



Rapid Iodination of Xylidines in Aqueous Medium: Kinetic verification of Speculated Reactivities

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Abstract

Comprehensive kinetic studies to investigate the relative nucleophilicities of the six isomers of xylidine have been carried out. Kinetic data presently obtained for iodination of xylidines in aqueous medium conclusively enlightened the order of the relative reactivities of xylidines in a quantitative manner. All the six reactions studied were found to be rapid, necessitating a special technique to follow the kinetics. The rotating platinum cathode method employed, yielded specific reaction rates that ranged from 52 to $893\text{M}^{-1}\text{s}^{-1}$ and energies of activation from 32.7 to 54.5kJ mol^{-1} at 25.0°C and 7pH . Stereochemical principles invoked, justified this observed reactivity order for the isomers under study. Thus the subtleties of the stereochemistry of xylidines were quantitatively ascertained using kinetics as an investigational tool.

Keywords: Xylidines, iodination, rotating platinum cathode (RPC), stereochemical principles.

Introduction

The six structural isomers of dimethyl aniline $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NH}_2$, commonly called xylidines are aromatic amines and are used in the production of antioxidants, pharmaceuticals, dyes, fertilizers and pesticides. Many of these are environmentally hazardous and care has to be taken in handling them¹. Like other aniline derivatives they undergo rapid halogenations in aqueous solution of which brominations are the fastest². Iodinations too become very rapid in aqueous solutions that contain molecular iodine devoid of excess iodide concentrations³. Presently, we have studied the rapid kinetics of iodination of the six xylidine isomers in aqueous solution using molecular iodine at 7pH . Since the iodide ion concentration influences the reaction rates, it has been kept constant in all the six reactions. The studies have been carried out at different temperatures to estimate the energies of activation for the six reactions. These kinetic data are invoked to justify the reactivities of xylidines in a quantitative manner. The rapidity of these reactions necessitates a special technique to follow the kinetics. These reactions being second order, their half – lives are extendable by diluting the solutions whereby convenient kinetic measurements are feasible. The rotating platinum cathode, RPC, based on the voltammetric principle, was used as a sensor to monitor the decaying low concentrations of iodine in these reactions^{4,5}. The saturated calomel electrode, SCE, is the anode and the diffusion current generated by iodine at the cathode is a measure of the decaying halogen concentration during the course of the reactions. The fact that the monoiodo isomer is the major product is ascertained stoichiometrically by iodimetric titrations and is in accord with known facts⁶. The investigations are aimed at providing a quantitative angle to the mechanisms of the organic reactions studied in aqueous medium since mechanisms in organic medium are better known⁷.

Material and Methods

Chemicals: AR grade samples of the six xylidine isomers, sodium dihydrogen phosphate, disodium hydrogen phosphate, potassium nitrate, iodine and potassium iodide were used to prepare the required stock solutions in double distilled water.

Electrodes: The cathode was a platinum electrode fused to a glass tube rotated at 600rpm with aid of a motor. The anode was a saturated calomel electrode.

Diffusion Current Measurement: Calibration: The RPC and SCE were dipped in solutions of different concentration of iodine containing a fixed iodide concentration along with the phosphate buffer components for maintaining 7pH and potassium nitrate which served as the supporting electrolyte. Use of phosphate buffer to maintain constant pH at about 7 is common⁸. The concentrations of iodine in terms of the diffusion currents were recorded. The plot of diffusion current Vs $[\text{I}_2]$ were linear.

Kinetic Measurements: Equimolar solutions of iodine and xylidine containing the supporting electrolyte and buffer components were kept in a thermostat in different containers. After attaining the desired temperature, these were mixed in the reaction vessel in which RPC and SCE were dipped and stop clock was simultaneously started. The bent shape of the glass tube to which the RPC is fused ensures efficient mixing of the reactants as the reaction proceeds. At every 10s the diffusion current in terms of galvanometer light spot is recorded until about the completion of the first half- life of the reaction. A plot of $[\text{I}_2]^{-1}$ Vs time was found to be linear the slope of which is the specific reaction rate. The kinetic measurements were repeated at five different temperatures. The study was carried out for all the six isomers of xylidine.

Table-1
Initial concentrations of the reagents in 50 cm³ of reaction mixtures

KNO ₃ / 10 ⁻³ M	4.00
Na ₂ HPO ₄ / 10 ⁻⁴ M	2.00
NaH ₂ PO ₄ / 10 ⁻⁴ M	3.20
KI / 10 ⁻⁴ M	8.00
Xylidine / 10 ⁻⁵ M	4.00
[I ₂] / 10 ⁻⁵ M	4.00

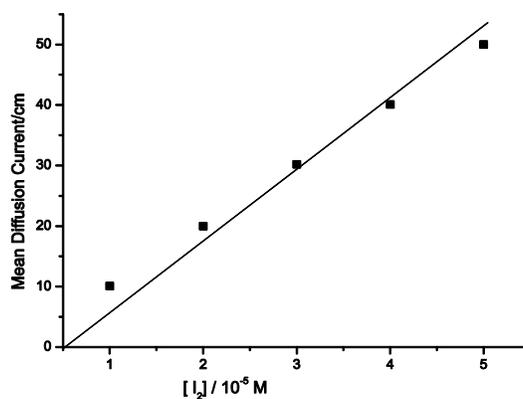


Figure-1
Calibration of diffusion current

Table 2
Calibration of diffusion current

Obs.No.	[I ₂] / 10 ⁻⁵ M	Mean Diffusion Current/cm
1	1.0	10.1
2	2.0	20.0
3	3.0	30.2
4	4.0	40.1
5	5.0	50.0

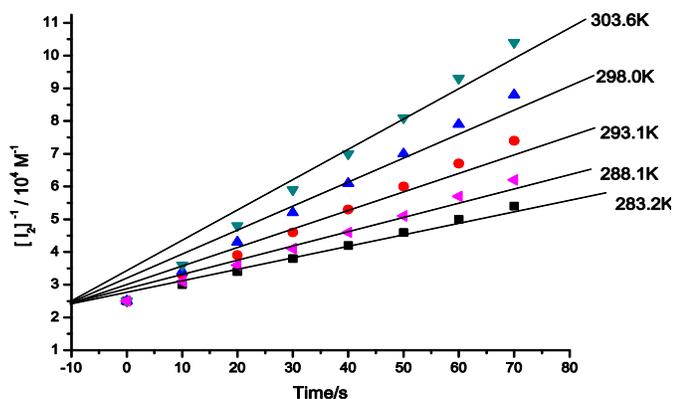


Figure-2
Kinetics of iodinations of 2, 5-xylidine at various temperatures

Results and Discussion

The six reactions studied follow second order kinetics, hence the plot of $[I_2]^{-1}$ Vs time is a straight line the slope of which is the specific reaction rate, unlike a first order reaction⁹. The kinetic investigation of the following six reactions at different temperatures has been studied by the RPC technique since the reactions are too rapid to be monitored by conventional methods. The typical results for the iodination of 2, 5-xylidine are shown in figure-3 and 4. The energy of activation for all the six reactions were obtained from Arrhenius plots.

Iodine is the sole iodinating agent in these reactions since the equilibrium



is predominantly shifted to the left in view of the low hydrolysis constant (2.0×10^{-13}) and since hypohalous acid is known to be a very weak electrophile¹⁰.

The kinetic evidences in table-4 quantitatively justify the speculations regarding the nucleophilicities of xylidines in the electrophilic substitution reactions considering steric hindrance of the different substituents in the different isomers. The $-NH_2$ group strongly activates the para and less strongly the ortho positions while $-CH_3$ activates positions ortho and para to it. The order of the decreasing magnitude the specific reaction rates observed in the study may be explained on the basis of stereochemistry principles.

Table 3
Kinetics of iodination of 2, 5-xylidine at 25.0°C

Obs. No.	Time/sec.	Mean diffusion current/cm	Unreacted $[I_2]/10^{-5} M$	$[I_2]^{-1}/10^4 M^{-1}$
1	0	40.0	4.00	2.5
2	10	29.4	2.94	3.4
3	20	23.3	2.33	4.3
4	30	20.0	2.00	5.0
5	40	19.2	1.92	5.2
6	50	16.4	1.64	6.1
7	52	14.3	14.3	7.0
7	60	12.7	1.27	7.9
8	70	11.4	1.14	8.8

Table-4
Summary of the kinetic investigations for the iodination of xylidines

Isomer of Xylidine	$t_{1/2}/s$	$k/M^{-1}s^{-1}$	$E_a/kJmole^{-1}$
2,5-xylidine	28	893	32.7
2,3-xylidine	52	481	38.0
3,5-xylidine	200	125	41.9
3,4-xylidine	260	96	49.7
2,4-xylidine	320	78	54.3
2,6-xylidine	480	52	54.5

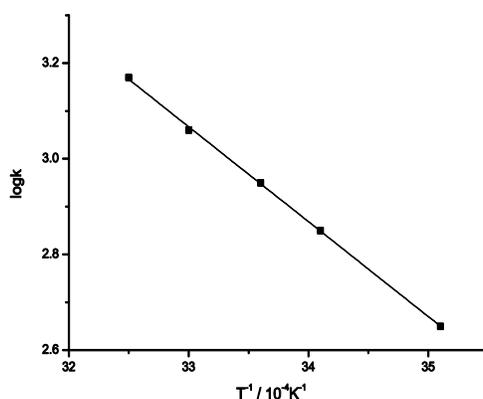
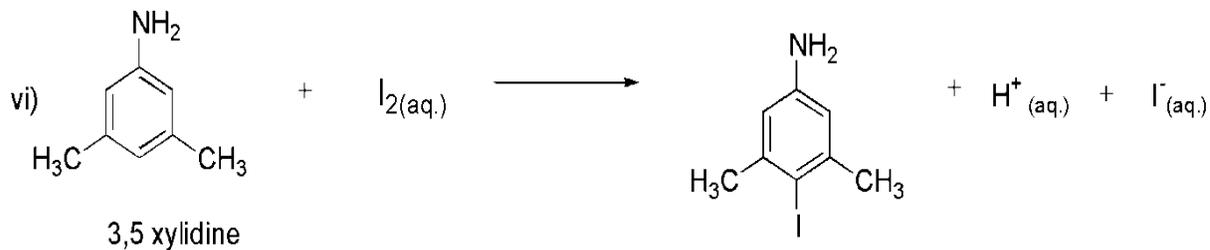
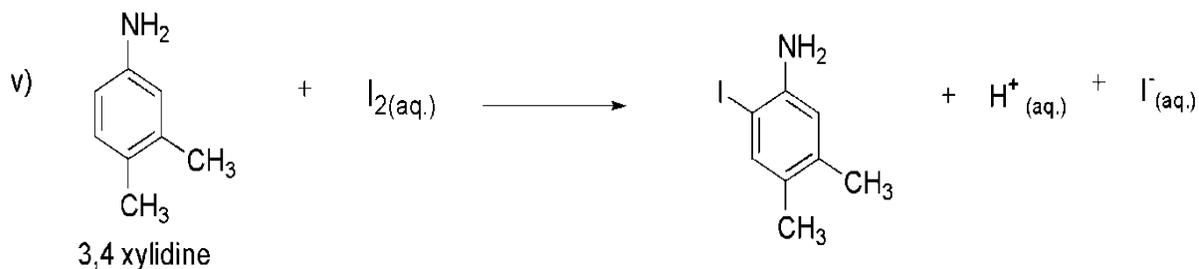
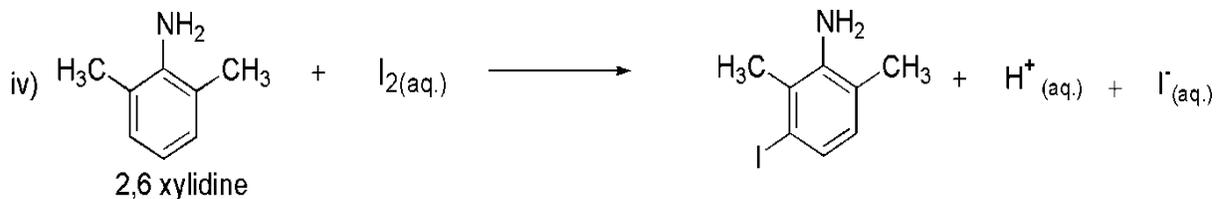
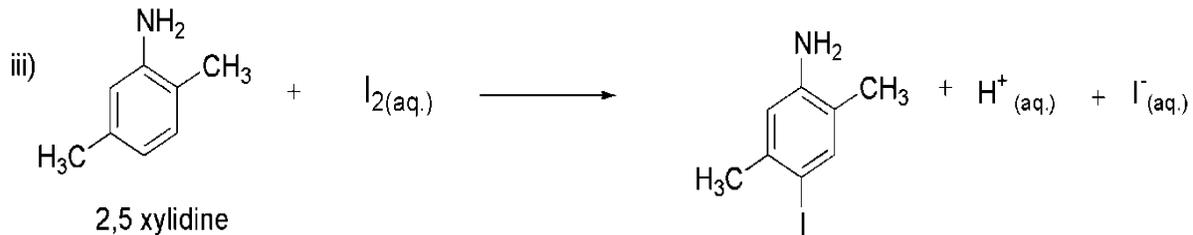
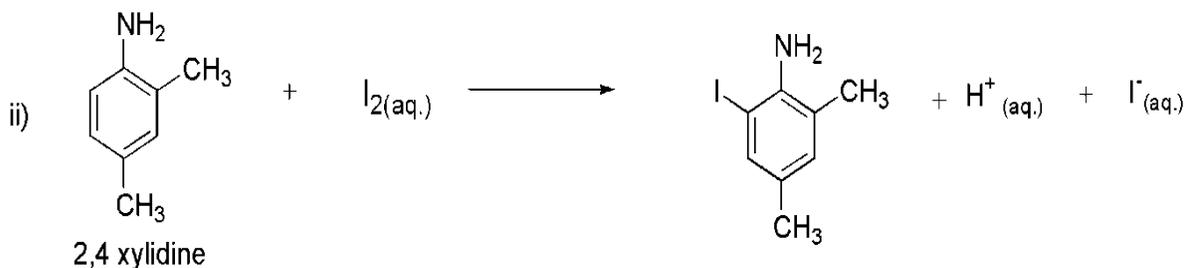
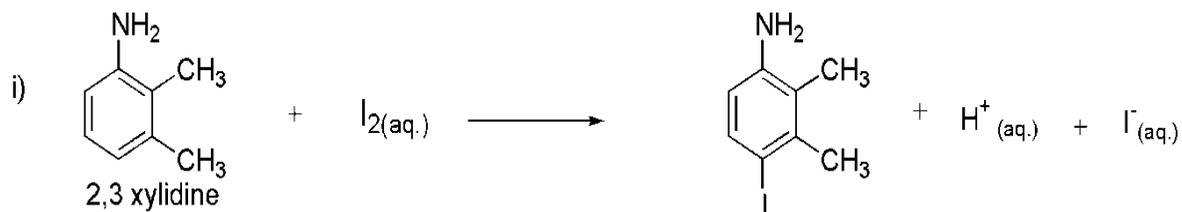


Figure-3
Arrhenius plot for the iodination of 2, 5-xylidine

The six reactions studied are represented as follows.



In 2, 5-xylylidine, the influence of the amino and methyl group operates in unison to direct the incoming iodo group at the position para to the amino group. This results in the high specific reaction rate for iodination of this isomer viz. $893 \text{ M}^{-1}\text{s}^{-1}$

In 2, 3-xylylidine, this combined influence is somewhat weakened due to the proximity of the two $-\text{CH}_3$ groups and a rate constant of $481 \text{ M}^{-1}\text{s}^{-1}$ is observed.

In 2,4 - xylylidine and 3,4 - xylylidine the position para to $-\text{NH}_2$ is blocked by $-\text{CH}_3$ and the reactivities are low as evinced by the specific reaction rates, $78 \text{ M}^{-1}\text{s}^{-1}$ and $96 \text{ M}^{-1}\text{s}^{-1}$. The relatively lower rate of 2,4- xylylidine is presumably due to the steric congestion of $-\text{NH}_2$ with $-\text{CH}_3$ and the incoming bulky iodo group.

3, 5-xylylidine, undergoes iodination at a specific reaction rate of $125 \text{ M}^{-1}\text{s}^{-1}$. In this case, the para iodo product is formed but at a reduced rate because of the steric hindrance encountered among the two methyl groups and the incoming bulky iodo group.

2, 6-xylylidine, undergoes iodination at a rate that is slowest, $52 \text{ M}^{-1}\text{s}^{-1}$, among the six isomers. The extreme proximity of the two methyl groups with the amino groups results in lack of coplanarity of the latter with the benzene ring. The perpendicular position of the amino group with the benzene ring disables its para directing ability. Hence the substitution is dominated by the ortho-para directing nature of the methyl groups and iodo group enters the position 3 instead of 4.

Conclusion

The relative reactivities of xylylidines considered in these reactions have been speculated only qualitatively on stereochemical principles but direct kinetic measurements for a quantitative assessment was lacking presumably due to the rapidity of these reactions. Such verification is provided by this study of the kinetics of iodination of the six isomers of xylylidine by molecular iodine in aqueous solution. Though these reactions are rapid and cannot be studied by conventional methods, the RPC has been used to monitor the progress of these reactions to evaluate the specific reaction rates. These are a measure of the relative nucleophilicities of xylylidines and portray the steric compulsions in these reactions in a quantitative manner.

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