

Kinetics & Mechanism of Oxidation of Tellurium(IV) by Cerium(IV) in Nitric & Sulphuric Acid Media

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A notable feature of the title reaction is that one of the products, viz. Ce(III) retards while the other, viz. Te(VI) accelerates the reaction rate. The order with respect to [Ce(IV)] is unity and that with respect to [Te(IV)] is fractional in both the acid media. Variation in ionic strength has little effect on the rate of the reaction in either medium. While increase in [H⁺] is found to retard the reaction considerably in nitric acid medium, a linear increase in rate is noticed in sulphuric acid medium. Activation parameters have also been determined. A suitable mechanism has been proposed.

IN a recent paper on the kinetics of oxidation of Te(IV) by Ce(IV) in perchloric acid medium¹, we could not propose a mechanism for the reaction for want of some more details. An interesting feature of this reaction is that one of the products, viz. Ce(III) retards the reaction while the other, viz. Te(VI) accelerates. We have now studied the kinetics of this reaction in nitric and sulphuric acid media also and succeeded in proposing a suitable mechanism.

Materials and Methods

Stock solutions (0.1M) of Te(IV) (in water) and Te(VI) (in the corresponding acid) were prepared from LR, BDH samples of sodium tellurite and sodium tellurate respectively and standardised². Stock solutions of Ce(IV) were prepared by dissolving ceric ammonium nitrate (or ceric ammonium sulphate) of 99.9% purity (Indian Rare Earths Ltd.) in 2M nitric (or sulphuric) acid. Ce(IV) and acid contents of the solutions were determined as reported in literature^{3,4}. Stock solutions of Ce(III) in these two acid media were prepared by reducing the Ce(IV) solutions in the corresponding acid with H₂O₂ and boiling off the excess H₂O₂. The acid and cerium contents of these solutions were determined by the method described elsewhere^{4,5}.

Lithium perchlorate was prepared by neutralising lithium carbonate (LR, BDH) with perchloric acid (70%, E. Merck, proanalysis).

A Shimadzu UV-VIS double beam spectrophotometer (140-02) with 1 cm glass cells was used for absorbance measurements.

Stoichiometry of the reaction — Aliquots of Te(IV) were mixed with a known excess of Ce(IV) and the [H⁺] was adjusted to 1M with nitric (or sulphuric) acid and the solutions were kept at room temperature in nitric acid medium and at 60°C in sulphuric acid medium for two days. The unreacted Ce(IV) was estimated spectrophotometrically at 360 nm in nitric acid medium and at 400 nm in sulphuric acid medium

and the stoichiometry was found to correspond to the equation: $\text{Te(IV)} + 2\text{Ce(IV)} \rightarrow \text{Te(VI)} + 2\text{Ce(III)}$.

Kinetic procedure — All kinetic runs were carried out at a constant temperature of $35 \pm 0.1^\circ\text{C}$ in nitric acid medium and at $60 \pm 0.1^\circ\text{C}$ in sulphuric acid medium, unless otherwise mentioned. Requisite amounts of all reactants except Ce(IV) were equilibrated at the desired temperature. Cerium(IV) was equilibrated separately. The reaction was initiated by transferring the calculated amounts of Ce(IV) into the reactants. The rates were measured keeping at least a ten-fold excess of [Te(IV)] and [H⁺] over [Ce(IV)] and following [Ce(IV)] at 360 nm in nitric and at 400 nm in sulphuric acid medium. Log (absorbance) versus time plots showed that the reaction followed pseudo-first order rate behaviour at least upto 80% completion of the reaction in both the acid media. The pseudo-first order rate constants were represented by k' .

Results

Pseudo-first order rate constants, k' , are independent of the ionic strength (adjusted by adding LiClO₄) in both the acid media.

It is observed that one of the reaction products, viz. Ce(III), retards the reaction while the other, viz. Te(VI), accelerates (Table 1).

Since the plots of log (absorbance) versus time are linear even upto 80% of the reaction in both the acid media, it may be concluded that the reaction is first order in Ce(IV). This is supported by the plots of log (initial rate) versus log [Ce(IV)] (6.0×10^{-4} to $16.0 \times 10^{-4}M$) which also indicated the order with respect to Ce(IV) to be unity in both the acid media at a constant [Te(IV)] and [H⁺] ($8.0 \times 10^{-3}M$ and $2.0M$ in nitric acid and $1.0 \times 10^{-2}M$ and $1.0M$ in sulphuric acid medium).

Varying [Te(IV)] from $6.0 \times 10^{-3}M$ to $20.0 \times 10^{-3}M$, keeping [Ce(IV)] and [H⁺] constant at $8.0 \times 10^{-3}M$ and $2.0M$ in nitric acid medium and at $1.0 \times 10^{-3}M$ and $1.0M$ in sulphuric acid medium respectively, the

TABLE 1 — EFFECT OF PRODUCTS ON THE PSEUDO-FIRST ORDER RATE CONSTANTS, k'

 A : HNO₃ medium — [Ce(IV)] = 8.0 × 10⁻⁴M; [Te(IV)] = 8.0 × 10⁻³M; [H⁺] = 2.0M; temp. = 35 ± 0.1°C

 B : H₂SO₄ medium — [Ce(IV)] = 1.0 × 10⁻³M; [Te(IV)] = 1.0 × 10⁻²M; [H⁺] = 1.0M; temp. = 60 ± 0.1°C

10 ³ [Ce(III)] (M)	10 ³ [Te(VI)] (M)	10 ⁶ k' (sec ⁻¹)		10 ³ [Ce(III)] (M)	10 ³ [Te(VI)] (M)	10 ⁶ k' (sec ⁻¹)	
		A	B			A	B
—	—	82.3	55.0	1.0	—	57.0	42.5
—	1.0	88.0	63.5	5.0	—	38.5	27.0
—	5.0	94.8	77.5	10.0	—	35.0	23.0
—	10.0	97.8	82.0	15.0	—	34.0	22.0
—	15.0	98.2	82.5	1.0	10.0	91.0	65.0
10.0	1.0	44.5	29.5	5.0	10.0	78.5	48.0
10.0	5.0	70.4	40.0	10.0	10.0	75.5	43.3
10.0	10.0	76.9	44.0	15.0	10.0	75.0	43.0
10.0	15.0	77.0	44.5				

 TABLE 2 — EFFECT OF VARYING [H⁺] ON THE PSEUDO-FIRST ORDER RATE CONSTANTS k'

 A : HNO₃ medium — [Ce(IV)] = 8.0 × 10⁻⁴M; [Ce(III)] = 1.0 × 10⁻²M = [Te(VI)]; [Te(IV)] = 8.0 × 10⁻³M; [NO₃⁻] = 6.0M; temp. = 35 ± 0.1°C.

 B : H₂SO₄ medium — [Ce(IV)] = 1.0 × 10⁻³M; [Ce(III)] = 1.0 × 10⁻²M = [Te(VI)]; [Te(IV)] = 1.0 × 10⁻²M; [HSO₄⁻] = 1.0M; temp. = 60 ± 0.1°C

Nitric acid medium		Sulphuric acid medium	
[H ⁺] (M)	10 ⁶ k' (sec ⁻¹)	[H ⁺] (M)	10 ⁶ k' (sec ⁻¹)
2.0	47.1	1.0	44.6
3.0	34.4	1.5	48.4
4.0	23.0	2.0	52.0
5.0	15.3	3.0	59.6
6.0	9.8	4.0	67.5

 TABLE 3 — EFFECT OF VARYING [NO₃⁻] AND [HSO₄⁻] ON THE PSEUDO-FIRST ORDER RATE CONSTANTS, k'

 HNO₃ medium — [Ce(IV)] = 8.0 × 10⁻⁴M; [Ce(III)] = 1.0 × 10⁻²M = [Te(VI)]; [Te(IV)] = 8.0 × 10⁻³M; H⁺ = 2.0M; temp. = 35 ± 0.1°C

 H₂SO₄ medium — [Ce(IV)] = 1.0 × 10⁻³M; [Ce(III)] = 1.0 × 10⁻²M = [Te(VI)]; [Te(IV)] = 1.0 × 10⁻²M; [H⁺] = 1.0M; temp. = 60 ± 0.1°C

Nitric acid medium		Sulphuric acid medium	
[NaNO ₃] (M)	10 ⁶ k' (sec ⁻¹)	[NH ₄ HSO ₄] (M)	10 ⁶ k' (sec ⁻¹)
2.0	75.3	1.0	44.0
2.5	70.0	1.25	28.0
3.0	65.2	1.50	19.0
3.5	55.6	2.0	11.0
4.0	50.4	2.5	6.8
5.0	40.0		

plots of log k' versus log [Te(IV)] are linear indicating fractional order dependence on [Te(IV)] in both the acid media (0.5 in HNO₃ and 0.64 in H₂SO₄). The initial rates method also indicates the fractional order dependence on [Te(IV)].

In both the acid media the [H⁺] was varied with perchloric acid keeping the concentration of nitrate or bisulphate ion constant. In nitric acid medium the rate decreases with increase in [H⁺], while in sulphuric

acid medium it increases linearly with increase in [H⁺] (Table 2).

Increase in [NO₃⁻] in nitric acid medium and increase in [HSO₄⁻] in sulphuric acid medium retard the reaction (Table 3). Further, in sulphuric acid medium the rate has an inverse second order dependence on [HSO₄⁻].

The reaction obeys Arrhenius temperature dependence in the temperature range 303–318°K in nitric acid medium and in the temperature range 313–333°K in sulphuric acid medium. The activation parameters E_a , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger are found to be 74.5 kJ mol⁻¹, 72.0 kJ mol⁻¹, -50.2 JK⁻¹ mol⁻¹ and 87.5 kJ mol⁻¹ in nitric acid medium and 108.8 kJ mol⁻¹, 105.9 kJ mol⁻¹, 27.2 JK⁻¹ mol⁻¹ and 97.1 kJ mol⁻¹ in sulphuric acid medium respectively.

Discussion

The nature of cerium (IV) species varies from one acid medium to another and is dependent upon the concentration of acid and of Ce(IV). In perchloric acid medium the reactive species is CeOH³⁺ as discussed in our earlier publication¹. The possible species of cerium(IV) in nitric acid medium are Ce⁴⁺, CeOH³⁺, Ce(NO₃)_x^{4-x}(Ce—O—Ce)⁶⁺ etc. At low nitric acid and cerium (IV) concentrations, the latter mainly exists⁶ as Ce⁴⁺ and CeOH³⁺ and if [Ce(IV)] is high, part of the hydrolysed species may be polymerised to give dimers and trimers⁷. On the other hand, when the nitric acid concentration is very high, the concentrations of the hydrolysed and polymerised species decrease and those of the nitrate-complexes increase⁸. Literature reports indicate that dimers and trimers do not exist under the present experimental conditions⁷. In view of the observed retardation with increase in [H⁺] and [NO₃⁻] (Tables 2 and 3) the reactive species in nitric acid medium also may be regarded as CeOH³⁺ as in perchloric acid medium. Such a species has also been assumed to be the reactive one in the oxidations of acetone⁹, isopropyl alcohol¹⁰, substituted mandelic acids¹¹, 3-bromopropionic acid¹² and thallium (I)¹³ by Ce(IV) in nitric acid medium.

In sulphuric acid medium, Ce(IV) exists in the form of sulphatocomplexes only. Moore and Anderson¹⁴ have shown that in 0.01M sulphuric acid, the complex

CeSO_4^{2+} predominates while in more concentrated acid solutions complexes like $\text{Ce}(\text{SO}_4)_2$ and $\text{Ce}(\text{SO}_4)_3^-$ may exist. Spectrophotometric studies of Hardwick and Robertson¹⁵ also indicate the formation of similar sulphato-complexes. Although the higher sulphato-complexes of Ce(IV) are the predominant species under the present experimental conditions (1M H_2SO_4) the linear increase in rate with increase in $[\text{H}^+]$ (Table 2) and the inverse second order dependence of rate on $[\text{HSO}_4^-]$ (Table 3) indicate CeSO_4^{2+} to be the reactive species. Such a species has also been assumed to be the reactive one in the oxidation of antimony(III)¹⁶, benzoic acid¹⁷, manganese(IV) catalysed oxidation of thallium(I)¹⁸, mercury(I)¹⁹ and hydroxylamine²⁰ by cerium(IV) in sulphuric acid medium.

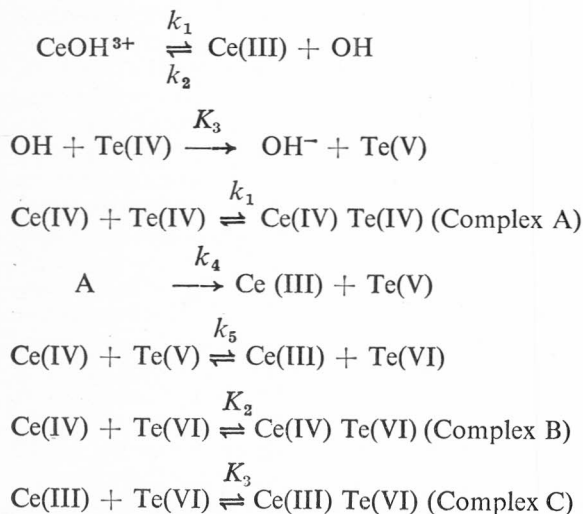
As has already been discussed in our earlier communication¹, Te(IV) exists as $\text{TeO}(\text{OH})^+$ or $\text{Te}(\text{OH})_3^+$ under the present experimental conditions.

Mechanism — When Ce(IV) is mixed with Te(IV) or Te(VI) in perchloric acid medium, an increase in the absorbance of Ce(IV) is noticed. Spectrophotometric study revealed the existence of 1 : 1 complexes of Ce(IV) with both the tellurium species¹. Though no spectrophotometric evidence has been obtained in nitric and sulphuric acid media, the plots of $1/k'$ versus $1/[\text{Te}(\text{IV})]$ and $1/k'$ versus $1/[\text{Te}(\text{VI})]$ are linear with an intercept on the rate axis in all the three acid media, thus providing kinetic evidence for the existence of 1 : 1 complexes of Ce(IV) with Te(IV) and Te(VI).

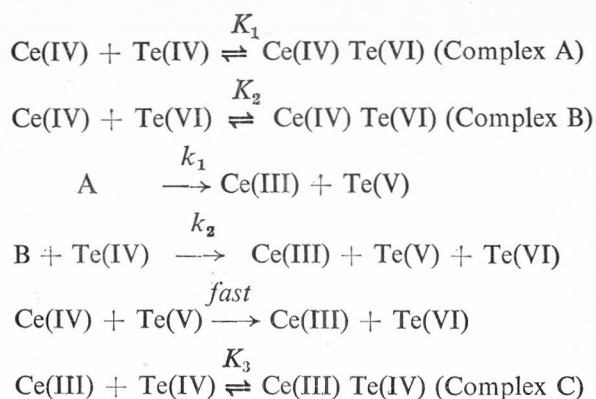
In order to explain the experimental observations in these three acid media, the following probable mechanisms (Schemes 1 to 3) may be considered.

Since, the kinetic pattern observed in the three acid media is almost similar and since, CeOH^{3+} does not exist in sulphuric acid medium, the mechanism shown in Scheme 1 has been ruled out.

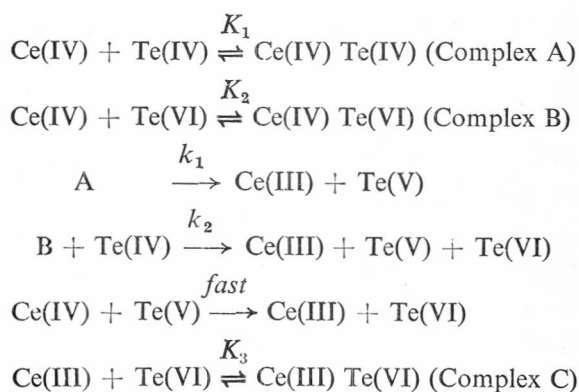
The assumption that Ce(III) forms complexes with Te(IV) or Te(VI) (Schemes 2 and 3 respectively)



Scheme 1



Scheme 2



Scheme 3

appears reasonable in view of the fact that Ce(III) is known to form complexes like CeClO_4^{2+} even with perchlorate ion^{21,22}. In the Fe(III) catalysed oxidation of As(III) by Ce(IV), Miller and Grosse²³ also attributed the inhibition by Ce(III) to the formation of a Ce(III)-Fe(III) complex. Further, in perchloric acid medium, under the conditions $[\text{Ce(III)}] \gg [\text{Te(IV)}] \approx [\text{Te(VI)}] \gg [\text{Ce(IV)}]$ the plot of $1/k'$ versus $[\text{Ce(III)}]$ is linear with an intercept on the rate axis thus furnishing evidence for the formation of a complex of Ce(III) with the reactive species.

The main difference between Schemes 2 and 3 is that, in the former, inhibition by Ce(III) is attributed to the formation of Ce(III)-Te(IV) complex, whereas, in the latter, it is ascribed to the formation of Ce(III)-Te(VI) complex. Both the Schemes explain all the experimental observations equally well. But during a study of Os(VIII)²⁴ and Ru(III) unpublished work catalysed oxidation of Te(IV) by Ce(IV) in sulphuric acid medium we have noticed that there is neither inhibition by Ce(III) nor acceleration by Te(VI). Had the inhibitory effect of Ce(III) been due to the formation of Ce(III)-Te(IV) complex as assumed in Scheme 2, such an inhibition should have been noticed in the catalysed reactions also. In view of these facts Scheme 3 appears to be more probable. Based on this, the following rate law may be derived :

$$[\text{Ce(IV)}]_t = [\text{Ce(IV)}]_e + [\text{A}]_e + [\text{B}]_e$$

$$\text{So } [\text{A}]_e = \frac{K_1[\text{Ce(IV)}]_t [\text{Te(IV)}]_t}{1 + K_1[\text{Te(IV)}]_t + K_2[\text{Te(VI)}]_e}$$

$$[\text{B}]_e = \frac{K_2[\text{Ce(IV)}]_t [\text{Te(VI)}]_e}{1 + K_1[\text{Te(IV)}]_t + K_2[\text{Te(VI)}]_e}$$

$$[\text{Te(VI)}]_e = \frac{[\text{Te(VI)}]_t}{1 + K_3[\text{Ce(III)}]_t}$$

$$\left(\because [\text{Ce(III)}] \gg [\text{Te(VI)}] \gg [\text{Ce(IV)}] \right)$$

$$\text{Rate} = k_1[\text{A}]_e + k_2[\text{B}]_e [\text{Te(IV)}]_t$$

Substituting the values of $[\text{A}]_e$, $[\text{B}]_e$ and $[\text{Te(VI)}]_e$

$$\text{Rate} = \frac{k_1 K_1 [\text{Ce(IV)}]_t [\text{Te(IV)}]_t}{(1 + K_3 [\text{Ce(III)}]_t)}$$

$$\frac{(1 + K_3 [\text{Ce(III)}]_t) + k_2 K_2 [\text{Ce(IV)}]_t [\text{Te(IV)}]_t [\text{Te(VI)}]_t}{(1 + K_1 [\text{Te(IV)}]_t) + K_2 [\text{Te(VI)}]_t}$$

It may be seen that the above rate equation neatly explains all the experimental observations.

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References

1. DIKSHITULU, L. S. A., HANUMANTHA RAO, V. & SATYANARAYANA, DINDI, *Indian J. Chem.*, **19A** (1980), 203.

2. DIKSHITULU, L.S.A. & SATYANARAYANA, DINDI, *Talanta*, **22** (1975), 313.
3. MATHAI, I. M. & VASUDEVAN, R., *J. chem. Soc., (B)*, (1970), 1361.
4. MCAULEY, *J. chem. Soc.*, (1965), 4054.
5. VOGEL, A. I., *Text book of quantitative inorganic analysis* (Longmans Green, London), 1968, 324.
6. YOST, D. M., RUSSEL, H. & GARNER, C. S., *The rare earth elements and their compounds* (John Wiley, New York), 1947.
7. BLAUSTEIN, B. D. & GRYDER, J. W., *J. Am. chem. Soc.*, **79** (1957), 540.
8. WYLIE, A. W., *J. chem. Soc.*, (1951), 1474.
9. SHORTER, J., *J. chem. Soc.*, (1962), 1868.
10. MATHUR, D. L. & BAKORE, G. V., *J. Indian chem. Soc.*, **48** (1971), 363.
11. BANERJI, K. K., *J. Indian chem. Soc.*, **52** (1975), 573.
12. SINGH, B., SAXENA, P. K., SHUKLA, R. K. & KRISHNA, B., *J. Indian chem. Soc.*, **54** (1977), 378.
13. DORFMAN, M. K. & GRYDER, J. W., *Inorg. Chem.*, **1** (1962), 799.
14. MOORE, R. L. & ANDERSON, R. C., *J. Am. chem. Soc.*, **67** (1945), 167.
15. HARDWICK, T. J. & ROBERTSON, E., *Can. J. chem.*, **29** (1951), 828.
16. MISHRA, S. K. & GUPTA, Y. K., *J. inorg. nucl. Chem.*, **30** (1968), 2991.
17. HANNA, SAMEI, B. & SARACSEZAI, A., *J. org. Chem.*, **42** (1977), 2063.
18. CYFERT, M. & URONSKA, *Mh. Chem.*, **108** (1977), 397.
19. MCCURDY (JR.), W.H. & GUILBAULT, G. G., *J. phys. Chem.*, **64** (1960), 1825.
20. TREINDL, L. & VILUDOVA, A., *Colln. Czech. Chem. Commun.*, **39** (1974), 3456.
21. HEIDT & BERSTICKE, *J. Am. chem. Soc.*, **77** (1955), 2049.
22. SUTCLIFFE, L. H. & WEBER, J. R., *Trans. Faraday. Soc.*, **52** (1956), 1225.
23. MILLER, A. D. & GROSSE, Yu. I., *Kinet. Katal.* **13** (1972), 859.
24. DIKSHITULU, L. S.A., HANUMANTHA RAO, V. & VANI, P., *React. Kinet. Catal. Lett.*, (in press).