

Voltammetric Kinetics of Bromination of the Regio-Isomers of Nitrophenol by N-Bromosuccinimide in Aqueous Solution

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Abstract: The rapid bromination kinetics of the regio-isomers of nitrophenol in aqueous solution by N-bromosuccinimide at 1.0×10^{-2} ionic strength has been studied by the rotating platinum electrode (RPE) techniques. The specific reaction rates for the bromination of the ortho, meta and para nitrophenol have been found to be 40.0, 5.67 and $20.0 \text{ m}^{-1}\text{s}^{-1}$ at 25°C respectively. The energy of activation, e_a and frequency factor, a , are evaluated. presumably due to rapidity of the reactions in aqueous solution necessitated a special technique rpe to measure unreacted NBS which is the only electro reducible species in the reaction. The kinetic data provides the relative substrate reactivity. The thermodynamic parameters are calculated.

Background: In voltammetry, dropping mercury electrode can not be used in rapid reactions due to its markedly positive potential of 0.4 volt against saturated calomel electrode because at this potential oxidation of mercury takes place. In place of dropping mercury electrode an inert platinum electrode can be used to extend the range of voltammetric measurements. The attainment of the steady diffusion current is very slow with stationary platinum electrode. This difficulty has been overcome by rotating platinum electrode at constant speed. In order to establish relation between diffusion current and concentration of the reactant, the speed of stirring must be kept constant during the reaction. The relative reactivity during bromination of regioisomers of nitrophenol were studied voltammetrically.

Materials And Methods: In this kinetic study the three regio-isomers of nitrophenol namely o-nitrophenol, m-nitrophenol and p-nitrophenol were subjected to bromination using the brominating reagent N-bromosuccinimide at temperature range of 15 to 30°C . The voltammetric technique was used with the employment of rotating platinum electrode at 600 rpm. The various kinetic parameters such as specific reaction rates, k , frequency factor, A , energy of activation, E_a , were evaluated. The thermodynamic parameters such as enthalpy of activation, Δh^\ddagger , entropy of activation, Δs^\ddagger and free energy of activation, ΔG^\ddagger were also determined.

Results: The relative reactivities of the regio-isomers of nitrophenol have been speculated quantitatively. The quantitative assessment was decided due to the rapidity of these reactions. Hence rotating platinum electrode was used to evaluate the specific reaction rates. The specific reaction rates of bromination of o-nitrophenol, m-nitrophenol and p-nitrophenol by NBS in aqueous solution at 25°C were found to be $40.0 \text{ m}^{-1}\text{s}^{-1}$, $5.67 \text{ m}^{-1}\text{s}^{-1}$ and $20.0 \text{ m}^{-1}\text{s}^{-1}$ respectively.

Conclusion: The relative reactivity for the bromination of regio-isomers of nitrophenol is $k_{(m\text{-nitrophenol})} < k_{(p\text{-nitrophenol})} < k_{(o\text{-nitrophenol})}$. The bromination of nitrophenol by NBS is overall second order reaction. The probable mechanism for this reaction is proposed. The RPE technique has been conveniently used rather than DME technique to study the rapid bromination reactions of regio-isomers of nitrophenol.

Key Word: Bromination; Kinetics; Voltammetry; Nitrophenol; Rotating Platinum Electrode (RPE).

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I. Introduction

Organic compound containing bromine molecules are of considerable commercial importance. They can be used as potential antiviral, antineoplastic, antifungal, antibacterial, antitumor and autooxidising agents. They can also be used as industrial intermediates in manufacture of agrochemicals, pharmaceuticals and other products such as medicinal, herbicides, pesticides and flame retardants¹⁻⁸, such compounds are also playing key role in preparation of organometallic reagents⁹⁻¹² and transition metal coupling reactions.¹³⁻¹⁶

Use of all the halogenated compounds in organic synthesis is well known.¹⁷ Generally, halogenations of organic compounds are electrophilic aromatic substitution reactions.¹⁸ Among these, electrophilic aromatic bromination are important reactions known to organic chemist. Brominations are rapid as compared to iodinations¹⁹. Therefore, it is necessary to study halogenation of aromatic compounds.

In present study, we have studied the kinetics of bromination of regio-isomers of nitrophenol by N-bromosuccinamide in aqueous medium (Figure -1) using (1×10^{-2} M) potassium chloride as supporting

electrolyte. The reactions under study are too rapid to be studied by conventional technique and hence has been studied by the voltammetric technique using rotating platinum electrode (RPE)²⁰. NBS gives diffusion current proportional to its concentration at RPE, whereas neither the isomers of nitrophenol nor the product yield diffusion current. Hence the course of reaction can be followed by measuring diffusion current at various intervals of time. Voltammetry is quite accurate and reproducible²¹⁻²².

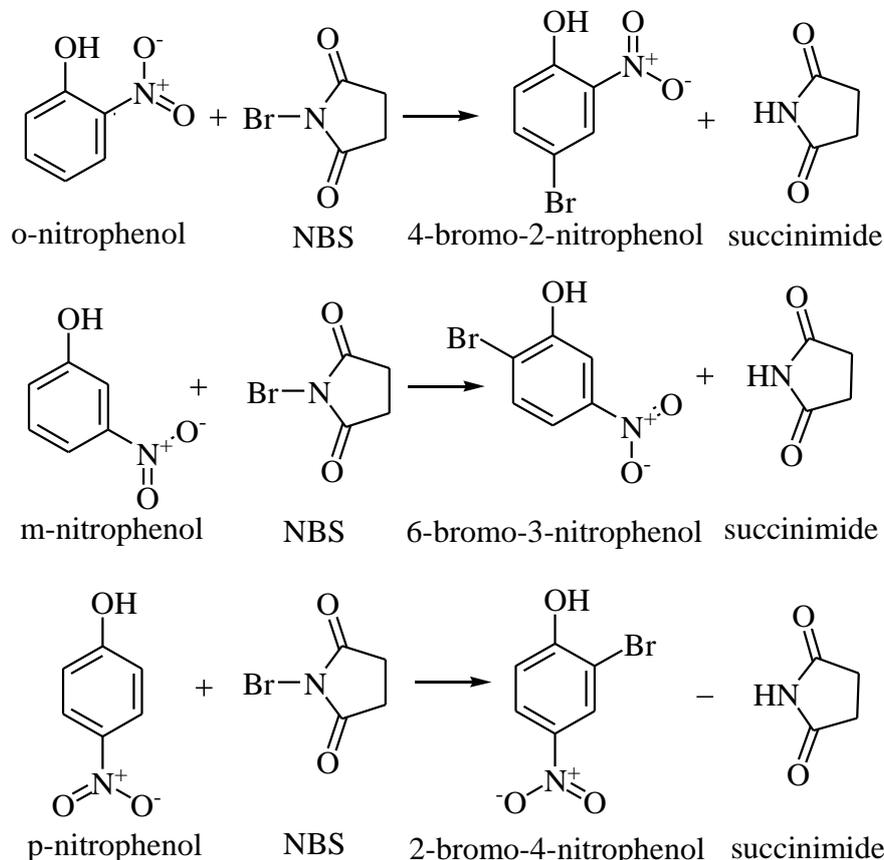


Figure 1: Bromination of ortho, meta and para-nitrophenols by N-Bromosuccinimide.

The kinetic measurement of the bromination of o-nitrophenol, m-nitrophenol and p-nitrophenol by NBS in aqueous solution has been carried out at four different temperatures to determine specific reaction rates, k , frequency factor, A , energy of activation, E_a , for reactions and hence the thermodynamic parameters such as enthalpy of activation, ΔH^\ddagger , entropy of activation, ΔS^\ddagger and free energy of activation, ΔG^\ddagger .

II. Material And Methods

2.1 Materials

Analytical grade o-nitrophenol, m-nitrophenol, p-nitrophenol and potassium chloride were used to prepare the stock solutions in doubly distilled water. Freshly prepared NBS solution was used throughout the experimental studies. The NBS solution was stable enough for a couple of days.

2.2 Electrodes

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

2.3 Rotating Platinum Electrode (RPE)

RPE consist of piece of platinum wire of 0.5 mm diameter. It is fused at the end of glass tube of 10 mm diameter so that 10 mm of the wire protrudes out. The electrode is fixed to a pulley and rotated at a speed of 600 rpm with the help of synchronous motor. This electrode is used in conjunction with saturated calomel electrode (SCE). It operates on the principle of 0.0 volt versus saturated calomel electrode applied at RPE. The diffusion current due to NBS is measured by a moving coil mirror galvanometer with lamp and scale arrangement and shunt.

2.4 Calibration of diffusion current

The rotating platinum electrode (RPE) and saturated calomel electrode (SCE) were introduced in several NBS solutions of concentration 0.5×10^{-4} M to 2.0×10^{-4} M, each in 1.0×10^{-2} M potassium chloride. The diffusion current was measured and plotted against concentrations of NBS (Table-1 and Figure-2).

2.5 Kinetic Measurements

Equimolar solutions of NBS and o-nitrophenol, m-nitrophenol and p-nitrophenol, containing 1.0×10^{-2} M potassium chloride supporting electrolyte were thermostated at 25.0°C . After the thermostat temperature was attained by all the solutions, the two reactant solutions were simultaneously added to reaction vessel kept in the thermostat in which the RPE was rotating and SCE was dipped. At the moment of mixing stop watch was already started. The diffusion current due to NBS reduced at RPE was measured with galvanometer deflection with lamp and scale arrangement. The Galvanometer deflections were already 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.

III. Result

Table-1: Calibration of the diffusion current in terms of the galvanometer deflection with respect to the concentration of the N-Bromosuccinimide at various temperatures (± 0.2 Error).

[NBS] / 10^{-4} M	Diffusion current / cm = μA (Galvanometer deflection)			
	15.0 $^\circ\text{C}$	20.0 $^\circ\text{C}$	25.0 $^\circ\text{C}$	30.0 $^\circ\text{C}$
0.5	10.5	11.2	12.0	12.5
1.0	21.2	22.5	24.0	25.0
1.5	32.0	34.0	35.5	37.0
2.0	42.5	45.0	47.5	50.0

Concentration of potassium chloride: 1.0×10^{-2} M, Potential applied at RPE vs. SCE: 0.0 Volt.

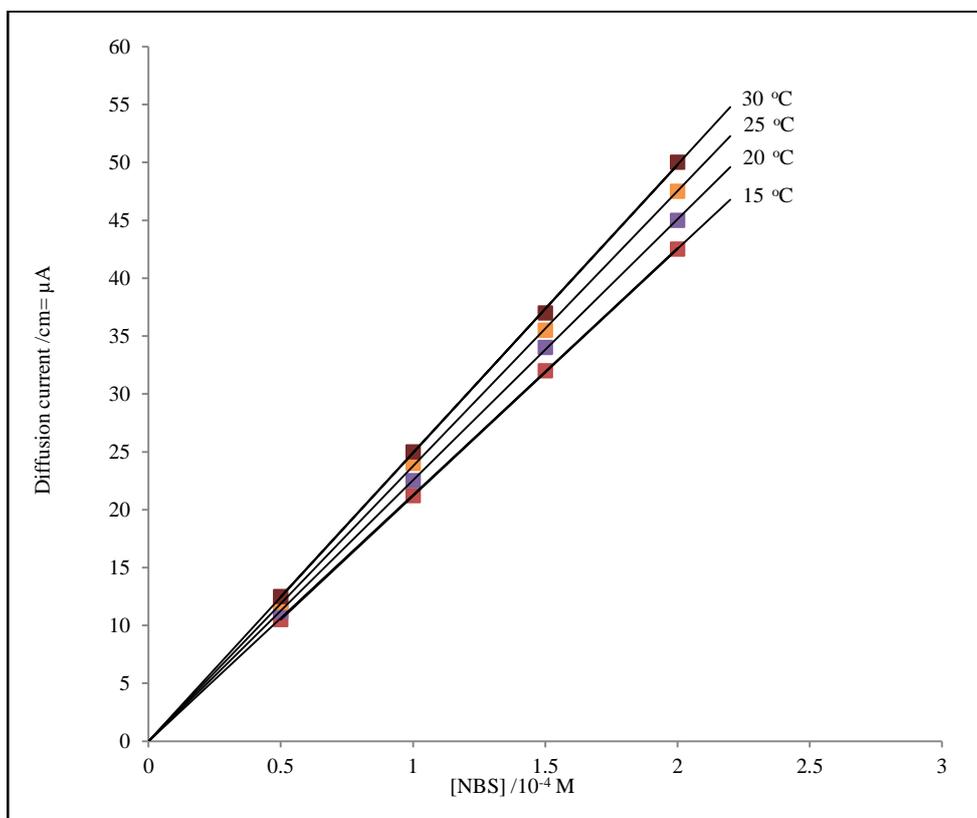


Figure 2: Calibration of the diffusion current in terms of the galvanometer deflection with respect to concentration of the N-Bromosuccinimide at various temperatures.

Table 2: Kinetics of bromination of o-nitrophenol by N-Bromosuccinimide in aqueous solution.

Concentration of o-nitrophenol : 2.0×10^{-4} M
 Concentration of N-Bromosuccinimide : 2.0×10^{-4} M
 Ionic Strength of supporting electrolyte : 1.0×10^{-2} M
 Temperature : 25.0 °C

Time in seconds	Diffusion current (Galvanometer deflection/cm)	Concentration of NBS unreacted(a - x)/ 10^{-4} M	$\frac{1}{(a-x)}/10^3M^{-1}$
0	47.0	2.00	5.00
10	43.5	1.85	5.40
20	40.4	1.72	5.81
30	37.5	1.61	6.21
40	35.5	1.51	6.62
50	33.6	1.43	7.00
60	31.7	1.35	7.40
70	30.1	1.28	7.81
80	28.7	1.22	8.20
90	27.3	1.16	8.62
100	26.1	1.11	9.00
110	24.9	1.06	9.43
120	24.0	1.02	9.80

Slope of plot of $\frac{1}{(a-x)}$ versus time = Specific reaction rate (k_2) = $40.0 M^{-1} S^{-1}$

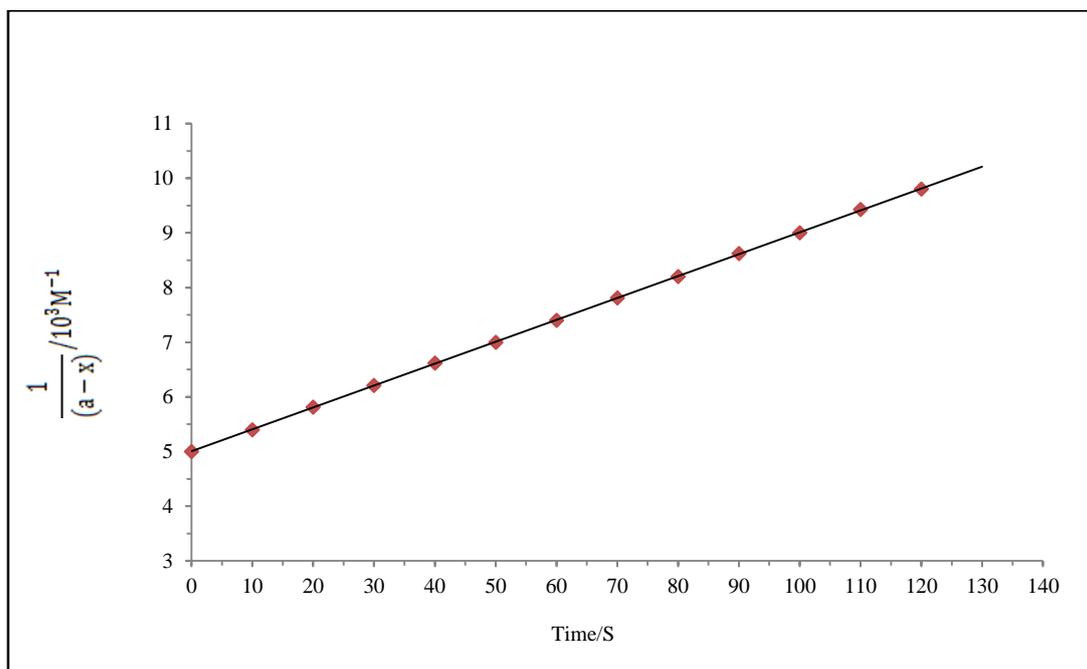


Figure 3: Kinetics of bromination of o-nitrophenol by N-Bromosuccinimide in aqueous solution.

Table-3: Kinetics of bromination of m-nitrophenol by N-Bromosuccinimide in aqueous solution.

Concentration of m-nitrophenol : 2.0×10^{-4} M
 Concentration of N-Bromosuccinimide : 2.0×10^{-4} M
 Ionic Strength of supporting electrolyte : 1.0×10^{-2} M
 Temperature : 25.0 °C

Time in seconds	Diffusion current (Galvanometer deflection/cm)	Concentration of NBS unreacted (a - x)/ 10^{-4} M	$\frac{1}{(a-x)}/10^3M^{-1}$
0	43.6	2.00	5.00
10	43.2	1.98	5.06
20	42.7	1.96	5.10
30	42.1	1.93	5.18
40	41.6	1.91	5.23
50	41.2	1.89	5.29
60	40.8	1.87	5.34
70	40.3	1.85	5.40
80	39.9	1.83	5.46

90	39.5	1.81	5.52
100	39.2	1.80	5.55
110	38.8	1.78	5.62
120	38.4	1.76	5.68

Slope of plot of $\frac{1}{(a-x)}$ versus time = Specific reaction rate (k_2) = $5.67 \text{ M}^{-1} \text{ S}^{-1}$

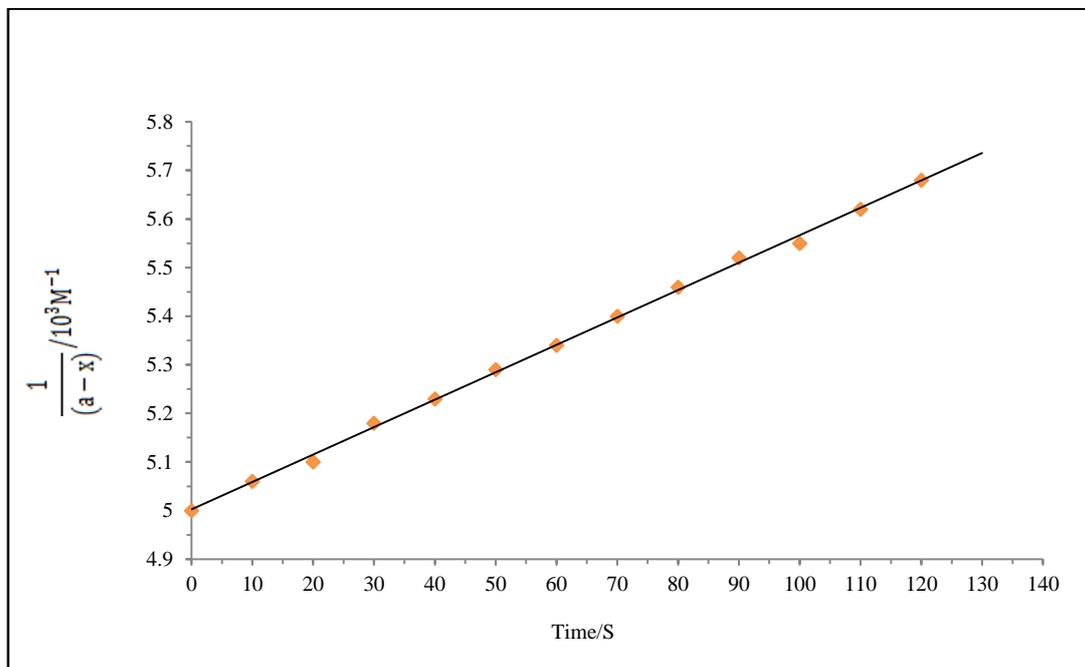


Figure 4: Kinetics of bromination of m-nitrophenol by N-Bromosuccinimide in aqueous solution.

Table 4: Kinetics of bromination of p-nitrophenol by N-Bromosuccinimide in aqueous solution.

Concentration of p-nitrophenol : $2.0 \times 10^{-4} \text{ M}$
 Concentration of N-Bromosuccinimide : $2.0 \times 10^{-4} \text{ M}$
 Ionic Strength of supporting electrolyte : $1.0 \times 10^{-2} \text{ M}$
 Temperature : $25.0 \text{ }^\circ\text{C}$

Time in seconds	Diffusion current (Galvanometer deflection/cm)	Concentration of NBS unreacted (a - x)/ 10^{-4}M	$\frac{1}{(a-x)}/10^3\text{M}^{-1}$
0	43.5	2.00	5.00
10	41.8	1.92	5.21
20	40.2	1.85	5.40
30	38.7	1.78	5.62
40	37.4	1.72	5.81
50	36.3	1.67	5.99
60	35.0	1.61	6.21
70	33.9	1.56	6.41
80	32.8	1.51	6.62
90	32.0	1.47	6.80
100	31.1	1.43	6.99
110	30.2	1.39	7.19
120	29.4	1.35	7.40

Slope of plot of $\frac{1}{(a-x)}$ versus time = Specific reaction rate (k_2) = $20.0 \text{ M}^{-1} \text{ S}^{-1}$

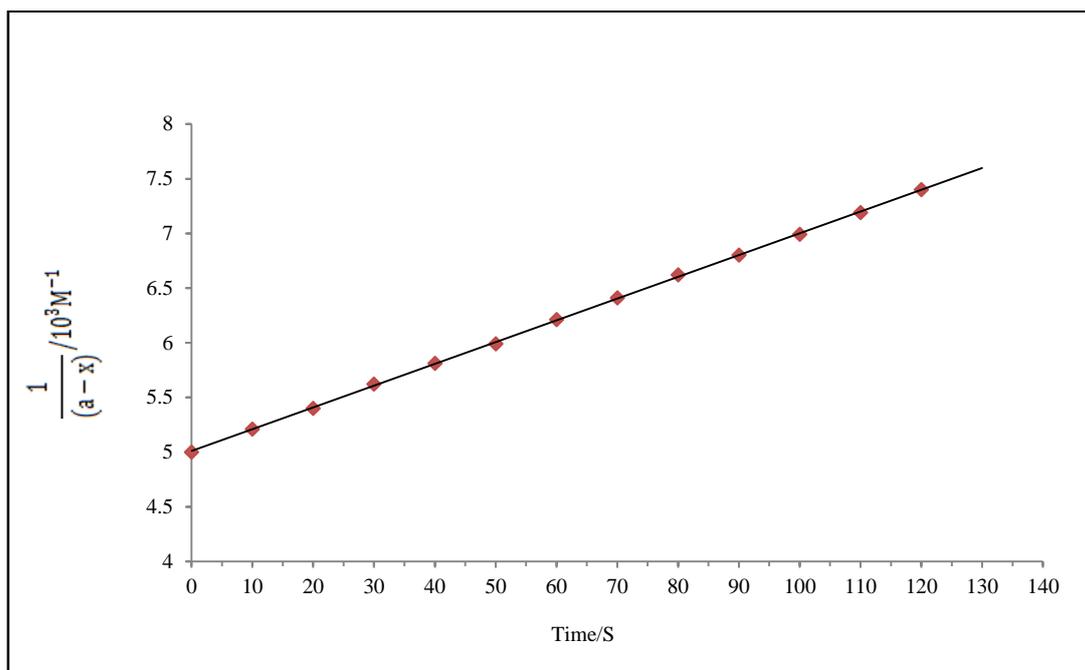


Figure 5: Kinetics of bromination of p-nitrophenol by N-Bromosuccinimide in aqueous solution.

Table 5: Comparison of the kinetics and thermodynamic parameters for the bromination of nitrophenols by NBS in aqueous solution at 25.0 °C.

Parameters	o-nitrophenol	m-nitrophenol	p-nitrophenol
Initial reactant concentration / M	2.0×10^{-4}	2.0×10^{-4}	2.0×10^{-4}
Specific reaction rate, $k / M^{-1} S^{-1}$	40.0	5.67	20.0
Energy of activation, $E_a / KJ \text{ mole}^{-1}$	36.0	53.0	48.4
Frequency factor, $A / M^{-1} S^{-1}$	0.81×10^8	110.0×10^8	60.6×10^8
Free energy of activation, $\Delta G^\ddagger / KJ \text{ mole}^{-1}$	63.85	68.69	65.57
Enthalpy of activation, $\Delta H^\ddagger / KJ \text{ mole}^{-1}$	30.27	18.11	19.59
Entropy of activation, $\Delta S^\ddagger / KJ \text{ mole}^{-1}$	-101.81	-61.00	-65.96

IV. Discussion

4.1 Kinetic study

The plot of diffusion current versus concentration is linear. From the observed galvanometer deflection during the kinetic study the concentration of unreacted NBS at various instant of time were evaluated. A plot of $[NBS]^{-1}$ versus time is satisfactorily linear in each nitrophenol. It indicates that bromination of nitrophenol isomers by NBS in aqueous solution is first order with respect to each reactant and hence the overall reaction is second order. The slope of the plot gives the specific reaction rate.

The specific reaction rates of bromination of o-nitrophenol, m-nitrophenol and p-nitrophenol by NBS in aqueous solution at 25 °C are found to be $40.0 M^{-1}S^{-1}$, $5.67 M^{-1}S^{-1}$ and $20.0 M^{-1}S^{-1}$ respectively (Table 2,3,4 and Figure 3,4,5).

The experiments are repeated at various temperature in the range of 15.0 °C to 30.0 °C to determine energy of activation, E_a , and frequency factor, A, and thermodynamics parameters such as free energy of activation, enthalpy of activation and entropy of activation at 25.0 °C of reaction (Table-5).

The activation energy (E_a) decreases from m-nitrophenol to p-nitrophenol to o-nitrophenol. Hence reactivity of bromination of o-nitrophenol > p-nitrophenol > m-nitrophenol. The negative entropy of activation obtained in all the three isomers of nitrophenol indicates that there is decrease in entropy of formation of transition state, which also indicates the associative mechanism for the single activated complex formation.

From the observed kinetic and thermodynamic data, the reactivity relation for the bromination of isomers of nitrophenol is;

$$k_{(m\text{-nitrophenol})} < k_{(p\text{-nitrophenol})} < k_{(o\text{-nitrophenol})}$$

4.3 Brominating Agent

There are variety of opinions on bromination by NBS²³⁻²⁴. According to some workers, NBS hydrolyse to form HOBr in aqueous solution and it may act as a brominating agent. If NBS hydrolyses to HOBr, it would be rate determining step (RDS) in bromination of isomers of nitrophenol and hence the specific reaction rates of

bromination of all the isomers of nitrophenol would be the same. But the observed data showed that the specific reaction rates for all the three isomers of nitrophenol are different. It implies that NBS is the only brominating agent and not a HOBr.

4.4 Mechanism of Bromination

On the basis of all the above observations, the most probable mechanism for the bromination of isomers of nitrophenol by NBS in aqueous solution would be as shown in Figure 6,7 and 8.

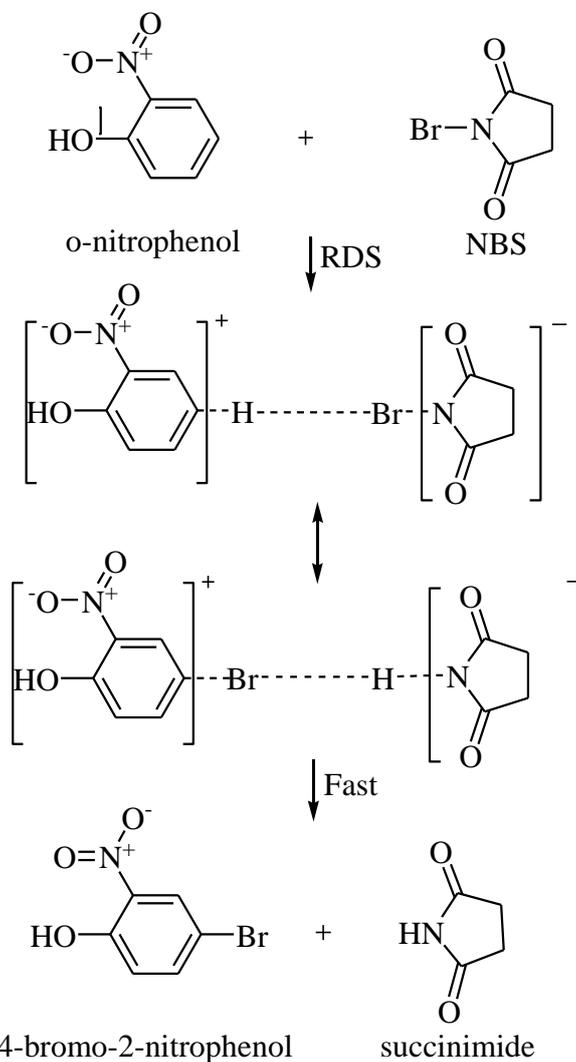


Figure 6: Proposed mechanism of bromination of o-nitrophenol

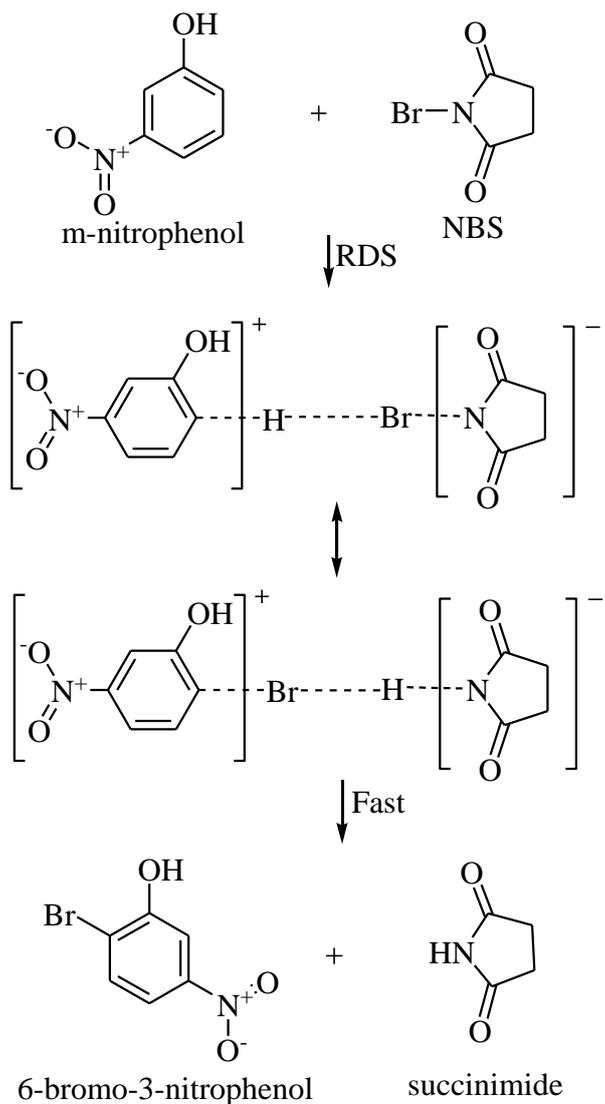


Figure 7: Proposed mechanism of bromination of m-nitrophenol

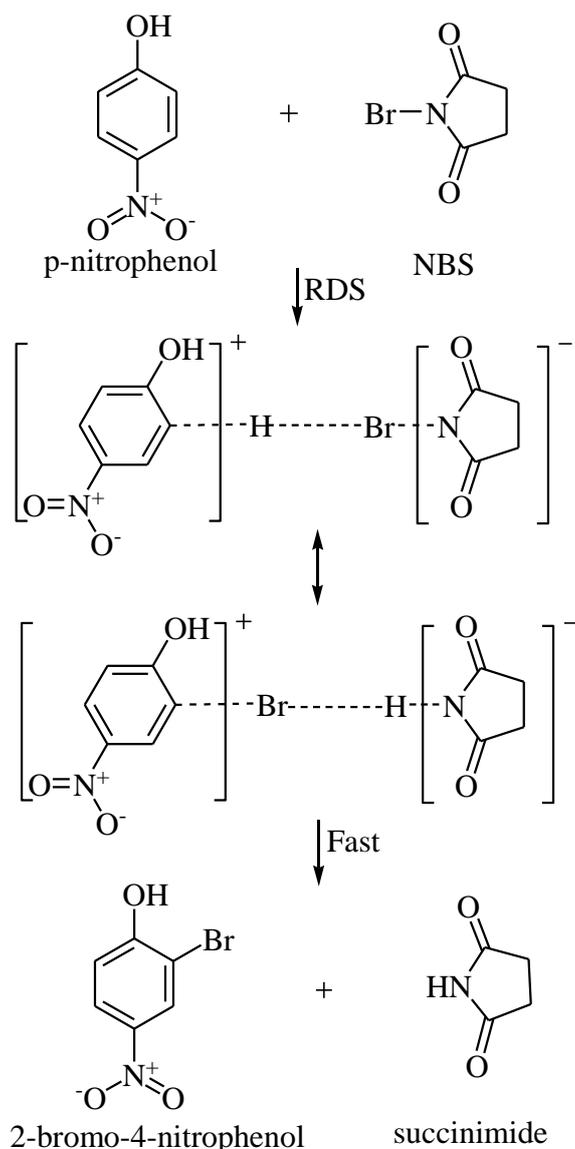


Figure 8: Proposed mechanism of bromination of p-nitrophenol

In NBS, N-atom is more electronegative than Br-atom, hence N atom carry incipient negative charge and Br atom carry incipient positive charge. Therefore, it is possible that NBS can complex with isomers of nitrophenol in RDS to give intermediate complex which further decomposes by Br atom transfer and in fast step H atom will be abstracted by NBS anions to give succinimide and bromo-nitrophenol as product.

4.5 Comparative Kinetic Study

It was observed that the reactivity of bromination of isomers of nitrophenol by NBS increases from m-nitrophenol to p-nitrophenol to o-nitrophenol. All the isomers contain -OH group which is ortho-para directing. In such a situation the stereo specificity decides the reactivity towards bromination of these isomers. The incoming electrophile (Br^+) was having more steric-hindrance in m-nitrophenol than p-nitrophenol than o-nitrophenol. Hence due to more steric-hindrance the bromination of m-nitrophenol was slowest with specific reaction rate $5.67 \text{ M}^{-1} \text{ S}^{-1}$. The p-nitrophenol at the same concentration of Br^+ ion gives specific reaction rate $20.0 \text{ M}^{-1} \text{ S}^{-1}$. The o-nitrophenol at the same concentration of Br^+ ion gives specific reaction rate $40.0 \text{ M}^{-1} \text{ S}^{-1}$.

V. Conclusion

The bromination of isomers of nitrophenol by NBS in aqueous solution gives bromo derivatives of nitrophenols. The overall reaction is second order. The relative reactivities of isomers of nitrophenol have been verified on qualitative as well as quantitative basis. These reactions were rapid and could not be studied by the

conventional techniques. The RPE technique has been conveniently used to study the rapid reactions of isomers of nitrophenol. On the basis of kinetic and thermodynamic data more probable mechanism has been proposed.

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