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Hydrolysis of Organophosphate: Reaction Mechanism of 2,4,6-Trichloroaniline Phosphoro Triamidate via Conjugate Acid Species

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2,4,6-Trichloroaniline phosphoro triamidate undergoes hydrolysis in acidic medium ranging from 1 M HCl to 6 M HCl. The product of hydrolysis increases with increasing temperature and time until 4 M acid value and then decreases afterwards. The parameters such as substrate concentration and Arrhenius parameter have also been studied. The linear curves of Arrhenius parameter reflect the uniformity of the reaction. The influence of the nature of reactive species is determined by the study of ionic strength. Further, the study of solvent effect indicates the formation of transitional state, during hydrolysis. Bunnett-Olsen parameter suggests that water is not involved in the rate determining step of the reaction.

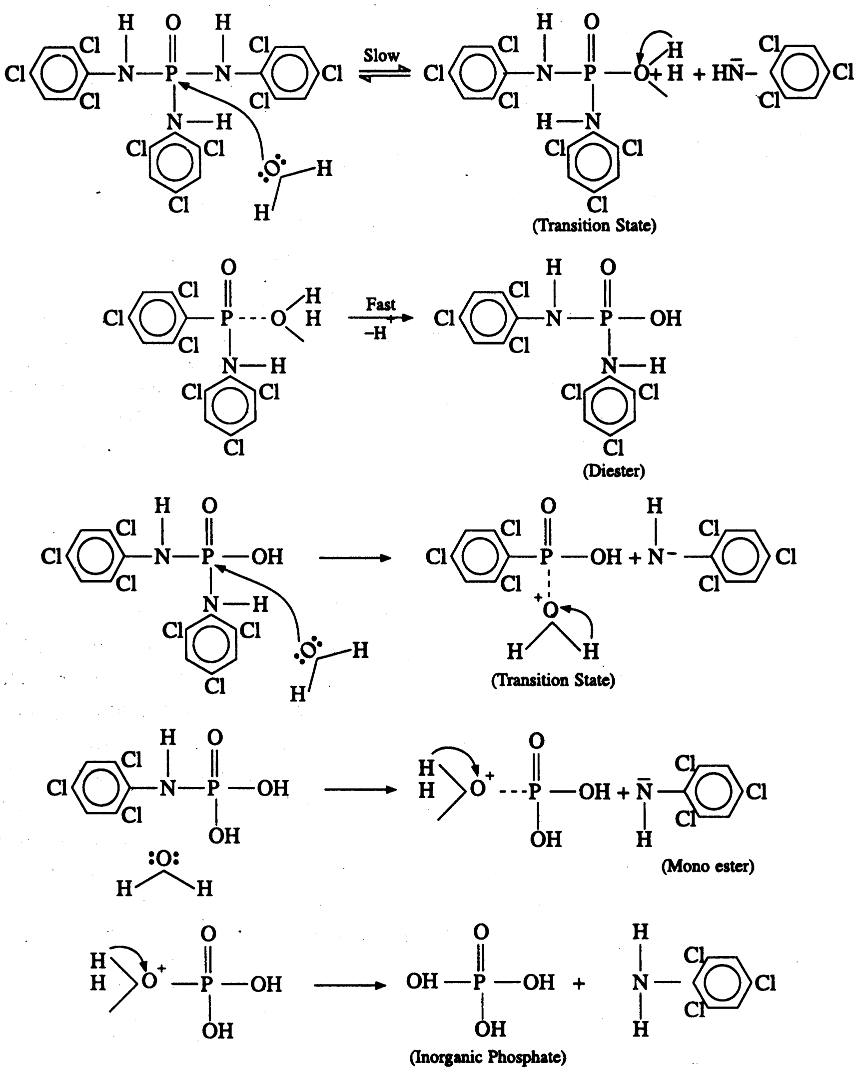
INTRODUCTION

The present investigation reports the hydrolysis of 2,4,6-trichloroaniline posphoro triamidate. It comprises a group of mono, di and tri esters. The phosphate esters having C—N—P linkage[1] known under the name of phosphoroamides, phosphoroamidic acids, phosphoroamidates undergo hydrolysis by different mechanisms. The reason of polymechanistic behaviour has been attributed to the fact that the ester may exist as an equilibrium mixture of different kind of species, varying in their degree of protonation and thereafter each of these species may react with nucleophile by more than one mechanism simultaneously[2].

Taking in to account that the cleavage of P—N bond can be used to study the condition of hydrolytic reaction, a series of kinetic runs were carried out at constant ionic strength. The concentration of tri-amidate is maintained at 5.0×10^{-4} M. For the present hydrolytic reaction 10% dioxane-water (v/v) binary mixture is used as a solvent medium. The molecularity of the hydrolytic reaction of triamidate in acidic medium is determined on the basis of Zucker-Hammett[3] hypothesis and Bunnett parameter[4] and to some extent by Arrhenius parameter[5]. The nature of acid catalysed reaction, *i.e.*, whether the hydrolysis is due to specific acid catalysis or subjected to ionic strength effect, is rationalised by Zucker-Hammett hypothesis and pH log rate profile.

For the study of the effect of dielectric constant on the rate of the hydrolytic reaction, the runs were carried in different percentage of dioxane-water mixture (v/v). The validity of Arrhenius equation is confirmed by carrying out runs in the temperature range of 60°, 70° and 80°C. The magnitudes of these parameters are helpful in establishing the molecularity of the reaction in the rate-determining step.

Bimolecular hydrolysis of conjugate acid species (S_N^2)



Reaction mechanism of the 2,4,6-trichloroaniline phosphoro triamidate hydrolysis

EXPERIMENTAL

A number of phosphorylating systems have been devised for preparing the ester of phosphoric acid by intermolecular dehydration. In the present study, synthesis is carried out by phosphorylation[6] using $POCl_3$. The characterisation of the synthesised compound was accompained with the aid of elemental analysis, UV and IR analysis. The study of reaction rates was done by using Allen's modified method[7]. All the chemicals used were either AR quality or Merc extra pure quality. The kinetic study of hydrolysis of amides formed during the course of hydrolysis was quantitatively carried out using ELICO colorimeter, at 608 μ red filter.

Kinetic study of the hydrolysis of 2,4,6-trichloroaniline phosphoro triamidate was done in 1 M to 6 M HCl at 70°C. The rate of hydrolysis was measured by colorimeter. The concentration was kept constant at 5.0×10^{-4} M. The results obtained are shown in Table-1.

TABLE-1
RATE CONSTANT FOR HYDROLYSIS OF 2,4,6-TRICHLOROANILINE PHOSPHORO TRIAMIDATE AT 70°C

HCl (M)	$\log CH^+$	$Ke \times 10^{-3}$ (min^{-1})	$(4 + \log k_e)$	$(4 + \log k_e) - \log CH^+$	$-H_0$	$\log (a_{H_2O})$	$\log CH^+ + H_0$	$4 + \log k_e + H_0$
1	0.0000	11.32	2.0538	2.0538	0.21	0.017	–0.2100	1.8538
2	0.3010	17.42	2.2400	1.9400	0.67	0.039	–0.3690	1.5510
3	0.4771	22.76	2.3571	1.8800	1.05	0.070	–0.5271	1.3070
4	0.6021	33.19	2.5210	1.9189	1.41	0.107	–0.8079	1.1210
5	0.6990	13.83	2.1408	1.4718	1.76	0.155	–1.0610	0.3808
6	0.7782	11.51	2.0610	1.2828	2.12	0.211	–1.3418	0.0590

It has been observed that with the increase in acidity up to 4 M HCl there is an increase in the rate of hydrolysis, with maximum at 4 M. An series of kinetic runs, in which ionic strength[8] is kept constant, were made in appropriate mixture of HCl and KCl. Three linear curves for three different ionic strengths (μ) are obtained. The rate axis indicates small contribution of hydrolysis *via* neutral species in strong acid medium.

Ionic strength is represented by:

$$K_e = K_H^+ \cdot C_H^+ \quad (1)$$

where K_e and K_H^+ are total acid and specific catalysed rate at that ionic strength. Estimated rates are obtained by applying

$$K_e = K_H^+ \cdot C_H^+ + K_N \quad (2)$$

On further applying empirical term of Debye-Huckel equation, the relationship may be represented as

$$\log K_H^+ \cdot C_H^+ = \log K_{H_0}^+ + \log C_H^+ + b'_{H^+} \cdot \mu \quad (3)$$

where b'_N is equal to $b'_{N/2.303}$ an K_N are specific natural rates at zero ionic strength.

Rates above 5 M HCl deviate from normal values which is attributed to decreasing reactivity of neutral forms. Therefore rates are calculated by applying Bronsted equation,

$$K^{+}_{H_0} = K^{+}_{H_0} \exp b^{+}_{H} \cdot \mu(a_{H_2O})^n \qquad \ldots (4)$$

$$K_N = K_{N_0} \exp b_N \cdot \mu(a_{H_2O})^n \qquad \ldots (5)$$

where $(a_{H_2O})^n$ represent the water activity[9] form.

In agreement with the foregoing analysis, Hammett parameter (slope 0.50) and Zucker-Hammett hypothesis (slope 1.20) indicate the bimolecularity of the reaction. Bunnett parameter (w = 10, w* = 5.0), emphasise that water affects the rate of reaction (Fig. 1).

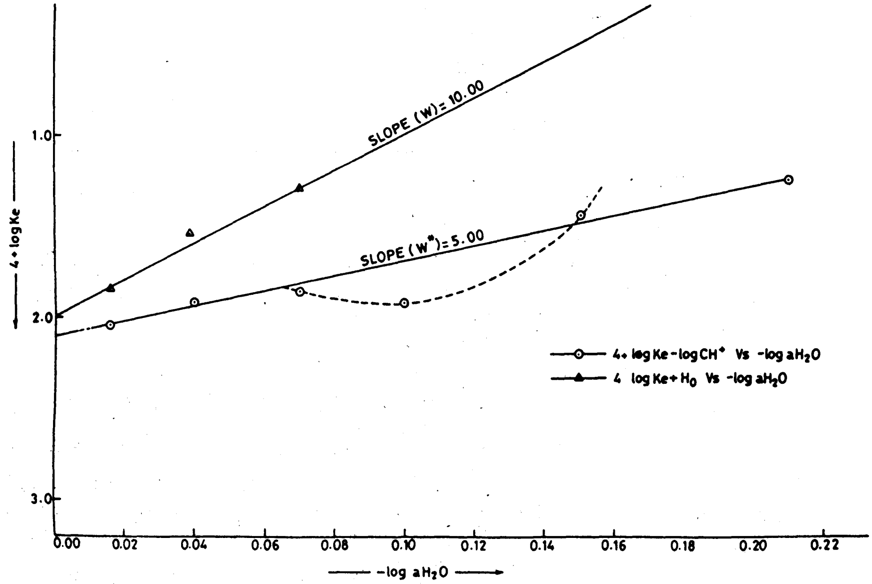


Fig. 1 Bunnett plot hydrolysis of 2,4,6 trichloroaniline phospohoro triamidate at 70°C

Thermodynamic parameter indicate that reaction is mainly governed by conjugate acid species[10]. The slope of linear curves were used to determine the value of energy of activation (E kcal/mol), frequency factor (A sec^{-1}) and entropy of activation ($\Delta s^{\neq}$ e.u). Comparative higher negative value of $\Delta s^{\neq}$ indicates that reaction is bimolecular. Results are shown in Table-2.

TABLE-2
ARRHENIUS PARAMETER FOR THE HYDROLYSIS OF 2,4,6-TRI CHLOROANILINE PHOSPHORO TRIAMIDATE AT 70°C

HCl	Energy of activation (E kcal/mol)	Frequency factor (A sec^{-1})	Entropy of activation ($\Delta s^{\neq}$ e.u.)
4 M	5.084	13.31	−56.48

The concentration effect was observed by varying concentration of substrate performed at 4 M HCl, where hydrolysis is independent of concentration. The effect of solvent on the rate of reaction depends upon the change of free energy of transition state relative to initial state. The success of Bronsted-Bjerrun rate equation[11, 12] has been limited because dieletric constant is not a good measure of short range interaction between solvent and reactants and it is these short range interactions which are dominant specially in dipolar protonic solvents.

RESULTS AND DISCUSSION

The difference observed in rate of hydrolysis is an apparent consequence of proton transfer agent in the rate determining step. The kinetics of hydrolysis of 2,4,6-trichloroaniline phosphoro triamidate has been carried out using acid buffer solution in aqueous medium. It is observed that rise in acidity increases the rate upto 4 M HCl and then decreases with increasing acidity. The cause has been attributed to either salt effect or the effect of water activity or both.

The valucs obtained by using the concept of molecularity favours the bimolecular nature of hydrolysis and dependence of acid catalysis role on water activity parameter involved as proton transfer agent in rate determining step. The values calculated for E kcal/mol, $\Delta S^{\neq}$ e.u. and A sec^{-1} fall in the range of bimolecular reaction path.

The effect of solvent shows rise in rate of hydrolysis, dioxane being better proton donor than water and increase in the concentration of conjugate acid species resulting in increasing rates. The concentration effect on the rate of hydrolysis also confirms the order of reaction to be of first order.

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