

Kinetics & Mechanism of Oxidation of Tellurium(IV) by Thallium(III) in Perchloric Acid Medium

L S A DIKSHITULU*, R RAM BABU & P VANI

Department of Inorganic and Analytical Chemistry, School of Chemistry, Andhra University, Waltair 530 003

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The kinetics of oxidation of Te(IV) by Tl(III) has been studied in 2.0-3.0 mol dm⁻³ perchloric acid medium. The order in [Te(IV)] and [Tl(III)] is unity each. Increase in [H⁺] causes a marked decrease in the rate of the reaction. Added Cl⁻, Br⁻ and NO₃⁻ ions retard the rate of reaction, while SO₄²⁻ ion does not have any effect. Consistent with the results, a mechanism involving hydrolysis of Tl³⁺ to TlOH²⁺ followed by the oxidation of the hydroxo species of tellurium, TeO(OH)⁺, by TlOH²⁺ in a slow step is proposed.

Depending on the nature of oxidant, oxidation of Te(IV) to Te(VI) proceeds either in a single step¹⁻⁶ or in two successive one-electron steps involving the formation of Te(V) as an intermediate⁷⁻¹⁰. The oxidation of Te(IV) by Tl(III), though complimentary, may proceed through either of the two possible mechanisms especially because both the oxidant and reductant are capable of exhibiting intermediate oxidation states. We have, therefore, undertaken the title investigation with a view to elucidating its mechanism.

Solution of Te(IV) (0.1 mol dm⁻³) was always prepared fresh by dissolving sodium tellurite (LR, BDH) in doubly distilled water and its strength checked. A 0.1 mol dm⁻³ solution of Te(VI) in 1.0 mol dm⁻³ perchloric acid was prepared from sodium tellurate (LR, BDH) and its strength verified¹¹.

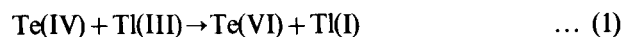
Stock solution of thallium(III) perchlorate (0.1 mol dm⁻³) was prepared as follows: Thallium(III) oxide (LR, BDH) was dissolved in conc. nitric acid, the solution evaporated and thallic hydroxide precipitated by adding potassium hydroxide¹². The precipitate was washed free from even traces of chloride, dissolved in perchloric acid and the solution standardized iodometrically¹³. A 0.04 mol dm⁻³ aqueous solution of thallium(I) was prepared from thallium(I) sulphate (AR, BDH), which was recrystallised from water to free it from traces of chloride. The solution of thallium(I) was standardized against bromate¹⁴.

All other chemicals used were of AR grade.

The kinetics of the reaction were studied at 70 ± 0.1°C in perchloric acid medium, keeping [Te(IV)]

in large excess over [Tl(III)]. The reaction was followed bromometrically¹⁴, estimating the amount of Tl(I) formed, after quenching the reaction by pouring the reaction mixture into 0.5 N HCl. The course of the reaction was followed upto two half-lives and the plots of log [Tl(III)] versus time were linear. The pseudo-first order rate constants (*k'*) were reproducible within ± 5%.

The stoichiometry of the reaction corresponds to 1:1 in accordance with Eq. (1)



The reaction products Te(VI) and Tl(I) did not affect the rate of reaction. However, anions like Cl⁻, Br⁻ and NO₃⁻ had considerable retarding effect although SO₄²⁻ did not have any effect on the rate of reaction.

The effect of varying ionic strength on the rate of reaction was studied by varying it from 2.0-6.0 mol dm⁻³ using sodium perchlorate. Even sodium perchlorate prepared by the neutralization of sodium carbonate (AR, BDH) with perchloric acid (Merck, proanalysis) was found to contain a little chloride. Similar observation was made by Roig and Dodson¹⁵ and by Favier and Zador¹⁶. Ionic strength variation studies were, therefore, carried out in the presence of a small amount of silver sulphate, to precipitate out the chloride. The results, thus obtained showed a slight decrease in rate with increase in ionic strength. For example, under the conditions: [Te(IV)] = 2.0 × 10⁻² mol dm⁻³; [Tl(III)] = 5.0 × 10⁻⁴ mol dm⁻³; [H⁺] = 2.0 mol dm⁻³; [Ag⁺] = 5.0 × 10⁻⁴ mol dm⁻³ and temp. = 70°C, the *k'*(× 10⁵, s⁻¹) value of 10.6 at μ = 2.0 mol dm⁻³ decreased to 8.5 at μ = 6.0 mol dm⁻³. This may be merely a medium effect.

The order with respect to Te(IV) was determined by carrying out the kinetic runs in 3.0 mol dm⁻³ HClO₄ [in view of the formation of a small amount of white precipitate in 2.0 mol dm⁻³ HClO₄ when the concentration of Te(IV) was high], keeping the concentrations of all other ions constant but varying the [Te(IV)] from 5.0-30.0 × 10⁻³ mol dm⁻³. The *k'* values thus obtained were found to increase with increase in [Te(IV)], the plot of *k'* versus [Te(IV)] being linear passing through origin, indicating the order in [Te(IV)], to be unity.

The fact that the plots of log [Tl(III)] versus time are linear [when Tl(III) was isolated] indicates that the order in [Tl(III)] is one. However, when [Tl(III)] was varied, keeping the concentrations of all other ions constant, the value of *k'* decreased with increase in [Tl(III)]. For example under the conditions: [Te(IV)]

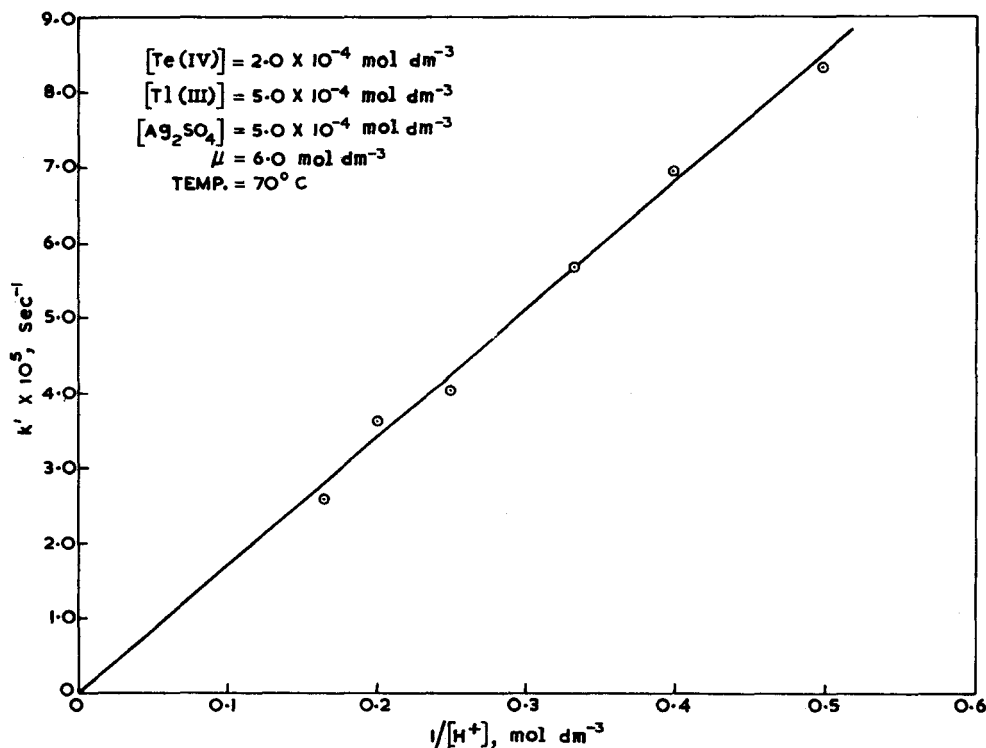


Fig. 1—Plot of k' (=rate/[Tl(III)]) versus $1/[H^+]$

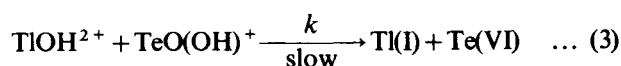
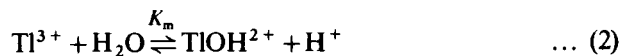
$= 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = 3.0 \text{ mol dm}^{-3}$ and temp. $= 70^\circ C$, the k' ($\times 10^5, \text{ s}^{-1}$) values were 10.4, 6.9, 5.4, 3.2, 1.9, 1.1 and 0.6 at $[Tl(III)]$ of 2.5, 5.0, 10.0, 15.0, 20.0, 25.0 and $30.0 \times 10^{-4} \text{ mol dm}^{-3}$ respectively. This may be attributed to the formation of less reactive dimeric Tl(III) species at higher concentrations.

At $[Te(IV)] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[Tl(III)] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ the effect of varying $[H^+]$ was studied in the range of 2.0 to 6.0 mol dm^{-3} using perchloric acid [a little silver sulphate ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) was added to precipitate out the chloride present in sodium perchlorate] and maintaining the ionic strength constant at 6.0 mol dm^{-3} (NaClO_4). With increase in $[H^+]$ from 2.0 mol dm^{-3} to 6.0 mol dm^{-3} the rate constant ($k' \times 10^5, \text{ s}^{-1}$) decreased from 8.4 to 2.6.

The effect of temperature on the rate of reaction was studied at $60^\circ, 65^\circ, 70^\circ$ and $75^\circ C$ and the k' ($\times 10^5, \text{ s}^{-1}$) values were found to be 5.0, 7.2, 11.1 and 17.3 respectively. E_a and ΔS^\ddagger were calculated using linear-least squares method and were found to be $80.4 \pm 6.3 \text{ kJ mol}^{-1}$ and $-63.7 \pm 18.4 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively.

Under the experimental conditions employed in the present investigations Te(IV) exists¹⁷ as $\text{TeO}(\text{OH})^+$ or $\text{Te}(\text{OH})_3^+$. The hydrolysis constant of Tl^{3+} at $25^\circ C$ was reported by Biedermann¹⁸ to be $0.073 \text{ mol dm}^{-3}$ at $\mu = 3.0 \text{ mol dm}^{-3}$, whereas Rogers and Waind¹⁹

reported the value to be $0.086 \text{ mol dm}^{-3}$ at $\mu = 1.5 \text{ mol dm}^{-3}$. Hence, under our present experimental conditions (2.0 to $3.0 \text{ mol dm}^{-3} \text{ HClO}_4$) Tl(III) exists mainly as Tl^{3+} with a small fraction existing as TlOH^{2+} . Since the plot of rate constant versus $1/[H^+]$ is linear passing through origin, the reactive species of Tl(III) may be regarded as TlOH^{2+} . In the presence of Cl^- the hydroxo species TlOH^{2+} gets converted into relatively unreactive TlCl^{2+} ion²⁰, thus causing a decrease in rate with increase in $[\text{Cl}^-]$. Similar unreactive species are probably formed with Br^- and NO_3^- ions also. Based on these observations Eqs (2) and (3) are proposed for the oxidation of Te(IV) by Tl(III) in perchloric acid medium.



This mechanism leads to the rate law (4)

$$\begin{aligned} \text{Rate} &= \frac{d[\text{Tl(I)}]}{dt} = -d[\text{Tl(III)}] dt \\ &= k[\text{Tl}(\text{OH}^{2+})]_e [\text{TeO}(\text{OH})^+] \quad \dots (4) \end{aligned}$$

But

$$[\text{Tl}^{3+}]_t = [\text{Tl}^{3+}]_e + [\text{TlOH}^{2+}]_e \quad \dots (5)$$

and

$$K_h = \frac{[\text{TlOH}^{2+}]_e [\text{H}^+]}{[\text{Tl}^{3+}]_e} \quad \dots (6)$$

Substituting for $[\text{TlOH}^{2+}]_e$ from Eqs (5) and (6) in Eq. (4), we get

$$\text{Rate} = \frac{k K_h [\text{Tl}^{3+}]_i [\text{Te(IV)}]}{[\text{H}^+] + K_h} \quad \dots (7)$$

Under our present experimental conditions, K_h can be neglected in the denominator of Eq. (7) and the simplified rate law is then given by Eq. (8)

$$\text{Rate} = \frac{k K_h [\text{Tl}^{3+}] [\text{TeO(OH)}^+]}{[\text{H}^+]} \quad \dots (8)$$

Equation (8) predicts that the plot of k' (rate/ $[\text{Tl}^{3+}]$) versus $1/[\text{H}^+]$ should be linear passing through the origin. This is found to be the case (see Fig. 1), thus substantiating the proposed mechanism.

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