Tetrahedron Vol. 42, No. 2, pp. 715 to 717, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

KINETICS AND MECHANISM OF OXIDATION OF SOME ALCOHOLS BY OSMIUM TETROXIDE

Bharat Singh,* A. K. Singh, M. B. Singh and **A. P. Singh**
Department of Chemistry, University of Allahabad, Allahabad 211002, India

(*Received in UK* 19 *January* 1985)

Abstract—Spectrophotometric studies of the kinetics of oxidation of 2-methylpropan-1-ol and 2-butanol by an alkaline solution of osmium tetroxide have been reported. A first-order dependence to osmium tetroxide was observed. A first-order dependence to both 2-methylpropan-1-ol and alkali at low concentration tends to zero order at higher concentrations. In the case of 2-butanol, first-order kinetics is exhibited with respect to 2-butanol but first-order kinetics observed at lower concentrations of alkali decrease at higher concentrations. A negligible ionic strength effect of the medium was observed. Activation parameters have been computed. A suitable mechanism in conformity with our kinetic observations has been suggested.

Very little data are reported on Os(VIII) as an independent oxidant,[1–8] although it has been widely used as a catalyst.[9–13] Recently some attempts have been made on kinetic studies of Os(VIII) oxidation of some substrates[14–17] but the literature on kinetic investigations of oxidation of reducing substances by Os(VIII) is scanty. This paper reports the kinetics and mechanism of oxidation of 2-methylpropan-1-ol and 2-butanol by osmium tetroxide in alkaline media.

EXPERIMENTAL

Materials and methods. All the reagents used were of highest purity available. B.D.H. (A.R.) samples of 2-methylpropan-1-ol and 2-BuOH were used, all other reagents were of A.R. grade. Triple distilled water was used throughout the course of the reaction and the soln of OsO_4 (Johnson and Matthey) was prepared by dissolving OsO_4 (1 g) in 393.4 ml of KOH aq (0.05 M).

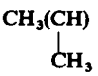
The reaction was initiated by adding a known volume of OsO_4 to requisite volumes of the substrate and NaOH maintained at the desired temp ($\pm 0.1°$).

Osmate ion absorbs strongly in the visible region at 400 nm ($\varepsilon = 400$). The kinetics of the reaction were followed by spectrophotometric estimation of unconsumed OsO_4 using a Beckman spectrophotometer model 26 with an auto recorder.

Stoichiometry and product analysis. Different sets of experiments were carried out with varying OsO_4 substrate ratios. Spectrophotometric estimation of unconsumed OsO_4 in each set indicated consumption of 2 and 4 mol of OsO_4 per mol oxidation of 2-methylpropan-1-ol and 2-BuOH, respectively. Isobutyric acid was identified as an end product in the oxidation of 2-methylpropan-1-ol while propionic and formic acids were characterized spectrophotometrically as end products in the oxidation of 2-BuOH. Stoichiometric Eqs (1) and (2) may, accordingly be written as

$$RCH_2OH + 2OsO_4 + 4OH^- = RCOOH + 2[OsO_2(OH)_4]^{2-} \quad (1)$$

where, R represents the



$\mathrm{CH_3(\underset{\underset{CH_3}{|}}{CH})}$

group in the 2-methylpropan-1-ol molecule.

$$CH_3CH_2CHOHCH_3 + 4OsO_4 + 10OH^- + H_2O \rightarrow 4[OsO_2(OH)_4]^{2-} + CH_3CH_2COO^- + HCOO^-. \quad (2)$$

RESULTS AND DISCUSSION

The kinetic observations covering a wider range of reactant concentrations and showing complicated features of the reactions are summarized in Tables 1 and 2 and Fig. 1. First-order kinetics with respect to osmium tetroxide were observed at all initial concentrations of osmium tetroxide (Table 1). The first-order constants (k_{obs}) were obtained on dividing ($-dA/dt$) values (obtained from the slopes of unconsumed OsO_4 vs time plots) by $[OsO_4]$ at which the slopes were taken. The kinetic data collected at various temperatures show a marked effect of temperature on the rate. The energy and entropy of activation were found as 8.08 K cal mol^{-1} and -26.96 e.u., respectively (2-methylpropan-1-ol) and 13.91 K cal mol^{-1} and -15.61 e.u., respectively (2-butanol).

Table 2 records the kinetic results at various

Table 1. Effect of varying $[OsO_4]$ and temperature on reaction rate

$[S] = 2.00 \times 10^{-2}$ M $[OsO_4] \times 10^3$ M	$[NaOH] = 2.00 \times 10^{-2}$ M $k_{obs} \times 10^4$ s^{-1}
1.00†	9.58[a]
1.34†	9.42[a]
1.60†	10.52[a]
2.00	9.50[a]
2.50†	10.00[a]
3.34†	10.40[a]
4.00†	9.51[a]
1.00†	6.31[b]
1.00†	7.76[c]
1.00†	12.59[d]
1.00‡	24.86[e]
1.34‡	23.62[e]
1.67‡	23.56[e]
2.50‡	23.71[e]
3.37‡	24.90[e]
4.00‡	24.23[e]
1.00‡	10.40[f]
1.00‡	15.15[g]
1.00‡	33.88[h]

† [2-methylpropan-1-ol]: a at 35°; b at 27°; c at 31°; d at 40°.

‡ [2-butanol]: e at 37.5°; f at 27°; g at 31°; h at 41°.

---

* Author to whom correspondence should be addressed.

Table 2. Effect of varying [substrate] and [NaOH] on reaction rate

[Substrate] × 10^2 (M)	[NaOH] × 10^2 (M)	$k_{obs} \times 10^4$ (s^{-1})	$10^2 k_2 = \frac{k_{obs}}{[\text{substrate}] \text{ or } [OH^-]}$ ($l\ mol^{-1}\ s^{-1}$)
1.00[a]	1.25	5.12[b]	5.12
1.25[a]	1.25	6.68[b]	5.34
2.00[a]	1.25	10.04[b]	5.02
2.50	1.25	11.60[b]	4.67
3.34[a]	1.25	14.96[b]	4.49
4.00[a]	1.25	16.08[b]	4.02
5.00[a]	1.25	19.78[b]	3.96
1.25[a]	0.66	7.09[c]	10.75
1.25[a]	0.83	7.89[c]	9.51
1.25[a]	1.11	8.88[c]	8.00
1.25[a]	1.66	9.66[c]	5.82
1.25[a]	2.50	10.68[c]	4.27
1.25[a]	3.33	10.24[c]	3.07
1.25[a]	5.00	10.84[c]	2.17
1.00[d]	1.25	9.44	9.44
1.66[d]	1.25	14.30	8.61
2.50[d]	1.25	22.54	9.00
3.34[d]	1.25	31.27	9.34
5.00[d]	1.25	41.75	8.35
10.00[d]	1.25	82.30	8.23
1.25[d]	1.00	10.89	10.89
1.25[d]	1.25	12.57	10.06
1.25[d]	1.66	15.12	9.11
1.25[d]	2.50	18.42	7.37
1.25[d]	3.30	23.67	7.10
1.25[d]	5.00	26.67	5.13
1.25[d]	7.50	33.00	4.40
1.25[d]	10.00	36.56	3.66

[a] [2-methylpropan-1-ol], $[OsO_4] = 1.00 \times 10^{-3}$ M.
[b] At 36°.
[c] At 37°.
[d] [2-butanol], $[OsO_4] = 2.00 \times 10^{-3}$ M, at 37.5°.

concentrations of alcohols and hydroxyl ions. The trend in shifting of order from first to zero is obvious from the constant values of k_2 (second-order constant) up to a certain limit of concentration of either 2-methylpropan-1-ol or hydroxyl ions and beyond which k_2 values show a decreasing trend (last column of Table 2), while constancy of k_2 values clearly indicates first-order kinetics in 2-butanol. At constant [substrate] a plot of $1/v_i$ (where v_i is the initial velocity in terms of $-d[OsO_4]/dt$) against $1/[OH^-]$ was linear making an intercept on the $1/v_i$ axis, which confirms the existence of octahedral complexes of osmium tetroxide. Addition of acrylonitrile to the reaction mixtures did not influence the rate of the reactions, which rules out the possibility of a free radical mechanism in the present case.

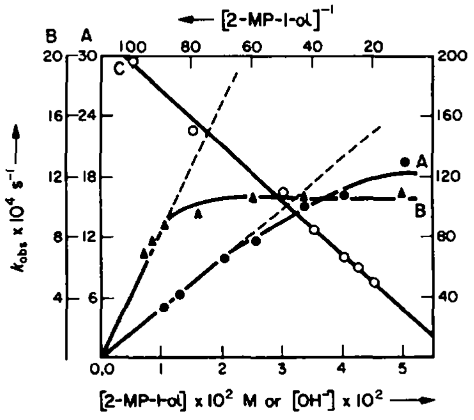


Fig. 1. (A) Effect of varying [2-MP-1-ol] on reaction rate at 36°: $[OsO_4] = 1.00 \times 10^{-3}$ M, $[OH^-] = 1.25 \times 10^{-2}$ M. (B) Effect of varying $[OH^-]$ on reaction rate at 37°: $[OsO_4] = 1.00 \times 10^{-3}$ M, [2-MP-1-ol] $= 1.25 \times 10^{-2}$ M. (C) Plot of $[v_1]^{-1}$ vs [2-MP-1-ol]$^{-1}$ at 36°: $[OsO_4] = 1.00 \times 10^{-3}$ M and $[OH^-] = 1.25 \times 10^{-2}$ M.

Octahedral complexes of the form *trans* $[OsO_4(OH^-)_2]^{2-}$ and $[OsO_4(OH^-)(H_2O)]^-$ are reported by Griffith.[18] The latter species is involved in step (i) of the proposed reaction scheme. The real reactive species formed by osmium tetroxide is $[OsO_4(OH^-)_2]^{2-}$ and the equilibrium lies entirely in its favour.[19] In alkaline medium Os(VIII) does not exist as OsO_4, which is confirmed by the formation[20] of $[OsO_4(OH^-)_2]^{2-}$ with OH^- ions.

In the light of the above statements and the kinetic results collected on the systems, the oxidation mechanism proposed is given as

$$\underset{(C_1)}{[OsO_4(OH^-)(H_2O)]^-} + OH^- \overset{K_1}{\rightleftharpoons} \underset{(C_2)}{[OsO_4(OH^-)_2]^{2-}} + H_2O \qquad \text{(i)}$$

$$[OsO_4(OH^-)_2]^{2-} + S \underset{slow}{\overset{K_2}{\rightleftharpoons}} \underset{(C_3)}{X} \quad \text{(intermediate or complex)} \qquad (ii)$$

where S represents 2-methylpropan-1-ol or 2-butanol.

$$X \xrightarrow{k_1} [OsO_2(OH)_4]^{2-} + \text{products.} \qquad (iii)$$

slowest and rate determining step

Step (ii) is slow but not as slow as step (iii) which is the rate determining step. The total [Os(VIII)] may be obtained from Eq. (3) on the basis of the above proposed scheme

$$[Os(VIII)]_{Total} = [C_1] + [C_2] + [C_3]. \qquad (3)$$

The final rate law in terms of the rate of consumption of $[OsO_4]$ may be derived by considering the equilibrium conditions for steps (i) and (ii) and solving in terms of total [Os(VIII)] with the help of Eq. (3). Thus the rate law obtained is given by Eq. (4)

$$\frac{-d[OsO_4]}{dt} = \frac{nk_1K_1K_2[Os(VIII)]_{Total}[OH^-][S]}{1 + K_1[OH^-] + K_1K_2[S][OH^-]} \qquad (4)$$

where n represents the number of mol of OsO_4 consumed by per mol of substrate, or

$$\frac{-d[OsO_4]}{dt} = \frac{nk_1K_2K_2[Os(VIII)]_{Total}[OH^-][S]}{1 + K_1[OH^-]\{1 + K_2[S]\}}. \qquad (5)$$

In the case of 2-butanol, Eq. (5) may be changed to Eq. (6) with the assumption $K_2[S] \ll 1$

$$\frac{-d[OsO_4]}{dt} = \frac{nk_1K_1K_2[Os(VIII)]_{Total}[OH^-][S]}{1 + K_1[OH^-]}. \qquad (6)$$

Rate law (6) conforms to the observed kinetics. At low $[OH^-]$, $1 \gg K_1[OH^-]$ holds good and rate law (7) is obtained

$$\frac{-d[OsO_4]}{dt} = nk_1K_1K_2[Os(VIII)]_{Total}[OH^-][S]. \qquad (7)$$

At higher $[OH^-]$, the inequality $1 \gg K_1[OH^-]$ is not strictly maintained and hence the order in OH^- shows the decreasing trend. The value of $k_1K_1K_2$ obtained from the slope of the curve (obtained from the plot of $1/v_i$ against $1/[OH^-]$) is 1.02×10^3 which is sensibly nearer to its value of 0.92×10^3 calculated from Eq. (7). In the case of 2-methylpropan-1-ol, the inequality $1 + K_1K_2[S][OH^-] \gg K_1[OH^-]$ holds good and thus Eq. (8) is obtained from Eq. (4)

$$\frac{-d[OsO_4]}{dt} = \frac{nk_1K_1K_2[Os(VIII)]_{Total}[OH^-][S]}{1 + K_1K_2[S][OH^-]}. \qquad (8)$$

Rate law (8) fully explains the observed kinetics. At low [S] and $[OH^-]$, the inequality $1 \gg K_1K_2[S][OH^-]$ holds good and Eq. (9) results which explains first-order kinetics in OH^- ions and 2-methylpropan-1-ol at low concentrations

$$\frac{-d[OsO_4]}{dt} = nk_1K_1K_2[Os(VIII)]_{Total}[S][OH^-]. \qquad (9)$$

At higher $[OH^-]$ and [S] the inequality $K_1K_2[S][OH^-] \gg 1$ holds good and Eq. (8) is reduced to Eq. (10), which explains zero-order kinetics in hydroxyl ions and 2-methylpropan-1-ol at higher concentrations

$$\frac{-d[OsO_4]}{dt} = nk_1[Os(VIII)]_{Total}. \qquad (10)$$

The value of $k_1K_1K_2$ calculated from the slope of the plot (between $1/v_i$ against $1/[S]$ at constant $[OH^-]$) was found to be 2.18×10^3 which agrees well with its value of 2.08×10^3 obtained from the slope of the plot (between the rate and [S] at constant $[OH^-]$). The closeness in $k_1K_1K_2$ values obtained from Eqs (8) and (9) confirms the proposed mechanism. The formation of $[OsO_2(OH)_4]^{2-}$ in step (iii) is supported by the fact[21] that Os(VI) exists as $[OsO_2(OH)_4]^{2-}$. The suggested mechanism is only known to apply during the initial period and could be different in the latter stages.

REFERENCES

[1] J. W. Cook and R. Schoental, *Nature* **161**, 237 (1948).

[2] P. J. Besufils, *Bull. Soc. Chim. Fr.* **4**, 166 (1969).

[3] V. S. Khan, E. V. Fomina and A. A. Volskov, *Zh. Neorg. Khim.* **21**, 1257 (1976).

[4] W. H. Theilmann and E. Hecker, *Justus Liebigs Annln Chem.* **13**, 735 (1970).

[5] B. L. Chandwani and G. D. Menghani, *Indian J. Chem.* **15A**, 560 (1977).

[6] B. L. Chandwani and G. D. Menghani, *Z. Naturforsch.* **291**, 336 (1978).

[7] N. L. Wendler, *J. Am. Chem. Soc.* **72**, 234 (1950).

[8] R. Toyo, *Tetrahedron Lett.* 2259 (1964).

[9] B. Singh, B. B. Singh and R. P. Singh, *J. Inorg. Nucl. Chem.* **43**, 1283 (1981).

[10] F. Solymosi, *Naturwissenschaften* **44**, 374 (1957).

[11] B. Krishna and H. S. Singh, *Z. Phys. Chem.* **231**, 399 (1966).

[12] V. N. Singh, H. S. Singh and B. B. L. Saxena, *J. Am. Chem. Soc.* **91**, 2645 (1969).

[13] M. P. Singh, H. S. Singh, B. Singh, A. K. Singh and A. K. Singh, *Proc. Ind. Nat. Acad. Sci.* **41A**, 331 (1975).

[14] B. H. Anand and G. D. Menghani, *J. Indian Chem. Soc.* LVIII, 374 (1981).

[15] B. L. Chandwani and G. D. Menghani, *J. Inorg. Nucl. Chem.* **40**, 1946 (1981).

[16] B. Singh, A. P. Singh, N. Mishra, K. B. Lal and A. K. Singh, communicated.

[17] B. Singh, A. P. Singh and A. K. Singh, *Nat. Acad. Sci. Lett.* (1986), in press.

[18] W. P. Q. Griffith, *Rev.* **19**, 254 (1965).

[19] W. P. Griffith, *The Chemistry of Rare Platinum Metals.* Interscience, New York (1967–70).

[20] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, p. 1007. Wiley Eastern, New Delhi (1966).

[21] F. A. Cotton and G. Wilkinson, *Adv. Inorg. Chem.* 831 (1962).