CHAPTER - III

RESULTS

RESULTS

In the present chapter, the results of oxidation of n-butanol and ethylene glycol by cerium(IV) catalysed by chromium(III) in mixture of perchloric and sulphuric acid medium are given . Since the uncatalysed reaction was also occurring with considerable rate, in order to account its contribution to the total rate the uncatalysed reaction was also studied.

All reactions were carried out under pseudo-first order condition and pseudo-first order rate constants were obtained from linear plots of log[Ce(IV)] against time. The pseudo-first order rate were denoted as k_u for the uncatalysed and k_c for the catalysed one. The results of this study involves effect of oxidant, substrate, perchloric acid and temperature and are given in this chapter.

EFFECT OF OXIDANT, CERIUM(IV)

During the study of effect Cerium(IV) concentration on the uncatalysed and chromium(III) catalysed reaction, the alcohol concentration (4.0 x 10^{-2} M), perchloric acid concentration (2.0M), sulphuric acid concentration (6.0 x 10^{-2}M) and chromium concentration (2.0 x 10^{-4}M) were kept constant. The cerium(IV) concentration was varied from 2.0 x 10^{-3} to 6.0 x 10^{-3}M. The ionic strength was maintained at 2.1 M with sodium perchlorate and the temperature was kept constant at 30 ± 0.1°C. Pseudo-first order ~~of~~ plots of log[Ce(IV)] against time were linear upto 75% or more, in most of the runs indicating order of unity with respect to the oxidant. The data of the example runs for uncatalysed and cataylsed reactions are given in Table 3.1 to 3.4 with respective pseudo-first order plots in Figure 3.1 to 3.4. As the concentration of Cerium(IV) increases, the pseudo-first order rate constants (k_u & k_c) decreases as shown in Table 3.5.

EFFECT OF ALCOHOL CONCENTRATION

The order with respect to alcohol was determined by Ostwald's isolation method, by keeping cerium(IV) (4.0 x 10^{-3}M), perchloric acid (2.0M), sulphuric acid (6.0 x 10^{-2}M) and chromium(III) (2.0 x 10^{-4}M) concentration constant. The alcohol concentration was varied from 2.0 x 10^{-2} M to 6.0 x 10^{-2} M at an ionic strength of 2.1M using sodium perchlorate and temperature of 30 ± 0.1°C. The pseudo-first order rate constant (k_u & k_c) are given in Table 3.6 and 3.7 for uncatalysed and chromium(III) catalysed reactions respectively. It is observed that rate of reaction increases as alcohol concentration increases. Plots of log of pseudo-first-order rate constants k_u and k_c against log[alcohol]$_o$ are shown in Figure 3.5 to 3.8 which yield order with respect to alcohol as 0.66 to 0.81 for the uncatalysed reaction and 0.57 and 0.69 for the chromium(III) catalysed

Table 3.1: Example run uncatalysed cerium(IV) oxidation of n-butanol

[Ce(IV)] = 4.0×10^{-3} [Alcohol] = 4.0×10^{-2}M
[$HClO_4$] = 2.0M [H_2SO_4] = 6.0×10^{-2}M
I = 2.1 M ~~M~~ Temp = 30°c.

Time in minutes	Burette* Readings	[Ce(IV)$\times 10^{-3}$M]	-log [Ce(IV)]
00	8.4	3.90	2.4089
15	7.8	3.62	2.4411
30	7.5	3.48	2.4584
45	6.5	3.02	2.5203
60	6.0	2.79	2.5544
75	5.5	2.55	2.5928
90	5.2	2.41	2.6172

* [Fe^{2+}] = 2.32×10^{-3}M

Figure 3.1: Plot of log [Ce(IV)] Vs time for the uncatalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.1)

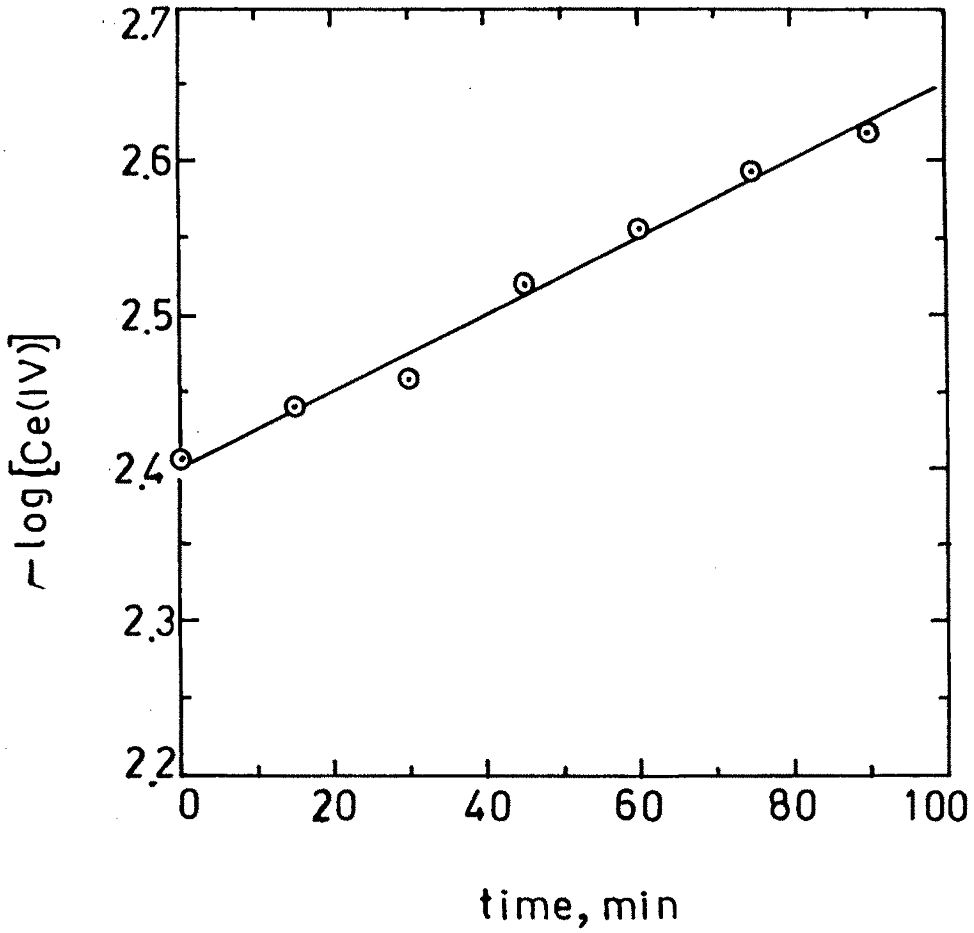


Table 3.2: Example run: uncatalysed cerium(IV) oxidation of Ethylene glycol

[Ce(IV)] = 3.0×10^{-3}
[$HClO_4$] = 2.0M
I = 2.1 M
[Alcohol] = 4.0×10^{-2}M
[H_2SO_4] = 6.0×10^{-2}M
~~M~~ Temp = 30°c.

Time in minutes	Burette* Readings	[Ce(IV)x10^{-3}M]	-log [Ce(IV)]
00	6.8	2.89	2.5384
15	6.4	2.72	2.5648
30	6.2	2.64	2.5785
45	6.0	2.55	2.8928
60	5.7	2.43	2.6151
75	5.3	2.26	2.6467
90	5.1	2.17	2.6634

* [Fe^{2+}] = 2.12×10^{-3}M

Figure 3.2: Plot of log [Ce(IV)] Vs time for the uncatalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.2)

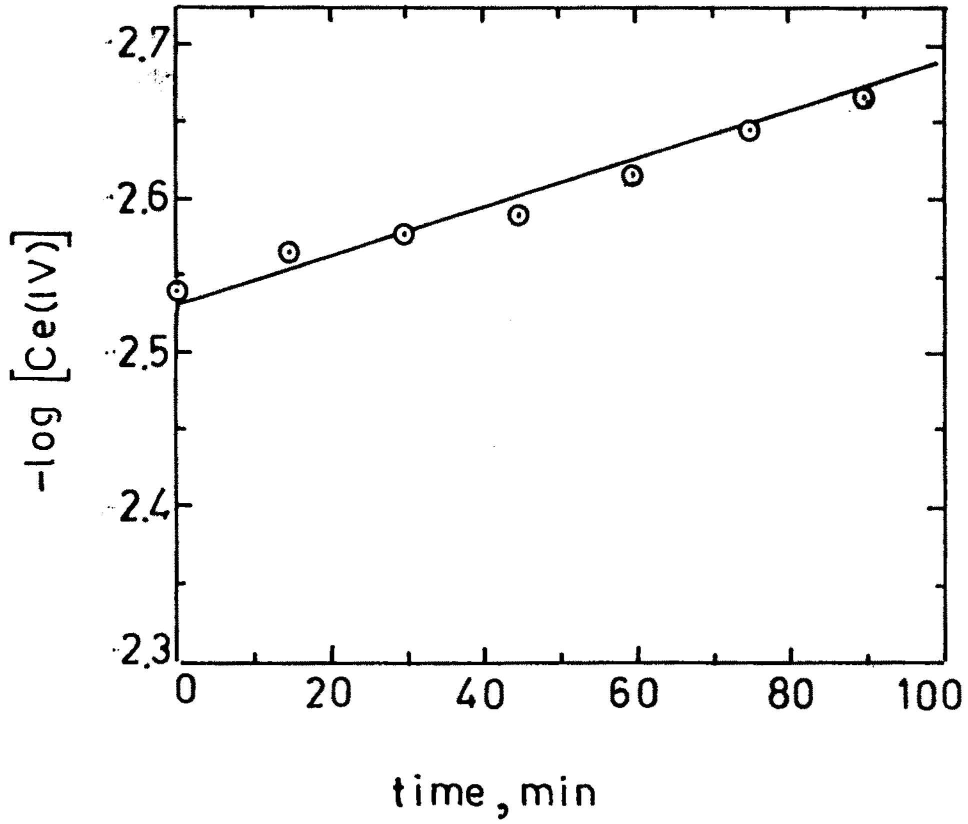


Table 3.3: Example run catalysed cerium(IV) oxidation n-butanol

$[Ce(IV)]$ = 4.0×10^{-3} [Alcohol] = $4.0\times10^{-2}M$
$[Cr(III)]$ = $2\times10^{-4}M$ $[HClO_4]$ = 2.0M
$[H_2SO_4]$ = $6.0\times10^{-2}M$ I = 2.1 M
Temp = 30°c.

Time in minutes	ml of $FeSO_4(NH_4)_2SO_4$* for 5 ml of aliquot	$[Ce(IV)\times10^{-3}M]$	-log [Ce(IV)]
00	8.7	3.86	2.4126
10	6.4	2.84	2.5460
20	4.4	1.95	2.7087
30	2.8	1.24	2.9050
40	1.7	0.75	3.1217
50	1.1	0.49	3.3108
60	0.5	0.22	3.6532

* $[Fe^{2+}] = 2.22\times10^{-3}M$

Figure 3.3: Plot of log [Ce(IV)] Vs time for chromium(III) catalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.3)

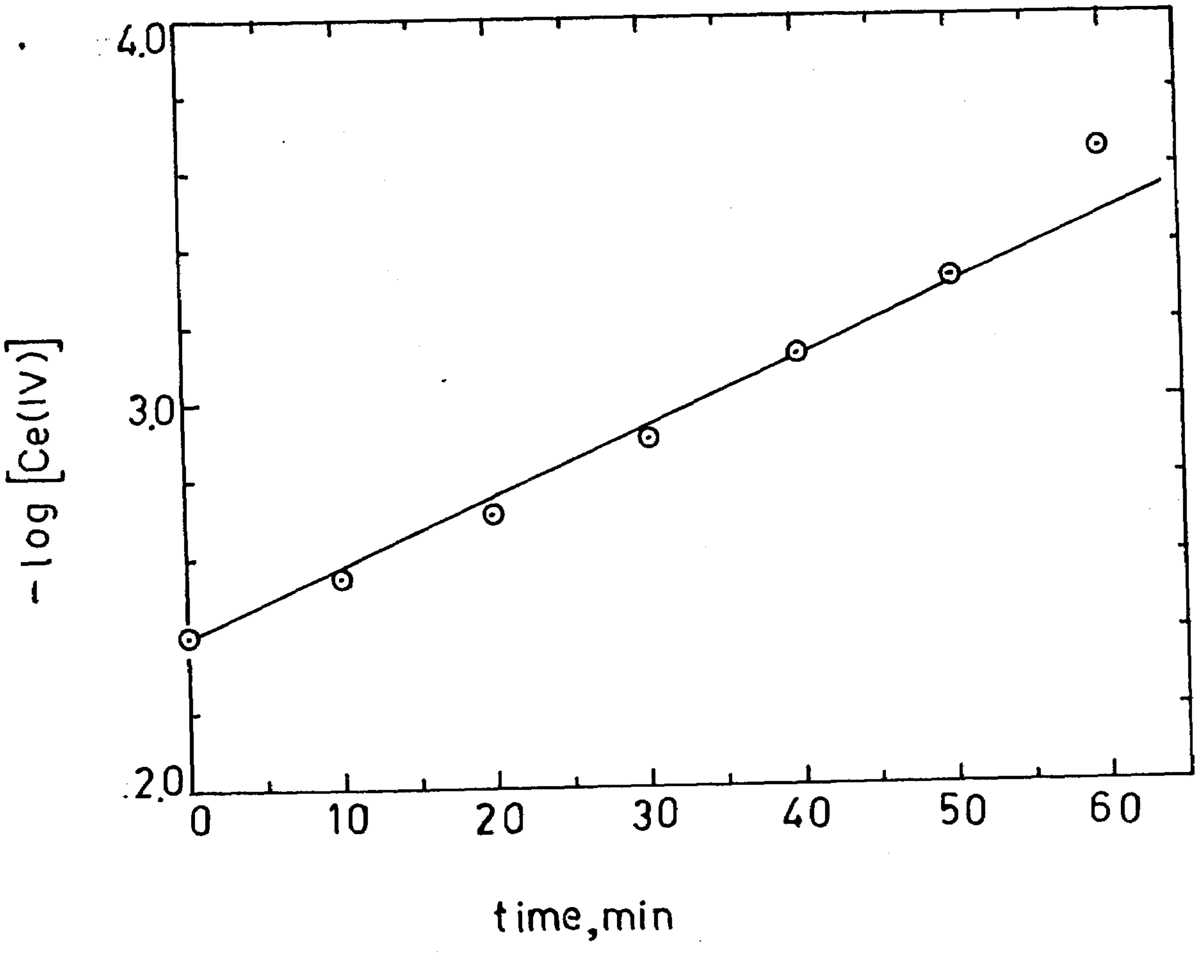


Table 3.4: Example run: ~~catalysed cerium(III~~ chromium(III)) catalysed cerium(IV) oxidation Ethylene glycol

[Ce(IV)] = 2.0×10^{-3} [Alcohol] = 4.0×10^{-2}M

[Cr(III)] = 2×10^{-4}M [$HClO_4$] = 2.0M

[H_2SO_4] = 6.0×10^{-2}M I = 2.1 M

Temp = 30°c.

Time in minutes	Burette* Readings	[Ce(IV)$\times 10^{-3}$M]	-log [Ce(IV)]
00	4.3	2.00	2.6988
05	3.8	1.76	2.7525
10	3.4	1.58	2.8008
15	3.0	1.39	2.8552
20	2.6	1.20	2.9173
30	2.0	0.93	3.0313
40	1.5	0.73	3.1356

* [Fe^{2+}] = 2.32×10^{-3}M

Figure 3.4: Plot of log [Ce(IV)] Vs time for chromium(III) catalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.4)

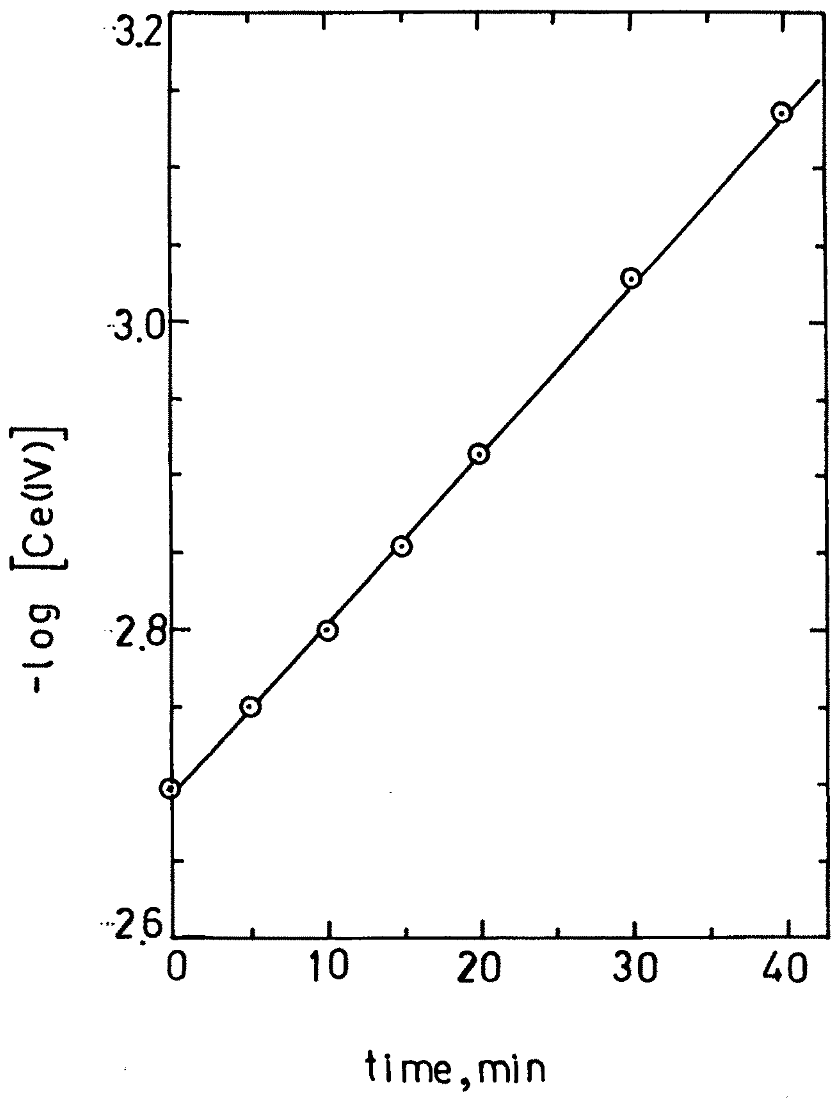


Table 3.5: Effect of cerium(IV) on pseudo-first order rate constants of uncatalysed (ku) and chromium(III) catalysed (kc) cerium(IV) oxidation of n-butanol and ethylene glycol.

[Alcohol] = 4.0×10^{-2}M, [$HClO_4$] = 2.0M

[H_2SO_4] = 6.0×10^{-2}M

I = 2.1 M, Temp. = 30°c

[Ce(IV)]x10^3 M	n butanol		ethylene glycol	
	kux10^5 s^{-1}	kcx10^4 s^{-1}	kux10^5 s^{-1}	kcx10^4 s^{-1}
2.0	15.0	8.21	6.9	3.76
3.0	12.0	8.03	6.1	2.97
4.0	9.8	6.82	5.6	2.44
5.0	8.10	4.60	5.3	1.96
6.0	6.80	3.80	4.7	1.60

* [Cr(III)] = 2.0×10^{-4} M

Table 3.6: Effect of alcohol concentration on pseudo-first order rate constants of (ku) uncatalysed ~~and~~ cerium(IV) oxidation of n-butanol and ethylene glycol.

$[Ce(IV)] = 4.0\times10^{-3}M$, $[HClO_4] = 2.0M$

$[H_2SO_4] = 6.0\times10^{-2}M$

I = 2.1 M, Temp. = 30°c

[Alcohol] 10^2 M	$ku\times10^5$ s^{-1}		-log[Alcohol]	-log ku	
	n-butanol	ethylene glycol		n-butanol	ethylene glycol
2.0	6.20	3.1	1.6989	4.2076	4.5086
3.0	7.20	4.6	1.5228	4.1426	4.3372
4.0	9.70	5.7	1.3979	4.0132	4.2441
5.0	11.00	6.6	1.3010	3.9586	4.1804
6.0	13.00	7.8	1.2218	3.8860	4.1079

Figure 3.5: Order in alcohol: uncatalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.6)

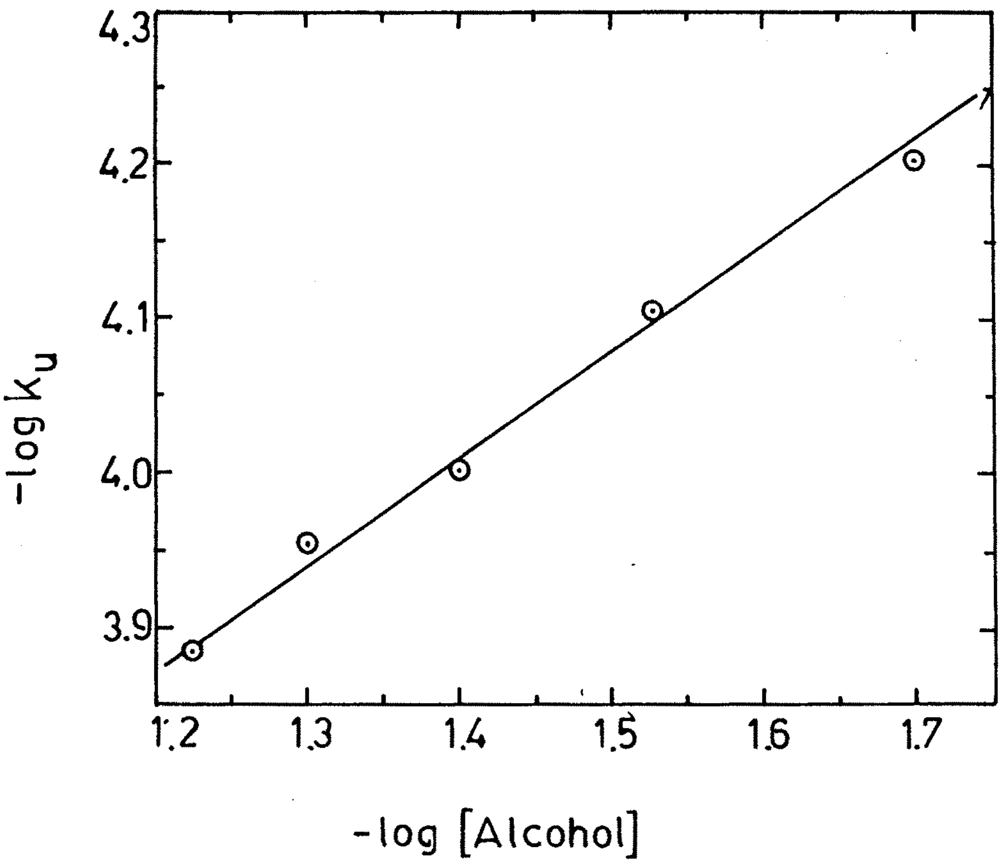


Figure 3.6: Order in alcohol: uncatalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.6)

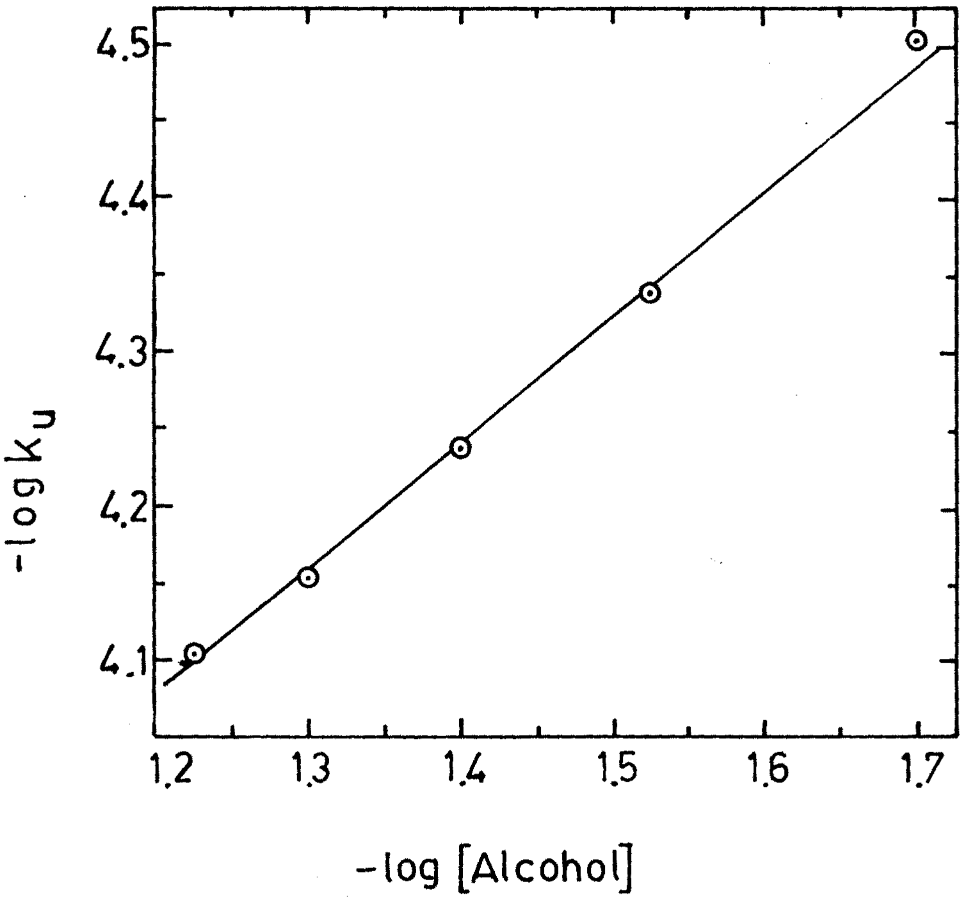


Table 3.7: Effect of alcohol concentration on pseudo-first order rate constants (k_c) of chromium(III) catalysed cerium(IV) oxidation of n-butanol and ethylene glycol.

[Ce(IV)] = 4.0×10^{-3}M, [$HClO_4$] = 2.0M

[H_2SO_4] = 6.0×10^{-2}M, [Cr(III)] = 2.0×10^{-4}M

I = 2.1 M, Temp. = 30°c

[Alcohol] 10^2 M	ku$\times10^5$ s^{-1}		-log[Alcohol]	-log kc	
	n-butanol	ethylene glycol		n-butanol	ethylene glycol
2.0	4.67	1.64	1.6989	3.3307	3.7851
3.0	5.90	2.18	1.5228	3.2291	3.6615
4.0	6.80	2.50	1.3979	3.1675	3.6020
5.0	7.40	3.09	1.3010	3.1307	3.5100
6.0	8.77	3.50	1.2218	3.0570	3.4559

Figure 3.7: Order in alcohol: chromium(III) catalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.7)

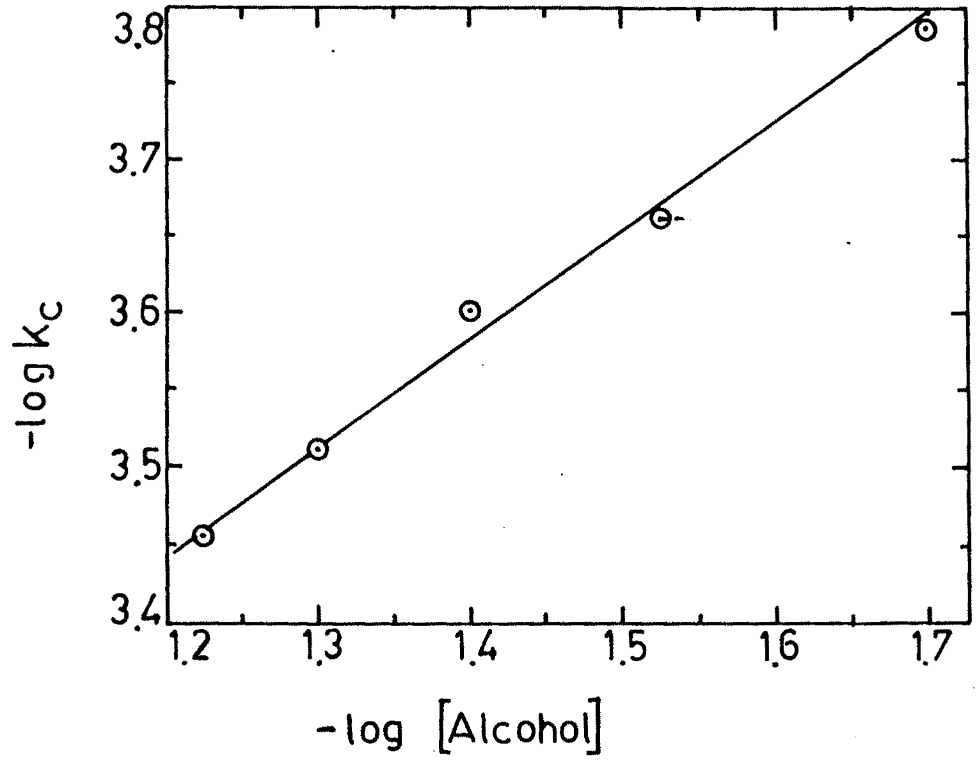
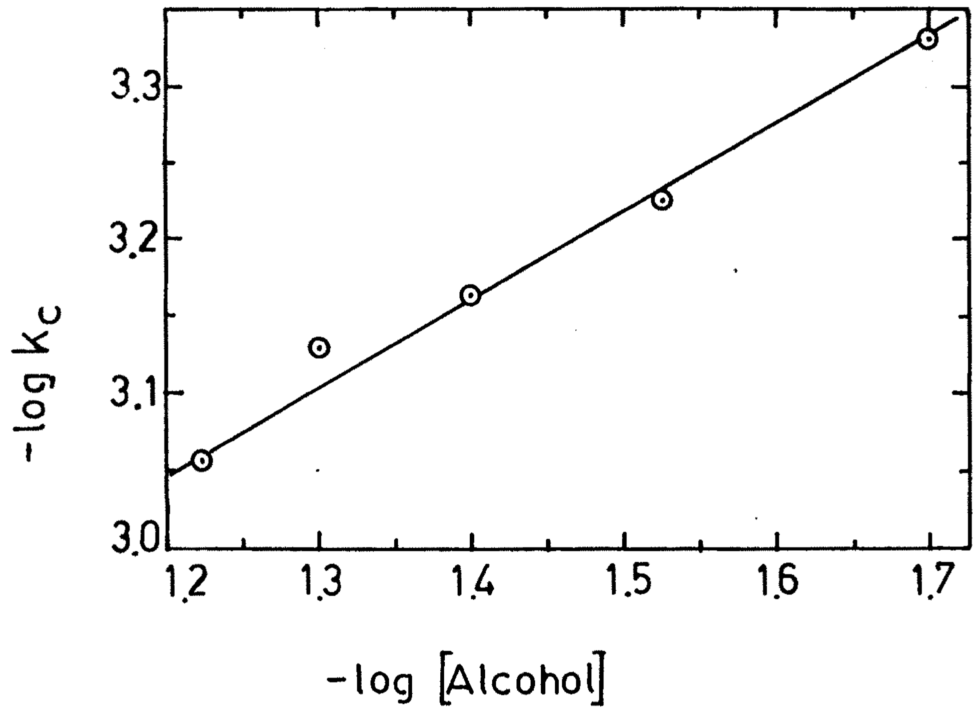


Figure 3.8: Order in alcohol: chromium(III) catalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.7)



reaction for n-butanol and ethylene glycol respectively.

EFFECT OF PERCHLORIC ACID CONCENTRATION

To study the effect of perchloric acid concentration on the reaction rate, cerium(IV) (4.0×10^{-3} M), alcohol (4.0×10^{-2}), sulphuric acid (6.0×10^{-2}) and chromium(III) (2.0×10^{-4} M) concentration were kept constant. the perchloric acid concentration was varied from 1.0 to 2.0 M. The total ionic strength was maintained at 2.1M using sodium perchlorate and temperature was kept constant at 30 ± 0.1°C. The data of example runs are given in Table 3.8 to 3.11 with respective pseudo-first order plots in Figures 3.9 to 3.12. As the perchloric acid concentration increases the pseudo-first order rate constant increases as shown in Table 3.12 and Table 3.13 for uncatalysed and catalysed reactions respectively. The plots of log K_u and log K_c against log $[HClO_4]_o$ are shown in Figure 3.13 to Figure 3.16. The order with respect to perchloric acid as found from Figure 3.13 to 3.15 are 1.26 and 1.43 for the uncatalysed reaction and 1.44 and 1.87 for the chromium(III) catalysed reaction of n-butanol and ethylene glycol respectively.

EFFECT OF CHROMIUM(III) CONCENTRATION

To study the effect of chromium(III) on the reaction, Cerium(IV) (4.0×10^{-3}), alcohol (4.0×10^{-2}M), perchloric acid (2.0M) and sulphuric acid (6.0×10^{-2}M)

Table 3.8: Example run uncatalysed cerium(IV) oxidation n-butanol.

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

[$HClO_4$] = 2.0M [H_2SO_4] = 6.0×10^{-2}M

I = 2.1 M Temp = 30°c.

Time in minutes	Burette* Readings	[Ce(IV)x10^{-3}M]	-log [Ce(IV)]
00	8.6	4.09	2.3878
15	8.1	3.85	2.4143
30	7.9	3.76	2.4247
45	7.1	3.37	2.4723
60	6.6	3.14	2.5028
75	6.3	2.99	2.5233
90	5.9	2.80	2.5519

* [Fe^{2+}] = 2.38×10^{-3}M

Figure 3.9: Plot of log[Ce(IV)] 'Vs time: uncatalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.8)

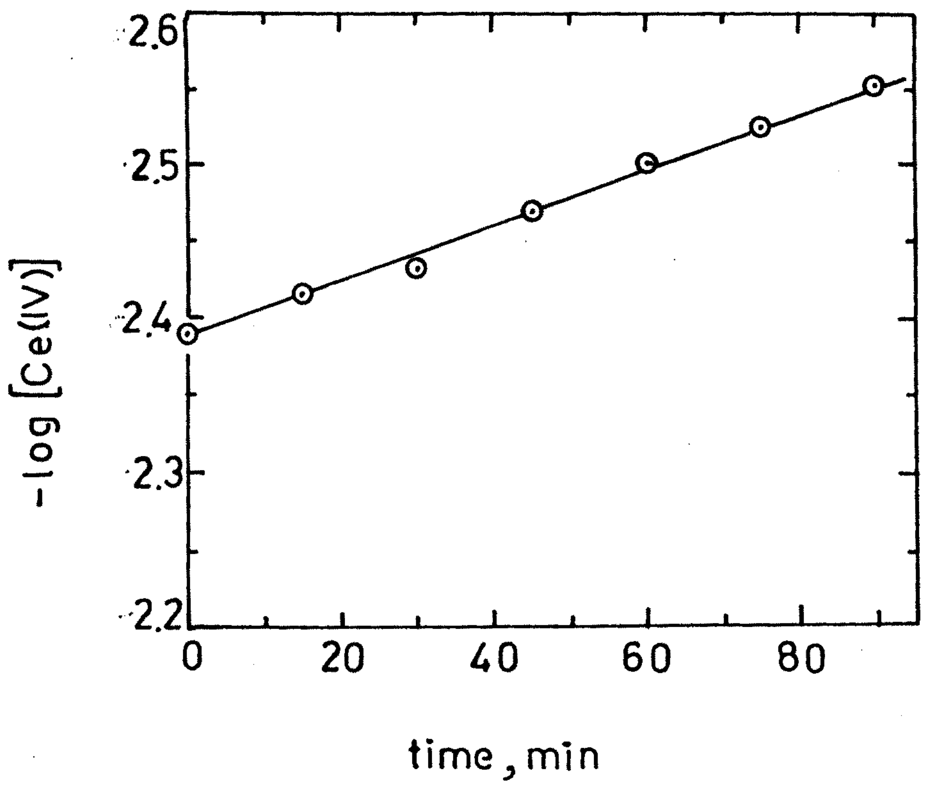


Table 3.9: Example run uncatalysed cerium(IV) oxidation Ethylene glycol

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

[$HClO_4$] = 1.8 M [H_2SO_4] = 6.0×10^{-2}M

I = 2.1 M Temp = 30°c.

Time in minutes	Burette* Readings	[Ce(IV)$\times10^{-3}$M]	-log [Ce(IV)]
00	10.0	3.84	2.4152
15	9.7	3.74	2.4284
30	9.2	3.53	2.4514
45	8.8	3.38	2.4707
60	8.4	3.23	2.4909
75	7.9	3.04	2.5175
90	7.6	2.92	2.5344

* [Fe^{2+}] = 1.92×10^{-3}M

Figure 3.10: Plot of log[Ce(IV)] Vs time: uncatalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.9)

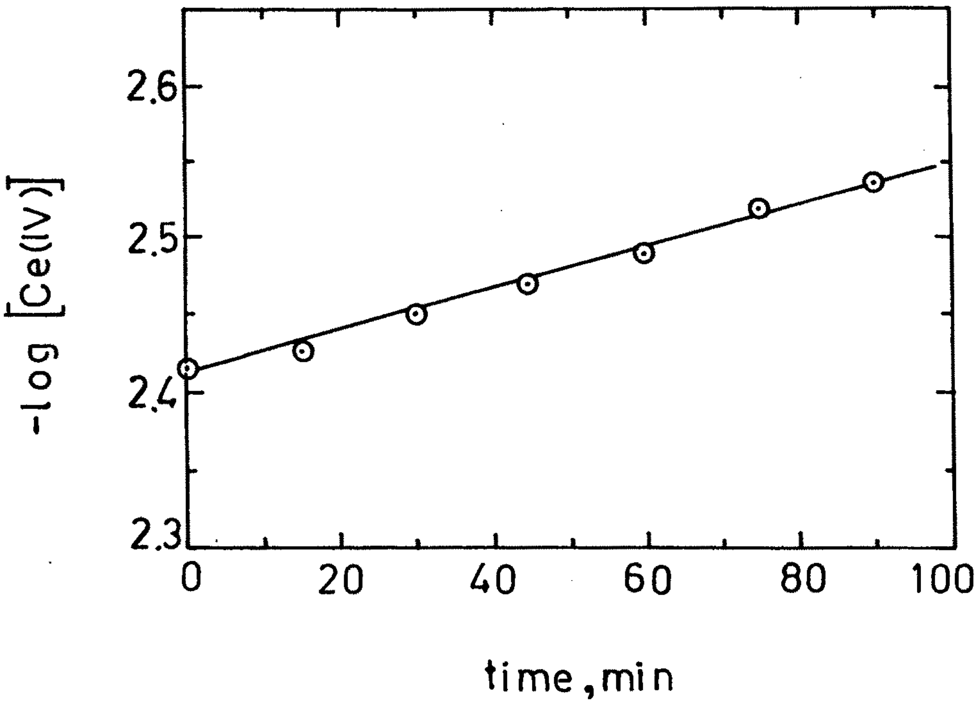


Table 3.10: Example run ~~uncatalysed~~ chromium(III) catalysed cerium(IV) oxidation n-butanol

[Ce(IV)] = 4.0×10^{-3} [Alcohol] = 4.0×10^{-2}M
[Cr(III)] = 2×10^{-4}M [$HClO_4$] = 1.6M
[H_2SO_4] = 6.0×10^{-2}M I = 2.1 M
Temp = 30°c.

Time in minutes	ml of $FeSO_4(NH_4)_2SO_4$* for 5 ml of aliquot	[Ce(IV)x10^{-3}M]	-log [Ce(IV)]
00	9.2	3.8332	2.4164
05	8.1	3.3749	2.4717
10	7.1	2.9600	2.5289
15	6.1	2.5400	2.5948
20	5.3	2.2100	2.6559
30	3.9	1.6200	2.7891
40	2.8	1.1700	2.9330
50	1.8	0.7500	3.1249
60	1.2	0.5000	3.3010

* [Fe^{2+}] = 2.08×10^{-3}M

Figure 3.11: Plot of log[Ce(IV)] Vs time: chromium(III) catalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.10)

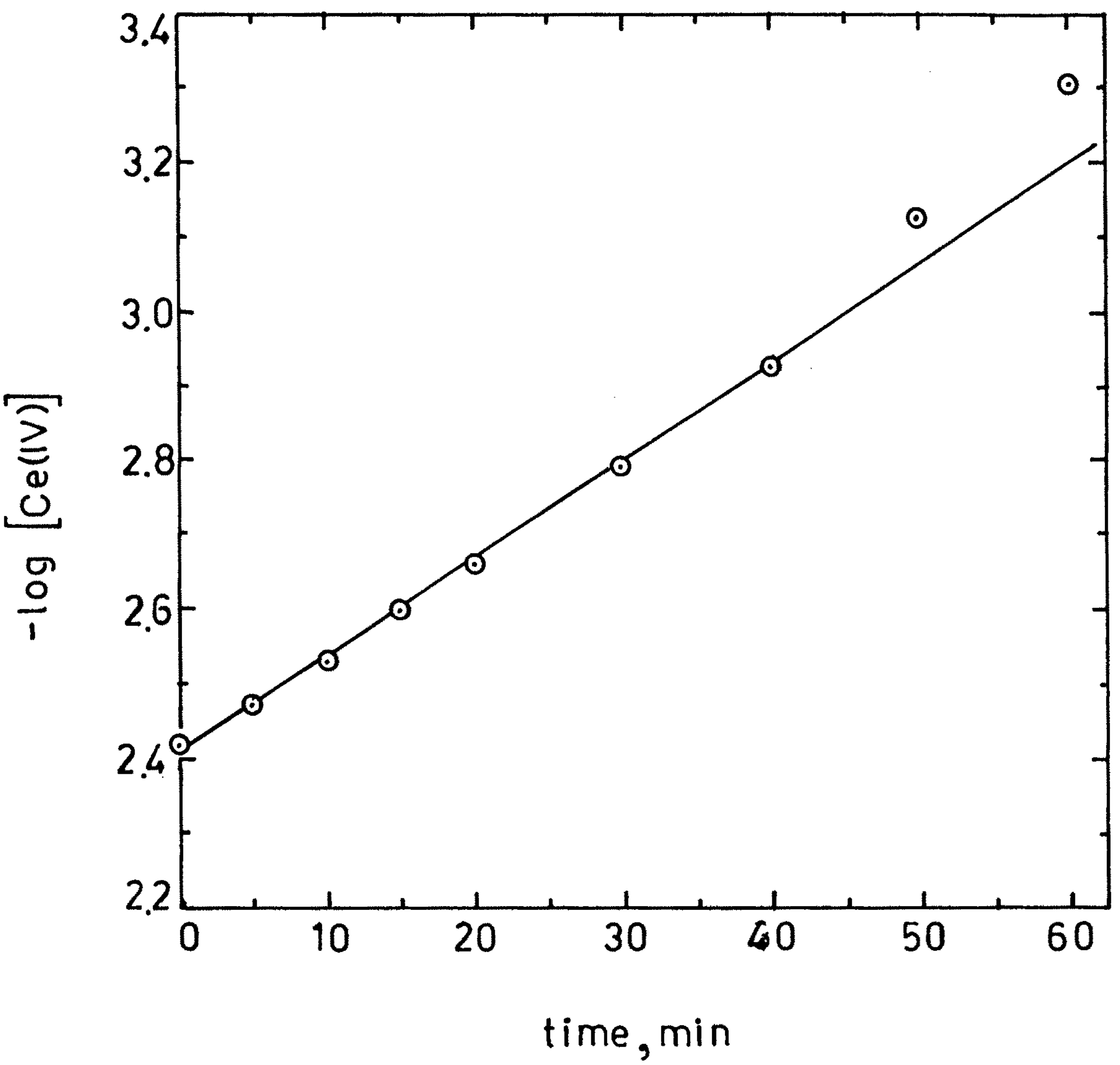


Table 3.11: Example run chromium(III) catalysed cerium(IV) oxidation Ethylene glycol

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

[Cr(III)] = 2.0×10^{-4}M [$HClO_4$] = 1.2 M

[H_2SO_4] = 6.0×10^{-2}M I = 2.1 M

Temp = 30°c.

Time in minutes	Burette* Readings	[Ce(IV)$\times10^{-3}$M]	-log [Ce(IV)]
00	9.4	4.00	2.3978
05	9.3	3.95	2.4025
10	9.1	3.87	2.4119
15	8.4	3.79	2.4216
20	8.7	3.70	2.4324
30	8.3	3.50	2.4517
40	7.9	3.36	2.4733
50	7.4	3.14	2.4971
60	6.9	2.94	2.5321

* [Fe^{2+}] = 2.13×10^{-3}M

Figure 3.12: Plot of log[Ce(IV)] Vs time: chromium(III) catalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.11)

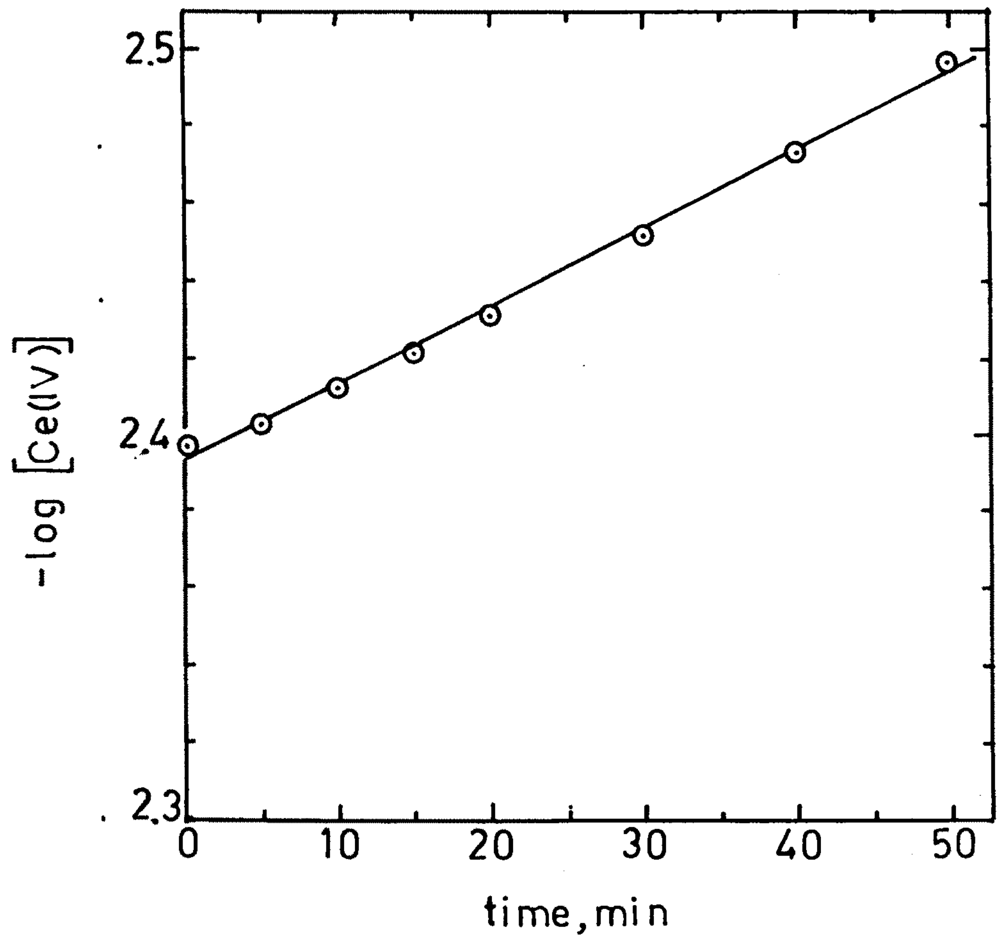


Table 3.12: **Effect of perchloric acid concentration on pseudo-first order rate constants (ku) of uncatalysed cerium(IV) oxidation of n-butanol and ethylene glycol.**

[Ce(IV)] = $4.0\text{x}10^{-3}$M, [Alcohol] = 2.0 $\text{x}10^{-2}$ M

[H_2SO_4] = $6.0\text{x}10^{-2}$M

I = 2.1 M, Temp. = 30°c

[$HClO_4$] M	ku$\times10^5$ s^{-1}		log[$HClO_4$]	-log ku	
	n-butanol	ethylene glycol		n-butanol	ethylene glycol
1.0	4.8	2.2	0.0000	4.3187	4.6576
1.2	5.1	3.1	0.0792	4.2924	4.5086
1.4	6.9	3.8	0.1461	4.1611	4.4202
1.6	7.3	4.3	0.2041	4.1367	4.3665
1.8	8.0	5.2	0.2553	4.0969	4.2839
2.0	10.0	5.8	0.3010	4.0000	4.2366

Figure 3.13: Order in $HClO_4$: uncatalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.12)

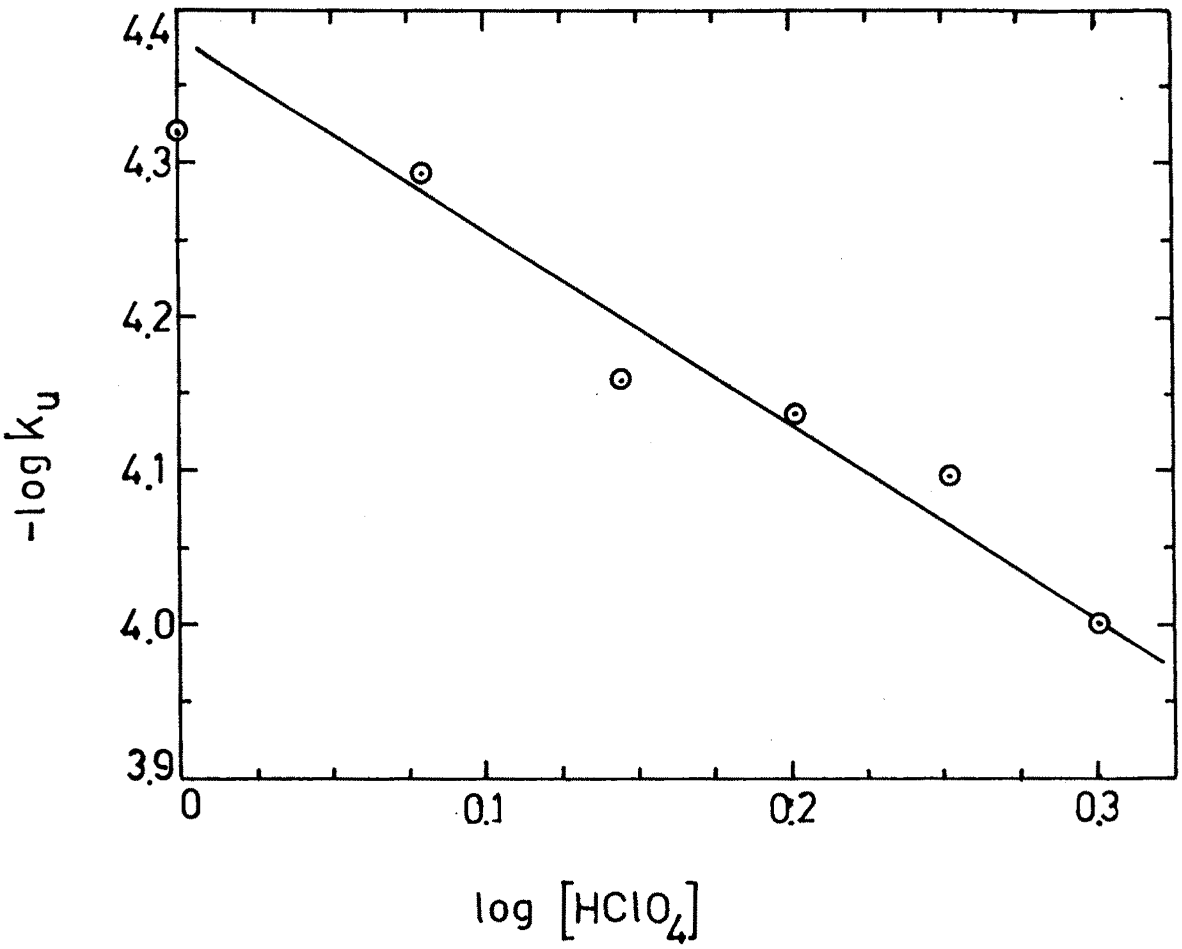


Figure 3.14: Order in $HClO_4$: uncatalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.12)

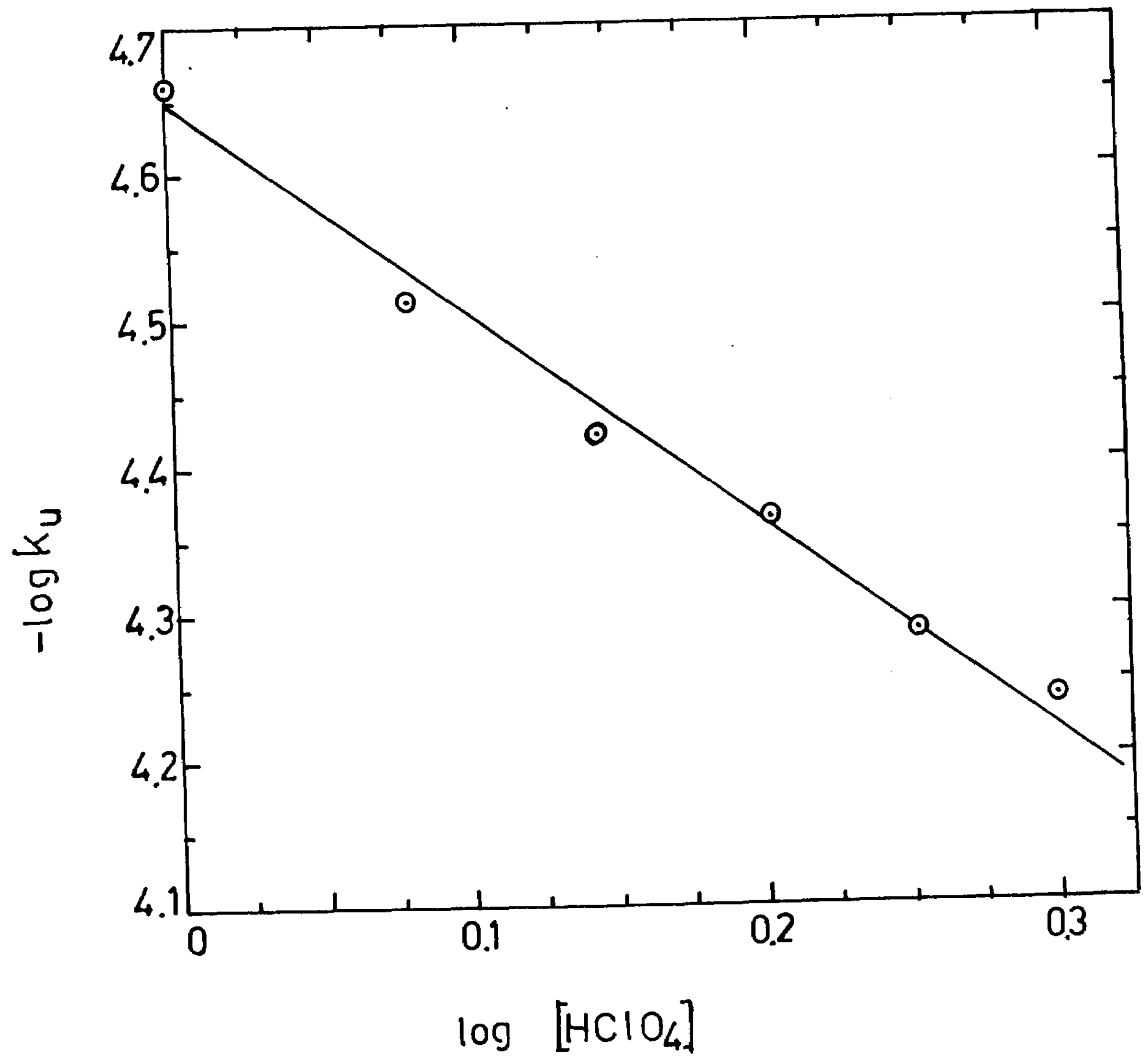


Table 3.13: Effect of perchloric acid concentration on pseudo-first order rate constants kc of chromium(III) catalysed cerium(IV) oxidation of n-butanol and ethylene glycol.

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

[Cr(III)] = 2.0×10^{-4}M [H_2SO_4] = 6.0×10^{-2}M,

I = 2.1 M, Temp. = 30°c

[$HClO_4$] M	$k_c \times 10^5$ s^{-1}		log[$HClO_4$]	-log kc	
	n-butanol	ethylene glycol		n-butanol	ethylene glycol
1.0	2.55	0.69	0.0000	3.5934	4.1611
1.2	3.50	1.00	0.0792	3.4559	4.0000
1.4	4.60	1.23	0.1461	3.3372	3.9100
1.6	5.11	1.66	0.2041	3.2915	3.7798
1.8	6.10	2.02	0.2553	3.2146	3.6946
2.0	6.90	2.38	0.3010	3.1611	3.6234

Figure 3.15: Order in $HClO_4$: chromium(IV) catalysed cerium(IV) oxidation of n-butanol (conditions as in Table 3.13)

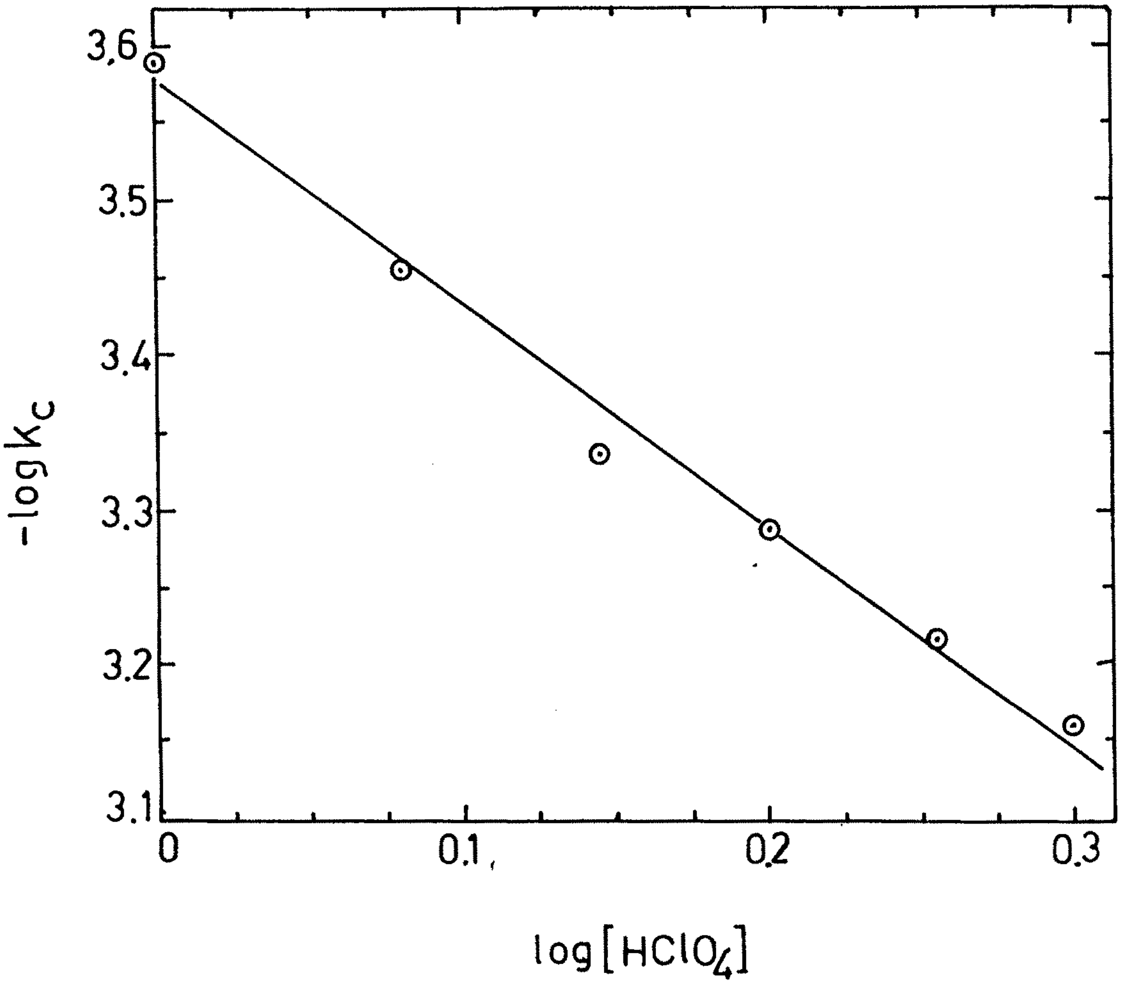
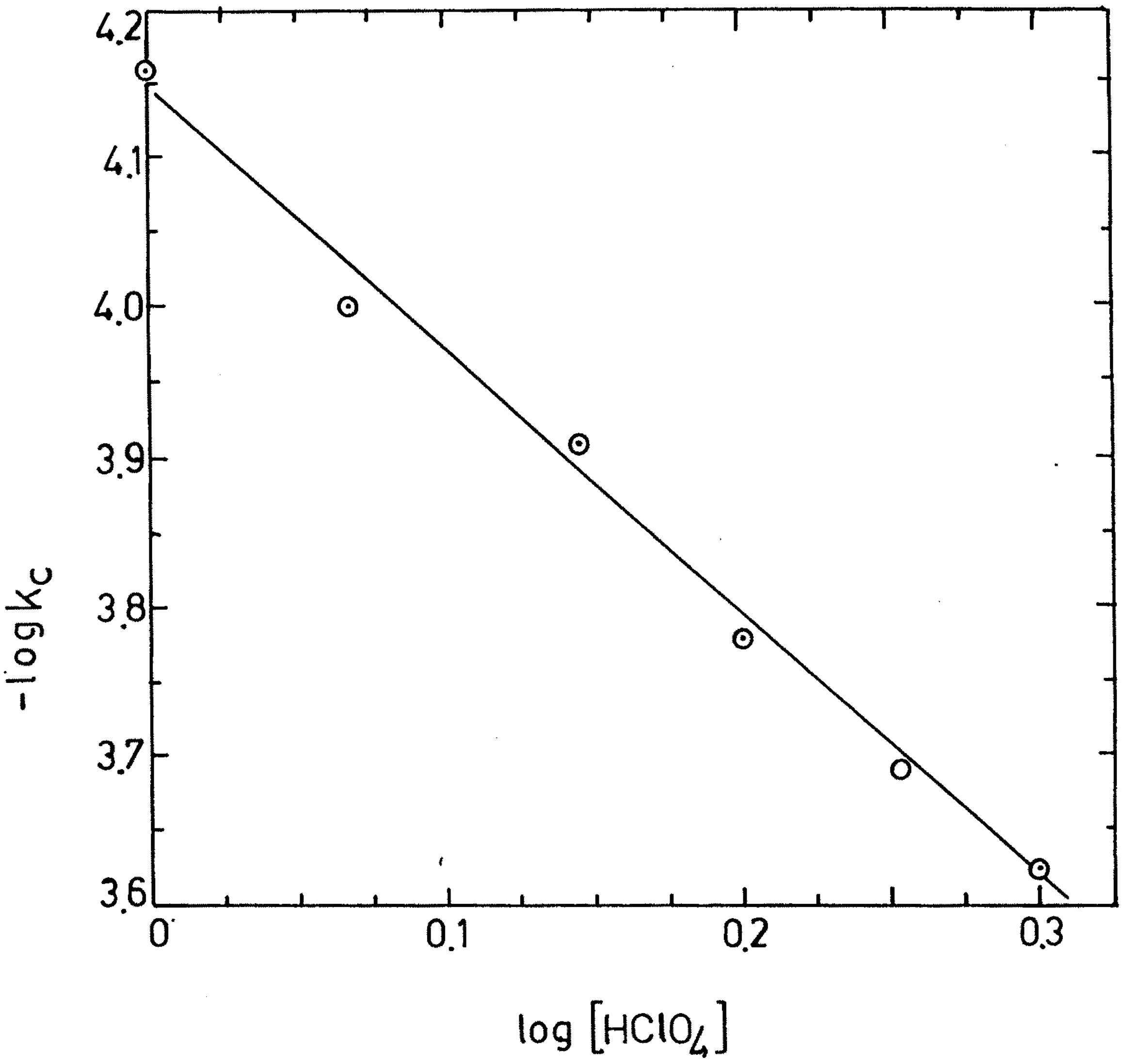


Figure 3.16: Order in $HClO_4$: chromium(IV) catalysed cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.13)



concentrations were kept constant Chromium(III) concentration was varied from 1.0×10^{-4}M to 16.0×10^{-4}M in case of n-butanol and 1.0×10^{-4}M to 20.0×10^{-4}M in case of ethylene glycol at constant ionic strength of 2.1M and temperature of 30 ± 0.1°C.

The pseudo first order rate constants (k_C) are given in Table 3.14. The order with respect to catalyst, chromium(III), were obtained from logk_C against log[(Cr(III)] plots which are shown in Figures 3.17 and 3.18 for n-butanol and ethylene glycol respectively. The order in catalyst were found to be 0.54 and 0.83 for n-butanol and ethylene glycol respectively.

EFFECT OF ADDED CERIUM(III)

The effect of added cerium(III) was studied between the concentration range of 1.0×10^{-3} to 3.0×10^{-3}M by keeping cerium(IV) (4.0×10^{-3}M), alcohol (4.0×10^{-2}M), chromium(III) (2.0×10^{-3}M) perchloric acid (2.0M) and sulphuric acid (6.0×10^{-2}M) concentrations constant. The ionic strength was maintained at 2.1M with sodium perchlorate and at temperature 30 ± 0.1°C. The data are given in Table 3.15. From the data of Table 3.15 it can be seen that added cerium(III) did not have any significant effect on the catalysed reaction.

Table 3.14: Effect of catalyst concentration on pseudo-first order rate constants kc of chromium(III) catalysed cerium(IV) oxidation of n-butanol and ethylene glycol.

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

$[H_2SO_4] = 6.0 \times 10^{-2} M$, $I = 2.1$ M, $[HClO_4] = 2{\cdot}0 M$

Temp. = 30°c

$[Cr(III)] \times 10^4 M$	$kc \times 10^4$ s^{-1}		$-\log[Cr(III)]$	$-\log kc$	
	n-butanol	ethylene glycol		n-butanol	ethylene glycol
1.0	3.5	1.47	4.0000	3.4559	3.8327
2.0	6.9	2.40	3.6989	3.1611	3.6198
3.0	7.67	3.40	3.5228	3.1152	3.4685
4.0	10.2	4.50	3.3979	2.9914	3.3468
5.0	12.2	5.50	3.3010	2.9136	3.2596
6.0	13.6	6.80	3.2218	2.8664	3.1675
8.0	15.3	7.10	3.0969	2.8153	3.1487
10.0	16.4	8.50	3.0000	2.7851	3.0706
12.0	17.4	8.40	2.9208	2.7594	3.0757
14.0	19.1	8.60	2.8538	2.7189	3.0655
16.0	20.3	8.60	2.7959	2.6925	3.0655
18.0	22.2	-	2.7447	2.6536	-
20.0	22.5	-	2.6989	2.6478	-

Figure 3.17: Order in chromium(III): cerium(IV) oxidation of n-butanol (conditions as in Table 3.14)

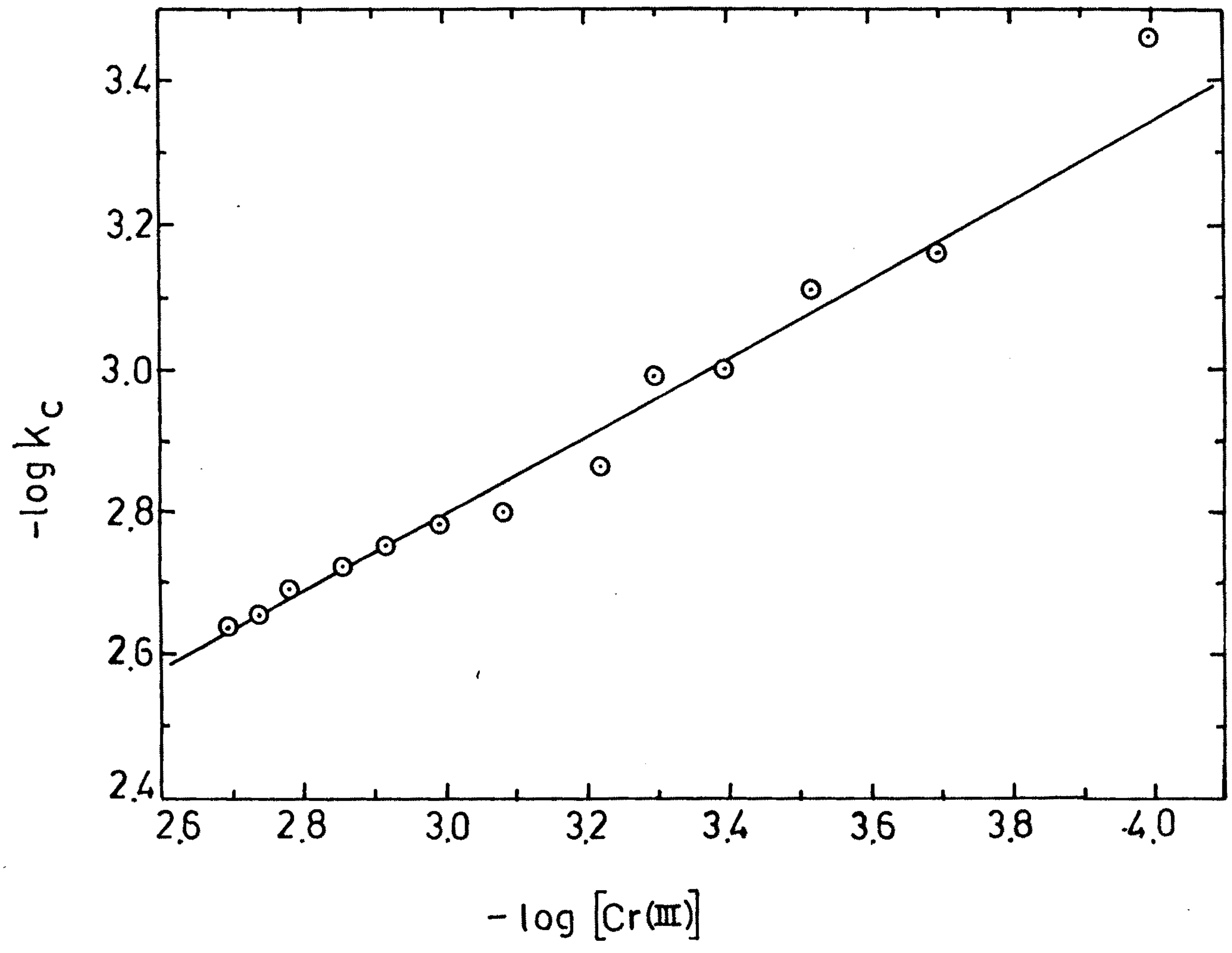


Figure 3.18: Order in chromium(III): cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.14)

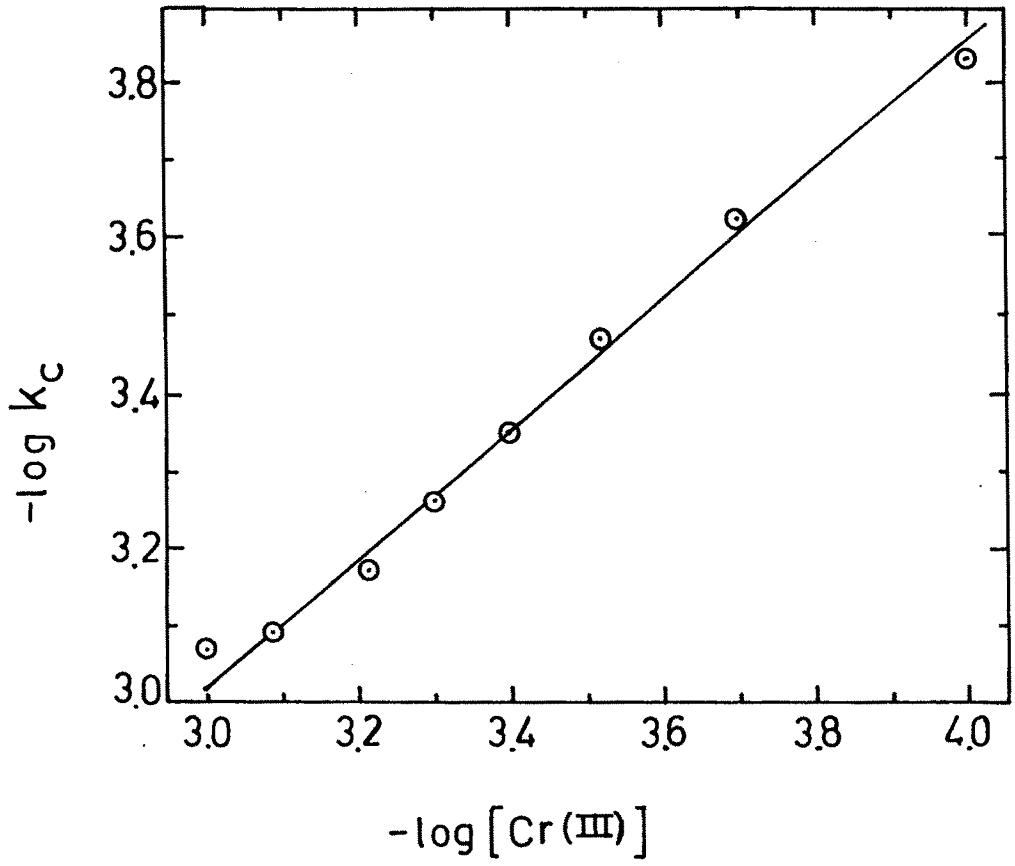


Table 3.15: Effect of added cerium(III) on the pseudo-first order rate constant of chromium(III) catalysed(kc) cerium(IV) oxidation of n-butanol and ethylene glycol.

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

[$HClO_4$] = 2.0M, [H_2SO_4] = 6.0×10^{-2}M

I = 2.1M, Temp. = 30°C

[Cr(III)]= 2.0×10^{-4}M.

[Ce(III)]$\times10^3$M	kc$\times10^4$ s^{-1}	
	n-butanol	ethylene glycol
1.0	5.8	2.51
2.0	6.4	2.32
3.0	5.8	2.51

EFFECT OF TEMPERATURE

The study of effect of temperature on the reaction was carried out in order to evaluate the thermodynamic parameters. The activation energy, Ea was determined with the help of Arrhenius equation 1. The

$$Kr = Ae^{-Ea/RT} \qquad ....(1)$$

Where

Kr = Rate constant of the reaction
A = Frequency factor
Ea = Energy of activation
T = Absolute temperature and
R = Molar gas constant

logarithmetic form of equation 1 is

$$\log Kr = \log A - \frac{Ea}{2.303\ RT} \qquad ....(2)$$

In order to study the temperature effect on the rate of oxidation of alcohols under study, namely n-butanol and ethylene glycol following conditions were maintained.

[Alcohol] = $4.0\text{x}10^{-2}$M
[Cerium(IV)] = $4.0\text{x}10^{-3}$M
[$HClO_4$] = 2.0M
[H_2SO_4] = $6.0\text{x}10^{-2}$M and
[Chromium(III)] = $2.0\text{x}10^{-4}$M

The uncatalysed and catalysed oxidation of n-butanol and ethylene glycol were studied at four different temperature (298, 303, 308 and 313°K). The pseudo-first order rate constants (k_u & k_c) at different temperatures are included in Table 3.16-3.19. Further, by utilizing pseudo-first order rate constants at different temperatures, plots of log k against 1/T was plotted and are shown in Figures 3.19-3.22. The values of 1/T, k_c, k_u, log k_u, ~~log k_u/T~~, log $k_c/\cancel{T}$ and the values of Ea, are tabulated in Table 3.16-3.19.

IDENTIFICATION OF END PRODUCTS AND STOICHIOMETRY

The products would be corresponding aldehydes as reported in an earlier report of uncatalysed reactions[24.25], Accordingly, for n-butanol, butaraldehyde is expected and it was confirmed by preparing a derivative of 2,4. Dinitro phenyl hydrazone[28]. The reaction mixture was distilled and the fraction collected at boiling point of bataraldehyde (74°c) was collected. To the fraction 3ml of 2.4 dinitrophenyl hydrazine reagent was added and allowed to stand for 5-10 minutes. The crystalline precipitate obtained was dried and its melting point was determined. The melting point of the compound was found to be 124°c (expected 123°c) which confirms the butaraldehyde as the product. The 2,4 dinitro phenyl hydrazine reagent was prepared by dissolving 2 gms of substance in 100 ml of methanol and 4.0 ml of concentrated

Table 3.16: Effect of temperature on pseudo-frist order rate constant (k_u) of uncatalysed cerium(IV) oxidation of n-butanol.

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

[$HClO_4$] = 2.0 M, [H_2SO_4] = 6.0×10^{-2} M,

I = 2.1 M

Temperature °K	298	303	308	313
$1/T \times 10^3$	3.3557	3.3003	3.2468	3.1949
$k_u \times 10^5 s^{-1}$	3.4000	10.0000	18.0000	29.0000
$- \log k_u$	4.4685	4.0000	3.7447	3.5376
Ea kJ M^{-1}	114.9 ± 0.05			

Figure 3.19: Plot logk_u Vs 1/T: cerium(IV) oxidation n-butanol (condition as in Table 3.16).

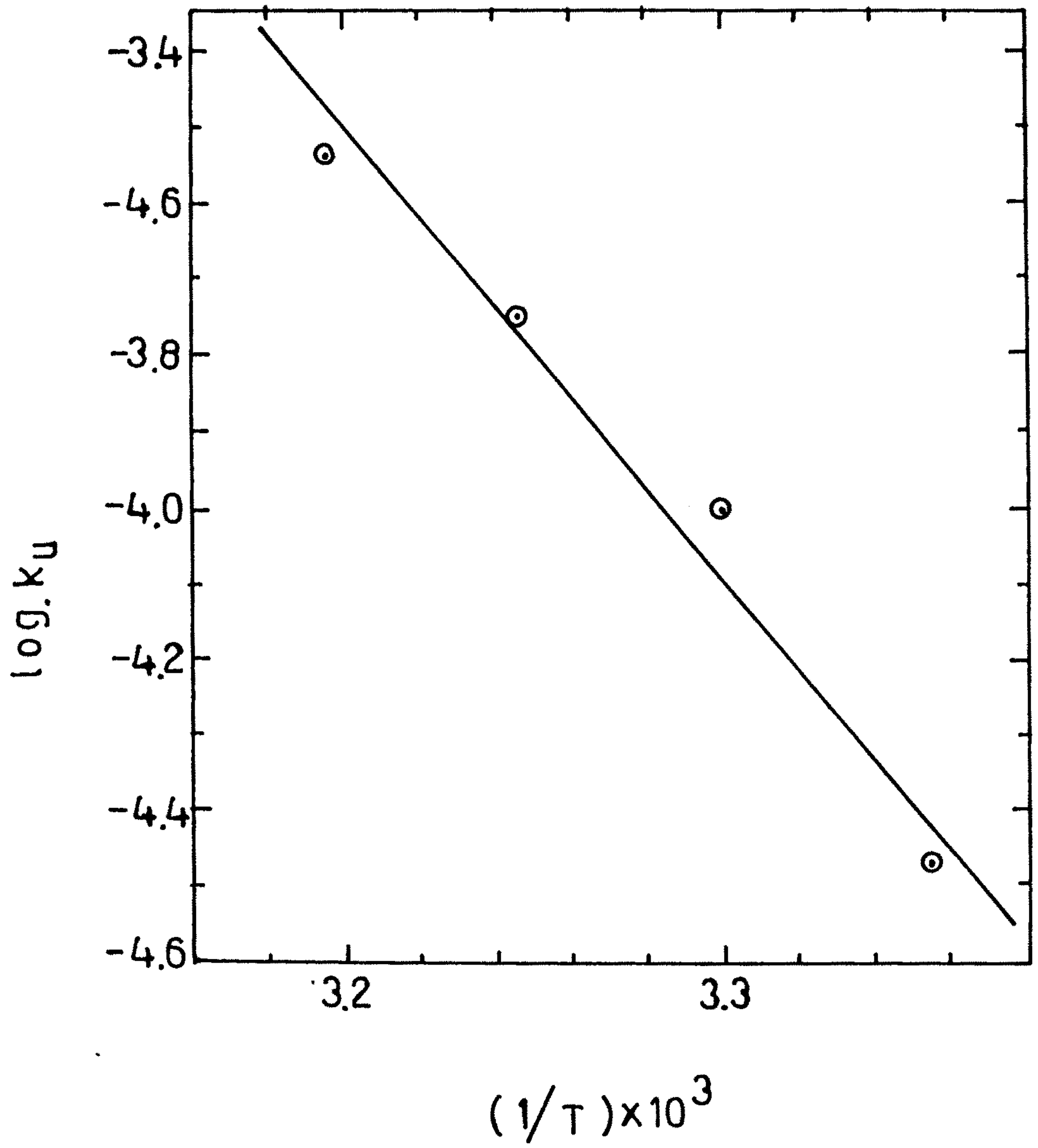


Table 3.17: Effect of temperature on pseudo-frist order rate constant (k_c) of chromium(III) catalysed cerium(IV) oxidation of n-butanol.

$[Ce(IV)] = 4.0x10^{-3}$ M, [Alcohol] = $4.0x10^{-2}$ M

$[Cr(III)] = 2.0x10^{-4}$ M, $[HClO_4] = 2.0$ M,

$[H_2SO_4] = 6.0x10^{-2}$ M, I = 2.1 M

Temperature °K	298	303	308	313
$1/T\ x10^3$	3.3557	3.3003	3.2468	3.1949
$k_c x10^5 s^{-1}$	3.7900	6.8200	9.2200	12.1500
$-\log k_c$	3.4213	3.1662	3.0352	2.9154
Ea kJ M^{-1}	58.78 ± 0.05			

Figure 3.20: Plot log k_c Vs 1/T: cerium(IV) oxidation of n-butanol (conditions as in Table 3.17)

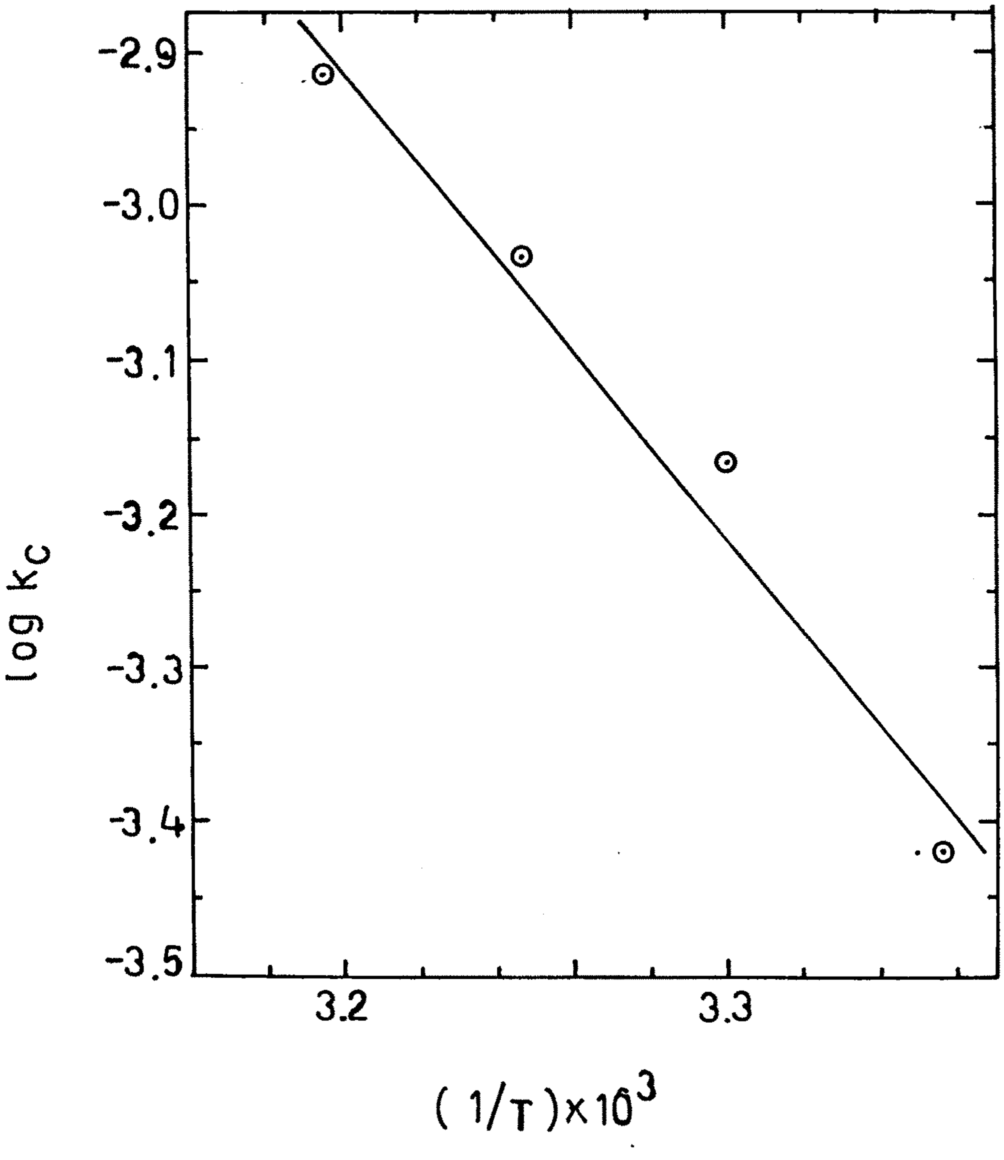


Table 3.18: Effect of temperature on pseudo-frist order rate constant (k_u) of uncatalysed cerium(IV) oxidation of ethylene glycol.

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

[$HClO_4$] = 2.0 M, [H_2SO_4] = 6.0×10^{-2} M,

I = 2.1 M

Temperature °K	298	303	308	313
$1/T \times 10^3$	3.3557	3.3003	3.2468	3.1949
$k_u \times 10^5 s^{-1}$	3.1000	5.6000	12.4000	29.8000
$- \log k_c$	4.5086	4.2518	3.9066	3.5257
Ea kJ M^{-1}	119.7 ± 0.05			

Figure 3.21: Plot $\log k_u$ Vs 1/T: cerium(IV) oxidation ethylene glycol (condition as in Table 3.18)

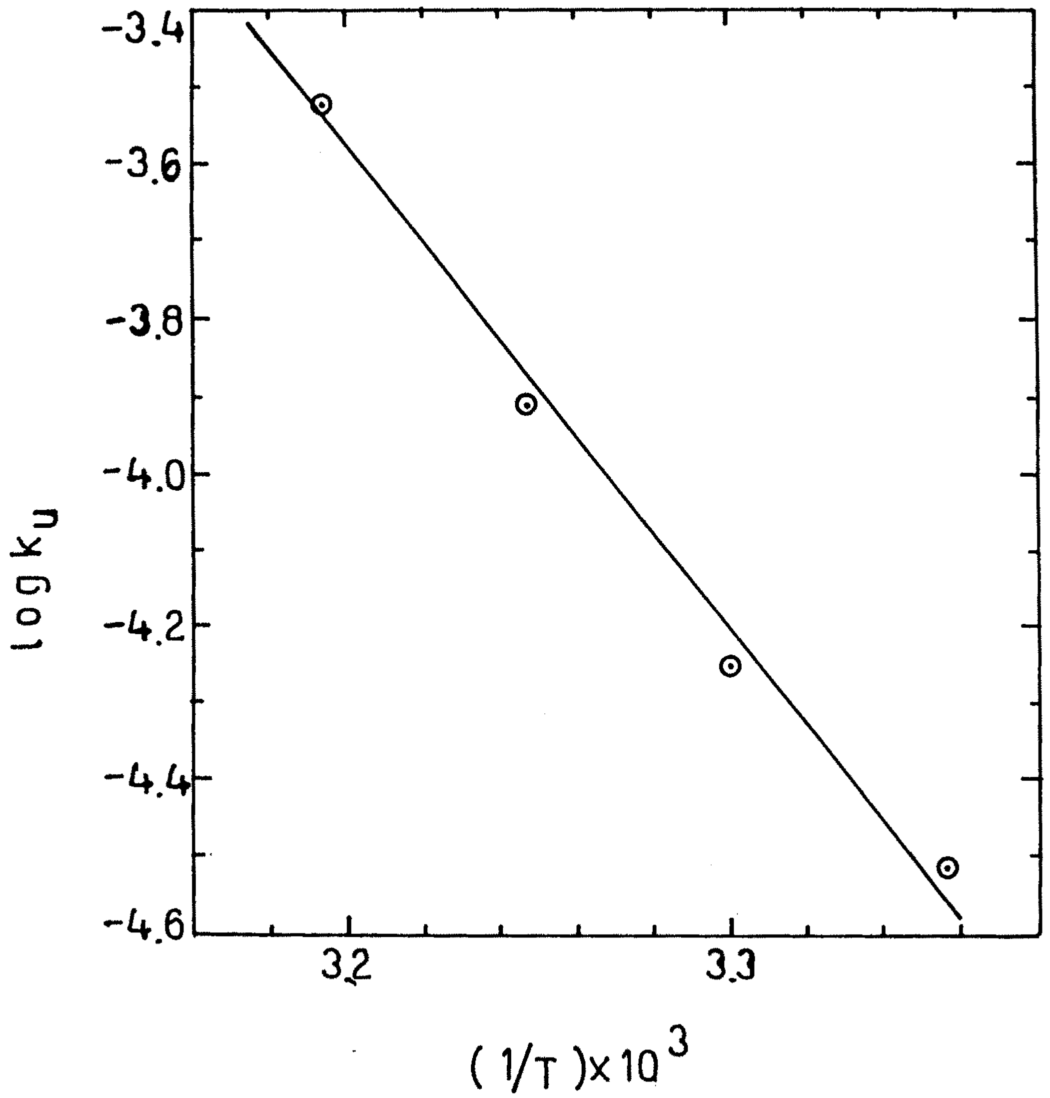


Table 3.19: Effect of temperature on pseudo-frist order rate constant (k_c) of chromium(III) catalysed cerium(IV) oxidation of ethylene glycol.

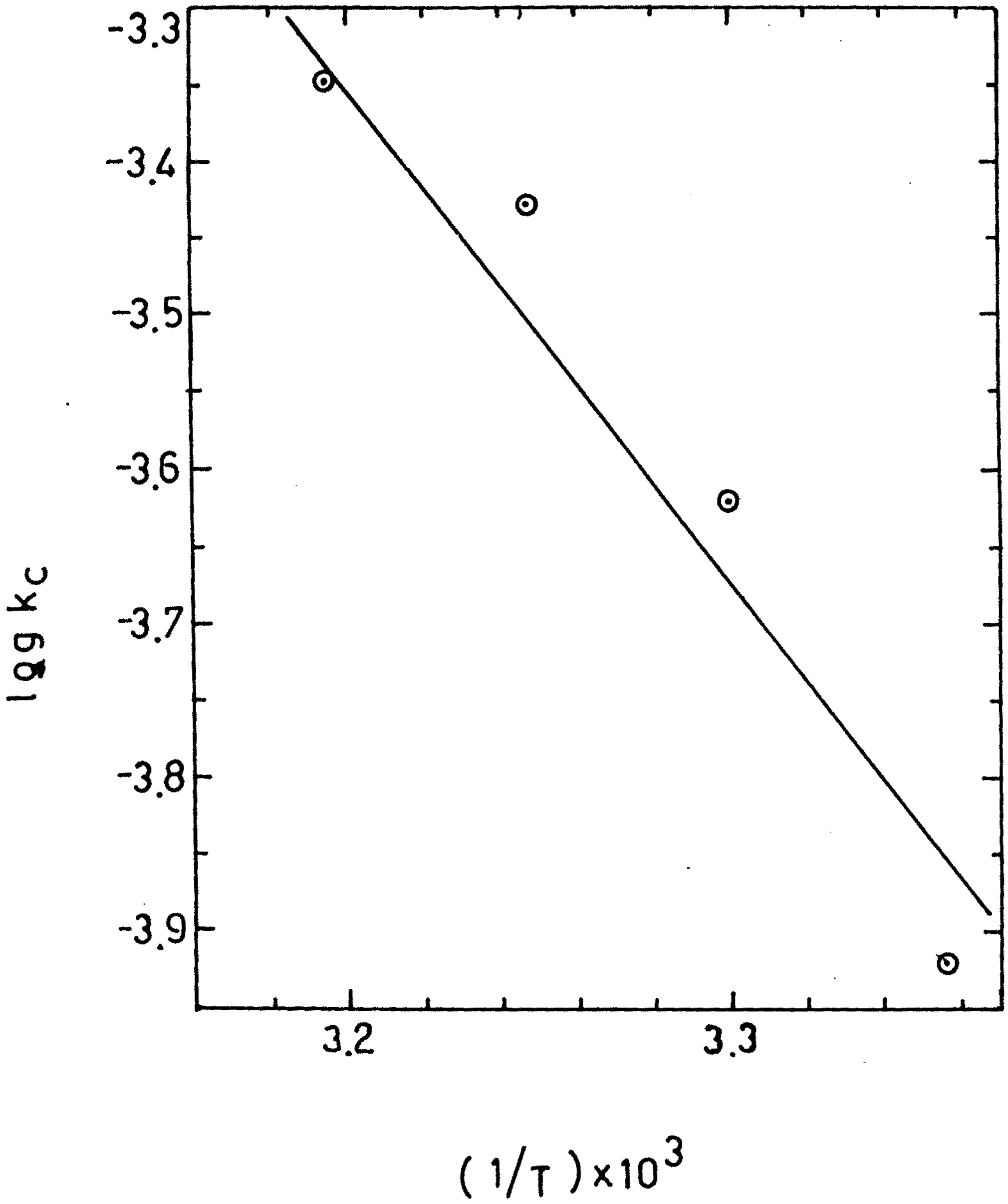
$[Ce(IV)] = 4.0x10^{-3}$ M, [Alcohol] = $4.0x10^{-2}$ M

$[Cr(III)] = 2.0x10^{-4}$ M, $[HClO_4] = 2.0$ M,

$[H_2SO_4] = 6.0x10^{-2}$ M, I = 2.1 M

Temperature °K	298	303	308	313
1/T $x10^3$	3.3557	3.3003	3.2468	3.1949
$k_c x10^5 s^{-1}$	1.2000	2.4000	3.7300	4.5000
- log k_c	3.9208	3.6198	3.4283	3.3468
Ea kJ M^{-1}	61.46 ± 0.05			

Figure 3.22: Plot log k_c Vs 1/T: cerium(IV) oxidation of ethylene glycol (conditions as in Table 3.19)



sulphuric acid was added slowly and the resulting solution was filtered and used.

The product formaldehyde in case of ethylene glycol was confirmed by resorcinol test[29]. To the reaction mixture two drops of 0.5 percent aqueous resorcinol solution was added. The resulting solution was slowly added down the side of an inclined test tube containing 3 ml concentrated sulphuric acid. A reddish-voilet ring formed confirmed the presence of formaldehyde.

Therefore the stoichiometry for n-butanol and ethylene glycol can be represented as in equations 6 and 7 for both uncatalysed as well as chromium(III) catalysed oxidation by cerium(IV).

$$\underset{\text{n-butanol}}{CH_3\ (CH_2)_3}\overset{OH}{\wedge} + 2Ce(IV) \longrightarrow \underset{\text{butyraldehyde}}{CH_3\ CH_2\ CH_2\ CHO} + 2H^+ + 2Ce(III) \quad .....(3)$$

$$\underset{\text{ethylene glycol}}{HO\ CH_2\ CH_2\ OH\cancel{O}} + 2Ce(\overset{(IV)}{\cancel{III}}) \longrightarrow \underset{\text{Formaldehyde}}{2HC\cancel{O}HO} + 2Ce(III) + 2H^+ \quad ......(4)$$

DETECTION OF FREE RADICALS

Test for free radicals was performed by adding acryllonitrile to the reaction mixture. A copious precipitation was observed in both uncatalysed and catalysed reactions indicating formation of free radicals. Such precipitation was not observed in absence of alcohol.