Oxidation of cyclanols by 1-chloro benzimidazole in aqueous acetic acid medium: A kinetic approach

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ABSTRACT

Kinetic investigation on oxidation of some Cyclanols (Cyclopropanol, Cyclobutanol, Cyclopentanol, Cyclohexanol and Cycloheptanol) by 1- chlorobenzimidazole (CBI) has been studied in 80% acetic acid - water (v/v) medium. The reaction exhibits first order rate dependence each with respect to [CBI], [Cyclanols] and [H^+]. The increase in dielectric constant of the medium increases the rate of the reaction. The variation of ionic strength has no significant effect on the reaction rate. The reaction does not induce any polymerization of acylonitrile. The addition of benzimidazole has no appreciable effect on the reaction rate. Thermodynamic parameters have been evaluated from Eyring plots by studying the reaction at different temperatures. A most probable mechanism and an appropriate rate law have been deduced for the observed kinetic data.

Key Words: Kinetics, CBI, Oxidation, Cyclic alcohols, Potentiometry.

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INTRODUCTION

In the recent years, the study of kinetics of oxidation of aromatic compounds by N- halo compounds has received considerable attention [1- 6]. Kinetics of oxidation of cyclanols (cyclic alcohols) with a variety of metal oxidants such as Ce (IV)[7], potassium hexacyanoferrate[8], thallium(III)acetate[9-10], barium manganate[11], quinolinium dichromate[12-17], quinolinium bromochromate[18] have been studied earlier.

A few N- halocompounds such as N- bromoacteamide[19], N- bromopthallimide[20], chlroamine – T[21] have also been utilized for the oxidation of cyclanols. An extensive literature reveals that no systematic kinetic work hitherto has been done on the oxidation of cyclanols by using 1 – chloro benzimidazole (CBI) though CBI has been used as an oxidant for benzaldehydes[22] and furfural[23]. In the present work, the reaction kinetics of cyclic alcohols with CBI has been studied in aqueous acetic acid medium.

EXPERIMENTAL SECTION

All the cyclic alcohols used were AnalaR Grade. CBI was prepared by literature method [24]. Acetic acid was refluxed over chromic oxide for 6 hours and the fraction distilling at 118°C was collected and used. The standard solutions of cyclanols were prepared by weighing its sample (AnalaR Grade) and dissolving it in acetic acid. Double distilled water was employed for all kinetic runs.

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Kinetic Measurements

Kinetic measurements were made under pseudo – first order conditions, by keeping a large excess of cyclanols (10 folds or more) over oxidant CBI. A thermostated water bath was used to maintain the desired temperature with in $\pm 0.1^0$C. The reactions were initiated by the addition of CBI solution to other reagents equilibrated separately at 303 K. The progress of the reaction were followed potentiometrically[22] upto 70% completion of reaction by following the potentials of the reaction mixture containing varying concentration of [CBI/BI] couple at regular time intervals using a platinum – saturated calomel electrode assembly.

The pseudo – first order rate constants were obtained from the linear plots (r>0.99) plots of log (E_t- E_∞) Vs time. The rate constants were in good agreement ($\pm 2\%$) with the rate constant values obtained when the kinetic runs were repeated by iodometry. Preliminary experiments showed that the reaction were not sensitive to change in ionic strength, hence no attempt was made to keep it constant.

Stoichiometry and product anlaysis

The stoichiometry of the reaction was determined by equilibrating varying ratios of [CBI] Vs [Cyclanol] at 303K for 48 hours under kinetic conditions. Estimation of unconsumed CBI revealed that 1 mole of CBI was required to oxidize 1 mole of the Cyclanol.

$$\text{Cyclanol} \;+\; \text{CBI} \longrightarrow \text{BI} \;+ \text{Cyclanone} \;+ \text{HCl}$$
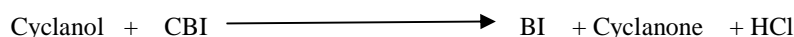
The reaction mixture from the actual kinetic run after sufficient time, was then evaporated with ether. The layer was then separated and dried. The product obtained was corresponding cyclanones which were characterized by TLC, spot test analysis[25], 2-4 dinitrophenyl hydrazine (DNP) derivatives[26] and their melting points.

RESULTS AND DISCUSSION

Effect of varying concentration of oxidant:

The kinetics of cyclanols by CBI was investigated at several initial concentrations of the oxidant. Under pseudo first order conditions of [cyclanol] >>> [CBI], the oxidation proceeds smoothly at 308K in aqueous acetic acid medium. The order of the reaction with respect to CBI (oxidant) was found to be unity as shown by the linearity of log (E_t- E_∞) Vs time plots, over 70% completion of the reaction (Table. 1).

Table.1. Effect of varying [oxidant] on the reaction rate

[Cyclanol] = 2 x 10^{-2} mol.dm^{-3} Solvent = 80% AcOH
[HClO$_4$] = 2.5 x 10^{-2} mol.dm^{-3} Temp. = 303 K

[CBI] x 10^3 mol.dm^{-3}	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
0.5	2.99	4.10	4.83	5.52	6.40
1.0	2.95	4.02	4.87	5.58	6.47
1.5	2.97	4.13	4.80	5.53	6.52
2.0	2.90	4.05	4.92	5.49	6.46
2.5	2.92	4.09	4.88	5.63	6.49

Table.2. Effect of varying [substrate] on the reaction rate

[CBI] = 1 x 10^{-3} mol.dm^{-3} Solvent = 80% AcOH
[HClO$_4$] = 2.5 x 10^{-2} mol.dm^{-3} Temp. = 303 K

[Cyclanol] x 10^2 mol.dm^{-3}	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
1.0	1.32	1.90	2.29	2.75	2.95
2.0	2.95	4.02	4.87	5.58	6.47
3.0	4.37	6.02	7.24	8.51	10.00
4.0	6.17	8.32	10.00	11.75	13.80
5.0	7.77	10.47	12.58	14.45	17.37

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Effect of varying concentration of substrate:
The oxidation reaction was also carried out with various concentrations of cyclanols, keeping other solution variables as constant at 303K. An increase in the concentration of cyclanols increases the rate of oxidation (Table.2.) The plots of log k_{obs} Vs log [cyclanol] were linear with unit slope showing first order dependence on the cyclanol.

Effect of varying concentration of hydrogen ions:
Effect of [H^+] was investigated by varying [$HClO_4$] and keeping other parameters constant. Increase in [H^+] increases the rate constants of the reaction (Table.3). The plot of log k_{obs} Vs log [H^+] is linear with unit slope, indicating direct first order dependence on [$HClO_4$].

Table.3. Effect of varying [H^+] on the reaction rate

[CBI]   = 1 x 10^-3 mol.dm^-3   *Solvent = 80% AcOH*
[Cyclanol] = 2 x 10^-2 mol.dm^-3   *Temp.   = 303 K*

[H^+] x 10^3 mol.dm^{-3}	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
1.0	1.07	1.73	1.77	2.23	2.51
2.5	2.95	4.02	4.87	5.58	6.47
4.0	4.78	7.94	8.32	9.12	11.22
6.0	7.58	12.58	13.18	13.80	17.37
7.5	9.77	16.21	16.98	17.37	22.38

Effect of varying dielectric constant:
The effect of varying dielectric constant of the reaction was studied by varying the concentrations of acetic acid from 70% to 90%. It was found that the rates of the reactions increase with increase in dielectric constant (acetic acid content) of the solvent mixture and the plot log k_{obs} Vs log [1/D] was linear with positive slope suggesting the involvement of ion- dipole interaction in rate determining step of the reaction (Table.4)

Table.4. Effect of varying dielectric constant on the reaction rate

[CBI]   = 1 x 10^-3 mol.dm^-3   *[HClO_4]   = 2.5 x 10^-2 mol.dm^-3*
[Cyclanol] = 2 x 10^-2 mol.dm^-3   *Temp.   = 303 K*

AcOH : H_2O	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
90:10	7.42	8.14	8.73	13.21	11.00
80:20	2.95	4.02	4.87	5.58	6.47
2.94	2.04	2.94	3.80	3.81	5.14
60:40	1.56	2.04	3.16	2.82	4.36

Table. 5. Effect of varying temperature on the reaction rate

[CBI]   = 1 x 10^-3 mol.dm^-3   *[HClO_4]   = 2.5 x 10^-2 mol.dm^-3*
[Cyclanol] = 2 x 10^-2 mol.dm^-3   *Solvent   = 80% AcOH*

Temp. (K)	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
293	1.63	2.56	3.12	3.56	4.02
303	2.95	4.02	4.87	5.58	6.47
313	4.51	6.09	7.82	8.99	10.03
323	6.60	9.37	12.03	14.12	15.45

The ionic strength of the reaction varied by the addition of $NaClO_4$ and its influence on reaction rate was studied. It was found that the variation in ionic strength of the reaction has negligible effect on rate. The addition of benzimidazole and nickel (II) chloride have no appreciable effect on reaction rates. Similarly, polymerization is not observed when acrylonitrile is added to reaction mixture. This observation rules out the formation of any free radical in the reaction.

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Effect of varying temperature:
The oxidation of cyclanols has been studied at different temperatures (293K – 323K). The results are shown in Table 5. The rates of the reactions increase with increase in temperature. The Eyring plots of ln k/T Vs 1/T were all linear. From the plots, the thermodynamic parameters were evaluated and displayed in Table.6.

Table. 6. Thermodynamic parameters

Parameter	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
$\triangle H^{\#}$ (+ve)	33.38	30.91	32.54	33.24	32.24
$\triangle S^{\#}$ (-ve)	202.00	208.10	200.86	197.51	199.70
$\triangle G^{\#}$ (+ve)	94.87	93.96	93.40	93.10	92.75
E_a	35.90	33.43	35.06	35.76	34.76
lnA	6.12	5.44	6.29	6.70	6.45

Mechanism and Rate law:
Under experimental conditions studied, the following five oxidizing species, viz. Cl_2, HOCl, H_2OCl^+, $CBIH^+$ and CBI in aqueous are possible. Molecular chlorine may not be the oxidizing species, since the rate is not influenced by added nickel (II) chloride which is a well known chlorine scavenger. The dependence of reaction rate on H^+ rules out the possibility of CBI as such and HOCl being the oxidizing species suggesting that $CBIH^+$ the most probable oxidizing species. This is also confirmed by the effect of solvent polarity on reaction rate suggesting the reaction between positive ion ($CBIH^+$) and cyclanol molecule.

All the cyclic alcohols follow the same mechanism for oxidation. The mechanism of oxidation of cyclohexanol by CBI is given below.
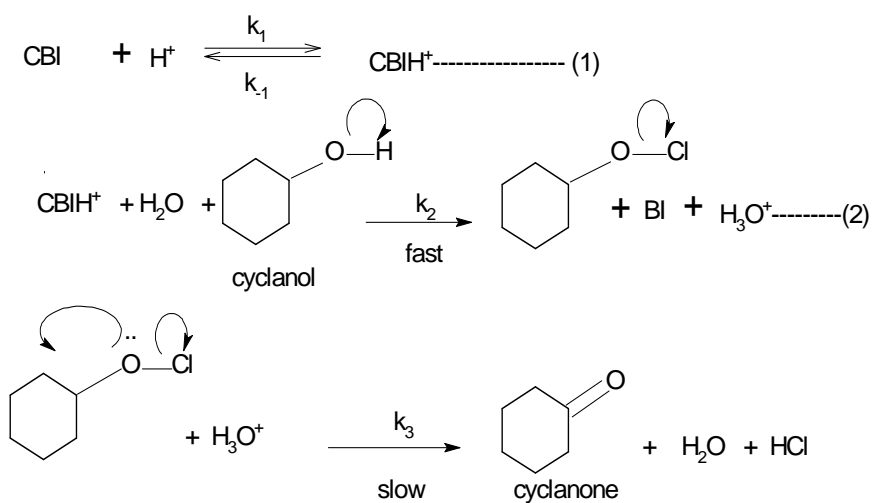
Applying steady state approximation,

Rate = k_2 [CBIH$^+$] [cyclanol] --------(1)

but

k_1[CBI] [H$^+$] = k_{-1}[CBIH$^+$]

or

k_1/k_{-1} = [CBIH$^+$]/[CBI] [H$^+$]--------(2)

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$K = [CBIH^+]/[CBI] [H^+]$ --------(3)

Where $K= k_1/k_{-1}$

Hence $[CBIH^+] = K [CBI] [H^+]$--------(4)

Substituting equation (4) in (1),

Rate = $k_2 K$[cyclanol] [CBI] [H$^+$] --------- (5)

The rate law is given by

$$\boxed{\text{Rate} \;=\; k_{obs} [CBI] [cyclanol] [H^+]}$$

Where $k_{obs} = k_2 K$

CONCLUSION

The kinetics of oxidation of cyclanols (cyclic alcohols) by 1- chlorobenzimidazole (CBI) in aqueous acetic acid medium clearly shows that the order of the reaction with respect to [CBI], [cyclanols], and [H$^+$] are unity. The product analysis also shows the formation of cyclanones (cyclic ketones) as the major product. The mechanism proposed for oxidation kinetics is in accordance with the observed kinetic facts. It is also known that all cyclanols follow the same mechanism.

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