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Reactivity of cyclanols with 1-bromobenzimidazole in acid medium: A kinetic perspective

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ABSTRACT

The kinetics of oxidation a few cyclanols (cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol and cycloheptanol) by 1-bromobenzimidazole (BBI) has been studied in 80% acetic acid - water (v/v) medium in presence of mercuric acetate. The reaction exhibits first order rate dependence each with respect to [BBI], [cyclanols] and [H^+]. The rates of the reactions increase with increase in acetic acid content of the solvent medium. The variation of ionic strength has no significant effect on the reaction rate. The reaction does not induce any polymerization with acrylonitrile. The addition of benzimidazole has no appreciable effect on the reaction rate. The reactions were studied at different temperatures and the thermodynamic parameters were calculated. A plausible mechanism and an appropriate rate law have been deduced for the observed kinetic data.

Key words: Kinetics, BBI, Oxidation, cyclanols.

INTRODUCTION

In the recent years, the studies of kinetics of oxidation of organic compounds have attracted considerable attention of the researchers[1-8]. Kinetics of oxidation of cyclanols (cyclic alcohols) with a variety of metal oxidants such as Ce(IV)[9], $KBrO_3$[10], $NaIO_4$[11], potassiumhexa cyanoferrate[12], thallium(III)acetate [13&14], bariummanganate[15], quinolinium dichromate[16-18] and quinoliniumbromochromate[19] have been studied earlier.

Oxidation of cyclanols by various N-halo oxidants such as N-bromosuccinimide[20], N-bromoacetamide[21], N-chloronicotinamide[22], N-bromobenamide[23], Chloramine–T[24], Bromamine–T[25], 1-chlorobenzotriazole[26], N-bromosaccharin[27], N-bromophthalimide[28] and 1-chlorobenzimidazole[29] have been reported. An extensive literature reveals that no systematic kinetic work hitherto has been done on the oxidation of cyclanols using 1–bromobenzimidazole (BBI) though BBI has been used as an oxidant for benzaldehydes[30], furfural[31], cyclohexanone[32], aromatic and aliphatic primary alcohols[33]. In the present investigation, the reaction kinetics of a few cyclanols with BBI has been studied in aqueous acetic acid medium in presence of mercuric acetate.

MATERIALS AND METHODS

All the cyclanols used were of AnalaR Grade. The oxidant BBI was prepared by literature method [34]. Acetic acid was refluxed over chromic oxide for 6 hours and the fraction distilling at 118^{o}C was collected and used. The standard solutions of cyclanols were prepared in glacial acetic acid. Double distilled water was employed for all kinetic runs.

KINETIC MEASUREMENTS

All kinetic measurements were made under pseudo first order conditions by keeping large excess of [cyclanol] over oxidant [BBI]. Mixtures containing requisite amounts of solutions of cyclanol, perchloric acid and mercuric acetate were equilibrated at 303K. A measured amount of pre-equilibrated (303K) standard solution of BBI was added to this mixture and the kinetics of the reaction was followed iodometrically by withdrawing aliquots of the reaction mixture at regular time intervals. To maintain the desired temperature (within $\pm$ 0.1^{o}C) the reaction mixture was kept in a thermostated water bath. Duplicate kinetic runs showed that the rate constants were reproducible within $\pm$ 3%.

The plot of log [BBI] Vs time was found to be linear (r>0.99) indicating the first order dependence of the reaction rate and from the slopes of such plots pseudo first order rate constants were calculated. 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 [BBI] Vs [cyclanol] at 303K for 48 hours under kinetic conditions. Estimation of unconsumed BBI revealed that 1 mole of BBI was required to oxidize 1 mole of the cyclanol.

Cyclanol + BBI $\longrightarrow$ BI + Cyclanone + HBr

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[35], 2-4dinitrophenylhydrazine(DNP) derivatives[36] and their melting points.

RESULTS AND DISCUSSION

The oxidations of cyclanols were carried out in 80% acetic acid –20% water medium (v/v) in presence of a large excess of substrate and perchloric acid of suitable concentration as the catalyzing acid source and mercuric acetate. The function of added mercuric acetate is only to fix up Br^- formed in the course of reaction as $HgBr_4^{2-}$.

The oxidation kinetics of cyclanols by BBI has the following salient features.

1. Effect of varying concentration of oxidant:

The kinetics of cyclanols by BBI was investigated at several initial concentrations of the oxidant. Under pseudo first order conditions of [cyclanol] >>> [BBI], the oxidation proceeds smoothly at 303K in aqueous acetic acid medium. The order of the reaction with respect to [BBI] was found to be unity as shown by the linearity of log [BBI] Vs time plots, over 70% completion of the reaction (Table. 1).

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

[Cyclanol] = 3.0 x 10^{-2} mol.dm^{-3} Solvent = 80% AcOH
[$HClO_4$] = 2.5 x 10^{-2} mol.dm^{-3} Temp. = 303 K
[$Hg(OAc)_2$] = 5.0 x 10^{-3} mol.dm^{-3}

[CBI] x 10^3 mol.dm^{-3}	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
1.5	3.99	4.81	5.81	6.23	7.46
3.0	3.95	4.80	5.72	6.50	7.38
4.5	3.97	4.80	5.91	6.49	7.18
6.0	3.90	4.67	5.68	6.31	7.20
7.5	3.92	4.83	5.78	6.48	7.48

2. Effect of varying concentration of substrate:

The oxidation reaction was carried out with various concentrations of cyclanols, keeping the concentrations of other reactants constant at 303K. The rates of the reactions increase with increase in the concentration of cyclanols (Table.2). The slope of plots of log k_{obs} Vs log [cyclanol] were found to be unity showing first order dependence on the [cyclanol].

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

[BBI] = 3.0 x 10^{-3} mol.dm^{-3} Solvent = 80% AcOH
[$HClO_4$] = 2.5 x 10^{-2} mol.dm^{-3} Temp. = 303 K
[$Hg(OAc)_2$] = 5.0 x 10^{-3} mol.dm^{-3}

[Cyclanol] x 10^2 mol.dm^{-3}	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
1.5	2.32	2.50	2.80	3.00	3.45
3.0	3.95	4.80	5.72	6.50	7.38
4.5	5.37	7.03	8.01	9.41	10.41
6.0	7.17	9.91	10.90	13.23	13.90
7.5	8.77	12.52	14.30	14.50	17.52

3. Effect of varying concentration of hydrogen ions:

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

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

[BBI] = 3.0 x 10^{-3} mol.dm^{-3} Solvent = 80% AcOH
[Cyclanol] = 3.0 x 10^{-2} mol.dm^{-3} Temp. = 303 K
[$Hg(OAc)_2$] = 5.0 x 10^{-3} mol.dm^{-3}

[H^+] x 10^2 mol.dm^{-3}	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
1.0	2.07	2.10	2.28	2.80	3.10
2.5	3.95	4.80	5.72	6.50	7.38
4.0	5.78	7.90	8.67	12.80	12.12
6.0	8.58	11.80	13.80	16.81	17.63
7.5	10.77	15.80	16.81	20.13	23.50

4. Effect of varying dielectric constant:

The effect of varying dielectric constant of the reaction was studied by varying the concentrations of acetic acid from 60% to 90%. It was found that the rates of the reactions increase with decrease in dielectric constant (increase in acetic acid content) of the solvent mixture and the plot of 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

[BBI] = 3.0 x 10^{-3} mol.dm^{-3} [$HClO_4$] = 2.5 x 10^{-2} mol.dm^{-3}
[Cyclanol] = 3.0 x 10^{-2} mol.dm^{-3} Temp. = 303 K
[$Hg(OAc)_2$] = 5.0 x 10^{-3} mol.dm^{-3}

AcOH : H_2O	k_{obs} x 10^4(s^{-1})				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
90:10	8.42	9.73	11.31	13.89	15.54
80:20	3.95	4.80	5.72	6.50	7.38
70:30	3.04	3.35	4.53	4.03	5.03
60:40	2.56	2.61	3.70	3.15	4.15

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 has no appreciable effect on reaction rates. Similarly, polymerization was not observed when acrylonitrile was added to reaction mixture. This observation rules out the formation of any free radical in the reaction.

5. Effect of varying temperature:

The oxidation of cyclanols has been studied at different temperatures (298K – 313K). 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 presented in Table.6.

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

[BBI] = 3.0×10^{-3} mol.dm^{-3} [$HClO_4$] = 2.5×10^{-2} mol.dm^{-3}
[Cyclanol] = 3.0×10^{-2} mol.dm^{-3} Solvent = 80% AcOH [$Hg(OAc)_2$] = 5.0×10^{-3} mol.dm^{-3}

Temp. (K)	$k_{obs} \times 10^4 (s^{-1})$				
	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
298	2.63	3.70	4.65	5.21	5.70
303	3.95	4.80	5.72	6.50	7.38
308	5.51	6.21	7.34	8.52	9.22
313	7.60	7.80	8.93	10.12	11.50

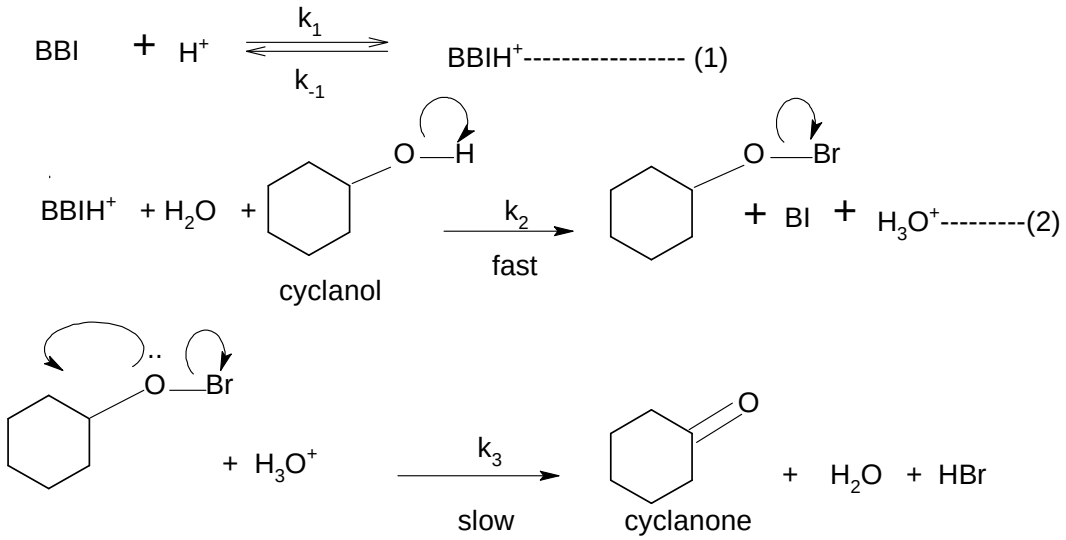
Table. 6. Thermodynamic parameters

Parameter	Cyclopropanol	Cyclobutanol	Cyclopentanol	Cyclohexanol	Cycloheptanol
$\Delta H^{\#}$ (+ve)	34.38	35.98	31.68	32.52	33.58
$\Delta S^{\#}$ (-ve)	205.00	205.10	202.39	198.59	200.82
$\Delta G^{\#}$ (+ve)	93.87	98.12	93.01	92.69	94.43
E_a	34.90	38.54	34.24	35.08	36.14
lnA	6.32	7.65	6.13	6.37	7.13

Mechanism and Rate law:

In acidified aqueous acetic acid solution of BBI, the possible oxidizing species are BBI itself, Br_2, HOBr, H_2OBr^+ and $BBIH^+$. The strict first order dependence of the reaction rate on [BBI] rules out the possibility of molecular bromine as oxidizing species. The dependence of reaction rates on [H^+] precludes the involvement of BBI as such and HOBr being the oxidizing species and suggesting $BBIH^+$ the most probable oxidizing species. This is also evidenced by the absence of any effect of added benzimidazole on the reaction rate.

The kinetic results obtained for all the cyclanols were the same. The mechanism of oxidation of cyclohexanol (cyclanol) by BBI is given below.



Applying steady state approximation,

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

but

$k_1[BBI] [H^+] = k_{-1}[BBIH^+]$

or

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

$K = [BBIH^+]/[BBI] [H^+]$ (3)

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

Hence

$[BBIH^+] = K [BBI] [H^+]$ (4)

Substituting equation (4) in (1),

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

The rate law is given by

$Rate = k_{obs} [BBI] [cyclanol] [H^+]$

Where $k_{obs} = k_2K$

CONCLUSION

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

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