

## Kinetics and Mechanism of Oxidation of Tellurium(IV) by Periodate in Alkaline Medium

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Recently Ram Babu and coworkers<sup>1</sup> have studied the kinetics of oxidation of tellurium(IV) by periodate in aqueous perchloric acid medium and reported that the mechanism of oxidation involves a two-electron transfer from tellurium(IV) to periodate in the rate step. We found that tellurium(IV) is also oxidised by periodate in alkaline medium at about 60° at a rate convenient for kinetic investigation. Since the species of both tellurium(IV) and periodate are different in alkaline and in acid media, we have taken up a detailed kinetic study of the oxidation of tellurium(IV) by periodate in alkaline medium with a view to comparing the mechanisms of oxidation in the two media. It is interesting to note that the rate step involves a two-electron transfer from tellurium(IV) to periodate in alkaline medium also, although the kinetic pattern is somewhat different from that in the acid medium.

### Results and Discussion

The product iodate does not have any effect on the rate of the reaction, but the other product, tellurate, causes considerable retardation in rate (Table 1). This retardation is due to complex formation between  $\text{Te}^{\text{VI}}$  and periodate, which is evidenced by an increase in the absorbance of periodate on mixing with  $\text{Te}^{\text{VI}}$ . Ardon's plot<sup>2</sup> of  $1/\text{absorbance}$  vs  $1/[\text{Te}^{\text{VI}}]$  was found to be a straight line with an intercept on the absorbance axis indicating the formation of a 1 : 1 complex. The formation constant of the complex calculated from the ratio of intercept to slope of the plot was found to be  $67.1 \text{ mol}^{-1} \text{ dm}^3$ .

The order with respect to periodate was determined in  $0.1 \text{ mol dm}^{-3}$  alkali, keeping  $[\text{Te}^{\text{IV}}]$  and ionic strength constant and varying  $[\text{periodate}]$  in the range  $5.0\text{--}30.0 \times 10^{-4} \text{ mol dm}^{-3}$ . When the initial rates of the runs (Table 1) were plotted against the corresponding  $[\text{periodate}]$ , a straight line passing through origin was obtained showing the order with respect to periodate to be unity. The order with respect to  $\text{Te}^{\text{IV}}$  was determined in  $0.1 \text{ mol dm}^{-3}$  alkali keeping the  $[\text{periodate}]$  and ionic strength constant and varying  $[\text{Te}^{\text{IV}}]$  from  $6.0 \times 10^{-3}$  to  $30.0 \times 10^{-3} \text{ mol dm}^{-3}$ . The constancy of initial rates at different  $[\text{Te}^{\text{IV}}]$  (Table 1) indicates the order with respect to  $\text{Te}^{\text{IV}}$  to be zero.

The effect of  $[\text{OH}^-]$  was studied keeping the concentrations of the reactants constant and varying  $[\text{OH}^-]$  from  $0.01$  to  $0.2 \text{ mol dm}^{-3}$  at an ionic strength of  $1.0 \text{ mol dm}^{-3}$ . The initial rates were found to decrease with increase in  $[\text{OH}^-]$  (Table 1). Since  $\text{Te}^{\text{IV}}$  species remain unchanged in the alkali concentration range studied, the decrease in rate is probably due to the conversion of  $\text{H}_3\text{IO}_6^{2-}$  species of periodate into less electrophilic  $\text{H}_2\text{IO}_6^{3-}$  species.

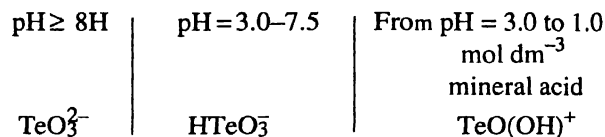
Ionic strength variation studies were carried out in  $0.1 \text{ mol dm}^{-3}$  alkali keeping the concentrations of the reactants constant and varying the ionic strength from  $0.15$  to  $1.0 \text{ mol dm}^{-3}$  using sodium perchlorate. The initial rates at different ionic strengths were found to be nearly the same (Table 1) indicating that the rate of the reaction is independent of ionic strength.

The activation parameters for the reaction were determined by carrying out kinetic runs at 45, 50, 55 and 60° in 0.1 mol dm<sup>-3</sup> alkali keeping the concentration of Te<sup>IV</sup> constant at 0.01 mol dm<sup>-3</sup> and that of periodate constant at 0.001 mol dm<sup>-3</sup>. The initial rates at 45, 50, 55 and 60° were found to be 2.68 × 10<sup>-7</sup>, 3.92 × 10<sup>-7</sup>, 5.62 × 10<sup>-7</sup> and 7.42 × 10<sup>-7</sup> mol dm<sup>-3</sup> s<sup>-1</sup> respectively. The values of E<sub>a</sub> and ΔS<sup>‡</sup> at 60° calculated from these data using linear least-squares method were found to be 60.3 ± 4.6 kJ mol<sup>-1</sup> and -94.7 ± 13.8 JK<sup>-1</sup> mol<sup>-1</sup> respectively.

TABLE 1—EFFECT OF [Te<sup>VI</sup>], [Per], [Te<sup>IV</sup>], [OH<sup>-</sup>] AND IONIC STRENGTH(I) ON INITIAL RATE AT 60°

[Te <sup>VI</sup> ] × 10 <sup>3</sup> mol dm <sup>-3</sup>	[Per] × 10 <sup>3</sup> mol dm <sup>-3</sup>	[Te <sup>IV</sup> ] × 10 <sup>2</sup> mol dm <sup>-3</sup>	[OH <sup>-</sup> ] × 10 mol dm <sup>-3</sup>	I mol dm <sup>-3</sup>	Initial rate × 10 <sup>7</sup> mol dm <sup>-3</sup> s <sup>-1</sup>
0.0	1.0	1.0	1.0	0.15	7.4
1.0	1.0	1.0	1.0	0.15	5.9
2.0	1.0	1.0	1.0	0.15	3.9
4.0	1.0	1.0	1.0	0.15	2.4
6.0	1.0	1.0	1.0	0.15	2.0
8.0	1.0	1.0	1.0	0.15	1.6
10.0	1.0	1.0	1.0	0.15	1.4
0.0	0.5	3.0	1.0	0.15	3.1
0.0	1.0	3.0	1.0	0.15	5.7
0.0	1.5	3.0	1.0	0.15	8.5
0.0	2.0	3.0	1.0	0.15	10.8
0.0	2.5	3.0	1.0	0.15	13.7
0.0	3.0	3.0	1.0	0.15	16.0
0.0	1.0	0.6	1.0	0.15	7.1
0.0	1.0	1.0	1.0	0.15	7.4
0.0	1.0	1.5	1.0	0.15	7.4
0.0	1.0	2.0	1.0	0.15	7.1
0.0	1.0	2.5	1.0	0.15	7.4
0.0	1.0	3.0	1.0	0.15	7.1
0.0	1.0	1.0	0.1	0.15	13.9
0.0	1.0	1.0	0.25	1.0	7.7
0.0	1.0	1.0	0.5	1.0	4.2
0.0	1.0	1.0	0.75	1.0	3.9
0.0	1.0	1.0	1.0	1.0	3.7
0.0	1.0	1.0	2.0	1.0	3.4
0.0	1.0	1.0	1.0	0.15	7.4
0.0	1.0	1.0	1.0	0.2	7.1
0.0	1.0	1.0	1.0	0.4	7.1
0.0	1.0	1.0	1.0	0.6	7.4
0.0	1.0	1.0	1.0	0.8	7.1
0.0	1.0	1.0	1.0	1.0	7.1

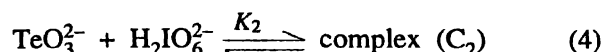
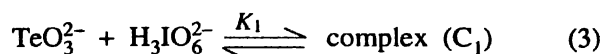
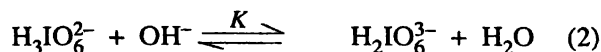
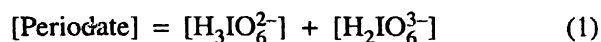
Havezov and Jordanov<sup>3</sup> summarised the most probable species of tellurium(IV) as follows :



Therefore, in the [OH<sup>-</sup>] range employed in the present investigation Te<sup>IV</sup> species present in solution is unambiguously TeO<sub>3</sub><sup>2-</sup>.

In 1.0–5.0 mol dm<sup>-3</sup> acid solutions, periodate exists in the form of the undissociated acid, H<sub>5</sub>IO<sub>6</sub>. From pH = 1 onwards, H<sub>5</sub>IO<sub>6</sub> starts undergoing dissociation leading to the formation of H<sub>4</sub>IO<sub>6</sub> (Refs. 4, 5). Between pH 2.5 and 7, periodate exists in the form of H<sub>4</sub>IO<sub>6</sub> or in its dehydrated form IO<sub>4</sub><sup>-</sup> depending on the temperature. At pH 7, H<sub>4</sub>IO<sub>6</sub> commences to dissociate to give H<sub>3</sub>IO<sub>6</sub><sup>2-</sup>, the two species being of nearly equal concentration at pH 8. Beyond pH 12.5, H<sub>3</sub>IO<sub>6</sub><sup>2-</sup> further dissociates to give H<sub>2</sub>IO<sub>6</sub><sup>3-</sup>, which however does not dissociate any further. Therefore, in the 0.01–0.02 mol dm<sup>-3</sup> alkali employed in the present study, periodate exists mainly in the form of H<sub>3</sub>IO<sub>6</sub><sup>2-</sup> and partly in the form of H<sub>2</sub>IO<sub>6</sub><sup>3-</sup>. However, in view of its greater electrophilic nature and its considerably higher concentration H<sub>3</sub>IO<sub>6</sub><sup>2-</sup> may be regarded as the predominant reactive species of periodate. This conclusion is also supported by the observed decrease in rate with increase in [OH<sup>-</sup>]. Although the reactive species of both the reactants are negatively charged the absence of ionic strength effect need not be considered anomalous since the order with respect to Te<sup>IV</sup> is zero.

On the basis of the experimental observations the following mechanism has been proposed for the oxidation of Te<sup>IV</sup> by periodate :





This mechanism leads to the rate equation,

$$\text{Rate} = -\frac{d[\text{Per}]}{dt} = \frac{[\text{TeO}_3^{2-}][\text{Per}]}{1 + K[\text{OH}^-]} \left\{ \frac{k_1 K_1}{1 + K_1[\text{TeO}_3^{2-}]} + \frac{k_2 K_2 K [\text{OH}^-]}{1 + K_2[\text{TeO}_3^{2-}]} \right\} \quad (7)$$

Chaudhuri and Mukherjee<sup>6</sup> in their review on periodates, stated that complex periodates are more stable in alkaline than in acid medium. It may, therefore, be presumed that  $K_1$  and  $K_2$  are fairly large under the present experimental conditions. No spectrophotometric evidence for complexation could be obtained probably because there is no significant difference in the absorbances of the periodate species and their complexes with  $\text{Te}^{\text{IV}}$ .

If  $K_1 [\text{TeO}_3^{2-}]$  and  $K_2 [\text{TeO}_3^{2-}]$  are large compared to unity, equation (7) reduces to

$$\text{Rate} = \frac{[\text{Per}]}{1 + K[\text{OH}^-]} \{k_1 + k_2 K [\text{OH}^-]\}$$

This equation explains the observed zero order with respect to  $\text{Te}^{\text{IV}}$ , first order with respect to periodate and decrease in rate with increase in  $[\text{OH}^-]$ .

In the oxidation of  $\text{Te}^{\text{IV}}$  by periodate in acid medium the order with respect to both  $\text{Te}^{\text{IV}}$  and periodate is unity, whereas in alkaline medium, although the order with respect to periodate is unity, that with respect to  $\text{Te}^{\text{IV}}$  is zero. This difference in order with respect to  $\text{Te}^{\text{IV}}$  in the two media may be attributed to the fact that the complex species formed between  $\text{Te}^{\text{IV}}$  and periodate are quite stable in alkaline medium but much less so in acid medium. Thus the mechanism of oxidation of  $\text{Te}^{\text{IV}}$  by periodate is broadly the same in the two media and might involve the transfer of an oxygen atom from periodate to  $\text{Te}^{\text{IV}}$ .

### Experimental

A 0.1 mol  $\text{dm}^{-3}$  solution of  $\text{Te}^{\text{IV}}$  was prepared afresh by dissolving sodium tellurite (L.R., B.D.H.) in water and its strength determined by titrating an aliquot volume of the solution with excess of

standard dichromate solution and back-titrating the excess with iron(II) solution of known strength<sup>7</sup>.

A 0.02 mol  $\text{dm}^{-3}$  aqueous solution of  $\text{Te}^{\text{VI}}$  was prepared from sodium tellurate (L.R., B.D.H.). Aqueous solutions (0.1 mol  $\text{dm}^{-3}$ ) of periodate and iodate were prepared from sodium metaperiodate and potassium iodate (AnalaR) respectively. A 4.0 mol  $\text{dm}^{-3}$  solution of sodium perchlorate was prepared by neutralising sodium carbonate (AnalaR) with 70% perchloric acid (Merck, Proanalysis). All other chemicals used were of A.R. grade. Double-distilled water was used throughout. A Shimadzu UV-140 spectrophotometer was used for absorption measurements. A U-10 (Germany) thermostat was used.

Kinetic runs were carried out at  $60 \pm 0.1^\circ$  in 0.1 mol  $\text{dm}^{-3}$  sodium hydroxide medium keeping  $[\text{Te}^{\text{IV}}]$  in 10-fold excess over [periodate]. The reaction was monitored spectrophotometrically following the absorbance of periodate at 280 nm, where all other ions involved in the reaction had negligible absorption. Under these conditions log concentration versus time plots were found to deviate from linearity after about 50% completion of the reaction, due to retardation by  $\text{Te}^{\text{VI}}$ ; hence initial rate method was employed. The rate constants were found to be reproducible within  $\pm 5\%$ .

Two- to four-fold excess of periodate was allowed to react with  $\text{Te}^{\text{IV}}$  at  $60^\circ$  in 0.1 mol  $\text{dm}^{-3}$  alkaline medium. After the completion of the reaction, the concentration of the unreacted oxidant was determined spectrophotometrically at 280 nm. The stoichiometry of the reaction was found to be in the mole ratio of 1 : 1, the same as that in acid medium.

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