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Synthesis Ofsome Benzothiazole Derivatives and Kinetic Studies of Their Oxidation Using Chloramine-T in Acid Medium

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Abstract: *The kinetics of oxidation of 2-phenyl-benzothiazole (BzlH), 2-(4-methoxyphenyl) benzothiazole (OMeBzlH), 2-(4-nitrophenyl)-benzothiazole (NO_2BzlH) by chloramine-T; (CAT) in presence of $HClO_4$ has been investigated at 296 K. Under similar experimental conditions, the oxidation reactions follow identical kinetics for all the three benzothiazoles with first order dependence each on $[CAT]_0$ and $[substrate]_0$ and inverse fractional order dependence on $[H^+]$. Solvent composition shows negative effect indicating the involvement of negative ion-dipolar molecule in the rate determining step. Variation of ionic strength of the medium and addition of halide ions had no effect on the reaction rate. Addition of p-toluenesulphonamide (PTS), the reduction product also has no effect on the rate of reaction. The reactions were studied at different temperatures and the composite activation parameters have been computed. Relative reactivity of oxidation of these follow the order: OMeBzlH>BzlH> NO_2BzlH. This trend may be attributed to inductive effects. The observed results have been explained by a plausible mechanism and the related rate law has been deduced.*

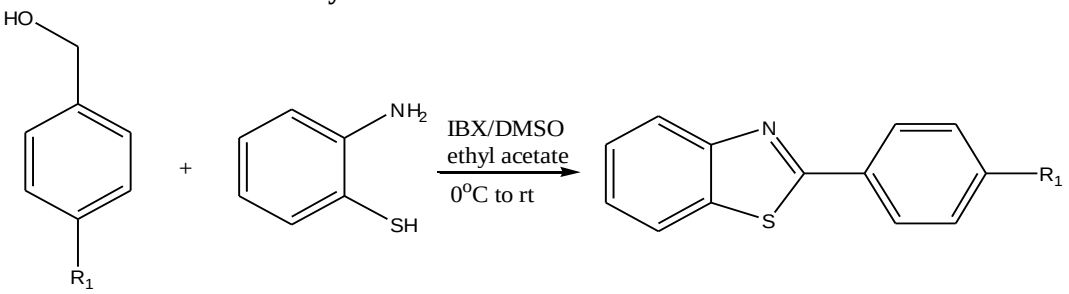
Key words: *activation parameters, dielectric constant, halide effect, Order,reaction mechanism*

I. Introduction

Benzothiazole, a well-known heterocyclic compound and also a weak base, which has a varied biological activities and is of great scientific from last few years. Benzothiazole and its derivatives are widely found in medicinal and bioorganic chemistry with various application in drug discovery. Benzothiazolemoites are part of compounds showvarious biological activities such as antimicrobial [1-5], anticancer [6-8,], anti-diabetic [9], anthelmintic [10] activities. They also find applications in industry asvulcanization accelerators, anti-oxidants. Various benzothiazoleslike 2-phenylbenzothiazolehas received much attention because of its unique structure and its uses as radioactive amyloid imagining agents [11], and anticancer agents. [12].Benzothiazoles are bicyclic ring system with numerous multiple applications for various purposes. In the 1950s, number of 2-aminobenzothiazoles were studied intensively, as the 2-amino benzothiazole scaffold is one among the privileged structure in medicinal chemistry [11,13] and reported cytotoxic on cancer cells[13]. It is noteworthy that the combination of 2- aminobenzothiazoles with other heterocyclic compounds is a well-known approach in order to design new drug like molecules, which allows achieving new pharmacological profile, action, toxicity lowering. The 2-(4-aminophenyl) benzothiazoles is one of the novel class of potent and e antitumor agents and they display characteristic profile of cytotoxic response along the cell lines. In addition, benzothiazole ring is present in various other compounds like terrestrial or marine natural compounds, which have numerous biological properties. P.R. Bhagat et al., reported kinetics of oxidation of benzothiazoles and its derivatives using ruthenium as catalysis in acid medium. Oxidation products of the reactions are orthanilic acid and its derivatives. On the basis of these observations, we will explore the oxidation and mechanistic investigation of benzothiazole derivatives. But only less information reported in the literature on the oxidation kinetics of benzothiazole derivatives using an oxidant.

Nandibewoor et al., reported the kinetics of oxidation of pyridylmethylsulphinylbenzimidazole by cerium (IV) in perchloric acid medium. Puttaswamy et al., oxidized imidazole, benzimidazole and its derivatives (2-HyBzlH, 2-AmBzlH, and 2-PhBzlH) by sodium-N-chloro-*p*-toluenesulfonamide (Chloramine-T) using ruthenium chloride as catalyst in acid medium. Oxidation product of the reactions is o-phenylenediamine and benzoic acid. Puttaswamy et al., also reported, oxidation of imidazole, benzimidazole and its derivatives(2-HyBzlH, 2-AmBzlH, and 2-PhBzlH) by sodium-N-chloro-p-toluenesulfonamide (Chloramine-T) using Os(VIII) as catalyst in alkaline medium at room temperature. Oxidation products of the reactions are orthanilic acid and its derivatives. On the basis of these observations, we will explore the oxidation and mechanistic investigation of benzothiazoleand derivatives by Sodium N-chloro-p-toluenesulfonamide (Chloramine-T). The main Objectives were 1. Synthesis of benzothiazole2. Development of efficient synthetic process for the facile conversation of benzothiazole derivatives to corresponding oxidation products. 3. Elucidation of plausible mechanism and to deduce an appropriate rate law. 4. Ascertain the various reactivity species. 5. Finally, assess the relative relativities of the substrates.

II. Synthesis Of Benzothiazole Derivatives



Where R_1= -H and R_2= -H, -OCH_3, -NO_2

To a solution alcohol (0.5-0.6mmol) and IBX (1.1 equiv) were stirred in DMSO at 20^{o}C. Once the oxidation of alcohol to aldehyde was complete, as judged from TLC analysis, O-aminothiophenol (1.1 equiv) was introduced in to the reaction mixture and the reaction mixture was allowed to stir at room temperature until the aldehyde disappeared. At the end of the reaction, DMSO was removed under high vacuum, and the residue was treated with 1.0M NaOH solution until the PH was 6-7. The organic matter was extracted with ethyl acetate. Regular work up followed by silica gel chromatography led to pure benzothiazoles, which were characterized

2.1 Experimental

2.1CAT (Sigma Aldrich) was purified by the method of Morris et al [14]. An aqueous solution of CAT was prepared, standardized iodometrically and stored in amber colored stoppered bottles until further use to prevent its photochemical deterioration. The concentrations of stock solutions were periodically determined. An aqueous solution of NO_2BzlH, BzlH and OMeBzlH, were freshly prepared whenever required. All other chemicals used were of analytical grade.Triple distilled water was used for preparing solutions.

2.2 Kinetic measurement

The kinetic runs were performed under pseudo-first-order conditions by ensuring an excess of CAT over substrate in sodium hydroxide at 296 K using UV-Vis spectrophotometry (Shimadzu-1800). A constant temperature was maintained with an accuracy of ±0.1^{o}C. Reactions were carried out in glass stoppered Pyrex boiling tubes whose outer surface were coated black to eliminate any photochemical effects. The oxidant as well as requisite amounts of substrate, $HClO_4$solutions and water (to keep the total volume constant for all runs) were taken in separate tubes. The absorbance reading were thermo stated for nearly 30 minutes at 296 K. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. 3 ml of aliquot of the solution was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at λ_{max} = 258nm, 283 nm and 276nm forBzlH, OMeBzlH, NO_2BzlH respectively for more than 75% of completion of the reaction. Plots log (abs) Vs time were made to evaluate the pseudo-first-order rate constants k' (s^{-1}). Regression analysis of the experimental data was carried out on fx-991MS scientific calculator to evaluate the regression coefficient.

2.3 Reaction stoichiometry

Reaction mixtures containing different ratios of CAT and substrate in 5×10^{-3}mol $dm^{-3}HClO_4$were allowed to react for 24hrs at 296 k. The determination of unreacted CAT in the reaction mixture showed that one mole of the substrate consumed one mole of CAT

III. Resultsand Discussion

3.1 Effect of varying reactant concentration on the rate

With the oxidant in excess and keeping $[CAT]_o$, $[HClO_4]$ and temperature constant, plot of log(abs) Vs time was found to be linear (R^2=0.99) indicating a first order dependence on $[subs]_o$. The values of Pseudo-First order rate constants ($k' s^{-1}$) are listed in Table 1. Also under the same experimental conditions an increase in $[CAT]_o$ increased the value of k' (Table1). Plot of log k' Vs log [CAT] were linear (R^2=0.99) with aslope of 0.92, 0.90 and 0.90forNO_2BzlH, BzlH, OMeBzlH, respectively which indicated a fractional order dependence on [CAT] (Figure 1).

3.2 Effect of varying $HClO_4$ concentration on the rate

The effect of $HClO_4$ on the rate of the reaction was studied by varying in the concentration of $[HClO_4]$ (table 1). Plot of log k' versus log $[HClO_4]$ were linear (R^2= 0.99) with a negative slope of 0.52, 0.52 and 0.51 for NO_2BzlH, BzlH, OMeBzlHrespectively which indicated an inverse fractional order dependence on $[H^+]$ (Figure 2).

Table 1. Effect of varying concentrations of oxidant, substrate and medium on the rate at 296 K

10^4×[CAT] mol dm-^{3}	10^5×[Subs] mol dm^{-3}	10^4 ×[H^+] mol dm^{-3}	10^4 k′ (s^{-1})		
			NO_2BzlH	BzlH	OMeBzlH
1.0	3.0	4.0	1.98	2.33	3.01
2.0	3.0	4.0	3.87	4.55	5.82
3.0	3.0	4.0	5.46	6.92	8.27
4.0	3.0	4.0	7.67	8.76	11.33
5.0	3.0	4.0	8.22	9.34	12.55
3.0	1.0	4.0	5.22	6.88	8.22
3.0	2.0	4.0	5.35	6.91	8.24
3.0	3.0	4.0	5.46	6.92	8.27
3.0	4.0	4.0	5.61	7.14	8.36
3.0	5.0	4.0	5.68	7.19	8.41
3.0	3.0	1.0	11.22	14.48	16.89
3.0	3.0	2.0	7.82	10.11	12.28
3.0	3.0	3.0	6.42	8.36	9.76
3.0	3.0	4.0	5.46	6.92	8.27
3.0	3.0	5.0	4.87	6.23	7.45

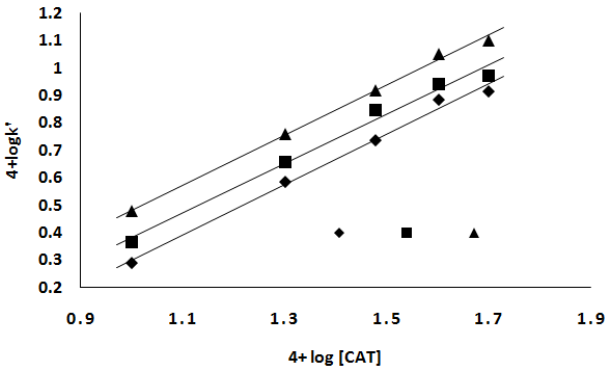


Fig.1: Plot of log k' Vs log [CAT]

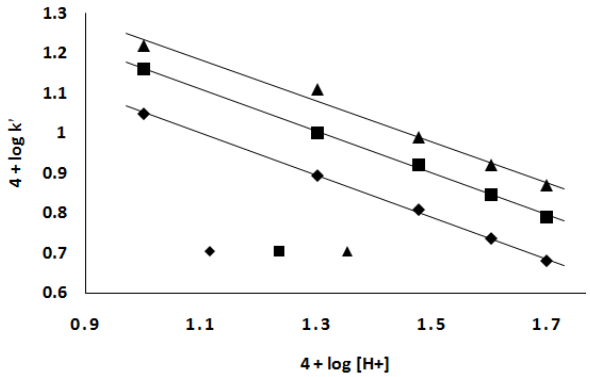


Fig.2: Plot of log k' Vs log [CAT]

3.3 Effect of halide ions, ionic strength and *p*-toluenesulphonamide on the rate

Addition of halide ions, Cl^- and Br^- ions in the form of their sodium salts (1.0×10^{-3}- 5.0×10^{-3} mol dm^{-3}) had negligible effect on the reaction rate. This suggests that no interhalogen or free halogen is formed in the reaction sequence. Ionic strength (μ) of the medium was varied byvarying the concentration of Sodium perchlorate ($NaClO_4$) (0.1-0.4mol dm^{-3}). No significant effect was noticed. It indicates the involvement of non-ionic species in the rate determining step. Hence no attempt was made to keep ionic strength of the medium constant during kinetic runs. The addition of p-toluene sulfonamide (reduction product of CAT) had negative effect on the rate of the reaction which indicates the involvement of the reduction product in a fast pre-equilibrium to the rate limiting step. Plot of log k′ versus log [PTS] were linear (R^2= 0.99) with a negative slope of 0.48, 0.36 and 0.40 for NO_2BzlH, BzlH, OMeBzlH respectively which indicated an inverse fractional order dependence on [PTS] (Figure 3).

Table 2. Effect of PTS on the rate of the reaction with [subs] =3.0x10^{-5} mol dm^{-3} [CAT] =3.0x10^{-4} mol dm^{-3} [H^{+}] =4.0x10^{-4} mol dm^{-3}

10^4× [PTS] mol dm^{-3}	10^4 k′ (mol dm^{-3} s^{-1})		
	NO_2BzlH	BzlH	OMeBzlH
1.0	5.22	6.87	8.15
1.5	4.44	6.11	7.39
2.0	3.87	5.34	6.35
3.0	3.10	4.66	5.21

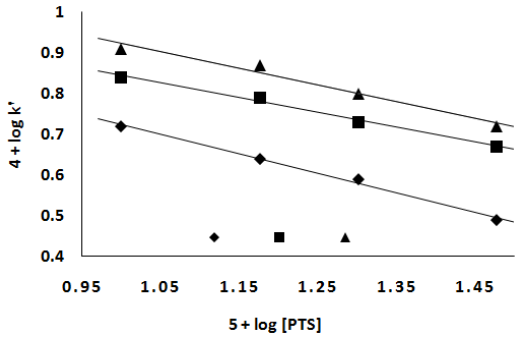


Fig. 3: Plot of log k' Vs log [PTS]

3.4 Effect dielectric constant (D) on the rate

The effect of solvent on the reaction kinetics has been discussed in detail in the well-known monographs of Moelwyn-Hughes [15] Benson [16] Frost and pearson [17] Laidler [18] Amis [19] and Entelis and Tiger [20].The solvent composition was varied by adding methanol (0%-30%). The rate of the reaction decreased with the increase in the methanol content of the reaction medium (table 3) and plot of log$k^{'}$ vs 1/D was linear (figure 4, R^2= 0.98) with negative slope. Blank experiments with methanol indicated that the oxidation of methanol was negligible. The values of D for various MeOH-H_2O mixtures reported in the literature [21] were employed

Table 3. Effect of dielectric constant on the rate of the reaction with [subs] =3.0x10^{-5} mol dm^{-3} [CAT] =3.0x10^{-4}mol dm^{-3} [H^{+}] =4.0x10^{-4} mol dm^{-3}

% MeOH (v/v)	D	10^4 k′ (mol dm^{-3} s^{-1})		
		NO_2BzlH	BzlH	OMeBzlH
0	76.73	5.46	6.92	8.27
10	74.50	4.85	6.22	7.43
20	72.37	4.11	5.11	6.71
30	67.48	3.38	5.39	6.05

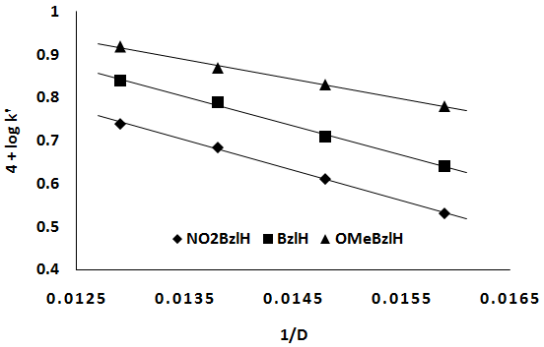


Fig. 4: Plot of log k' Vs 1/D

3.5 Effect of temperature on the rate and calculation of activation parameters

The reaction was studied ad different temperatures in the range 296-312 K keeping other experimental conditions constant. Arrhenius plot of log k′ Vs 1/T were plotted (Figure 5) and with the help of the graph, activation parameters were evaluated and average values for each parameter is reported along with errors (table 4)

Table 4. Effect of temperature on the rate of the reaction and corresponding values of activation parameters for the oxidation of NO_2BzlH, BzlH and OMeBzlH by CAT in acid medium with [sub] =$4.0x10^{-5}$ mol dm^{-3} [CAT] = $3.0x10^{-4}$ mol dm^{-3} $[H^+]$ = $4.0x10^{-4}$ mol dm^3

T(K)	$10^4k'$(mol dm^{-3} s^{-1})			Activation parameters			
	NO_2BzlH	BzlH	OMeBzlH		NO_2BzlH	BzlH	OMeBzlH
296	5.46	6.92	8.27	Ea(KJ mol^{-1})	73.13	49.87	39.59
300	8.02	8.99	9.85	$\triangle H^{\#}$(KJ mol^{-1})	59.09 ± (0.04)	41.30± (0.05)	31.97 ± (0.04)
304	10.88	11.93	12.49	$\triangle G^{\#}$(KJ mol^{-1})	93.77 ± (0.06)	93.88± (0.04)	93.61 ± (0.06)
308	15.49	15.43	13.31	$\triangle S^{\#}$($JK^{-1}mol^{-1}$)	-137.03± (0.1)	-167.22±(0.2)	-197.60± (0.2)
312	21.43	20.39	19.03	log A	5.85 ± (0.05)	4.43± (0.04)	3.20 ± (0.02)

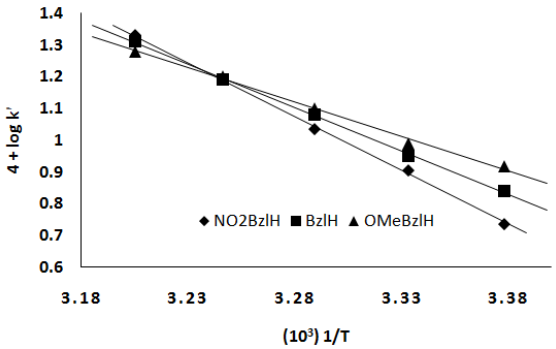


Fig. 5: Plot of log k' Vs 1/D

3.6 Test for free radicals

Addition of reaction mixture to aqueous acrylamide monomer solutions did not initiate polymerization, indicating the absence of in situ formation of free radical species in the reaction sequence

IV. Discussions

Chloramine-T behaves as a strong oxidizing species in aqueous solutions [22]. Depending on the pH of the medium; CAT furnishes [22-24] following types of reactive species in solutions:

$$TsNClNa \rightleftharpoons TsNCl^{\ominus} + Na^{\oplus} \quad (2)$$

$$TsNCl^{\ominus} + H^{\oplus} \rightleftharpoons TsNHCl \quad (3)$$

$$2TsNHCl \rightleftharpoons TsNH_2 + TsNCl_2 \quad (4)$$

$$TsNHCl + HO_2 \rightleftharpoons TsNH_2 + HOCl \quad (5)$$

$$TsNCl_2 + HO_2 \rightleftharpoons TsNHCl + HOCl \quad (6)$$

$$HOCl \rightleftharpoons H^{\oplus} + OCl^{\ominus} \quad (7)$$

$$HOCl + H^{\oplus} \rightleftharpoons HOCl_2^{\oplus} \quad (8)$$

Therefore the possible oxidizing species in acidified CAT solutions are TsNHCl, $TsNCl_2$,HOCl, and possibly H_2O^+Cl. Further, formation of species of the type $TsNH_2Cl^+$ has been reported [25, 26] with CAT and the protonation constant for the reaction,

$$TsNHCl + H^{\oplus} \rightleftharpoons TsNHCl_2^{\oplus} \quad (9)$$

Is found to be 1.02×10^2 at 25^0C

If $TsNCl_2$ were to be the reactive species, then the rate law predicts a second order dependence of rate on $[CAT]_o$, which is contrary to the experimental observations. Since the rate of the reaction is retarded by the addition of $TsNH_2$, HOCl is the most probable oxidizing reactive species for the oxidation of benzothiazole derivatives in the present system. From the above discussion and experimental facts, **scheme 1** is proposed to explain the reaction mechanism for the oxidation of benzothiazole derivatives by CAT in HCl medium In the first step there is a formation of an unprotonated CAT due to deprotonation of $TsNH_2$ Cl^+. In the second step unprotonated CAT undergoes hydrolysis to give $TsNH_2$ and HOCl. Here HOCl is the most probable oxidizing

species for the oxidation of Benzothiazole derivatives. In the next step (rate determining step) the reactive species forms a complex (X) with Benzothiazole derivative (S) and finally the complex formed undergoes series of changes to give the oxidized products.

$TSNH_2Cl^+ \xrightleftharpoons{K_1} TsNHCl + H^+$ i) fast

$TsNHCl + H_2O \xrightleftharpoons{K_2} TsNH_2 + HOCl$ ii) fast

$HOCl + S \xrightarrow{K_3} X$ iii) slow and rds

$X + H_2O \xrightarrow{K_4} Products$ iv) fast

Scheme 1: A general scheme for the oxidative decolorization of benzothiazole derivatives by CAT in $HClO_4$ medium.

If $[CAT]_t$is the total effective concentration of CAT, then

$[CAT]_t = [TsNH_2Cl^+] + [TsNHCl] + [HOCl]$ (10)

From step (i) of scheme 1,

$$K_1 = \frac{[TsNHCl]\ [H^+]}{[TsNH_2Cl^+]} \quad \text{or} \quad [TsNH_2Cl^+] = \frac{[TsNHCl]\ [H^+]}{K_1} \tag{11}$$

From step (ii) of scheme 1,

$$K_2 = \frac{[HOCl]\ [TsNH_2]}{[TsNHCl]\ [H_2O]} \quad \text{or} \quad [TsNHCl] = \frac{[HOCl]\ [TsNH_2]}{K_2\ [H_2O]} \tag{12}$$

By substituting for [TsNHCl] from equation (12) into equation (11) we get

$$[TsNH_2Cl^+] = \frac{[H^+]\ [HOCl]\ [TsNH_2]}{K_1K_2\ [H_2O]} \tag{13}$$

By substituting for $[TsNH_2Cl^+]$ [TsNHCl] and [HOCl] from equation (13) and (12) into equation (10) and solving for [HOCl], we get

$$[HOCl] = \frac{k_1\ k_2[\ CAT]\ [H_2O]}{[H^+][TsNH_2] + K_1[TsNH_2] + K_1K_2\ [H_2O]} \tag{14}$$

From slow step of Scheme 1,

Rate = k_3 [HOCl] [S] (15)

By substituting for [HOCl] from equation 14, the following rate law is obtained

$$Rate = \frac{k_1\ k_2K_3[\ CAT][S][H_2O]}{[H^+][TsNH_2] + K_1[TsNH_2] + K_1K_2\ [H_2O]} \tag{16}$$

Rate law (16) satisfactorily fit well to the observed kinetic data wherein a first order dependence of rate on [S] and [CAT] and inverse fractional order on each [TsNH2] and $[H^+]$ on the rate of the reaction .

V. Conclusions

All the benzothiazole derivatives exhibit an identical kinetic behavior and the rate of oxidation of benzothiazole derivatives was found to decrease in the order: OMeBzlH>BzlH> NO_2BzlH. The Kinetics of Oxidation was studied by CAT as an oxidant in acid medium at 296 K. The experimental rate law was $-d[CAT]/dt = k[NO_2BzlH]^1[CAT]^{0.92}[H^+]^{-0.52}[PTS]^{-0.48}$and $-d[CAT]/dt = k\ [BzlH]^1[CAT]^{0.90}[H^+]^{0.52}[PTS]^{-0.36}$ and $-d[CAT]/dt = k[OMeBzlH]^1[CAT]^{0.90}[H^+]^{-0.51}[PTS]^{-0.40}$. The oxidation kinetics was also studied by varying the ionic strength, dielectric constant of the medium. Finally the reaction was studied at different temperatures. Finally based on the observations made an appropriate rate law was derived.

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