

Platinum Catalysed Thallium(III) Oxidation of Vanadium(IV) in Aqueous Sulphuric Acid

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Thallium(III) oxidation of V(IV) in the presence of bright platinum metal in sulphuric acid and sulphate medium at ionic strength 5 mol dm^{-3} and 70°C occurs at a faster rate than the reaction in the absence of platinum. The details of the uncatalysed and catalysed reactions and the nature of the active species are discussed.

The non-complementary Tl(III) oxidation of V(IV) in aqueous sulphuric acid as well as in aqueous perchloric acid¹ was shown to occur by a two-step process involving a reactive Tl(II) species. However, details of the active species and the complete rate law in terms of such active species were not given. Platinum metal catalyses the non-complementary Tl(III)-Fe(II) reaction². We present herein the results of the platinum catalysis of Tl(III)-V(IV) reaction and the details of the mechanism of the uncatalysed as well as the catalysed reaction.

Thin plates of platinum metal were repeatedly washed with aqua regia followed by distilled water. The surface area was found from the thickness and other dimensions of the plates. The method of preparation of solutions, stoichiometric experiments, the details of kinetic runs and calculation of rate constants etc. were similar to those employed for the uncatalysed reaction reported earlier¹.

The Tl(III) oxidation of V(IV) in the presence of bright platinum in sulphuric acid and sulphate medium at 70°C and at an ionic strength of 5 mol dm^{-3} parallels the uncatalysed reaction in stoichiometry, reaction order and effects of added products and acid. The stoichiometry was 1:2 and of the products, viz. Tl(I) and V(V), only the latter retarded the reaction and Tl(I) had no effect. As a result the second order plots developed curvature similar to that in the uncatalysed reaction. The second order rate constants (k), used for a comparison of different effects, were obtained from the slopes of the best linear plots of $1/(a-x)$ versus time (see Fig. 1). It is seen from Fig. 1 that the intercepts (0.60 and 0.56) are somewhat larger than the experimental value of 0.5. At fixed $[\text{V(IV)}]$ and varying $[\text{Tl(III)}]$ (4.0×10^{-3} to $12.0 \times 10^{-3} \text{ mol dm}^{-3}$) and

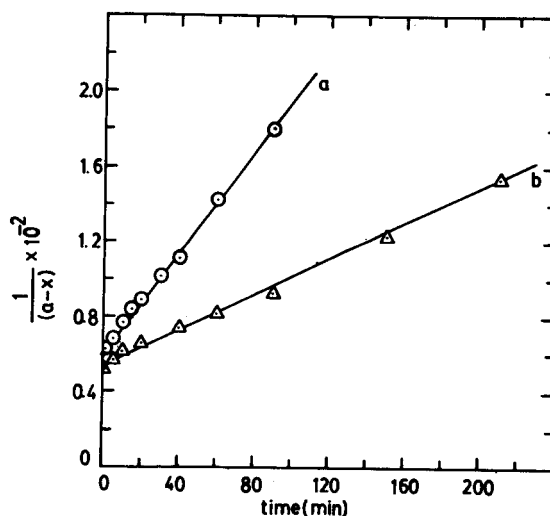


Fig. 1—Plot of $1/(a-x)$ versus time ($[\text{H}_2\text{SO}_4] = 1 \text{ mol dm}^{-3}$ (a) at 70°C and (b) at 60°C . Other conditions are same as in Table 1)

Table 1—Effect of Sulphuric Acid Concentration on the Platinum Catalysed Tl(III)-V(IV) Reaction

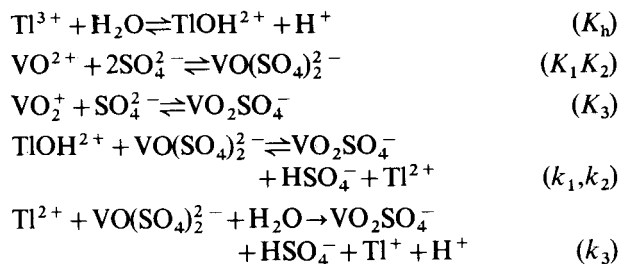
$2[\text{Tl(III)}] = [\text{V(IV)}] = 0.02 \text{ mol dm}^{-3}$; $\mu = 5 \text{ mol dm}^{-3}$; temp. 70°C ;
Surface area of platinum = 27.51 cm^2

$[\text{H}_2\text{SO}_4]$ mol dm^{-3}	$[\text{H}^+]$ † mol dm^{-3}	$[\text{SO}_4^{2-}]$ † mol dm^{-3}	$[\text{HSO}_4^-]$ † mol dm^{-3}	$k \times 10^2$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0.50	0.004	0.62	0.996	18.4
0.75	0.026	0.15	1.47	6.31
1.00	0.39	0.012	1.61	2.04
1.5	1.38	0.003	1.62	0.667

†Calculated from added sulphuric acid and sulphate concentrations and the acid sulphate equilibrium constant³.

fixed $[\text{Tl(III)}]$ and varying $[\text{V(IV)}]$ (7.7×10^{-3} to $22.0 \times 10^{-3} \text{ mol dm}^{-3}$), the reaction orders in $[\text{V(IV)}]$ and $[\text{Tl(III)}]$ were unity each in the presence of platinum metal of surface area 27.51 cm^2 . The second order rate constant (k) increased linearly with the surface area of platinum with a gradient of $3.81 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ cm}^{-2}$.

The second order rate constant (k) also decreased with increase in acidity in the presence of platinum (Table 1) as in the case of the uncatalysed reaction. In sulphuric acid and sulphate medium, $[\text{H}^+]$ and $[\text{sulphate}]$ were determined by the acid sulphate equilibrium ($K = 0.0026$ at 70°C)³. Over the range of the added $[\text{sulphuric acid}]$ (0.5 to 1.5 mol dm^{-3}), it was found that the reaction was inverse fractional order (0.27) in $[\text{H}^+]$ and direct fractional order (0.30) in



Scheme 1

[sulphate]. The probable active species of Ti(III), V(IV) and V(V) under the reaction conditions are TiOH^{2+} , $\text{VO}(\text{SO}_4)_2^-$ and VO_2SO_4^- . The detailed mechanism in terms of these species must take into account prior equilibria of formation of these species as shown in Scheme 1. This mechanism accounts for all the experimental results. The rate law is given by Eq. (1) where the formation of a lower complex of V(IV), VOSO_4 , is also taken into account. According to Eq. (1), a plot of $[\text{V(IV)}][\text{Ti(III)}]/(\text{rate})$ versus $[\text{V(V)}]/[\text{V(IV)}]$ should be linear. This is found to be so.

$$\frac{-d[\text{V(IV)}]}{dt} = \frac{2k_1 k_3 k_2^2 k_h^2 K_h [\text{V(IV)}]^2 [\text{Ti(III)}] [\text{SO}_4^{2-}]^4}{(1 + K_1 [\text{SO}_4^{2-}] + K_1 K_2 [\text{SO}_4^{2-}]^2)^2 (K_h + [\text{H}^+]) \left\{ \frac{k_2 K_2 [\text{V(V)}] [\text{SO}_4^{2-}] [\text{HSO}_4^-]}{(1 + K_3 [\text{SO}_4^{2-}])} + \frac{k_3 K_1 K_2 [\text{V(IV)}] [\text{SO}_4^{2-}]^2}{(1 + K_1 [\text{SO}_4^{2-}] + K_1 K_2 [\text{SO}_4^{2-}]^2)} \right\}} \quad \dots (1)$$

From the slopes and intercepts of such plots as well as the known⁴ values of K_1 , K_2 , K_3 and K_h (55.0, 5.82, 6.9 and 0.072 respectively) the values of k_1 and k_2/k_3 are obtained as $0.30 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and 0.30 respectively for the platinum catalysed reaction, the surface area of the platinum used being 27.51 cm^2 . For the uncatalysed reaction under comparable conditions, the value of k_1 was virtually the same but the k_2/k_3

ratio was slightly larger (0.36). This shows that the catalysis, which is not large, occurs with respect to the second step of the reaction (k_3) while the first step remains unaffected. Thus platinum catalyst facilitates the electron transfer between V(IV) and Ti(II) (see ref. 5). The catalytic effect of platinum in Ti(III)-V(IV) reaction is also somewhat lower as compared to that for Ti(III)-Fe(II) reaction in aqueous perchloric acid².

The activation parameters of the Ti(III)-V(IV) reaction with respect to the forward reaction of the first step, k_1 , are determined as 125 kJ mol^{-1} and 117 JK^{-1} , both for the catalysed and uncatalysed reactions. The formation of complexes such as VOSO_4 and $\text{VO}(\text{SO}_4)_2^-$ in sulphate-rich media is facile. In cases where the sulphate concentration is small as compared to $[\text{V(IV)}]$, very little $\text{VO}(\text{SO}_4)_2^-$ is formed and a partial formation of VOSO_4 may be expected. Thus, an analysis of the results of the Ti(III)-V(IV) reaction in low sulphate (high H^+) medium has shown that while $\text{VO}(\text{SO}_4)_2^-$ is not formed to any appreciable extent, VOSO_4 is rather inactive and VO^{2+} is reactive under such conditions. Thus, rate law (1) is directly applicable to the reaction in high sulphate media.

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