × 10⁻² mol dm⁻³, of sulphuric acid coming from the original stock solution of cerium(IV) is also present in all cases.
† Data taken from ref. 6
(i) Cerium(IV) species, viz. Ce(OH)³⁺, CeSO₄⁺, Ce(SO₄)₂⁺ and HCe(SO₄)₃⁺ are not shown as CeSO₄⁺ concentration is almost constant and the other three decrease with increasing acidity.
(ii) Free [H⁺] was calculated from the total [H⁺] and acid sulphate equilibrium constant of ref. 9 and the different cerium(IV) sulphate complexes were calculated as in ref. 3 from the respective equilibrium constants of ref. 6. Ce(OH)³⁺ equilibrium constants used were from ref. 10.
(iii) kₑ and kₑ refer to pseudo-first order rate constants of the uncatalysed and catalysed reaction respectively.

The order of the reaction in [Cr(III)] is ~0.9 and this may be due to the active catalyst form being an ion pair complex, Cr³⁺·SO₄⁻², with a low equilibrium constant. Inner sphere complexes of chromium(III) are unlikely to be of much importance in the reaction.

The mechanism in Scheme 1 leads to rate law (1) which can be rearranged to Eq. (2).

\[
\frac{[\text{Ce(IV)}][\text{Cr(III)}][\text{DMSO}]}{\text{rate}_\text{cat} - \text{rate}_\text{u}} = \frac{k_{-1}}{2k_1k_2} \frac{[\text{Ce(III)}]}{[\text{DMSO}]} + \frac{1}{2k_1k_2} \frac{[\text{Ce(III)}]}{[\text{DMSO}]} \quad (2)
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\]
different temperatures, $E_a$ and $\Delta S^\circ$ values pertaining to the reaction of Ce(IV) and Cr(III) yielding Cr(IV) and Ce(II) have been obtained as 41 kJ mol$^{-1}$ and $-134$ JK$^{-1}$ mol$^{-1}$ respectively for catalysed reaction ($E_a$ and $\Delta S^\circ$ are 53 kJ mol$^{-1}$ and $-222$ JK$^{-1}$ mol$^{-1}$ for uncatalysed reaction). It may be noted here that the value of $k_1$ (9.3 x 10$^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 30°C) referring to the Ce(IV) − Cr(III) reaction (forward reaction of first step of Scheme 1) is that which may be expected on the basis of the value of $5.0 \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25°C obtained for the overall Ce(IV) − Cr(III) reaction$^8$.

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References


