Thallium(III) Oxidation of Oxovanadium(IV)

S A CHIMATADAR, S T NANDIBEWOOR & J R RAJU*

Department of Chemistry, Karnatak University, Dharwad 580003

Thallium(III) oxidation of oxovanadium(IV) has been studied in sulphuric acid-sulphate medium at constant ionic strength of 5 mol dm^{-3} and 70°. Results are in accord with a two-step mechanism with participation of thallium(II). An inverse dependence of rate on [acid] indicates the active oxidant species to be a hydrolysed thallium(III) species and participation of sulphate complexes of oxovanadium(IV) and oxovanadium(V) in the reaction.

The kinetics and mechanism of thallium(III) oxidation of a number of reductants in perchlorate-perchloric acid medium have been investigated earlier[1]. However, in view of the slow decomposition of the oxidant[2] in this medium in the presence of oxovanadium(IV) at 60-80°C, we decided to carry out the title investigation in sulphuric acid medium. We have earlier shown that Tl(III) is quite stable in sulphuric acid medium[3]. Even in the presence of oxovanadium(IV) the oxidant is stable in sulphuric acid medium.

Stock solution of Tl(III) was prepared by dissolving thallium(III) oxide (BDH) in hot 2 N sulphuric acid and standardised with EDTA (Analar) solution[4]. Oxovanadium(IV) sulphate (Loba) was dissolved in 1 N sulphuric acid and standardised titrimetrically using standard Ce(IV) solution. Sodium vanadate (BDH) was the source of the oxovanadium(V) used. Other chemicals used were of reagent grade. Doubly distilled water was used for the preparation of solutions.

Reactant solutions preequilibrated at 70°C, were mixed, the acidity (2 N) and ionic strength (5.0 mol dm^{-3}) being adjusted by adding sulphuric acid and sodium sulphate respectively. Aliquots from the reaction mixture were withdrawn at regular time intervals and titrated in the presence of acetic acid against standard Ce(IV) solution using ferroin as indicator[5]. The reaction in most cases was followed up to 75% completion. Stoichiometric experiments, carried out under similar conditions, showed that one mol of Tl(III) reacted with two mol of V(IV).

Under the conditions of the titration there was virtually no reaction between Ce(IV) and Tl(I). The oxovanadium content found in this way by titration with Ce(IV) was in agreement with that found spectrophotometrically by measuring the absorbance

at 765 nm using Spectronic 2000 Bausch and Lomb spectrophotometer. The E^{765} for oxovanadium(IV) concentrations up to 10^{-2} mol dm^{-3} in 1 mol dm^{-3} sulphuric acid at an ionic strength of 5 mol dm^{-3} was 17.25. Duplicate runs agreed within 3%.

The order with respect to thallium(III) was one in the concentration range of 4×10^{-3} to 12×10^{-3} mol dm^{-3} and the order in vanadium(IV) was 1.24 in the concentration range of 7.7×10^{-3} to 22×10^{-3} mol dm^{-3} as found by log (rate)-log (conc) plots. Added vanadium(V) decreased the second order rate while added thallium(I) had no effect (Table 1). Second order plots also showed curvature quite early in a run as compared to the thallium(III)-iron(II) reaction[6]. These results are compatible with the mechanism shown in Scheme 1.
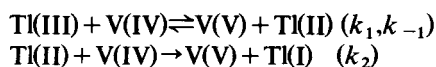
$$Tl(III) + V(IV) \rightleftharpoons V(V) + Tl(II) \quad (k_1, k_{-1})$$
$$Tl(II) + V(IV) \rightarrow V(V) + Tl(I) \quad (k_2)$$
Scheme 1

This mechanism was suggested earlier for Tl(III) oxidation of V(IV) in perchloric acid-perchlorate medium[2]. In accord with Scheme 1, the rate law is given by Eq. (1) which can be rearranged to Eq. (2). The plot of left hand side of Eq. (2) against [V(V)]/[V(IV)] is linear, the intercept and slope of which give the values of k_1 and k_{-1}/k_2. The plots at

$$-\frac{d[V(IV)]}{dt} = \frac{2k_1 k_2 [V(IV)]^2 [Tl(III)]}{k_{-1}[V(V)] + k_2[V(IV)]} \quad \cdots (1)$$

$$-\frac{[V(IV)] [Tl(III)]}{d[V(IV)]/dt} = \frac{k_{-1} [V(V)]}{2k_1 k_2 [V(IV)]} + \frac{1}{2k_1} \quad \cdots (2)$$

four different acid concentrations are shown in Fig. 1. At constant ionic strength and different [H$_2$SO$_4$] of 0.5, 0.75, 1.0 and 1.5 mol dm^{-3}, values of k_1 and k_{-1}/k_2 were 0.24, 0.10, 0.038, 0.015 dm^3 mol^{-1} s^{-1} and 0.20, 0.59, 1.97, 3.94 respectively. The decrease in k_1 with increase in [H$_2$SO$_4$] is expected if a hydrolysed thallium(III) species is the active oxidant. In fact, the

Table 1—Effect of Added Product on Thallium(III)-Oxovanadium(IV) Reaction

2[Tl(III)] = [V(IV)] = 0.02 mol dm^{-3}; [H$_2$SO$_4$] = 1 mol dm^{-3};
temp. 70°; μ = 5 mol dm^{-3}

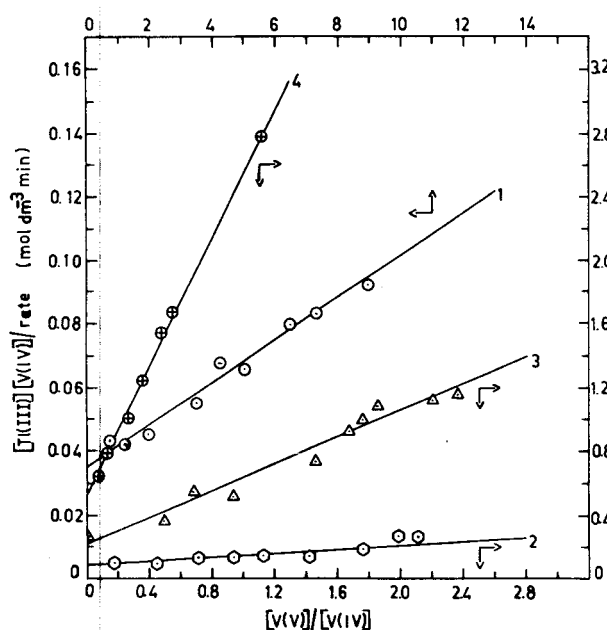| [Tl(I)] (mol dm^{-3})	$k \times 10^3$ (dm^3 mol^{-1} s^{-1})	[V(V)] (mol dm^{-3})	$k \times 10^3$ (dm^3 mol^{-1} s^{-1})
Nil	13.4	Nil	13.4
0.005	13.2	0.005	8.91
0.010	13.4	0.010	7.47
0.015	13.5	0.015	6.47

Fig. 1—Plot of $[V(IV)][Tl(III)]/(d[V(IV)]/dt)$ versus $[V(V)]/[V(IV)]$ at $[H_2SO_4]$ of 0.5 (1), 0.75 (2), 1.0 (3) and 1.5 mol dm^{-3} (4)

concentrations of $TlOH^{2+}$ calculated from its equilibrium constant[1] (0.072), added $[Tl(III)]$ and [acid] parallel the decreases in k_1. When such $TlOH^{2+}$ concentrations were used in place of Tl(III) in the plots of the left hand side of Eq. (2) against $[V(V)]/[V(IV)]$ in Fig. (1), a common intercept of approximately 0.025 dm^3 mol^{-1} min^{-1} ($k_1 \simeq 0.3$ dm^3 mol^{-1} s^{-1}) resulted at four different acid concentrations.

The increase in k_1/k_2 ratio with increase in [acid] in the reaction medium may be due to either increase of k_{-1} or decrease of k_2 with increase in [acid] or both. In aqueous sulphuric acid-sulphate medium, the main V(IV) and V(V) species are known to be $VO(SO_4)_2^{2-}$ and $VO_2H(SO_4)_2^{2-}$ which may chiefly be responsible for the changes in the rate constants. Thus, the concentration of $VO(SO_4)_2^{2-}$ is inversely proportional to acidity in view of the sulphate-bisulphate equilibrium: $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$, and hence may cause lowering of k_2 (and also of k_1) with increase in [acid]. Similarly, the concentration of $VO_2H(SO_4)_2^{2-}$ may be expected to increase marginally with increase in [acid], thereby causing an increase in k_{-1}. The equilibrium constants of the V(IV) and V(V) species are known[7,8] to be 320 and 110 respectively in a medium of $\mu = 3$ mol dm^{-3}. Since other sulphate complexes are also possible in the reaction medium, the prevailing multiple equilibria preclude a more detailed analysis of this effect.

References

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