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Insecticidal Activity, Kinetics and Mechanism of Hydrolysis of Bis-3-nitro-*p*-touidine Phosphate via Conjugate Acid Species

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Bis-3-nitro-*p*-toluidine phosphate was found to be a good insecticide. Kinetic study has been investigated in acid region from 0.1 to 6.0 mol dm^{-3} at 98°C in 30% dioxane-water mixture (v/v). Ionic strength data exhibits the participation of conjugate and neutral species. Bimolecular behaviour has been decided by molecularity data studies. Solvent isotope effect study favours specific acid catalysis. The formation of a transsition state has been observed by solvent effect study. Phosphorus-nitrogen bond fission has been further strengthened by isokinetic relationship.

INTRODUCTION

Bis-3-nitro-*p*-toluidine phosphate has been synthesised with a view to investigate various reaction paths involved in its hydrolytic reaction. The use of organophosphates is widely acclaimed as insecticides. The organophosphorus insecticides today account for approximately 30% of the registered synthetic insecticides in the USA.[1] Bunton *et al.*.[2] found that acid catalysed hydrolysis occurred only when electron attracting substituent was present in the aryl moiety, as in nitrophenyl phosphate ester.

EXPERIMENTAL

The present phosphate ester was prepared by $POCl_3$ method[3], m.p. = 159°C. It was characterised by elemental analysis (% of observed P = 8.42) and IR spectrum at 3340 cm^{-1} (—NH stretching); 3220 cm^{-1} (—OH stretching); 3080 cm^{-1} (=CH stretching in aromatics); 1616 and 1625 cm^{-1} ν(C=C) in aromatic nuclei); 1270 cm^{-1} ν(P=O)); 1340 and 1520 cm^{-1} $\nu(NO_2)$.

Periplaneta americana, the common cockroaches, were used for insecticidal activity[4].

The acid hydrolysis of the present ester (5×10^{-4} mol dm^{-3}) in the acid range (0.1 to 6.0 mol dm^{-3} HCl at 98 ± 0.5°C) was carried in 30% aqueous dioxane (v/v) medium. The inorganic phosphate obtained during hydrolysis was estimated colorimetrically by Allen's modified method[5].

RESULTS AND DISCUSSION

There are several ways to administer insecticides to an insect[6]. Contact method was employed for the application of the compound in acetone medium. Death of the cockroaches occurred after 10 h of application of the compound which indicates its toxicity.

Good pseudo-first order rate coefficients were obtained (Table-1). Acid and pH log rate profile (Figure not shown) showed that rates increased with decrease in pH up to 4.0 mol dm^{-3} HCl,[7, 8] then decreased with increase in acid molarity up to 6.0 mol dm^{-3}. The initial increase in the rate of hydrolysis is due to incursion of conjugate acid species. The cause of the bend at 4.0 mol dm^{-3} HCl may not be due to maximum protonation because ester as a class are feebly basic substances; therefore, the cause of the bend has been attributed either to water activity or to the effect of ionic strength or may be due to both. To examine the above cause kinetic runs may be carried out at constant ionic strength[9] by using appropriate mixture of NaCl and HCl at different ionic strengths (Fig. not shown). The acid catalysed rates are subjected to positive salt effect, as the slopes are progressing with the increase in ionic strength. The intercepts on the rate axis show the presence of a side reaction via neutral species. Since the intercepts on the rate axis decrease in magnitude with the increase in ionic strength, neutral hydrolysis is subjected to negative ionic strength effect. Such results are obtained in case of hydrolysis of glycollides[10]. The reaction in the acid range can be represented by:

TABLE-1

ESTIMATED AND EXPERIMENTAL PSEUDO-FIRST ORDER RATE COEFFICIENTS FOR THE HYDROLYSIS OF BIS-3-NITRO-*p*-TOLUIDINE PHOSPHATE AT 98°C

HCl mol dm^{-3}	$10^3 K_H^{\oplus} C_H^{\oplus}$ min^{-1}	$10^3 K_N$ min^{-1}	$10^3 K_e$ estimated from Eq. (2)	$-\log (a_{H_2O})^n$	$10^3 K_e$ estimated from eqn. (4)	$10^3 K_e$ experimental min^{-1}
0.1	0.96	16.82	17.78	—	17.78	17.63
0.2	1.98	16.66	18.59	—	18.59	19.60
0.5	4.90	16.19	21.09	—	21.09	20.65
1.0	10.09	15.45	25.54	—	25.54	25.94
1.5	15.56	14.74	30.30	—	30.30	30.53
2.0	21.33	14.06	35.39	—	35.39	37.13
2.5	27.40	13.41	40.81	—	40.81	41.00
3.0	33.81	12.79	46.60	—	46.60	46.96, 34.08[a], 26.02[b] 47.80[c], 49.45[d]
4.0	47.65	11.64	59.29	—	59.29	59.98
4.5	55.10	11.10	66.20	$(0.130)^2$	41.38	41.28
5.0	62.93	10.59	73.52	$(0.155)^3$	32.16	32.50, 24.73[a], 18.64[b] 35.03[c], 38.81[d]
5.5	71.17	10.58	81.75	$(0.181)^4$	24.01	23.26
6.0	79.81	9.64	89.45	$(0.211)^5$	16.67	16.48

Note: a = 90°C, b = 80°C, c = 40% dioxane, d = 45% dioxane.

$$K_e = K_H^{\oplus} \cdot C_H^{\oplus} + K_N \qquad (1)$$

Using second empirical term of Debye-Huckel equation[11], Eq. (1) becomes Eq. (2).

$$K_e = K_{H_0^{\oplus}} \cdot \exp b_{H^{\oplus}}\mu C_{H^{\oplus}} + K_{N_0} \exp b_N \cdot \mu \qquad (2)$$

where $K_{H_0^{\oplus}}$ and K_{N_0} are specific conjugate acid and specific neutral rate coefficients at zero ionic strength respectively and $b_{H^{\oplus}}$ and b_N are constants.

The rates estimated from equation (2) 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. (3).

$$K_e = 9.54 \times 10^{-3} \exp (0.024 \times 2.303) + 16.98 \times 10^{-3} \exp (-0.041 \times 2.303)\mu \quad (3)$$

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[12] (Eq. (4)).

$$K_e = K_{H_0^{\oplus}} \cdot CH^{\oplus} \cdot \exp b_{H^{\oplus}} \cdot \mu (a_{H_2O})^n + K_{N_0} \cdot \exp b_N \cdot \mu \qquad (4)$$

Hence the rate law beyond 4.0 mol dm^{-3} HCl may be represented as Eq. (5).

$$\begin{aligned} K_e = {} & 9.54 \times 10^{-3} \cdot C_{H^{\oplus}} \cdot \exp (0.024 \times 2.303)\mu \\ & + a(H_2O)^n + 16.98 \times 10^{-3} \exp (-0.041 \times 2.303)\mu \qquad (5) \end{aligned}$$

where $(a_{H_2O})^n$ is water activity term[13] 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 bis-3-nitro-*p*-toluidine phosphates in acid solutions occur *via* both conjugate acid and neutral species and their rates are subjected to both ionic strength and water activity.

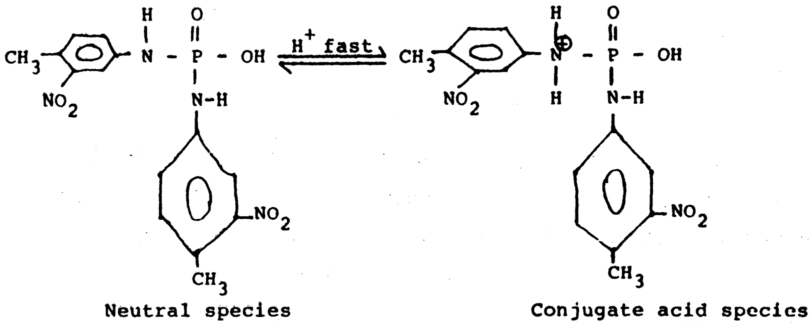
Solvent effect (Table-1) shows a significant rise in rates; dioxane being a better proton donor than water increases the concentration of conjugate acid species resulting in the increase in rates. Effect of solvent on the rate of hydrolysis may, therefore, be taken to indicate the formation of transition state in which charge is dispersed; this is in accordance with Chanley's observation[14].

Thermodynamic parameters[15] for the reaction in 3.0 mol dm^{-3} HCl were found to be $E = 8.28$ kcals/mol, $A = 0.591 \times 10^{+2}$ sec^{-1}, $\Delta S^{\neq} = -52.87$ e.u. The corresponding values at 5 mol dm^{-3} HCl were $E = 8.55$ kcals mol^{-1}, $A = 0.608 \times 10^{+2}$ sec^{-1}, $\Delta S^{\neq} = -52.81$ e.u. These values are indicative of bimolecular nature of hydrolytic reaction. Biomecular nature of reaction is further supported by slopes of the plots of Zücker and Hammett[16] (1.03), Hammett[17] (0.3) and Bunnett[18] ($w = 8.0$, $w^* = 3.33$). Bunnett and Olsen[19] ($\phi = 1.33$ which is greater than 0.58) (plots not shown) suggests that water is involved as a proton transfer agent in the rate determining step.

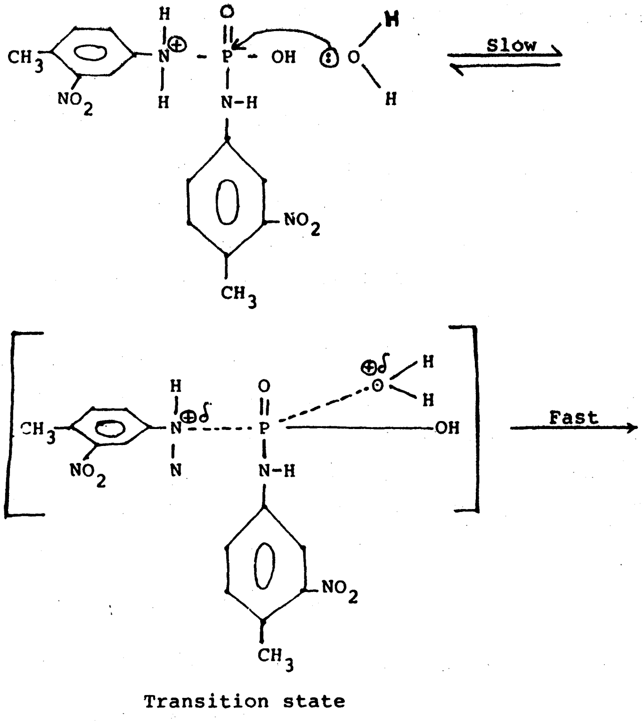
Since the rate coefficients are fairly similar and are independent of initial concentration of (diester) the reaction may be taken to be kinetically of first order[20]. The hydrolysis of the diester occurs via the cleavage of P—N bond; fission follows the isokinetic relationship[21] (figure not shown).

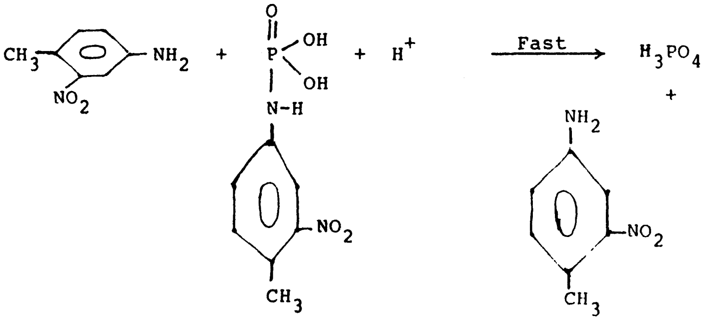
By observing the above evidences and discussions the most tentative mechanistic routes for the conjugate acid species may be formulated as:

(a) Formation of conjugate acid species by fast pre-equilibrium proton transfer:



(b) Bimolecular nucleophilic attack of water on phosphorus of the conjugate acid species $S_N{}^2(P)$





REFERENCES

1. Fumio Matsumura, Toxicology of Insecticides, Plenum Press, N.Y. and London (1976).
2. P.W.C. Barnard, C.A. Bunton, D. Kellerman, M.M. Mhala, B. Silver, C.A. Vernon and V.A. Welch, *J. Chem. Soc. B*, 227 (1966).
3. P. Rudert, *J. Chem. Soc. A*, 323 (1893).
4. R.D. O'Brien, Insecticides: Action and Metabolism, Academic Press, New York and London (1967).
5. R.J.L Allen, *Biochem. J.*, **34**, 838 (1940).
6. P.J. Oppenoorth, *Entomol. Exptt. Appl.*, **2**, 216 (1959).
7. M.M. Mhala and Shashi Prabha, *Indian J. Chem.*, **8**, 972 (1976).
8. M.M. Mhala, M.D. Patwardhan and G. Kasturi, *Indian J. Chem.*, **7**, 145 (1969).
9. K.J. Laidler, Chemical Kinetics, Tata McGraw-Hill, New Delhi, 229 (1965).
10. J.P. Mishra, Mechanism of the hydrolysis of some lactides, Ph.D. Thesis, Jiwaji University, Gwalior (1967).
11. M.C. Bailly, *Bull. Soc. Chim. Fr.*, **2**, 340, 405 (1942).
12. P.W.C. Barnard, C.A. Bunton, D. Kellerman, M.M. Mhala, B. Silver, C.A. Vernon and V.A. Welch, *J. Chem. Soc. B*, 227 (1966).
13. J.F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956, 4982 (1961).
14. J.D. Chanley and E.J. Feageson., *Am. Chem. Soc.*, **80**, 2686 (1958).
15. S.Z. Arrhenius, *Phys. Chem.*, **4**, 226 (1889).
16. L. Zücker and P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1932).
17. L.P. Hammett, Physical Organic Chemistry, McGraw-Hill, London, 335 (1940).
18. J.F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).
19. J.F. Bunnett and F.P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).
20. E.S. Swinbourne, Analysis of Kinetic Data, Nelson, London, p. 53 (1971).
21. E.M. Kosower, An Introduction to Physical Organic Chemistry, Wiley, New York, pp. 51–59 (1968).

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