Kinetic Study and Mechanism of Mono-β-Naphthylamine Phosphate (Ba-Salt) via Conjugate Acid Species

R. PATIL*, C.P. SHINDE, A. SAMADHIYA and K.B. DAS
School of Post Graduate Studies in Chemistry
Jiwaji University, Gwalior-474 011, India

Hydrolysis of mono-β-naphthylamine phosphate (Ba-salt) was carried out in the acid region (0.1–7.0 mol dm^{-3}) at 98°C in aqueous media. The acid log rate profile has a rate maxima at 4.0 mol dm^{-3}. Here mainly contribution of mono-β-naphthylamine phosphate (Ba-salt) is involved in hydrolysis. The participation of conjugate acid species and determination of theoretical rates has been exhibited by ionic strength data. The observed rates were also found in close agreement with the estimated theoretical rates derived from the 2nd empirical term of Debye-Hückel equation. By molecularity data the bimolecular nature of reaction is detected and P-N bond fission has been stengthened by isokinetic relationship.

INTRODUCTION

Kinetic Study & Mechanism of Mono-β-Naphthylamine Phosphate

The phosphate esters with C-N-P linkages have also been used as plasticizers[1], polymeric substances[2], synthetic lubricants[3] and hydraulic brake fluid[4], particularly cyclic amine phosphate in combination with phosphoramidic acid media and sulpha drugs are very important for their pharmaceutical and medicinal value[5] and as cancer chemotherapeutic agents. The present work is an extension of the previous work.[6]

EXPERIMENTAL

Mono-β-naphthylamine phosphate (Ba-salt) was prepared by P_2O_5 method by phosphorylation of β-naphthylamine in the mixture of benzene and pyridine. The reaction was carried out at 98°C employing (5.0×10^{-4} mol dm^{-3}) solution of the compound which was followed by colorimetic estimation by Allen's[6] modified method in aqueous media. While constant ionic strengths were maintained using appropriate mixture of NaCl and HCl.

RESULTS AND DISCUSSION

Investigation was carried out at 98°C in the range of 0.1 to 7.0 mol dm^{-3} in aqueous media and it was found that the pseudo-first order rate coefficients increase with the subsequent increase in acid molarity[7, 8] upto 4.0 mol dm^{-3} (Table-1) and then on further rise in molarity decrease in rate coefficients has

been found which can be attributed to the complete conversion of the basic (ester) molecules into respective conjugate acid species with simultaneous lowering in concentration of neucleophile (water) playing an important role in the rate determining step of bimolecular reactions.

Hydrolysis at each ionic strength (1, 2 and 3 μ) is denoted by linear curve, the increase in rates with the increase in acid concentration at each ionic strength (1.0, 2.0 and 3.0 μ) indicates the specific acid catalysis. Here the neutral rates are subjected to a positive ionic strength effect, since increase in intercepts with increase in μ has been observed. The slopes of the linear curves suggest a positive contribution of ionic strength effect to the acid catalysed species.

The reaction in the acid range can be represented by:

$$K_e = K_{H^\oplus} \cdot C_{H^\oplus} + K_N \qquad (i)$$

Using second empirical, term of Debye-Hückel equation,[9] Eq. (i) becomes Eq. (ii).

$$K_e = K_{H_0^\oplus} C_{H^\oplus} \exp b_{H^+}\mu + K_{N_0} \exp b_n \cdot \mu \qquad (ii)$$

where $K_{H_0^+}$ and K_{N_o} are specific conjugate acid and specific neutral rate coefficients at zero ionic strength respectively and b_H^+ and b_N are constants.

The rates estimated from Eq. (ii) are in close agreement with the experimentally observed rates, upto 4.0 mol dm^{-3} HCl (Table-1)

In the region of 0.1 mol dm^{-3} to 4.0 mol dm^{-3} the rate law is represented by Eq (iii).

$$K_e = 2.065 \times 10^{-3} C_{H^+} \exp (0.01662 \times 2.303)\mu$$
$$+ 2.398 \times 10^3 \exp (0.1945 \times 2.303)\mu \qquad (iii)$$

The rates above 4.0 mol dm^{-3} HCl, however, deviate probably due to decrease in the reactivity of the neutral form as a result of decrease in water activity. Therefore, the rates beyond 4.0 mol dm^{-3} HCl were calculated employing Bronsted-Bjerrum[10] [Eq. (iv)].

$$K_e = K_{H_o} + C_{H^+} \exp b_{H^+} \cdot \mu(a_{H_2O})^n + K_{N_o} \exp b_n \cdot \mu(a_{H_2O})_n \qquad (iv)$$

Hence the rate law beyond 4.0 mol dm^{-3} HCl may be represented as Eq. (v).

$$K_e = 2.065 \times 10^{-3} C_{H^+} \exp (0.01662 \times 2.303)\mu (a_{H_2O})^n$$
$$+ 2.398 \times 10^3 \exp (0.1945 \times 2.303\mu (a_{H_2O})^n) \qquad (v)$$

where $(a_{H_2O})^n$ is water activity term[11] and n is an integer, which increases with increase in acidity. The revised estimated rates now agree well with the experimentally observed rates (Table-1). It is clear from the above results that mono-β-naphthylamine phosphates in acid solutions occur via both conjugate acid and neutral species and their rates are subjected to both ionic strength and water activity.

Solvent effect (Table-1) shows a significant rise in rates; dioxane being a better proton donor than water increases the concentration of conjugate acid species resulting in the increase in rates. Effect of solvent on the rate of hydrolysis may,

TABLE-1

ESTIMATED AND EXPERIMENTAL RATES FOR HYDROLYSIS OF MONO-β-NAPHTHYLAMINE PHOSPHATE (Ba SALT) AT 98°C

HCl mol dm^{-3}	$K_N \times 10^3$ min^{-1} $K_N = K_N \exp b'_N$	$K_N \times 10^3$ min^{-1} $K_N = K_{N_0} \exp b'_N \mu \cdot (a_{H_2O})^n$	n	$K_H^+ C_H^+ \times 10^3$ min^{-1} $= K_H^+ C_H^+ \exp b'_H$	n	$K_H^+ C_H^+ \times 10^3$ min^{-1} $= K_H^+ C_H^+ \exp b'_H \mu \cdot (a_{H_2O})^n$	$K_e \times 10^3$ min^{-1} (estd.)	$K_e \times 10^3$ min^{-1} (expt.)	$4 + \log K_e$ (estd.)	$4 + \log K_e$ (expt.)
0.1	2.508			0.207			2.715	1.790	1.446	1.252
0.2	2.623			0.417			3.040	2.100	1.490	1.322
0.5	2.999			1.040			4.039	2.990	1.604	1.457
1.0	3.749			2.145			5.894	5.754	1.759	1.759
2.0	5.861			4.458			10.319	11.012	2.040	2.013
3.0	9.162			6.947			16.119	16.509	2.217	2.207
								6.320[c]		1.801
								3.430[d]		1.540
4.0	14.321			9.624			23.945	24.599	2.390	2.379
								26.599[a]		
								37.229[b]		
5.0	22.387	15.667	1	12.502	2	6.123	21.790	20.789	2.317	2.338
								8.709[c]		1.940
								3.881[d]		1.589
6.0	34.994	14.387	2	12.387	3	3.628	18.015	18.447	2.265	2.255
7.0	34.701	8.770	3	18.886	4	1.446	10.216	9.291	1.968	2.009

a, b are solvent effect data of 10.0% and 20.0% dioxane respectively.   c, d are temperature effect data at 80° and 70° respectively.

therefore, be taken to indicate the formation of transition state in which charge is dispersed; this is in accordance with Chanley's observation.[12] Bimolecular nature is further supported by Hammett[13] (0.556), Zücker-Hammett[14] (1.00), Bunnett[6] (W = 7.00, W* = 2.5) Bunnett-Olsen[15] (ϕ = 1.434) plots.

Arrhenius parameters[16] for the reaction in 3.0 mol dm^{-3} HCl where.found to be E = 14.566 kcal/mol, A = 3.353 × 10^4 sec^{-1}, $\Delta S^{\neq}$ = −39.43 e.u. The corresponding values at 5.0 mol dm^{-3} HCl were E = 13.728 kcal/mol, A = 4.496 × 10^4 sec^{-1}, − $\Delta S^{\neq}$ = 38.85 e.u. respectively.

The concentration effect of the present ester confirms the order of reaction to be one with respect to the present ester by reducing either half (24.37 × 10^{-3} min^{-1}) or double (K$_e$ = 24.729 ×10^{-3} min^{-1}) and normal concentration (K$_e$ = 24.599 × 10^{-3} min^{-1}) at 4.0 mol dm^{-3} HCl.

The hydrolysis of the mono-β-naphthylamine occurring via the cleavage of P-N bond fission[17-19] follows the isokinetic relationship (figure not shown).

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