Oxidation of thallium(I) by permanganate in aqueous perchloric acid

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Permanganate oxidation of thallium(I) in aqueous perchloric acid has 2:3 stoichiometry (oxidant: reductant) and manganese(IV) and thallium(III) are the products. A clean second order kinetics is followed by the reaction with fractional dependence on [acid]. The results are explained by a mechanism involving $HMnO_4$ as the active oxidant species.

Thallium(I) is a two-electron reductant and is easily oxidised by permanganate in acid medium but the mechanism is not known and hence the title investigation. Reduction of permanganate to either manganese(IV) or manganese(II) is possible, the former state being attained in reactions with two electron reductants[1].

Experimental

Reagent grade chemicals and doubly distilled water were used. Aqueous solutions of potassium permanganate (BDH, AR) and thallium(I) sulphate were standardised by titrating against oxalic acid and potassium bromate respectively. Thallium(III) solution was prepared by dissolving thallium(III) oxide (BDH) in 2.0 mol dm^{-3} perchloric acid and standardised against EDTA solution. Manganese(IV) solution was prepared in hot 1:1 perchloric acid and standardised as reported in literature. Manganese(IV) solution of concentration higher than around 1.0×10^{-3} mol dm^{-3} was unstable under the experimental conditions employed. Therefore, solutions of manganese(IV) with concentrations less than $\sim 7.0 \times 10^{-4}$ mol dm^{-3} which were stable over 5-6 hrs under the experimental conditions were used in the study.

Kinetic procedure

Thermally equilibrated solutions of MnO_4^- and Tl(I), which also contained the required quantities of perchloric acid and sodium perchlorate to give the required acidity and ionic strength, were mixed and the reaction was followed spectrophotometrically by measuring the absorbance of MnO_4^- in the reaction mixture at 526 nm on a Bausch and Lomb Spectronic 2000 instrument. The application of Beer's law under the reaction conditions had earlier been verified in the concentration range of 0.50×10^{-4} to 4.0×10^{-4} mol dm^{-3} of MnO_4^- in 1.0 mol dm^{-3} perchloric acid with $\varepsilon = 2400 \pm 25$. Initial rates were reproducible within $\pm 5\%$.

Stoichiometry

Different reaction mixtures containing different [reactants] in 1.0 mol dm^{-3} perchloric acid solution and sodium perchlorate ($I = 1.10$ mol dm^{-3}) were kept at 25° for over 4 hrs. The oxidant, MnO_4^-, was found by measuring its absorbance at 526 nm. Tl(III) formed was analysed as the Tl(III)-PAN complex[2] by extraction of the latter into chloroform at $pH = 2.4$-5 and measuring its absorbance at 570 nm. Manganese(IV) was found from the absorption spectrum of the reaction mixture in 9 M sulphuric acid[3].

Manganese(IV) formed in the reaction showed no insoluble form under the reaction conditions as observed by Nepheloturbidimeter. However, under the conditions of [Mn(VII)] greater than around 1.0×10^{-3} mol dm^{-3}, the product formed showed a precipitate of manganese dioxide. The results of the reaction showed that two moles of oxidant were required for the oxidation of three moles of thallium(I).

$$2Mn(VII) + 3Tl(I) = 2Mn(IV) + 3Tl(III) \qquad \ldots (1)$$
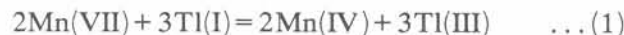
Results

Under the conditions of $[MnO_4^-]$ in the range of 0.25×10^{-4} to 2.5×10^{-4} mol dm^{-3}, $[Tl(I)] = 3.0 \times 10^{-4}$ mol dm^{-3}, acidity $= 1.0$ mol dm^{-3} and ionic strength $= 1.10$ mol dm^{-3}, log-log plots of initial rates versus $[MnO_4^-]$ led to an order of approximately unity in [oxidant]. Under similar conditions, the order in [Tl(I)] in the concentration range of 0.50×10^{-4} to 6.0×10^{-4} mol dm^{-3}, at $[Mn(VII)] = 2.0 \times 10^{-4}$ mol dm^{-3}, was also found to be unity. Measurement of initial rates at different [acid] ranging from 0.25 to 1.25 mol dm^{-3} perchloric acid, other conditions being constant, led to an order of around 0.83 in [acid]. Initially added product, Tl(III), did not affect the reaction significantly; but, initial addition of varying amounts of [Mn(IV)] increased the rate leading to an order of around 0.40 in [Mn(IV)].

The Mn(VII)-Tl(I) reaction has a stoichiometry of 2:3 ([Mn(VII)]:[Tl(I)]) and intervention or forma-
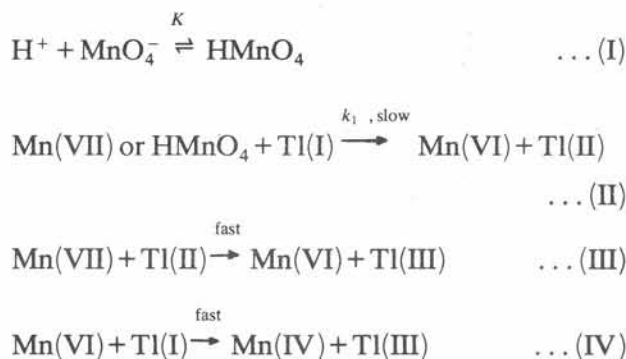
tion of Mn(III) and Mn(II) may be regarded as unlikely. This conclusion was supported by the non-detection of both Mn(III) and Mn(II) at the end of the reaction. Manganese(VI), Mn(V) and Tl(II) might be involved in the reaction. However, while Mn(VI) and Mn(V) are known only in basic solution[4]. Tl(II) is rather shortlived[5]. Hence, no experimental tests could be carried out in these cases.

Variation of ionic strength between 1.1 and 2.0 mol dm^{-3} by addition of the requisite [NaClO$_4$] reduced the rate. For example, under the conditions $3[MnO_4^-] = 2[Tl(I)] = 6.0 \times 10^{-4}$ mol dm^{-3}, [HClO$_4$] = 1.0 mol dm^{-3} at 24°C, an increase in ionic strength from 1.1 to 2.0 mol dm^{-3} decreased the initial rate from 11.3×10^{-7} to 5.17×10^{-7} mol dm^{-3}s^{-1}. On the other hand, the initial rate increased with increase in dielectric constant (decrease in acetic acid content) of the medium. Under identical conditions as mentioned above, when the acetic acid content (%v/v) was increased from 0 to 50, the initial rate decreased from 11.3×10^{-7} to 2.77×10^{-7} mol dm^{-3}s^{-1}. Salt effects on the reaction were also studied and, while added sodium nitrate and sodium sulphate did not affect the reaction rate to any significant extent, added chloride influenced the reaction rate appreciably.

At constant acidity, ionic strength and other constant conditions, the effect of increasing temperature between 24° and 34°C was studied (values of k_2 at 24.0°, 29.0° and 34.0°C were 41.3, 47.2 and 55.6 dm^{3}mol^{-1}s^{-1} respectively) and the activation parameters obtained are: $E_a = 22.6 \pm 3$ kJmol^{-1} and $\Delta S^{\neq} = -148.3 \pm 4$ JK^{-1}mol^{-1}.

Discussion

The Mn(VII)-Tl(I) reaction is a noncomplementary one with the oxidant undergoing a three equivalent reduction and Tl(I) undergoing a two equivalent change. No evidence for the lower oxidation states of manganese such as Mn(III) and Mn(II) was found. Again, Mn(VI) and Mn(V) are unstable in acid media[4] and could not be detected. The intervention of Tl(II) in many cases of oxidation reaction of Tl(I) in acid solutions is well established although its intervention is difficult to detect since it is very short-lived[5]. Manganese(IV) which is a product, catalyses the reaction and hence the second order plot of $1/(a-x)$ versus time deviates from linearity (Fig. 1). The other product, Tl(III), has no effect on the reaction. The reaction order of two (unity in each reactant) and fractional order in acid can be accommodated by a mechanism shown in Scheme 1. The active oxidant species is likely to be the monoprotonated species of Mn(VII)(HMnO$_4$) as indicated by the

$$H^+ + MnO_4^- \overset{K}{\rightleftharpoons} HMnO_4 \qquad \ldots (I)$$

$$Mn(VII) \text{ or } HMnO_4 + Tl(I) \xrightarrow{k_1, \text{ slow}} Mn(VI) + Tl(II) \qquad \ldots (II)$$

$$Mn(VII) + Tl(II) \xrightarrow{\text{fast}} Mn(VI) + Tl(III) \qquad \ldots (III)$$

$$Mn(VI) + Tl(I) \xrightarrow{\text{fast}} Mn(IV) + Tl(III) \qquad \ldots (IV)$$

Scheme 1

effect of acidity on the reaction. Oxidation by unprotonated oxidant occurs to a negligible extent, around 0.4% of the total oxidation. That permanganic acid (HMnO$_4$) is a stronger oxidant than MnO$_4^-$ has also been observed in other cases[6]. The steps beyond the slow step are all likely to be fast in view of the fact that short-lived intermediates of manganese or thallium are involved. Since none of the intermediates could be identified, Scheme 1 is only one of the different possible mechanisms for the reaction, steps beyond step(II) being uncertain. It may be noted that both Mn(V) and Mn(VI) are stable only in strongly basic media[4]. However, Tl(II) has been found to intervene[5] in oxidation of Tl(I) in acid solutions. Scheme 1 leads to rate law (2) which may be rearranged to the form (3) suitable for verification. A plot
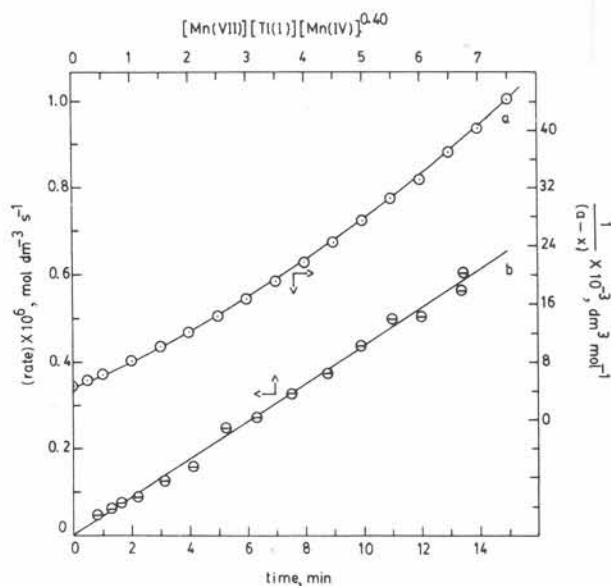

Fig. 1—Mn(VII)-Tl(I) reaction in aqueous perchloric acid at 24°C—(a) Plot of $1/(a-x)$ versus time; (b) Plot of rate versus [Mn(VII)][Tl(I)][Mn(IV)]$^{0.4}$ ($3[MnO_4^-] = 2[Tl(I)] = 6.0 \times 10^{-4}$ mol dm^{-3}; [HClO$_4$] = 1.0 mol dm^{-3}; $I = 1.3$ mol dm^{-3}).

$$-\frac{d[\text{Mn(VII)}]}{dt}=\frac{Kk_1[\text{Mn(VII)}]_T[\text{Tl(I)}]_T[\text{H}^+]_T}{(1+K[\text{H}^+]_T)}$$

$$\dots (2)$$

$$\frac{[\text{Mn(VII)}]_T[\text{Tl(I)}]_T}{(\text{Initial rate})}=\frac{1}{k_1K[\text{H}^+]_T}+\frac{1}{k_1} \qquad \dots (3)$$

of the left hand side of Eq. (3) against $1/[\text{H}^+]_T$ must be linear with rate constant, k_1, and formation constant of HMnO_4, K, being obtainable from slope and intercept of such plot. The plot is linear and the values of k_1 and K are 50 $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ and 0.61 $\text{dm}^3\text{mol}^{-1}$ respectively. Using these values, initial rates for several situations as used in experiment were calculated and compared with experimental results. It is found that a fair agreement is obtained. The value of K of 0.61 $\text{dm}^3\text{mol}^{-1}$ for the formation of HMnO_4 in the equilibrium step is much higher than may be expected on the basis of the reported pK_a values of permanganic acid of -2.25 in perchloric acid and -4.6 in sulphuric acid[7].

The role of Mn(IV), a product, is amply borne out by the linearity of the plot of rate versus $[\text{Mn(VII)}][\text{Tl(I)}][\text{Mn(IV)}]^{0.4}$. Soluble forms of Mn(IV) exist under certain conditions[8]. Thus, the catalysis by Mn(IV) (fractional order) of the reaction may be due to soluble species like $\text{H}_2\text{MnO}_4^{2-}$.

The effect of ionic strength and dielectric constant on the reaction may be understood in terms of their opposing effects on the first and second steps of Scheme 1. While step(I) is favoured by decreasing polarity of the solvent, the formation of the activated (charged) state (step (II)) may occur to a lesser extent[9]. The effect of ionic strength is that, while step(II) is favoured by the increase in ionic strength, step(I) is not. The rather small activation energy and the large entropy of activation indicate that the activated state is considerably ordered. The particular effect of chloride ions on the reaction is likely to be due to the fact that the product, Tl(III), forms highly stable chloride complexes[10] as compared to Tl(I), the product stabilisation accounting for the rate increase.

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