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Kinetic study of chlorination of p-methoxyacetanilide by chloramine-T in hydrochloric acid medium

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ABSTRACT

The kinetics of chlorination of p-methoxyacetanilide by sodium N-chloro-p-toulenesulphonamide, chloramine-T (CAT) in the presence of HCl has been investigated at 30 °C. The reaction shows first-order dependence each on (CAT) and [H^+] and is independent on [substrate]. The variation of the ionic strength of the medium has no significant effect on the reaction rate, Addition of the reaction product (p.toluenesulphonamide) retards the rate while addition of chloride ion or an increase in the ethanol proportion (decrease he dielectric constant of the medium) accelerate the reaction rate. The chlorination process under condition employed in the present investigation has been shown to proceed via either the interaction of p.methoxy acetanilide with H_2O+Cl or HOCl with protonated p-methoxy acetanilide to give the product. Finally, the activation parameters for the reaction were also calculated.

Key words: Kinetic study, chloramine-T and HCl.

INTRODUCTION

The chemistry of sodium salt of N-chloro-p-toluensulphonamide (PCH_3-$C_6H_4SO_2NClNa.3H_2O$) well known as chloramine T(CAT;RNClNa) and other related N-halogeno-N-metallo reagents is particularly important ,since they react as sources of both haloniumcations and nitrogen anions. As a results,they have been extensively exploited in effecting molecular modifications and transformation of a wide range of organic and inorganic substances.the existing literature on the chemistry of these reagents have been reviewed[1] recently. Although CAT has been widely used as an oxidizing agent in the qantitive determination of variety of compounds[2] very kinetic studies have been carried out with this reagent.these include decomposition of hydrogen peroxide[3], oxidation of cyanide[4], thio cyanates[5], hexa cyanoferrate ii[6], sulfoxides[7,8], hydroxy acid[9], hydroxylamine[10], primary[11,12] and secondary alcohols[13],aliphatic aldehydes[14] and ketones[15],aldoses[16].amino acids[17,18], formic acid[19] by CAT.In addition chlorination reactions of aniline[20],tolune[21] furan-2carboxylic acid[22] and substituted acetanilide[23a,b] have also been studied The present work also an attempt to explore the mechanistic pathway involved in the chlorination of p-methoxyacetanilide in acidic medium.

EXPERIMENTAL

Materials

Chloramine-T was prepared[24] and purified by method of Morris *et al.,*[25]. An aqueous solution of chloramine-T was standardized by he iodometric method. P-methoxyacetanilide and all other chemicals were of analytical grade and used as receive. The ionic strength of the medium was kept at a high value by using a concentrated solution of sodium perchlorate.

Kinetic Measurements

The reaction was carried out in glass stoppard pyrex flask under pseudo-first-order condition by keeping the p-methoxyacetanilide acetanilide concentration large in comparison with CAT. A typical experiment was performed in the following manner; appropriate amount of p-methoxyacetanilide, hydrochloric acid, ethanol, sodium perchlorate solution, acid and water (to kept the total volume flask constant for all runs) taken in the and thermostated at 30 °C for at least one-half hour for equilibrium. A measured amount of CAT solution (thermostated at the same temperature) was rapidly added to the mixture. The progress of the reaction was followed by with drawing samples at various time intervals, to the quenched. solution (5% potassium iodide solution, 2 M sulphuric acid and water) in a fixed volumetric flask. The liberated iodine was estimated spectrophotometrically at 353 nm[26].

The course of the reaction was followed for at least two half-lives. The pseudo-first-order rate constants k1‘ were obtained from the slope of the plots of log [CAT] versus time.

Stoichiometry

Reaction solutions containing varying ratios of chloramine-T to pmethoxy acetanilide in the presence of 0.04 M HCl were equilibrated at 30 °C for 24 h. Estimation of the residual chloramine-T showed that one mole of chloramine-T is consumed by one mole of acetanilide.

$$C_6H_5NHCOCH_3\ R{+}NHCl \rightarrow C_6H_5NC_lCOCH_3\ R{+}NH_2$$

Where (R‘= $CH_3C_6H_4SO_2$)

The reaction product p-toluenes ulphonamide (R‘NH_2) has been detected by paper chromatography(27,28), Benzyl alcohol saturated with water was used as the solvent with 0.5% vaniline in 1% HCl solution in ethanol as spray reagent (R_f = 0.905). The N-chloro-p-methoxy acetanilide produced as a yellow crystal was identified by I. R. Spectroscopy (815, 1160, 1350 cm^{-1})(8,20), m.p. (91°C) and from elemental analysis test for chlorine.

RESULTS

The kinetics of chlorination of p-methoxyacetanilide by chloramine-T was investigated at several initial concentration of reactant in acid media. At constant acid concentration with the substrate in excess plot of log [CAT] versus time were linear (r > 0.9987), indicating a firstorder dependence of rate on [CAT]. The pseudo-first-order constants, k1‘, are given in Table 1.

The values of k1‘ were unaffected with the increase in [p-methoxyacetanilide]o indicating that the rate is independent on p-methoxyacetanilide concentration (Table 1).

The rate increased with an increase [H^+] (Table 2) . Plots of log k1‘ versus log [H^+] at constant [Cl^-] gave straight line (r>0.9984) with a unit slope.

Variation of ionic strength of the medium (0.1-0.60 M) using sodium perchlorate, or sodium nitrate, and addition of the reaction product p-toluenesulphonamide [PTSA] (up to 0.002 M) had no significant effect on the rate in acid media (Table 3).

The reaction was also studied in aqueous ethanol of varying composition. An increase in the

Table 1: Effect of varying reactant concentration on rate of chlorination of p-methoxy acetanilide by chloramine-T in acid media at 30 °C. [HCl] = 0.04 M, m=0.4 M. 3:2 (v/v) ethanol:water

10^3 [CAT] M	10^2 [P-oCH³ ceta]	M 10^4 k_1‘ sec^{-1}
0.	8 1.6	9.0200
0.8	2.4	9.0584
0.8	3.2	9.1350
0.8	4.0	8.9433
0.8	4.8	9.0960
0.8	1.6	9.0200
1.0	1.6	8.5211
1.2	1.6	8.2140
1.6	1.6	7.2546
2.0	1.6	6.7170

Table 2: Effect of hydrogen ion concentration and chloride ion concentration, [Cl-]t on reaction rate at 30 °C, [CAT]o = 0.00081M, [p-oCH$_3$ aceta]o = 0.016, [NaClO$_4$] = 0.1 M, 3:2 (v/v) ethanol:water

10 [H+]M	10 [Cl$^-$]t M	10^4 k_1' sec^{-1}	102 k_1'/[H$^+$]	10^2 k_1' [Cl]t
0.4	1.2	18.0384	4.5096	
0.6	1.2	24.2940	4.0490	
0.8	1.2	34.7696	4.3462	
1.0	1.2	45.4046	4.5404	
1.2	1.2	53.2353	4.4362	
0.4	0.56	8.9043		1.5900
0.4	0.72	11.9922		1.6655
0.4	0.88	14.1221		1.6047
0.4	1.04	17.3700		1.6701
0.4	1.2	19.3063		1.6088

Table 3: Effect of ionic strength and p-toluenesulphonamide [PTSA] concentration on reaction rate at 30 °C, [CAT] = 0.0008 M , [p-oCH$_3$ aceta]o = 0.016 M, [H+] = 0.04 M, 3:2 (v/v) ethanol:water. While varying [PTSA] m=0.5 M

[NaClO$_4$]M	10^4 k1' sec^{-1}	10^3 PTSA sec^{-1}	10^4 k_1' sec^{-1}
0.1	9.0584	0.4	7.3696
0.2	9.1352	0.8	6,9090
0.3	9.0200	1.2	6.5251
0.4	9.0968	1.6	6.2181
0.5	8.9433	2.0	5.7958

ethanol content increase the rate of reaction with ethanol =50, 60, 65, 70, 80 % the 104 k1' values were 7.29, 9.02, 9.94, 14.50 and 19.88 S^{-1}, respectively at 30 °C with [CAT] =0.008 M, [aceta] = 0.1 M, [H$^+$] = 0.04 M and m= 0.2 M.

A plot of log k1' versus 1/D (where D is dielectric constant of the medium, calculated as given in the literature)(29) gave a straight line with positive slope (r>0.998). The rate of reaction were measured at 22, 26, 30, 34 and 38 °C. The pseudo-first-order rate constant k1'were obtained as 4.22, 6.34, 9.02, 11.20 and 14.39 x 10-4 sec^{-1}, respectively. With [CAT] = 0.0008 M, [p-oCH$_3$ aceta] = 0.016 M, [HCl]= 0.04 M, μ= 0.1 M and 60% (v/v) ethanol:water. The activation energy of chlorination process (computed from straight line plot of log k1' versus (1/T, r > 0.9982) was found to be 57.46KJ/mole, and the other activation parameter, ΔH^+ = 54.94 KJ/mole, ΔS^1 = -122.77 J/mole. °K and log A = 6.6465 were also computed.

DISCUSSION

The rate dependence on [H$^+$] indicates protonation of either the p-methoxyacetanilide or chloramine-T. The former is of some importance, since SH+ is an acid, and the conc. of protonated species in solution must be taken into consideration. The protonation of CAT has been thoroughly investigated by many workers[5,19,25,30], chloramine-T behaves like a strong electrolyte in aqueous solution and dissociates as:

$$RNClNa \rightleftharpoons R'NCl^- + Na^+ \quad \text{....(2)}$$

Where (R'= P-CH$_3$-C$_6$H$_5$SO$_2$)

The anion picks up a proton in acid solution to give the free acid monochloramine-T, R'NHCl. (N-chloro-p-toluenesulphonamide)

$$R'NCl+H^+ \rightleftharpoons R'NCl \quad ...(3)$$

K_a =2-82 × 10^{-5}

Although the free acid has not been isolated, there is experimental evidence for its formation in acid solution[30]. It undergoes disproportionation giving rise to p-toluene sulphonamide (R'NH2) and dichloramine-T (R'NCl_2):

$$2R'NHCl \overset{k_d}{\rightleftharpoons} RNH_2 + RNCl_2 \quad ...(4)$$

K_d= 6.1 × 10^{-2} at 25 °C

The dichloramine-T and the free acid hydrolyse to give hypochlorous acid (HOCl)[11,31].

$$R'NCl_2 + H_2O \overset{k_d}{\rightleftharpoons} R'NHCl + HOCl \quad ...(5)$$

K_d= 8.0 × 10^{-7} at 25 °C

$$R'NHCl + H_2O \overset{k_b}{\rightleftharpoons} RNH_2\ HOCl \quad ...(6)$$

Kb= 4.88 × 10^{-8} at 25 °C

In addition, protonaion of the free acid in pH less 2.8 give (RN^+H_2Cl)[32].

$$R'NHCl + H^+ \overset{k_p}{\rightleftharpoons} R'N^+H_2Cl \quad ...(7)$$

The potonated monochloamine-T (RN^+H_2Cl) can also hydrolyzed to give hypochlorous acidium ion[33], H_2O^+Cl.

$$R'N^+H_2Cl+H_2O \rightleftharpoons R'NH_2+H_2O^+Cl \quad ...(8)$$

Finally, HOCl ionizes to

$$HOCl \overset{k_a}{\rightleftharpoons} H^+OCl^- \quad ...(9)$$

Ka = 3.3 × 10^{-8} at 25 °C

Free chlorine has also been detected in acid medium in the presence of chloride ion, It may be formed through the following steps(19).

$$R'N+H_2Cl + Cl^- \rightleftharpoons Cl_2 + R'NH_2 \quad ...(10)$$

$$Cl_2\ H_2O \overset{K}{\rightleftharpoons} HOCl + H^+Cl^- \quad ...(11)$$

K = 4.66 x 10^{-4}

Therefore, the possible reactive species in acidified CAT solution are R'NHCl, R'NCl_2, HOCl, H_2O+Cl, Cl_2.

If R'NCl_2, were to be the reactive species then the rate predicts a second-order dependence of rate on $[CAT]^o$, which is contrary to the experimental observations. The absence of significant ionic strength effect and the enhancement of reaction rate with the addition of ethanol lead to the conclusion that the reaction take place between positive ion and netural molecule. In view of this, either H_2O+Cl or RN+H_2Cl seems to be efecive species. First-approximation calculations by bishop and Jennings[28] on 0.05 M solution of CAT have shown that the concentrations of RNHCl and HOCl are 10^{-2} and 10^{-7} respectively, at pH < 3 . Protonaion of monochloramine-T R'HCl (equation 7) at pH < 2.8 has also been reported[33]. The protonated monochloramine-T produced can under hydrolysis to from R'NH2 and H_2O+Cl (equation 8). Since, there is no first-order retardation of the rate by the added reaction product (PTSA), the forward reaction is the rate determining step and the subsequent steps of the reaction sequence are fast. Furthermore, there is small equilibrium constant between protononated and deprotonated p-methoxy acetanilide (S^+ H^+ SH^+). The protonated from is expected to be less reaction than deprotonated form to word the (HOCl) due to fact that the nucleophilic nitrogen site is attacked by (H^+) and there is on possibility of the electrophile to attack the nitrogen. In addition swain and Crist[34] have pointed out in their studies on the chlorination of anisole by HOCl that hypochlorous acidium ion H_2O^+Cl is a better electrophile than HOCl. So rate of direct interaction

of protonated p-methoxy acetanilide with HOCl is expected to be very small may be negligated. Thus, under the assumption that H_2O^+Cl is the reaction species, a reaction scheme can be formulated in which the p-methoxy acetanilide is attacked at the nucleophilic nitrogen site by the oxidant to from a nitronium-type intermediate, then elimination of H^+ and H_2O results in the formation of -chloro-p-methoxyacetanilide. The overall rate law for the chlorination of p-methoxyacetanilide by chlormine-T is;

$$-d[CAT]/dt = k_1'[CAT][H^+] \quad ...(9)$$

Further, an increase in the initial concentration of chloroamine-T (Table 1) results in a slight decrease in the first-order rate constant which may by due to deactivation caused by the formation of small quantities(8,35,36) of $NaClO^3$ in a side reactions

$$H_2O^+Cl + Na^+ \rightleftharpoons NaOCl + 2H^+ \quad ...(10)$$

$$3NaOCl \rightarrow NaClO_3 + 2NaCl \quad ...(11)$$

Finally, the proposed mechanism is supported by the negative value of entropy of activation which is an indication of rigid transitionstate configuration, with fairly high positive value of free energy of activation[22,36,37].

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