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Kinetic of iodination of phenol and substituted phenols by pyridinium iodochloride in methanol

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Abstract

The kinetics of iodination of the phenol and substituted phenols using pyridinium iodochloride in methanol has been studied under varying conditions. The rates show first order kinetics each in pyridinium iodochloride and phenols. The rates of reactions are measured at different temperature and activation parameters for all phenols 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 359.55 K. Similarly log A values of all the phenols are optimized corresponding to E_a of phenols through the equation, log A = log k_{obs} + E_a / 2.303 RT.

Keywords: Kinetics; Iodination; Phenols; Pyridinium iodochloride

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1. 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] has 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 tools 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 focuses on the study of kinetics and mechanism of iodination of phenols by pyridinium iodochloride in methanol.

2. Experimental

All the chemicals and solvent used were of analytical grade. The anilines used were substituents *m*-CH_3, -H, *m*-Cl, *p*-Cl, *p*-OH, *p*-NO_2. The solid phenols were used as such, and the

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liquid phenols were used after vacuum distillation. Pyridinium iodochloride was prepared by reported method [16], by mixing the equimolar quantaties of pyridine and iodine monochloride in acetic acid. Its purity was checked by the iodometric method.

2.1. 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%.

2.2. Stoichiometry and product analysis

Stoichiometry of pyridinium iodochlroide and phenol reaction was determined by allowing the reaction mixture containing phenol 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.

3. Results and discussion

The results of iodination of substituted phenols by pyridinium iodochloride are presented in Tables 1-4.

3.1. 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], [PyICl] = 0.01 mol L^{-1}, temperature = 301 K, solvent = methanol.

[Substrate]	$k_1 \times 10^{-3}\ s^{-1}$					
	m -CH_3	-H	*m* Cl	*P* Cl	*p* OH	*p* NO_2
0.4 M	62.17	55.42	47.89	42.60	36.09	32.07
0.2 M	34.54	19.17	24.56	23.03	19.95	16.88
0.1 M	17.65	14.58	9.21	10.74	8.44	7.67
0.05 M	9.97	5.37	4.60	3.83	3.07	2.30
0.0025 M	4.48	2.98	2.35	2.01	1.57	1.24

3.2. 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).

Table 2
Dependence of rate constant on [PyICl], [substrate] = 0.01 mol L^{-1}, temperature = 301 K, solvent = methanol.

[PyICl]	$k_1 \times 10^{-3}$ s^{-1}					
	m -CH_3	-H	*m* Cl	*P* Cl	*p* OH	*p* NO_2
0.04 M	18.02	14.12	10.69	9.26	8.49	7.78
0.02 M	17.80	14.95	10.82	9.36	8.67	7.83
0.01 M	17.65	14.58	10.74	9.21	8.44	7.67
0.005 M	18.08	14.89	10.97	9.59	4.82	8.06
0.0025 M	17.98	13.27	10.13	9.32	4.73	7.95

3.3. Effect of temperature

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

Table 3
Effect of temperature variation on reaction rate constant, [substate]=0.1 mol L^{-1}, [PyICl]=0.01 mol L^{-1}.

No.	Temperature (K)	288	293	301	308	313
	Name of Substrate	$k \times 10^{-3}$ s^{-1}				
1	*m*-Creasol	9.68	13.07	17.65	25.59	34.54
2	Phenol	7.65	10.56	14.58	20.41	28.16
3	*m* chlorophenol	5.32	7.45	11.74	15.46	21.65
4	*p* chlorophenol	4.41	6.30	9.21	13.44	19.22
5	*p* Hydroxyphenol	3.90	5.70	8.44	12.49	18.23
6	*p* Nitrophenol	3.44	5.09	6.64	11.64	16.96

Table 4
Thermodynamic parameters, [substrate] = 0.1 mol L^{-1}, [PyICl] = 0.01 mol L^{-1}, temperature=301 K, solvent = Methanol.

No.	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
1	*m*-cresol	17.65	41.48	39.14	144.69	82.73	5.84
2	Phenol	14.58	44.67	42.17	137.10	83.43	5.92
3	*m*-chlorophenol	11.74	45.51	43.01	130.11	83.97	5.93
4	*p*-chlorophenol	9.21	47.86	45.36	128.09	83.91	6.27
5	*p*-hydroxyphenol	8.44	51.05	48.55	119.60	84.54	6.37
6	*p*-nitrophenol	6.64	54.25	51.75	109.73	84.77	6.86

3.4. Energy-entropy relationship

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

$$\Delta H^{\#} = \Delta H^{\circ} + \beta \Delta S^{\#} \qquad (1)$$

were β is the isokinetic temperature Fig. 1 give the isokinetic plot for the reaction between phenols and pyridinium iodochloride in methanol. The isokinetic tempeature (359.55 K) 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. These 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.

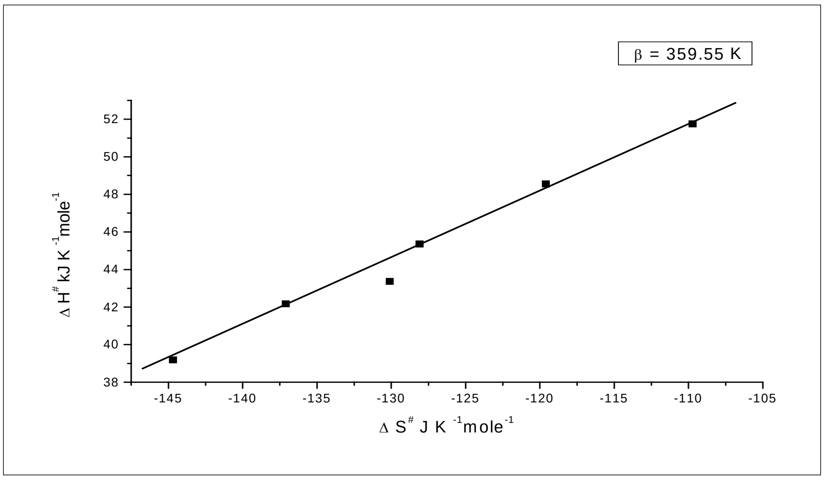


Fig.1. Isokinetic plot for the reaction between phenols and pyridinium iodochloride in methanol.

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 -

0.53 (Fig. 2). The negative value of rate constant suggests that the reactions are electrophilic substitution reaction. The magnitude of reaction constant (ρ) and its negative sign suggest that the iodination reaction is accelerated by electron donating groups and rate is retarded by electron withdrawing groups [20].

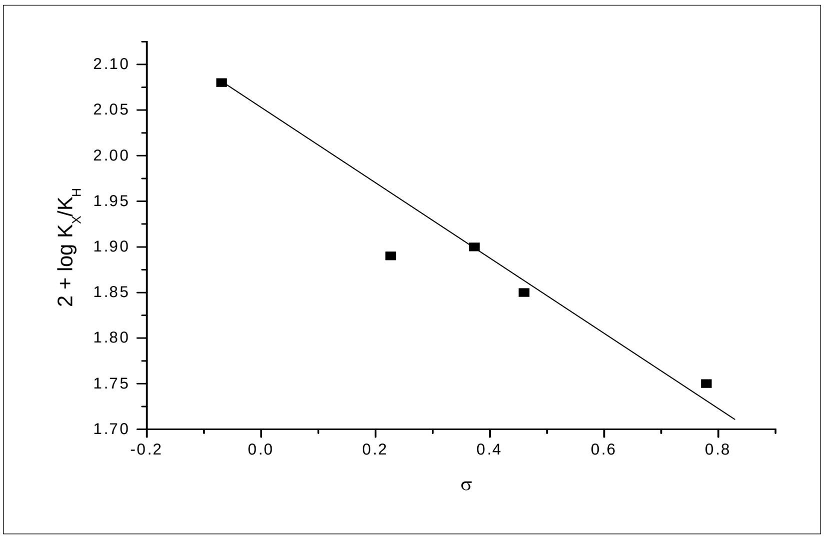
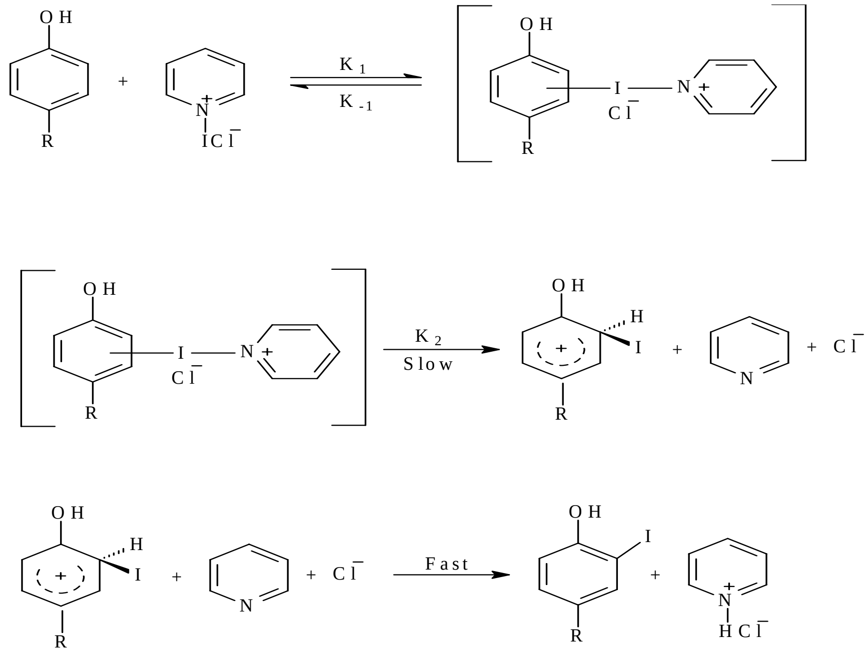


Fig. 2. A Hammett plot showing linear free energy relationship between phenols and pyridinium iodochloride.

The order of reactivities with substituents is *m*-CH_3 > -H > *m*-Cl > *p*-Cl> *p*-OH > *p*-NO_2 based on above experimental observations and a probable mechanism (Scheme 1) is suggested and rate law is derived.



$$\frac{-d[PyICl]}{dt}\alpha[Phenol][PyICl]$$

Scheme 1 Probable mechanism of iodination phenols and rate law.

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