THEMODYNOMICAL STUDY OF OXIDATION OF CYCLOPENTANOLE BY N CHLOROPHTHALIMIDE: KINETIC APPROCH

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Abstract:

The kinetic and mechanistic study of some cyclopentanol by N-chlorophthalimide in acetic acid medium was carried out at 308^0k. The follows pseudo first order kinetics each in [NCP] and [cyclopentanol], and reaction is acid catalysed. The study completely discarded the formation of complex and rules out the involvement of cations in mechanism. The study reveals that the reaction velocity retarded with increases in solvent composition. Thermodynamic parameters were computed. A suitable mechanism with the kinetics results has been proposed.

Key words:

Involvement, consistent, composition, deterioration.

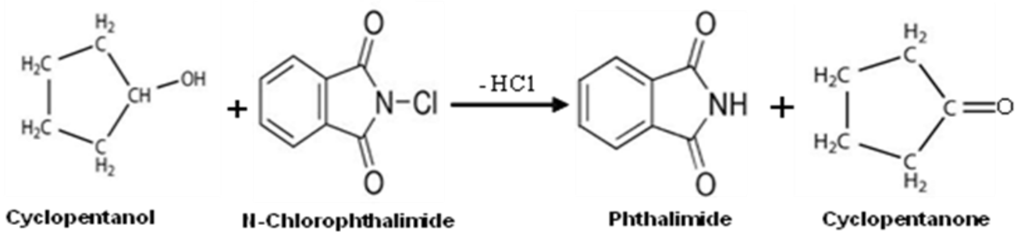
Introduction:

The present proposed study investigated with the kinetic of reactions involving the redox system.[1] The N-chlorophthalimide can be successfully exploited as an input technology and first of all employed as an oxidant for kinetic aspect by *Bhavani et al.*[2] for the oxidation of phenyl methyl sulphoxide. Kinetic and mechanism of oxidation of cyclopentanol with NCP have been received much attention and attracted to chemists in several laborites kinetic of cyclopentanol with variety of oxidants such as cerium (IV)[3], $KBrO_3$[4], Qinolium dichromate[5], pyridinium chlorochromate[6,7]and Chloramine-T[8] have been reported earlier.

Experimental:

All the chemicals employed in this investigation were of analytical grade. The solution of N-chlorophthalimide was obtained by (99% purity) whose melting point was found to be 481^0K was obtained by dissolving its weighed quantity in 100% acetic acid and kept in either amber colored flask or black paper wrapped around it to save it from the action of diffused day light which alters appreciably its concentration i.e. to avoid occurrence of photochemical deterioration.

The standardization of N-chlorophthalimide was carried out by taking 1ml of its solution in conical flask to which 10ml of 2% KI solution followed by 5ml of 2N-H_2SO_4 was added to it. The liberated iodine was estimated against standard hypo ($Na_2S_2O_3$. $5H_20$) solution using starch solution as indicator.



Result and Discussion:

The reaction follow first-order kinetic with respect to [NCP] all these reactions are homogenous and characterized by induction period. It is found that under the condition.

[NCP]<< [cyclopentanol]

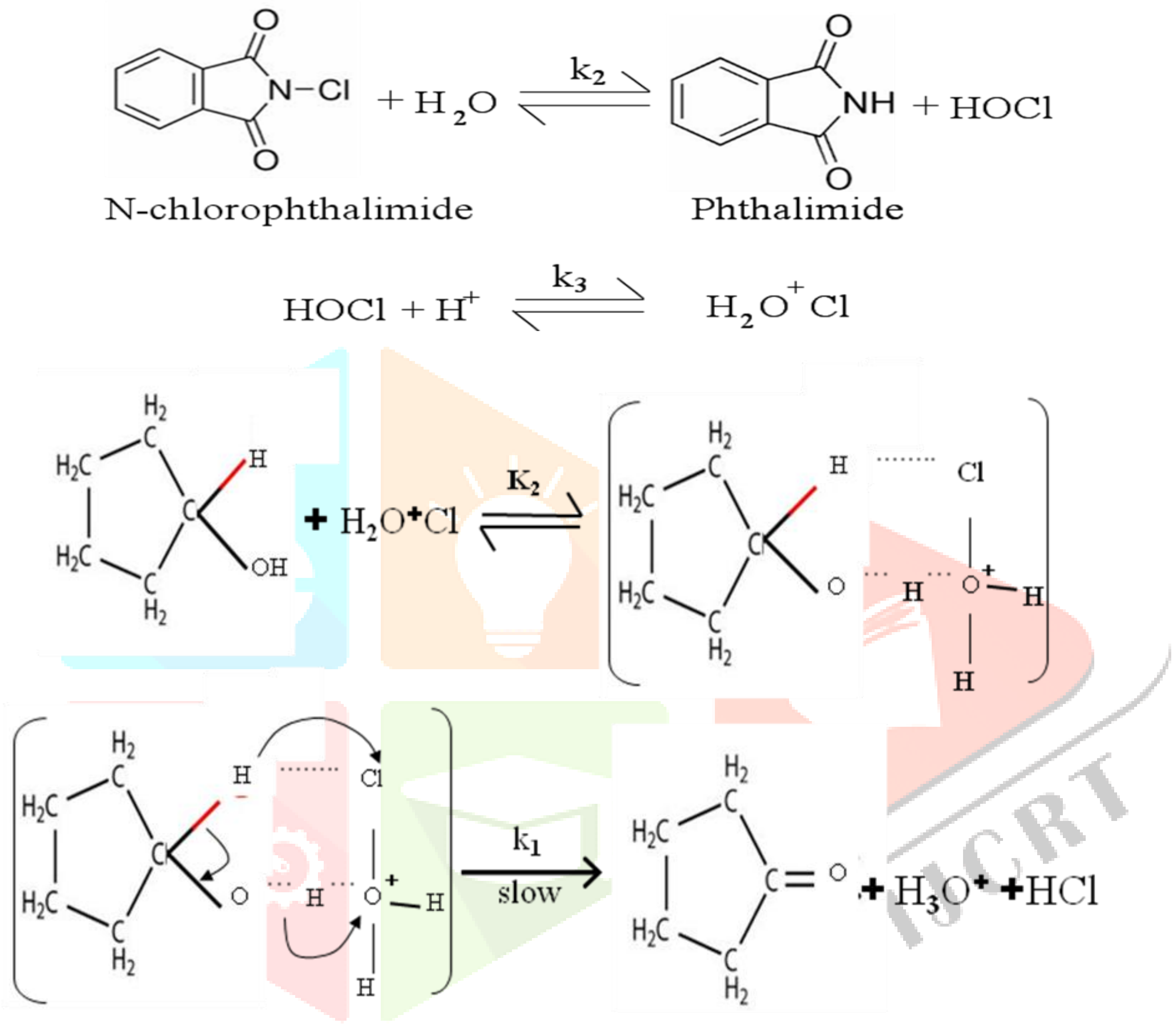
The rate constant was determined at different hydrogen ion concentration for cyclopentanol the plot of log k_1 verses log $[H^+]$ is obtained linear with passing through origin, suggesting that reaction involve only acid catalyzed independent path as recorded in Table No.-1 at constant temperature. The effect of increasing concentration of Cu^{++} ions show an acceleration in the reaction velocity while Mn^{++} ions show a retardation in the rate of reaction. Table No.-2

Mechanism:

In the present study, the effect of dielectric constant of the medium shows the first order rate constant increase with increasing composition of acetic acid. i.e. rate slightly accelerated with decrease in dielectric constant of the medium.

In the presence investigation the powerful prime remote reactive cationic electrophile is H_2O^+Cl which interact with cyclopentanol in the process to form chloronium ion. The transfer of electons, take place from substrate to active species of

NCP during the formation of HOCl. Considering these facts a plausible mechanism for the oxidation of cyclopentanol with N-chloropthilime could be proposed as per following scheme.



The rate law was derived as.

$$K_{obs} = \frac{\text{Rate}}{[\text{NCP}]_T} = \frac{k\,k_1\,k_2[\,C_6H_4(CH_2)OH][H^+]}{[\text{Phthalimide}]+k_2+k_2+k_1+[H^+]}$$

The proposed mechanism is also supported by the moderate value of energy of activation and other thermodynamic parameters.

Cyclopentanone was identified as end-product in the study with 1:1 stichiometrically

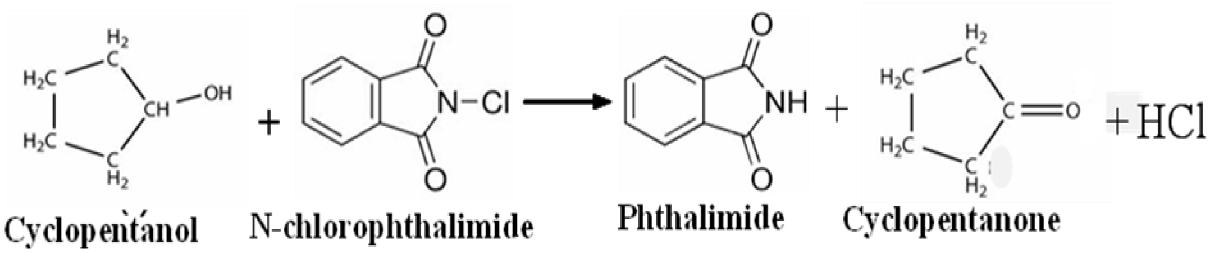

Cyclopentanol
N-chlorophthalimide
Phthalimide
Cyclopentanone
+HCl

Table No. - 1

Dependence of rate on the concentration of Sulphuric acid

$10^3 \times$ [NCP] (mol dm^{-3}) = 2.50;
$10^2 \times$ [substrate] (mol dm^{-3}) = 2.50;
HOAc-H_2O % (v/v) = 30;
Temperature^0 K = 308.

Sr.No.	**[H^+] × 10^2 (mol dm^{-3})**	**cyclopentanol 10^4 k_1 (s^{-1})**
1.	0.25	-
2.	0.50	1.72
3.	1.00	3.71
4.	1.25	4.35
5.	1.50	5.20
6.	2.00	6.95

Table No. -2

Dependence of rate on the concentration of metal ion catalyst Cu^{++}

10^3 [NCP] (mol dm^{-3}) = 2.50 ;
10^2 [Substrate] (mol dm^{-3}) = 2.50;
10^2 [H^+] (mol dm^{-3}) = 1.0;
HOAc-H_2O, % v/v = 30;
Temperature^o K = 308

Sr. No.	**[Cu^{++}] ×10^3 (mol dm^{-3})**	**Cyclopentanol 10^4 k_1 (s^{-1})**
1.	0.00	3.71
2.	0.50	3.96
3.	1.25	4.01
4.	2.00	4.51
5.	2.50	4.69
6.	4.00	4.98
7.	5.00	5.03

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References:-

1. Pauling, L. Franklin : "General Chemistry" Allied Pacific Pvt. Ltd. Bombay, 245 **(1962)**.
2. Bhavani, N. and Lily, K. : Current Science Sept. 20 No. 18 **(1983)**.
3. Tandon, P.K., Singh, A.K., Sahgal, S. and Kumar, S. : J. Mode Catal. A. Chem., 282, 136 **(2008)**.
4. Shrivastava, S., Sharma, R.K. and Singh, S. : J. Indian, Chem. Soc., 83, 282 **(2006)**.
5. Lee, D.G. and Gai, H. : Can. J. Chem., 71, 1394 **(1993)**.
6. Jain, S., Hiran, B.L., and Bhatta, C.V. : E. Journal of Chemistry 6(1), 237-246 **(2009)**.
7. Devassy, Biju M., Lefebvre, F. and Halligudi, S.B. : Journal of Catalysis 231, 1 **(2009)**.
8. S. Kutti Rani. D. Eswaramoorthy, Mohamed Bilal, T. and M. Palanichmg. : Appl. Catal A: General 369 (102), 1-7, (2009).