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Short Communication

Protonation Behaviour of Hydroxamic Acids

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ABSTRACT

N-Aryl Substituted hydroxamic acids behave as weak organic bases in presence of mineral acid solution. Their protonation parameters have been estimated in aqueous sulphuric acid solution.

Keywords: Hydroxamic Acid, Protonation Behaviour.

INTRODUCTION

Hydroxamic acids are N-acyl derivatives of hydroxylamine (I) and the hydroxamic acid functional group (II) has the outstanding chemical feature. The field of hydroxamic acid is very vast and lots of strenous work has been already done in different aspects of these versatile metal extractants. These reagents posses great importance in recent years because of their analytical [1-3], agricultural [4-6], biological [7-10], antioxidant [11] and technical applications [12-16]. Knowledge of base strength of weak organic bases is a useful diagnostic tool to understand a biological reaction, structure reactivity relationship and to study the reaction kinetics. N-Arylsubstituted hydroxamic acids behave as weak organic bases in presence of mineral acid solution. Their protonation parameters have been estimated in aqueous sulphuric acid solution following Excess Acidity Method. The present investigation also discussed substituent effect on protonation behaviour of these reagents.

MATERIALS AND METHODS

Electronic Corporation of India, Hyderabad, model GS 5700, a digital spectrophotometer having 10mm matched cells was employed for the absorption measurement at fixed wavelength. Analytical grade Carbon tetrachloride and sulphuric acid were used for determing distribution ratios. Acid was standarised with Sodium hydroxide solution which was titrated against potassium hydrogen Phthalate. In both the cases phenolphthalein was used as indicatior. Acidic solutions of different concentrations were prepared by diluting standard acid with glass distilled water.

RESULTS AND DISCUSSION

$pK_{H_2A^+}$ values for the protonation reaction of hydroxamic acids are calculated following Excess Acidity Method, EAM [17-19]. Excess acidity method also known as X-function method [20] is used to evaluate the acidity constants of weak bases, from ionisation ratio measurement in strong solution by the extrapolation to the aqueous standard state. This extrapolative method was an earlier approach proposed by Morziano and Passerini [21]. For proton transfer to a base HA, they proposed the general thermodynamic equation which involves proton concentration C_{H+} and the concept of excess medium acidity.

$$\log I = pK_{H2A+} + \log C_{H+} + m^*X \qquad [1]$$

where X = Excess acidity of the medium.

The term, excess medium acidity X, was first used by Perrin [22]. It is the difference between the abserved acidity and that which the system would have, if it is ideal [17-18]. X-scale is derived from indicator ratio data, Values of X are available for the aqueous sulphuric acid system [23] and are given in table 1 along with corresponding H_0 and H_A values. Slopes m*, the plots of log I versus X are presented in fiqures 1 to 5. It expresses the sensitivity of the substrate to the changing acidity and describes the protonation behavior of the base, H_A. Values of $pK_{H_2A^+}$, m* and r are presented in Table 2.

Table 1: Values of H_0, H_A and X as a function of sulphuric acid concentration.

Acidity %	Acidity Functions		
	$-H_0$	$-H_A$	X
10	0.31	0.15	0.231
15	0.66	0.40	0.387
20	1.01	0.67	0.573
25	1.37	0.92	0.790
30	1.72	1.17	1.038
35	2.06	1.41	1.317
40	2.41	1.67	1.628
45	2.85	1.91	1.969
50	3.38	2.18	2.345
55	3.91	2.44	2.763

Table 2. Protonation parameters of n-arylhydroxamic acids in sulphuric acid by EAM.

S. No.	Hydroxamic Acid	EAM H_0			
		$pK_{H_2A^+}$	m*	r	σ
1.	N-phenyl-2-chlorobenzo-	-2.2870	1.1361	0.9958	0.9449
2.	N-phenyl-2-iodobenzo-	-2.0828	1.2240	0.9985	0.8735
3.	N-phenyl-2-nitrobenzo-	-2.5451	1.1749	0.9967	1.0233
4.	N-o-Totyl-2-chlorobenzo-	-2.5997	1.2642	0.9992	0.9492
5.	N-o-Totyl-2,4-dichlorobenzo-	-2.6660	1.2453	0.9992	0.9811

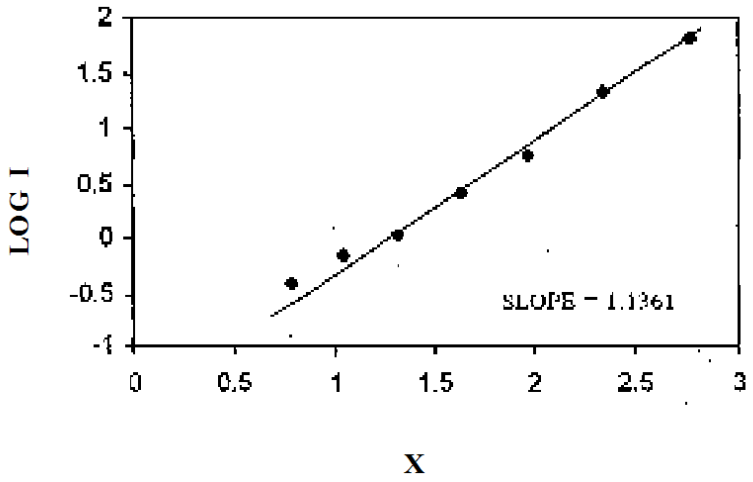

Fig. 1: N-Phenyl-2-chlorobenzohydroxamic acid

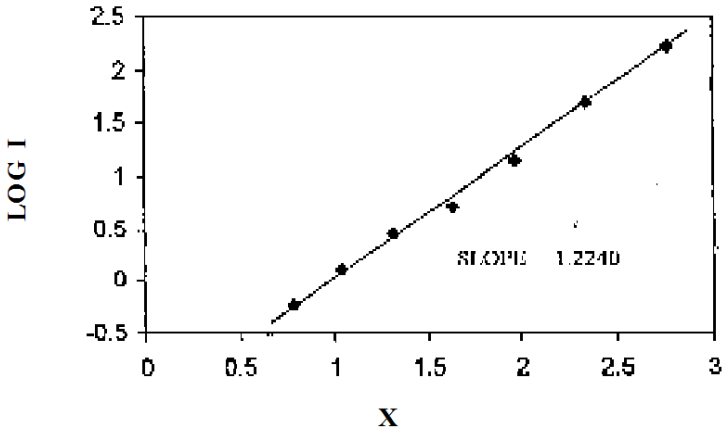

Fig. 2: N-Phenyl-2-iodobenzohydroxamic acid

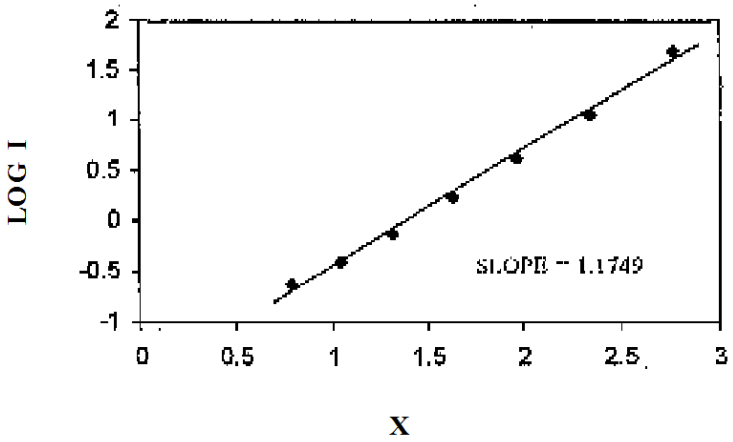

Fig. 3: N-Phenyl-2-nitrobenzohydroxamic acid

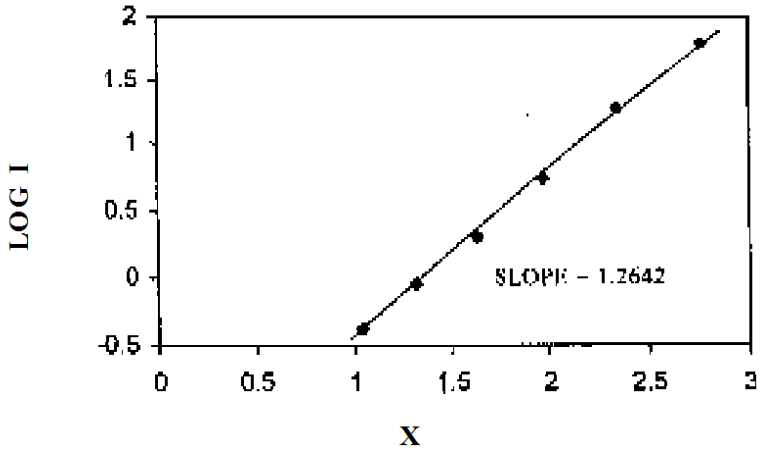

Fig.4: N-o-Tolyl-2-chlorobenzohydroxamic acid

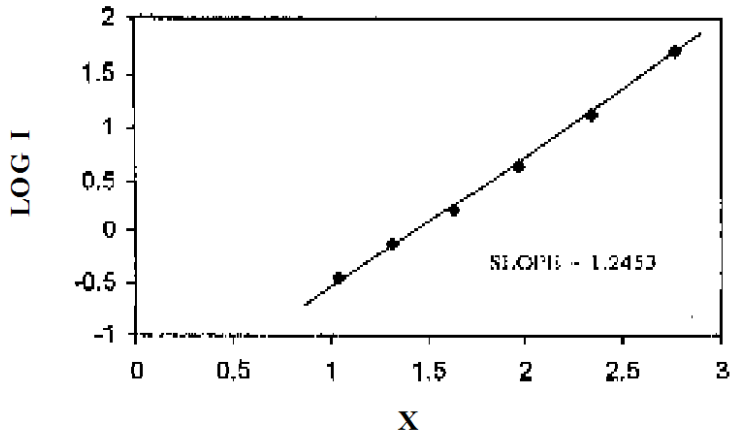

Fig.5: N-o-Tolyl-2,4-dichlorobenzohydroxamic acid

The slopes for the equation (1) are the measure of the protonation behaviour of the substrate and express the sensitivity of the substrate to the changing acidity. In EAM slopes m* are the plots of log I versus X obtained in the range from 1.1367 to 1.2931. $pK_{\mathbf{H2A+}}$ is a measure of acid strength of the conjugate acid H_2A^+ of the base HA. The stronger is the acid H_2A^+, the weaker will be the base HA. The values of $pK_{\mathbf{H2A+}}$ determined by EAM are least negative. The values of $pK_{\mathbf{H2A+}}$ is from -1.9145 to 2.6660 for EAM. These data suggest that hydroxamic acids behave as weak bases in presence of sulphuric acid.

APPLICATIONS

This study is useful to know the protonation behavior of N-Aryl hydroxamic acids

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