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Kinetics Of Iodination Of Aniline And Substituted Anilines By Pyridinium Iodochloride In Methanol

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ABSTRACT

The kinetics of iodination of the aniline and substituted anilines using pyridinium iodochloride in methanol has been studied under varying conditions. The rates shows first order kinetics each in pyridinium iodochloride and anilines. The rates of reactions are measured at different temperature and activation parameters for all amines computed. Hammett plot is found to be valid and the corrletion between the enthalpies and free energies of activations is reasonably linear with an isokinetic temperature 347K. Similarly log A values of all the amines are optimized corresponding to Ea of amines through the equation, $\log A = \log k_{obs} + Ea/2.303RT$.

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KEYWORDS

Kinetics;
Iodination
Anilines;
Pyridinium iodochloride.

INTRODUCTION

Iodination of aromatic rings is an electrophilic substitution reaction with wide applications in organic synthesis particularly in the synthesis of pharmaceuticals[1-6]. Aromatic iodides have been used in the synthesis of many interesting natural products[7] and also as bioactive materials[8]. They also have importance in medicinal and pharmaceutical research[9].

To study the kinetics of organic compounds number of reagents such as molecular iodine[10-11], iodine monochloride[12], N-iodosuccinimide[13] have been used. But most of reagents used are toxic, expensive and generates hazardous waste[14]. The pyridinium iodochloride is an efficient solid iodinating agent which has no hazardous effect and ecofriendly.

Further one of the important tool in deciding the mechanism of reaction is the study of substituent effect and thermodynamic parameters. The Hammett equation[15] and its modified form, all known as linear free energy relationship (LFER), have been found useful for correlating reaction and equilibrium constants. The isokinetic relationship is also an important tool for deciding the nature of a mechanism.

This article focus on the study of kinetics and mechanism of iodination of aromatic amines by pyridinium iodochloride in methanol.

EXPERIMENTAL

All the chemicals and solvent used were of analytical grade. The anilines used were substituents H, m-

CH_3, m-NO_2, p-NO_2, p-Cl, p-Br. The solid anilines were used as such, and the liquid anilines were used after vacuum distillation. Pyridinium iodochloride was prepared by reported method[16] and its purity was checked by the iodometric method.

Kinetic measurements

The reactions were carried out under pseudo first order conditions by keeping an excess of substrate over pyridinium iodochloride. The progress of reaction was followed by estimating the unreacted pyridinium iodochloride iodometrically. The rate constants were determined by least square method, from the linear plots of log [PyICl] versus time. Replicate runs showed that the rate constants were reproducible to within ±3%.

Stoichiometry and product analysis

Stoichiometry of pyridinium iodochlroide and aniline reaction was determined by allowing the reaction mixture containing aniline and pyridinium iodochloride in 1:1 molar ratio in methanol to go to completion at room temperature. Then the reaction mixture was poured in water to get solid product. The iodinated product was analyzed using preparative TLC on silica gel, and comparing the melting point of product with the known sample.

RESULTS AND DISCUSSION

The results of iodination of substituted anilines by PylCl are presented in TABLES 1-4.

Effect of variation of [substrate]

At constant [PylCl], the increase in[substrate] enhances the reaction rate. The plot of log k_{obs} versus log [substrate] for different initial concentration of substrate is linear with unit slope indicating the first order dependence on substrate TABLE 1.

TABLE 1 : Dependence of rate constant on [substrate]

[Substarate]	$k_1 \times 10^{-3}$ sec^{-1}					
	m -CH_3	-H	p Br	m NO_2	p NO_2	p Cl
0.2 M	39.91	35.34	30.70	27.43	23.02	15.35
0.1 M	19.19	18.42	15.35	13.43	12.28	9.97
0.05 M	11.51	8.44	7.29	6.14	5.75	4.03
0.025 M	6.39	4.26	3.83	3.07	2.87	2.01
0.0125 M	3.27	2.36	1.91	1.61	1.51	1.06

[PyICl]= 0.01M, Temp=301K, Solvent=methanol

TABLE 2 : Dependence of rate constant on [PyICl]

[PyICl]	$k_1 \times 10^{-3}$ sec^{-1}					
	m -CH_3	-H	p Br	m NO_2	p NO_2	p Cl
0.02 M	19.03	18.80	15.73	13.58	12.66	10.36
0.01 M	19.19	18.42	15.35	13.43	12.28	9.97
0.005 M	19.95	18.65	15.96	13.54	12.43	10.20
0.0025 M	19.04	18.12	15.90	13.32	12.41	10.03
0.00125 M	20.02	18.77	16.01	13.17	12.29	10.11

[substrate]= 0.01M, Temp=301K, Solvent=methanol

TABLE 3 : Effect of temperature variation on reaction rate constant

Temperature (K) →	288	293	301	308	313
Name of substrate	$k \times 10^{-3}$ s^{-1}				
m-Toludine	14.31	16.68	19.19	39.72	45.68
Aniline	12.74	15.29	18.42	38.68	46.41
p-Bromoaniline	9.36	11.99	15.35	35.30	45.19
m-Nitroaniline	7.98	10.38	13.43	31.59	41.06
p-nitroaniline	6.26	8.77	12.28	22.10	30.94
p-chloroaniline	4.43	6.64	9.97	19.87	29.76

[substrate]= 0.1M, [PyICl]=0.01M

Effect of variation of [PyICl] :

At constant [substrate], the increase in [PyICl] did not affect the rate of reaction. The first order plots of log [PyICl] versus time were linear. The pseudo first order rate constants computed from the plots remained unaffected by the change in [PyICl], establishing the first order dependence of the rate on pyridinium iodochloride in all cases (TABLE 2).

Effect of temperature

The study of iodination of different anilines has been subjected to different temperature range 288K to 313K by keeping the concentration of substrate and reagent

TABLE 4 : Thermodynamic parameters

Name of Substrate	$k \times 10^{-3} s^{-1}$	E_a kJmole^{-1}	$\Delta H^{\#}$ kJmole^{-1}	$-\Delta S^{\#}$ Jmole^{-1}K^{-1}	$\Delta G^{\#}$ kJmole^{-1}	Freq. factor log A L/mole/Sec
m-Toludine	19.19	19.14	16.64	218.96	85.04	1.60
Aniline	18.42	25.52	23.02	198.29	85.20	2.69
p-Bromoaniline	15.35	31.91	29.41	178.65	85.48	4.75
m-Nitroaniline	13.43	35.10	32.60	168.10	85.89	5.27
p-nitroaniline	12.28	47.86	45.36	127.33	86.18	7.47
p-chloroaniline	9.97	57.44	54.94	97.23	86.70	9.09

[Amine]=0.1M, [PyICl]=0.01M, Temperature=301K, Solvent=methanol

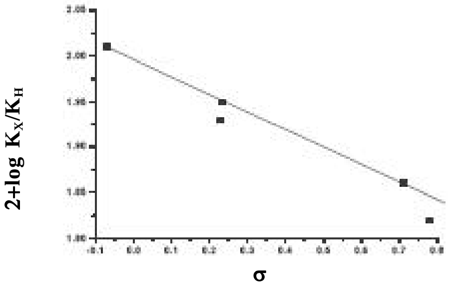

Figure 1 : Hammett plot

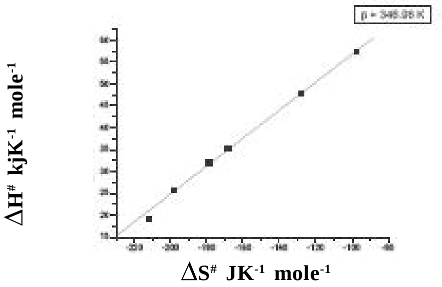

Figure 2 : Isokinetic plot

constant. The rate constants are given in TABLE 3. The plots of log k versus 1/T are linear. Activation parameters are presented in TABLE 4.

Energy-entropy relationship

The entropy of activation and heat of reaction are correlated by the equation 1.

$$\Delta H^{\#}=\Delta H^{0}+\beta\Delta S^{\#}$$

Where β is the iokinetic temperature figure 2 give the isokinetic plot for the reaction between anilines and pyridinium iodochloride in methanol. The isokinetic tempeature(347K) is greater than experimental temperature.

The values of entropy of activation also suggest that the reaction is entropy as well as enthalpy controlled. The values of free energies of activation of reaction were found to be move or less similar. This trends also support the identical reaction mechanism being followed in these reactions[17]. The linear relationship in Exner plot[18,19] at 3+log k_{293K} and 3+log k_{288K} observed in present study also supports the conclusion drawn from isokinetic temperature.

A linear free energy relationship is attempted by casting the data in Hammett equation. The value of slope of Hammett plot is known as the reaction constant(ρ) and which is found to be -0.35. The negative value of rate constant suggest than the reaction are electrophilic substitution reaction. The magnitude of reaction constant(ρ) and its negative sign suggest the iodination reaction is accelerated by electron donating groups and rate is retarded by electron withdrawing groups[20,21]. The order of reactivities with substituents is m-CH_3>-H>m-NO_2>p-NO_2>p-Cl>p-Br>, based on above experimental observations and a probable mechanism (SCHEME 1) is suggested and rate law is derived.

Probable mechanism of iodination amines and rate law

$$\text{Ar-NH}_2 + \text{PyICl} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\text{Complex}]$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products}$$

Rate law

$$\frac{-d[\text{PyCl}]}{dt} \;\alpha[\text{Ar-NH}_2][\text{PyCl}]$$

SCHEME 1

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