# Kinetics of Oxidation of Tellurium(IV) by Cerium(IV) in Perchloric Acid Medium

L. S. A. DIKSHITULU*, V. HANUMANTHA RAO & S. N. DINDI

Department of Chemistry, Andhra University, Waltair 530 003

A very interesting feature of the title reaction is that one of the products, viz Ce(III) retards while the other, viz. Te(VI) accelerates the reaction. The reaction is found to be of first order with respect to Ce(IV) and of fractional order with respect to Te(IV). The rate of the reaction is found to decrease slightly with increase in [H+] in 2-5M range. Variation in ionic strength is found to have no effect on the rate of the reaction. $E_a$, $\triangle H\ddagger$, $\triangle S\ddagger$ and $\triangle G\ddagger_{308}$ for the reaction are found to be 12.1 kcal mol⁻¹, 11.5 kcal mol⁻¹,—29.1 cal mol⁻¹ degree⁻¹ and 20.5 kcal mol⁻¹ respectively. Spectrophotometric and kinetic evidences have been obtained for the formation of 1:1 complexes of Ce(IV) with Te(IV) as well as with Te(VI).

DURING our attempts to develop oxidimetric methods for the determination of tellurium(IV), we noticed that the oxidation of Te(IV) by Ce(IV) is much slower than by Cr(VI). Since this is contrary to what is normally expected from the redox potentials of Ce (IV)/ Ce(III) and Cr(VI)/ Cr(III) couples [in fact, Ce(IV) oxidises Cr(III) to Cr(VI)], we thought it worthwhile to investigate the kinetics of oxidation of Te(IV) by Cr(VI) as well as by Ce(IV) expecting to get a clue to the mechanisms of these oxidations. We have already reported our results pertaining to the kinetics of oxidation of Te(IV) by Cr(VI)[1]. In this paper we present our results on the kinetics of oxidation of Te(IV) by Ce(IV) in perchloric acid medium. An interesting feature of this reaction is that one of the products, viz. Ce(III) retards while the other, viz. Te(VI) accelerates the reaction. So far only two reactions exhibiting similar behaviour have been reported in the literature. In the oxidation of V('II) by Fe(III) giving rise to V(IV) and Fe(II), V(IV) accelerates the reaction, while the Fe(II) retards[2]. Similarly, in the oxidation of V(III) by Np(V) leading to the formation of V(IV) and Np(IV) the former retards while the latter accelerates[3].

## Materials and Methods

A solution of (0.1M) Te(IV) was prepared afresh by dissolving twice recrystallised sodium tellurite (LR, BDH) in water and standardised by the literature method[4]. Identical results were obtained even when twice recrystallised sodium tellurite (LR, H & W, England) or Te(IV) prepared from 99.999% tellurium (gift from Nuclear Fuel Complex, Hyderabad) was used.

A. O. 1M solution of Te(VI) in 1M perchloric acid was prepared from twice recrystallised sodium tallurate (LR, BDH) and its strength was also verified[4]. The results were also checked with tell-

urate prepared from 99.999% tellurium (gift from Nuclear Fuel Complex, Hyderabad).

An approximately 0.2 M stock solution of Ce(III) in perchloric acid was prepared starting from Ce(III) chloride (E. Merck, GR) and heating it with perchloric acid to expel chloride ion[5]. The solution was analysed for the acid and cerium contents[6,7]. A solution of Ce(III) perchlorate prepared from 99.9% pure Ce(III) chloride (The Indian Rare Earths Limited, Udyogamandal) gave identical results.

A 0.2M stock solution of Ce(IV) was prepared by the electrolytic oxidation of 0.2M Ce(III) perchlorate in 2M perchloric acid medium using a diaphragm cell. The electrolysis was carried out for 8 hr using a Toshniwal Electrolytic Analyser, Type CM 16, at a constant voltage of 12 V. A bright platinum rod was used as the cathode and a platinum gauze as the anode. The oxidation was found to be 99.8% complete when its strength was checked[8]. The acid content of this solution was also determined[6]. The solution was found to be free from chloride.

'Proanalysi' grade Perchloric acid (70%) (E. Merck) was used throughout the study. All other reagents used were of AR grade.

*Stoichiometry of the reation* — Aliquots of Te(IV) solution were mixed with known excess of Ce(IV) perchlorate, the [H–] adjusted to 2M with perchloric acid and the solution kept at room temperature for over 100 hr. The unreacted Ce(IV) was determined with standard ammonium iron(II) sulphate solution (suitable blanks were also carried out). The stoichiometry was found to correspond to the equation.

$$Te(IV) + 2Ce(IV) \rightarrow Te(VI) + 2Ce(III)$$
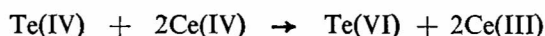
*Kinetic procedure* — All kinetic runs were carried out at a constant temperature of $35 \pm 0.1°C$, unless otherwise mentioned. The activity coefficients were controlled by maintaining a constant ionic strength with sodium perchlorate. Requisite amounts of all reactants except Ce(IV) [or Te(IV)] were equilibrated at the desired temperature. Cerium(IV) [or Te(IV)] was equilibrated at the desired temperature separately. After the solutions attained the temperature of the bath, the reaction was initiated by transferring the calculated amount of Ce(IV) [or Te(IV)] into the reaction bottle. The rate measurements were made, keeping [Te(IV)] and [H+] constantly in excess and following [(Ce(IV)] which was isolated. Aliquots of the reaction mixture were taken at known intervals of time and run into excess ammonium iron(II) sulphate of known strength to quench the reaction. The excess Fe(II) was back titrated with Ce(IV) sulphate to ferroin endpoint. The reaction could not be followed spectrophotometrically because of the increase in the absorbance of Ce(IV) when mixed with either Te(IV) or Te(VI), probably due to complexation of Ce(IV) with the latter.

## Results and Discussion

An inspection of log $(T_\infty - T_t)$ versus time plot (Fig. 1) (where $T_\infty$ and $T_1$ represent titre values at time $\infty$ and $t$) reveals that the reaction follows pseudo-first order behaviour even upto 80% of the reaction. As is evident from Fig. 1, the initial presence of Ce(III) caused considerable retardation in the reaction rate while in the presence of Te(VI) considerable enhancement of rate is observed. So as to minimise the effect of Ce(III) and Te(VI) produced during the course of the reaction, kinetic runs were performed keeping a ten-fold molar excess of the products over the initial [(Ce(IV)]. The pseudo-first order rate constants were calculated from the plots thus obtained and they were represented by the symbol $k'$. The variation in $k'$ with changes in [Ce(III)] and [Te(VI)] is shown in Table 1.



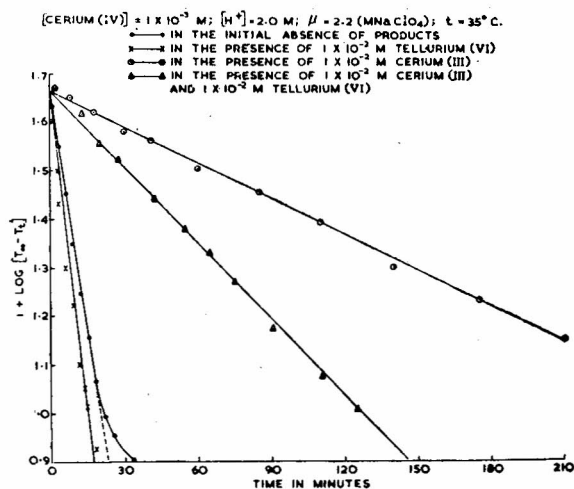Fig. 1 — Effect of addition of products Ce(III) and Te(VI) on the reaction rate.

*Order with respect to Ce(IV)* — The fact that the log [Ce(IV)] versus time plot was linear over a considerable range of concentration when Ce(IV) was isolated, suggested the order with respect to Ce(IV) to be unity.

Further, order with respect to Ce(IV) was also determined by the initial rate method. In this method kinetic runs were carried out [ in the absence of Ce(III) and Te(VI) at varying initial [Ce(IV)] ($6 \times 10^{-4}$ to $16 \times 10^{-4}M$) keeping the concentrations of the other ions constant at [tellurium(IV)] $= 1 \times 10^{-2}M$; [H+] $= 2.0M$ and $\mu = 2.2M$ (NaClO$_4$). The initial rates were determined employing the mirror technique[9]. The plot of log (initial rate) versus log [Ce(IV)]$_0$ was found to be linear with a slope of 0.97 thus confirming the order with respect to Ce(IV) to be unity.

*Order with respect to tellurium(IV)* — Kinetic runs were carried out keeping the initial concentration of Ce(IV) at $1.0 \times 10^{-3}M$, [H–] at $2.0M$, [Ce(III)] and [Te(VI)] at $1 \times 10^{-2}M$ each, $\mu$ at $2.2M$ (NaClO$_4$) and varying the initial [Te(IV)]$_0$ from $6 \times 10^{-3}$ to $16 \times 10^{-3}M$. When log (pseudo-first order rate constant) was plotted against log[TeIV)]- a linear plot with a slope of 0.5 was obtained indicating the order with respect to Te(IV) to be fractional. Further, when the pseudo-first order rate constant, $k'$, was plotted against [Te(IV)]$_0$ a linear plot with a positive intercept on the $y$-axis was obtained showing that both Te(IV) independent and Te(IV) dependent paths existed.

*Effect of varying ionic strength* — The increase of ionic strength from 2.2 to 5.2 $M$ (NaClO$_4$) was found to have negligible effect on the pseudo-first order rate constant, $k'$.

TABLE 1 — EFFECT OF VARYING [Ce(III)] AND (Te(VI)] ON THE PSEUDO-FIRST ORDER RATE CONSTANT

{[Te(IV)]$_0$ $= 1 \times 10^{-2}$ $M$; [Ce(IV)]$_0$ $= 1 \times 10^{-3}$ $M$; [H+]$_0$ $= 2.0M$; $\mu = 2.2$ $M$ (NaClo$_4$); temp $= 35° \pm 0.1°$C}

| $10^3$[Ce(III)]$_0$ $M$ | $10^3$[Te(VI)] $M$ | $10^4 k'$ (sec$^{-1}$) | $10^3$[Ce(III)]$_0$ $M$ | $10^3$[Te(VI)] $M$ | $10^4 k'$ (sec$^{-1}$) |
|---|---|---|---|---|---|
| — | — | 12.12 | 10.0 | 1.0 | 1.24 |
| 1.0 | — | 4.00 | 10.0 | 2.5 | 1.47 |
| 2.5 | — | 2.00 | 10.0 | 5.0 | 1.75 |
| 5.0 | — | 1.30 | 10.0 | 7.5 | 1.88 |
| 7.5 | — | 1.05 | 10.0 | 10.0 | 1.95 |
| 10.0 | — | 0.99 | 10.0 | 15.0 | 2.02 |
| 15.0 | — | 0.98 | 1.0 | 10.0 | 2.43 |
| — | 1.0 | 13.65 | 2.5 | 10.0 | 2.16 |
| — | 2.5 | 14.75 | 5.0 | 10.0 | 2.07 |
| — | 5.0 | 15.70 | 7.5 | 10.0 | 2.05 |
| — | 7.5 | 16.20 | 10.0 | 10.0 | 2.03 |
| — | 10.0 | 16.50 | 15.0 | 10.0 | 2.025 |
| — | 15.0 | 16.66 | | | |
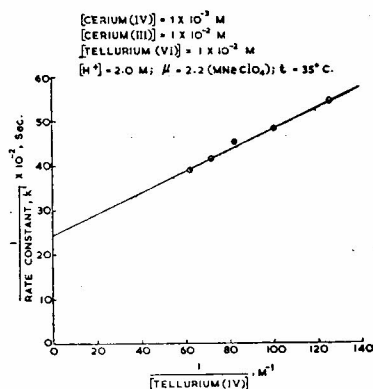
Fig 2 — Plot of 1/[Tellurium (IV)] versus 1/rate constant

TABLE 2 — EFFECT OF VARYING [H⁺] ON PSEUDO-FIRST ORDER
RATE CONSTANT

{$[Te(IV)]_0 = 1 \times 10^{-2} M$; $[Ce(IV)]_0 = 1 \times 10^{-3} M$; $[Ce(III)]_0$
$= 1 \times 10^{-2} M$; $[Te(VI)]_0 = 1 \times 10^{-2} M$; $\mu = 5.2 M$ (Na ClO₄)
temp. $= 35° \pm 0.1°C$}

| $[H^+]$, $M$ | $10^4 k'$ (sec⁻¹) | $[H^+]$ $M$ | $10^4 k'$ (sec⁻¹) |
|---|---|---|---|
| 2.0 | 1.96 | 4.0 | 1.81 |
| 2.5 | 1.90 | 5.0 | 1.72 |
| 3.0 | 1.84 | | |

*Effect of varying* $[H^+]$ — It may be seen from Table 2 that the rate of the reaction decreases slightly with increase in $[H^+]$.

*Activation parameters* — The reaction was carried out at four different temperatures and the activation parameters determined from the linear Arrhenius plot. From this plot, the activation energy of the reaction, $E_a$ was calculated to be 12.1 kcal mol⁻¹ and $\triangle H\ddagger$, $\triangle S\ddagger$ and $\triangle G\ddagger_{308}$ were found to be 11.5 kcal mol⁻¹, −29.1 cal mol⁻¹ degree⁻¹ and 20.5 kcal mol⁻¹ respectively.

Depending on the concentrations of perchloric acid and Ce(IV), the latter may be present[10] as Ce⁴⁺ and CeOH³⁺ besides the polymeric forms like (Ce—O—Ce)⁶⁺ and (Ce₂O₃)⁶⁺. From the data of King and Pandow[11], Baker *et al*[12] estimated that at least 90% of Ce(IV) was present as the monomer in 0.85-2.5M perchloric acid medium. However, Offner and Skoog[13] and Amjad and Mc-Auley[14], from their spectrophotometric studies in 1M perchloric acid, showed that Ce(IV) was present as the monomeric species only, upto a concentration of about 1.5 × 10⁻³M Calculations based on their data showed that Ce(IV) was present as Ce⁴⁺ to the extent of about 90% and the remainder as CeOH³⁺ at 25°C. As the concentrations of Ce(IV) and perchloric acid employed in the present investigation are similar to those in the above reports[13,14], all the Ce(IV) may be regarded as existing in the form of monomer only. Further, since the rate of the reaction decreases, though slightly, with increase in [H⁺], CeOH³⁺ may be reagarded as more reactive than Ce⁴⁺.



Fig 3 — Plot of 1/[Tellurium (VI)] versus 1/rate constant

From the solubility studies of TeO₂ in 0.1-0.74 M perchloric acid Schuhmann[15] concluded that Te(IV) existed as Te(OH)₃⁺ or TeO(OH)⁺. Awad[16] reported that Te(IV) existed as TeO(OH)⁺ in the pH range 0-0.8. Havezov and Jordanov[17] summarised the most probable ionic species of Te(IV) at different pH values as follows : TeO₃²⁻ (>pH8), HTeO₃⁻ (pH 3-7.5), H₂TeO₃ (pH3.5) and TeO(OH)⁺ (pH 3 to 1M mineral acid). From these reports it may be presumed that Te(IV) exists as TeO(OH)⁺ or Te(OH)₃⁺ under our experimental conditions.

During the investigation of this reaction we have obtained evidence for complexation of Ce(IV) with Te(IV) as well as with Te(VI). The composition of these complexes has been studied spectrophotometrically, the former at 280 nm and the latter at 265 nm. Using Jobs and mole ratio methods both the complexes correspond to 1:1 stoichiometry. Kinetic evidence for the formation of these complexes is also obtained from the linear plots of $1/k'$ versus $1/[Te(IV)]$ and $1/k'$ versus $1/[Te(VI)]$. We could not succeed in proposing a mechanism which could account for all the observations made in this investigation. Further work in nitric and sulphuric acid media is in progress to obtain better insight into the mechanism of this reaction.

**References**

1. DIKSHITULU, L. S. A. & SATYANARAYANA, DINDI, *J. inorg. nucl. Chem.*, **38** (1976), 1843.

2. HIGGINSON, W. C. E. & SYKES, A. G., *J. chem. Soc.*, (1962), 2841.

3. APPELMAN, E. H. & SULLIVAN, J. C., *J. phys. Chem.*, **66** (1962), 442.

4. DIKSHITULU, L. S. A. & SATYANARAYANA, DINDI, *Talanta* **22** (1975), 313.

5. SMITH, G. F., *Analyt. Chem.*, **27** (1955), 1142.

6. MCAULEY, A., *J. chem. Soc.*, (1965), 4054.

7. VOGEL A. I., *Text book of quantitative inorganic analysis* (Longmans Green, London), 1968, 324.

8. MATHAI, I. M. & VASUDEVAN, R., *J. chem. Soc.*, (B), (1970), 1361.

9. LATSHAW, M, *J. Am. chem. Soc.*, **47** (1925), 793.

10. ADAMSON, M. G., DAINTON, F. S. & GLENTWORTH, P. *Trans. Faraday Soc.*, **61** (1965), 689.

11. KING, E. L. & PANDOW, M. L., *J. Am. chem. Soc.*, **74** (1952), 1966.

12. BAKER, F. G., NEWTON, T. W. & KAHN, M., *J. phys. Chem.*, **64** (1960), 109.

13. OFFNER, H. G. & SKOOG, D. A., *Analyt. Chem.*, **38** (1966), 1520.

14. AMJAD, Z. & MCAULEY, A., *J. chem. Soc.*, Dalton, (1974), 2521.

15. SCHUHMANN, K., *J. Am. chem. Soc.*, **47** (1925), 356.

16. AWAD, S. A., *Electrochim. Acta*, **13** (1968), 925.

17. HAVEZOV, I. & JORDANOV, N., *Talanta* **21** (1974), 1013.