

## RESEARCH ARTICLE

## A Quantitative Assessment of the Comparative Reactivity of Pyridine in Bromination and Chlorination Reactions in Aqueous Solution by Molecular Halogens Using Hydrodynamic Voltammetry

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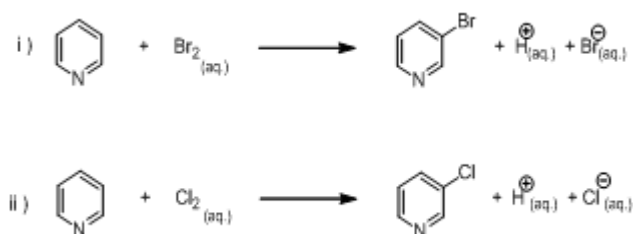
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Manuscript Details	ABSTRACT
<p>Received : 14.07.2015 Accepted: 02.09.2015 Published:05.10.2015</p> <p><b>ISSN: 2322-0015</b></p> <p><b>Editor: Dr. Arvind Chavhan</b></p> <p><b>Cite this article as:</b> Maske PD, Sangpal RR, Borkar VT and Dangat VT. A Quantitative Assessment of the Comparative Reactivity of Pyridine in Bromination and Chlorination Reactions in Aqueous Solution by Molecular Halogens Using Hydrodynamic Voltammetry, <i>Int. Res. J. of Science &amp; Engineering</i>, 2015; Vol. 3 (5):197-201.</p> <p><b>Copyright:</b> © Author(s), This is an open access article under the terms of the Creative Commons Attribution Non-Commercial No Derivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.</p>	<p>The rapid kinetics for the bromination and chlorination of pyridine by molecular halogens in aqueous medium at pH 7 using hydrodynamic voltammetry has been studied. The specific reaction rates at 295 K for the bromination and chlorination of pyridine are found to be respectively, <math>800 \text{ M}^{-1}\text{s}^{-1}</math> and <math>56 \text{ M}^{-1}\text{s}^{-1}</math> implying the greater reactivity for bromination. The energy of activation, entropy change and the pre-exponential factor for both these reactions are evaluated from the studies carried out at different temperatures. These data establish the relative reactivities of the two halogens toward the heterocycle in quantitative terms.</p> <p><b>Keywords:</b> Hydrodynamic Voltammetry, Pyridine, Molecular Halogens.</p> <p><b>INTRODUCTION</b></p> <p>Halogenations of aromatic substrate are known to be electrophilic substitution reactions and are rapid in aqueous medium (Berliner 1966). The rates of these reactions depend upon the electrophilicity of the electrophile, nucleophilicity of the aromatic ring and the nature of the aromatic substrate. As the electrophilicity of the electrophile and nucleophilicity of aromatic ring increase, the rates of these reactions increase. With greater steric hindrance, the reaction rates are lowered (Bonde <i>et al.</i>, 2013). Mono-halo derivatives of most aromatic substrates are carcinogenic in nature, while di and tri derivatives are known to have several pharmaceutical applications. Hence the rates and mechanisms of the formation of these derivatives are of significance.</p>

In aqueous medium, halogenations of aromatic substrates follow rapid kinetics necessitating the use of special techniques to measure their rates. (Bhore *et al.*, 1990) These include temperature jump, competition technique, stopped flow and pulse radiolysis technique.

Pyridine is a basic heterocyclic organic compound with the chemical formula  $C_5H_5N$ . It is structurally related to benzene, with one methine group replaced by a nitrogen atom and has pharmacodynamic significance. There seems to be a dearth of literature on the kinetics of halogenation of pyridine in aqueous medium presumably due to the rapidity of these reactions. (Borkar *et al.*) Herein it is attempted to establish on a quantitative basis the relative reactivity of pyridine in the bromination and chlorination reactions in the aqueous medium, by molecular halogens. For this purpose, the kinetics of the two reactions are investigated.

The reactions under study for the bromination and chlorination of pyridine can be represented as:



## MATERIALS AND METHOD

### Chemicals

**Molecular bromine:** A stock solution of  $\text{Br}_2$  is prepared in double distilled water and standardized iodometrically.

**Pyridine:** The required weight of A.R. grade Pyridine is used to prepare the stock solution in aqueous medium.

**Buffer Solutions:** Sodium dihydrogen phosphate and disodium hydrogen phosphate each 0.4 M is prepared.

**Potassium Nitrate:** A.R. grade Potassium nitrate is used to prepare a stock solution that is the supporting electrolyte.

### Electrodes

A platinum electrode fused to a glass tube rotated at 600 rpm with the aid of an A.C Motor is the cathode [RPE]. A saturated calomel electrode [SCE] is the anode. A constant potential of + 0.1V versus the saturated calomel electrode (SCE) is applied at the RPE, using a potentiometer.

A galvanometer with a sensitivity of  $0.10 \text{ nA cm}^{-1}$  provided with a lamp & scale arrangement is used for the measurement of the diffusion current due to the halogen in terms of the deflection of the galvanometer light spot. The current passing through the galvanometer is controlled by employing a shunt so that the deflection of the light spot is within scale limit.

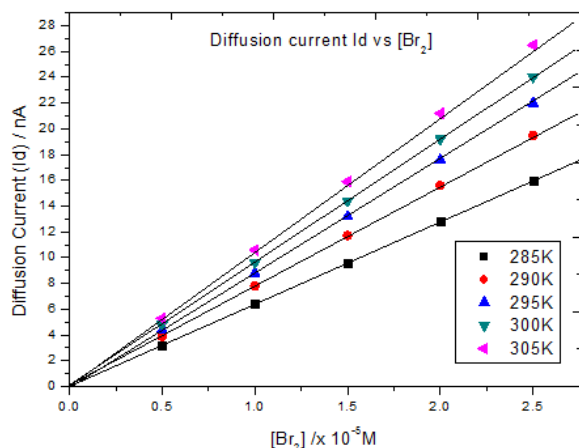
### Calibration

The RPE and SCE are dipped in 100 mL of  $5 \times 10^{-3} \text{ M}$  potassium nitrate which is the supporting electrolyte. A potential of + 0.1V at the RPE with respect to the SCE, is applied and the galvanometer light spot is adjusted to zero deflection on the scale. The potassium nitrate solution is replaced by  $5 \times 10^{-5} \text{ M}$  bromine solution containing  $5 \times 10^{-3} \text{ M}$  potassium nitrate. The shunt is adjusted and the galvanometer light spot is observed at 42 cm. The shunt is kept constant throughout the experiment. The diffusion current values, in terms of the position of the light spot on the scale is noted for various concentrations of bromine in the range of  $0.5 \times 10^{-5} \text{ M}$  to  $2.5 \times 10^{-5} \text{ M}$  for different temperatures from 285K to 305K.

**Table 1: Calibration of diffusion current at different temperatures**

[Br <sub>2</sub> ]/ 10 <sup>-5</sup> M	Diffusion Current (I <sub>d</sub> ) / nA				
	285 K	290 K	295 K	300 K	305 K
0.5	3.2	3.9	4.4	4.8	5.3
1.0	6.4	7.8	8.8	9.6	10.6
1.5	9.6	11.7	13.2	14.4	15.9
2.0	12.8	15.6	17.6	19.2	21.2
2.5	16	19.5	22.0	24	26.5

A plot of diffusion current versus concentration of  $\text{Br}_2$  is drawn for the five different temperatures. The readings are recorded only after allowing the solution to attain the thermostat temperature at which the kinetic study is to be studied subsequently.



**Fig 1: Calibration Plot of diffusion current at different temperatures at different temperatures.**

### Kinetic measurements

50 mL each of  $5 \times 10^{-5}$  M pyridine and bromine containing  $5 \times 10^{-3}$  M potassium nitrate are taken in two separate flasks and kept in a thermostat to attain the desired temperature. The solutions contain the required buffers to maintain pH 7. After the solutions have reached the thermostat temperature, they are mixed in the thermostated reaction vessel containing the RPE and SCE noting the time. As the reaction proceeds, the galvanometer deflection is observed to be gradually decreasing. The readings are noted at every 20 seconds for about two minutes.

The procedure of calibration and kinetic measurement is repeated thrice to crosscheck the reproducibility of the readings. These were found to be within an error limit of 0.2cm/nA.

Similar kinetic study is carried out by using Chlorine to compare the difference in their rate of the chlorination reaction at different temperatures.

During this kinetic study, from the observed deflections, the concentrations of unreacted  $\text{Br}_2$ ,

(a-x) at various instants can be determined using the calibration curve (Fig 1).

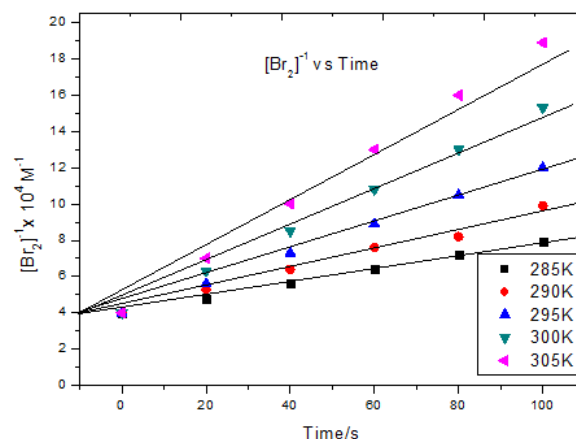
Where 'a' - initial concentration of reactants.

'x' - concentration of reacted  $\text{Br}_2$ .OR  $\text{Cl}_2$

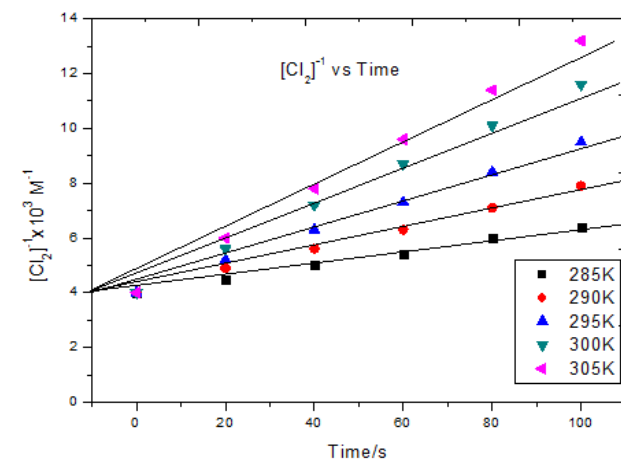
't' - time of reaction.

From Fig. 3, a plot of  $1/[\text{Br}_2]$  i.e.  $1/(a-x)$  versus 't' is linear. Thus the reaction is concluded to be of the second order. The slope of this plot gives the specific reaction rate 'k'. This study is carried out at different temperatures in the range of 285 K to 305 K and the energy of activation of the reactions ( $E_a$ ) are calculated. The frequency factor (A) and entropy change ( $\Delta S$ ) for the reactions are also evaluated.

The procedure is repeated for chlorination of pyridine.



**Fig: 2 Kinetics of bromination of Pyridine at different temperatures**



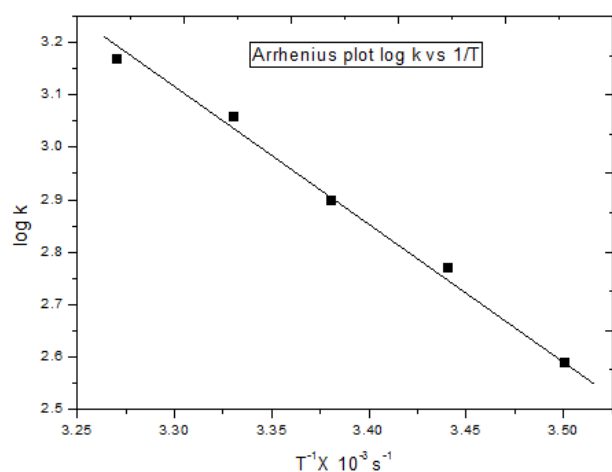
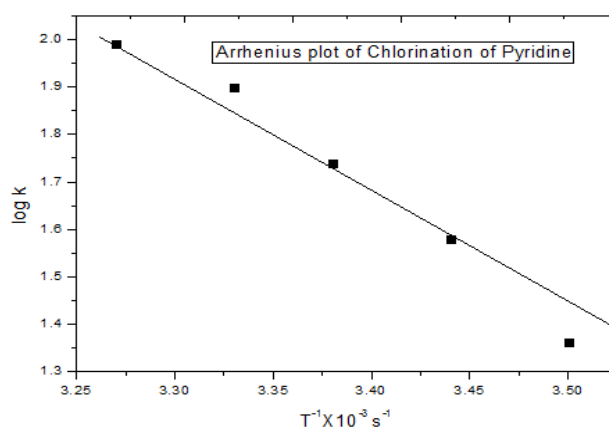
**Fig: 3 Kinetics of Chlorination of Pyridine at different temperatures**

**Table 2:** The Variation of specific reaction rates of Bromination & Chlorination of Pyridine with temp.

Temp /K	T· 1x10 <sup>-3</sup> / K <sup>-1</sup>	Bromination of pyridine		Chlorination of pyridine	
		k/M <sup>-1</sup> s <sup>-1</sup>	log k	k/M <sup>-1</sup> s <sup>-1</sup>	log k
285	3.50	390	2.59	23.0	1.36
290	3.44	595	2.77	38.5	1.58
295	3.38	800	2.90	55.5	1.74
300	3.33	1150	3.06	80.0	1.90
305	3.27	1500	3.17	98.0	1.99

**Table 3:** Parameters evaluated for Bromination and Chlorination of Pyridine

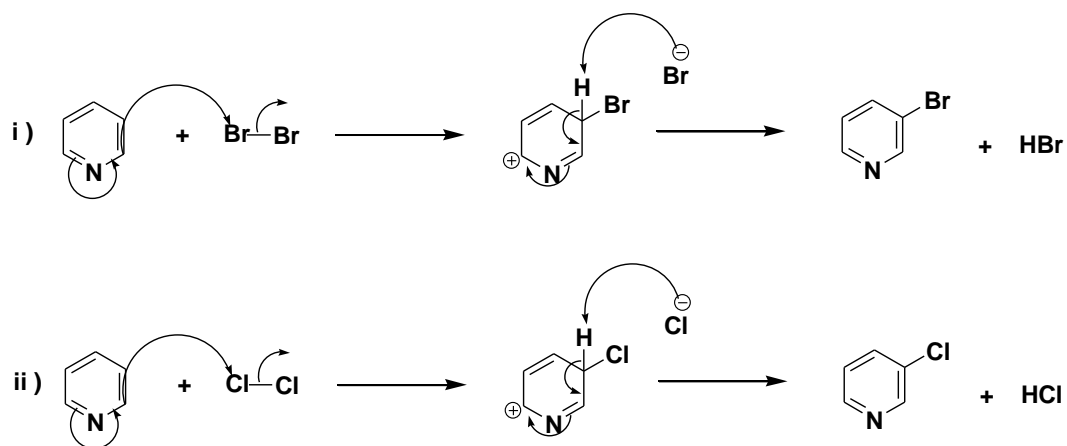
Sr. No.	Parameters evaluated at 295 K	Bromination of Pyridine	Chlorination of Pyridine
1	Specific reaction rate /M <sup>-1</sup> s <sup>-1</sup>	800	56
2	Energy of activation / k J mol <sup>-1</sup>	42.0	48
3	Frequency factor / M <sup>-1</sup> s <sup>-1</sup>	2.18 x 10 <sup>10</sup>	1.18 x 10 <sup>10</sup>
4	Entropy of activation / J mol <sup>-1</sup> K <sup>-1</sup>	- 68.5	- 63.5

**Fig. 4:** Arrhenius plot of bromination of pyridine**Fig. 5:** Arrhenius plot of Chlorination of pyridine

## RESULTS AND DISCUSSION

### Mechanism:

The probable mechanistic route for the reactions under study may be proposed as follows;



The sole halogenating agent in these two reactions under study is the halogen atom in the aqueous equilibria, considering the equilibrium constant values (Wang *et al.*, 1994).

Both the reactions are found to follow second order kinetics since the plots of  $1/\text{Br}_2$  and  $1/\text{Cl}_2$  versus time are straight lines. The gradient of these lines are the specific reaction rates for the bromination and chlorination reactions respectively.

The products in the two reactions are 3-bromo pyridine and 3-chloro pyridine respectively confirmed from NMR data and from stoichiometry.

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## CONCLUSION

The bromination rate is much faster than that of chlorination. The energy of activation for bromination of pyridine is lower than that for chlorination. The higher reactivity of bromine as compared to that of chlorine is quantitatively established in this study.

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