



## 2.2 Electrodes

A platinum microelectrode was fused to a glass tube and rotated at 600 rpm with the aid of a synchronous A.C. motor (RPC). A saturated calomel electrode (SCE) was the anode.

## 2.3 Measurement of the diffusion current

A constant potential of + 0.1V versus the saturated calomel electrode (SCE) was applied at the RPC, using a potentiometer.

A galvanometer with a sensitivity of 0.10 nA cm<sup>-1</sup> provided with a lamp & scale arrangement was used for the measurement of the diffusion current due to iodine in terms of the deflection of the galvanometer light spot. The current passing through the galvanometer was controlled by employing a shunt so that the deflection of the light spot was within scale limit.

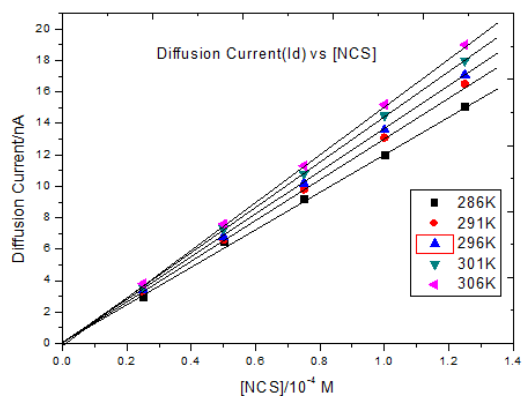
## 2.4 Calibration

The electrodes RPC and SCE were dipped in 100 cm<sup>3</sup> of 2.5 x 10<sup>-2</sup> M potassium nitrate solution. After applying a potential of ± 0.1V at the RPC with respect to the SCE, the galvanometer light spot was adjusted to zero deflection on the scale. The potassium nitrate solution was then replaced with 2.5 x 10<sup>-4</sup> M NCS solution containing 2.5 x 10<sup>-2</sup> M potassium nitrate and the shunt was adjusted for the galvanometer light spot to be within scale limit. This shunt value was kept constant throughout the experiment. The diffusion current value in terms of the position of the light spot on the scale was noted for different known concentrations of NCS from 0.25 x 10<sup>-4</sup> M to 1.25 x 10<sup>-4</sup> M.

A plot of diffusion current versus concentration of NCS was the calibration curve at different temperatures [Fig.1]. The readings were recorded only after allowing the solutions to attain the thermostat temperature at which the kinetic study were to be undertaken.

**Table 1:** Calibration of diffusion current

| [NCS] / 10 <sup>-4</sup> M | Diffusion Current (Id) / nA |       |       |       |       |
|----------------------------|-----------------------------|-------|-------|-------|-------|
|                            | 286 K                       | 291 K | 296 K | 301 K | 306 K |
| 0.25                       | 3.0                         | 3.3   | 3.4   | 3.6   | 3.8   |
| 0.50                       | 6.5                         | 6.6   | 6.8   | 7.3   | 7.6   |
| 0.75                       | 9.2                         | 9.8   | 10.2  | 10.8  | 11.3  |
| 1.00                       | 12.0                        | 13.1  | 13.6  | 14.5  | 15.2  |
| 1.25                       | 15.1                        | 16.5  | 17.1  | 18.0  | 19.0  |



**Figure 1:** Calibration of diffusion current

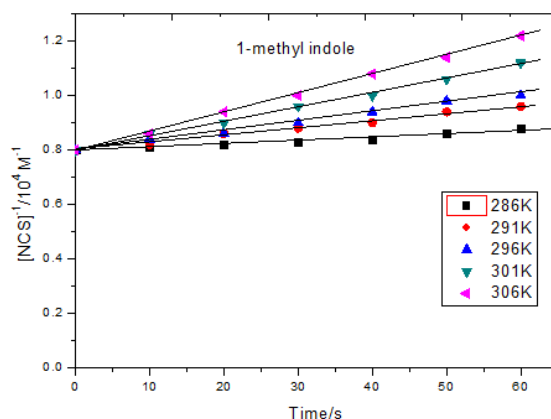
## 2.5 Kinetic Measurements

50 cm<sup>3</sup> of 2.5x10<sup>-4</sup> M 1-methyl indole and 50 cm<sup>3</sup> of 2.5 x 10<sup>-4</sup> M NCS both containing 2.5 x 10<sup>-2</sup> M potassium nitrate were taken in two separate flasks and kept in a thermostat to attain the desired temperature. After the solutions reached the thermostat temperature, they were mixed in the reaction vessel kept in the thermostat. RPC and SCE were dipped in the reaction vessel. A stopwatch was started while the solutions were mixed. As the reaction proceeded, the decreasing galvanometer deflection due to un-reacted NCS in the reaction was observed at every 10 seconds for about a minute.

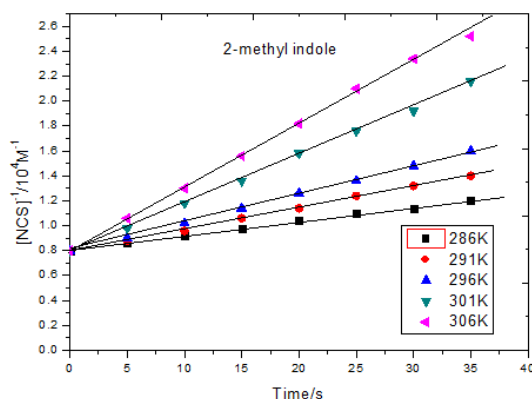
The procedures of calibration and kinetic measurements were repeated thrice to ascertain the reproducibility of the reaction which is found to be within an error limit of 0.2 cm.

From the observed deflections, the concentration of un-reacted NCS at various instants was determined using the calibration curve (Fig 1).

Fig 2, the plot of 1/ [NCS] versus time was linear. Thus the reaction was concluded to be of the second order [6,7]. The slope of this plot gave the specific reaction rate 'k'. This study was carried out at different temperatures in the range of 286 K to 306 K and the energy of activation for the reactions (Ea) was calculated. Further, the frequency factor (A) and entropy change (ΔS) for the reaction were also evaluated. Similar kinetic study was then carried out for the other two regioisomers, 2-methyl indole and 3-methyl indole.



**Figure 2:** Kinetics of Chlorination of 1- methyl indole



**Figure 3:** Kinetics of Chlorination of 2- methyl indole

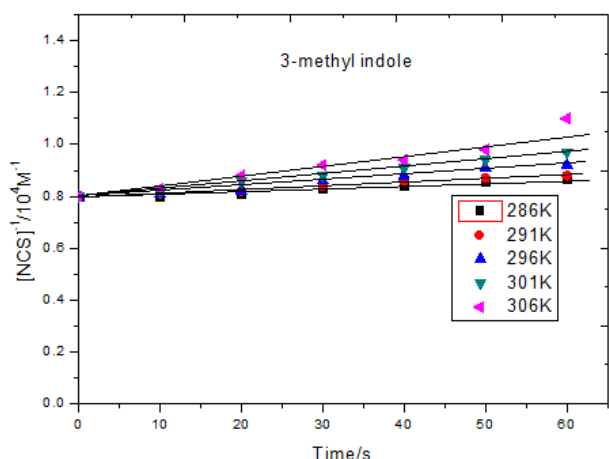


Figure 4: Kinetics of Chlorination of 3- methyl indole

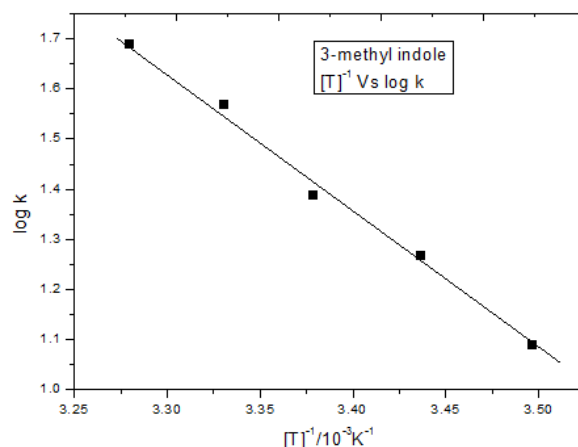


Figure 5 (c):  
 Figure: 5(a), 5(b), 5(c): Arrhenius Plots

Table 2: The variation of specific reaction rates of chlorination of isomers of methyl indole with temperature

| T/K | T <sup>-1</sup> /10 <sup>-3</sup> K <sup>-1</sup> | 1-methyl indole                   |       | 2-methyl indole                   |       | 3-methyl indole                   |       |
|-----|---|-----------------------------------|-------|-----------------------------------|-------|-----------------------------------|-------|
|     |   | k/M <sup>-1</sup> s <sup>-1</sup> | log k | k/M <sup>-1</sup> s <sup>-1</sup> | log k | k/M <sup>-1</sup> s <sup>-1</sup> | log k |
| 286 | 3.496   | 17.2                              | 1.24  | 115.0                             | 2.06  | 12.5                              | 1.09  |
| 291 | 3.436   | 25.8                              | 1.41  | 172.5                             | 2.24  | 18.7                              | 1.27  |
| 291 | 3.378   | 34.4                              | 1.54  | 230.0                             | 2.36  | 25.0                              | 1.39  |
| 301 | 3.330   | 51.2                              | 1.71  | 345.0                             | 2.54  | 37.5                              | 1.57  |
| 306 | 3.279   | 68.8                              | 1.84  | 460.0                             | 2.66  | 50.0                              | 1.69  |

Table 3: Kinetic and thermodynamic parameters for chlorination of region-isomers of methyl-indole

| Parameter  | 1-methyl indole | 2- methyl indole | 3-methyl indole |
|--|-----------------|------------------|-----------------|
| Specific reaction rate /M <sup>-1</sup> s <sup>-1</sup> at 306 K   | 68.8            | 460.0            | 50.0            |
| Energy of activation /kJmol <sup>-1</sup>                          | 48              | 44               | 49.78           |
| Frequency factor /10 <sup>10</sup> M <sup>-1</sup> s <sup>-1</sup> | 1.0717          | 1.4878           | 1.569           |
| Entropy of activation /J mol <sup>-1</sup> K <sup>-1</sup>         | -69.70          | -66.93           | -66.53          |

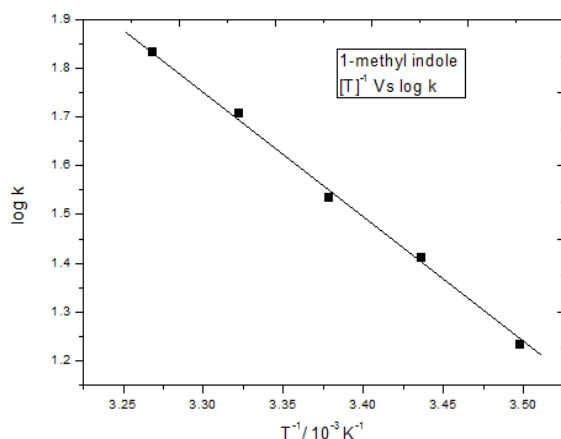


Figure 5 (a):

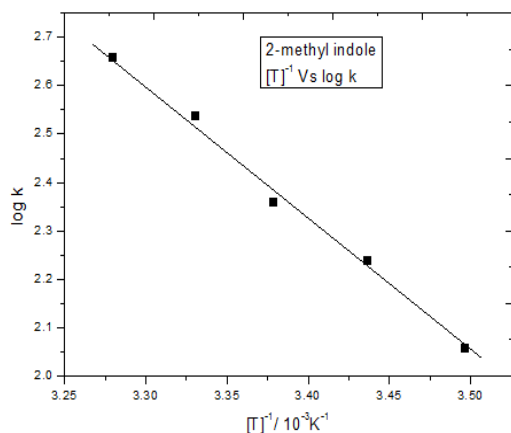


Figure 5 (b):

### 3. Results and Discussion

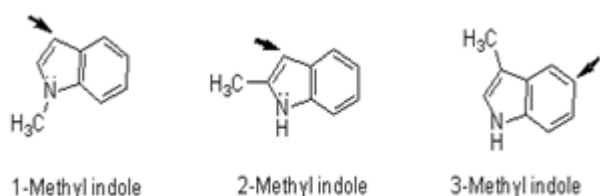
The products of chlorination of 1-methyl indole, 2-methyl indole and 3-methyl indole were found to be 3-chloro-1-methyl indole, 3-chloro-2-methyl indole and 5-chloro-3-methyl indole, respectively as ascertained from NMR studies.

In the study of the chlorination reactions of the three regio-isomers of methyl indole, the reactivity order was found to be 3-methyl indole < 1-methyl indole < 2-methyl indole.

This is justified on the basis of the stereo-specificity of the compounds. The path of the incoming electrophile Cl<sup>+</sup> is shown in the figure by arrows.

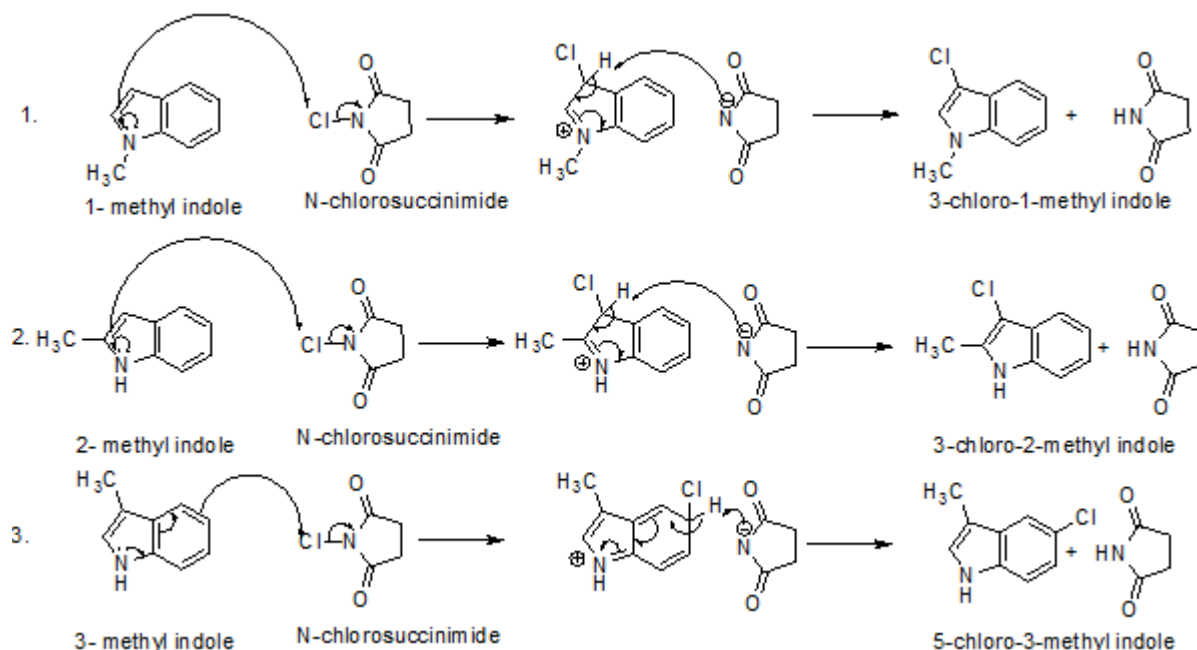
In 1-methyl indole, the presence of methyl group attached to -N provides steric hindrance and makes the lone pair of electrons less available to attack the electrophile. Thus has the least specific reaction rate of 68.80 M<sup>-1</sup>s<sup>-1</sup> at 306 K. In 3-methyl indole the presence of methyl group at the 3 position causes the electrophile to get attached at position 5. Due to less steric hindrance the reaction was faster as compared to 1-methyl indole, having a specific reaction rate of 50.00 M<sup>-1</sup>s<sup>-1</sup> at 306 K.

In 2-methyl indole, the lone pair of electrons on -N was readily available to attack the electrophile Cl<sup>+</sup>. Position 3 is more conducive to the entry of electrophile due to the combined effect of activating this position by both, the methyl group at position 2 and the nitrogen at position 1. Thus the reaction is rapid and has specific reaction rate of 460.00 M<sup>-1</sup>s<sup>-1</sup> at 306 K.



#### 4. Mechanism

The plausible mechanisms for the three chlorination reactions are suggested as follows.



#### 5. Conclusion

A comparative study of the reactivities of the regio-isomers of methyl indole have been qualitatively speculated hitherto but by direct kinetic measurements yielding quantitative assessment has herein been provided. These reactions being rapid could not be studied by conventional methods, and the use of hydrodynamic voltammetry technique facilitated to monitor the progress of these reactions to evaluate their specific reaction rates. The data obtained in this study is expected to complement those related to the investigation of chlorination of other aromatic substrates.

[6] Borkar, V.T., Dangat, V.T. and S.L. Bonde, S.L. (2013) A Quantitative Structure – Reactivity Assessment of Phenols by Investigation of Rapid Iodination Kinetics Using Hydrodynamic Voltammetry: Applicability of the Hammett Equation in Aqueous Medium International Journal of Chemical Kinetics Wiley Pub. (USA) Vol.46,9,

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