

Osmium(VIII)-mediated oxidation of arsenic(III)/antimony(III) by 1-equivalent oxidants

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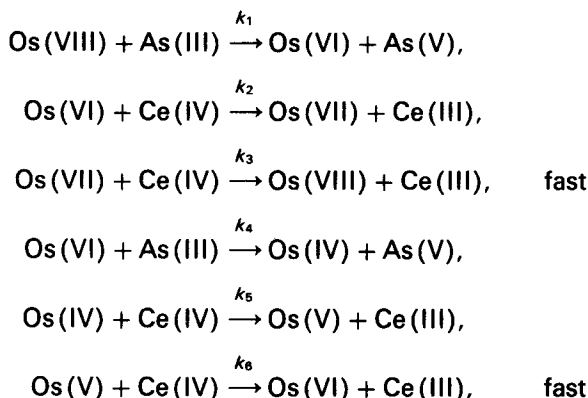
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Abstract. Os(VIII) catalysis of oxidation of As(III)/Sb(III) by 1-equivalent oxidants like Ce(IV) and Mn(III) in acid medium is studied. A multistep mechanism involving the intervention of the intermediate oxidation states of osmium is found to apply. Specific rates of different steps in the mechanism are estimated and used to calculate reaction rates which are in reasonable agreement with those of experiment.

Keywords. Osmium(VIII); oxidation; arsenic(III); antimony(III).

1. Introduction

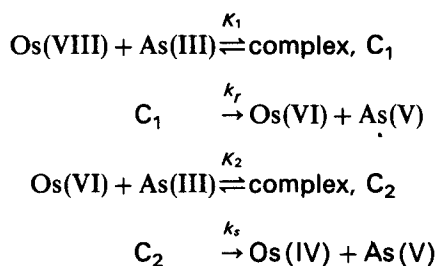
Osmium(VIII) catalysis of redox reactions may occur in acid, neutral and alkaline media but very few studies are available in acid media (Agrawal and Upadhyay 1983). In non-complementary redox reactions involving 1-electron oxidants, osmium(VIII) catalysis may occur with intervention of one or more of the intermediate oxidation states of osmium such as (VII), (VI) and (V). An example is the case of the cerium(IV)–arsenic(III) reaction in aqueous sulphuric acid (Robert *et al* 1967) and the multistep mechanism suggested involved all the above intermediates (scheme 1). As seen in the first step of this mechanism, the osmium(VIII)–arsenic(III) interaction results in osmium(VI) and arsenic(V) formation following by other steps.



Scheme 1.

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With reference to this first step it may be noted that no complex formation between osmium(VIII) and arsenic(III) was observed in this case. However, in the osmium(VIII)-catalysed vanadium(V)-arsenic(III) reaction. (Sambrani and Raju 1991) and, more particularly in the direct osmium(VIII)-arsenic(III) case (Tuwar *et al* 1991) in acid medium, a complex between osmium(VIII) and arsenic(III) was found to form followed by the oxidation steps. The direct reaction also involved the formation of an osmium(VI)-arsenic(III) complex as in scheme 2.



Scheme 2.

Furthermore, it was found in the osmium(VIII)-catalysed vanadium(V)-arsenic(III) reaction that the rate corresponding to k_1 (which may be approximately identified with $K_1 k_r$ of scheme 2), as compared with the osmium(VIII)-catalysed cerium(IV)-arsenic(III) case in acid medium, differed by approximately 10^4 although both reactions involved the same elementary osmium(VIII)-arsenic(III) reaction. Such results prompted us to examine the osmium(VIII)-catalysed oxidation reactions of arsenic(III)/antimony(III) with 1-electron oxidants like cerium(IV) and manganese(III). The results of a similar reaction with vanadium(V) in acid medium are given elsewhere (Sambrani and Raju 1991). Our study particularly concerned the applicability or otherwise of scheme 1 for such reactions.

2. Experimental

Reagent grade chemicals were used. Doubly distilled water was used throughout. The Ce(IV) stock solution was obtained by dissolving $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ in aqueous H_2SO_4 and standardising with Fe(II) solution (Vogel 1978). The Mn(III) solution had to be freshly prepared as it was found to degrade by approximately 3% in 24 h. Addition of $0.01 \text{ mol dm}^{-3} \text{KMnO}_4$ to $0.10 \text{ mol dm}^{-3} \text{MnSO}_4$ (Riedel) dissolved in $3.0 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ yielded an Mn(III) solution (Ubbelohde 1935) which was standardised with iron(II) solution. The Mn(III) solution thus obtained gave rise to a spectrum in the visible region in agreement with that reported earlier (Salim and Lingane 1959). The stock solution of Mn(III) prepared contained a small concentration of Mn(II) which did not interfere in the catalysed reactions (see *infra*, product effect). The presence of such concentrations of Mn(II) also help to prevent the disproportionation of Mn(III). The Os(VIII) stock solution was prepared by dissolving 1 g of OsO_4 (Johnson and Mathey) in aqueous H_2SO_4 and standardising with Ce(IV) solution (Saxena 1967). The As(III) solution was made by dissolution of As_2O_3 (BDH, AR) in $1.0 \text{ mol dm}^{-3} \text{NaOH}$ and its concentration was ascertained by titration with KBrO_3 solution (Vogel 1978). The base in the As(III) solution was neutralised with the required amount of acid in the preparation of the reaction

solution. The Sb(III) solution was made by dissolving Sb_2O_3 (S. Merck) in aqueous H_2SO_4 and standardised (Vogel 1978). The aqueous HClO_4 solution of Sb(III) was made by keeping Sb_2O_3 in 6.0 mol dm^{-3} HClO_4 overnight. The solution was then filtered and standardised. The stock solutions were diluted in presence of acid as required before each run. Dilute solutions of Os(VIII), however, were made from the stock solution before each series of related runs. Ionic strength was maintained with Na_2SO_4 in case of the H_2SO_4 reaction medium and with NaClO_4 for the HClO_4 medium. Ionic strength was maintained constant by taking the calculated H^+ , HSO_4^- and SO_4^{2-} concentrations by making use of the bisulphate equilibrium constant. The Sb(V) solution employed was made by mixing equivalent amounts of Sb(III) and KBrO_3 in solution and As(V) solution was obtained by dissolving K_3AsO_4 (BDH) in water. The temperature was constant within $\pm 0.05^\circ\text{C}$.

2.1 Kinetic measurements

Kinetic runs were initiated by mixing the previously thermostatted reactant solutions which also contained the required concentrations of Os(VIII), H_2SO_4 (or HClO_4) and Na_2SO_4 (or NaClO_4). The reaction was followed by periodically measuring absorbance of the reaction mixture in a 1 cm cell placed in the thermostatted compartment of a Bausch and Lomb Spectronic 2000 spectrophotometer at the required wavelength. The absorbances of Ce(IV) at 360 nm and of Mn(III) at 500 nm were found to obey Beer's law under the reaction conditions at 25°C ($\epsilon_{360} = 3555 \pm 1.5\%$ for Ce(IV) in the range of 5.50×10^{-5} to $4.0 \times 10^{-4} \text{ mol dm}^{-3}$ in 4.0 mol dm^{-3} H_2SO_4 at $\mu = 4.6 \text{ mol dm}^{-3}$ and $\epsilon_{360} = 3150 \pm 1.5\%$ between 5.0×10^{-5} and $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ Ce(IV) in 1.6 mol dm^{-3} HClO_4 at $\mu = 3.0 \text{ mol dm}^{-3}$; $\epsilon_{500} = 114 \pm 1.0\%$ for Mn(III) between 5.0×10^{-4} and $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ in 5.0 mol dm^{-3} H_2SO_4 at $\mu = 5.6 \text{ mol dm}^{-3}$). There was a marginal variation of molar absorptivity in H_2SO_4 ($\pm 1\%$) in both cases of Mn(III) and Ce(IV) with variation of the H_2SO_4 concentration. Os(VIII) did not have any perceptible absorption in all the cases studied and did not interfere to any extent in following the kinetics. Initial rates were reproducible within $\pm 4.0\%$ in case of runs with Ce(IV) whereas the errors were higher, $\pm 6.0\%$ in case of runs of Mn(III).

The log [Ce(IV)] vs. time plots are linear in the initial stages upto 50% ([reductant] > [oxidant]) the deviation from linearity beyond this stage being presumably due to the interference of the Os(VIII)-reductant direct reaction, the Os(VIII) tending to be reduced by the excess reductant as the oxidant is much decreased. First-order rate constants obtained from the initial linear portions for a few results are as follows. At [Ce(IV)] $\times 10^4$ of 0.5, 2.0, 3.0, 4.0 and 6.0 mol dm^{-3} , the pseudo-first order constants are 3.3, 3.1, 2.9, 2.8 and $2.8 \times 10^{-3} \text{ s}^{-1}$ respectively ([Sb(III)] = 5.0×10^{-4} , [Os(VIII)] = 3.5×10^{-8} , [H_2SO_4] = 4.0, $\mu = 4.30/\text{mol dm}^{-3}$, temp. 25°C).

2.2 Stoichiometry

Reactants of different sets of concentrations with a constant concentration Os(VIII) ($3.5 \times 10^{-8} \text{ mol dm}^{-3}$ and $2.0 \times 10^{-7} \text{ mol dm}^{-3}$ in the case of the oxidations by Ce(IV) and Mn(III), respectively, under the respective reaction conditions (see tables 1 to 3) were allowed to react over 24 h at 25°C and then analysed. The unreacted oxidants were found by measuring their absorbances at 360 and 500 nm whereas the reductants

Table 1. Effect of [Ce(IV)], [Sb(III)] and [Os(VIII)] on Os(VIII) mediated Ce(IV)-Sb(III) reaction in aq. H₂SO₄ at 298 K.(A) [Sb(III)] > [Ce(IV)]; [H₂SO₄] = 4.0, $\mu = 4.30/\text{mol dm}^{-3}$

10 ⁴ × [Ce(IV)]	10 ⁴ × [Sb(III)]	10 ⁸ × [Os(VIII)]	10 ⁷ × Rate (mol dm ⁻³ s ⁻¹)	
			Exp.*	Calc.
0.50	5.0	3.5	1.1	1.1
1.0	5.0	3.5	2.5	2.4
2.0	5.0	3.5	4.6	4.6
3.0	5.0	3.5	6.8	6.7
4.0	5.0	3.5	8.7	8.7
6.0	5.0	3.5	13.0	13.0
1.0	1.0	3.5	2.5	2.6
1.0	8.0	3.5	2.4	2.3
1.0	10.0	3.5	2.4	2.3
1.0	30.0	3.5	2.5	2.3
1.0	40.0	3.5	2.4	2.2
1.0	5.0	2.4	1.7	1.6
1.0	5.0	4.8	3.2	3.2
1.0	5.0	6.0	4.0	4.0
1.0	5.0	7.2	4.7	4.8
1.0	5.0	8.4	5.6	5.6

(B) [Ce(IV)] > [Sb(III)]; [H₂SO₄] = 4.0; $\mu = 4.30/\text{mol dm}^{-3}$

10 ⁴ × [Ce(IV)]	10 ⁴ × [Sb(III)]	10 ⁸ × [Os(VIII)]	10 ⁷ × Rate (mol dm ⁻³ s ⁻¹)	
			Exp.*	Calc.
0.50	2.5	3.5	1.9	2.1
1.0	2.5	3.5	2.5	2.5
2.0	2.5	3.5	2.6	2.6
4.0	2.5	3.5	2.5	2.5
5.0	2.5	3.5	2.5	2.5
3.5	3.5	3.5	3.3	3.5
3.5	5.0	3.5	4.8	4.8
3.5	7.5	3.5	6.9	6.8
3.5	10.0	3.5	8.5	8.0
3.5	15.0	3.5	8.7	8.9
3.5	20.0	3.5	8.9	9.3
4.0	2.5	0.60	0.68	0.66
4.0	2.5	1.2	1.1	1.0
4.0	2.5	2.4	1.9	1.8
4.0	2.5	4.8	3.0	3.0

*Exp. – experimental; calc. – calculated

were analysed by titration with KBrO₃ and one of the products (Sb(V)/As(V)) was also estimated. The results indicated a 2:1 stoichiometry as given below.

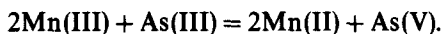
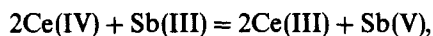


Table 2. Effect of [Ce(IV)], [Sb(III)] and [Os(VIII)] on Os(VIII) mediated Ce(IV)–Sb(III) reaction in aq. HClO₄ at 25°C.(A) [Sb(III)] > [Ce(IV)]; [H₂SO₄] = 4.0, [Ce(IV)] = 1.0 × 10⁻⁴; μ = 3.0/mol dm⁻³

10 ⁴ × [Sb(III)]	10 ⁸ × [Os(VIII)]	[HClO ₄]	10 ⁷ × Rate (mol dm ⁻³ s ⁻¹)	
			Exp.	Calc.
5.0	0.6	1.6	1.9	1.8
5.0	1.2	1.6	3.3	3.4
5.0	3.5	1.6	6.9	8.0
5.0	4.8	1.6	9.8	9.8
5.0	6.0	1.6	11.0	12.0
1.0	3.5	2.6	8.2	8.2
5.0	3.5	2.6	8.9	9.1
10.0	3.5	2.6	9.8	10.0
15.0	3.5	2.6	10.6	10.4
20.0	3.5	2.6	10.7	11.3

(B) [Ce(IV)] > [Sb(III)]; [H₂SO₄] = 0.40; [HClO₄] = 1.6, μ = 3.0/mol dm⁻³.

10 ⁴ × [Ce(IV)]	10 ⁵ × [Sb(III)]	10 ⁸ × [Os(VIII)]	10 ⁷ × Rate (mol dm ⁻³ s ⁻¹)	
			Exp.	Calc.
0.50	2.0	1.8	1.1	1.2
1.0	2.0	1.8	1.4	1.3
2.0	2.0	1.8	1.4	1.4
4.0	2.0	1.8	1.3	1.4
5.0	2.0	1.8	1.3	1.4
4.0	4.0	1.8	2.8	2.8
4.0	5.8	1.8	4.0	3.9
4.0	7.8	1.8	5.6	5.1
4.0	9.7	1.8	6.3	6.2
4.0	16.0	1.8	9.3	9.3
4.0	20.0	1.8	11.0	11.0
4.0	2.0	0.30	0.45	0.42
4.0	2.0	1.2	0.89	0.82
4.0	2.0	3.0	1.5	1.40
4.0	2.0	4.2	2.0	2.00
4.0	2.0	6.0	2.4	2.45

Abbreviations as in table 1

3. Results

3.1 Rate law

In view of the complexity of the reaction, the order of the reaction was determined under different conditions extending from excess [oxidant] over [reductant] through [oxidant] ~ [reductant] to [oxidant] much less compared to [reductant]. The orders were determined from log–log plots of initial rates vs. concentrations. The order in catalyst, osmium(VIII), was found under two extreme conditions: oxidant concentration being around eightfold excess over that of the reductant and vice versa (see

Table 3. Effect of [Mn(III)], [As(III)] and [Os(VIII)] on Os(VIII) mediated Mn(III)–As(III) reaction in aq. H₂SO₄ at 25°C.(A) [As(III)] > [Mn(III)]; [H₂SO₄] = 5.0, $\mu = 5.6/\text{mol dm}^{-3}$

10 ³ × [Mn(III)]	10 ² × [As(III)]	10 ⁸ × [Os(VIII)]	10 ⁵ × Rate (mol dm ⁻³ s ⁻¹)	
			Exp.	Calc.
1.0	3.0	20.0	1.0	1.1
3.0	3.0	20.0	3.0	3.1
5.0	3.0	20.0	5.0	4.8
7.5	3.0	20.0	7.8	6.8
10.0	3.0	20.0	11.0	9.0
5.0	1.0	20.0	3.7	3.6
5.0	5.0	20.0	5.1	5.1
5.0	6.5	20.0	5.2	5.2
5.0	8.0	20.0	5.3	5.3
5.0	3.0	3.1	2.3	2.2
5.0	3.0	9.3	3.4	3.3
5.0	3.0	16.0	4.8	4.9
5.0	3.0	31.0	7.2	7.1
5.0	3.0	37.0	9.0	9.0

(B) [Mn(III)] > [As(III)]; [Os(VIII)] = 2.0 × 10⁻⁷; [H₂SO₄] = 5.0, $\mu = 5.6/\text{mol dm}^{-3}$.

10 ² × [Mn(III)]	10 ³ × [As(III)]	10 ⁵ × Rate (mol dm ⁻³ s ⁻¹)	
		Exp.	Calc.
0.25	0.40	0.21	0.21
0.50	0.40	0.21	0.21
1.0	0.40	0.22	0.22
1.2	0.40	0.21	0.22
1.5	0.40	0.23	0.23
1.0	0.20	0.10	0.10
1.0	0.80	0.41	0.43
1.0	1.40	0.90	0.80
1.0	2.0	1.0	1.0

tables 1 to 3). The order in osmium(VIII) was slightly less than unity in both reactions under both extreme conditions. Since the catalyst osmium(VIII) activity had been found to be very much lower in the case of the vanadium(V)–arsenic(III) reaction (Sambrani and Raju 1991) an attempt was made in this study to compare the effect of catalyst at a catalyst concentration of $\sim 10^{-8} \text{ mol dm}^{-3}$ in the cerium(IV)–antimony(III) reaction with a similar catalyst effect at a catalyst concentration on the range $\sim 10^{-5} \text{ mol dm}^{-3}$ in the vanadium(V)–arsenic(III) reaction at 25°C. The high concentration of catalyst used in the latter case was needed (as in the case of many other studies in alkali media (Mehrotra and Mushran 1968; Sengupta and De 1975; Mohan and Gupta 1977; Sengupta and Basu 1977, 1978) to bring about suitable rate acceleration. The results found in this regard at constant concentrations of reactants are shown as rate vs osmium(VIII) concentration in figure 1 and table 4. The order in reductant and oxidant were also determined at different intermediate

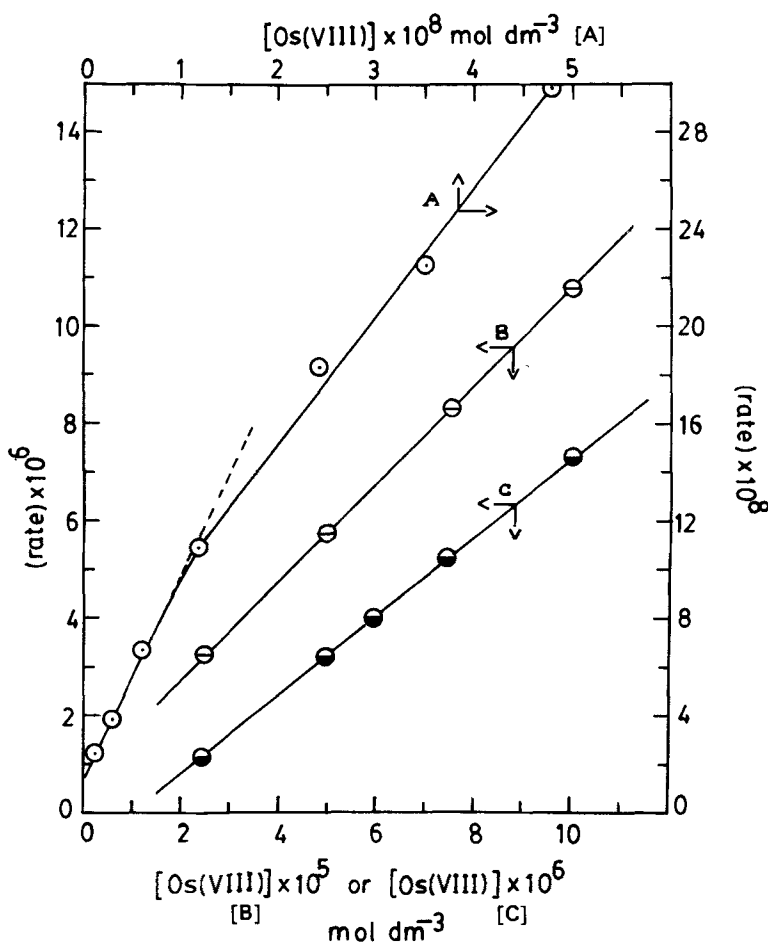


Figure 1. Plot of rate vs osmium(VIII) concentration (conditions as in table 4).

Table 4. Effect of [Os(VIII)] on oxidation of Sb(III)/As(III) by one equivalent oxidants at 25°C.

[Os(VIII)](mol dm ⁻³)	Rate/[Os(VIII)](s ⁻¹)
4.0 × 10 ⁻⁵ to 3.6 × 10 ⁻⁴	0.03 ^a
2.4 × 10 ⁻⁸ to 8.4 × 10 ⁻⁸	6.3 ^b
1.2 × 10 ⁻⁸ to 4.8 × 10 ⁻⁸	5.0 ^c
1.5 × 10 ⁻⁹ to 6.0 × 10 ⁻⁹	9.8 ^c

^a[V(V)] = 4.0 × 10⁻³; [As(III)] = 2.0 × 10⁻²; [H₂SO₄] = 4.0 (Sambrani and Raju 1991); μ = 4.3/mol dm⁻³

^b[Ce(IV)] = 1.0 × 10⁻⁴; [Sb(III)] = 5.0 × 10⁻⁴; [H₂SO₄] = 4.0; μ = 4.6/mol dm⁻³

^c[Ce(IV)] = 4.0 × 10⁻⁴; [Sb(III)] = 2.5 × 10⁻⁵; [H₂SO₄] = 4.0; μ = 4.3/mol dm⁻³

stages covering entire range of the two extremes of oxidant concentration being eight-to tenfold excess over the reductant concentration and the reductant concentration being eight-to tenfold excess over the oxidant concentration. In both reactions studied, the order of unity in oxidant decreases through fractions to zero as the conditions change from [reductant] > [oxidant] through [reductant] ~ [oxidant] to the case where [reductant] < [oxidant]. Likewise, as the conditions are changed in the reverse order from excess oxidant to the stage of excess reductant, the order in reductant changes from unity through fraction to zero. In both reactions, neither product influenced the reaction. At all other conditions, being constant, the variation of H⁺ concentration led to rates which indicated a fractioned order in H⁺ in case of cerium(IV) oxidations and inverse fractional order in case of the manganese(III) oxidation. Variation of ionic strength in both reactions did not cause appreciable changes.

Independent studies were also made to ascertain the intervention of intermediate oxidation states of osmium as was done in the study of cerium(IV)–arsenic(III) reaction (Robert et al 1967) and osmium(VIII)–arsenic(III) case (Tuwar *et al* 1991). When [As(III)] > 2[Os(VIII)], osmium(IV) resulted and when [As(III)] = [Os(VIII)], the resulting osmium(VI) could be characterised from its spectrum (Tuwar *et al* 1991). These results indicated that intervention of lower oxidation states than osmium(IV) in the catalysed reaction were unlikely, and, while it was difficult to detect osmium(VII) and osmium(V), such species may also be involved in the catalytic cycle of Os(VIII)–Os(IV)–Os(VIII).

In view of the possibility of the interaction of SO₄²⁻ in the reactions, experiments were performed with varying concentrations of SO₄²⁻ keeping all other conditions constant in perchlorate-perchloric acid media in both cases. It was found that added sulphate did not lead to any recognizable effect on the rate of reactions and hence its interaction is precluded.

4. Discussion

The title reaction displays a complex rate law as indicated below. While the Os(VIII) order remains almost constant throughout the wide range of relative concentration variation of the reactants, the orders in the two reactants vary as shown,

$$\frac{-d}{dt}[(As(III))] \text{ or } \frac{-d[Sb(III)]}{dt} = \text{rate} = k[\text{oxidant}]^x[\text{Os(VIII)}][\text{reductant}]^y,$$

x and *y* can have values of unity through fractional to zero depending on the conditions.

(*x* → 0 as [oxidant] → 8[reductant] or higher;

y → 0 as [reductant] → 8[oxidant] or higher)

such results may be accounted for in terms of scheme 1.

Scheme 1 seems to be general to all cases of osmium(VIII)-catalysed oxidation of arsenic(III) (or antimony(III), by 1-electron oxidants like manganese(III) and

cerium(IV) in acid media. A direct verification of the applicability of this mechanism to the cases of manganese(III) and cerium(IV) can be made using the rate law (1) derived for scheme 1.

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{2k_1 k_5 [\text{Ce(IV)}][\text{Sb(III)}][\text{Os(VIII)}]_t (k_2 [\text{Ce(IV)}] + k_4 [\text{Sb(III)}])}{k_2 k_5 [\text{Ce(IV)}]^2 + k_1 k_5 [\text{Ce(IV)}][\text{Sb(III)}] + k_1 k_4 [\text{Sb(III)}]^2} \quad (1)$$

A similar rate law with Mn(III) for [Ce(IV)] in (1) applies for the manganese(III)–arsenic(III) case. Rate law (1) is comprehensive enough to include all experimental orders determined. Thus, for example, under conditions of [Ce(IV)] \gg [Sb(III)], it reduces to the form (2) and, when [Sb(III)] \gg [Ce(IV)] to the form (3).

$$\text{Rate} = 2k_1 [\text{Sb(III)}][\text{Os(VIII)}]_t,$$

$$\text{Rate} = 2k_5 [\text{Ce(IV)}][\text{Os(VIII)}]_t. \quad (3)$$

when [Ce(IV)] \gg [Sb(III)], osmium(VIII) in scheme 1 can be seen to be restricted to the catalytic cycle of Os(VIII)–Os(VI)–Os(VIII) as it is unlikely that the excess cerium(IV) will allow reduction below osmium(VI) stage. Again, under conditions when the reductant is in excess, the osmium(VIII) is quickly reduced to the osmium(IV) state and is now restricted to the cycle Os(VI)–Os(IV)–Os(VI) as in the excess of reductant higher oxidation states than the osmium(VI) are improbable. The simplified rate laws (2) and (3) obtain because of these simplified schemes and because steps 3 and 6 in scheme 1 are fast.

A start for verification of (1) can be made with values of k_1 and k_5 obtained from the extreme cases when (2) and (3) apply. Use of these k_1 and k_5 values to other experimental conditions along with rate law (1) permits evaluation of k_2 and k_4 ; this set of rate constants now enables calculation of rates for all experimental conditions from (1). The values of k_1 , k_2 , k_4 and k_5 obtained were 1.4×10^5 , 2.3×10^5 , 7.1×10^5 and $3.3 \times 10^4/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the Os(VIII)-catalysed Ce(IV)–Sb(III) case in aqueous sulphuric acid and 2.0×10^5 , 0.96×10^5 , 1.6×10^5 and $2.3 \times 10^5/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in perchloric acid and 1.3×10^4 , 0.96×10^4 , 2.1×10^4 and $2.8 \times 10^4/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the Os(VIII)-catalysed Mn(III)–As(III) case. Rates thus calculated are compared in tables 1 to 3 with the experimentally found rates and show reasonable agreement.

Scheme 1 seems to be satisfactory for the two cases studied. No evidence of complex formation between osmium(VIII) and arsenic(III) (or antimony(III)) was obtained in this study unlike in the case of the osmium(VIII) catalysed vanadium(V)–arsenic(III) and the osmium(VIII) oxidation of arsenic(III). In the latter two cases, an osmium(VIII)–arsenic(III) complex first formed and then split up into osmium(VI) and arsenic(V) followed by other steps. It can be seen that an approximate comparison of K_1 of $1.4 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (of scheme 1 Ce(IV)–Sb(III) reaction : table 1) may be made with $K_1 k_r$ of $4.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (of V(V)–As(III) reaction) showing that the vanadium(V) reaction is extremely slow because of the intervention of the complex (Sambrani and Raju 1991). It was also found elsewhere (Sandell 1959) that when large concentrations of osmium(VIII) catalyst were used, quantitative reoxidation of reduced osmium is difficult. A comparison of the effectiveness of the catalyst in the oxidations with cerium(IV) and vanadium(V) is shown in table 4 where

rate/[Os(VIII)] is shown at different ranges of osmium(VIII) concentrations used, other conditions and reactant concentrations in the particular ranges being constant. It is seen in table 4, that the catalyst is most effective at the lowest concentrations of $\sim 10^{-9}$ and when no catalyst substrate complex is intervening in the reaction. As osmium(VIII) concentration increases its effectiveness is found to decrease.

The effect of increasing sulphuric acid on the osmium(VIII) catalysed cerium(IV)–antimony(III) reaction resulting in fractional order is due to the fact that several cerium(IV) sulphate complexes are involved in the reaction, the more active among them being the $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$ species as shown elsewhere (Kampli 1988). Since a small amount of sulphuric acid was used in the dissolution of cerium(IV) which is also present in the runs when the effect of perchloric acid on the reaction was studied, sulphate complexes of cerium(IV) as well as $\text{Ce}(\text{OH})^{3+}$ are likely to be involved in the oxidation in presence of perchloric acid (Kampli 1988). This accounts for the comparatively less fractional order (~ 0.3) in perchloric acid media as compared to the order of 0.43 in sulphuric acid–sulphate media. Rates in case of manganese(III) oxidation decrease with increase of sulphuric acid and it has been shown elsewhere (Kampli *et al* 1989) that the chief oxidant species of manganese(III) in such media is MnOH^{2+} and since MnOH^{2+} is more potent than Mn^{3+} , rates tend to decrease with increase of acidity in this case. The osmium(VIII) species in acid media (Mehrotra and Mushran 1970) is understood as H_2OsO_5 with very low dissociation constant and hence qualitatively it may be inferred that ionic strength would not significantly affect the reaction as noted in the experiment.

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