Kinetics & Mechanism of Oxidation of m-Cresol by Osmium Tetroxide in Alkaline Medium

A K SINH*, SANGEETA SAXENA, MADHU SAXENA, RANJANA GUPTA & R K MISHRA
Chemistry Department, University of Allahabad, Allahabad
Received 10 June 1987; revised 31 August 1987; accepted 15 October 1987

The title reaction is first order each in [OsO₄] and [substrate]. First order dependence in OH⁻ at low [OH⁻] becomes zero at higher [OH⁻]. Kinetic results indicate the formation of a complex between the substrate and reactive species of Os(VIII) i.e. [OsO₄(OH)₂]²⁻ which disproportionates in a slow step into the products and Os(VI) species.

Although osmium tetroxide has been extensively used as a catalyst, it has been seldom used as an oxidant. Silverton¹ has reported the oxidation of 4,5-dihydrobenzophrine by osmium tetroxide. The title investigation is an extension of our earlier work²,³ on the application of OsO₄ as an oxidising agent.

The standard solution of OsO₄ was prepared by dissolving the sample (Johnson Matthey) in KOH solution. Standard solution of m-cresol was prepared by weight. The progress of reaction was followed spectrophotometrically at 420 nm.

Kinetic results can be summarised as follows:
(i) Order in [OsO₄] is unity as revealed by the constancy in k₁ values (both graphical as well as calculated) at varying [OsO₄]. For example, under the conditions, [m-cresol] = 1.2 × 10⁻² mol dm⁻³, [NaOH] = 1.6 × 10⁻² mol dm⁻³ at 32.7°C the value of k₁ × 10³ s⁻¹ remained constant at 3.61 ± 0.30 when [OsO₄] x 10³ was varied from 1.2 to 4.2 mol dm⁻³.
(ii) Order in m-cresol is one as revealed by the constancy of k₁/[m-cresol] values at varying [m-cresol]. Under the conditions [OsO₄] = 1.25 × 10⁻¹ mol dm⁻³, [NaOH] = 2.5 × 10⁻² mol dm⁻³ and temp. = 31.7°C, k₁/[m-cresol] remained constant (0.27 ± 0.01) when [m-cresol] × 10³ was varied from 4 to 20 mol dm⁻³.
(iii) Order in [OH⁻] changed from unity at low [OH⁻] to zero at high [OH⁻].
(iv) There is no change in reaction rate by varying ionic strength of medium.
(v) Activation parameters have been calculated (temp. = 35.3°C) to be Eₐ = 71.65 kJmol⁻¹, A=9.49 × 10⁹ mol⁻¹ dm⁻³ s⁻¹, ΔG°=67.58 kJmol⁻¹, ΔS° = 4.96 JK⁻¹ mol⁻¹.

It is reported⁴ that OsO₄ in alkaline medium exists mainly as [OsO₄(OH)₂]²⁻ species. Based on the kinetic results the mechanism in Scheme 1 has been proposed.

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

\[\text{CH}_3\text{C}_6\text{H}_4\text{OH} + \text{[OSO}_4\text{(OH)}_2\text{]^{2-}} \rightarrow \text{[CH}_3\text{C}_6\text{H}_4\text{O}^- \ldots \ (2)\]

\[\text{CH}_3\text{C}_6\text{H}_4\text{O}^- \ldots \ (3)\]

Scheme 1

Scheme 1 leads to rate law (4)

\[\frac{d[\text{Os(VIII)}]}{dt} = \frac{-2kK_1K_2[\text{[Os(VIII)]}_1[S][\text{OH}^-]}{1 + K_1[\text{OH}^-][1 + K_2[S]]} \ldots \ (4)\]

since 1 ≫ K₁[S], Eq. (4) reduces to Eq. (5)

\[1 = \frac{1}{k_1} \left[ \frac{1}{2kK_1K_2[\text{OH}^-]} + \frac{1}{2kK_2} \right] \ldots \ (5)\]

where \(k_1 = \frac{d[\text{Os(VIII)}]}{dt}/[\text{[Os(VIII)]}_1\text{)]} \)

The rate equation (5) predicts that the plot of 1/k₁ versus 1/[OH⁻] should be linear with a positive intercept. It is found to be so and from the slope value of kK₁K₂ (13.54) and from intercept the value of kK₂ (0.416) are calculated.

Similarly a plot of 1/k₁ and 1/[S] is linear passing through origin. From the slope the value of kK₂ has been calculated to be 0.422.

References