Kinetics and Mechanism of Oxidation of Cyclopentanone and Cyclohexanone by Bromamine-B in Perchloric Acid Medium

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Kinetics of oxidation of cyclopentanone (Cyp) and cyclohexanone (Cyh) by bromamine-B (BAB) in perchloric acid medium have been reported. The rate shows zero order dependence in BAB and first order dependence on both cyclic ketones and hydrogen ion concentration have been observed. Variation of ionic strength of the medium, addition of bromide ion and benzenesulphonamide which is one of the reaction products have no effect on the rate. The rate of the reaction increases with decrease in the dielectric constant of the medium. The proposed mechanism involves acid catalysed enolisation of cyclic ketones in the slow and rate determining step, followed by its fast interaction with BAB giving corresponding 1,2-diketones as final products. Thermodynamic parameters have been computed by studying the reaction at different temperatures (303–318 K).

INTRODUCTION

The kinetics and mechanism of oxidation by aromatic sulphonyl haloamines have attracted the attention of chemists due to their diverse properties to act as halonium cations, hypohalites and N-anions. They can behave as both bases and nucleophiles depending on the reaction conditions. They interact with a wide range of functional groups, effecting a variety of molecular transformations. The monohaloamines are two electron oxidants and the prominent member of this class is chloramine-T (CAT). Kinetics of reactions of chloramine-T and chloramine-B are reviewed[1,2] but information about the bromine analogues is scanty. Sodium salt of N-bromobenzenesulphonamide or bromamine-B (BAB) has received considerable attention as an oxidimetric reagent.[3–7] Kinetic investigations involving aliphatic, cyclic and aromatic ketones with various oxidising agents have been reported earlier by many workers.[8–12] Studies on oxidation of aliphatic ketones by BAB[13] and cyclic ketones by bromamine-T (BAT)[14] in perchloric acid medium have been reported. Recently, Ru(III) catalysed oxidation of *m*-hydroxy benzoic acid with BAB has been reported[15]. A survey of literature reveals that almost no information is available on the oxidation of cyclopentanone and cyclohexanone by BAB. The present work constitutes an investigation on the kinetics and mechanism of the oxidation of cyclopentanone (Cyp) and cyclohexanone (Cyh) by the less widely used but potent oxidising agent BAB in perchloric acid medium.
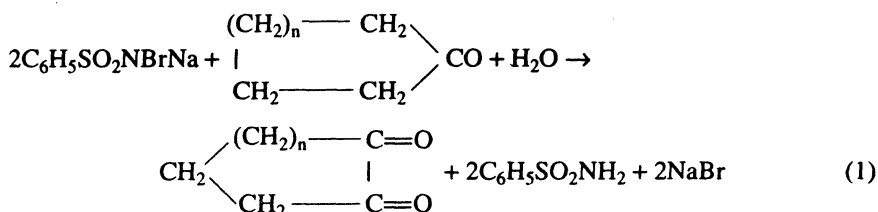
EXPERIMENTAL

BAB was prepared as reported in literature.[16] Its purity was checked iodometrically through its active bromine content and further characterized by ^1H and ^{13}C NMR spectroscopy. An aqueous solution of BAB (0.1 mol dm^{-3}) was standardized iodometrically and preserved in brown bottle to prevent its photochemical deterioration. Cyp (E. Merck) was used as such, while Cyh (BDH) was used after distillation. A 0.5 mole dm^{-3} aqueous solution of cyclic ketone was used. The ionic strength of the reaction mixture was maintained at a constant value using a 2.0 mol dm^{-3} solution of $NaClO_4$. All other chemicals were of analytical grade. Triply distilled water was used throughout the course of investigation.

Kinetic measurements

Kinetic runs were all performed under pseudo-first order conditions of a large excess of substrate over the oxidant at 308 K. The reaction was carried out in a glass-stoppered pyrex boiling tube whose outer surface was blackened to eliminate photochemical effects. Requistite amount of substrate, acid, sodium perchlorate (to keep the ionic strength constant) and water (to keep the total volume constant throughout) were taken in the tube and thermostated at 308 K. A measured quantity of BAB solution pre-thermostated at the same temperature was rapidly added to the mixture. The progress of reaction was monitored up to three half-lives by iodometric determination of unreacted BAB in a measured aliquot of the reaction mixture withdrawn at regular time intervals. The kinetic runs showed reproducible results within ±3%.

Stoichiometry and product analysis

The stoichiometry of the reaction was ascertained by carrying out several sets of measurements with varying proportions of BAB and cyclic ketones (BAB $\gg$ cyclic ketones). The estimation of unreacted BAB showed that one mole of each ketone consumed two moles of BAB. Accordingly, the following stoichiometric equation can be formulated.

$$2C_6H_5SO_2NBrNa + \begin{array}{c} (CH_2)_n \!-\! CH_2 \\ | \qquad\qquad\quad \\ CH_2 \!-\!-\! CH_2 \end{array}\!\!\Big\rangle CO + H_2O \rightarrow$$

$$CH_2\!\!\Big\langle \begin{array}{c} (CH_2)_n \!-\! C\!=\!O \\ | \qquad\qquad \\ CH_2 \!-\!-\! C\!=\!O \end{array} + 2C_6H_5SO_2NH_2 + 2NaBr \qquad (1)$$

where $n = 1$ in Cyp and $n = 2$ in Cyh.

Benzenesulphonamide among the reaction products was detected by TLC. A mixture of petroleum ether, chloroform and n-butanol (2 : 2 : 1, v/v) was used as the solvent and iodine as the developing reagent ($R_f = 0.88$). The corresponding 1,2-diketones were identified by adopting TLC followed by conventional spot test analysis,[17] and also by preparing dinitrophenyl hydrazine (DNP) derivative[18]. The 1,2-diketones were further confirmed by their PMR spectra. A triplet

due to the proton in position-3 is found at δ 5.2 and a singlet at δ 7.2 due to the enolic OH which is in equilibrium with the ketonic form of the 1,2-diketone was observed.

Regression analysis of experimental data (to obtain regression coefficient 'r' and standard deviation 's' of points from the regression line) was carried out on an fx-115D statistical calculator.

RESULTS AND DISCUSSION

The kinetics of oxidation of Cyp and Cyh by BAB were investigated at several initial concentrations of the reactants in perchloric acid medium.

TABLE-1

EFFECT OF [BAB], [SUBSTRATE], [HClO$_4$], IONIC STRENGTH (μ) AND [Br$^-$]
VARIATION OF REACTION RATE AT 308 K (μ = 0.25 mol dm^{-3})

[BAB] 10^3 mol dm^{-3}	[Substrate] 10^2 mol dm^{-3}		[HClO$_4$] 10^2 mol dm^{-3}		$k_s \times 10^6$ mol dm^{-3} sec^{-1}	
	cyp	cyh	cyp	cyh	cyp	cyh
1.0	—	6.0	—	2.0	—	1.599
2.0	6.0	6.0	8.0	2.0	2.054	1.592
3.0	6.0	6.0	8.0	2.0	2.067	1.603
4.0	6.0	6.0	8.0	2.0	2.096	1.598
5.0	6.0	6.0	8.0	2.0	2.080	1.586
6.0	6.0	—	8.0	—	2.040	—
4.0	2.0	2.0	8.0	2.0	0.782	0.437
4.0	4.0	4.0	8.0	2.0	1.437	1.093
4.0	8.0	8.0	8.0	2.0	2.707	2.187
4.0	10.0	10.0	8.0	2.0	3.488	2.812
4.0	6.0	6.0	2.0	0.5	0.489	0.322
4.0	6.0	6.0	5.0	1.0	1.246	0.677
4.0	6.0	6.0	10.0	3.0	2.641	2.097
4.0	6.0	6.0	12.0	4.0	3.264	3.042
4.0[a]	6.0	6.0	8.0	2.0	2.098	1.602
4.0[b]	6.0	6.0	8.0	2.0	2.020	1.596
4.0[c]	6.0	6.0	8.0	2.0	2.102	1.608
4.0[d]	6.0	6.0	8/0	2.0	2.088	1.598

(a) μ = 0.5 mol dm^{-3}; (b) and (c) [Br$^-$] = 0.05 and 0.1 mol dm^{-3} (d) Excess of BSA

With the cyclic ketones in excess, plots of [BAB]$_0$–[BAB] *vs.* time were found to be linear (r > 0.9994, s ≤ 0.02) passing through the origin indicating zero order dependence on [BAB]. The standard zero order rate constant k$_s$ was obtained by the equation k$_s$ = SN/V where S is the slope of the plot, N the normality of

thiosulphate and V is the volume of the reaction mixture titrated. k_s was not affected by a change in $[BAB]_0$. The values of k_s are shown in Table-1. The rate increases with [cyclic ketone] and plot of log k_s vs. log [cyclic ketone] was linear ($r > 0.9978$, $s \leq 0.05$) with unit slope (1.02) showing first order dependence on [cyclic ketone]. The rate also increases with increase in $[HClO_4]$ and plot of log k_s vs. log $[HClO_4]$ was linear ($r > 0.9996$, $s \leq 0.02$) with a slope of unity (0.998) indicating first order dependence on $[H^+]$. It is observed that addition of benzenesulphonamide (BSA), Br^- ion and excess of ClO_4^- ion had no effect on the rate (Table-1). The solvent composition was varied by adding methanol (0–40%). The rate increases with increase in the methanol content of the reaction mixture (Table-2). A plot of log k_s vs. 1/D where D is the dielectric constant of the medium gives a straight line ($r > 0.9993$, $s \leq 0.03$) with a positive slope..

TABLE-2

EFFECT OF SOLVENT COMPOSITION AND TEMPERATURE ON REACTION RATE

$[BAB] = 0.004$ mol dm^{-3}; $\mu = 0.25$ mol dm^{-3}

$[Cyp] = 0.06$ mol dm^{-3} and $[HClO_4] = 0.08$ mol dm^{-3}

$[Cyh] = 0.06$ mol dm^{-3} and $[HClO_4] = 0.02$ mol dm^{-3}

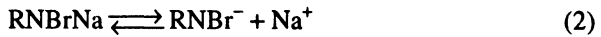| T (K)	Methanol-Water v/v (%)		$k_s \times 10^6$ mol dm^{-3} sec^{-1}	
	Cyp	Cyh	Cyp	Cyh
303	0–100	0–100	1.300	0.916
308	0–100	0–100	2.068	1.599
313	0–100	0–100	3.300	2.776
318	0–100	0–100	4.800	4.371
308	5–95	5–95	2.536	1.678
308	10–90	10–90	3.145	1.921
308	15–85	20–80	3.913	2.208
308	20–80	30–70	5.136	2.760
308	—	40–60	—	3.533

The reaction was studied at different temperatures (303–318 K). From the linear plot ($r > 0.9991$, $s \leq 0.01$) of log k' vs. 1/T, where the first order rate constant $k' = k_s/[\text{cyclic ketone}]_0$, the values of activation parameters were computed (Table-3).

TABLE-3

KINETIC AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF CYCLIC KETONES

Cyclic ketones	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	log A
Cyp	67.74	65.15 ± 0.05	-119.07 ± 0.16	102.07 ± 0.63	7.02 ± 0.01
Cyh	79.71	77.13 ± 0.045	-82.29 ± 0.2	102.64 ± 0.40	8.94 ± 0.01

Addition of acrylamide solution to the reaction mixture in an inert atmosphere did not initiate polymerization indicating the absence of free radical formation in the reaction sequence.
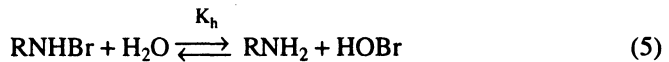
BAB is analogous to CAT and behaves as a strong electrolyte in aqueous solution. The work of Hardy and Johnston[3] and our work on conductometric studies[19] indicate the following equilibria with BAB in acid solutions.

$$RNBrNa \rightleftharpoons RNBr^- + Na^+ \tag{2}$$

$$RNBr^- + H^+ \overset{K_a}{\rightleftharpoons} RNHBr \tag{3}$$

$$K_a = 1.5 \times 10^{-5} \text{ at } 25°C$$

$$2RNHBr \overset{K_d}{\rightleftharpoons} RNH_2 + RNBr_2 \tag{4}$$

$$K_d = 5.8 \times 10^{-2} \text{ at } 25°C$$

$$RNHBr + H_2O \overset{K_h}{\rightleftharpoons} RNH_2 + HOBr \tag{5}$$

$$K_h = 4.21 \times 10^{-3} \text{ at } 25°C$$

$$HOBr \overset{K_a}{\rightleftharpoons} H^+ + OBr^- \tag{6}$$

$$K_a = 2.0 \times 10^{-9} \text{ at } 25°C,$$

where $R = C_6H_5SO_2$.

Thus the possible oxidizing species in acidified BAB solution are RNHBr, $RNBr_2$ and HOBr. However, Soper[20] reported that [HOCl] is very small in acidified CAT solution and is independent of [CAT]. On this basis, the role of HOBr in oxidation reactions involving BAB can be ignored under high acid conditions. The remaining species, *i.e.*, either RNHBr or $RNBr_2$ seems to be the real oxidizing species of BAB. It is not possible to establish the predcminance of one species over the other with the present kinetic data. Therefore, BAB as such has been used in the reaction mechanism. Strict zero order dependence on $[BAB]_0$ observed does not help in distinguishing either of the two species as real oxidizing species of BAB. The rate is also independent of the concentration of benzenesulphonamide (BSA) suggesting the formation of BSA after slow and rate determining step. Zero order dependence of the reaction on BAB suggests involvement of BAB in a fast step, preceded by slow and rate determining enolisation step[21].

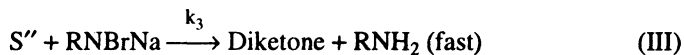Ketones are known to enolise in acidic media as follows:

$$\underset{(S)}{\overset{R}{\underset{R'}{>}}CO + H^+} \rightarrow \underset{(S')}{\overset{R}{\underset{R'}{>}}C^+—OH} \rightarrow \underset{(S'')}{\overset{R}{\underset{R''CH}{>}}C—OH + H^+} \tag{7}$$
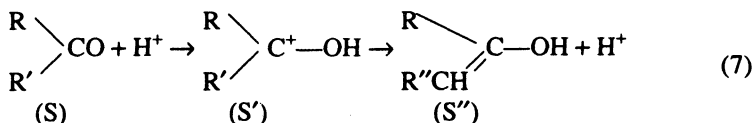
where S represents the ketone, S′ is the conjugate acid and S″ is its enolic form.

With the above facts in view, the following mechanism is suggested for the acid catalysed oxidation of both cyclic ketones (S) by BAB.

$$S + H^+ \underset{}{\overset{k_1}{\rightleftharpoons}} S' \text{ (fast)} \tag{I}$$

$$S' \xrightarrow{k_2} S'' + H^+ \tag{II}$$

(Slow and rate determining step)

$$S'' + RNBrNa \xrightarrow{k_3} \text{Diketone} + RNH_2 \text{ (fast)} \tag{III}$$

where $R = C_6H_5SO_2$.

Application of steady state treatment to [S'] gives the rate law as:

$$-\frac{d[BAB]}{dt} = \frac{2k_1k_2}{k_{-1} + k_2} [S][H^+] \tag{8}$$

The rate law (8) is in agreement with the observed stoichiometry and kinetic orders. Variation of ionic strength of the medium and addition of Br^- ion had no effect on the reaction rate. These facts support the above mechanism. The proposed mechanism is also supported by the negative dielectric effect. The negative dielectric effect indicates a charge dispersal in the transition state pointing towards positive ion-dipole interaction[22]. The constancy of $\Delta G^{\neq}$ values however indicate that a similar mechanism is operative in the oxidation of cyclic ketones by BAB. The rate of oxidation of cyclic ketones by BAB is nearly 2.5 times faster than BAT. The oxidation in alkaline medium could not be followed under present experimental conditions, since the rate was very high.

ACKNOWLEDGEMENT

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