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Research Article

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Kinetics of Bromination of Benzofurans by Phenyltrimethylammonium Tribromide

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ABSTRACT

The kinetics of the reaction between different 2-acetyl benzofuran (BF) and phenyltrimethylammonium tribromide (PTT) has been studied spectrophotometrically in acetic acid under varying conditions. The results indicate first order kinetic with respect to 2-acetyl benzofurans (BF) and inverse first order due to phenyltrimethylammonium tribromide (PTT). Effect of ionic strength and dielectric constant on reaction rate was observed. The rates of reaction are measured at different temperature and activation parameters have been calculated. The products of the bromination are the corresponding 2-bromoacetyl benzofurans.

Keywords: Kinetics; Benzofuran; Phenyltrimethylammonium tribromide; Bromination; Acid catalyst

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INTRODUCTION

α-Bromo derivatives have been attracting increasing attention in view of their high reactivity [1-3]. Benzo [b]furan derivatives an important class of organic compounds, which are known to be present in many natural products [4] and possess physiological activity. They find applications in agrochemicals [5], pharmaceuticals [6] and cosmetics [7]. Bromo derivatives have been used to produce different substituted benzo [b] furans derivatives with raised biological activity [8]. To study the kinetics of bromination of organic compounds number of reagents such as, iodine monobromide [9], bromate-bromide [10], bromine with oxygen [11], NBS [12], HOBr [13], alkali metal bromide [14], sodium hypo bromide – NBS [15], Br_2 + $FeCl_3.6H_2O$ and dibenzoyl peroxide [16], $CuBr_2$- HNO_3 - HBr - $HClO_4$ - O_2 - H_2O system [17], trimethylbromosilane dimethyl sulfoxide [18], N - halo compounds [19] etc., has been used. But most of the reagents used are toxic and hazardous, expensive, difficult to handle and cause severe burns in contact with skin. The phenyltrimethylammonium tribromide [20] (PTT) is an efficient, selective, versatile, stable, crystalline, easy to handle and worked well as a 'greener' substitute of bromine for bromination reaction. Literature survey reveals that no report is available on the kinetics of bromination of 2- acetyl benzofuran by phenyltrimethylammonium tribromide; hence it was thought worthwhile to undertake the investigation.

EXPERIMENTAL SECTION

Material and Methods

All the chemicals used were of AR grade (Thomas Baker). The 2-acetyl -5-substituted benzofurans were prepared by Stoermer and Schaffer method [21,22]. The brominating reagent PTT was prepared by standard procedure [20], the purity of prepared 2-acetyl -5-substituted benzofurans and PTT were checked by TLC, elemental analysis, IR, NMR and mass spectra. Digital spectrophotometer of 'ELICO PVT. LTD. HYDERABAD.' Make model CL- 27 was used to monitor the decrease in concentration of PTT.

Kinetic Measurements

Solutions of brominating reagent, 2 ml of 0.80 N H_2SO_4 and substrate were thermo stated in requisite proportion in two separate flasks for half an hour. After attaining the same temperature the solutions were mixed with shaking to initiate the reaction then requisite quantity of aliquots of the reaction mixture was withdrawn at different time intervals and the absorbance of PTT at 405 nm was recorded using glacial acetic acid as a solvent. The reaction rate was studied up to 80% of completion of reaction. The rate constants were determined by a least square method from the linear plot of log [PTT] *vs*. time. Replicate runs were reproducible to within ± 4%.

Stoichiometry and Product Analysis

Stoichiometry of Phenyltrimethylammonium tribromide and 2-acetyl-5-substituted benzofuran reaction was determined by allowing the reaction mixture containing 2-acetyl-5-substituted benzofuran and Phenyltrimethylammonium tribromide in 1:1 molar ratio in acetic acid for completion of reaction. Then the reaction mixture was poured on crushed ice to get solid product. The brominated product was characterized by IR, NMR and Mass spectra. Interesting observation was the base catalyzed bromination reaction leads to give ring bromination with mixture of mono, di and tribromo derivatives, while in present work bromination reaction occurs on - $COCH_3$ group gives monobromoacyl derivatives as a product.

RESULTS AND DISCUSSION

The results of bromination of 2- acetyl benzofuran and PTT are presented in Tables 1-5.

Effect of Variation of Substrate

At constant [PTT], the increase in (substrate) enhances the reaction rate (Table 1). The plot of log k_{obs} versus log (substrate) for different initial concentration of substrate is linear with unit slope, indicating the first order dependence on substrate.

Table 1: Dependence of rate constant on [substrate], [PTT]=0.0040 M, [H_2SO_4]=0.80 N temperature=303 K, solvent=acetic acid

[substrate] M	$k \times 10^5$ s^{-1}			
	5-CH_3O	5-H	5-Br	5-NO_2
0.004	32.62	16.12	9.17	6.14
0.0035	28.78	14.58	7.96	5.18
0.003	24.5	12.47	6.33	4.03
0.0025	20.72	9.21	5.01	3.02

Effect of Variation of [PTT]

At constant [substrate], the increase in [PTT] decreases the reaction rate (Table 2). The plot of log k_{obs} versus log [PTT] with a negative slope, indicating that velocity constant is inversely proportional to PTT concentration due to decrease in concentration of a reactive species [15,23] establishing the inverse first order dependence of the rate on PTT in all cases.

Table 2: Dependence of rate constant on [PTT], [substrate]=0.0040 M, [H_2SO_4]=0.80 N, temperature=303 K, solvent=acetic acid

[PTT] M	$k \times 10^5$ s^{-1}			
	5-CH_3O	5-H	5-Br	5-NO_2
0.004	40.67	22.07	10.36	6.04
0.0035	46.82	24.6	12.91	7.94
0.003	54.12	29.91	14.91	9.59
0.0025	65.63	36.82	16.88	10.65

Effect of Variation of [H^+]

The reaction is catalyzed by hydrogen ion; the rate of reaction increases with increase in H_2SO_4 concentration, the plot of log k_{obs} versus log [H^+] are also straight line with unit slope, indicating a first order dependence on [H^+] (Table 3).

Table 3: Dependence of rate constant on [H_2SO_4], [substrate]=0.0040 M, [PTT]=0.0040 M, temperature=303 K, solvent=acetic acid

[H_2SO_4] N	k × 10^5 s^{-1}			
	5-CH_3O	5-H	5-Br	5-NO_2
0.15	13.58	5.987	4.018	3.045
0.3	16.25	8.004	7.31	5.121
0.45	17.99	11.35	10.12	6.472
0.6	23.27	17.25	14.72	7.994

Effect of Variation of Temperature

The kinetic measurements were carried out at different temperature range 298 K to 313 K using concentration of 2-acetyl-5-substituted benzofuran and PTT and sulphuric acid to study the effect of temperature on the rate of bromination reaction. The rate constants are given in Table 4. The plots of log k_{obs} versus 1/T are linear. Activation parameters are presented in Table 5. The relatively small $\Delta H^{\#}$ and negative $\Delta S^{\#}$ were consistent with the reaction generally proceed through highly organized transition state [13]. The negative values of entropy of activation indicates that the reaction involve the transfer of electron between ions of same charges [10].

The values of $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ are calculated by using following equations:

$$\Delta H^{\#} = Ea - RT$$

$$\Delta S^{\#} = 19.16 (\log k - 10.576 - \log T + Ea/19.16T)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

Table 4: Effect of temperature variation on reaction rate constant, [H_2SO_4]=0.80 N, [substrate]=0.0040 M, [PTT]=0.0040 M, solvent=acetic acid

No.	Temperature (K) Name of Substrate	298	303 k × 10^5 s^{-1}	308	313
1	5-CH_3O	26.67	35.92	48.89	68.98
2	5-H	11.8	18.23	22.07	36.24
3	5-Br	7.89	14.11	17.26	30.69
4	5-NO_2	4.578	7.777	9.689	12.37

Table 5: Thermodynamic parameters, [substrate]=0.0040 M, [PTT]=0.0040 M, [H_2SO_4]=0.80 N, temperature=303 K, solvent=acetic acid

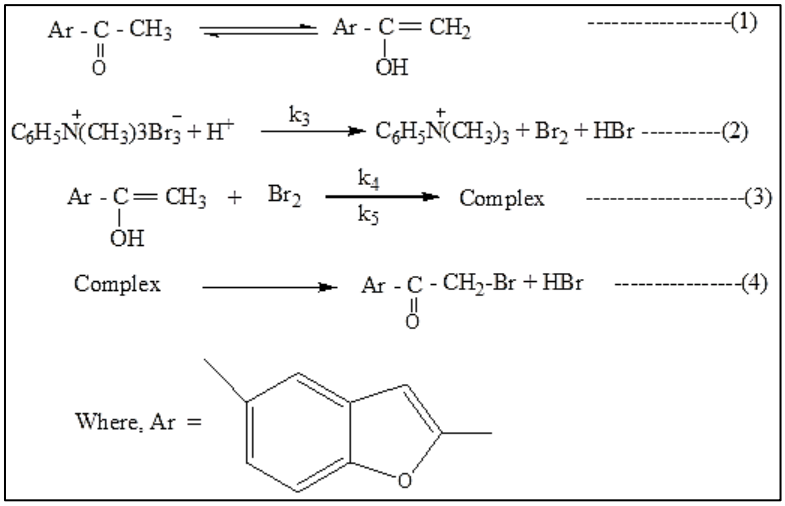
Sr.	Substrate	k ×10^5 s^{-1}	Ea kJmole^{-1}	Δ H kJmole^{-1}	Δ $S^{\#}$ Jmole^{-1}K^{-1}	Δ$G^{\#}$ kJmole^{-1}	Freq. Factor (LogA) L/mole/sec
1	5-CH_3O	35.92	38.43	35.91	190.06	93.99	1.468×10^3
2	5-H	18.23	73.03	70.7	81.76	95.04	6.323×10^8
3	5-Br	14.11	78.66	76.39	77.79	95.79	1.019×10^9
4	5-NO_2	7.777	80.85	78.32	62.09	97.13	6.686×10^9

Energy-Entropy Relationship

The entropy of activation and heat of reaction are correlated by the equation 1.

$$\Delta H^{\#} = \Delta H^{\#} + \beta\Delta S^{\#} (1)$$

Where β is the isokinetic temperature. The isokinetic temperature for the reactions between 2- acetyl benzofurans and PTT in acetic acid is 333 K, which is obtained from the linear plots of $\Delta H^{\#}$ verses $\Delta S^{\#}$ are in agreement with the values obtained from log k verses 1/T plot. The isokinetic temperature was greater than the experimental temperature which indicates that the reactions are entropy controlled. The values of free energies of activation of the reaction were found more or less similar. This trend also supports the identical reaction mechanism being followed in these reactions [24]. The effect of substituents on rate was studied by varying the substituents in 2- acetyl -5-substituted benzofurans. The order of reactivates with substituents was 5-methoxy > 5- H > 5-bromo > 5- nitro. The rate retards with the introduction of electron withdrawing groups into the aromatic ring while rate of reaction was accelerated due to electron donating groups. The electron donating group donates electrons by resonance, increases the relative stability of keto form and shows higher reactivity. Based on above experimental observations and a probable mechanism (Scheme 1) is suggested.



Scheme 1: Probable mechanism of bromination of 2- acetyl benzofuran and rate law

CONCLUSION

Effect of ionic strength and dielectric constant on reaction rate was observed. The rates of reaction are measured at different temperature and activation parameters have been calculated. The products of the bromination are the corresponding 2-bromoacetyl benzofurans.

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