Kinetic study of bromination of 5-substituted-2-hydroxy acetophenones using phenyl trimethylammoniumtribromide

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ABSTRACT

The bromination of 5-substituted-2-hydroxy acetophenones by using phenyl trimethylammoniumtribromide (PTT) in presence H_2SO_4 catalyst at different temperature have been carried out. In the present study, it is observed that first order kinetics due to ketones, inverse first order kinetics due to PTT and first order kinetics due to sulphuric acid. The effect of temperature have been discussed.

Key words: Kinetic study, bromination, acetophenones.

INTRODUCTION

Organic bromoderivatives are important due to their biological activities. These are widely used as reactive intermediates in various organic synthesis. Kinetics of bromination of substituted acetophenones is carried out by various workers[1-2]. The use of phenyl trimethylammoniumtribromide (PTT) as selective α-brominating agent for arylakyl ketones in organic synthesis has been reported by Noland[3]. Hence it encourage to use the PTT as a brominating agent for the kinetic study of bromination of 5-substituted-2-hydroxyacetophenones.

EXPERIMENTAL

All the chemicals used were of AR grade. The 2,5-dihydroxyacetophenone (AP-I), 2-hydroxyacetophenone (AP-II) and 2-hydroxy-5-nitroacetophenone (AP-III) were prepared by standard method[4]. Glacial acetic acid was purified by literature procedure[5]. PTT was prepared by standard procedure[4]. The purity of 5-substituted-2-hydroxyacetophenones and PTT were confirmed by TLC, melting point, NMR spectra and elemental analysis. The required amount of the solution of PTT, substrate and H_2SO_4 separately kept in a thermostatic waterbath to maintain the required temperature. Aliquots of the reaction mixture were withdrawn at a different tiem intervals and absorbance were noted at reference as 405nm in acetic acid as a solvent. The absorbance of all the samples were recorded on UV-visible Spectrophotometer (ELICO Model No. SL 159). The product of the reaction was analysed and confirmed by melting point, TLC and NMR spectra.

RESULTS AND DISCUSSION

The results of bromination of 5-substituted-2-hydroxyacetophenones.

The order was inverse first with respect to [PTT]. The plot of logk against log [PTT] with a negative slope indicated that the rate constant is inversely proportional to [PTT] due to decrease in concentration of reactive species. The plot of 1/k Vs 1/[PTT] does not pass through the origin indicating the formation of intermediate complex. The order with respect to subtrate was also one as revealed by unit slope of the plot of logk against log [substrate]. The plot of 1/k against 1/[substrate] was also linear with intercept on the Y-axis, suggesting complex formation between reactant molecules. The similar observations have been reported in the bromination between reactant molecules. The similar observations have been reported in the

bromination reactions by N. Rath and *et al.*,[6]. The rate of reaction increased with increase in [H_2SO_4]. The plot of logk Vs log [H^+] was linear with unit slope. The rate constant increases with increase in dielectric constant of the medium. The distance between two interacting ions has been calculated from the slope of logk Vs 1/D plot of 5-substituted-2-hydroxyacetophenones. The value was found to be 4.98 in agreement with Laidler's predictions[7].

The plot of logk Vs square root of ionic strength was linear with positive slope. The trend indicates that the reacting species are ionic with same charges, hence as the ionic strength increases the constant increases. The rate of reaction increases with increase in temperature according to Arrhenius equation. The relatively small $\Delta H^{\#}$ Vs negative $\Delta S^{\#}$ are consistent with highly organized transition state[8-9]. The negative value of entropy of activation indicates that the reaction involves the transfer of electron between ions of the same charge[10]. The slopes at 336K and 335K obtained from the linear plots of $\Delta H^{\#}$ Vs $\Delta S^{\#}$ and Ea Vs logA respectively are in agreement with the values obtained from logk Vs 1/T plot, that the isokinetic temperature is greater than the experimental temperature, indicates that the reactiosn are entropy-controlled. The values of entropy of activation also suggest that the reaction are entropy controlled.

The values of free energy of activaiton of the reaction were found to be more of less are similar. This trend also support the identical reaction mechanism being followed in these reaction. The slope at 335K for linear relationship in Exner plots of 5+logK_2 (308 K) Vs 5+logk_1 (303 K) observed in the present study also support the conclusion drawn from isokinetic temperature.

Based on the above experimental observation, a probable mechanism (Scheme 1) is suggested and the rate law is derived as,

$$Dx/dt \; \alpha \; [substrate][Acid]/[PTT]$$

The effect of substituents on rate was studied by varying the substrate in 5-substituted-2-hydroxyacetophenones. The order of reactivity with substituents in acetophenones is 2,5-

Table 1: Effect of variation of [PTT] on rate constant

[Substrate] = 3.5×10^{-3} M, [H_2SO_4] = 0.6 N and Temp. = 303 K

[PTT] x10^{-3} M	AP-I k × 10^{-4} S^{-1}	AP - II k × 10^{-4} S^{-1}	AP - III k × 10^{-4} S^{-1}
3.5	4.58	3.04	0.85
3.0	5.28	3.61	1.08
2.5	5.98	4.40	1.44
2.0	7.22	5.76	1.85

Table 2: Effect of variation of [Substrate] on rate constant

[PTT] = 3.5×10^{-3} M, [H_2SO_4] = 0.6 N and Temp. = 303 K

[Substrate] x10^{-3} M	AP-I k × 10^{-4} S^{-1}	AP - II k × 10^{-4} S^{-1}	AP - III k × 10^{-4} S^{-1}
3.5	4.58	3.04	0.85
3.0	4.01	2.52	0.70
2.5	3.42	2.00	0.57
2.0	2.88	1.68	0.42

Table 3: Effect of variation of [H_2SO_4] on rate constant

[Substrate] = 3.5×10^{-3} M, [PTT] = 3.5×10^{-3} M, and Temp. = 303 K

[H_2SO_4] N	AP-I k × 10^{-4} S^{-1}	AP - II k × 10^{-4} S^{-1}	AP - III k × 10^{-4} S^{-1}
0.2	3.87	2.00	0.42
0.4	4.15	2.52	0.63
0.6	4.58	3.04	0.85
0.8	4.72	3.58	1.07
1.0	4.96	4.02	2.28

hydroxyacetophenones. The order of reactivity with substituents in acetophenones is 2,5-hydroxyacetophenones>2-hydroxyacetophenone>2-hydroxy-5-nitroacetophenone. The similar observations are reported by Jadhav *et al.*,[11]. In the present study is observed that electron withdrawing

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### Table 4: Effect of variation of ionic strength on rate constant

[Substrate] = 3.5×10^{-3} M, [PTT] = 3.5×10^{-3} M, [H_2SO_4] = 0.6 and Temp. = 303 K

[CH_3COONa] $\times 10^{-3}$ M	AP-I $k \times 10^{-4}$ S^{-1}	AP - II $k \times 10^{-4}$ S^{-1}	AP - III $k \times 10^{-4}$ S^{-1}
5.00	5.05	4.23	1.25
7.50	5.84	4.88	1.51
10.0	6.55	5.42	1.83
12.5	7.28	6.10	2.10
15.0	8.01	6.90	2.43

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### Table 5: Effect of temperature on bromination of 5-substituted-2-hydroxyacetophenones

[Substrate] = 3.5×10^{-3} M, [PTT] = 3.5×10^{-3} M, and [H_2SO_4] = 0.6 N

Temp. K	AP-I $k \times 10^{-4}$ S^{-1}	AP - II $k \times 10^{-4}$ S^{-1}	AP - III $k \times 10^{-4}$ S^{-1}
298	3.80	2.09	0.32
303	4.58	3.04	0.85
308	4.96	4.02	1.29
313	6.19	5.03	1.78
318	7.53	6.27	2.29
323	8.31	7.42	2.69

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Table 6: Thermodynamic parameters

[Substrate] = 3.5×10^{-3} M, [PTT] = 3.5×10^{-3} M, and [H_2SO_4] = 0.6 N and Temp. = 303 K

Compound	Frequencey factor (A) dm³ mol⁻¹ s⁻¹	Ea kJ/mol	$\Delta H^{\#}$ kJ/mol	$-\Delta S^{\#}$ J/mol	$\Delta G^{\#}$ Kj/mol
AP-I	14.23	26.24	23.71	230.32	93.49
AP-II	2473	40.19	37.67	184.25	93.49
AP-III	781600	64.67	62.14	103.47	93.49

Mechanism:
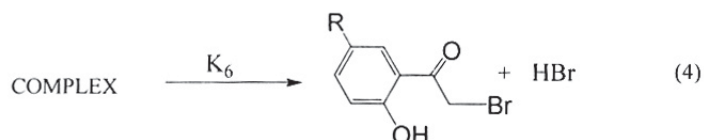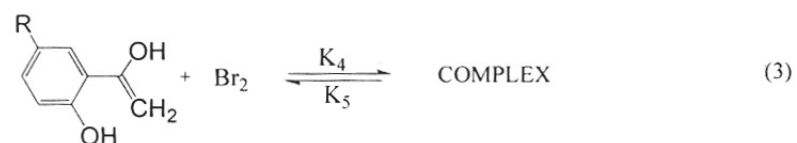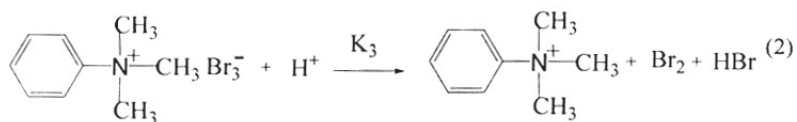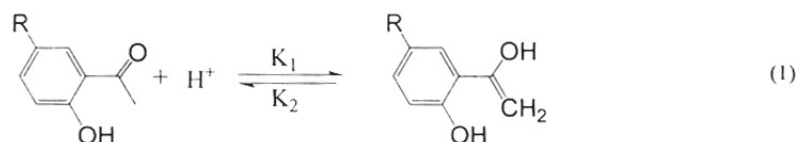
Where R = -H, -OH, -NO$_2$

Scheme 1

group that is Nitro group decrease the rate of bromiantion whereas the electron donating that is hydroxyl group donate electrons whcih cause increase in the relative stability of keto form and hence shows increase in the rate of reaction.

         The Hammett's constant were determined by plotting rate constant against σ values of various substituents. The linear nature of plots supports the

identical mechanism in all the brominations rections. The change in rate of reaction with respect to the change in substituents was studied. An interesting observation is that the base catalyzed bromination reaction give a mixture of mono-, di-, tri-bromo derivatives of 5-substituted-2-hydroxyacetophenone, while in the present work the reaction gives only mono-bromo 5-substituted-2-hydroxyacetophenone derivatives.

REFERENCES

1. D.N.Nanda, P.L. Nayak and M.K. Rout, *Indian J. Chem.,* **07**: 469 (1969).
2. Gopalan Raghaavachary and A. George Pincus, *J.C.S. Comm.* 1016 (1981).
3. Noland, *Organic Synthesis collective volume-VI Pub.* John. Wiley and Sons, 175 (1988).
4. V.S. Ingle *Ph. D. thesis* Dr. B.A.M. University, Aurangabad (1998).
5. K.S.P. Orton and A.E. Bradfield, *J. Chem. Soc.,* 983 (1927).
6. N. Rath and *et al.*, *Indian J. Chem.* **27**A: 1028 (1988).
7. K.J. Laidler, "Chemical Kinetics" *Tata McGraw Hills Pub.* New Delhi, 214 (1986).
8. E.V. Sundaram, G.V.S. Shaidhar and M. Satyanarayana, *J. Indian Chem. Soc.*, **65**: 346 (1988).
9. S.C. Basu, *Indian J. Chem.,* **23**A: 884 (1984).
10. N. Sutin and J.K. Yandell, *J. Bio-Chem,* **16**: 1741 (1977).
11. W.N. Jadhav, S.R. Bhusare, R.P. Pawar and B.R. Arbad, *J. Ind. Chem. Soc.*, **78**: 310-312 (2001).