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Kinetics and Mechanism of Bromination of 2,4-Dinitrophenol in Aqueous Acetic Acid

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The bromination of 2,4-dinitrophenol by molecular bromine at various concentrations, in (95:5% v/v), (90:10% v/v) and (85:15% v/v) acetic acid-water mixture medium is investigated. The effect of temperature is studied and kinetic parameters are determined.

INTRODUCTION

The kinetics of bromination of aromatic compounds like phenol[1], *p*-substituted phenols[2–9] have been investigated in acetic acid, carbon tetrachloride and water, but very few attempts have been made on the bromination of di-substituted phenols. In the present work the kinetics and mechanism have been studied on bromination of 2,4-dinitrophenol by molecular bromine at various concentrations, in (95:5% v/v), (90:10% v/v) and (85:15% v/v) acetic acid : water mixture medium.

EXPERIMENTAL

The preparation of pure anhydrous acetic acid (f.pt. 16.3°C) is carried out by the method of orton and Bradifield[10]. 2,4-Dinitrophenol of (Sigma) is used. Bromine ampoules, sodium thiosulphate and all other reagents were of analytical grade.

The kinetic investigation have been carried out by determining the concentration of bromine iodometrically as a function of time. Since reaction is faster, the *Batch method*[1] is adopted.

RESULTS AND DISCUSSION

The over all order determined by carrying out the study using equimolar concentrations of the reactants. The over all order in case of 2,4-dinitrophenol (95 : 5% v/v) and (90 : 10% v/v) acetic acid and water mixture medium, determined by fractional life method at higher concentration (0.3 to 0.05 M)

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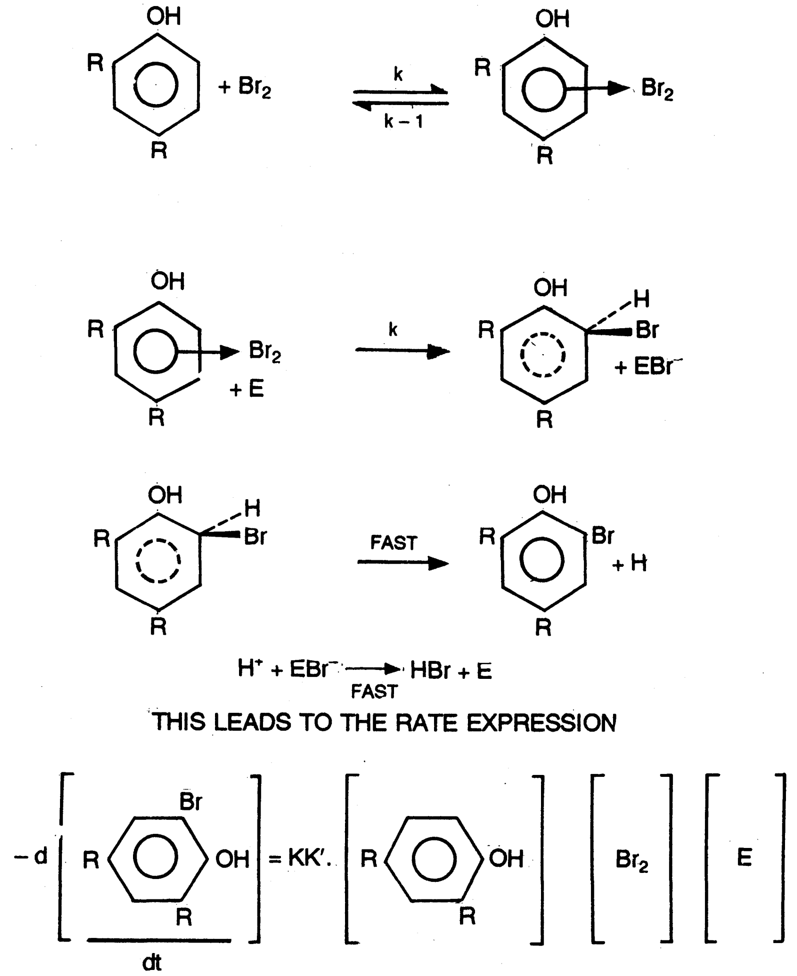

Fig. 1 General mechanism in case of bromination

region is *three* and the same is decreased and found *two* at lower concentration (0.02–0.005 M) region. Hence the over all order found to depend on the concentration of reactants. (Table 1).

In case of bromination of 2,4-dinitrophenol in (85:15% v/v) acetic acid and water mixture medium, the over all order is *2.4* at higher concentration region and *two* at lower concentration region (Table-1). The decrease in order from *three* to nearly *two* may be due to increase in the concentration of water in acetic acid. Since water plays a role of electrophile in the rate determining step.

The individual orders for the substrate and bromine are determined by *Isolation method.* The order with respect to substrate is *one* but the order with respect to bromine is nearly *one* (Table 2). The order initial rates for both the reactants have been determined from the log-log plot of initial rate against concentration. The slope of the linear plot gives the order (Fig. 2; Tables 2 and 3).

TABLE 1

DETERMINATION OF OVERALL ORDER IN AQUEOUS ACETIC ACID BY FRACTIONAL LIFE METHOD AT 30°C

[2,4-Dinitrophenol] = [Bromine]

Time (Sec)						Concentration (mol l^{-1})		Overall order ($AcOH : H_2O$)		
(95:5%) v/v		(90:10%) v/v		(85:15%) v/v		C_2	C_1	(95 : 5%) v/v	(90 : 10%) v/v	(85 : 15%) v/v
t_2	t_1	t_2	t_1	t_2	t_1					
30	120	—	—	2.0	5.5	0.2	0.1	3.0	—	2.45
60	300	—	—	4.0	10.0	0.2	0.1	3.3	—	2.32
120	450	—	—	5.5	14.5	0.1	0.05	2.9	—	2.40
300	1140	—	—	10.0	25.0	0.1	0.05	2.9	—	2.32
300	600	12	30	12.0	27.0	0.02	0.01	2.0	2.3	2.10
720	1350	24	54	21.0	39.0	0.02	0.01	1.9	2.1	1.90
600	1200	30	60	27.0	54.0	0.01	0.005	2.0	2.0	2.00
1350	2490	54	102	39.0	75.0	0.01	0.005	1.9	1.9	1.90
—	—	6	15	—	—	0.3	0.2	—	3.2	—
—	—	12	30	—	—	0.3	0.2	—	3.2	—
—	—	5	27	—	—	0.2	0.15	—	3.0	—
—	—	30	56	—	—	0.2	0.15	—	3.1	—
—	—	3	12	—	—	0.3	0.15	—	3.0	—
—	—	6	24	—	—	0.3	0.15	—	3.0	—
—	—	12	42	—	—	0.15	0.075	—	2.8	—
—	—	24	78	—	—	0.15	0.075	—	2.7	—

The effect of temperature on the rate constant is examined using mixture of substrate and bromine (0.02 M each) over the temperature range of 25°–45°C. The second order rate constant obtained for the reaction at different temperatures were plotted against $1/T$ and the activation energy and other activation parameters are calculated. $E_a = 38.3$ KJ mol^{-1}; $\Delta H^{*} = 35.7$ KJ mol^{-1} at 30°C; $\Delta F^{*} = 103.9$ KJ mol^{-1}at 30°C; $\Delta S^{*} = 216.8$ JK^{-1} mol^{-1} at 30°C.

The observed results can be explained on the basis of simultaneous occurance of second and third process in 2,4-dinitrophenol. The similar results have been observed in *p*-bromophenol[2], anisole[4], *o*-chlorophenol[6] and *p*-hydroxy benzaldehyde[9] in acetic acid by molecular bromine.

TABLE 2
DETERMINATION OF INDIVIDUAL ORDERS IN AQUEOUS ACETIC ACID
(AcOH : H_2O) AT 30°C BY FRACTIONAL LIFE METHOD
2,4-Dinitrophenol/Bromine (Varying)
2,4-Dinitrophenol/Bromine (Constant)

Concentration (mol l^{-1})		Order: by Fractional life method		Solvent (AcOH : H_2O)
Bromine (M)	2,4-Dinitrophenol (M)	Bromine	2,4-Dinitrophenol	
[0.02, 0.01, 0.05] (Phenol = 0.2 M)	[0.2, 0.1, 0.05] (Br = 0.1 M)	1.1	1.1	(95:5% v/v)
[0.03, 0.015, 0.0075] (Phenol = 0.2 M)	[0.4, 0.3, 0.2] (Br = 0.02 M)	1.2	0.95	(90:10% v/v)
[0.01, 0.005, 0.0025] (Phenol = 0.2 M)	[0.1, 0.05, 0.025] (Br = 0.005 M)	1.3	1.1	(90:10% v/v)
[0.03, 0.015, 0.0075] (Phenol = 0.2 M)	[0.3, 0.15, 0.075] (Br = 0.02 M)	1.3	1.0	(85:15% v/v)
[0.02, 0.01, 0.005] (Phenol = 0.2 M)	[0.2, 0.1, 0.05] (Br = 0.01 M)	1.3	1.0	(85:15% v/v)

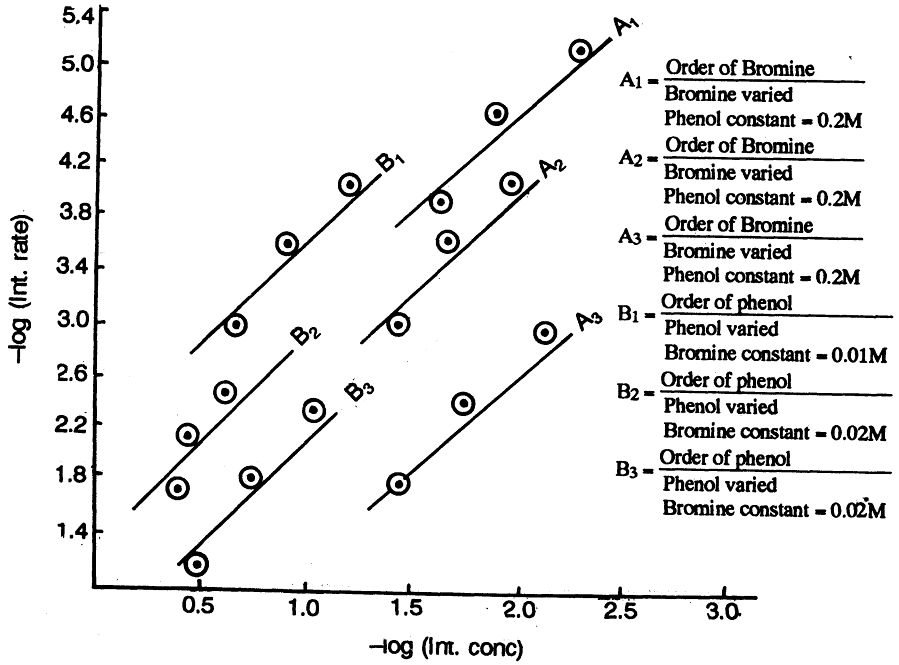

Fig. 2 Bromination of 2,4-Dinitrophenol; Solvent: (AcOH : H_2O)
$A_1 : B_1$ = (95.5% v/v); $A_2 : B_2$ = (90 : 10% v/v) : $A_3 : B_3$ = (85 : 15% v/v)

TABLE 3
INDIVIDUAL ORDERS DETERMINED FROM THE INITIAL RATE AT 30°C

Substrate	Bromine	Phenol	Solvent ($AcOH : H_2O$) v/v
2,4-Dinitrophenol	1.3	1.1	(95 : 5%)
–do–	1.3	1.0	(90 : 10%)
–do–	1.2	1.1	(85 : 15%)

In the overall third order process at higher concentration region (E) may be the bromine molecule, which acts as an electrophile at the rate determining step. In the overall second order process at lower concentration region in 95% and 90% aqueous acetic acid the reaction may be pseudo second order, as the solvent molecules ($AcOH:H_2O$) participates and acts as an electrophile in the rate determining step. Where as in 85% aqueous acetic acid order is decreased even at higher concentration, it may be due to H_2O, as it participate and acts as an electrophile at the rate determining step. (Fig-1)

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