

Kinetics of Oxidation of Methyl Glycol & Diacetone Alcohol by Osmium Tetroxide in Alkaline Medium

A K SINGH*, A K SISODIA, SANGEETA SAXENA & MADHU SAXENA

Chemistry Department, Allahabad University, Allahabad

Received 7 August 1986; revised 17 October 1986; accepted 10 November 1986

Oxidation of methyl glycol and diacetone alcohol by osmium tetroxide in alkaline medium shows first order dependence in $[\text{OsO}_4]$ and $[\text{substrate}]$. First order dependence in OH^- ion at lower concentration tends towards zero at higher $[\text{OH}^-]$. Kinetic results indicate that an activated complex is formed between the substrate and reactive species of Os(VIII) , i.e. $[\text{OsO}_4(\text{OH})_2]^{2-}$. This activated complex disproportionates into the products and Os(VI) species. On the basis of experimental observations, a probable reaction mechanism has been proposed.

Kinetic investigations on OsO_4 oxidation of organic substrates are comparatively less than those wherein OsO_4 has been used as a catalyst. An earlier paper from our laboratory¹ reported the application of OsO_4 as an oxidising agent. Presently we have studied the kinetics and mechanism of osmium tetroxide oxidation of methyl glycol and diacetone alcohol in alkaline medium.

Materials and Methods

Standard solutions of methyl glycol and diacetone alcohol were prepared by weight. Standard solution of osmium tetroxide was prepared by dissolving 1 g of osmium tetroxide (Johnson & Matthey) in aq KOH solution (393.4 ml). Stock solution of NaOH was prepared in doubly distilled water and standardised volumetrically against phenolphthalein indicator.

The progress of the reaction was studied spectrophotometrically using a Beckman UV-visible spectrophotometer model-26. Standard solution of osmium tetroxide absorbed maximally at 420 nm and this wavelength was chosen to monitor the progress of reaction.

The reaction mixture was prepared by mixing calculated amounts of osmium tetroxide, alkali, doubly distilled water and the substrate to be oxidised. The absorbance of the reaction mixture was noted immediately (zero time) against doubly distilled water as blank. Such absorbance measurements were made at regular time intervals. During the course of reaction Os(VIII) changed to Os(VI) and the absorbance decreased due to decrease in intensity of colour of the solution.

Results and Discussion

The initial rate of the reaction increased proportionally with increase in $[\text{OsO}_4]$ for both the

substrates indicating first order dependence in $[\text{OsO}_4]$. This was further verified by the uniform k_1 values presented in Table 1 at varying $[\text{OsO}_4]$. The first order rate constant (k_1) values were calculated by the following equation: $k_1 = \frac{2.303}{t} \log(A_0/A_t)$

where A_0 is the absorbance at zero time and A_t is the absorbance at a given time t .

The average first order rate constant (k_1) increased in direct proportion with increase in $[\text{substrate}]$ (Table 2) suggesting first order dependence in $[\text{substrate}]$.

The oxidation of methyl glycol and diacetone alcohol follows first order kinetics at low $[\text{OH}^-]$ which tends towards zero at higher $[\text{OH}^-]$ (see Table 3). Change in ionic strength of the medium has no effect on the reaction rate.

The energy of activation and entropy of activation have been obtained from the linear Arrhenius plots and the values for the oxidation of methyl glycol are $E_a = 11.8$ kcal/mol, $\Delta G^\ddagger = 19.3$ kcal/mol, and $\Delta S^\ddagger =$

Table 1—Effect of Varying [Oxidant] on Rate Constants of Oxidation of Methyl Glycol and Diacetone Alcohol

(A) For methyl glycol oxidation: $[\text{substrate}] = 0.4$ mol dm⁻³, $[\text{NaOH}] = 0.01$ mol dm⁻³; temp = 33°C. (B) For diacetone alcohol oxidation: $[\text{substrate}] = 2.0 \times 10^{-3}$ mol dm⁻³ $[\text{NaOH}] = 3.0 \times 10^2$ mol dm⁻³; temp = 23°C

Sl. No.	A		B	
	$[\text{OsO}_4] \times 10^3$ (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)	$[\text{OsO}_4] \times 10^3$ (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)
1	0.3	1.2	1.8	4.5
2	0.6	1.2	2.4	4.6
3	1.2	1.4	3.0	4.6
4	1.8	1.5	3.6	4.3
5	2.4	1.5	—	—
6	3.6	1.5	—	—

Table 2—Effect of Varying [Substrate] on Rate Constants of Oxidation of Methyl Glycol and Diacetone Alcohol

(A) For methyl glycol oxidation: $[\text{OsO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{NaOH}] = 0.1 \text{ mol dm}^{-3}$; $\text{temp} = 25 \text{ C}$. (B) For diacetone alcohol oxidation: $[\text{OsO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{NaOH}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{temp} = 23.7^\circ\text{C}$

Sl. No.	A			B		
	[Methyl glycol] (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)	$k_1/[\text{substrate}]$ (mol ⁻¹ dm ³ s ⁻¹)	[Diacetone alcohol] $\times 10^3$ (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)	$k_1/[\text{substrate}] \times 10^3$ (mol ⁻¹ dm ³ s ⁻¹)
1	0.2	1.3	6.5	2.0	0.98	0.49
2	0.4	2.6	6.5	4.0	2.0	0.51
3	0.7	4.4	6.3	6.0	3.0	0.51
4	1.0	6.1	6.1	8.0	3.9	0.49
5	—	—	—	10.0	5.1	0.51

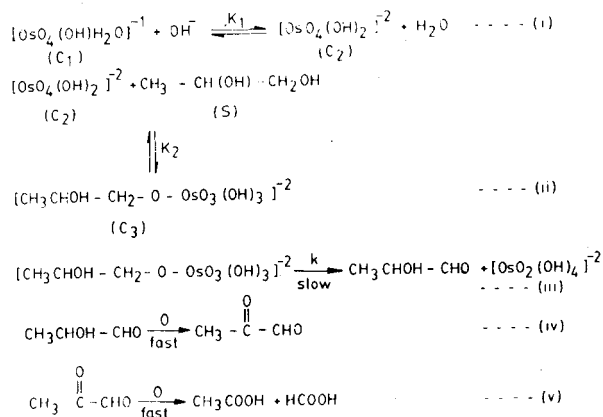
Table 3—Effect of Varying $[\text{OH}^-]$ on Rate Constants of Oxidation of Methyl Glycol and Diacetone Alcohol(A) For methyl glycol oxidation; [substrate] = 0.4 mol dm⁻³; $[\text{OsO}_4] = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{temp} = 26^\circ\text{C}$. (B) For diacetone alcohol oxidation; [substrate] = 6.25 $\times 10^{-3} \text{ mol dm}^{-3}$; $[\text{OsO}_4] = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{temp} = 33^\circ\text{C}$

Sl. No.	A		B	
	[NaOH] (mol dm ⁻³)	$k_1 \times 10^2$ (s ⁻¹)	[NaOH] $\times 10^2$ (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)
1	0.005	0.12	0.2	0.65
2	0.01	0.19	0.4	1.02
3	0.03	0.26	0.6	1.54
4	0.05	0.24	0.8	2.18
5	0.07	0.26	1.0	2.35
6	0.10	0.27	1.2	3.06
7	—	—	1.6	3.24

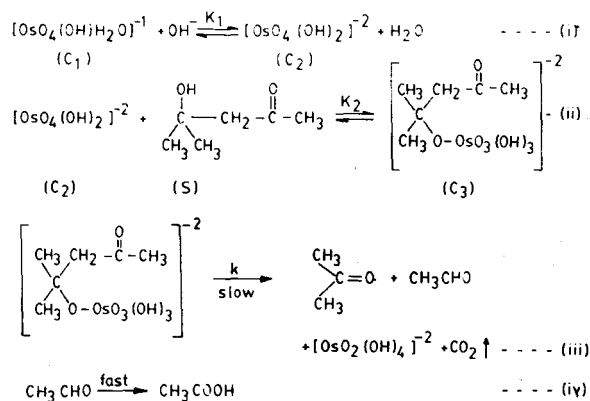
−26.3 e.u. Corresponding values for diacetone alcohol are 8.6 kcal/mol, 11.2 kcal/mol and −10.4 e.u.

On the basis of above experimental findings the probable mechanisms shown in Schemes 1 and 2, may be proposed for the oxidation of methyl glycol and diacetone alcohol respectively.

The mechanisms shown in Schemes 1 and 2 clearly indicate that a complex is formed between Os(VIII) and the alcohol molecule in step (ii) by the possible



SCHEME 1



SCHEME 2

displacement of coordinated OH. The complex thus formed disproportionates into the product and Os(VI) species. Total Os(VIII) concentration can be expressed by Eq. (1)

$$[\text{Os(VIII)}]_{\text{T}} = [\text{C}_1] + [\text{C}_2] + [\text{C}_3] \quad \text{--- (1)}$$

The rate of reaction in terms of decrease in concentration of OsO_4 can be expressed by Eq. (2).

$$-\frac{d[\text{Os(VIII)}]}{dt} = 2k[\text{C}_3] \quad \text{--- (2)}$$

Applying the equilibrium condition for steps (i) and (ii), Eqs (3) and (4) are obtained.

$$[\text{C}_1] = \frac{[\text{C}_2]}{K_1[\text{OH}^-]} \quad \text{--- (3)}$$

$$[\text{C}_2] = \frac{[\text{C}_3]}{K_2[\text{S}]} \quad \text{--- (4)}$$

Substituting the value of $[\text{C}_2]$ into Eq. (3), we get

$$[\text{C}_1] = \frac{[\text{C}_3]}{K_1 K_2 [\text{S}] [\text{OH}^-]} \quad \text{--- (5)}$$

Substituting the value of $[\text{C}_1]$ and $[\text{C}_2]$ in Eq. (1) we get

$$[\text{Os(VIII)}]_{\text{T}} = \frac{[\text{C}_3]}{K_1 K_2 [\text{S}] [\text{OH}^-]} + \frac{[\text{C}_3]}{K_2 [\text{S}]} + [\text{C}_3] \quad \text{--- (6)}$$

$$[C_3] = \frac{[Os(VIII)]_T K_1 K_2 [S][OH^-]}{1 + K_1 [OH^-] + K_1 K_2 [S][OH^-]} \quad \text{--- (7)}$$

Now substituting the value of $[C_3]$ from Eq. (7) into Eq. (2) we get

$$\frac{-d[Os(VIII)]}{dt} = \frac{2k K_1 K_2 [Os(VIII)]_T [S][OH^-]}{1 + K_1 [OH^-] + K_1 K_2 [S][OH^-]} \quad \text{--- (8)}$$

$$\frac{-d[Os(VIII)]}{dt} = \frac{2k K_1 K_2 [Os(VIII)]_T [S][OH^-]}{1 + K_1 [OH^-] \{1 + K_2 [S]\}} \quad \text{--- (9)}$$

The rate law (9) accounts for the first order dependence in $[Os(VIII)]$. The presence of $[S]$ and $[OH^-]$ in the denominator in Eq. (9) shows their retarding influence at higher concentration.

As the order of reaction in [substrate] is unity up to its ten-fold variation, the following inequality will hold good.

$$1 \gg K_2 [S]$$

With this assumption Eq. (9) will reduce to Eq. (10).

$$\frac{-d[Os(VIII)]}{dt} = \frac{2k K_1 K_2 [Os(VIII)]_T [S][OH^-]}{1 + K_1 [OH^-]} \quad \text{--- (10)}$$

At very low $[OH^-]$ the inequality $1 \gg K_1 [OH^-]$ will hold good and Eq. (10) will reduce to Eq. (11).

$$\frac{-d[Os(VIII)]}{dt} = 2k K_1 K_2 [S][OH^-][Os(VIII)]_T \quad \text{--- (11)}$$

At higher $[OH^-]$ the inequality $K_1 [OH^-] \gg 1$ will hold good and the rate will be given by Eq. (12).

$$\frac{-d[Os(VIII)]}{dt} = 2k K_2 [S][Os(VIII)]_T \quad \text{--- (12)}$$

Equation (12) clearly explains the zero order kinetics at higher $[OH^-]$.

Equation (10) can also be written as

$$k_1 = \frac{-d[Os(VIII)]}{dt} / [Os(VIII)]_T = \frac{2k K_1 K_2 [S][OH^-]}{1 + K_1 [OH^-]} \quad \text{--- (13)}$$

(S = methyl glycol / diacetone alcohol)

OR

$$\frac{1}{k_1} = \frac{1}{2k K_1 K_2 [S][OH^-]} + \frac{1}{2k K_2 [S]} \quad \text{--- (14)}$$

OR

$$\frac{1}{k_1} = \frac{1}{[S]} \left\{ \frac{1}{2k K_1 K_2 [OH^-]} + \frac{1}{2k K_2} \right\} \quad \text{--- (15)}$$

The fact that the plot of $1/k_1$ and $1/[OH^-]$ was linear with a positive intercept on Y axis supports the validity of the proposed reaction mechanism. The slope of the linear plot gives the value of kK_1K_2 and the intercept the value of kK_2 . The value of kK_2 thus calculated for methyl glycol and diacetone alcohol are 3.571×10^{-3} and 1.388 respectively.

Similarly a plot of $1/k_1$ and $1/[S]$ was linear passing through origin. From the slope of the linear plot, the value of kK_2 has been calculated by Eq. 16.

$$\text{Slope} = \frac{1}{2k K_1 K_2 [OH^-]} + \frac{1}{2k K_2} \quad \text{--- (16)}$$

Substituting the value of kK_1K_2 and $[OH^-]$, one can easily calculate the value of kK_2 . The kK_2 values for methyl glycol and diacetone alcohol are 3.405×10^{-3} and 1.620, respectively. The close agreement between the two set of values supports the proposed mechanism.

Negative entropy of activation for the oxidation of both the substrates reflects the loss of entropy incurred in bringing two reactant molecules into the single transition state. Energy of activation and free energy of activation both indicate that oxidation of diacetone alcohol is faster than that of methyl glycol.

References

- 1 Singh B, Singh M B, Singh A K & Singh A P, *Tetrahedron*, **42** (1986) 715.