Kinetics of Bromination of Phenols

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The kinetics of bromination of phenols with molecular bromine in acetic acid have been studied. The overall order was found to depend on the concentrations of the reactants: three at higher concentrations and two at low concentration region. Individual orders were found to be one in each reactant. Activation parameters for the bromination of phenols were calculated. The order of reactivity is in the order of o-cresol > phenol > m-chlorophenol > o-chlorophenol > o-bromophenol > p-chlorophenol > salicylic acid > vanilline.

INTRODUCTION

Kinetics of bromination of substituted phenols have been studied by some workers[1-4] but detailed study has not been done on bromination of phenols. To add more light on the kinetics of bromination of phenols, the bromination of phenols in acetic acid medium was investigated with a view to find out overall order at different concentrations, individual Orders and kinetic parameters for o-substituted phenols.

EXPERIMENTAL

The glacial acetic acid (S. Merck) was purified according to orton's[5] procedure. Phenols (BDH or E. Merck) were redistilled and used. Bromine (BDH) and potassium iodide (BDH) were used.

The kinetic measurements have been carried out by determining the concentration of bromine, iodometrically as a function of time. Since reaction is faster, the batch method recommended by Gnanapragasam and Yeddanapalli[6] was adopted. The halogen and phenol solution in acetic acid (5 ml) each in several glass stoppered bottles and test tubes respectively were placed in a thermostat at required temperature. After solution reached the bath temperature, the phenol solution was quickly added into the bromine solution and mixture was allowed to react for a definite time, after which the reaction was arrested by quick addition of potassium iodide (10%, 5 ml). The reaction mixture was kept for one

†Deceased.

minute and then the liberated iodine was titrated against standard sodium thiosulphate.

Temperature control was maintained with accuracy of $\pm0.05°$, using automatic thermostatic bath.

RESULTS AND DISCUSSIONS

The overall order was determined by carrying out the study using equimolar concentrations of the reactants. The overall order determined by fractional life method was three at higher concentration (Table 1). As the concentration decreases the order decreased.

TABLE 1

DETERMINATION OF OVERALL ORDER: IN ACETIC ACID AT 35°,
BY FRACTIONAL LIFE METHOD (Phenol=Br)

Concentrations mol l^{-1}		Overall order					
C$_2$	C$_1$	o-bromo-phenol	o-chloro-phenol	m-chloro-phenol	Phenol	p-chloro-phenol	Salicylic acid
0.2	0.1	2.84	—	2.87	—	2.90	3.58
0.2	0.1	3.00	—	2.95	—	2.88	3.38
0.1	0.05	2.67	2.97	2.24	—	2.79	2.58
0.1	0.05	2.58	3.15	2.18	—	2.54	2.50
0.02	0.01	2.55	—	2.32	2.05	2.26	1.80
0.02	0.01	2.13	—	2.35	1.94	2.35	1.79
0.01	0.005	1.71	1.93	2.66	2.00	—	—
0.01	0.005	1.80	2.32	2.17	1.65	—	—

Individual orders were determined by the isolation method and also from initial rate were found to be one (Table 2) in phenols as well as in bromine.

TABLE 2

INDIVIDUAL ORDERS DETERMINED BY FRACTIONAL LIFE METHOD
AND BY THE INITIAL RATES

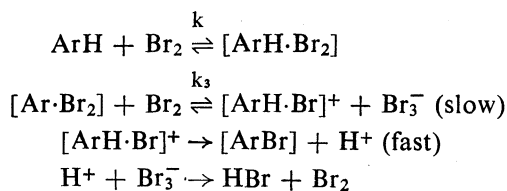| Substrate	Order: by fractional life method				Order: from the initial rates	
	Concentration mol l^{-1}		Order			
	Phenol	Bromine	Bromine	Phenol	Bromine	Phenol
o-chloro phenol	0.05–0.0125	0.003–0.0007	1.10	0.99	0.80	0.90
m-chloro phenol	0.2 –0.05	0.02 –0.005	0.94	0.95	0.88	1.09
o-bromo phenol	0.1 –0.025	0.02 –0.005	0.88	1.18	0.804	1.18
p-chloro phenol	0.2 –0.05	0.04 –0.01	0.93	1.04	0.90	0.92
Salicylic acid	0.2 –0.05	0.04 –0.01	0.90	1.00	0.86	1.04

In order to determine various activation parameters, the effect of temperature on the rate constant was studied using mixture of phenols and bromine (0.01 M each) over the temperature range at 35–50°. The pseudo-second order rate constant obtained for the reaction at different temperatures were plotted against $1/T$ and the activation energy and other activation parameters were calculated (Table 3). Since the bromination of o-cresol is highly fast, a detailed investigation was not made. Only over all order at lower concentration was determined and was found to be two.

TABLE 3

ACTIVATION PARAMETERS FOR THE BROMINATION OF PHENOLS
IN ACETIC ACID

Substrate	$k_1 \times 10^2$ sec^{-1} at 35°	Ea kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1} at 35°	$\Delta F^{\neq}$ kJ mol^{-1} at 35°	$-\Delta S$ JK^{-1} mol^{-1} at 35°	log 10^A
Phenol	541.6	18.4	15.9	71.0	178.7	3.89
m-chlorophenol	75.0	27.6	24.6	76.3	164.9	4.56
o-chlorophenol	11.3	35.9	33.9	81.2	153.2	5.22
o-bromophenol	· 9.6	31.8	29.3	81.5	169.1	4.39
p-chlorophenol	1.9	30.1	27.6	102.1	188.4	3.39
Salicylic acid	9.0	40.1	37.2	86.6	161.2	4.81
Vanilline	0.6	37.2	34.7	88.5	174.2	4.14
o-cresol	1600.0	—	—	—	—	—

The bromination of phenols in acetic acid medium was third order at higher concentrations and at low concentration it was of second order (Table 1). The values given in (Table 1) indicate the simultaneous occurrence of second and third order process. Similar results were reported by Rajaram and Kuriacose[2] for p-bromophenol in acetic acid. The over all second order reaction at lower concentration may be pseudo-second order with the solvent molecules participating in the reaction[7].
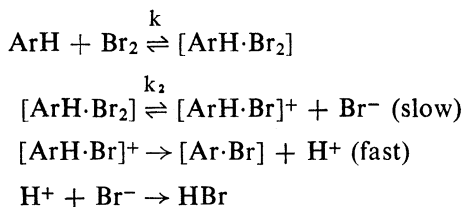
The results agree with the general mechanism proposed[8] involving the attack of one molecule of electrophile (E), on one of the complex ArH-Br$_2$ in the rate determining step. In the third order process (E) is another molecule of bromine. So the mechanism suggested for the third order is as follows;

$$ArH + Br_2 \stackrel{k}{\rightleftharpoons} [ArH \cdot Br_2]$$
$$[Ar \cdot Br_2] + Br_2 \stackrel{k_3}{\rightleftharpoons} [ArH \cdot Br]^+ + Br_3^- \text{ (slow)}$$
$$[ArH \cdot Br]^+ \rightarrow [ArBr] + H^+ \text{ (fast)}$$
$$H^+ + Br_3^- \rightarrow HBr + Br_2$$

This leads to the rate expression

$$\frac{-d\ Ar \cdot Br}{dt} = kk_3[ArH][Br_2]^2$$

In the pseudosecond order process (E) is one molecule of solvent[2, 7]. So the mechanism suggested for second order is as follows.

$$ArH + Br_2 \overset{k}{\rightleftharpoons} [ArH \cdot Br_2]$$

$$[ArH \cdot Br_2] \overset{k_2}{\rightleftharpoons} [ArH \cdot Br]^+ + Br^- \text{ (slow)}$$

$$[ArH \cdot Br]^+ \rightarrow [Ar \cdot Br] + H^+ \text{ (fast)}$$

$$H^+ + Br^- \rightarrow HBr$$

This leads to the rate expression

$$\frac{-d\ ArH \cdot Br}{dt} = kk_2[ArH][Br_2]$$

Comparison of the rates and bromination of phenols (Table 3) reveals that the reactivity of different substituted phenols is in the order of o-cresol > phenol > m-chlorophenol > o-chlorophenol > o-bromophenol p-chlorophenol > salicylic acid > vanilline. This clearly emphasizes that electron withdrawing groups retard the rate and electron releasing groups enhance the reaction rate as has been observed for other similar electrophilic substitution reactions.

The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values (Table-3) are nearly similar with those reported previously for the electrophilic substitution reactions[9]. The large negative values of $\Delta S^{\neq}$ indicate that the formation of intermediate complex is the rate determining step[10].

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