Kinetics of Oxidation of Iodide Ion by Ce(IV)

R. VENKATA NADH, B. SYAMA SUNDAR* and P.S. RADHAKRISHNAMURTI
Department of Chemistry
Nagarjuna University, Nagarjunanagar-522 510, India

Kinetics of oxidation of iodide ion by Ce(IV) was studied. The reactions
are found to be of 1.5 order in case of iodide, first order in Ce(IV) and
first order in case of [H^+] in the case of uncatalysed reaction. In the case
of catalysed reactions both by Ru(III) and Os(VIII) it was noticed that the
order with respect to iodide is 1.5, the order with respect to Ce(IV) is one
and the dependence on hydrogen ion is found to be one while the reactions
are found to be first order in case of both the catalysts Ru(III) and Os(VIII).
Plausible mechanisms have been postulated both in the case of uncatalysed
and catalysed reactions based upon the experimental observations.

INTRODUCTION

Kinetics of oxidation of iodide ion by cerium(IV) at pH 3 has been studied by
Swain and Hedberg.[1] Subsequently King and Pandow[2] carried out a few
measurements involving iodide ion and Ce(IV). They observed that at pH about
2.5 a certain amount of Ce(IV) was in the colloidal form and the reaction is
composed of two steps: (a) iodide ion and colloidal Ce(IV) species, (b) dispersed
Ce(IV) species and iodide ion. In addition the conclusions were that the former
reaction is slow and the latter reaction is fast. In view of these conflicting
observations it was decided to study the oxidation reaction of iodide ion and
Ce(IV) in perfectly homogeneous conditions in aqueous acetic acid, aqueous
DMSO and in aqueous medium at pH below 2.

EXPERIMENTAL

Potassium iodide, ceric ammonium nitrate, perchloric acid and other reagents
used in these experiments are of analytical reagent grade. The reaction kinetics
was followed by the following procedures: 50.0 mL reagent solution was used
for the kinetic experiments. First the substrate solution was pipetted out into the
reaction vessel by means of a calibrated standard 50 mL pipette. Later 50.0 mL
of the oxidant solution was added with a standard rapid delivery pipette, the
instant of half delivery being noted as zero times. The vessel was stoppered and
shaken well. The progress of reaction was followed by withdrawing 5.0 mL
aliquots at various time intervals, discharging into a flask containing ice cold
water. The liberated iodine was analysed using standard thiosulphate solution.

The rate constants were calculated from the slopes of log (a–x) versus time
curves using regression analysis from the experimental results. Linearity was
observed in most of the cases up to 50% of Ce(IV) consumption, after that slowing
down of the reaction was observed due to the competition of I_3^- reaction with the
oxidant along with the main reaction. Hence rate constants were calculated up to

50% of the reaction in all the cases, as it represens clearly the oxidation reaction of I^- by Ce(IV). In all kinetics experiments I^- was taken in excess.

When the concentrations of potassium iodide and Ce(IV) are equal irrespective of the concentration of H^+ whether it is equal or larger the reaction becomes sluggish at about 30% of consumption of Ce(IV) indicating clearly that there is no free I^- at this point as I_2 formed is complexed with I^- to form I_3^- which reacts with Ce(IV) at very much slower rate and hence in all the experiments excess of potassium iodide was used to study the kinetics of the consumption of Ce(IV) till about 70% of the reaction.
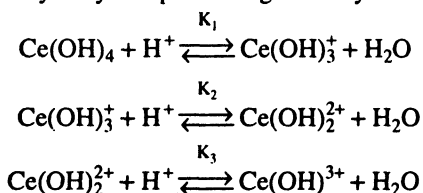
RESULTS AND DISCUSSION

Reaction between iodide ion and cerium(IV) in aqueous medium

Dependence of the reaction on Ce(IV):   It is observed that the reaction is first order with respect to Ce(IV). Plots of log $(b - x)$ *vs.* time are fairly linear establishing first order dependence on the oxidant. It is also observed that there is a constancy in the first order rate constants with increase in the concentration of the oxidant (Table-1).

Dependence of reaction on iodide ion: Variation of the concentration of iodide ion at a fixed concentration of Ce(IV) and at constant acidity resulted in an increase in kinetic rate. The order is found to be 1.5 (Table-1).

Dependence of reaction on acidity: Variation of acid has been carried out at two different concentrations of substrate. The data indicate that it is first order with respect to H^+. Plot of log k *vs.* log H^+ is linear with a slope of one indicating the first order dependence on acidity (Table-1).

The oxidative power of Ce(IV) depends largely on its state in sloution. The increase in kinetic rate with increase in acidity points to the fact that the hydrolysed species of Ce(IV) participate more effectively in the reaction rate than the non hydrolysed species. he hydrolysed species might be any one of the following:

$$Ce(OH)_4 + H^+ \overset{K_1}{\rightleftharpoons} Ce(OH)_3^+ + H_2O$$

$$Ce(OH)_3^+ + H^+ \overset{K_2}{\rightleftharpoons} Ce(OH)_2^{2+} + H_2O$$

$$Ce(OH)_2^{2+} + H^+ \overset{K_3}{\rightleftharpoons} Ce(OH)^{3+} + H_2O$$

This has been fairly established by the works of Hardwick and Robertson[3], Haidt and Smith[4], Gryder and Dadson[5], Beer and Stein[6], Duke and Parchan[7], Baker and coworkers[8], Wells and Hussain[9] and Glass and Martin[10]. The reactions are much faster in perchloric acid medium than in sulphuric acid medium. This shows that sulphuric acid exhibits considerable inhibitory effect on the reaction rate. One way to explain the differential effect of perchloric acid and suphuric acid on the kinetics is to compare the redox potentials of Ce(IV) in perchloric acid and sulphuric acid systems. The redox potentials are 1.7 V in perchloric acid medium and 1.4 V in sulphuric acid medium. Hence the observed reduced reactivity in sulphuric acid system.

TABLE-1
OXIDATION OF IODIDE BY CERIUM(IV)-UNCATALYSED
REACTIONS (TEMP. = 28.5°C)

Variant	Concentration of non-variant	Concentration of variant	$k_1 \times 10^4$ sec^{-1}
Cerum(IV)	$I^- = 3.5 \times 10^{-2}$ M	2.5×10^{-3} M	5.757
	$H^+ = 5.0 \times 10^{-2}$ M	5.0×10^{-3} M	5.757
		10.0×10^{-3} M	5.224
I^-	Ce(IV) = 5.0×10^{-3} M	1.5×10^{-2} M	0.690
	$H^+ = 2.5 \times 10^{-2}$ M	3.5×10^{-2} M	3.166
		5.0×10^{-2} M	4.500
		10.0×10^{-2} M	17.600
		15.0×10^{-2} M	29.550
H^+	Ce(IV) = 5.0×10^{-3} M	2.5×10^{-2} M	3.166
	$I^- = 3.5 \times 10^{-2}$ M	5.0×10^{-2} M	5.757
		10.0×10^{-2} M	9.200
		15.0×10^{-2} M	19.345
	Ce(IV) = 5.0×10^{-3} M	2.5×10^{-2} M	4.500
	$I^- = 5.0 \times 10^{-2}$ M	15.0×10^{-2} M	23.030
Mn^{2+}	Ce(IV) = 5.0×10^{-3} M	zero	30.13
	$I^- = 3.5 \times 10^{-2}$ M	5.0×10^{-4} M	32.06
	$H^+ = 5.0 \times 10^{-2}$ M	10.0×10^{-4} M	47.90
	AcOH = 20%	20.0×10^{-4} M	89.82
AcOH	Ce(IV) = 5.0×10^{-3} M	zero	5.757
	$I^- = 3.5 \times 10^{-2}$ M	10%	25.563
	$H^+ = 5.0 \times 10^{-2}$ M	20%	30.130
		30%	36.848
DMSO	Ce(IV) = 5.0×10^{-3}M	Zero	3.166
	$I^- = 3.5 \times 10^{-2}$ M	5%	6.961
	$H^+ = 5.0 \times 10^{-2}$ M	10%	10.522
		20%	32.745
Mineral acid	Ce(IV) = 5.0×10^{-3} M	5.0×10^{-2} M HClO$_4$	30.130
	$I^- = 3.5 \times 10^{-2}$M	5.0×10^{-2} M H$_2$SO$_4$	5.964
	AcOH = 20%		
Sodium perchlorate	Ce(IV) = 5.0×10^{-3} M	zoro	3.166
	$I^- = 3.5 \times 10^{-2}$ M	3.0×10^{-2} M	3.173
	$H^+ = 2.5 \times 10^{-2}$ M	6.0×10^{-2} M	3.195

This is at variance with the dependence observed in the Ce(IV)-bromide reaction. The dependence in Ce(IV)-bromide reaction has been found to be complex. The authors could not rationalize the dependence of acidity observed at constant bisulphate concentration with varying amounts of acid. It was said that the dependence of acid was 1.7 but the inverse dependence of bisulphate concentration and direct dependence of H^+ are not consistent. Similarly in the Ce(IV)-iodide reaction, King and Pandow[2] postulated that the initial reaction was acid dependent and later reaction was acid independent. Hence, the present

observation that there is unit dependence on H^+, in the concentration range studied, is significant. The dependence on H^+ is quite obvious even up to 70% of the reaction which supports that there are no two pathways in this reaction. The only pathway is acid dependent reaction.

Effect of addition of sodium perchlorate: The results indicate that the kinetic rate is unaffected by the addition of sodium perchlorate in the range studied. This shows that this reaction is not subject to ionic strength effect (Table-1).

Effect of addition of solvent—acetic acid: The reaction rates increase with increasing proportions of acetic acid. The theory predicts that for the reactions between ions of opposite charge decrease of delectric constant results in an increase in kinetic rate. The experimental observations are in consistence with the theory of solvent effects (Table-1).

Effect of addition of solvent—dimetyl sulphoxide (DMSO): Dimethyl sulphoxide is a dipolar aprotic solvent and it has a dielectric constant less than that of water and more than that of acetic acid. Increasing proportions of DMSQ also result in an increase in kinetic rate as observed with acetic acid-water mixtures. A comparison of kinetic rates shows that the reaction rates are lesser in DMSO-water mixtures as compared to acetic acid-water mixture. This is quite in order as acetic acid- water mixtures have less dielectric constant than DMSO-water mixtures. Hence, the reaction rates are higher in acetic acid-water mixtures than in DMSO-water mixtures. (Table-1).

Effect of Mn(II): It is clear from Table-1 that there is acceleration in the presence of Mn(II). The acceleration may be ascribed to the formation of complex.The iodide ion and Mn(II) form a complex which is oxidised to Mn(III)-iodide complex. This complex breaks down into products in a slow rate determining step. Similar acceleration in the presence of Mn(II) had been observed by Shaffer[11] in the oxidation of thallous ion by Ce(IV). Radhkrishna-murti and Behera[12] observed that similar acceleration in the presence of Mn(II) in the oxidation of lactic acid by Ce(IV) (Table-1).

Effect of Ru(III): It was of interest to study the effect of addition of Ru(III). In this reaction it was found that Ru(III) functions as a catalyst. The dependence of Ru(III) has been found to be one. The dependence of Ce(IV) has been also found to be one. This is at variance with other reactions where Ru(III) has a dependence of one and other co-oxidant has a dependence of zero. This means that I^- forms a complex with Ru(III) which breaks down in rate determining step in the presence of Ce(IV) to form products. The dependence of I^- has been found to be 1.5. (Table-2)

Effect of Os(VIII): The work has been extended using another catalyst Os(VIII). It functions by a mechanism of alternate oxidation-reduction process. Even in this reaction with Os(VIII) the dependence on co-oxidant Ce(IV) found to be one and depencence on Os(VIII) is also one. This is comparable to the results obtained with Ru(III). The dependence on I^- is 1.5 as observed in Ru(III) catalysed process (Table-3).

TABLE-2

OXIDATION OF IODIDE BY CERIUM(IV) CATALYSED BY Ru(III) (TEMP = 28.5°C)

Varian.	Concentration of non-variant	Concentration of variant	$k_1 \times 10^4$ sec^{-1}
Ru(III)	Ce(IV) = 5.0×10^{-3} M	0.95×10^{-5} M	12.521
	I$^-$ = 3.5×10^{-2} M	1.9×10^{-5} M	25.33
	H$^+$ = 5.0×10^{-2} M	2.85×10^{-5} M	29.0
		3.8×10^{-5} M	40.76
Ce(IV)	I$^-$ = 3.5×10^{-2} M	5.0×10^{-3} M	25.33
	H$^+$ = 5.0×10^{-2} M	7.5×10^{-3} M	27.175
	Ru(III) = 1.9×10^{-5} M	10.0×10^{-3} M	26.023
		12.5×10^{-3} M	26.77
I$^-$	Ce(IV) = 5.0×10^{-3} M	1.75×10^{-2} M	7.735
	H$^+$ = 5.0×10^{-2} M	3.50×10^{-2} M	25.33
	Ru(III) = 1.9×10^{-5} M	5.0×10^{-2} M	34.545

TABLE-3

OXIDATION OF IODIDE BY CERIUM(IV) CATALYSED BY Os(VIII) (TEMP = 28.5°C)

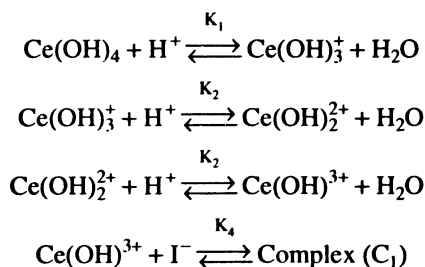| Variant	Concentration of non-variant	Concentration of variant	$k_1 \times 10^4$ sec^{-1}
Os(VIII)	Ce(IV) = 5.0×10^{-3} M	0.4×10^{-5} M	20.00
	I$^-$ = 3.5×10^{-2} M	0.8×10^{-5} M	27.14
	H$^+$ = 5.0×10^{-2} M	1.120×10^{-5} M	40.00
Ce(IV)	I$^-$ = 3.5×10^{-2} M	2.5×10^{-3} M	20.75
	H$^+$ = 5.0×10^{-2} M	5.0×10^{-3} M	20.00
	Oe(VIII) = 0.4×10^{-5} M	10.0×10^{-3} M	20.15
I$^-$	Ce(IV) = 5.0×10^{-3} M	1.75×10^{-2} M	8.54
	H$^+$ = 5.0×10^{-2} M	3.5×10^{-2} M	20.00
	Os(VIII) = 0.4×10^{-5} M	5.0×10^{-2} M	32.24

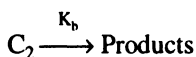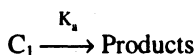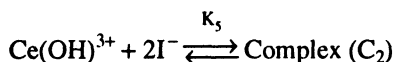**Mechanism and rate law**

Based upon the results obtained the rate equation is of the form:

$$\text{Rate} = k_a[Ce(IV)][I^-][H^+] + k_b[Ce(IV)][I^-]^2 [H^+]$$

For the uncatalysed reaction the reaction sequences are:

$$Ce(OH)_4 + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} Ce(OH)_3^+ + H_2O$$

$$Ce(OH)_3^+ + H^+ \underset{}{\overset{K_2}{\rightleftharpoons}} Ce(OH)_2^{2+} + H_2O$$

$$Ce(OH)_2^{2+} + H^+ \underset{}{\overset{K_2}{\rightleftharpoons}} Ce(OH)^{3+} + H_2O$$

$$Ce(OH)^{3+} + I^- \underset{}{\overset{K_4}{\rightleftharpoons}} \text{Complex (C}_1)$$

$$Ce(OH)^{3+} + 2I^- \overset{K_5}{\rightleftharpoons} \text{Complex } (C_2)$$

$$C_1 \overset{K_a}{\longrightarrow} \text{Products}$$

$$C_2 \overset{K_b}{\longrightarrow} \text{Products}$$

$$[Ce(IV)]_T = Ce(OH)_4 + Ce(OH)_3^+ + Ce(OH)_2^{2+} + Ce(OH)^{3+} + C_1 + C_2$$

$$= Ce(OH)^{3+}\left[\frac{1}{K_1K_2K_3[H^+]} + \frac{1}{K_2K_3[H^+]^2} + \frac{1}{K_3[H^+]} + 1 + K_4[I^-] + K_5[I^-]^2\right]$$

As the major species in the hydrolysis of Ce(IV) are $Ce(OH)_2^{2+}$ and $Ce(OH)^{3+}$, the terms which include $Ce(OH)_4$ and $Ce(OH)_3^+$ are excluded as they are of negligiable concentration.
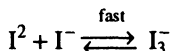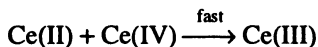
Hence,

$$Ce(IV)_T = Ce(OH)^{3+}\left[\frac{1 + K_3[H^+] + K_3K_4[H^+][I^-] + K_3K_5[H^+][I^-]^2}{K_3[H^+]}\right]$$

$$\text{Rate} = \frac{k_aK_3K_4[H^+][I^-][Ce(IV)]_T}{1 + K_3[H^+] + K_3K_4[H^+][I^-] + K_3K_5[H^+][I^-]^2}$$

$$+ \frac{k_bK_3K_5[H^+][I^-]^2[Ce(IV)]_T}{1 + k_3[H^+] + K_3K_4[H^+][I^-] + K_3K_5[H^+][I^-]^2}$$

The above rate law explains the observed kinetic orders 1.5 with regard to I^-, one with regard to Ce(IV) and one with regard to H^+.

The rate determining decomposition of C_1 and C_2 into products may be visualised further as follows:
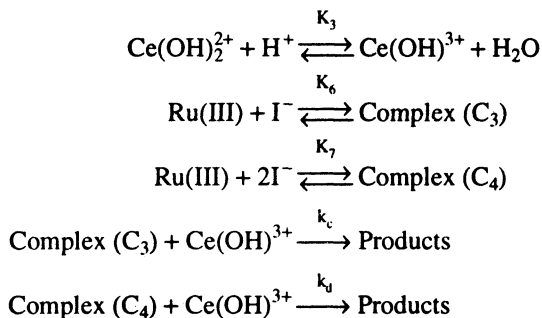
$$C_1 \overset{slow}{\longrightarrow} Ce(III) + I^\bullet$$

$$C_2 \overset{slow}{\longrightarrow} Ce(II) + 2I^\bullet$$

followed by

$$I^\bullet + I^\bullet \overset{fast}{\longrightarrow} I_2$$

$$Ce(II) + Ce(IV) \overset{fast}{\longrightarrow} Ce(III)$$

$$I^2 + I^- \overset{fast}{\rightleftharpoons} I_3^-$$

Besides the above possibilities of disappearance of $I^\bullet$ atoms as I_2 molecules, there are other roots possible like

$$I^\bullet + Ce(IV) \overset{fast}{\longrightarrow} I^+ + Ce(III)$$

$$I^+ + I^- \overset{fast}{\longrightarrow} I_2$$
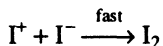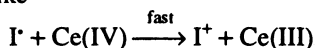
All these reactions subsequent to the rate determining steps are fast and their influence on the kinetic orders will not be felt.

The sequence of reactions for catalysed reactions is as follows:

$$Ce(OH)_2^{2+} + H^+ \xrightleftharpoons{K_3} Ce(OH)^{3+} + H_2O$$

$$Ru(III) + I^- \xrightleftharpoons{K_6} Complex\ (C_3)$$

$$Ru(III) + 2I^- \xrightleftharpoons{K_7} Complex\ (C_4)$$

$$Complex\ (C_3) + Ce(OH)^{3+} \xrightarrow{k_c} Products$$

$$Complex\ (C_4) + Ce(OH)^{3+} \xrightarrow{k_d} Products$$

Hence

$$Rate = \frac{k_c K_3 K_6 [H^+][I^-][Ce(IV)]_T [Ru(III)]}{1 + K_3[H^+]} + \frac{k_d K_3 K_7 [H^+][I^-]^2 [Ce(IV)]_T [Ru(III)]}{1 + K_3[H^+]}$$

The above rate law explains the observed kinetic orders of 1.5 with respect to I^-, one with respect to Ce(IV), one with respect to Ru(III) and one with respect to $[H^+]$. Similar rate law will explain the catalysed reaction with Os(VIII).

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