

Manganese(II) catalysed cerium(IV) oxidation of arsenic(III) in aqueous sulphuric acid

S A Chimatadar, S T Nandibewoor & J R Raju*
Department of Chemistry, Karnatak University,
Dharwad 580 003

Received 5 August 1988; revised 9 February 1989;
accepted 22 February 1989

Manganese(II) catalysed Ce(IV) oxidation of arsenic(III) in aqueous sulphuric acid takes place with intervention of a Mn(III) species, presumably MnOH^{2+} . The active oxidant is understood to be a Ce(IV) sulphate complex of the formula, $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$.

The chromium(III) catalysis of Ce(IV)-As(III) reaction is understood to occur via a Cr(IV) species and involves Ce(IV) sulphate complexes as active species¹. Manganese(II) also catalyses this reaction in aqueous sulphuric acid and in view of the several oxidation states possible for Mn, an investigation dealing with the kinetics and mechanism of Mn(II)-catalysed reaction is of interest and hence the title investigation.

Experimental

The reagents and the kinetic procedure employed were similar to those adopted earlier¹. Runs were usually followed at 30° and 40° and the rates of reaction were reproducible within $\pm 5\%$. The same sample of manganese(II) sulphate (Riedel) was used throughout. Different reaction mixtures with varying $[\text{Ce(IV)}]$, $[\text{As(III)}]$ and $[\text{Mn(II)}]$ were allowed to stand at 30°C for over 2 hr and then analysed as in earlier work¹ and a 2:1 stoichiometry between Ce(IV) and As(III) was observed for the reaction; the catalyst, $[\text{Mn(II)}]$, remained unchanged as found by estimating² it with EDTA at pH = 10.

Results and discussion

At a fixed ionic strength of 5.0 mol dm^{-3} , $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ and $[\text{Mn(II)}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$, the approximate orders in Ce(IV) and As(III) were 1.0 and 0.8 respectively in the Ce(IV) and As(III) concentration ranges of 0.001-0.010 and 0.010-0.10 mol dm^{-3} , respectively. Orders were determined from log-log plots of initial rates and concentrations. The orders in Mn(II) and initially added product Ce(III) were approximately +1 and -0.5 respectively in the concentration ranges of 0.005-

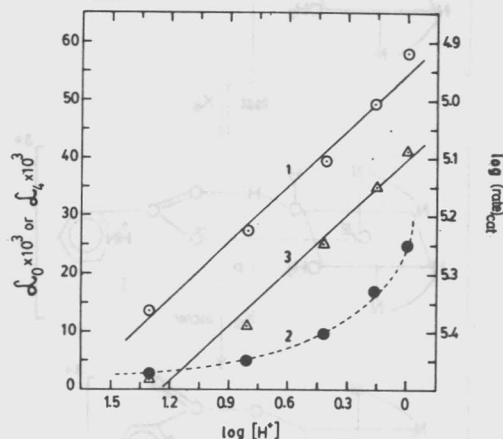


Fig. 1—Variation of fractions of total $[\text{Ce(IV)}]$ of the different Ce(IV) species and $(\text{rate})_{\text{cat}}$ (1) with $[\text{H}^+]$. (α_0) (2) and α_4 (3) refer to the species Ce^{4+} and $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$. α_1 , α_2 and α_3 , relating to CeSO_4^+ , $\text{Ce}(\text{SO}_4)_2$ and $\text{HCe}(\text{SO}_4)_3^-$ respectively, did not change appreciably over the $[\text{acid}]$ used and hence are not shown).

0.050 and 0.004-0.012 mol dm^{-3} , respectively. Initially added As(V) did not have significant effect.

The initial rates increased with increase in $[\text{H}_2\text{SO}_4]$, at fixed concentrations of the other reactants (Table 1). In sulphuric acid media, Ce(IV) forms different sulphate complexes³ and the concentrations of the different species, Ce^{4+} , $\text{Ce}(\text{SO}_4)_2^{2+}$, $\text{Ce}(\text{SO}_4)_2$, $\text{HCe}(\text{SO}_4)_3^-$ and $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$ were calculated as in earlier work¹ making use of the respective stability constants, β_1 , β_2 , β_3 , β_4 , added $[\text{Ce(IV)}]$, $[\text{H}^+]$ and $[\text{HSO}_4^-]$; these H^+ and HSO_4^- concentrations, in turn, were calculated from the added concentrations of sulphuric acid and sulphate and the known equilibrium constant of the acid sulphate equilibrium⁴. Figure 1 shows the variation of $\log(\text{initial rate})$ with the fractions, α , of the total Ce(IV) constituting the species Ce^{4+} (α_0) and $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$ (α_4) over $[\text{H}_2\text{SO}_4]$ used. The concentrations of the other Ce(IV) species do not change appreciably or even decrease with increase in $[\text{acid}]$ used (Table 1). The order in free $[\text{H}^+]$ was found from initial rates as ~ 0.4 .

Cerium(IV) oxidation of arsenic(III) in acid sulphate medium proceeds with a measurable speed in the absence of the catalyst¹. Hence, in the presence of Mn(II), the reaction is understood to occur in parallel paths with contributions from the uncatalysed and catalysed paths.

The experimental results concerning the orders, effect of initially added products, acid and catalyst are well accommodated by the rate law (1); rate_{cat}

Table 1—Variation of different Ce(IV) species[†] with added sulphuric acid [Ce(IV)] = 2[As(III)] = 0.01, [Mn(II)] = 0.005, *I* = 3.5 mol dm⁻³, 40°C

[H ₂ SO ₄] mol dm ⁻³	10 ³ α ₀	α ₁	α ₂	10 ² α ₃	10 ³ α ₄	10 ⁶ (rate) _{cat} / mol dm ⁻³ s ⁻¹
0.2	2.7	0.72	0.22	4.7	1.7	4.3
0.4	5.0	0.79	0.14	5.5	11	5.9
0.6	9.8	0.84	0.083	4.1	25	7.8
0.8	17	0.87	0.051	2.8	35	9.8
1.0	25	0.88	0.036	2.1	41	12

[†]α₀, α₁, α₂, α₃ and α₄ are the fractions of total Ce(IV) of the species Ce⁴⁺, CeSO₄²⁺, Ce(SO₄)₂, HCe(SO₄)₃⁻ and H₃Ce(SO₄)₄⁻ respectively. The stability constants of the different Ce(IV) complexes are from ref. 3 and the acid sulfate equilibrium constant used is from ref. 4.

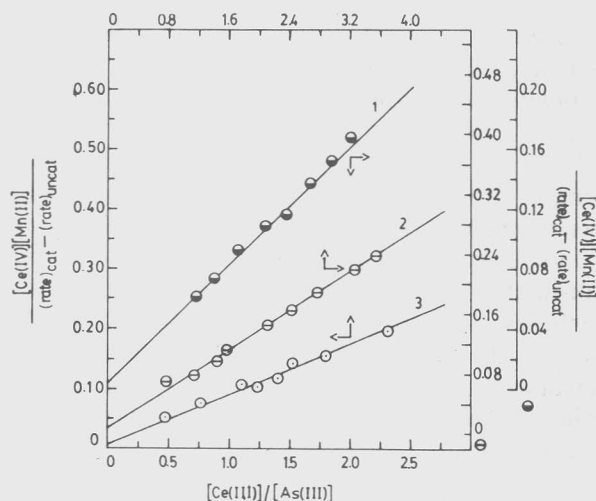


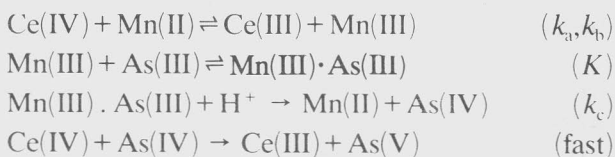
Fig. 2—Verification of rate law (1) (Effect of acid concentrations: 0.6 (1), 0.8 (2) and 1.0 (3) mol dm⁻³ conditions as in Table 1)

and rate_{uncat} represent initial rates of catalysed and uncatalysed reactions respectively.

$$(\text{rate})_{\text{cat}} - (\text{rate})_{\text{uncat}} =$$

$$\frac{2k_a k_c K [\text{Ce(IV)}][\text{Mn(II)}][\text{As(III)}][\text{H}^+]}{k_b [\text{Ce(III)}] + K [\text{As(III)}] (1 - k_c [\text{H}^+])} \quad \dots (1)$$

Rate law (1) is in agreement with the mechanism shown in Scheme 1 where the oxidation occurs in single electron transfer steps. Scheme 1 does not take into account the reported disproportionation⁵ of Mn(III) into Mn(II) and Mn(IV) as it would



Scheme 1

lead to a different rate law. Moreover, in media of high [H₂SO₄] the disproportionation is unimportant and Mn(III) is comparatively stable⁵.

In view of the very low dissociation constant⁶ of H₃AsO₃ (2.8 × 10⁻¹⁰), the predominant form of As(III) is H₃AsO₃ itself. As regards Ce(IV), of the different sulphate complexes it forms, only the H₃Ce(SO₄)₄⁻ concentrations parallel the rate data at different [H₂SO₄] and hence this species is concluded to be the prime active oxidant. Pseudo-first order conditions, at different initial [Ce(IV)] also support this conclusion. The catalyst intermediate, Mn(III), is likely to be active in the form of MnOH²⁺ as it has been noted that the latter form can exist even in highly concentrated perchloric acid solutions⁷. Indeed, somewhat low order in [H⁺] is presumably due to a mechanism (see Scheme 1) which results in rate law (1) and, in part, may be due also to MnOH²⁺ being the active form of manganese(III). Since Scheme 1 also leads to rate law (1), the latter is verified from plots of ([Ce(IV)][Mn(II)]/(rate_{cat} - rate_{uncat})) versus [Ce(III)]/[As(III)] for different [H⁺] which are found to be linear as expected (Fig. 2).

References

- Chimatadar S A, Nandibewoor S T, Sambrani M I & Raju J R, *J chem Soc Dalton Trans* (1987) 573.
- Vogel A I, *Textbook of quantitative inorganic analysis*, (ELBS, Longman, NY) 1978, 330.
- Kharzeova S E & Serebrennikov V V, *Russ J inorg Chem*, 12, (1967) 1601; Bugaenko K T & Huang Kuam-lin, *Russ J inorg chem*, 8 (1963) 1299.
- Kulba F Ya, Yakovlev Yu B & Mironov V L, *Russ J inorg chem*, 10 (1965) 1113.
- Diebler H & Sutin N, *J phys Chem*, 68 (1964) 174; Selim R G & Lingane J J, *Anal chim acta*, 21 (1959) 536.
- Pal B B, Mukherjee D C & Sengupta K K, *J inorg nucl chem*, 34 (1972) 3433; Ivakin A A, Vorobeva S V, Gertman E M & Voronova E M, *Russ J inorg chem*, 21 (1976) 237.
- Fackler Jr J P & Chawla I D, *Inorg Chem*, 3 (1964) 1130; Wells C F & Davies G, *Nature*, 205 (1965) 692.