

CHAPTER – III

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

3. CHROMIUM(III) CATALYSED CERIUM(IV) OXIDATION OF CYCLOHEXANOL

Carcinogenic nature of chromium compounds is predicted to be due to intervention³¹ of a typical Cr(IV) and Cr(V) species. These species are produced either by reduction⁶ of Cr(VI) by the substrate or in oxidation³ of Cr(III) by oxidants like peroxide or Ce(IV). In Cr(III) oxidation by Ce(IV), Cr(IV) is produced in an equilibrium prior to the rate determining step which has been utilized for catalysis of organic²⁸ and inorganic¹⁵ oxidations. Recently, it has been shown that for further reduction of Cr(IV) by the substrate, the hydride ion transfer path is more favorable than the free radical formation as reported in our earlier study²⁸. In continuation of our effort to understand the reactivity of Cr(IV) produced by Cr(III)-Ce(IV) system and its application in synthetic organic chemistry³¹ the oxidation of cyclohexanol was studied.

3.1 Experimental

3.1.1 Results

The uncatalysed oxidation of cyclohexanol was studied in detail²⁴ and found to proceed with an oxidant alcohol complex which decomposes in a rate determining step. Therefore, in the present study, the rate constant of uncatalysed reaction, k_{uncat} , is used for determination of contribution from the catalysed reaction, k_{cat} . The values of k_{cat} were calculated by subtracting k_{uncat} from the observed rate constant, k_{obs} . The order in oxidant was found to be unity as pseudo-first order plots were linear for both uncatalysed and Cr^{III} catalysed reactions. The pseudo-first order rate constants were found to decrease as the concentration of oxidant concentration increases [Table III(i)]. The effect of cyclohexanol on both uncatalysed and

Table III(i)

Effect of Ce^{IV} on Cr^{III} catalysed cyclohexanol oxidation by cerium(IV).

$10^5[\text{Cr}^{\text{III}}] = 4.0 \text{ mol dm}^{-3}$, $10^3 [\text{Cyclohexanol}] = 2.0 \text{ mol dm}^{-3}$

$[\text{HClO}_2] = 1.0 \text{ mol dm}^{-3}$, $10^2 [\text{H}_2\text{SO}_4] = 6.0 \text{ mol dm}^{-3}$, $T = 298 \text{ K}$.

$10^4[\text{Ce}^{\text{IV}}]$ mol dm^{-3}	$10^4 k_u \text{ s}^{-1}$	$10^4 k_c \text{ s}^{-1}$	$10^4 k_c - k_u \text{ s}^{-1}$
1.0	0.95	2.76	1.81
2.0	0.69	2.56	1.87
3.0	0.32	1.96	1.64
4.0	0.10	1.78	1.68
5.0	0.05	1.46	1.41

catalysed reactions are given in Table III(ii). The order in cyclohexanol was determined from the plot of $\log k$ against $\log [\text{cyclohexanol}]$ plots [Figure III(i)] and for both catalysed and uncatalysed reactions was found to be fractional (0.5). The order in catalyst concentration was also found to be 0.34 [Table III (iii) and Figure III (ii)]. The effect of perchloric acid concentration was studied between 0.1 to 1.0 mol dm^{-3} keeping all other concentrations constant. The rate of reaction increases with the concentration of perchloric acid [Table III(iv)]. The plot of k_{uncat} and $(k_c - k_u)$ against $[\text{H}^+]$ was found to be linear for catalysed reaction and a curve for uncatalysed reaction both passing through origin [Figure III(iv)]. The order in hydrogen ion concentration was found to be more than one (1.33) [Figure III(v)]. Added product Ce^{III} decreases the rate of the reaction slightly [Table III(v)]. The effect of temperature was studied between 25 to 40°C and the activation parameters were determined from the plots of $\log k$ and $\log k/T$ against $1/T$ [Figure III(vi) and Figure III(vii.)]. The kinetic data and the activation parameters are given in Table III(vi).

3.2 Discussion

3.2.1 Uncatalysed Reaction

According to the above observations and the stoichiometry of the uncatalysed reaction, the mechanism proceeds through an oxidant alcohol complex formation²⁴ followed by its decomposition in a slow step as shown in Scheme 1 and the corresponding rate law would be given by equation 1. The order in hydrogen ion concentration of more than one indicate involvement of two protonation.

Table III(ii)

Effect of cyclohexanol on Cr^{III} catalysed cyclohexanol oxidation by cerium(IV).

$10^5[\text{Cr}^{\text{III}}] = 4.0 \text{ mol dm}^{-3}$, $10^4[\text{Ce}^{\text{IV}}] = 4.0 \text{ mol dm}^{-3}$ $[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$,

$10^2[\text{H}_2\text{SO}_4] = 6.0 \text{ mol. dm}^{-3}$ $T = 298 \text{ K}$

$10^3 [\text{Cyclohexanol}]$ mol dm^{-3}	$1/[\text{Al}]$	$10^4 k_u$ s^{-1}	$10^4 k_c$ s^{-1}	$10^4 (k_c - k_u)$ s^{-1}	$10^3 [1/(k_c - k_u)]$
1.0	1000	0.57	1.28	0.71	1.41
2.0	500	0.69	1.78	1.09	0.92
4.0	250	0.82	2.20	1.38	0.73
6.0	167	1.20	2.80	1.60	0.63
8.0	125	1.41	3.40	1.99	0.50
10.0	100	1.65	3.80	2.15	0.47

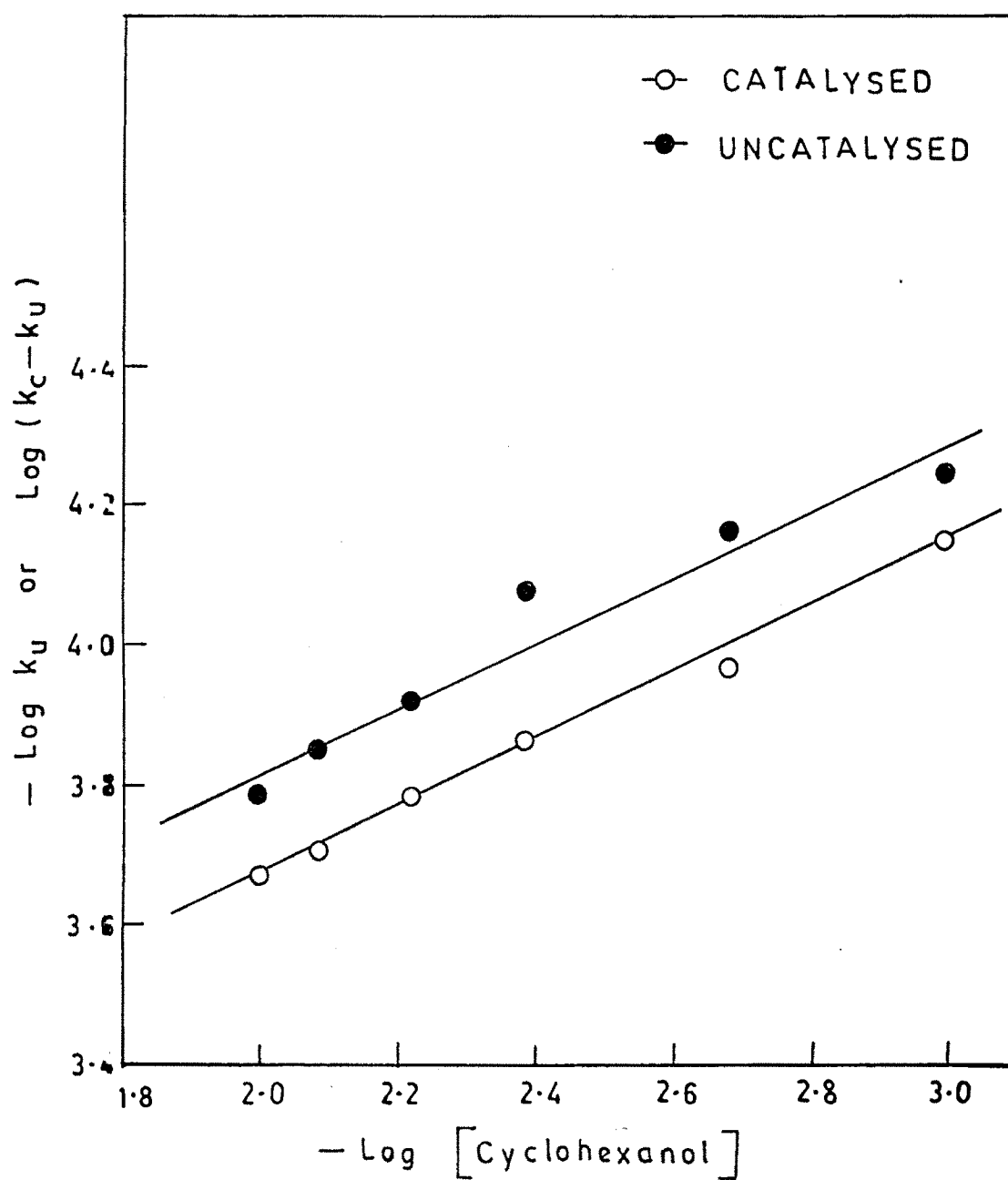


FIG.III(i) - ORDER IN CYCLOHEXANOL.

[CONDITIONS AS IN TABLE III (ii)].

Table III(iii)

Effect of catalyst on Cr^{III} catalysed cyclohexanol oxidation by cerium(IV).

$10^4[\text{Ce}^{\text{IV}}] = 2.0 \text{ mol dm}^{-3}$, $10^3[\text{Cyclohexanol}] = 2.0 \text{ mol dm}^{-3}$

$[\text{HClO}_4] = 1.0 \text{ mol. dm}^{-3}$, $10^2[\text{H}_2\text{SO}_4] = 6 \text{ mol dm}^{-3}$, $T = 298 \text{ K}$

$10^5[\text{Cr}^{\text{III}}]$ mol dm^{-3}	$10^4 k_c \text{ s}^{-1}$	$10^4 (k_c - k_u) \text{ s}^{-1}$	$-\log[\text{Cr}^{\text{III}}]$	$-\log(k_c - k_u)$
0.0	0.69	--	--	--
2.0	2.08	1.39	4.69	3.86
4.0	2.56	1.87	4.39	3.73
8.0	3.07	2.38	4.09	3.62
12.0	3.35	2.66	3.92	3.57
16.0	3.59	2.90	3.79	3.54
20.0	3.78	3.09	3.69	3.51

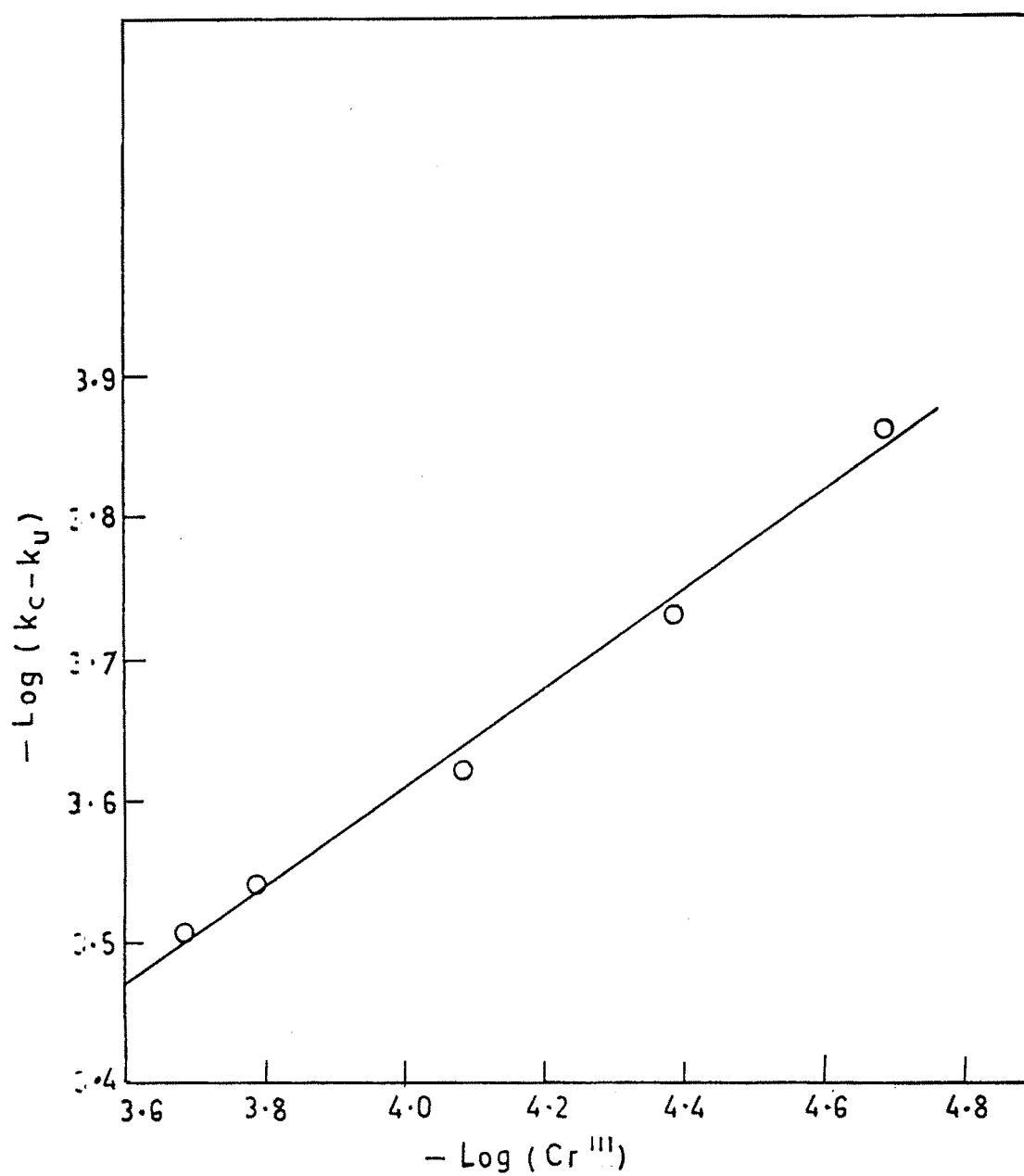


FIG III (ii) — ORDER IN CATALYST CONCENTRATION .
[CONDITIONS AS IN TABLE III (iii)] .

Table III(iv)

Effect of HClO_4 on Cr^{III} catalysed cyclohexanol oxidation by cerium(IV).

$10^4[\text{Ce}^{\text{IV}}] = 2.0 \text{ mol dm}^{-3}$, $10^3[\text{Cyclohexanol}] = 2.0 \text{ mol dm}^{-3}$,

$10^2[\text{H}_2\text{SO}_4] = 6.0 \text{ mol dm}^{-3}$, $10^4[\text{Cr}^{\text{III}}] = 4.0 \text{ mol dm}^{-3}$. $T = 298 \text{ K}$

$[\text{HClO}_4] \text{ mol dm}^{-3}$	$10^4 k_u \text{ s}^{-1}$	$10^4 k_c \text{ s}^{-1}$	$10^4(k_c - k_u)$
0.1	0.04	0.13	0.09
0.2	0.07	0.46	0.39
0.4	0.10	0.76	0.66
0.6	0.21	1.21	1.00
0.8	0.45	1.85	1.40
1.0	0.69	2.56	1.87

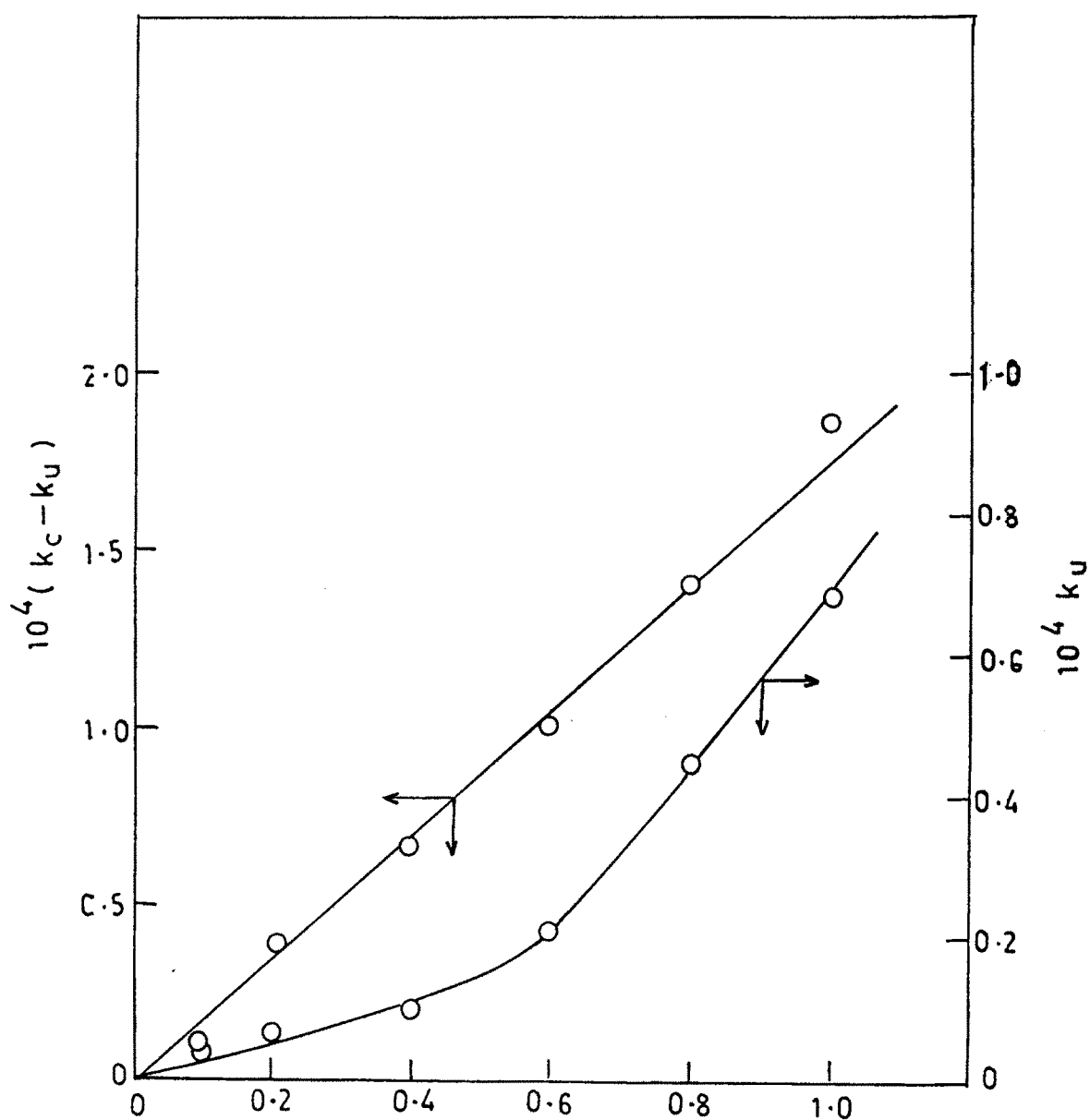


FIG. III(iv) — PLOT OF k_u AND $(k_c - k_u)$ AGAINST $[H^+]$.
[CONDITIONS AS IN TABLE III (iv)].

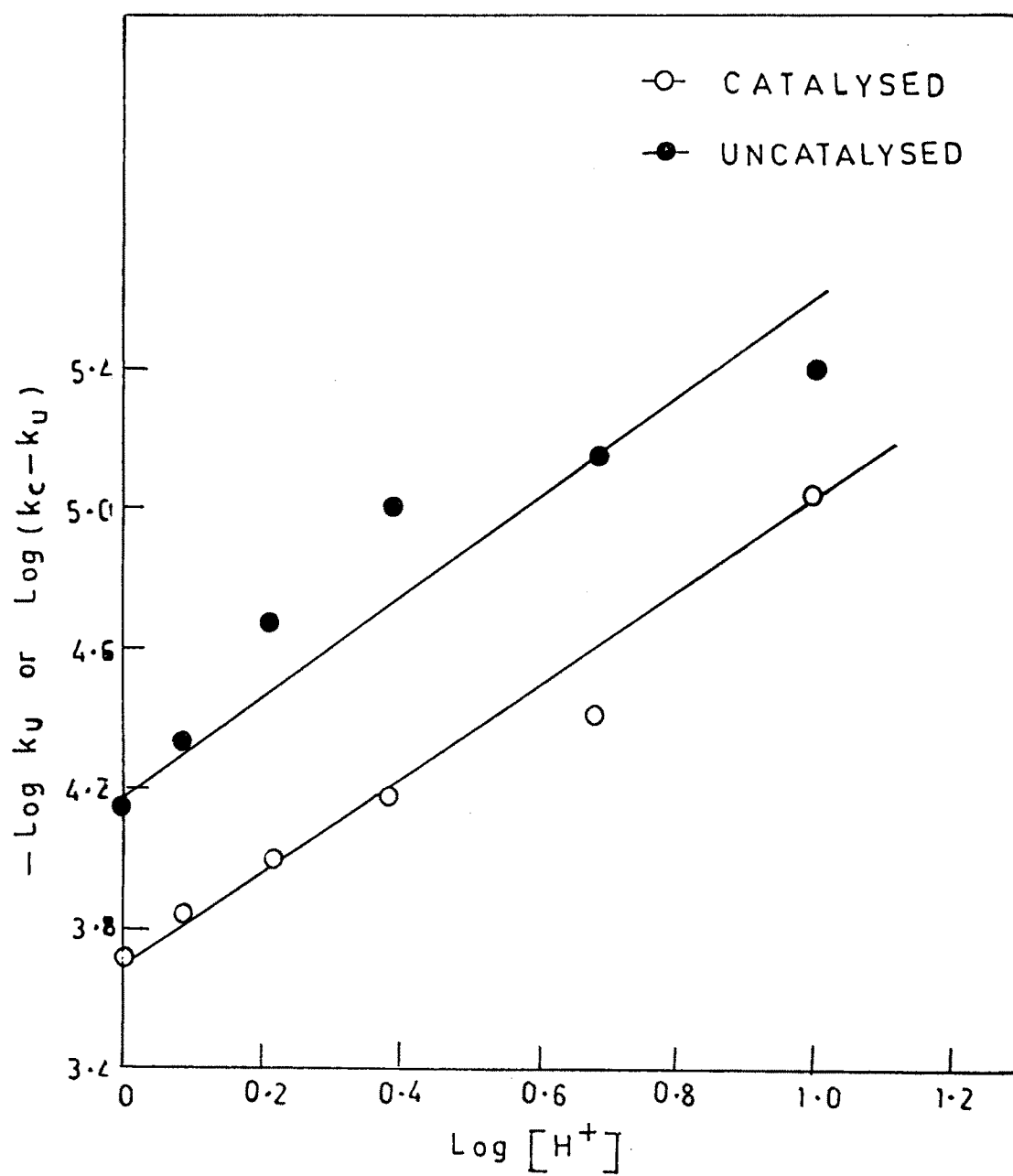


FIG.III(v) — ORDER IN $[H^+]$.

[CONDITIONS AS IN TABLE III(ii)]

Table III(v)

Effect of Ce^{III} on Cr^{III} catalysed cyclohexanol oxidation by cerium(IV).

$10^5 [\text{Cr}^{\text{II}}] = 4.0 \text{ mol dm}^{-3}$, $10^4 [\text{Ce}^{\text{IV}}] = 4.0 \text{ mol dm}^{-3}$,

$10^3 [\text{Cyclohexanol}] = 2.0 \text{ mol dm}^{-3}$ $[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$,

$10^2 [\text{H}_2\text{SO}_4] = 6.0 \text{ mol dm}^{-3}$, $T = 298 \text{ K}$

$10^3 [\text{Ce}^{\text{III}}]$ mol dm^{-3}	$10^4 k_c$ s^{-1}
1.0	1.78
3.0	1.72
6.0	1.64

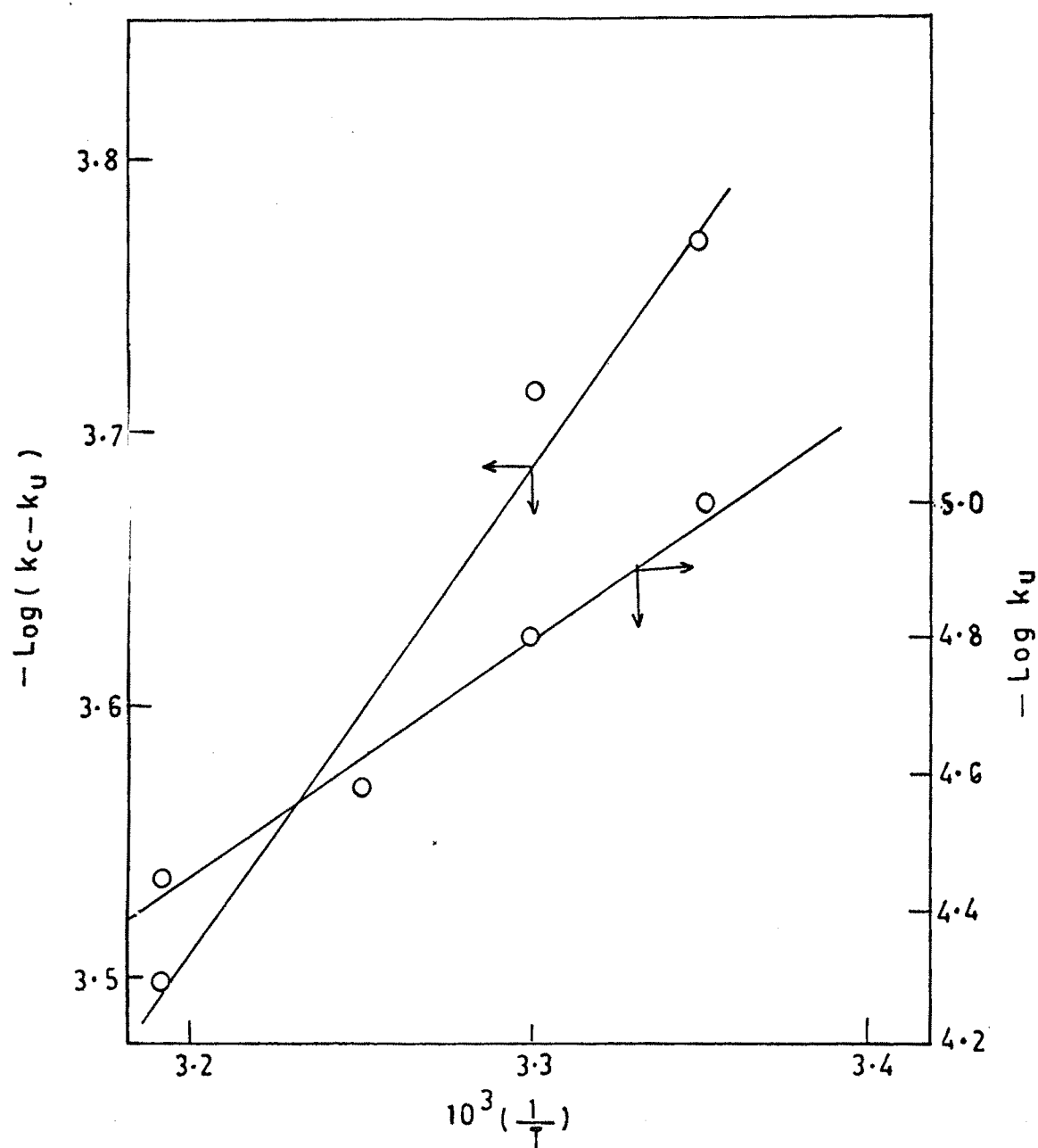


FIG. III(vi) — PLOT OF $\text{Log} k_u$ AND $\text{Log} (k_c - k_u)$
 AGAINST $1/T$.
 [CONDITIONS AS IN TABLE III(vi).]

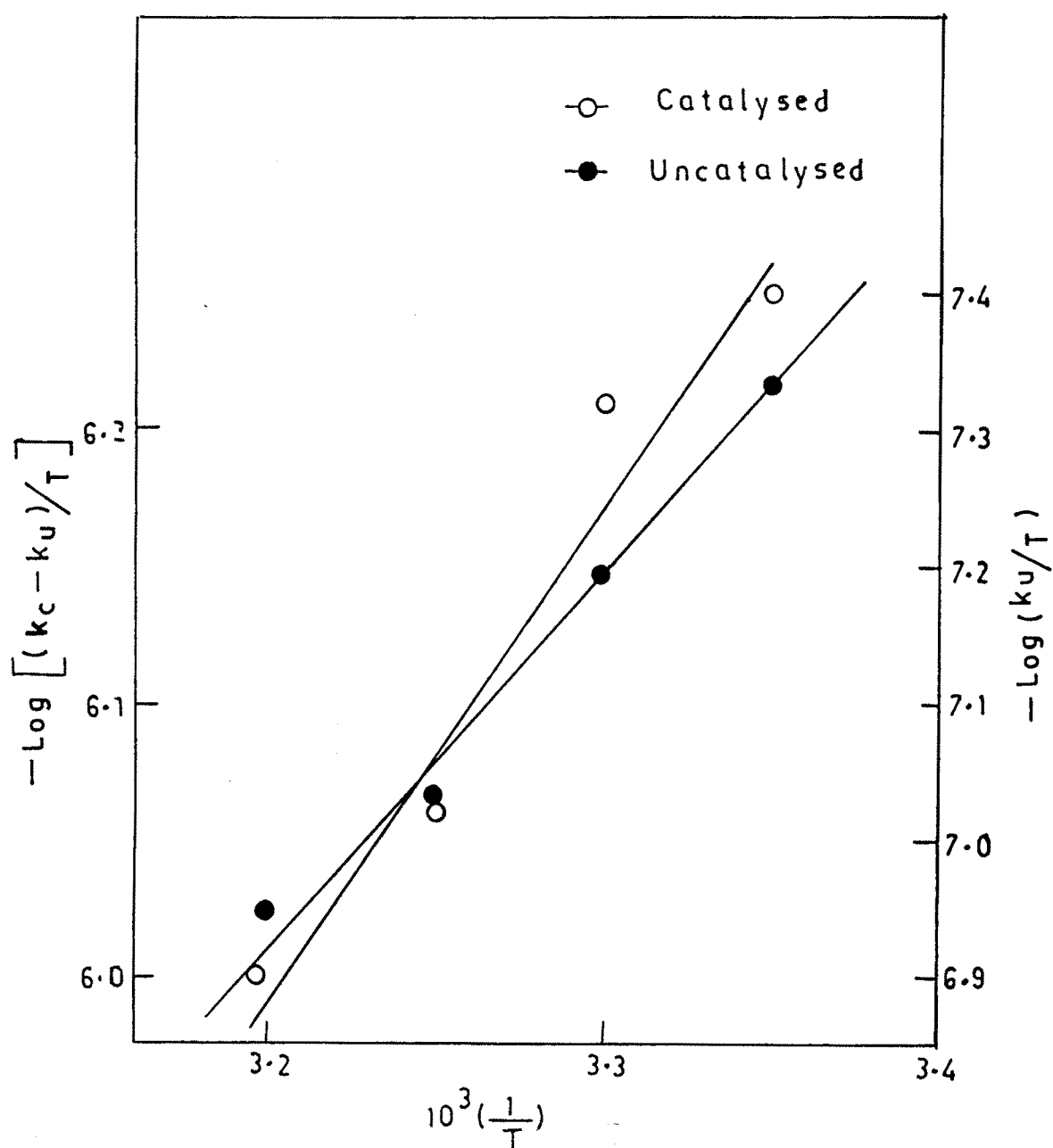


FIG.II (vii) — PLOT OF $\text{Log} (k_u/T)$ AND $\text{Log} [(k_c - k_u)/T]$
 AGAINST $1/T$.
 [CONDITIONS AS IN TABLE III(vi)] .

Table III(vi)

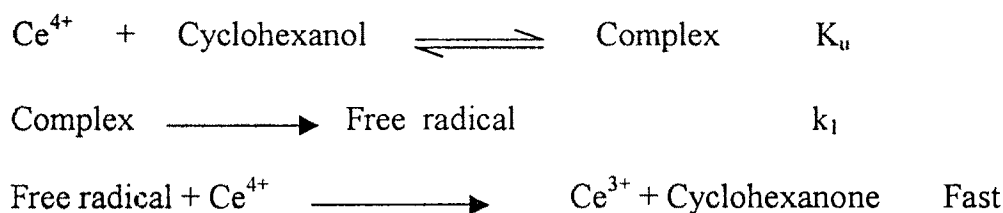
Effect of temperature on uncatalysed and Cr^{III} catalysed Ce^{4+} oxidation of cyclohexanol.

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

$[\text{Cyclohexanol}] = 2.0 \text{ mol dm}^{-3}$ $[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$ $10^2 [\text{H}_2\text{SO}_4] 6.0 \text{ mol dm}^{-3}$.

T	$10^4 k_u \text{ s}^{-1}$	$10^4 k_c \text{ s}^{-1}$	$10^4(k_c - k_u) \text{ s}^{-1}$
298	0.10	1.78	1.68
303	0.16	2.00	1.84
308	0.26	2.95	2.69
313	0.35	3.48	3.13

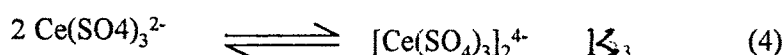
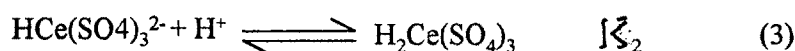
	Ea KJ mol^{-1}	ΔH^\ddagger KJ mol^{-1}	ΔS^\ddagger $\text{JK}^{-1} \text{ mol}^{-1}$	ΔG^\ddagger KJ mol^{-1}
Uncat	64.2 ± 4	52.6 ± 5	-133 ± 9	103.9 ± 5
cat	33.72 ± 5	35.4 ± 5	-212 ± 10	96.9 ± 5



Scheme 1

$$(\text{rate})_{\text{uncat}} = k_1 k_u [\text{Alcohol}] [\text{Ce}^{4+}] / (1 + K_u [\text{Alcohol}]) \dots\dots\dots (1)$$

prior equilibria. In solutions containing sulphate, cerium(iv) will be predominantly³² present as $\text{Ce}(\text{SO}_4)_3^{2-}$ and is further protonated as shown by equilibria 2 and 3. The decrease in the rate constants as the oxidant concentration increases [Table-I(i)] may be due to the dimerization³³ of Ce^{IV} as shown in equation 4 and only monomer is the active species in the present study. Since, the order in $[\text{H}^+]$ is



more than one therefore, diprotonated, $\text{H}_2 \text{Ce}(\text{SO}_4)_3$, species of the oxidant is active in both uncatalysed and catalysed reactions. In order to express the rate law (1) in terms of active species the concentration of $\text{H}_2 \text{Ce}(\text{SO}_4)_3$ is obtained in the following manner.

The total oxidant concentration is given by

$$\begin{aligned}
 [\text{Ce}^{4+}]_T &= [\text{Ce}(\text{SO}_4)_3^{2-}]_T \\
 &= [\text{Ce}(\text{SO}_4)_3^{2-}]_f + [\text{H Ce}(\text{SO}_4)_3^-] + [\text{H}_2 \text{Ce}(\text{SO}_4)_3] + [\text{Ce}(\text{SO}_4)_3]_2^{4-} \dots\dots\dots (5)
 \end{aligned}$$

where $[\text{Ce}(\text{SO}_4)_3^{2-}]_T$ and $[\text{Ce}(\text{SO}_4)_3^{2-}]_f$ are total and free $[\text{Ce}(\text{SO}_4)_3^{2-}]$ respectively.

Then from equilibria 2 to 4 we get

$$\begin{aligned} [\text{Ce}(\text{SO}_4)_3^{2-}]_T &= [\text{Ce}(\text{SO}_4)_3^{2-}]_f + K_1 [\text{H}^+] [\text{Ce}(\text{SO}_4)_3^{2-}]_f + K_1 K_2 [\text{H}^+]^2 [\text{Ce}(\text{SO}_4)_3^{2-}]_f \\ &\quad + K_3 [\text{Ce}(\text{SO}_4)_3^{2-}]_f^2 \\ &= [\text{Ce}(\text{SO}_4)_3^{2-}]_f \{ 1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + K_3 [\text{Ce}(\text{SO}_4)_3^{2-}]_f \} \end{aligned}$$

$$[\text{Ce}(\text{SO}_4)_3^{2-}]_f = \frac{[\text{Ce}(\text{SO}_4)_3^{2-}]_T}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + K_3 [\text{Ce}(\text{SO}_4)_3^{2-}]_f} \quad (6)$$

from equilibrium (3) substituting the value of $[\text{Ce}(\text{SO}_4)_3^{2-}]_f$ expressed by equation (6) we get

$$[\text{H}_2\text{Ce}(\text{SO}_4)_3] = \frac{K_1 K_2 [\text{H}^+]^2 [\text{Ce}(\text{SO}_4)_3^{2-}]_T}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + K_3 [\text{Ce}(\text{SO}_4)_3^{2-}]_f} \quad (7)$$

subtracting the values of $[\text{H}_2\text{Ce}(\text{SO}_4)_3]$ for $[\text{Ce}^{4+}]$ in equation 1 in the rate law in terms of active species $\text{H}_2\text{Ce}(\text{SO}_4)_3$ is obtained as in equation (8) and the

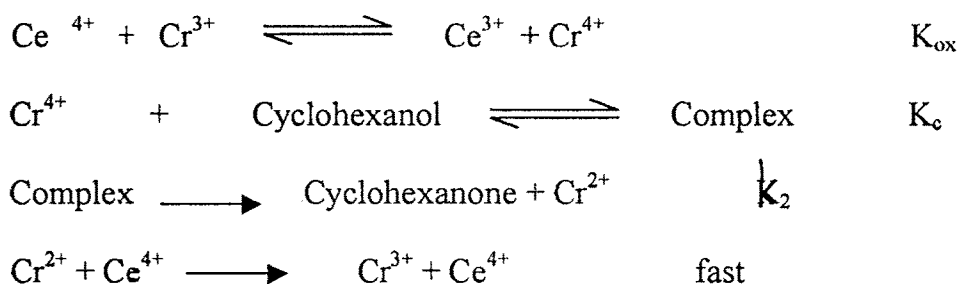
$$(\text{rate})_{\text{uncat}} = \frac{k_1 K_u K_1 K_2 [\text{H}^+]^2 [\text{Ce}(\text{SO}_4)_3^{2-}]_T [\text{Alcohol}]}{(1 + K_u [\text{Alcohol}]) + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + K_3 [\text{Ce}(\text{SO}_4)_3^{2-}]_f} \quad (8)$$

$$k_{\text{uncat}} = k_u = \frac{k_1 K_u K_1 K_2 [\text{H}^+] [\text{Alcohol}]}{(1 + K_u [\text{Alcohol}]) (1 + k_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + k_3 [\text{Ce}(\text{SO}_4)_3^{2-}]_f)} \quad (9)$$

The corresponding pseudo-first-order rate constant by equation (9).

3.2.2 Catalysed Reaction

The first order dependence on oxidant concentration and decrease in the rate of the reaction in presence of added product Ce^{III} [Table III(v)] indicate involvement of both in reversible equilibrium with the catalyst. The oxidation of Cr^{III} by Ce^{IV} is known to involve such an equilibrium³ with the formation of Cr^{IV} intermediate followed by its slow conversion to Cr^{V} due to change in co-ordination number from 6 to 4. The fractional order in the alcohol and the Michealis-Menten plot of $(1/k_{\text{cat}} - k_{\text{uncat}})$ against $1/[\text{Alcohol}]$ [Figure III (viii)] shows its involvement in the complex formation. Since, the catalyst, Cr^{III} is known for its inert nature, the probable path would be its reaction with oxidant generating labile Cr^{IV} in an equilibrium which may then form a complex with the alcohol. The complex formed may undergo internal oxidation reduction as shown in Scheme 2.



Scheme – 2

$$(\text{rate})_{\text{cat}} = \frac{k_2 K_{\text{ox}} K_c [\text{Alcohol}]}{[\text{Ce}^{3+}] [1 + K_c [\text{Alcohol}]]} \quad (10)$$

The complex formed may undergo either one electron or two electron transfer to produce Cr^{II} and Cr^{III} respectively. The former path will produce free radicals and the latter leads to the generation of Cr^{III} without any significant change in the rate law. Although, the two electron path is more favorable³⁴, it is difficult to

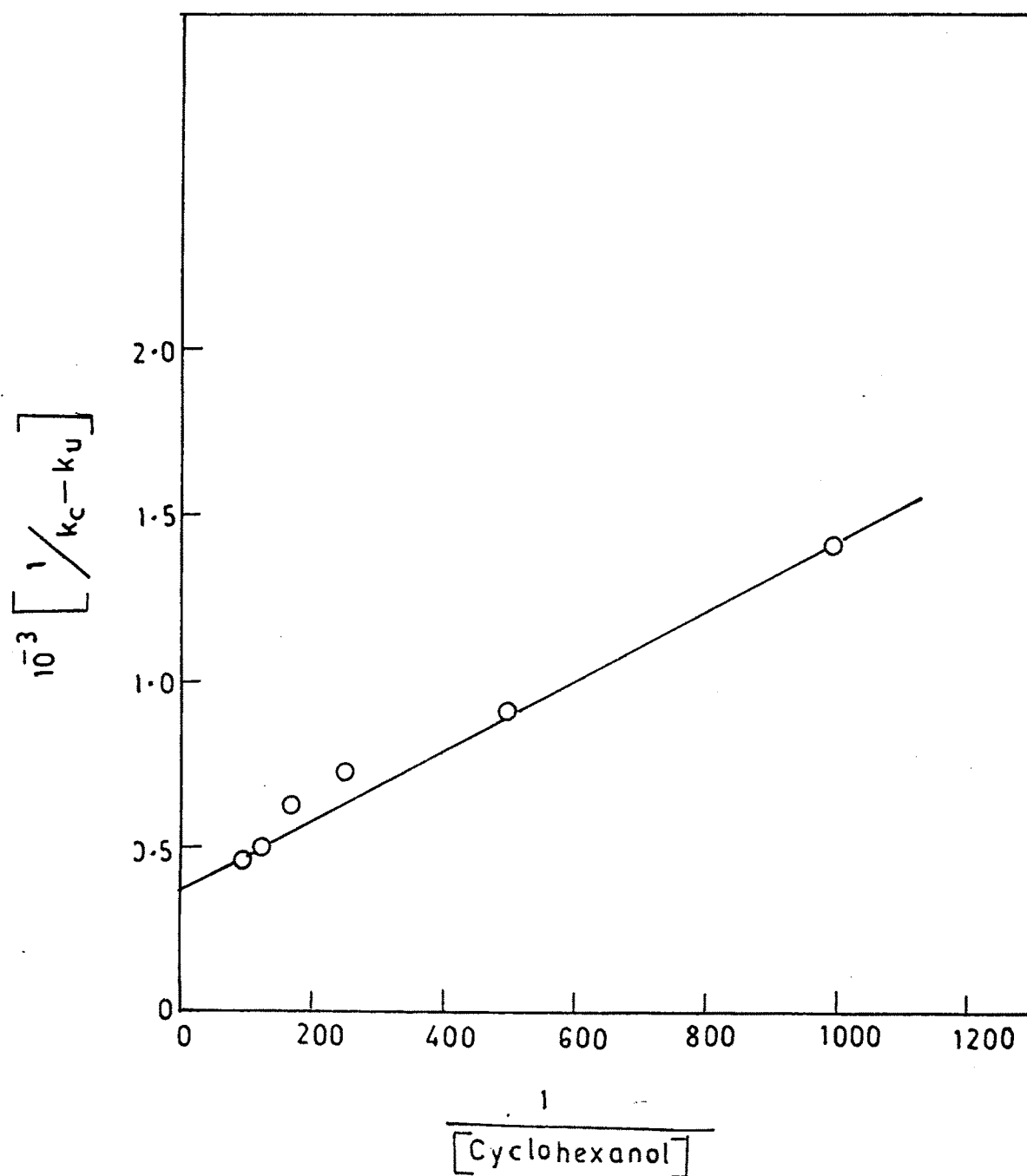


FIG. III.viii) — PLOT OF $\left[\frac{1}{k_c - k_u} \right]$ AND $\frac{1}{k_u}$ AGAINST $\frac{1}{[\text{Cyclohexanol}]}$.
 [CONDITIONS AS IN TABLE III(ii)].

differentiate between the two. Considering latter path as the probable the mechanism of catalysed reaction is represented in Scheme 2 and the corresponding rate law by equation (10). Since the hydrogen ion concentration is similar in both catalysed and uncatalysed reaction considering same oxidant species, $\text{H}_2\text{Ce}(\text{SO}_4)_3$ as the active one the rate law in terms of active species would be as in equation (11). The rate law (11) is verified by,

$$(k_c - k_u)_I = \left\{ \frac{k_2 K_{ox} K_c [\text{Alcohol}]}{[\text{Ce}^{3+}] [1 + K_c [\text{Alcohol}]]} \right\} \times \left\{ \frac{K_1 K_2 [\text{H}^+]^2}{(1 + k_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + k_3 [\text{Ce}(\text{SO}_4)_3^{2-}])} \right\} \quad (11)$$

plotting $1 / k_c - k_u$ against $1 / [\text{Alcohol}]$ [Figure III (viii)]

The activation energy for the catalysed path is lesser than that of the uncatalysed path as expected. Low entropy of activation for both catalysed and uncatalysed reaction support, the formation of complex due to which loss of degrees of freedom occurs.