Asian Journal of Chemistry Vol. 5, No. 3 (1993), 679–683

Kinetics and Mechanism of Hydrolysis of Mono-2-Chloro 4-Nitrophenyl Phosphate

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Kinetic study of mono-2-chloro 4-nitrophenyl phosphate has been carried out in acid medium at 98 ± 5°C. Colorimetric method has been employed for the estimation of inorganic phosphate, the ultimate product of hydrolysis. Pseudo-first order rate coefficients have been calculated. In the acid region protonate acid species and neutral species have been found to be reactive. The calculated rate coefficients are in good agreement with the experimentally observed rates. The effect of pH, salt, temperature, solvent, solvent isotope and substrate concentration have been studied on the rate of hydrolysis.

INTRODUCTION

Bunton and coworkers[1] found that acid catalysed hydrolysis occurred only when electron attracting substituent was present in the aryl moiety, as in nitrophenyl phosphate mono ester, 4-chlorophenyl phosphate[2] showed only feeble acid catalysis, while 4-chloro-3-methylphenyl phosphate[3] showed absence of acid catalysis. Recently Mhala and coworkers[4] reported the hydrolysis of 4-chloro3,5-dimethylphenyl phosphate in acid medium, and showed the absence of acid catalysis. In continuation to this, we now wish to report the mechanistic step for the hydrolysis of mono-2-chloro 4-nitrophenyl phosphate.

EXPERIMENTAL

Mono-2-chloro 4-nitrophenyl phosphate (cyclohexyl ammonium salt) was prepared by PCl_5 method[5, 6]. The crude product so obtained was finally recrystallized (m.pt. 122°) with the help of absolute alcohol (Found: C, 46.36%, H, 6.92%, N, 9.86%, P, 7.86%; Required: C, 47.84%, H, 6.86%, N, 9.30%, P, 7.86%). Colorimetric method[7] was used for the estimation of inorganic phosphate. The concentration of the mono ester in all the kinetic runs was maintained 5×10^{-4} mol dm^{-3} (unless otherwise specified) for kinetic study at 98°, 90° and 70°C respectively.

All other chemicals used were of B.D.H. (A.R.) quality. D_2O (99.4%) was obtained from Bhabha Atomic Research Centre, Trombay.

RESULTS AND DISCUSSION

A plot of log rate constants versus pH showed that rates of hydrolysis of mono-2-chloro 4-nitrophenyl phosphate increased with decrease in pH upto 1.0 mol dm^{-3} HCl, then increased with increase in acid molarity up to 4.0 mol dm^{-3} HCl. The initial increase in rate of hydrolysis may be due to the conversion of neutral and mononegative species into neutral and conjugate acid species[8]. The maximum rate at 4.0 mol dm^{-3} HCl exhibits a maximum percentage of protonated form of mono ester[9]. However, beyond 4.0 mol dm^{-3} HCl there is lowering in rates. In the region 1.0 to 4.0 mol dm^{-3} HCl, increase in rates may be due to either acid catalysed hydrolysis or increase in reactivity of neutral species by ionic strength effect.

Therefore, effect of ionic strength was studied by performing kinetic runs at different constant ionic strengths by using appropriate mixture of NaCl and HCl. Thus hydrolysis of mono-2-chloro 4-nitrophenyl phosphate at constant ionic strength shows that the increase in rate with the increase in acid concentration, at each ionic strength (μ) indicates specific acid catalysis. This is further supported by the fact that rates are slightly increased ($K_{D_2O}/K_{H_2O} = 1.1$) when water is replaced by D_2O. This also suggests a fast preequilibrium proton transfer generally observed for specific acid catalysed reactions[10]. Neutral rates are subjected to a positive ionic strength effect, since increase in intercept with increase in μ has been observed. Increased slopes (K_H+) of curves suggest a +ve but different contribution of ionic strength effect to the acid catalysed species, which are in good agreement with the results of the hydrolysis of 2,3-dimethoxyphenyl dihydrogen phosphate[8].

From this ionic strength effect, the total rates contributed by both neutral and conjugate acid forms have been calculated by the following 2nd empirical term of Debye-Huckel equation[11].

$$K_e = K_{H^+} \cdot C_{H^+} + K_N$$

$$K_e = K_{H_0^+} \cdot C_{H^+} \cdot \exp b_{H^+}\mu + K_{N_0} \exp b_N\mu \qquad (1)$$

where K_{H^+},·$K_{H_0^+}$ and b_{H^+} are specific acid catalysed rate at that ionic strength, specific acid catalysed rate at zero ionic strength and slope of the linear plot of log K_H vs ionic strength respectively. Similarly, K_N, K_{N_0} and b_N are specific neutral rate at that ionic strength, specific neutral rate at zero ionic strength and a constant, slops of the linear plot of log K_N vs ionic strength. The intercepts on the rate axis in both the plots i.e. log $K_{H_0^+}$ and log K_{N_0} are found to be constants. Thus increase in total rate is due to both $b_{H^+}\mu$ and $b_N\mu$ factors, supporting the ionic acceleration effect.

In the range 0.01 to 2.0 mol dm^{-3} HCl, the close concordance is due to the contribution of both the neutral and conjugate acid species. The rates estimated from equation (1) are in close agreement with the experimentally observed rates within this range. After 3.0 mol dm^{-3} HCl, the calculations are based on the following modified equation of Bronsted-Bjerrum[1] type using water activity term and considering the participation of both the neutral and conjugate acid forms:

$$K_e = K_{H_0^+} \cdot C_{H^+} \cdot \exp b_{H^+} \cdot \mu + K_{N_0} \cdot \exp b_N \cdot \mu (a_{H_2O})^n \quad (2)$$

Kinetic rate law for the hydrolysis of present mono ester may be formulated as:

$$K_e = 14.45 \times 10^{-3} \cdot C_{H^+} \cdot \exp 0.11 \times \mu (a_{H_2O})^n + 0.55 \times 10^{-3} \exp 0.36 \mu (a_{H_2O})^n \quad (3)$$

where n is an integer, its value varies with the increase in acidity.

The dependence of the reaction rate on water activity is also shown by Bunnett parameters[9]. The values 3.2 and 8.33 for W and W* are associated with a slow proton transfer[9], but these values were taken to be unsuitable because the treatment failed for hydrolysis in toluene *p*-sulphonic acid and in mixture of HCl and LiCl[1]. However, Bunnett Olsen[12] parameter (ϕ), the slope of plot between log k + H_0 and log C_{H^+} + H_0, has been shown to be suitable to explain the acid dependence on reaction rate of dinitrophenyl phosphate[1] ($\phi = 1.2$). Similar results are also observed for mono-2-chloro 4-nitrophenyl phosphate ($\phi = 1.6$). This also suggests that water acts as a proton transfer agent too. Zücker Hammett hypothesis,[13] when applied to solvolytic reactions in moderately strong acid solutions, suggests the

TABLE 1

ACID AND NEUTRAL RATES FOR THE HYDROLYSIS OF MONO-2-CHLORO 4-NITROPHENYL PHOSPHATE AT 98°C

HCl (M)	$10^3 K_N$ (min^{-1})	$10^3 K_{H^+} C_{H^+}$ (min^{-1})	$10^3 K_e$ (min^{-1}) (Calcd.)	$10^3 K_e$ (min^{-1}) (Obsd.)
0.01	0.55	0.14	0.70	0.69
0.05	0.57	0.73	1.31	1.26
0.1	0.60	1.48	2.08	2.05
0.2	0.65	3.04	3.69	3.50
0.3	0.70	4.68	5.39	5.23
0.4	0.76	6.40	7.17	6.62
0.5	0.83	8.2	9.04	8.75
1.0	1.26	18.62	19.88	20.70
2.0	2.88	47.98	50.86	50.59
3.0	5.62[a]	61.95[f]	67.57	67.75, 35.10, 5.76 (90°C) (70°C)
4.0	10.46[b]	89.00[g]	96.46	97.62, 107.82*
5.0	5.82[c]	61.53[h]	67.35	67.22, 33.70, 5.52 (90°C) (70°C)
6.0	4.42[d]	39.44[i]	43.81	44.14
7.0	7.33[e]	23.99[j]	31.32	32.59

For a to j, the value of $(a_{H_2O})^n$ in eq. (5) are 1.0, 1.5, 5.0, 5.0, 5.0, 2.5, 2.5, 4.0, 4.0 and 5.0 respectively.

*Rates in D_2O.

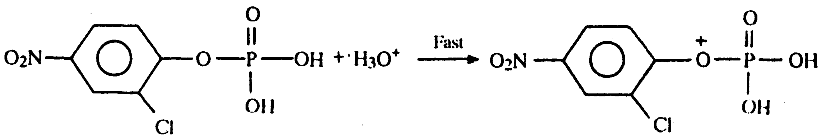
probable mechanism to be bimolecular, if the slope of the curve between log rate and log C_{H^+} is approximately unity. Zucker Hammett plot for the hydrolysis of mono-2-chloro 4-nitrophenyl phosphate ester gives a unit slope (curve not given when log $K_{H^+} \cdot C_{H^+} - b_{H^+} \cdot \mu$ is plotted against log C_{H^+}). Arrhenius parameters[14] ($E = 22.88$ Kcals mole^{-1}, $\lambda = 32.56 \times 10^9$ sec^{-1}, $\Delta S^+ = -12.86$ e.u. at 3.0 mol dm^{-3} HCl and $E = 22.88$ Kcal mole^{-1}, $\lambda = 32.56 \times 10^9$ sec^{-1}, $\Delta S^+ = 12.86$ e.u. at 5.0 mol dm^{-3} HCl) also lends support to the bimolecular nature of the reaction.

Hydrolysis of mono-2-chloro 4-nitrophenyl phosphate may proceed via bimolecular reaction either by P–O or C–O bond fission. The P–O bond rupture by the attack of water molecule on P is more probable because of the formation of resonance stabilized phenoxide ion intermediates. The probability of P–O bond rupture is also supported by comparative kinetic data or other monoaryl phosphates[15].

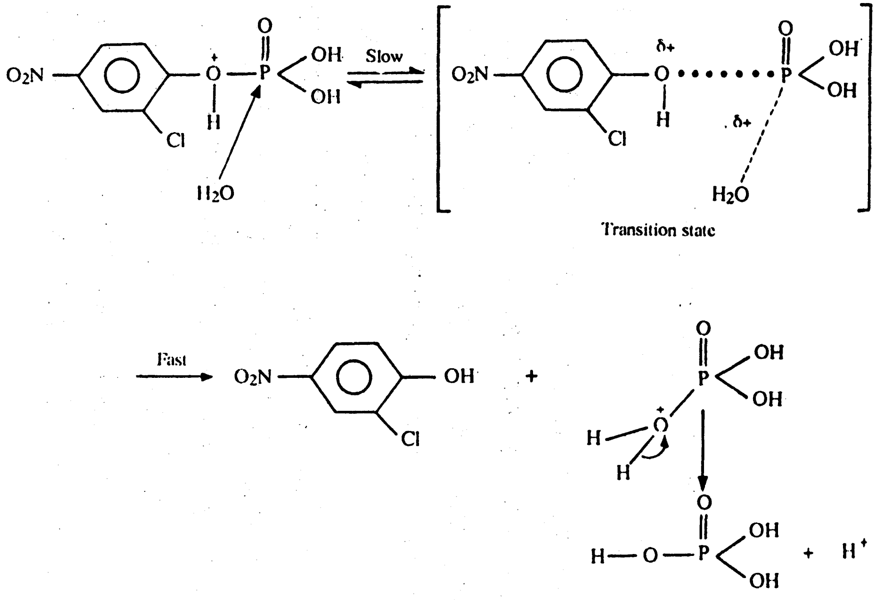
Thus on the basis of experimental data, the formulations of the probable mechanism paths for the acid catalysis is shown as follows:

Mechanism

1. Formation of conjugate acid species:



2. Bimolecular attack of water on phosphorus of the conjugate acid species:



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(*Received*: 1 February 1992; *Accepted*: 15 October 1992) AJC–507