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NOTE

Study of Hydrolysis of Mono 2,5-Diethoxy Aniline Phosphate in Acid Medium at Constant Ionic Strength

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The present work is focused on the mechanism of hydrolytic break down of mono 2,5-diethoxy aniline phosphate. The phosphate esters find application depending upon the kind of linkages involved. The hydrolysis was carried out at three different temperatures. Ionic strength data and the effect of concentration point to existence of conjugate species of mono 2,5-diethoxy aniline phosphate as reactive species in acid region.

Key Words: Mono 2,5-diethoxy aniline, Ionic strength.

The organic phosphates are the esters of organo phosphoric acid which are formed by the replacement of acidic hydrogen atoms by an alkyl and aryl or their substituted derivatives. It forms a series of esters with alcohols, phenols, thiols and their derivatives. When the ionic strength is adjusted in such a manner that it is not affected significantly during the progress of reaction, primary and secondary salt effects[1] are the two major interactions produced. When the reaction takes place directly between two ions, the effect of inert salts on the rate of reaction is known as primary salt effect[2]. This effect can be employed to deduce the changes on the reacting species in some cases. Debye Huckel limiting law is helpful for calculating the activity coefficient in dilute solutions.

Bunton[3] found that the rate of hydrolysis of dianion of dinitro phenyl phosphate. The hydrolysis of *p*-tolyl and *p*-nitro phenyl phosphate in pH range 2.0-7.0 was studied by Silver[4]. Organophosphate esters are the derivatives of orthophosphoric acid and raminifications are possible by making changes in substituent groups attached to phosphorus atom through specific linkages such as C-N-P[5] and C-O-P[6].

Phosphate esters, on hydrolysis produce inorganic phosphates and its quantitative estimation was possible by Allen's modified method[7]. (i) mono 2,5-diethoxy aniline phosphate (ii) HCl + NaCl (iii) solvent-water (iv) temperature 98 ± 0.5 ºC (v) ionic strength = 1 μ (vi) amidol reagent (vii) ammonium molybdate.

Ionic strength (1.0 μ) was maintained by taking 2.1 mL of 11.5 M HCl and 6.25 mL of 4 M NaCl.

Kinetic runs were made at different ionic strength in order to know whether or not there exists the effect of ionic strength or the presence of acid catalysis. The different ionic strength (1, 2 and 3 μ) were maintained by proportionate mixture of NaCl and HCl. Rate constants at different ionic strength are recorded in Table-2.

TABLE-1
HYDROLYSIS OF MONO ESTER AT CONSTANT IONIC STRENGTH (μ)

Time (min)	Optical density (x)	(a-x)	log k_e	log k_c (min)
24	0.04	0.38	3.7023	5.04
58	0.10	0.32	3.7034	5.05
93	0.15	0.27	3.6967	4.97
135	0.20	0.22	3.6943	4.95
173	0.24	0.18	3.7006	5.02
255	0.30	0.12	3.6986	4.99

Average value $k_c = 500 \times 10^{-3}$ (min)

TABLE-2
HYDROLYSIS OF MONO 2,5-DIETHOXY ANILINE PHOSPHATE AT
CONSTANT IONIC STRENGTH AT 98 ºC

Ionic strength (μ)	Composition		10^3 k_e exp. (min^{-1})
1	0.2	0.8	4.55
	0.4	0.6	5.00
	0.6	0.4	5.82
2	0.4	1.6	4.65
	1.0	1.0	5.50
	1.6	0.4	6.75
3	0.6	2.4	4.90
	1.4	1.6	5.75
	2.2	0.8	6.55

A plot between rate-coefficients and acid molarity (Table-3), three linear plots are obtained (not shown) and each denotes the kinetics at that ionic strength. The slopes of straight lines decrease with increase ionic strength. The acid catalysis is subjected to negative salt effect. Each of these lines makes an intercept on rate axis which is designated as neutral rate constant. It increases with increasing ionic strength indicating the positive influence of ionic strength on neutral rates.

Both neutral and acid catalyzed rates have been shown to be in relation with the ionic strength by the second empirical term of Debye Huckel equation.

Since the rates are proportional to the concentration of individual reactive species, the total rate due to neutral as well as conjugate acid species can be given as:

$$K_e = k_N^+ k_H^+ C_H^+$$

Both neutral and conjugate acid species of the monoester regularly contribute to the overall rate upto 3.5 M and beyond.

TABLE-3
HYDROLYSIS OF MONO 2,5-DIETHOXYANILINE PHOSPHATE *via* ITS
NEUTRAL AND CONJUGATE ACID SPECIES AT 98 ºC

Ionic strength (μ)	10^3 k_H^+ ($min^{-1}mol^{-1}$)	5 + log k_H^+	10^3 k_N (min^{-1})	5 + log k_N
1	4.28	2.63	3.25	2.51
2	1.63	2.21	4.00	2.60
3	0.91	1.96	4.50	2.65

Ionic strength data shows that the maximum at 3.5 M HCl is due to salt effect. It is consistent with the feebly basic nature of esters. In case of amide systems the maximum has been attributed to maximum protonation. Arhenius parameters for kinetic runs in acid solutions before and after the maximum are different. Unless heat of protonation is small, a difference between the activation energies before and after maximum protonation in the case of mono 2,5-diethoxyaniline phosphate has been found to be absent since the activation energies are not significantly different for kinetic runs in 3 M and 5 M HCl.

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