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Kinetic study of oxidation of cyclic alcohols by N-bromophthalimide

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ABSTRACT

Kinetic investigations of oxidation of some cyclic alcohols (cyclopentanol, cyclohexanol and cycloheptanol) by N-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been studied. The reaction exhibits a first order rate dependence with respect to oxidant, while it is fractional order in cyclic alcohols. The variation of ionic strength, $Hg(OAC)_2$, H^+ and phthalimide (reaction product) have insignificant effect on reaction rate. Activation parameters have been evaluated from Arrhenius plot by studying the reaction at different temperature.

KEYWORDS

Kinetics;
Oxidation;
Cyclic alcohols;
N-bromophthalimide.

INTRODUCTION

Kinetics of oxidation of cyclic alcohols with variety of oxidants such as Cerium (IV), $KBrO_3$, $NaIO_4$, Quinolinium dichromate, ferrate[1-5] etc are reported earlier. A number of reports on kinetic studies of oxidation of cyclic alcohols by N-halo compounds such as NBS, NBA, NCN, NBB, chloramine-T, Bromamine-T, CBT, NBSA[6-13], as an oxidants have been reported. N-bromopthalimide (NBP) is a potential oxidizing agent [14] and has some definite advantages over other N-halogeno oxidants[15], which has been extensively used in the estimation of organic substrates[16]. In the present investigation oxidation of some cyclic alcohols (cyclopentanol, cyclohexanol and cycloheptanol) by N-Bromophthalimide in 30 % acetic acid has been reported.

EXPERIMENTAL

Materials

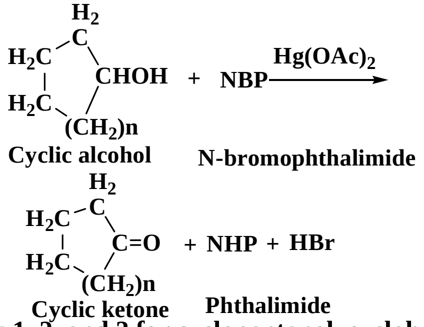
All the cyclic alcohols used were of AR grade. The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R.grade) was purified by the literature procedure. The standard solutions of cyclic alcohols were prepared in acetic acid. Double distilled water was employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of NBP was stored in an amber colored bottle and its strength was checked iodometrically[17] using 1 % solution of freshly prepared starch as an indicator.

Kinetics

Kinetic measurements were made under pseudo first order conditions, by keeping large excess of cyclic alcohol over oxidant. Mixture containing requisite amounts of solutions of cyclic alcohol and $Hg(OAC)_2$ in 30 % acetic acid were equilibrated at 303 K. To this mixture was added a measured amount of prequilibrated (303 K) standard solution of NBP. To maintain the desired temperature (within $\pm 0.1^0$C) the reaction mixture was kept in a thermostated water bath and the progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time of intervals. The pseudo first order rate constants k' were computed from linear least squares plot of -log [a-x] Vs time.

Stoichiometry and product analysis

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over cyclic alcohol and mercuric acetate in 30 % acetic acid for 24 hrs. at 30^{0}C. The unreacted oxidant (NBP) was determined by iodometrically. The estimated amount of unreacted NBP showed that one mole of cyclic alcohol consumes one mole of NBP.



(n = 1, 2, and 3 for cyclopentanol, cyclohexanol and cycloheptanol respectively)

TABLE 1 : Effect of variation of reactants on pseudo order rate constant k′ at 303K($Hg(OAc)_2$=2.00×10^3 (mol dm^{-3}) 30% AcOH medium)

10^2× [cycloalkanol] (mol dm^{-3})	10^3× [NBP] (mol dm^{-3})	k' × 10^4 (s^{-1})		
		Cyclopentanol	Cyclohexanol	Cycloheptanol
1.00	1.00	1.86	2.10	2.29
2.00	1.00	2.92	3.32	3.51
3.00	1.00	3.79	4.24	4.36
4.00	1.00	4.41	4.92	5.21
5.00	1.00	5.34	5.50	6.21
6.00	1.00	5.97	6.29	6.60
1.00	1.00	1.86	2.10	2.29
1.00	2.00	3.88	4.68	5.08
1.00	3.00	6.23	7.60	8.10
1.00	4.00	8.64	10.13	10.46
1.00	5.00	10.52	12.08	13.06
1.00	6.00	12.16	13.72	15.12

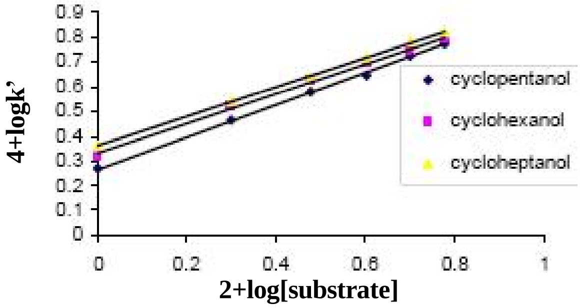


Figure 1 : Plot for order on substrate

Cyclic alcohol (0.2 Mole) and NBP (0.4 Mole) were mixed together with mercuric acetate (0.5 Mole) in 30 % aqueous acetic acid (total volume 100 ml). The reaction mixture was set-aside for about 24 hrs. to ensure completion of the reaction. It was then evaporated and extracted with ether. The layer was separated and dried. The product obtained was corresponding ketone, which is characterized by TLC, 2, 4- DNP derivatives[18] and its M.P.

RESULT AND DISCUSSION

Order of reaction

The kinetics of oxidation of cyclic alcohols by NBP in 30 % acetic acid was carried at 303 K under pseudo first order conditions. The concentration of $Hg(OAc)_2$ was kept higher than NBP. The Plot of log [NBP] Vs time found to be linear (plot not shown) indicating first order dependence of the reaction rate and from the slopes of such plots pseudo first order rate evaluated. The rate constant (k′) have been found to increase with increase in the concentration of cyclic alcohol and plot of log k′ Vs log [cyclic alcohol] was linear (figure 1) with slope less than unity for all the cyclic alcohols indicating a fractional order dependence on rate (TABLE 1). The dependence of the reaction rate on hydrogen ion concentration has been investigated at different ini-

TABLE 2 : Effect of variation of dielectric constant on reaction rate

AcOH (%)	Dielectric constant (D)	10^3/D	10^2 (D-1)/(2D+1)	k' × 10^4 (s^{-1})		
				Cyclopentanol	Cyclohexanol	Cycloheptanol
20	58.2	17.18	48.7	1.94	2.17	2.35
30	52.2	19.16	48.6	1.86	2.10	2.29
40	45.5	21.98	48.4	1.79	2.02	2.21
50	39.0	25.64	48.1	1.71	1.95	2.13
60	32.4	30.86	47.7	1.60	1.85	2.03
70	26.1	38.31	47.2	1.48	1.72	1.90

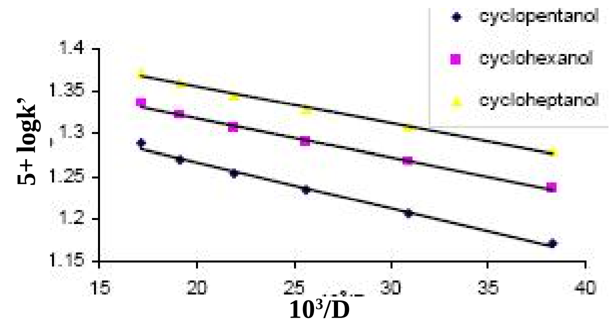


Figure 2 : Amis plot

tial concentrations of H_2SO_4 and keeping the concentration of the other reactants constant. There was no significant change in rate constant was observed with variation of H^+ ion.

The ionic strength of the reaction was varied by the addition of $NaClO_4$ and the influence of ionic strength on the reaction rate was studied. It was found that the ionic strength of the reaction medium has negligible effect. The concentration effect of mercury (II) acetate in our present study showed negligible effect on the reaction rate but found its utility to fix bromide ion during the course of reaction and avoiding the oxidation of the latter to molecule bromine[3,7]. Variation of Phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The reaction neither induces polymerization nor retards the reaction rate by variation of acrylonitrile, which may be attributed to the inertness shown by free radicals.

Effect of solvent composition

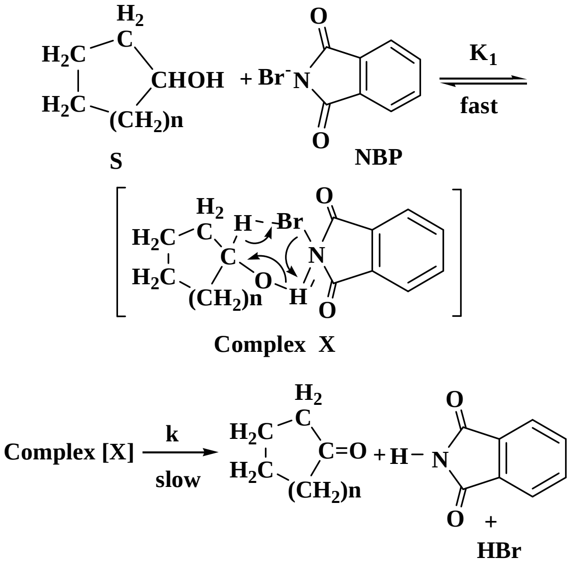
The effect of changing solvent composition on the reaction rate was studied by varying concentration of acetic acid from 20-70 %. The rate constants TABLE 2 suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. The plot of log k′ Vs 1/D was found to be linear with negative slope (Figure 2) indicating the involvement of two dipoles or a negative ion-dipole reaction. This reveals that there is formation of a charge separated complex in the rate-limiting step which is in agreement with Amis[19]. A plot of log k′ versus (D-1/2D+1) has been found to be linear (figure not shown) in accordance with Kirkwoods[20] theory of dipole-dipole type reaction.

Reactive species and mechanism

Earlier reports reveal that NBS, NBP and NBSA are stable oxidizing and brominating agents and behave in a similar way. NBP like other similar N-halo imides may exist in various forms in acid medium viz. free NBP, protonated NBP, Br^+, HOBr, H_2O^+Br. In absence of mineral acid, the possibility of Br^+, $NBPH^+$, or H_2OBr^+ being the reactive oxidizing species is ruled out. If HOBr is the reactive oxidizing species, then the rate of reaction should be an inverse function of phthalimide (NHP), which is not observed in the present study. Also the possibility of brominating action of bromide is ruled out due to the presence of mercury (II) acetate that eliminates Br^- through complexation. The rate constants suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. This observation coupled with slight enhancement in the reaction rate with ionic strength of the medium also supports the participation of neutral molecule in the rate-determining step. Therefore (free) NBP is the probable oxidizing species under the present experimental condition[16d].

Mechanism and rate law

Based upon the experimental observations, the most probable mechanism and rate expression can be derived applying steady state approximation.



$$\frac{-d[NBP]}{dt} = rate = \frac{kK_1[S][NBP]}{1+K_1[S]} \qquad (1)$$

$$K' = \frac{kK_1[S]}{1+K_1[S]} \qquad (2)$$

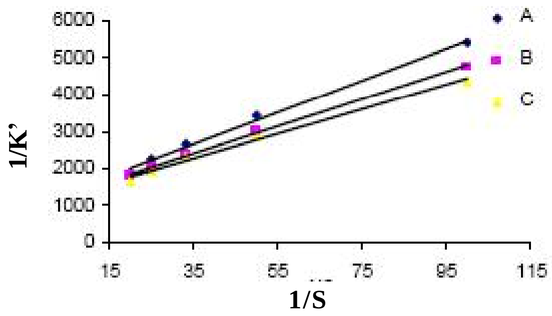


Figure 3 : Double reciprocal plot of cycloalkanols at 303K. A-cyclopentanol, B-cyclohexanol, C-cycloheptanol

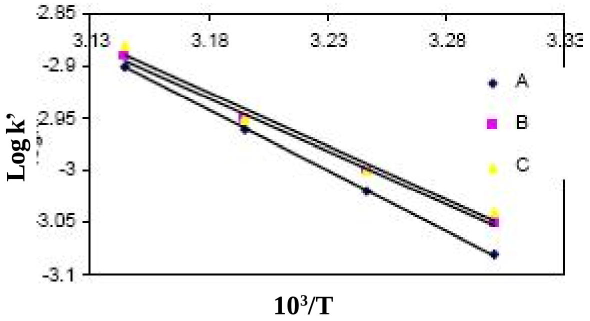


Figure 4: Arrhenius plot of cycloalkanols at 303K. A-cyclopentanol, B-cyclohexanol, C-cycloheptanol

TABLE 3 : Decomposition rate constant (*k*) and formation constant (K_1) at 303K

Cyclic alcohol	$k \times 10^4$ (s)$^{-1}$				K_1
	303 K	308 K	313 K	318 K	(dm^3 mol^{-1})
Cyclopentanol	8.56	9.59	10.87	12.52	27.40
Cyclohexanol	8.95	9.86	11.20	12.88	30.46
Cycloheptanol	9.12	10.06	11.34	13.05	33.04

TABLE 4 : Activation parameters of cyclic alcohols at 303K

Cyclic alcohol	Ea KJmol^{-1}	$\Delta H^\#$ KJmol^{-1}	$\Delta G^\#$ KJmol^{-1}	$\Delta S^\#$ JK^{-1}mol^{-1}	LogA
Cyclopentanol	20.30	17.78	75.22	-248.19	4.13
Cyclohexanol	19.53	17.01	75.21	-248.17	4.06
Cycloheptanol	19.12	16.60	75.20	-248.16	4.03

Reciprocal of eq^n (2) gives,

$$\frac{1}{k'} = \frac{1}{kK_1[S]} + \frac{1}{k} \qquad (3)$$

The kinetics results suggest the possibility of formation of binary complex involving of oxidant and substrate is strongly favored. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot of 1/k′Vs 1/[S] (figure 3). From the intercept and slopes of the plots of 1/k′ versus 1/[S] decomposition rate constant *k* and the formation constant K_1 were evaluated (TABLE 3). Evidence is also provided by the fractional order found in substrate. The results are interpreted in terms of a cyclic mechanism involving a rate determing abstraction of the α-H as a hydride anion[6,11]. The order of reactivity for these cyclic alcohols studied is Cycloheptanol > Cyclohexanol > Cyclopentanol. The rate is increasing with increasing ring size. Similar order of reactivity is observed in oxidation of cycloalkanols by NBS[6], $KBrO_3$[2], Quinolinium dichromate[4], NBSA[13].

Effect of temperature

The rate of oxidation was determined at different temperatures and the Arrhenius plots of log k versus 1/T were all linear (Figure 4). From these plots, the activation parameters were evaluated (TABLE 4). The thermodynamic parameter for equilibrium step and rate determining step of the scheme was evaluated. The observed negative values of $\Delta S^\#$ could be attributed to the greater rigidity and cyclic structure of the transition state. It may be interpreted that the fraction of collisions become more stringent and decomposition of activation complex is a quite slow process. $\Delta H^\#$ indicates that the reactions are enthalpy controlled. Further the constancy in the calculated values of $\Delta G^\#$ for this oxidation reaction indicates that the same type of the reaction mechanism could be operative for the reaction.

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