

CHAPTER – IV

CHROMIUM(III) CATALYSED CERIUM(IV) OXIDATION OF SELENIUM(IV)

4. CHROMIUM(III) CATALYSED CERIUM(IV) OXIDATION OF SELENIUM(IV)

The reduction potential of the couple Ce(IV)/Ce(III) depends both on the nature and concentration of the acid medium¹. Although the reaction between Te(IV) and Ce(IV) is thermodynamically feasible because the Te(IV)/Te(VI) couple has the redox potential¹ of 1.02.V. but it occurs² with a very low rate. Similarly the reaction² between Cr(VI) and Se(IV) occurs very slowly but when the oxidation of Se(IV) is carried out in presence of small amount of Cr(III) the reaction occurs with measurable rate. Such catalysis by Cr(III) is due to formation of a typical oxidation states of chromium, namely Cr(IV), which makes otherwise slow reactions to occur with considerable acceleration. Therefore, the oxidation of Se(IV) by Ce(IV) was studied in presence of Cr(III) to understand the mechanism of catalysis.

4.1 Results

The reaction was carried out under pseudo-first order conditions keeping [Se(IV)] excess than that of [Ce(IV)] and the pseudo-first order plots were found to be linear. Therefore, the order in [Ce(IV)] is unity. The pseudo-first order rate constants were found to decrease as the [Ce(IV)] increases [Table IV(i)]. The effect of reductant was studied between the concentration range of 8.0×10^{-4} to 8.0×10^{-3} mol dm⁻³ keeping all other concentrations constant. The pseudo-first-order rate constants were fairly constant [Table IV(ii)] indicating the first order dependence of the reaction on reductant concentration. At constant concentration of oxidant, reductant perchloric acid and sulphuric acid concentration the effect of catalyst,

Table IV(i)

Effect of Oxidant

 $10^3[\text{SeO}_2] = 2.0 \text{ mol dm}^{-3}$, $10^5[\text{Cr}^{\text{III}}] = 4.0 \text{ mol dm}^{-3}$ $[\text{HClO}_4] = 0.2 \text{ mol dm}^{-3}$, $10^2 [\text{H}_2\text{SO}_4] = 4.0 \text{ mol dm}^{-3}$

$10^5 [\text{Ce}^{\text{IV}}] \text{ mol dm}^{-3}$	$10^4 k \text{ s}^{-1}$
2.0	12.7
3.0	8.73
4.0	4.60
10.0	4.50
20.0	4.05
30.0	2.58
40.0	1.86

Table IV(ii)

Effect of SeO_2

$10^4 [\text{Ce}^{\text{IV}}] = 2.0 \text{ mol dm}^{-3}$, $10^5 [\text{Cr}^{\text{III}}] = 4.0 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.2 \text{ mol dm}^{-3}$,
 $10^2 [\text{H}_2\text{SO}_4] = 4.0 \text{ mol dm}^{-3}$,

$10^4 [\text{SeO}_2] \text{ mol dm}^{-3}$	10^4 k s^{-1}
8.0	4.20
20.0	4.05
40.0	4.10
60.0	4.20
80.0	4.15

Cr(III), was studied between 2.0×10^{-5} to 2.0×10^{-4} mol dm⁻³ [Table IV(iii)] and the plot of the K_{obs} against [Cr(III)] was found to be linear passing through origin [Figure IV(i)]. Therefore, the uncatalysed reaction occurs to negligible extent and its contribution to the overall catalysed rate is not considered. The order in catalyst concentration was found to be unity as determined from $\log k_{\text{obs}}$ against $\log[\text{Cr(III)}]$ plot [Figure IV(ii)]. The hydrogen ion has an accelerating effect on the reaction [Table IV(iv)] and the order in $[\text{H}^+]$ was found to be less than unity (0.6) as determined from $\log k_{\text{obs}}$ against $\log [\text{H}^+]$ plot [Figure IV(iii)]. The added product Ce(III) has slightly inhibiting effect [Table IV(v)]. The effect of temperature was studied between 25 to 40°C and the activation parameters were determined. The kinetic data for effect of temperature and the activation parameters are tabulated in Table IV(vi).

4.2 Discussion

The order of unity in oxidant and the catalyst is due to their involvement in an prior equilibria which is also supported by the inhibiting effect of the added product. The prior equilibria between catalyst and the oxidant which generate Cr(IV) oxidises the reductant, Se(IV), in the second step of the reaction. The estimated redox potential³ of the Cr^{IV}/Cr^{III} couple (> 1.5 V) is higher than the Ce^{IV}/Ce^{III} (1.40 V)¹ and Cr^{VI}/Cr^{III} (1.30 V)⁶ thus making the oxidation more feasible. The possibility of further oxidation of Cr(IV) to Cr(V) is ruled out due to stereochemical⁶ changes from co-ordination 4 to 6.

The effect of $[\text{H}^+]$ on the reaction may be explained due to the protonation of the Ce(IV) sulphate complex, $\text{Ce}(\text{SO}_4)_3^{2-}$, as explained in the previous chapter on cyclohexanol oxidation. The only difference would be that only monoprotonated species of the $\text{Ce}(\text{SO}_4)_3^{2-}$ is the active species in the present case. Therefore,

Table IV(iii)

Effect of catalyst

$10^4 [\text{Ce}^{\text{IV}}] = 2.0 \text{ mol dm}^{-3}$, $10^3 [\text{SeO}_2] = 2.0 \text{ mol dm}^{-3}$, $10^2 [\text{H}_2\text{SO}_4] = 4.0 \text{ mol dm}^{-3}$,
 $[\text{HClO}_4] = 0.2 \text{ mol dm}^{-3}$,

$10^5[\text{CrIII}]$	$10^4 k \text{ s}^{-1}$	$\log k$	$\log \text{Cr}^{\text{III}}$
2.0	2.20	-3.65	-4.69
4.0	4.10	3.38	4.39
6.0	6.05	3.22	4.22
8.0	8.50	3.07	4.09
10	10.6	2.97	4.00
12	12.3	2.91	3.92
14	14.0	2.85	3.85
16	16.0	2.79	3.79
18	17.9	2.75	3.75
20	19.2	2.72	3.69

FIG. IV(i)—PLOT OF k_{obs} AGAINST $[Cr^{iii}]$.
[CONDITIONS AS IN TABLE IV(iii)].

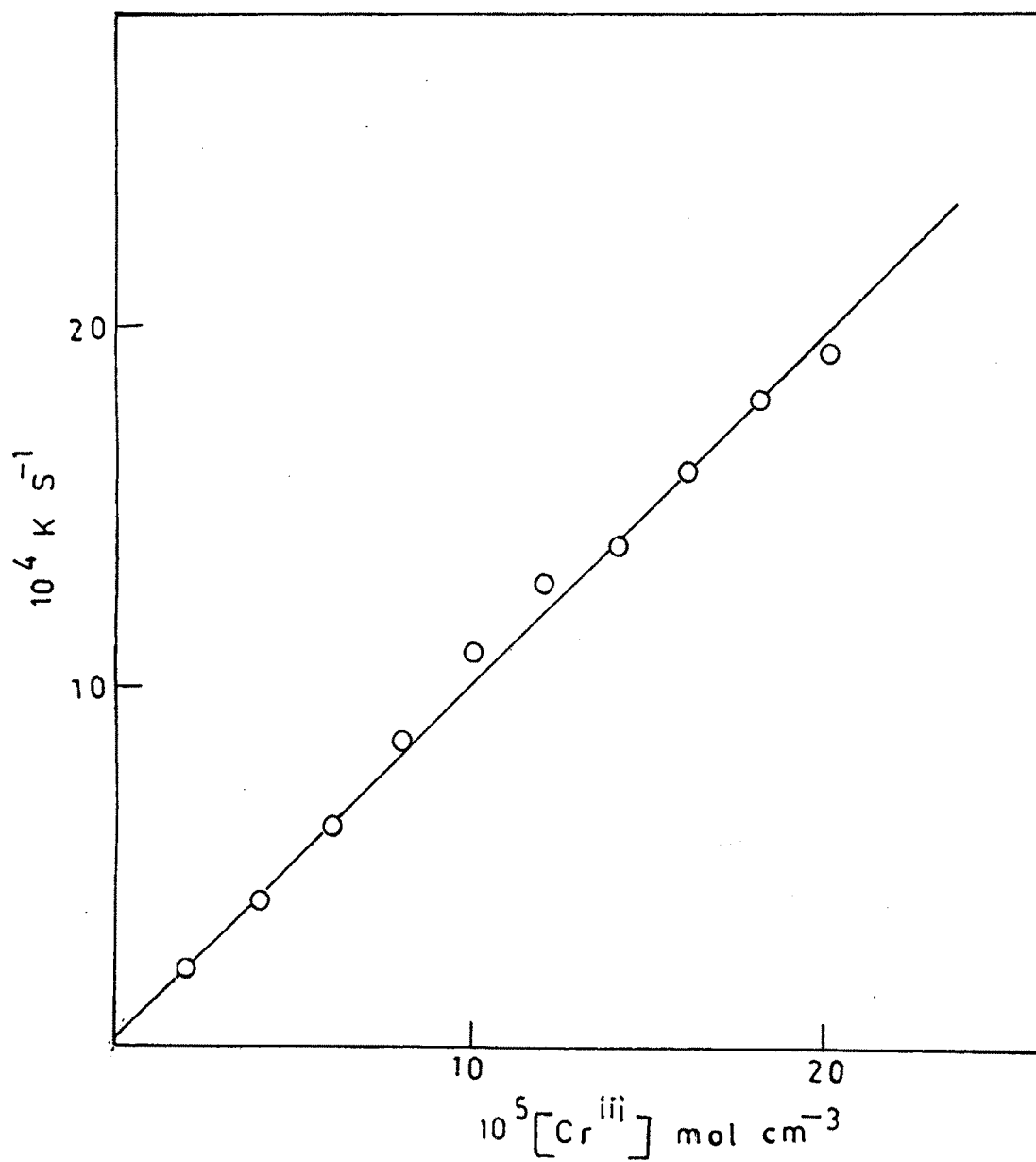


FIG. IV (ii) — ORDER IN CATALYST CONCENTRATION.
[CONDITIONS AS IN TABLE IV (iii)]

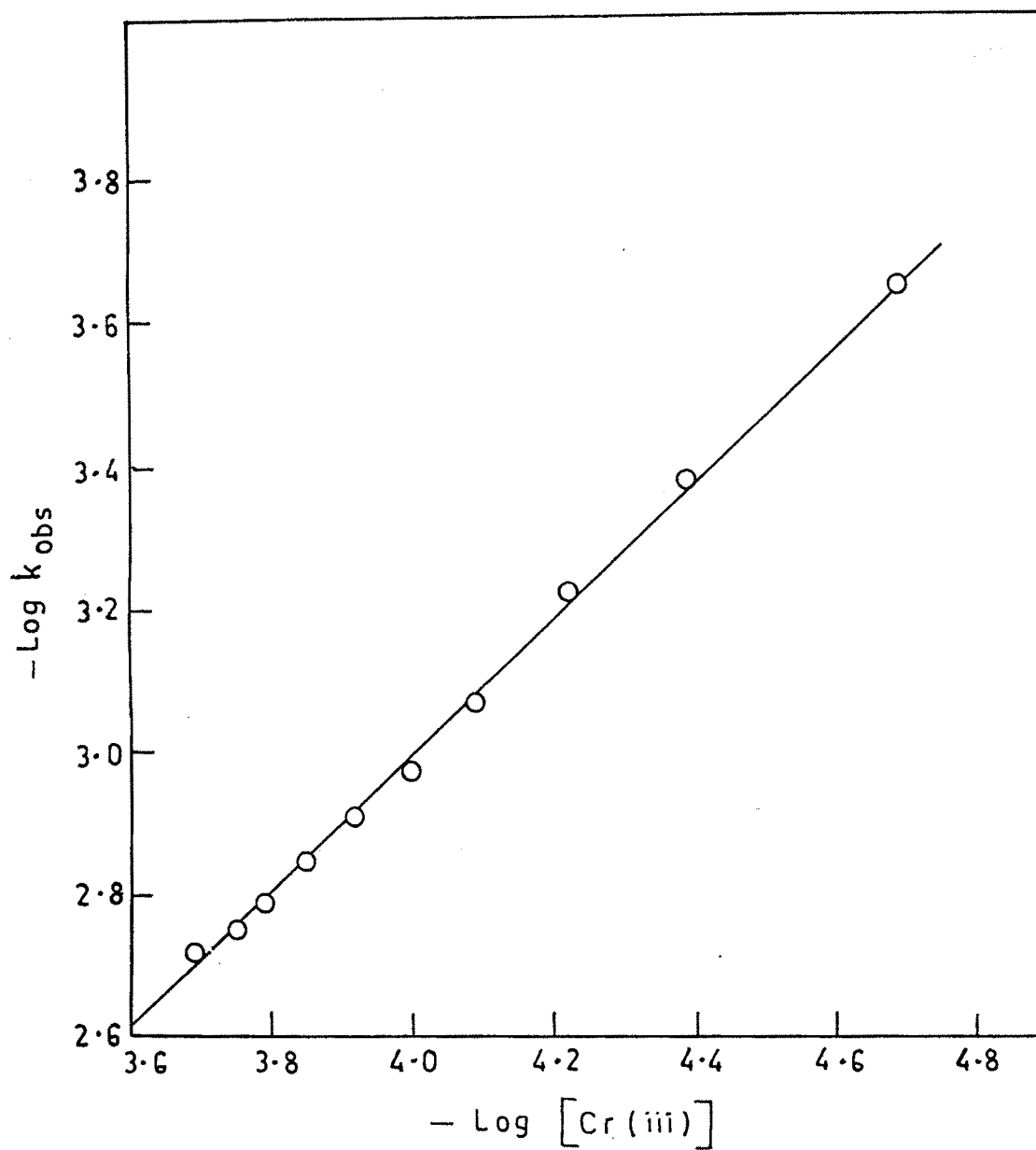


Table IV(iv)

Effect of $[H^+]$

$10^4 [Ce^{IV}] = 2.0 \text{ mol dm}^{-3}$, $10^5 [Cr^{III}] = 4.0 \text{ mol dm}^{-3}$, $10^3 [SeO_2] = 2.0 \text{ mol dm}^{-3}$,
 $10^2 [H_2SO_4] = 4.0 \text{ mol dm}^{-3}$,

$[H^+]$	$10^4 k \text{ s}^{-1}$	$\log [H^+]$	$\log k$
0.02	1.25	-1.69	-3.90
0.04	1.70	1.39	3.77
0.08	2.20	1.09	3.66
0.14	3.80	0.85	3.42
0.20	4.10	0.69	3.38

FIG. IV (iii) — ORDER IN HYDROGEN ION CONCENTRATION.
[CONDITIONS AS IN TABLE IV (iv)] .

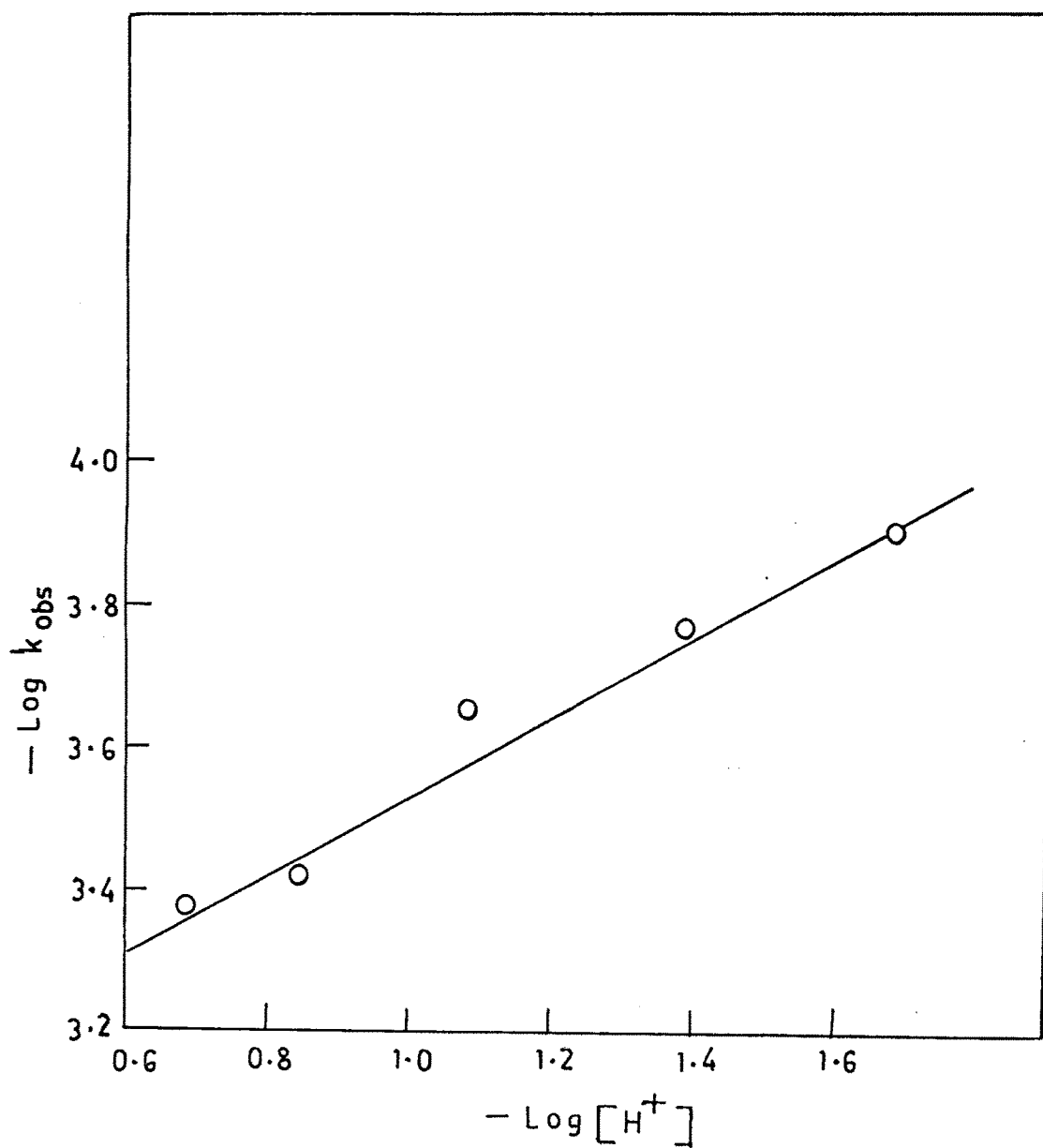


Table IV(v)

Effect of added product

$10^4 [\text{Ce}^{\text{IV}}] = 2.0 \text{ mol dm}^{-3}$, $10^5 [\text{Cr}^{\text{III}}] = 2.0 \text{ mol dm}^{-3}$, $10^3 [\text{SeO}_2] = 2.0 \text{ mol dm}^{-3}$,
 $[\text{HClO}_4] = 2.0 \text{ mol dm}^{-3}$, $10^2 [\text{H}_2\text{SO}_4] = 4.0 \text{ mol dm}^{-3}$,

$10^4 [\text{Ce}^{\text{III}}] \text{ mol dm}^{-3}$	10^4 k s^{-1}
0.0	4.10
0.4	4.00
0.6	3.92
0.8	3.86

Table IV(vi)

Effect of Temperature.

$10^4 [\text{Ce}^{\text{IV}}] = 2.0 \text{ mol dm}^{-3}$, $10^5 [\text{Cr}^{\text{III}}] = 2.0 \text{ mol dm}^{-3}$, $10^3 [\text{SeO}_2] = 2.0 \text{ mol dm}^{-3}$,
 $[\text{HClO}_4] = 0.2 \text{ mol dm}^{-3}$, $10^2 [\text{H}_2\text{SO}_4] = 4.0 \text{ mol dm}^{-3}$,

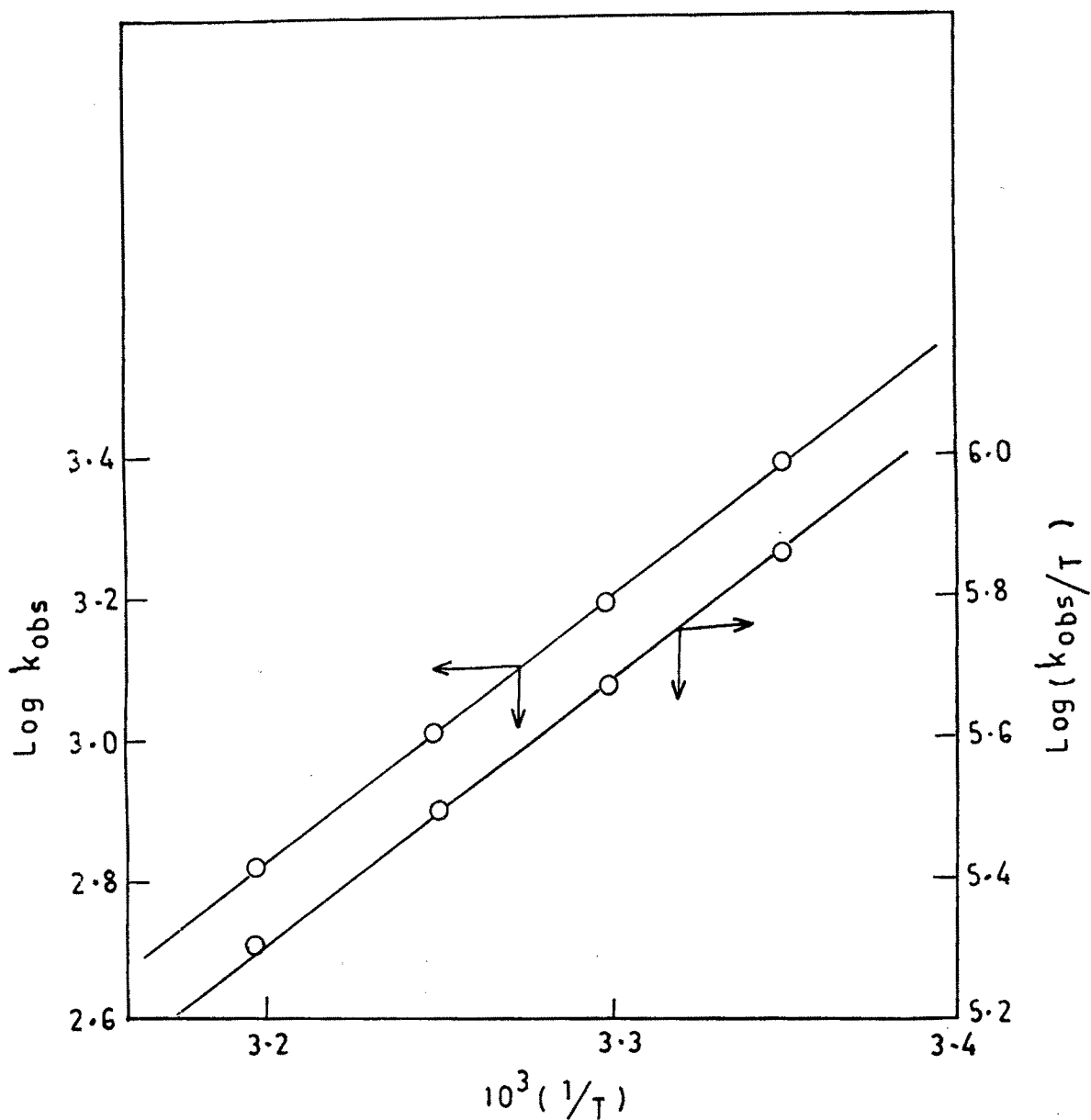
T	$10^4 k$	$1/T$	$\log k$	$\log (k/T)$
298	4.10	3.35×10^{-3}	-3.39	-5.86
303	6.45	3.30×10^{-3}	3.19	5.67
308	9.65	3.25×10^{-3}	3.01	5.50
313	15.13	3.19×10^{-3}	2.82	5.31

$$E_a = 70.8 \pm 5 \text{ kJ mol}^{-1}, \Delta S^\ddagger = -79.2 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$$

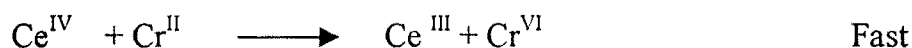
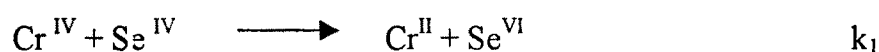
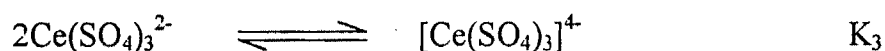
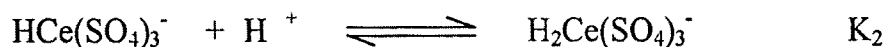
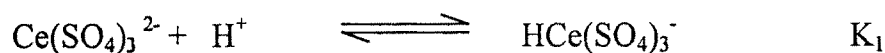
$$\Delta H^\ddagger = 72.1 \pm 6 \text{ kJ mol}^{-1}$$

$$\Delta G^\ddagger = 95.60 \pm 6 \text{ kJ mol}^{-1}$$

FIG. IV - PLOT OF $\text{Log } k_{\text{obs}}$ AND $\text{Log } (k_{\text{obs}}/T)$ AGAINST $1/T$.
(CONDITIONS AS IN TABLE IV)



considering $\text{HCe}(\text{SO}_4)_3^-$ as the active oxidant species the overall mechanism of the reaction can be represented as in Scheme 1. The



corresponding rate law can be derived as in case of cyclohexanol in Chapter I which is given in equation 1 and pseudo-first order rate constant by equation 2 respectively.

$$\text{rate} = \frac{k_1 K_1 K_{\text{ox}} [\text{H}^+] [\text{Ce}(\text{SO}_4)_3^{2-}] [\text{Se}^{\text{IV}}] [\text{Cr}^{\text{III}}]}{(1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + K_3 [\text{Ce}(\text{SO}_4)_3^{2-}])} \quad (1)$$

$$k_{\text{obs}} = \frac{k_1 K_1 K_{\text{ox}} [\text{H}^+] [\text{Se}^{\text{IV}}] [\text{Cr}^{\text{III}}]}{(1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + K_3 [\text{Ce}(\text{SO}_4)_3^{2-}])} \quad (2)$$

while deriving equations 2 and 3 the redox equilibrium between Cr^{III} and Ce^{IV} is considered to be rapid due to the fact that in this equilibrium the Cr^{IV} generated will be consumed by excess Se^{IV} present in the solution. The rate law derived explains satisfactorily the order in oxidant, substrate catalyst and hydrogen ion

concentration. The activation parameters obtained from the plots of $\log k$ and $\log k/T$ against $1/T$ [Figure IV(iv)] are given in Table IV(vi). Low entropy of activation suggests an outer-sphere transition state between Cr^{IV} and Se^{IV} .