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

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The title reaction is first order each in $[OsO_4]$ 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. $[OsO_4(OH)_2]^{2-}$ 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. Silverton[1] has reported the oxidation of 4,5-dihydrobenzophrine by osmium tetroxide. The title investigation is an extention of our earlier work[2,3] on the application of $OsO_4$ as an oxidising agent.

The standard solution of $OsO_4$ 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.
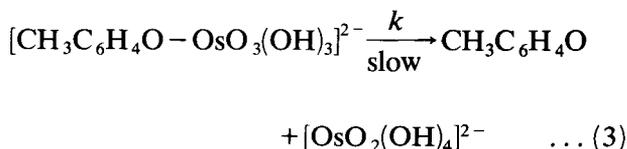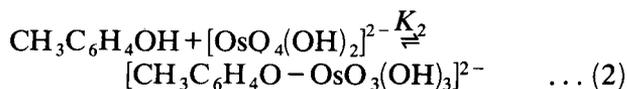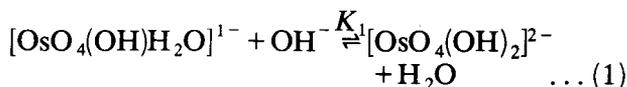
Kinetic results can be summarised as follows:

(i) Order in $[OsO_4]$ is unity as revealed by the constancy in $k_1$ values (both graphical as well as calculated) at varying $[OsO_4]$. For example, under the conditions, [m-cresol] = $1.2 \times 10^{-2}$ mol dm$^{-3}$, [NaOH] = $1.6 \times 10^{-2}$ mol dm$^{-3}$ at 32.7°C the value of $k_1 \times 10^3$ s$^{-1}$ remained constant at $3.61 \pm 0.30$ when $[OsO_4] \times 10^3$ was varied from 1.2 to 4.2 mol dm$^{-3}$.

(ii) Order in m-cresol is one as revealed by the constancy of $k_1/$[m-cresol] values at varying [m-cresol]. Under the conditions $[OsO_4]$ = $1.25 \times 10^{-3}$ mol dm$^{-3}$, [NaOH] = $2.5 \times 10^{-2}$ mol dm$^{-3}$ and temp. = 31.7°C, $k_1/$[m-cresol] remained constant $(0.27 \pm 0.01)$ when [m-cresol] $\times 10^3$ 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 $E_a = 71.65$ kJmol$^{-1}$,

$A = 9.49 \times 10^9$ mol$^{-1}$ dm$^{-3}$ s$^{-1}$, $\Delta G^{\ddagger} = 67.58$ kJmol$^{-1}$, $\Delta S^{\ddagger} = 4.96$ JK$^{-1}$ mol$^{-1}$.

It is reported[4] that $OsO_4$ in alkaline medium exists mainly as $[OsO_4(OH)_2]^{2-}$ species.

Based on the kinetic results the mechanism in Scheme 1 has been proposed.

$$[OsO_4(OH)H_2O]^{1-} + OH^- \overset{K_1}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \qquad \ldots (1)$$

$$CH_3C_6H_4OH + [OsO_4(OH)_2]^{2-} \overset{K_2}{\rightleftharpoons} [CH_3C_6H_4O - OsO_3(OH)_3]^{2-} \qquad \ldots (2)$$

$$[CH_3C_6H_4O - OsO_3(OH)_3]^{2-} \overset{k}{\underset{slow}{\longrightarrow}} CH_3C_6H_4O + [OsO_2(OH)_4]^{2-} \qquad \ldots (3)$$

Scheme 1

Scheme 1 leads to rate law (4)

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

since $1 \gg K_2[S]$, Eq. (4) reduces to Eq. (5)

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

where $k_1 = -\dfrac{d[Os(VIII)]}{dt}\Big/[Os(VIII)]_T$

The rate equation (5) predicts that the plot of $1/k_1$ versus $1/[OH^-]$ should be linear with a positive intercept. It is found to be so and from the slope value of $kK_1K_2$ (13.54) and from intercept the value of $kK_2$ (0.416) are calculated.

Similarly a plot of $1/k_1$ and $1/[S]$ is linear passing through origin. From the slope the value of $kK_2$ has been calculated to be 0.422.

## References

1 Silverton, *Tetrahedron Lett*, **19** (1976) 1557.
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3 A K Singh, A K Sisodia, Sangeeta Saxena & Madhu Saxena, *Indian J Chem*, **26A** (1987) 600-602.
4 Griffith, W P, *Quart Rev*, **19** (1665) 254.