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KINETICS AND MECHANISM OF OXIDATION OF CYCLOHEXANONE OXIME BY N-CHLOROPIPERAZINE-2, 5-DIONE

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ABSTRACT
The kinetics of oxidation of a cyclohexanone oxime by N-chloropiperazine-2,5-dione in aqueous acetic acid medium have been investigated. The reaction is first order with respect to oxidant and fractional order with respect to substrate and inverse order with respect to [H^+] ion. From the kinetic data obtained ,the activation parameters have been calculated using Eyring's plot and a suitable mechanism has been proposed. The oxidation product is cyclohexanone .A suitable rate law is derived.
Key words: Kinetics,Mechanism,Oxidation,cyclohexanone oxime, N-chloropiperazine-2,5-dione

INTRODUCTION

Kinetics of oxidation and halogination of organic substrate using a variety of N-halo compounds have been reported earlier[1-12]. Now report the kinetics and mechanism of oxidation of cyclohexanone oxime with a mild and selective oxidants, N-chloropiperazine-2,5-dione (NCPD)[13-14].

EXPRIMENTAL

Materials

Piperazine-2,5-dione was prepared as described by vogel[15] and it was chlorinated to get N-chloropiperazine-2,5-dione by usual procedure. All other chemicals used were of AnalaR. Doubly distilled water was used throughtout.

Stoichiometry and Product analysis

Solutions of cyclohexanone oxime containing an excess of NCPD were kept overnight at 30° C. Estimation of the remaining oxidant showed that the stoichiometry (cyclohexanone oxime : NCPD) as 1:1 .The reaction mixture from actual kinetic runs with excess of oxidant after slight warming was kept for two days and extracted with chloroform and dried over anhydrous sodium sulphate. The chloroform layer was then evaporated and the product obtained was cyclohexanone and it was identified by its 2,4-dinitriphenyl hydazone derivative(m.p 161° C).

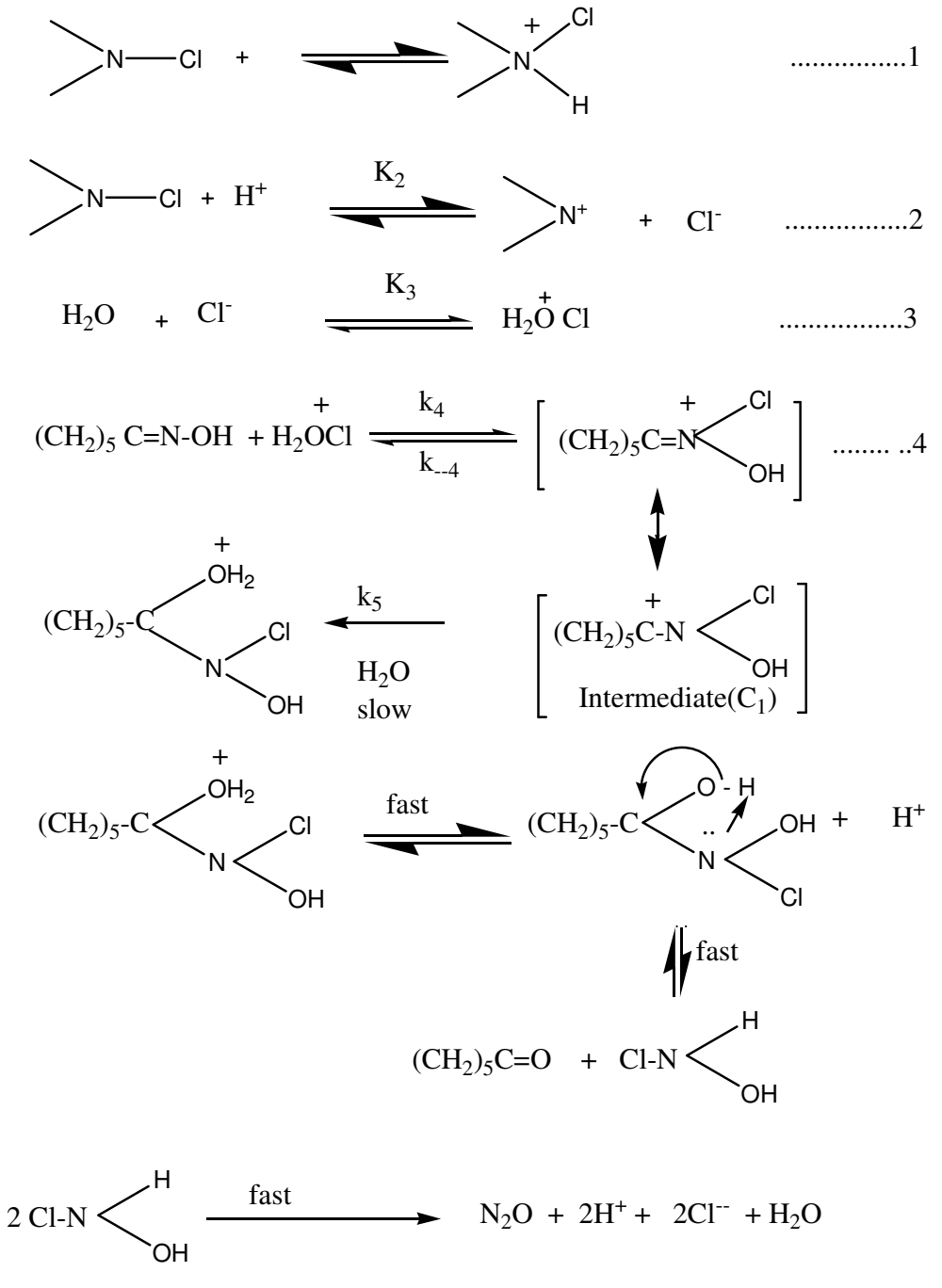
RESULTS AND DISCUSSION

From the observation(Table-1) it is clear that the reaction is showing unit order dependence with respect to oxidant and fractional order with respect to the substrate, as well as[H^+] ion.The rate increases with decrease in the dielectric constantof the medium and increase in the ionic strength has negligible effect on the rate.The reaction did not induce polymerization of acrylo nitrle indicating the absence of free radical path way. Based on the above observations, a possible mechanism has been proposed(scheme-1)

Mechanism and rate law

›N-Cl bond in NCPD is partially polar similar to N-bromosuccinimide.Here the various oxidizing species in acidified solution are the molecular NCPD,protonated NCPD(NCPDH^+) solvated chloro cation (H_2O^+Cl) and HOCl.

Scheme-1



Rate of the reaction $= k_5 C_1$

$$\text{But } C_1 = \frac{k_4 [H_2O^+ Cl] [\text{Oxime}]}{k_{-4} + k_5 + k_4 [\text{oxime}]}$$

$$[H_2O^+Cl] = K_2 K_3 [NCPD]_f$$

$$\text{But } [NCPD]_f = \frac{[NCPD]_f}{1 + K_1[H^+]}$$

where $[NCPD]_f = [NCPD]_{free}$

$[NCPD]_t = [NCPD]_{total}$

Hence

$$-\frac{d[NCPD]}{dt} = \frac{k_5 K_2 K_3 [NCPD]_{total} [\text{oxime}]}{\{k_{-4} + k_5 + k_4 [\text{oxime}]\} \; 1 + k_1[H^+]}$$

$$k_{obs} = \frac{k_5 K_2 K_3 [\text{oxime}]}{\{k_{-4} + k_5 + k_4 [\text{oxime}]\} \; 1 + k_1[H^+]}$$

Reaction involving chlorine atom is ruled out as no inhibition of the reaction is observed when vinyl monomer,acrylonitrile is added to the reaction mixture. As the reaction is fractional order dependence on substrate, the molecular NCPD is not considered as reactive species. Since the protonated and deprotonated are said to be fast, $NCPDH^+$ is likely to be the reactive species.Moreover ,as the reaction rate decreases with the increase of acidity, , $NCPDH^+$ is not considered as the reactive species. At low pH, among HOCl and H_2O^+Cl, the protonated form is predominating; also this is the strong electrophile and a more potent reactive species,Hence the H_2O^+Cl is peoposed to be reactive species. Based on the above facts, the following mechanism has been proposed.

Table-1: Rate constant for the oxidation of cyclohexanone oxime by NCPD in aqueous acetic acid medium.

[NCPD] (10^3 M)	[OXIME] 10^2M)	[$NaClO_4$](10^2M)	[H^+] (10^1 M)	AcOH -H_2O(% v/v)	Temp.° C	k_1 ($10^4 s^{-1}$)
0.50	2.00	-	2.00	35-65	40	2.36
0.75	2.00	-	2.00	35-65	40	2.20
1.00	2.00	-	2.00	35-65	40	2.16
1.25	2.00	-	2.00	35-65	40	2,23
1.00	1.00	-	2.00	35-65	40	2.35
1.00	1.50	-	2.00	35-65	40	2.56
1.00	2.00	-	2.00	35-65	40	3.53
1.00	2.50	-	2.00	35-65	40	3.68

1.00	2.00	2.50	2.00	35-65	40	2.99
1.00	2.00	5.00	2.00	35-65	40	3.49
1.00	2.00	7.20	2.00	35-65	40	4.05
1.00	2.00	10.00	2.00	35-65	40	4.69
1.00	2.00	-	0.92	35-65	40	3.33
1.00	2.00	-	0.72	35-65	40	2.80
1.00	2.00	-	0.65	35-65	40	2.98
1.00	2.00	-	0.62	35-65	40	2.76
1.00	2.00	-	2.00	25-75	40	2.05
1.00	2.00	-	2.00	30-70	40	2.74
1.00	2.00	-	2.00	35-65	40	3.53
1.00	2.00	-	2.00	40-60	40	3.12
1.00	2.00	-	2.00	35-65	35	2.19
1.00	2.00	-	2.00	35-65	40	3.17
1.00	2.00	-	2.00	35-65	45	5.32
1.00	2.00	-	2.00	35-65	50	10.49

$\Delta H^{\neq}$ = 69.93 kJ mol^{-1} $\Delta S^{\neq}$ = -68. 76 J K^{-1} mol^{-1} $\Delta G^{\neq}$ =91 .45 kJ mol^{-1}

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