
CHAPTER - IV

DISCUSSION

DISCUSSION

UNCATALYSED REACTIONS

The uncatalysed cerium(IV) oxidations of n-butanol and ethylene glycol were studied by Rangaswamy and Santappa²⁴ and by Sant and coworkers²⁵. In both the cases complex formation between alcohol and oxidant was predicted with its decomposition in a rate determining second step. In order to account for the contribution of uncatalysed reaction we ^{have} also studied the uncatalysed reactions under the conditions used for the catalysed reactions. The results of the study are given in chapter III and have the following characteristics.

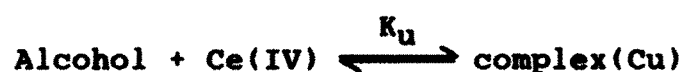
i) For both the alcohols the order in oxidant is unity and the orders in n-butanol and ethylene glycol were 0.66 and 0.81 respectively.

ii) Formation of free radicals was observed in both the cases.

iii) The end products were n-butyraldehyde and formaldehyde for n-butanol and ethylene glycol respectively.

The results of the study of uncatalysed reactions are in agreement with the formation of a complex between the oxidant and alcohol followed by its decomposition in a slow second step as observed in earlier studies^{24,25}. In order to confirm the complex formation kinetically the

values of $1/k_u$ were plotted against $1/[\text{Alcohol}]_0$ (Table 4.1 & 4.2). The plot was found to be linear with an intercept as shown in Figure 4.1 & 4.2 for n-butanol and ethylene glycol respectively. The general mechanism of uncatalysed oxidation of n-butanol and ethylene glycol can be written with formation of complex as primary step.



The complex so formed decomposes in a slow second step to give free radicals.



The free radical thus obtained is further oxidised in a fast step to give the products. Accordingly the rate is given by

$$-\frac{d[\text{Ce(IV)}]_T}{dt} = k'_u [\text{Ce(IV)}]_f [\text{C}_u] \dots\dots(1)$$

The concentration of complex $[\text{C}_u]$ is given by

$$[\text{C}_u] = K_u [\text{Ce(IV)}]_f [\text{Alcohol}] \dots\dots(2)$$

Where $[\text{Ce(IV)}]_f$ and $[\text{Alcohol}]$ are free cerium(IV) and total alcohol concentrations respectively. But the total cerium(IV) concentration will be sum of complexed and free cerium(IV) concentrations

$$\begin{aligned} [\text{Ce(IV)}]_T &= [\text{Ce(IV)}]_f + [\text{C}_u] \dots\dots(3) \\ &= [\text{Ce(IV)}]_f + K_u [\text{Ce(IV)}]_f [\text{Alcohol}] \end{aligned}$$

Table 4.1: Data for Michaelis Menten plot for uncatalysed and chromium(III) catalysed cerium(IV) oxidation of n-butanol.

$$[\text{Ce(IV)}] = 4.0 \times 10^{-3} \text{ M}, [\text{HClO}_4] = 2.0 \text{ M}$$

$$[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2} \text{ M}$$

$$I = 2.1 \text{ M}, \quad \text{Temp.} = 30^\circ\text{C}$$

$[\text{Alcohol}]$ 10^2 M	$k_u \times 10^4$ s^{-1}	$k^*c \times 10^4$ s^{-1}	$(k_c - k_u)$ 10^4 s^{-1}	$\frac{1}{[\text{Alcohol}]}$	$\left[\frac{1}{k_u} \right] 10^{-3}$	$\left[\frac{1}{k_c - k_u} \right] \times 10^{-2}$
2.0	0.62	4.67	4.05	50.0	16.13	24.7
3.0	0.72	5.90	5.18	33.3	13.89	19.3
4.0	0.97	6.82	5.85	25.0	10.31	17.1
5.0	1.10	7.40	6.30	20.0	9.09	15.9
6.0	1.30	8.77	7.47	16.7	7.69	13.4

$$* [\text{Cr(III)}] = 2.0 \times 10^{-4} \text{ M}$$

Figure 4.1: Plot of $1/k_u$ and $1/k_c - k_u$ against $1/[\text{Alcohol}]$ for cerium(IV) oxidation of n-butanol. (conditions as in Table 4.1)

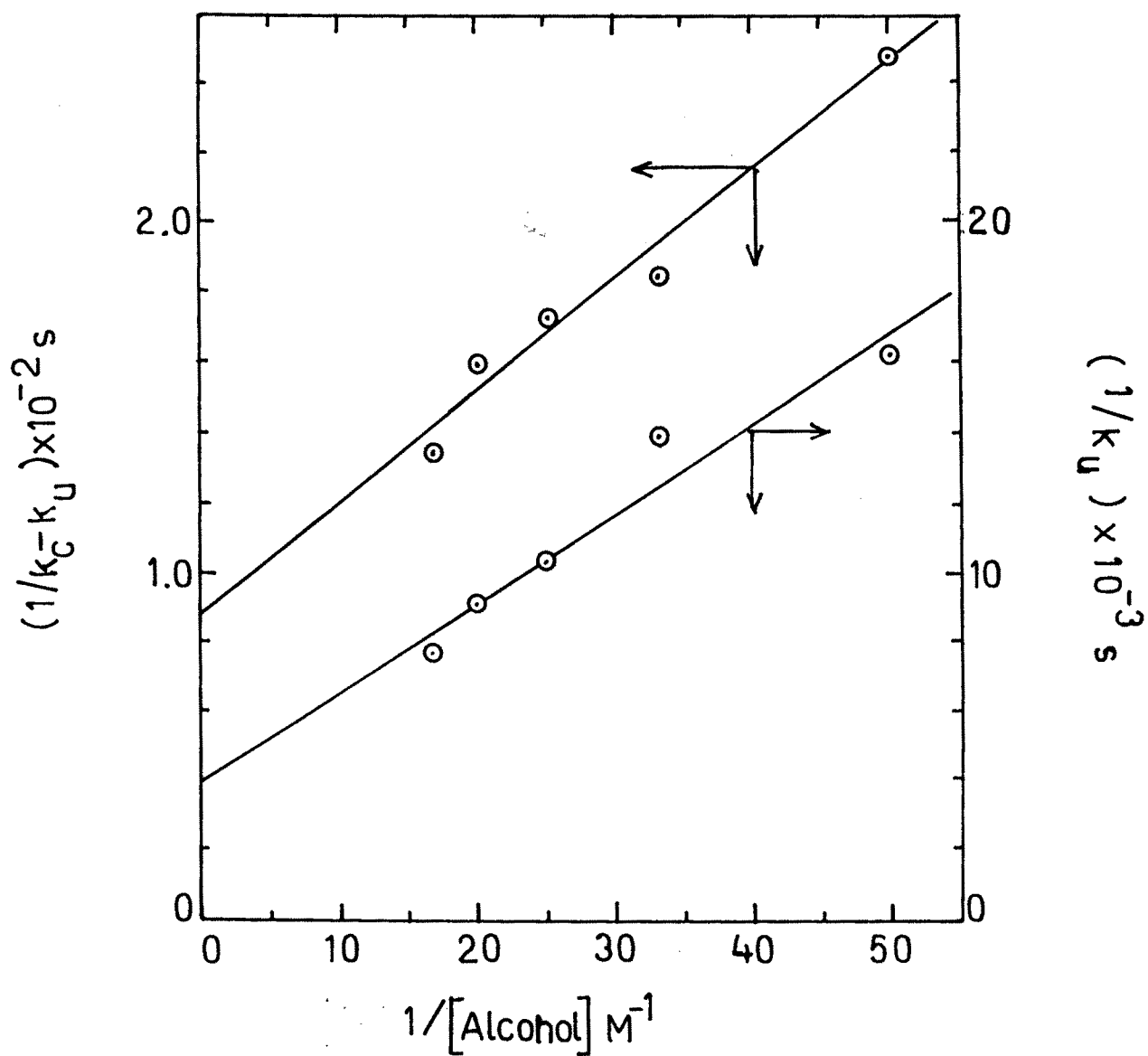


Table 4.2: Data for Michaelis-Menten plot for uncatalysed and chromium(III) catalysed cerium(IV) oxidation of ethylene glycol.

$$[\text{Ce(IV)}] = 4.0 \times 10^{-3} \text{ M}, [\text{HClO}_4] = 2.0 \text{ M}$$

$$[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2} \text{ M}$$

$$I = 2.1 \text{ M}, \quad \text{Temp.} = 30^\circ\text{C}$$

[Alcohol] 10^2 M	$k_u \times 10^4$ s^{-1}	$k^*c \times 10^4$ s^{-1}	$(k_c - k_u)$ 10^4 s^{-1}	$\frac{1}{[\text{Alcohol}]}$	$\left[\frac{1}{k_u}\right] 10^{-3}$	$\left[\frac{1}{k_c - k_u}\right] \times 10^{-2}$
2.0	0.31	1.64	1.33	50.0	32.3	75.2
3.0	0.46	2.18	1.72	33.3	21.7	58.0
4.0	0.57	2.50	1.93	25.0	17.5	51.8
5.0	0.66	3.09	2.43	20.0	15.2	41.2
6.0	0.78	3.50	2.72	16.7	12.8	36.7

$$* [\text{Cr(III)}] = 2.0 \times 10^{-4} \text{ M}$$

Figure 4.2: Plot of $1/k_u$ against $1/[\text{Alcohol}]$ for cerium(IV) oxidation of ethylene glycol. (conditions as in Table 4.2)

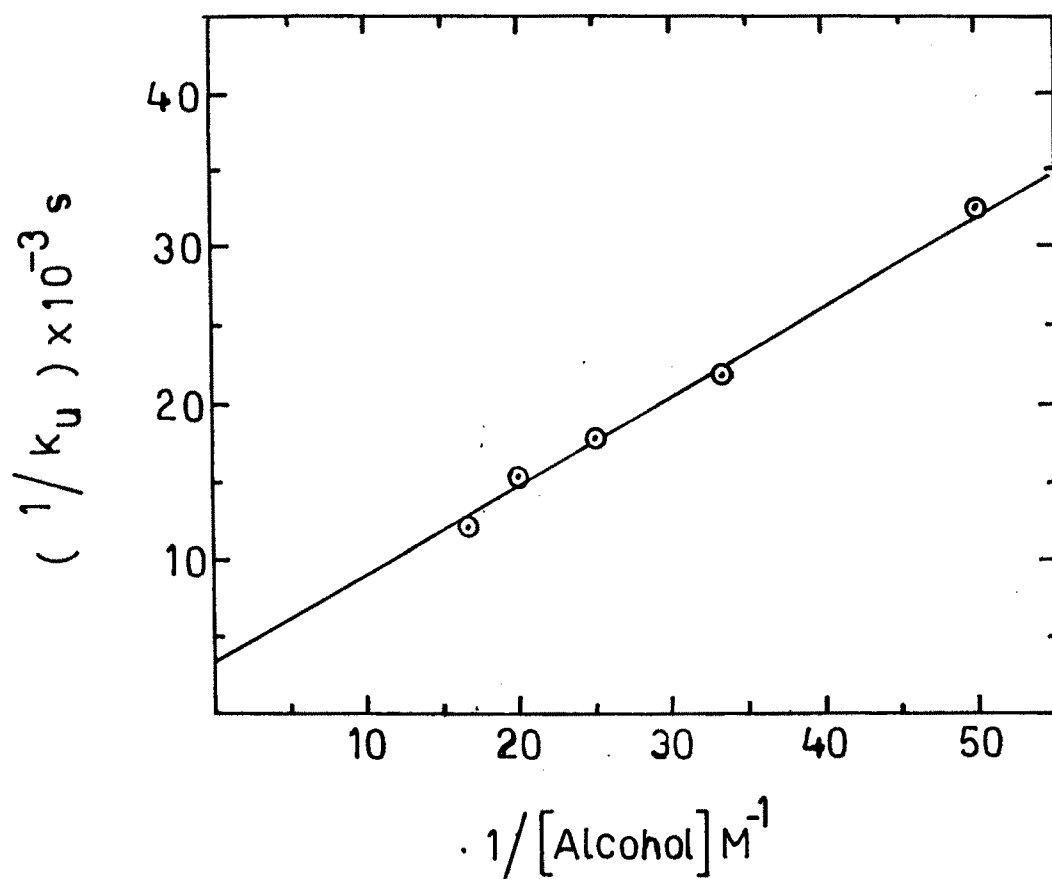
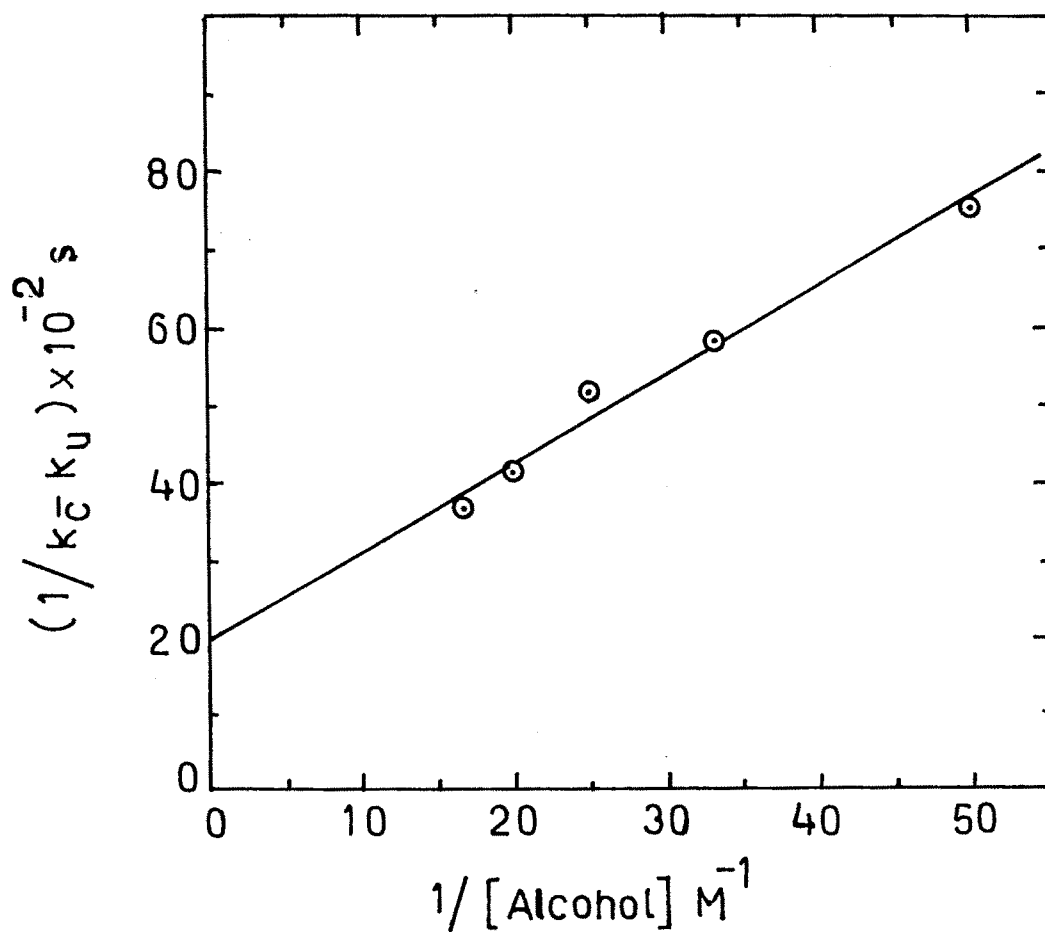


Figure 4.3: Plot of $1/k_C - k_U$ against $1/[\text{Alcohol}]$ for cerium(IV) oxidation of ethylene glycol. (conditions as in Table 4.2)



$$[\text{Ce(IV)}]_f = \frac{[\text{Ce(IV)}]_T}{1 + K_u[\text{Alcohol}]} \dots\dots(4)$$

Substituting the value of $[\text{Ce(IV)}]_f$ in equation (2).

$$[\text{C}_u] = \frac{K_u[\text{Ce(IV)}]_T [\text{Alcohol}]}{1 + K_u[\text{Alcohol}]} \dots\dots(5)$$

Then from equation (1) and (5) we get

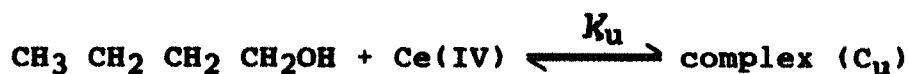
$$\frac{-d[\text{Ce(IV)}]_T}{dt} = \frac{k'_u K_u [\text{Ce(IV)}]_T [\text{Alcohol}]}{1 + K_u[\text{Alcohol}]} \dots\dots(6)$$

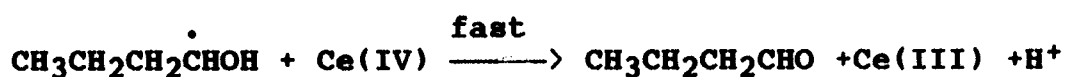
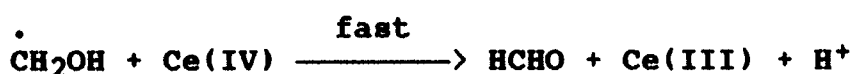
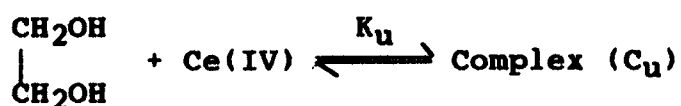
The pseudo-first order rate constant of the uncatalysed reaction k_u will be

$$k_u = \frac{k'_u K_u [\text{Alcohol}]}{1 + K_u [\text{Alcohol}]} \dots\dots(7)$$

Where K_u is the equilibrium constant of complex formation between alcohol and oxidant and k'_u is the rate constant for its decomposition.

The detailed mechanism for uncatalysed oxidations can be represented as in scheme I and scheme II for n-butanol and ethylene glycol respectively.



SCHEME ISCHEME II**CHROMIUM(III) CATALYSED REACTIONS**

The results of chromium(III) catalysed cerium(IV) oxidations of n-butanol and ethylene glycol have been included in chapter III. It can be seen from the results that n-butanol and ethylene glycol oxidations in presence of chromium(III) follow Michaelis Menten type of kinetics, the characteristics of which are as follows.

i) For both the alcohols order in oxidant is unity and order in alcohols are found to be 0.57 and 0.69 for n-butanol and ethylene glycol respectively.

ii) The order with respect to catalyst, chromium(III) are 0.54 and 0.83 for n-butanol and ethylene glycol respectively.

iii) Formation of free radicals is observed for both the reactions.

iv) The end products are butyraldehyde and formaldehyde for n-butnaol and ethylene glycol respectively.

The results of the study of chromium(III) catalysed reactions indicate formation of a complex between catalyst and alcohol followed by its oxidation by cerium(IV) in a slow step. The complex formation was confirmed by plotting $(1/k_C - k_U)$ values against $1/[\text{Alcohol}]$ (Tables 4.1 to 4.2) where k_C and k_U are observed pseudo-first order rate constants of the catalysed and uncatalysed reactions. The values $(k_C - k_U)$ were used in order to consider only the catalysed rate constant for catalyst-alcohol complex formation after subtracting the uncatalysed rate constant. The plots were found to be linear with intercept (Figures 4.1 and 4.3). An attempt to obtain spectroscopic evidence for the complex failed as there was no change in ultraviolet and visible spectrum of catalyst and alcohol in presence of one another. Therefore the complex formation between alcohol and catalyst is restricted to the kinetic data only. The general mechanism for the catalysed reactions can be written as



The complex formed is oxidised by cerium(IV) to form a free radical





The free radical thus formed is further oxidised by another cerium(IV) ion to respective aldehydes.



Therefore the rate of catalysed reaction will be given by

$$-\frac{d[\text{Ce(IV)}]}{dt} = k'_c [\text{Ce(IV)}] [\text{C}_c] \dots\dots(8)$$

The concentration of the complex is given by

$$[\text{Cc}] = K_c [\text{Cr(III)}]_f [\text{Alcohol}] \dots\dots(9)$$

Where $[\text{Cr(III)}]_f$ and $[\text{Alcohol}]$ are uncomplexed chromium(III) and total alcohol concentrations respectively. The constants K_c and k'_c are the equilibrium constant of the catalyst alcohol complex formation and rate constant of the slow second step respectively.

Since total chromium(III) concentration is sum of complexed and uncomplexed chromium(III) concentrations.

$$[\text{Cr(III)}]_T = [(\text{Cr(III)}]_f + [\text{Cc}]$$

$$[\text{Cr(III)}]_T = [\text{Cr(III)}]_f (1 + K_c[\text{alcohol}]) \dots\dots(10)$$

Substituting the value of $[\text{Cr(III)}]_f$ in equation(9) we get

$$[\text{C}_c] = \frac{K_c [\text{Cr(III)}]_T [\text{Alcohol}]}{1 + K_c[\text{Alcohol}]} \dots\dots(11)$$

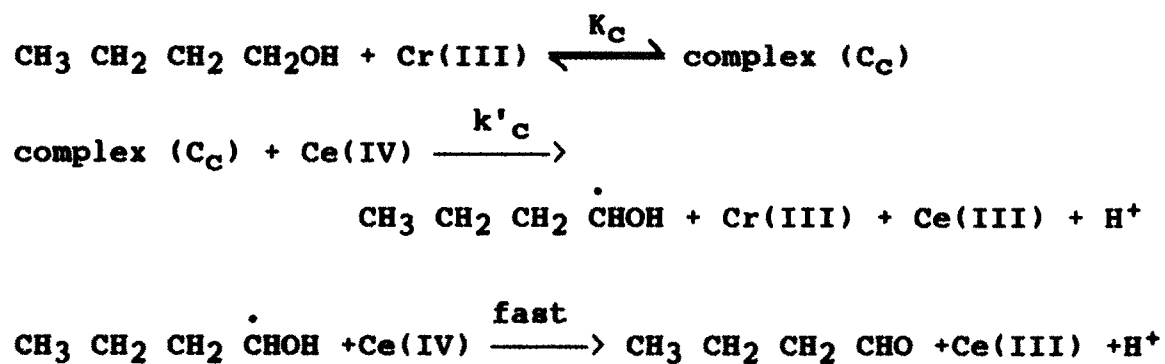
The from equations (11) and (8) the rate of the reaction is given by

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{k'_c K_c [\text{Cr(III)}]_T [\text{Ce(IV)}] [\text{Alcohol}]}{1 + K_c [\text{Alcohol}]} \dots (12)$$

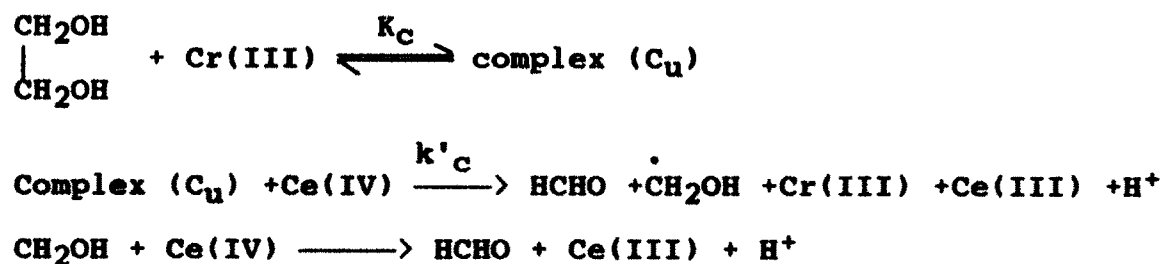
The pseudo-first order rate constant of the catalysed reaction is

$$k''_c = \frac{k'_c K_c [\text{Cr(III)}]_f [\text{Alcohol}]}{1 + K_c [\text{Alcohol}]} \dots (13)$$

The detailed mechanisms of chromium(III) catalysed oxidation of n-butanol and ethylene glycol are represented in scheme III and scheme IV.



SCHEME III



SCHEME IV

Since uncatalysed and catalysed reactions are occurring simultaneously the total rate of the reaction will be sum of rates of both the reactions.

$$-\frac{d[\text{Ce(IV)}]}{dt} = \text{rate of uncatalysed reaction} + \text{rate of catalysed reaction}$$

$$-\frac{d[\text{Ce(IV)}]}{dt} = \left[\frac{k'_u K_u}{1 + K_u [\text{Alcohol}]} + \frac{k'_c K_c [\text{Cr(III)}]}{1 + K_c [\text{Alcohol}]} \right] [\text{Ce(IV)}] [\text{Alcohol}] \dots (14)$$

The pseudo-first order rate constant will be

$$k = \frac{k'_u K_u [\text{Alcohol}]}{1 + K_u [\text{Alcohol}]} + \frac{k'_c K_c [\text{Cr(III)}] [\text{Alcohol}]}{1 + K_c [\text{Alcohol}]} = k_c$$

$$k_c = k_u + \frac{k'_c K_c [\text{Cr(III)}] [\text{Alcohol}]}{1 + K_c [\text{Alcohol}]}$$

$$k_c - k_u = \frac{k'_c K_c [\text{Cr(III)}] [\text{Alcohol}]}{1 + K_c [\text{Alcohol}]} \dots \dots (15)$$

Therefore in order to obtain the equilibrium constant of catalyst-alcohol complex formation the values of $(1/k_c - k_u)$ were plotted against $1/[\text{Alcohol}]$ (Fig. 4.1 & 4.3). The values of k_c obtained are given in Table 4.3 along with the values of k_u for the uncatalysed reactions.

Table 4.3: Values of K_u and K_c for uncatalysed and chromium(III) catalysed cerium(IV) oxidation of n-butanol and ethylene glycol. (conditions as in Table 4.2 and 4.3)

	$K_u \text{ M}^{-1}$	$K_c \text{ M}^{-1}$
n-butanol	15.7	27.8
ethylene glycol	5.6	17.5

EFFECT OF PERCHLORIC ACID CONCENTRATION

The variation of pseudo-first order rate constant with perchloric acid (Table 4.4 and 4.5) may be due to different cerium(IV) species forming in presence of sulphate. The order with respect to perchloric acid was found to be:

- i) 1.26 for uncatalysed n-butanol oxidation
- ii) 1.43 for uncatalysed ethylene glycol oxidation
- iii) 1.44 for the chromium(III) catalysed oxidation of n-butanol and
- iv) 1.87 for the chromium(III) catalysed oxidation of ethylene glycol
- v) The plots k_u and $(k_c - k_u)$ against $[H^+]^2$ are found to be linear with intercept (Figure 4.4 & 4.5) in case uncatalysed and chromium(III) catalysed cerium(IV) oxidation of n-butanol.
- vi) The plot of k_u vs $[H^+]^2$ is linear with intercept for the uncatalysed cerium(IV) oxidation of ethylene glycol. Where as the plot of $(k_c - k_u)$ against $[H^+]^2$ is linear without any intercept for the chromium(III) catalysed cerium(IV) oxidation of ethylene glycol as shown in Figure 4.6.

The results given above indicate involvement of more than one cerium(IV) species in the rate determining

Table 4.4: Effect of perchloric acid on uncatalysed and chromium(III) catalysed cerium(IV) oxidation of n-butanol.

[Ce(IV)] = 4.0×10^{-3} M, [Alcohol] = 4.0×10^{-2} M

[H₂SO₄] = 6.0×10^{-2} M

I = 2.1 M, Temp. = 30°C

[H ⁺]*	[H ⁺] ²	$k_u \times 10^4 \text{ s}^{-1}$	$k_c^{**} \times 10^4 \text{ s}^{-1}$	$(k_c - k_u) \times 10^4 \text{ s}^{-1}$
1.0	1.00	0.48	2.55	2.07
1.2	1.44	0.51	3.50	2.99
1.4	1.96	0.69	4.60	3.91
1.6	2.56	0.73	5.11	4.38
1.8	3.24	0.80	6.10	5.30
2.0	4.00	1.00	6.90	5.90

* [HClO₄] is taken as [H⁺]

** [Cr(III)] = 2.0×10^{-4} M

Figure 4.4: Plot of k_u against $[H^+]^2$: cerium(IV) oxidation of n-butanol (conditions as in Table 4.4)

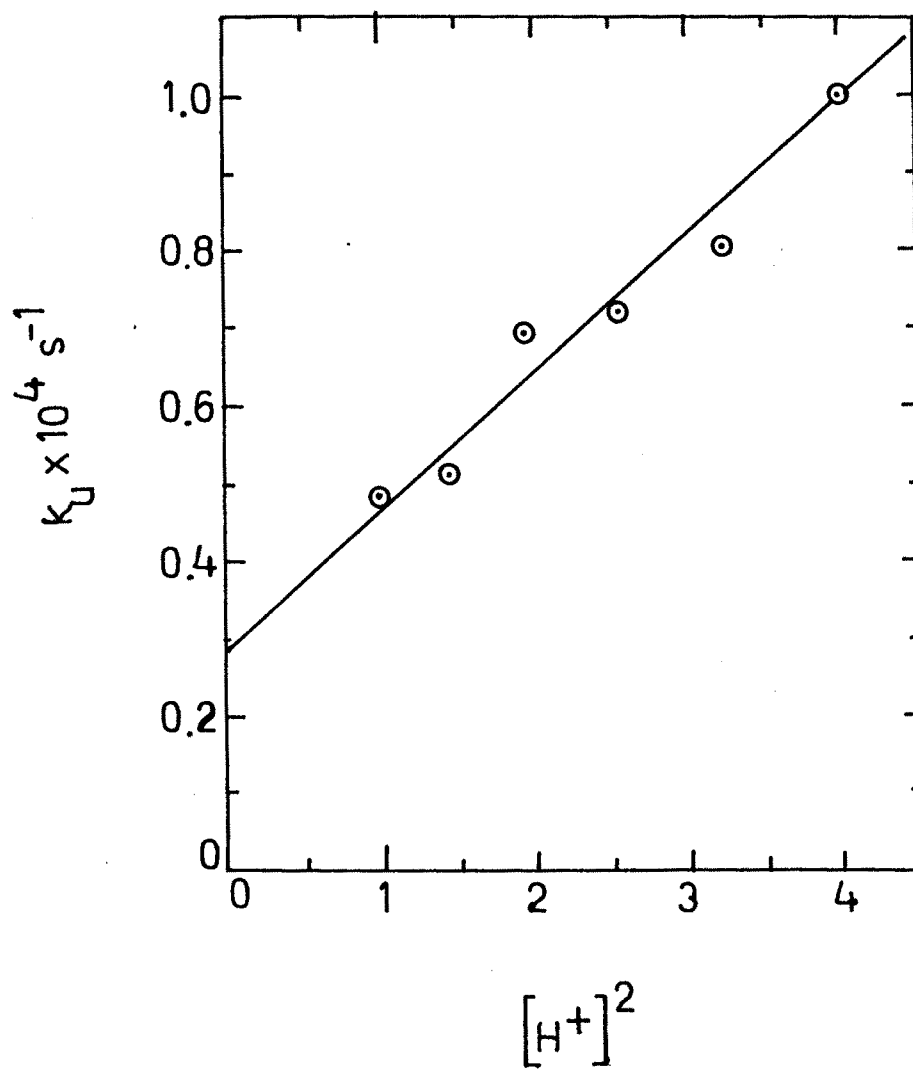


Figure 4.5: Plot of $(k_C - k_U)$ against $[H^+]^2$: cerium(IV) oxidation of n-butanol (conditions as in Table 4.4)

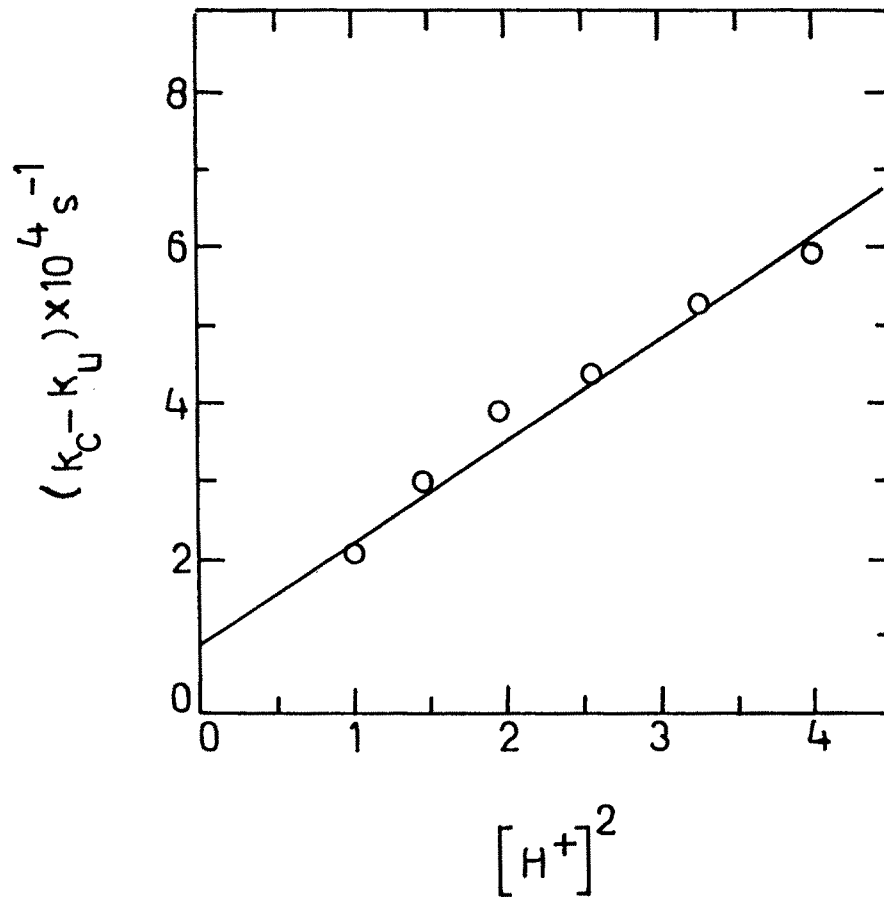


Table 4.5: Effect of perchloric acid on uncatalysed and chromium(III) catalysed cerium(IV) oxidation of ethylene glycol.

$[\text{Ce(IV)}] = 4.0 \times 10^{-3} \text{ M}$, $[\text{Alcohol}] = 4.0 \times 10^{-2} \text{ M}$

$[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2} \text{ M}$

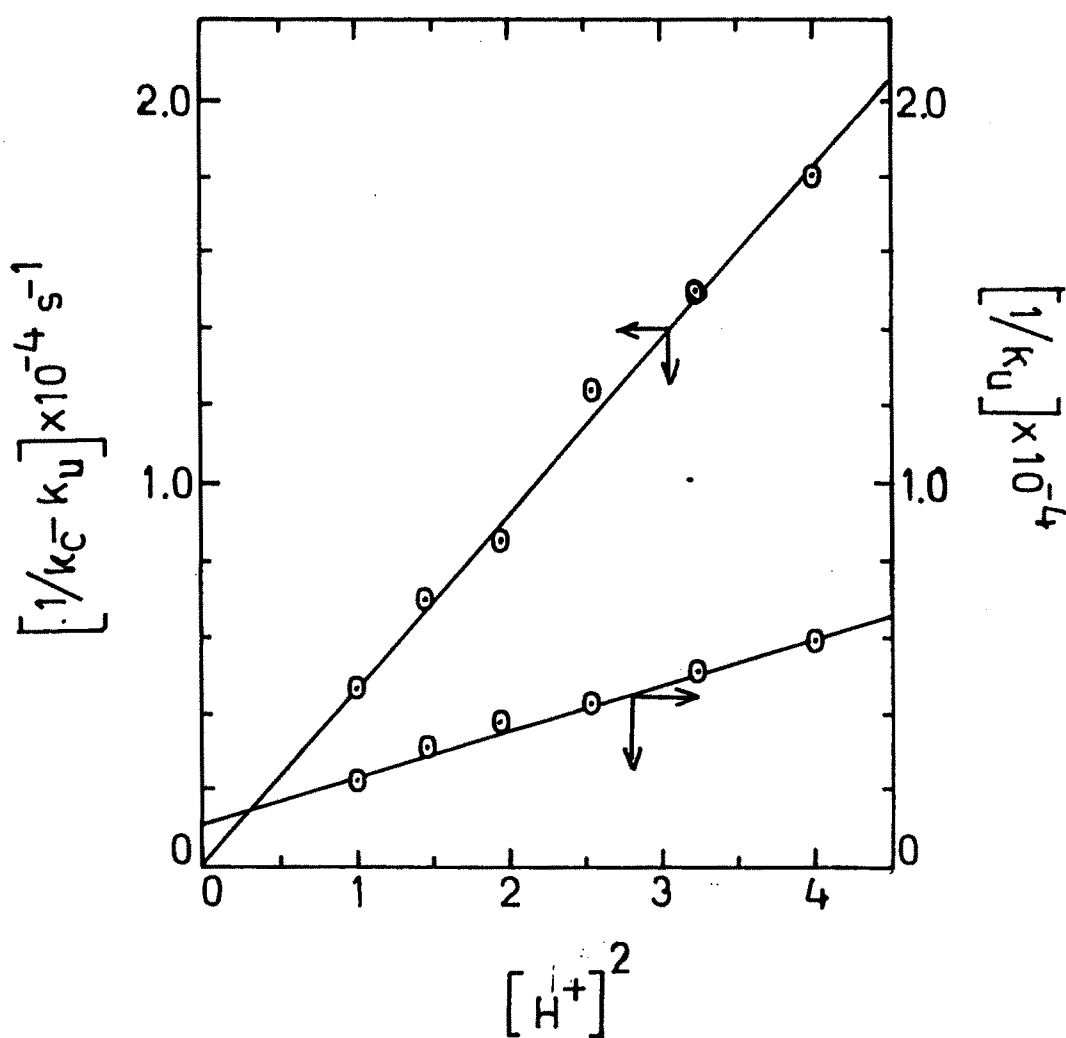
$I = 2.1 \text{ M}$, Temp. = 30°C

$[\text{H}^+]$ *	$[\text{H}^+]^2$	$k_u \times 10^4 \text{ s}^{-1}$	$k_c^{**} \times 10^4 \text{ s}^{-1}$	$(k_c - k_u) \times 10^4 \text{ s}^{-1}$
1.0	1.00	0.22	0.69	0.47
1.2	1.44	0.31	1.00	0.69
1.4	1.96	0.38	1.23	0.85
1.6	2.56	0.43	1.66	1.23
1.8	3.24	0.52	2.02	1.50
2.0	4.00	0.58	2.38	1.80

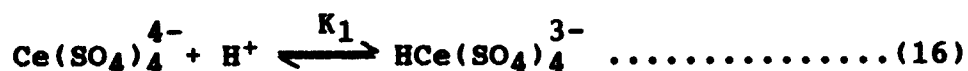
* $[\text{HClO}_4]$ is taken as $[\text{H}^+]$

** $[\text{Cr(III)}] = 2.0 \times 10^{-4} \text{ M}$

Figure 4.6: Plot of k_u and $(k_c - k_u)$ against $[H^+]^2$: cerium(IV) oxidation of ethylene glycol (conditions as in Table 4.5)



step. In solutions containing sulphate cerium(IV) will be predominantly present as $\text{Ce}(\text{SO}_4)_4^{4-}$ and it is further successively protonated³⁰ as shown by the equilibria 16 to 19.



From the orders obtained with respect to perchloric acid and Figures 4.4 to 4.6 the reasonable prediction of active species of oxidant would be as follows:

i) $\text{H Ce}(\text{SO}_4)_4^{3-}$ and $\text{H}_2 \text{Ce}(\text{SO}_4)_4^{2-}$ may be the active species for both uncatalysed reactions and chromium(III) catalysed oxidation of n-butanol.

ii) $\text{H}_2 \text{Ce}(\text{SO}_4)_4^{2-}$ may be the active species for the chromium(III) catalysed oxidation of ethylene glycol

iii) $\text{H Ce}(\text{SO}_4)_4^{3-}$ and $\text{H}_2\text{Ce}(\text{SO}_4)_4^{2-}$ may be the active species for uncatalysed cerium(IV) oxidation of ethylene glycol

The mechanism of oxidation of n-butanol and ethylene glycol by cerium(IV) both uncatalysed and chromium(III) catalysed reactions proceeds with the formation of either oxidant-substrate complex or catalyst-

substrate complex respectively. The formation free radicals in the reaction was confirmed by polymerization of acrylonitrile. The decrease observed in the values of pseudo-first order rate constants as cerium(IV) concentration increases is probably due to dimerization³¹ of the cerium(IV) species. Added cerium(III) did not affect the rate. Therefore no redox equilibria involving cerium(III) is likely to be involved. The activation energies obtained by studying the reaction at four different temperature are given in Table 3.16 to 3.19. The reaction in presence of chromium(III) is having less activation energy than the reaction in absence of chromium(III) as expected for a catalysed reaction.