



VOLTAMETRIC KINETICS OF BROMINATION OF REGIO-ISOMERS OF CHLOROPHENOL BY N-BROMOSUCCINAMIDE IN AQUEOUS SOLUTION

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Abstract: The rotating platinum electrode, RPE¹ has been used much less frequently than the Dropping Mercury Electrode in voltametric measurements. Nevertheless, it is for the study of the kinetics of fast reactions. The bromination of phenols and their derivatives are usually very fast and their kinetics have been studied only by indirect methods. Since these reactions follow second order kinetics, their half-lives can be made long enough for convenient kinetic measurements by making the solutions dilute enough and since, by means of RPE, it is possible to measure even very low concentrations of N-Bromosuccinimide (NBS), the course of such reactions can be directly followed. As typical instances, the kinetics of bromination of o-chlorophenol, m-chlorophenol and p-chlorophenol in aqueous solution have been studied. In these reactions only NBS is reducible at the RPE among the reactants and products.

Keywords - Regio-isomers, Bromination, Voltammetry, N-Bromosuccinimide, Rotating Platinum Electrode.

Introduction

Halogenated compounds are very important in organic synthesis. These compounds are often used in preparation of organometallic reagents^{2,3} and coupling reactions⁴⁻⁸. They are also used as pesticides, disinfectants⁹, herbicides and other commercially available products¹⁰. Halogenations of aromatic compounds are electrophilic aromatic substitution reactions¹¹. Electrophilic aromatic bromination is an important reaction known to organic chemist. Among these bromination reactions are rapid as compared to iodination reactions¹².

In present study, kinetics of bromination of regioisomers of chlorophenol has been carried out. Since the reactions are too rapid to be studied by conventional techniques, it has been studied by the use of rotating platinum electrode (RPE)¹³⁻¹⁷. RPE operates on the principle of zero potential versus saturated calomel electrode. At this principle, only N-Bromosuccinimide yields diffusion current equal to its concentration during the course of reaction. Neither the substrate nor the products of the reaction yield any diffusion current. Hence, the course of reaction can be followed by the monitoring the concentration of unreacted NBS by measuring diffusion current at various intervals of time.

The kinetic measurement of the bromination of o-chlorophenol, m-chlorophenol and p-chlorophenol by NBS has been carried out at four different temperatures. The specific reaction rate, K, energy of activation, E_a and Arrhenius factor, A, has been found out. Hence, the thermodynamic parameters such as enthalpy of activation, ΔH[‡], entropy of activation ΔS[‡] and free energy of activation, ΔG[‡] have been evaluated.

Material and Methods

Chemicals

Analytical grade chemicals were used in the present study. Stock solutions of 5.0 x 10⁻⁵ M NBS, o-chlorophenol, m-chlorophenol and p-chlorophenol were prepared in double distilled water. 1.0 x 10⁻² M potassium chloride was prepared as the supporting electrolyte. Required concentrations of reactants was prepared from stock solutions.

Electrodes

The electrodes used in the present study are rotating platinum electrode (as a cathode) and saturated electrode (as an anode).

Method

Rotating platinum electrode was constructed in the laboratory. It consists of inverted T-shaped glass tube 50 cm long and 5 mm in diameter, filled with mercury. About 5 mm of platinum wire protrudes from T-shaped glass tube. A copper wire is dipped in the glass tube for electrical contact. The assembly is mounted on a pair of pulleys. It was adjusted so that rotates at the speed of 600 rpm by synchronous motor. The T -shape of the glass tube acts as a stirrer while rotating. It operates on the principle of 0.0 Volt versus saturated calomel electrode applied at RPE. Only NBS yields diffusion current proportional to its concentration, whereas neither the substrate nor the product of the reaction yields any diffusion current. Therefore, the course of reaction can be followed by monitoring the concentration of unreacted NBS from measurement of the diffusion current at intervals of time.

Calibration of Diffusion Current

The diffusion currents at RPE for different concentrations of NBS, ranging from 1.0×10^{-5} M to 5.0×10^{-5} M, containing supporting electrolyte (1.0×10^{-2} M) are determined. The plot of diffusion current versus concentration of NBS is found to be linear at all the temperatures (Table 1 and Figure 1).

Table: 1
Calibration of the diffusion current of NBS at various temperatures for bromination of isomers of chlorophenol in aqueous medium

[NBS] / 10^{-5} M	Diffusion current (cm)			
	15.0 °C	20.0 °C	25.0 °C	30.0 °C
1	8.0	8.5	9.0	9.5
2	16.0	17.0	18.0	19.0
3	24.0	25.5	27.0	28.5
4	32.0	34.0	36.0	38.5
5	40.0	42.5	45.0	48.0

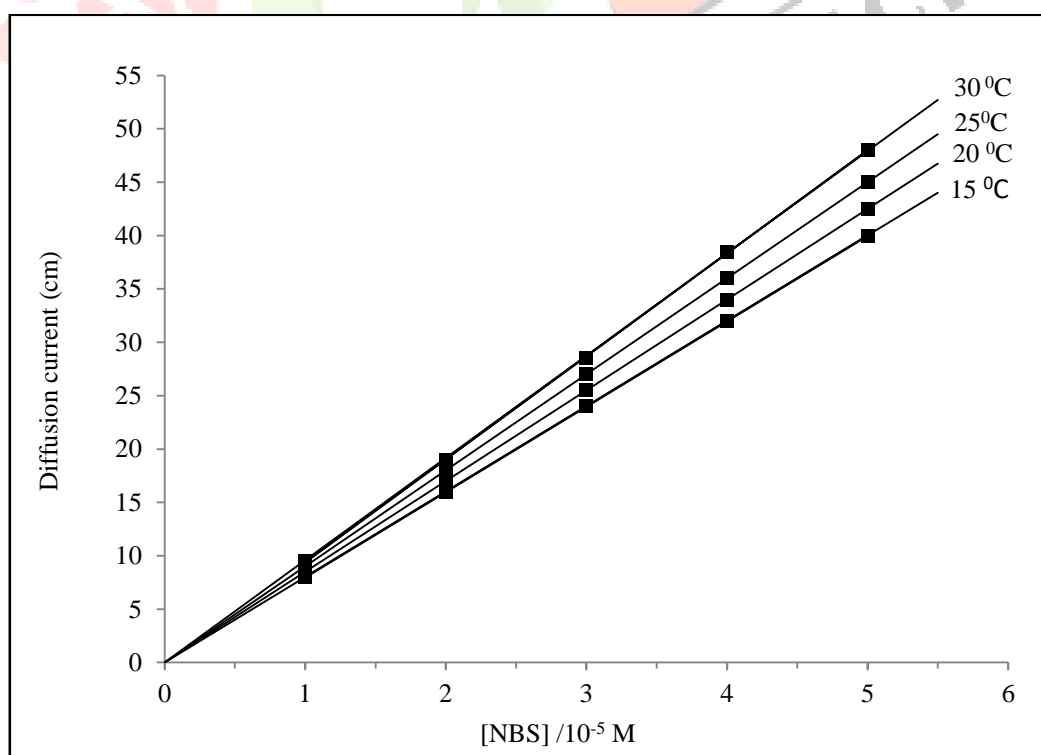


Figure: 1

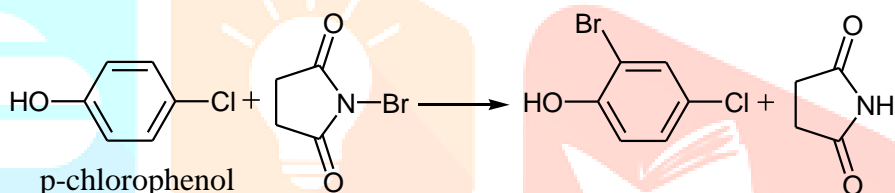
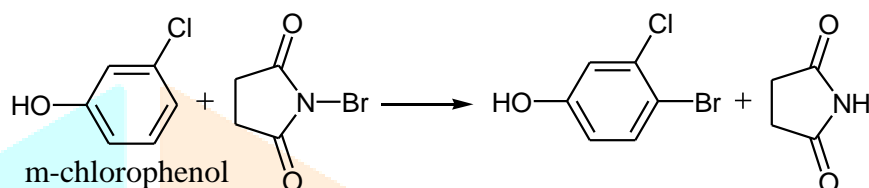
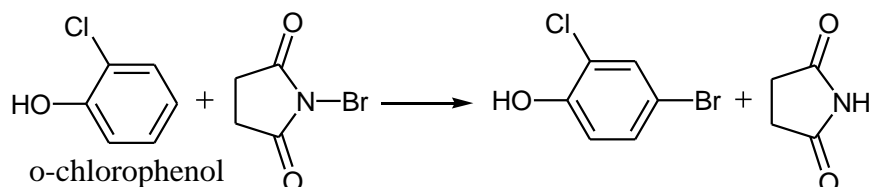
Calibration of the diffusion current of NBS at various temperatures for bromination of isomers of chlorophenol in aqueous medium

Kinetic Measurements

Equimolar solutions of NBS and o, m, and p-chlorophenol, containing 1.0×10^{-2} M potassium chloride as a supporting electrolyte were rapidly mixed in a 250 ml cell containing RPE and SCE. Simultaneously a stop-watch was started. The diffusion current due to NBS reduced at RPE was measured with Galvanometer deflection with lamp and scale arrangement. The Galvanometer deflections were calibrated previously with various concentrations of NBS under identical experimental conditions. From these, the concentrations of unreacted NBS were determined at various intervals of time.

Result and Discussion

In all reactions one mole of each chlorophenol reacts with one mole of NBS and gives one mole of bromo-chlorophenol and one mole of succinimide as a product.



The plot of $[\text{NBS}]^{-1}$ versus time is satisfactorily linear in each chlorophenol isomer. It indicates that bromination of chlorophenol isomers by NBS is first order with respect to each reactant and hence the overall reactions are of second order. In a typical case of o-chlorophenol the slope of the plot gives specific reaction rate (Table 2 and Figure 2).

Table: 2

Kinetics of bromination of o-chlorophenol by N-Bromosuccinimide in aqueous solution at 25.0 °C

Time in seconds	Diffusion current /cm	[NBS] unreacted / 10^{-5} M	$[\text{NBS}]^{-1} / 10^4 \text{ M}^{-1}$
0	45.0	5.00	2.00
10	39.2	4.35	2.30
20	34.7	3.85	2.60
30	31.0	3.45	2.90
40	28.5	3.17	3.15
50	26.1	2.90	3.45
60	24.0	2.67	3.75
70	22.2	2.47	4.05
80	20.7	2.30	4.35
90	19.4	2.15	4.65
100	18.2	2.02	4.95
110	17.1	1.90	5.25
120	16.4	1.82	5.50

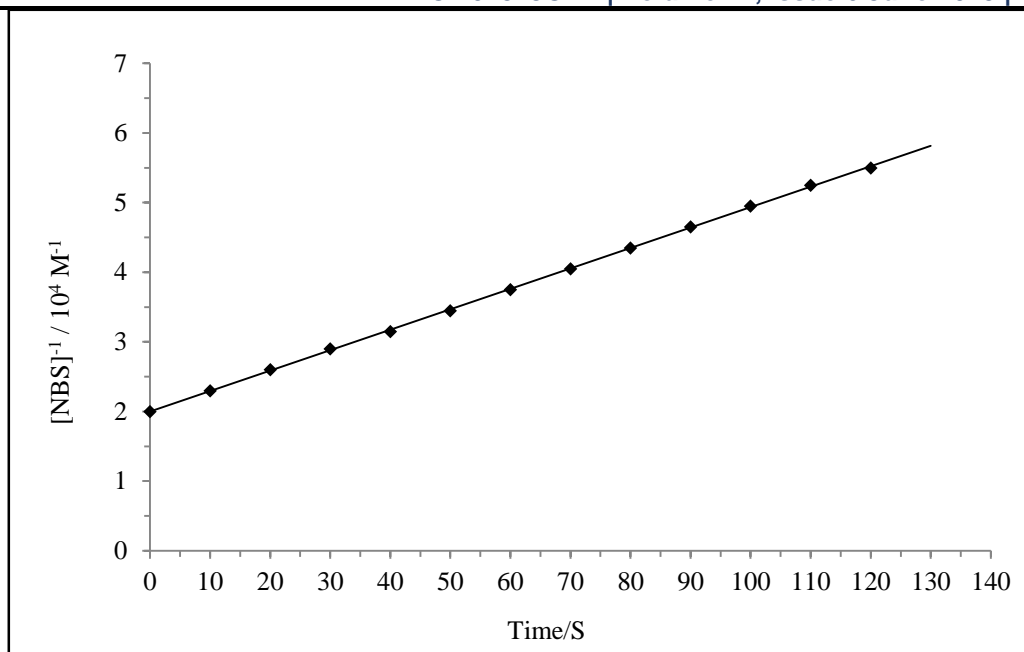


Figure: 2

Kinetics of bromination of o-chlorophenol by N-Bromosuccinimide in aqueous solution at 25.0 °C

Slope of plot of $[\text{NBS}]^{-1}$ versus time = Specific reaction rate, $(k) = 292 \text{ M}^{-1} \text{ S}^{-1}$

The specific reaction rates of bromination of o-chlorophenol, m-chlorophenol and p-chlorophenol by NBS in aqueous solution at 25.0 °C are found to be $292 \text{ M}^{-1} \text{ S}^{-1}$, $2983 \text{ M}^{-1} \text{ S}^{-1}$, $375 \text{ M}^{-1} \text{ S}^{-1}$ respectively.

For evaluation of thermodynamic parameters, the specific reaction rates were determined at four different temperatures, ranging from 15.0 °C to 30.0 °C. The plots of $\log k$ versus reciprocal of absolute temperature were satisfactorily linear.

From slopes of the plot, activation energies were evaluated. The energies of activation for o-chlorophenol, m-chlorophenol and p-chlorophenol were found to be $37.1 \text{ KJ mole}^{-1}$, $33.9 \text{ KJ mole}^{-1}$, and $40.0 \text{ KJ M}^{-1} \text{ S}^{-1}$ respectively. The corresponding Arrhenius factors are $9.25 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$, $26.0 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$ and $38.3 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$.

The free energies of activations (ΔG^\ddagger), enthalpies of activations (ΔH^\ddagger) and entropies of activations (ΔS^\ddagger) were evaluated and found to be as depicted in Table 3, Table 4, Table 5 and Table 6.

Table: 3

Kinetics of bromination of o-chlorophenol by NBS at various temperatures in aqueous solution.

Temperature/K	$[T]^{-1} 10^{-3} \text{ K}^{-1}$	$k/ \text{M}^{-1} \text{ S}^{-1}$	$\log k$
288	3.47	170	2.230
293	3.41	223	2.348
298	3.35	292	2.465
303	3.30	363	2.560

Table: 4

Kinetics of bromination of m-chlorophenol by NBS at various temperatures in aqueous solution.

Temperature/K	$[T]^{-1} 10^{-3} \text{ K}^{-1}$	$k/ \text{M}^{-1} \text{ S}^{-1}$	$\log k$
288	3.47	1817	3.2593
293	3.41	2341	3.3694
298	3.35	2983	3.4746
303	3.30	3633	3.5603

Table: 5
Kinetics of bromination of p-chlorophenol by NBS at various temperatures in aqueous solution.

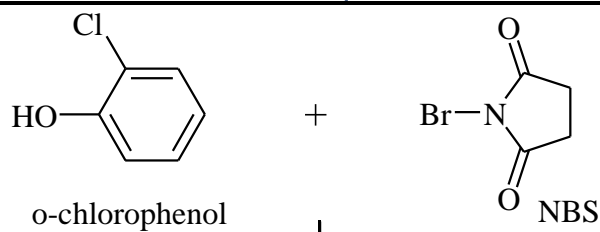
Temperature/K	$[T]^{-1} 10^{-3} K^{-1}$	$k / M^{-1} S^{-1}$	log k
288	3.47	209	2.3201
293	3.41	278	2.4440
298	3.35	375	2.5740
303	3.30	474	2.6757

Table: 6
Comparison of the kinetics and thermodynamic parameters for the bromination of chlorophenols by NBS in aqueous solution at 25.0 °C.

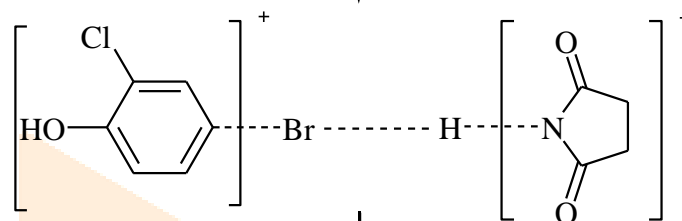
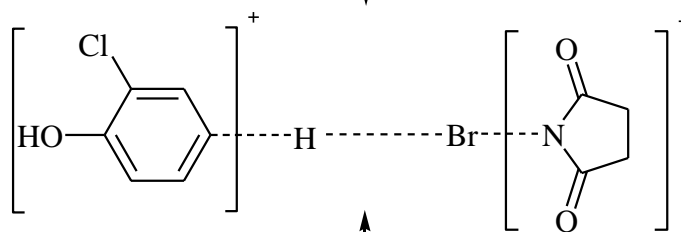
Sr. No.	Parameters	o-chlorophenol	m-chlorophenol	p-chlorophenol
1	Initial reactant concentration / M	5.0×10^{-5}	5.0×10^{-5}	5.0×10^{-5}
2	Specific reaction rate, $k / M^{-1} S^{-1}$	292	2983	375
3	Energy of activation, $E_a / KJ \text{ mole}^{-1}$	37.1	33.9	40.0
4	Frequency factor, $A / M^{-1} S^{-1}$	9.25×10^8	26.0×10^8	38.3×10^8
5	Free energy of activation, $\Delta G^\ddagger / KJ \text{ mole}^{-1}$	58.93	53.17	58.31
6	Enthalpy of activation, $\Delta H^\ddagger / KJ \text{ mole}^{-1}$	24.25	21.70	20.73
7	Entropy of activation, $\Delta S^\ddagger / KJ \text{ mole}^{-1}$	-81.58	-72.99	-69.77

There are different opinions on bromination by NBS¹⁸⁻¹⁹. According to some researchers, NBS may hydrolyze to form HOBr in aqueous solution and it may act as a brominating agent. If NBS slowly hydrolyses to HOBr, it would be rate determining step in bromination of o, m, and p-chlorophenol and hence the specific reaction rates of bromination of o, m, and p-chlorophenol would be the same. But experimental result shows that the specific reaction rates are $292 M^{-1}S^{-1}$, $2983 M^{-1}S^{-1}$, $375 M^{-1}S^{-1}$ respectively at 25.0 °C. It implies that NBS is the brominating agent and not HOBr.

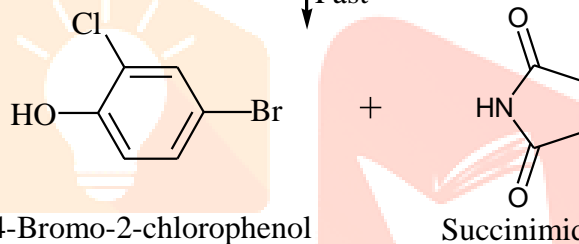
With these observations, the most probable mechanism for bromination of o, m, and p-chlorophenol by NBS is proposed as shown below in scheme 1, 2 and 3 respectively.



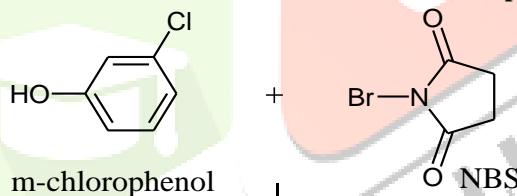
RDS



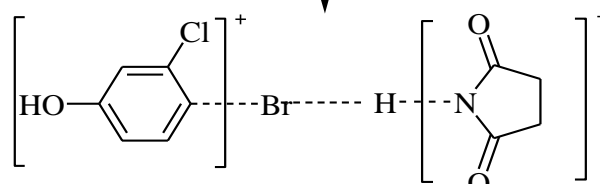
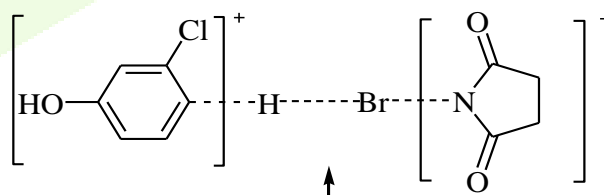
Fast



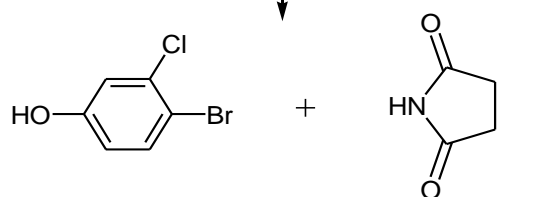
Scheme 1: Mechanism of bromination of o-chlorophenol



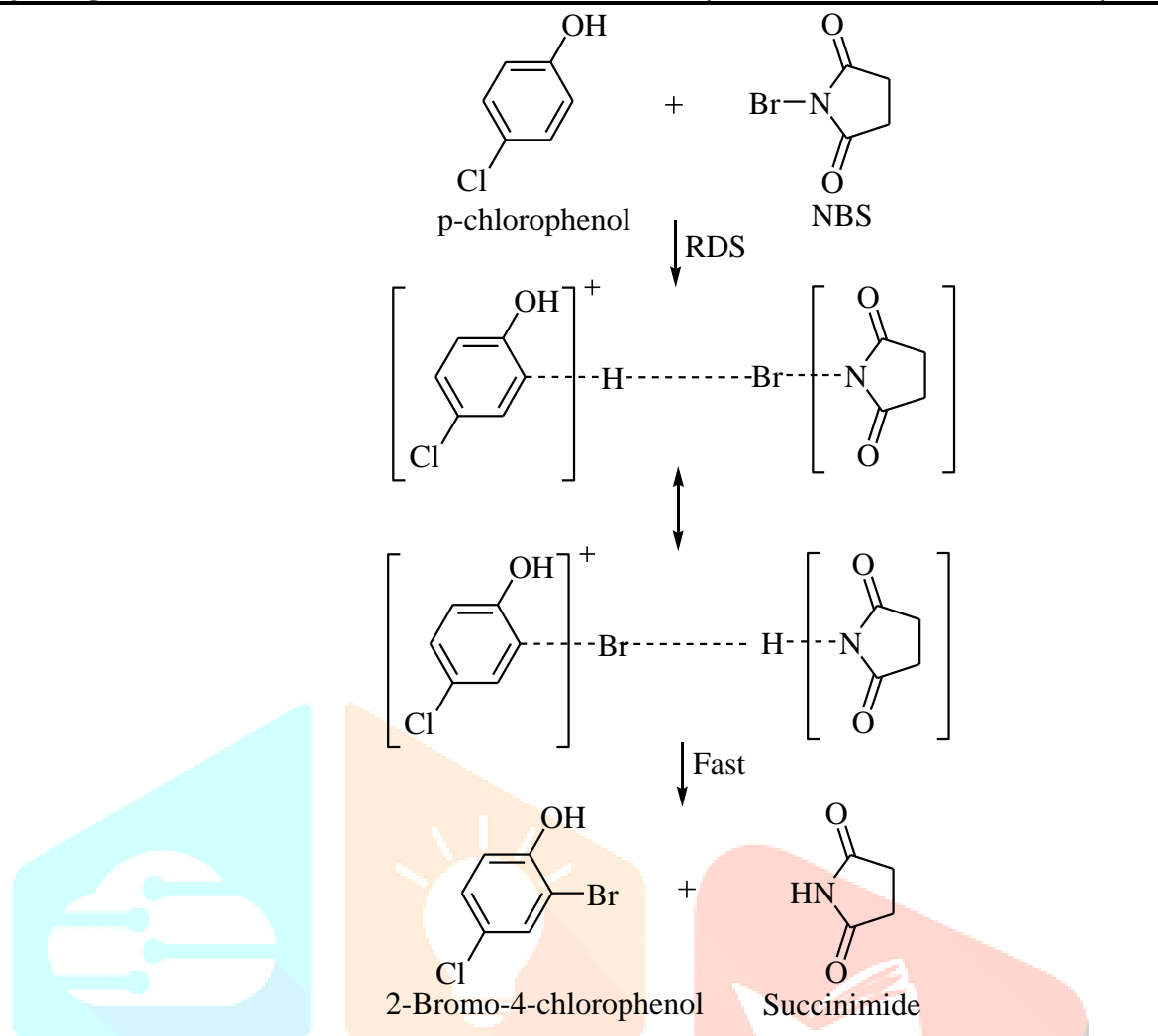
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Fast



Scheme 2: Mechanism of Bromination of m-chlorophenol



Scheme 3: Mechanism of Bromination of p-chlorophenol

In NBS, N-atom have more electronegativity than Br atom, hence N and Br atom carry incipient negative and positive charge respectively. Therefore, it is possible that NBS can complex with o, m, and p-chlorophenol in rate determining step to give intermediate complex, which decomposes by halogen transfer and in fast step, proton will be abstracted by NBS anion to lead succinimide and Bromo-chlorophenol.

Comparative Kinetic Study of Isomers of Chlorophenol

Comparison of rate of bromination of isomers of chlorophenol by NBS in aqueous solution (Table 6) reveals that the reactivity of o-chlorophenol, m-chlorophenol and p-chlorophenol is in the order of



In these isomers both the –OH and –Cl groups are ortho- para directing. In these cases, electronic effect plays more important role than the stereospecificity. Hence the rate of bromination decreases in the case of o-chlorophenol than p-chlorophenol than m-chlorophenol. Both the ortho- para directing effect operate in unison in m-chlorophenol, which is confirmed from the highest rate of bromination observed for this compound. The other two chlorophenols have relatively lower reactivity in terms of rate of bromination due to lack of unison activation effect of the two substituent groups. There is steric congestion of –OH and –Cl group in o-chlorophenol, which results in loss of co-planarity. It causes deteriorated aromaticity of the o-chlorophenol and shows lowest specific reaction rate among three isomers.

Conclusion

The bromination of chlorophenol isomers by NBS in aqueous solution gives very good bromo-derivatives of chlorophenols. The reaction followed first order kinetics in chlorophenols and first order in NBS. The overall reactions are of second order. The second order and moderate negative entropies of activation indicates that there is formation of intermediate complex and it is the rate determining step²⁰, which is followed by the transfer of Br⁺ electrophile to the aromatic ring of chlorophenol to lead a bromo-chlorophenol product. Thus, the relative speculated reactivities of chlorophenol isomers by NBS in aqueous solution is here by obtained.

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