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Catalysed Bromination of p-hydroxy Biphenyl and o-hydroxybiphenyl in Acetic Acid Solvent

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Kinetics of Iodine bromide catalysed bromination of p-hydroxybiphenyl and o-hydroxybiphenyl has been investigated in glacial acetic acid. Overall order is three and individual order being one with respect to each reactant and catalyst. The bromination phenomenon of catalytic maximum has been investigated. On the basis of the observed facts reaction mechanism is also discussed.

INTRODUCTION

In the bromination of phenols, a number of substances such as iodine[1], anhydrous aluminium chloride[2], ferric chloride[3] and zinc chloride[4] have been used as catalysts. In the case of iodine, the effective catalyst has been shown to be iodine bromide[5,6]. In the studies presented here, it is decided to investigate the iodine bromide catalysed bromination of p-hydroxy and o-hydroxybiphenyl under such conditions that the iodine-bromide can act as a catalyst instead of acting as the source of bromine. The very high equilibrium constant for the formation of iodine bromide in acetic acid[6,7] suggests that all the iodine is in the form of iodine bromide. Thus by maintaining the concentration of bromine at higher value compared to that of iodine, the free bromine present could act as the brominating agent and this process can be catalysed by the presence of iodine bromide. *Catalytic maxima in the bromination of p-hydroxy and o-hydroxy biphenyl compounds*:

It has been previously reported[6-9] that at the constant concentrations of bromine and the substrate, the rate of reaction passes through a maximum, by the addition of increasing amounts of iodine to the reaction mixture. In the IBr-catalysed bromination of p-hydroxy and o-hydroxy biphenyl compounds, it is observed that at the constant concentrations of phenol and bromine the increase in concentration of iodine resulted in passing the rate through a maximum. Hence iodine bromide is considered to be the effective catalyst. The composition of the effective catalyst has been determined from the ratios of the reactants at the catalytic maxima.

This method for determining catalytic maximum also helps in determining the order with respect to iodine bromide and with respect to free bromine.

EXPERIMENTAL

The phenol, iodine bromide and bromine mixture in acetic acid (5 ml. each) in test tube and glass stoppered bottles respectively were placed in a thermostat at the required temperature. Iodine bromide was prepared by mixing equimolar solutions of iodine and bromine in acetic acid in equal volumes. After the solutions reached the bath temperature, the phenol solution was added quickly into the iodine bromide and bromine solution and the mixture was allowed to react for a definite time, after which potassium iodide (10%, 5 ml) was added to stop the reaction. Immediately after one minute the liberated iodine was titrated against standard solution of sodium thiosulphate.

The glacial acetic acid (S. Merk) was purified according to Orton's[10] procedure. p-hydroxybiphenyl and o-hydroxybiphenyl (SISCO) were recrystallised and then used. Bromine, iodine and potassium iodide (BDH) were used.

The kinetic studies have been made by determining the concentration of bromine iodometrically and expressing it as the function of time. The overall orders have been evaluated by fractional life method and individual orders from the initial rates.

RESULTS AND DISCUSSION

Overall order for the IBr-catalysed bromination of p-hydroxy and o-hydroxybiphenyls has been found to be three. Order is independent of the concentrations of the reactants. The individual orders of phenols bromine and iodine bromide were determined by initial rates and found as one in each (Table 1).

The phenomenon of catalytic maximum has been investigated by plotting a graph between I_2/Br_2 and IBr/Br_2 against the initial rate values. The catalytic maxima for the order of bromine and iodine bromide were found to be 0.33 and 1.0 respectively. This indicates that at the maximum rate there are three moles of bromine for every one molecule of iodine and the concentrations of IBr and free bromine are equal. This stands an additional support for the view that iodine bromide is the effective catalyst.

The effect of temperature on the rate constant of p-hydroxy biphenyl and o-hydroxy biphenyl was established (using pseudofirst order formula) using a mixture of phenol (0.01M) bromine (0.02M) and iodine bromide (0.01M) over the temperature range 25°–45°C. The rate constants for the reaction at the different temperatures were plotted against 1/T and activation parameters calculated.

TABLE 1

DETERMINATION OF INDIVIDUAL ORDERS IN ACETIC ACID AT 30°C (BY INITIAL RATES)

Initial rate × 10^4 (mole L^{-1} sec^{-1})	Initial conc. (mol L^{-1})	Order
Substrate: p-hydroxy biphenyl		
Order of phenol: Br_2 and IBr 0.02M: constant, phenol varied		
85.7	0.1	
25.0	0.05	1.2
7.5	0.025	
Order of Br_2: Phenol=0.1M, IBr=0.02M: constant, Br_2 varied		
80.0	0.04	
30.0	0.02	1.1
12.0	0.01	
Order of IBr: Phenol=0.1M, Br_2=0.02M: constant, IBr varied		
5.0	0.025	
2.5	0.05	1.0
1.8	0.10	
Substrate: o-hydroxy biphenyl		
Order of phenol: Br_2=IBr=0.002M: constant, phenol varied		
66.0	0.1	
25.0	0.05	1.2
08.3	0.025	
Order of Br_2: Phenol 0.1M, IBr=0.02 M: constant, Br_2 varied		
80.0	0.04	
20.0	0.02	1.2
0.6	0.01	
Order of IBr: Phenol=0.1M, Br_2=0.02M: constant, IBr varied		
6.6	0.02	
3.3	0.04	1.1
2.1	0.08	

TABLE 2

ACTIVATION PARAMETERS

IBr-catalysed bromination of p-hydroxy and o-hydroxy biphenyls

Solvent: AcOH
(Phenol)=(IBr)=0.01M
(Br_2)=0.01M

Substrate	ΔE KJ mol^{-1}	ΔH KJ mol^{-1}	$-\Delta S$ KJ mol^{-1}	ΔF KJ mol^{-1}	log A
p-hydroxy biphenol	53.5	50.8	143.5	90.8	5.1
o-hydroxy biphenol	49.6	47.1	149.6	89.4	5.2

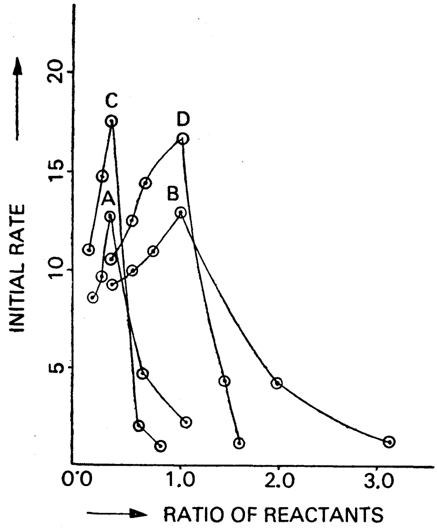

Fig. 1 IBr-catalysed bromination of o⁻ and p⁻-hydroxybiphenyl. Catalytic Maxima, Solvent: ACOH, Temp.: 30°C.
(1) o⁻-hydroxybiphenyl: (A) I_2/Br_2, (B) IBr/Br_2,
(2) p⁻-hydroxybiphenyl: (C) I_2/Br_2, (D) IBr/Br_2.

On the basis of the observed facts reaction mechanism is discussed.

I. $(ArH) + (Br_2) \overset{K}{\rightleftharpoons} (ArHBr_2)$
II. $(ArHBr_2) + (IBr) \rightarrow (ArHBr)^+ + IBr_2^-$ (slow)
III. $(ArHBr)^+ \rightarrow (ArBr) + H^+$ (fast)
IV. $IBr_2^- + H^+ \rightarrow HBr + IBr$ (fast)

This leads to the rate expression.

Rate = K_3 (ArH) (Br_2) (IBr). The IBr molecule acts as electrophile in the rate determining step. IBr reacts on aromatic substrate halogen complex and removes the bromide ion as IBr_2^-.

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