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Kinetics and Mechanism of Hydrolysis of Di-Ethyl Dithiophosphate in Acid Media

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Investigation of diethyl-dithio phosphate was carried out by using "Allen's" modified method of colorimetry, in aqueous medium from 0.1 to 7.0 mol dm^{-3} HCl at 98°C. Ionic strength data exhibit different contribution of neutral species and presence of acid catalysis. Theoretical rates estimated from 2nd empirical term of Debye-Hückel equation have been found in close agreement with experimental rates. Ionic strength, temperature, solvent and concentration of kinetic studies are provided to identify the reactive species and molecularity. Molecularity and bond fission are also discussed in terms of Zücker-Hammett hypothesis. Hammett acidity functions, Bünnet and Bünnett-Olsen parameters and isokinetic relationship.

INTRODUCTION

Phosphates having C-O-P linkages are of great importance. They are used as pesticides, insecticides[1], fire retardants[2], plasticizers[3], synthetic lubricants[4] etc. The undertaken compound *i.e.*, diethyl-dithiophosphate, was chosen for the kinetic study as this compound is reactive via different species depending upon the experimental conditions.

EXPERIMENTAL

Diethyl dithiophosphate compound is commercially available. The reactions were carried out at 98°C employing 5.0×10^{-4} mol dm^{-3} solution of diester which was subsequently followed by the Allen's[5] modified method of colorimetric estimation of organic phosphate in aqueous media maintaining constant ionic strength by means of HCl and NaCl. All the chemicals used were of BDH quality.

RESULTS AND DISCUSSION

The rate of hydrolysis of diethyl dithiophosphate was studied in HCl (0.1 to 7.0 mol dm^{-3} HCl at 98°C). In Table-1 the pseudo-first order rate constants are summarised, from which it is quite clear that rate of reaction increases up to 4.0 mol dm^{-3} HCl [6–9] but further increase in acid molarity really decreases the rate as it can be attributed to the complete conversion of the ester (basic) molecule into their respective conjugate acid species with the lowering of concentration of a nucleophile (water), which plays its role in rate determining step of bimolecular hydrolytic reaction.

In order to determine whether or not there is effect of ionic strength or presence of acid catalysis, kinetic runs were made at three different ionic strengths (1.0, 2.0 and 3.0 μ) which were maintained by adequate mixture of NaCl and HCl. Hydrolysis at each ionic strength is represented by a linear curve (figure not shown) that makes a positive slope. Since the K_{H^+} is slope increasing with increase in ionic strength, acid catalysis is subjected to positive effect of ionic strength.

From the study of ionic strength effect, the total rates contributed by conjugate acid and neutral can be calculated by the following 2nd empirical term of Debye-Hückel[10] equation

$$K_e = K_{H^\oplus} C_{H^\oplus} + K_N \qquad (1)$$

In the above equation the terms K_e, K_{H^+} and K_N are observed rate constants, the specific acid catalysed and specific neutral rates at that ionic strength respectively.

The sum of neutral and acid rates agree well with the experimentally observed rates (Table-1) up to 4.0 mol dm^{-3} HCl. The lowering in rates in 5.0, 6.0 and 7.0 mol dm^{-3} HCl can be explained by considering water activity[11-13] as an additional parameter represented as

$$K_e = K_{H^+} C_{H^+} (a_{H_2O})^n + K_N \qquad (2)$$

where a_{H_2O} is water activity and n is an integer. The revised estimated rates now agree well with the experimentally observed rates (Table-1). It is clear from the above result that diethyl dithiophosphate in acid solution occurs via both conjugate acid species and neutral species. The contribution of neutral species to overall hydrolysis is constant, while conjugate acid species is subjected to the positive salt effect.

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 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].

Arrhenius parameters[15] are determined for the hydrolysis at 3.0 and 5.0 mol dm^{-3} HCl (Table-2). The magnitude of Arrhenius parameter falls in the range of bimolecular reaction. Bimolecular nature of reaction is further supported by Hammett[16] (0.18), Zücker-Hammett[17] (1.062) and Bünnett[18] $W = 8.15$, $W^* = 2.5$. Bünnett-Olsen parameter[19] $0 = 1.66$ which is greater than 0.58 suggests that water involved as a proton transfer agent is the rate determining step.

The effect of concentration of diester on the rate of hydrolysis also confirms the order of reaction to be one with respect to the diester by reducing half ($K_e = 2.29 \times 10^{-4}$ min^{-1}) or double ($K_e = 22.12 \times 10^{-4}$ min^{-1}) the normal concentration ($K_e = 22.29 \times 10^{-4}$ min^{-1}) at 4.0 mol dm^{-3} HCl.

Comparative kinetic data (not shown) also support the bimolecular nature of hydrolysis involving attack of water molecule on phosphorus of the diester involving P-O bond fission[20].

TABLE-1
ESTIMATED AND EXPERIMENTAL DATA FOR THE HYDROLYSIS OF DIETHYL DITHIOPHOSPHATE AT 98°C

HCl (mol dm^{-3})	$K_N \times 10^4$ (min^{-1})	$K_{H^+}C_{H^+} \times 10^4$ (min^{-1})	$K_e \times 10^4$ (min^{-1}) (Estd)	$-\log(a_{H_2O})$	$K_e \times 10^4$ (min^{-1}) (Estd)	$K_e \times 10^4$ (min^{-1}) (Expt)
0.1	12.5	0.187	12.687		12.68	11.32
0.2	12.5	0.376	12.876		12.87	12.74
0.5	12.5	0.952	13.450		13.45	13.02
1.0	12.5	1.949	14.449		14.44	13.75
2.0	12.5	4.083	16.583		16.58	16.86
3.0	12.5	6.412	18.912		18.91	18.14
4.0	12.5	8.953	21.453		21.45	22.22 23.71[a] 25.03[b]
5.0	12.5	11.721	24.221	$(0.155)^3$	16.51	16.44
6.0	12.5	14.723	27.223	$(0.211)^4$	14.60	15.16
7.0	12.5	17.988	30.488	$(0.279)^5$	13.22	13.75

TABLE-2
CALCULATED ARRHENIUS PARAMETERS

HCl mol dm^{-3}	Temp. (°C)	$K_e \times 10^4$ min^{-1}	'E' kcal/mol	A sec^{-1}	$-\Delta S$ e.u.
3.0	98	18.14	11.44	1.65	50.828
3.0	85	10.28			
3.0	75	6.60			
5.0	98	16.44	12.36	5.22	48.544
5.0	85	8.91			
5.0	75	5.31			

REFERENCES

1. A.H. Schlesinger, *Chem. Abstr.*, **49**, 5517e (1955).
2. C.A. Vernon and V.A. Walch, *J. Am. Chem. Soc.*, **64**, 1553 (1942).
3. L.F. Audrieth and A.D.F. Toy, *J. Am. Chem. Soc.*, **64**, 1553 (1942).
4. E.F. Norman, Hitchcock, A.C. Robert, Rohar Corswell and E. Derbysire, 1, 042, 391 (1965).
5. R.J.L. Allen, Biochem. *J.*, **34**, 858 (1940).
6. M.M. Mhala and Shashi Prabha, *Indian J. Chem.*, **8**, 972 (1970).
7. M.M. Mhala, M.D. Patwardhan and G. Kasturi, *Indian J. Chem.*, **7**, 145 (1969).
8. R. Patil, C.P. Shinde and N. Kulshrestha, *Asian J. Chem.*, **7**, 342 (1995).
9. J.S. Chauhan, C.P. Shinde and R. Patil (Mhala), *Asian J. Chen.*, **8**, 411 (1996).
10. M.C. Bailey, *Bull. Soc. Chim. Fr.*, **2**, 340, 405 (1942).
11. J.E. Leffler and E. Gurnwald, The Rates and Equilibria of Organic Reactions, John Wiley and Sons Inc., New York, pp. 177, 286 (1963).
12. E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 224 (1933).
13. P.W.C. Barnard, C.A. Vernon and V.A. Welch, *J. Chem. Soc.*, 227, 229 (1966).
14. J.D. Chanley and E.J. Feageson, *J. Am. Chem. Soc.*, **80**, 2686 (1958).
15. S.Z. Arrhenius, *Phys. Chem.*, **4**, 226 (1889).
16. L.P. Hammett, Physical Organic Chemistry, McGraw-Hill, London, p. 335 (1940).
17. L. Zücker and P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1932).
18. J.F. Bünnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).
19. J.F. Bünnett and F.P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).
20. M.M. Mhala, (Miss) C.P. Holla, (Mrs.) G. Kasturi and (Miss) K. Gupta, *Indian J. Chem.*, **8**, 333 (1970).

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