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Kinetics of Uncatalysed & Ru(III) & Os(VIII) Catalysed Oxidations of Dimethyl Sulphoxide by Lead Tetraacetate

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Kinetics of uncatalysed and Ru(III) and Os(VIII) catalysed oxidations of DMSO by lead tetraacetate (LTA) in aqueous acetic acid and perchloric acid media have been studied. In the catalysed reactions the order in substrate is zero (Ru^{III}) and unity (Os^{VIII}) while in the uncatalysed reaction the order in substrate is zero. The order in oxidant for uncatalysed reaction is unity while the orders for catalysed reactions are unity (Ru^{III}) and zero (Os^{VIII}). The reaction is insensitive towards any change in acidity for Ru(III) catalysed oxidation. The acid dependence is unity in Os(VIII) catalysed reaction and fractional in the uncatalysed reaction. In both the catalysed reactions, the order in catalyst is unity. Increase in the percentage of acetic acid decreases the rate of reaction in both uncatalysed and catalysed reactions. Plausible mechanisms consistent with observed facts have been postulated.

Considerable work has been reported from our laboratory on the kinetics of both catalysed (Ru^{III} and Os^{VIII} as catalysts) and uncatalysed oxidations of dimethyl sulphoxide (DMSO) by various oxidants such as iron (III)[1], periodate[1], chloramine-T[2] in alkaline medium and bromate[3], iodate[3], N-chlorosuccinimide[4] and N-bromosuccinimide[4] in acid medium. The title investigation is an extension of the earlier work in which lead tetraacetate (LTA) is used as the oxidant in the presence and absence of Ru(III) and Os(VIII) catalysts.

Materials and Methods

All the compounds used were of AR(BDH) grade. Solutions of Os(VIII) and Ru(III) were prepared and standardised as reported earlier. The progress of the reaction was followed by estimating unreacted LTA iodometrically at regular time intervals.

Results and Discussion

Uncatalysed oxidation of DMSO

The rate data at varying concentrations of LTA, DMSO and $HClO_4$, given in Table 1, indicate first order dependence on [oxidant], zero order on [DMSO] and fractional order on $[H^+]$. The reaction rate decreases with increase in CH_3COOH content (Table 1) thereby suggesting that the active oxidant species is $[Pb(OAc)_3]^+[ClO_4]^-$, in aqueous medium (Table 1). The existence of this species is known in literature[5]. Added salts like $NaClO_4$, NaOAc, $Mg(OAc)_2$ cause retardation in rate. The values of the activation parameters have been evaluated at 60°C and found to be $E_a = 58.92$ kJ mol^{-1}, $\Delta H\ddagger = 56.20$ kJ mol^{-1}, $\Delta S\ddagger = -119.1$ JK^{-1} mol^{-1} and $\log A = 7.05$.

Based on the kinetic data the mechanism in Scheme 1 is proposed.

$$Pb(OAc)_4 + HClO_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pb(OAc)_3]^+[ClO_4]^- + HOAc$$

$$[Pb(OAc)_3]^+[ClO_4]^- \underset{slow}{\overset{k_2}{\rightleftharpoons}} Pb(OAc)_2 + OAc^+ + ClO_4^-$$

$$OAc^+ + (CH_3)_2S{=}O + H_2O \xrightarrow{fast} \text{Dimethyl sulphone} + HOAc + H^+$$

Scheme 1

Scheme 1 leads to rate equation (1)

$$-\frac{d[LTA]}{dt} = \frac{Kk_2[H^+][LTA]_T}{1+K[H^+]} \qquad \ldots(1)$$

where $K = k_1/k_{-1}$ and $[LTA]_T = [LTA] + [Pb(OAc)]^+ [ClO_4]^-$

Oxidation of DMSO catalysed by Os(VIII)

The reaction is zero order in [LTA] as indicated by the linear plot of the percentage of the reaction versus time, and by the constancy (Table 2) of the zero order rate constant (k_0). The order in [substrate] is unity as

Table 1—Pseudo-first Order Rate Constants at Varying [LTA], [DMSO] and [$HClO_4$]

[Solvent = 90% (v/v) aq. acetic acid; temp. = 60°C]

10^4[LTA] (mol dm^{-3})	10^3[DMSO] (mol dm^{-3})	10^2[$HClO_4$] (mol dm^{-3})	$10^3 k_1$ (min^{-1})
2.5	5.0	2.0	2.05
6.4	5.0	2.0	1.96
8.3	5.0	2.0	2.04
12.9	5.0	2.0	1.93
5.0	0.5	2.0	1.83
5.0	1.0	2.0	1.83
5.0	2.5	2.0	1.90
5.0	5.0	2.0	1.96
5.0	10.0	2.0	1.88
5.0	15.0	2.0	1.88
5.0	50.0	2.0	1.91
5.0	5.0	3.0	2.16
5.0	5.0	4.0	2.54
5.0	5.0	6.0	2.95
5.0	5.0	2.0	2.26[a]
5.0	5.0	2.0	0.96[b]
5.0	5.0	2.0	1.00[c]
5.0	5.0	2.0	3.76[d]

(a) In 85% (v/v) aq. acetic acid: (b) in 95% (v/v) aq. acetic acid; (c) at 50°C; and (d) at 70°C.

Table 2—Zero Order Rate Constants at Varying [LTA], [DMSO], [Os(VIII)] and [$HClO_4$]

[Solvent = 90% (v/v) aq. acetic acid; temp. = 60°C]

10^4[LTA] (mol dm^{-3})	10^3[DMSO] (mol dm^{-3})	10^6[Os(VIII)] (mol dm^{-3})	10^2[$HClO_4$] (mol dm^{-3})	$10^6 k_0$ (mol dm^{-3})
2.20	5.0	1.57	2	3.12
4.75	5.0	1.57	2	3.06
7.42	5.0	1.57	2	3.09
9.87	5.0	1.57	2	3.86
5.0	1.25	1.57	2	0.88
5.0	2.50	1.57	2	1.58
5.0	10.0	1.57	2	6.43
5.0	5.0	0.79	2	1.53
5.0	5.0	2.36	2	4.51
5.0	5.0	3.15	2	6.05
5.0	5.0	1.57	0.5	0.81
5.0	5.0	1.57	1	1.53
5.0	5.0	1.57	3	4.44
5.0	5.0	1.57	2	3.75[a]
5.0	5.0	1.57	2	1.57[b]
5.0	5.0	1.57	2	1.05[c]
5.0	5.0	1.57	2	5.69[d]

(a) In 85% (v/v) aq. acetic acid: (b) in 95% (v/v) aq. acetic acid (c) at 50°C; and (d) 70°C

revealed by the linear plot of log k_0 versus log [S] with unit slope and by the constancy of the first order rate constants ($k_1 = k_0$/[S]) (k_1 = 0.704, 0.632, 0.612, 0.643 $\times 10^{-6}$ min^{-1}) at different [substrate]. The order in Os(VIII) and [H^+] is unity each as revealed by the linear plots with unit slopes of log k_0 versus log [Os(VIII)] and log k_0 versus log [H^+] respectively.

Table 3—Pseudo-first Order Rate Constants at Varying [LTA] [DMSO], [Ru(III)] and [$HClO_4$]

[Solvent = 90% (v/v) aq. acetic acid; temp. = 35°]

10^4[LTA] (mol dm^{-3})	10^3[DMSO] (mol dm^{-3})	10^7[Ru(III)] (mol dm^{-3})	10^2[$HClO_4$] (mol dm^{-3})	$10^2 k_1$ (min^{-1})
2.8	5.0	1.54	2	2.04
5.3	5.0	1.54	2	2.12
7.9	5.0	1.54	2	1.96
10.4	5.0	1.54	2	1.96
5.0	2.5	1.54	2	1.95
5.0	7.5	1.54	2	2.11
5.0	10.5	1.54	2	2.26
5.0	15.0	1.54	2	2.42
5.0	5.0	0.77	2	0.98
5.0	5.0	2.31	2	3.08
5.0	5.0	3.08	2	4.24
5.0	5.0	1.54	1	2.12
5.0	5.0	1.54	3	1.96
5.0	5.0	1.54	4	2.04
5.0	5.0	1.54	2	2.68[a]
5.0	5.0	1.54	2	1.64[b]
5.0	5.0	1.54	2	1.16[c]
5.0	5.0	1.54	2	3.92[d]

(a) In 85% (v/v) aq. acetic acid: (b) in 95% (v/v) aq. acetic acid: (c) at 30°C and (d) at 40°C

The reaction rate decreases with increase in acetic acid content of the solvent system (Table 2). Rate constants decrease with the increase in concentrations of added salts like $NaClO_4$, NaOAc and $Mg(OAc)_2$. Activation parameters for Os(VIII) catalysed reaction at 60° are found to be $E_a = 82.7$ kJ mol^{-1}, $\Delta H^{\ddagger} = 79.9$ kJ mol^{-1}, $\Delta S^{\ddagger} = -120.8$ JK^{-1} mol^{-1} and log $A = 6.98$. These observations lead to the mechanism shown in Scheme 2, where S represents DMSO

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+$$

$$SH^+ + Os(VIII) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{(complex)}}{SH^+ \ldots Os(VIII)}$$

$$\text{Complex} \xrightarrow[\text{slow}]{k_3} Os(VI) + \text{dimethyl sulphone} + H^+$$

$$Os(VI) + Pb(IV) \xrightarrow[H_2O]{\text{fast}} Os(VIII) + Pb(II)$$

Scheme 2

Applying steady state approximation, Scheme 2 leads to rate law (2)

$$\text{Rate} = k_3[\text{Complex}] = \frac{\dfrac{K_1 K_2 k_3 [\text{S}][\text{H}^+]}{[\text{Os(VIII)}]}}{1 + \dfrac{k_3}{k_{-2}}} \quad \ldots(2)$$

Since $k_3/k_{-2} <<< 1$, Eq. (2) becomes Eq. (3) which explains all the observed facts.

$$\text{Rate} = k_3 K_1 K_2 [\text{S}][\text{H}^+][\text{Os(VIII)}] \quad \ldots(3)$$

Oxidation of DMSO catalysed by Ru(III)

The reaction is first order in [LTA] (Table 3). The reaction is insensitive towards change in [substrate]. The order in [Ru(III)] is unity. Increase in [$HClO_4$] has no effect on the reaction rate showing the absence of participation of acid in the reaction course (Table 3). The reaction rate decreases with increase in acetic acid content of the solvent and increase in concentrations of added salts like [$NaClO_4$], [NaOAc] and [$Mg(OAc)_2$]. The Arrhenius activation parameters computed at 35° are: $E_a = 94.2$ kJ mol^{-1}, $\Delta H^\ddagger = 91.6$ kJ mol^{-1}, $\Delta S^\ddagger = -30.1$ JK^{-1} mol^{-1} and log A = 14.82.

The mechanism of oxidation is given by Scheme 3.

$$\text{LTA} + \text{Ru(III)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex}$$

$$\text{Complex} \underset{k_2}{\overset{\text{slow}}{\rightarrow}} \text{Ru(V)} + \text{Pb}^{+2}$$

$$\text{DMSO} + \text{Ru(V)} \overset{\text{fast}}{\rightarrow} \text{Dimethyl sulphone} + [\text{Ru(H}_2\text{O)}_6]^{+3}$$

Scheme 3

Scheme 3 leads to rate law (4)

$$\text{Rate} = \frac{K_h k_2 [\text{LTA}]_T [\text{Ru(III)}]}{1 + K_h [\text{Ru(III)}]} \quad \ldots(4)$$

where $K_h = k_1/(k_{-1} + k_2)$.

Since Ru(III) concentration is of the order 10^{-7} mol dm^{-3} and the order in Ru(III) is unity the second term in the denominator is negligible. Hence the rate becomes,

$$-\frac{d[\text{LTA}]_T}{dt} = k_2 K_h [\text{Ru(III)}][\text{LTA}]_T \quad \ldots(5)$$

which explains all the observed facts.

References

1 Radhakrishnamurti P S & Padhi S C, *Curr Sci*, **46** (1977) 1097.
2 Radhakrishnamurti P S & Padhi S C, *Indian J Chem*, **17(A)** (1979).
3 Sahu N C, Ph.D. thesis, Berhampur University (1982).
4 Radhakrishnamurti P S & Panda H P, *J Indian chem Soc*, **56** (1979) 1247.
5 Robert J Ouellette, Daniel Miller, Aurbeysonth Jr. & Richard D Robins, *J Am chem Soc*, **91** (1969) 971.