KINETIC STUDY OF THE HYDROLYSIS OF MONO-2-AMINO-4-CHLOROPHENYL PHOSPHATE ESTER AT 97°C:

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ABSTRACT:

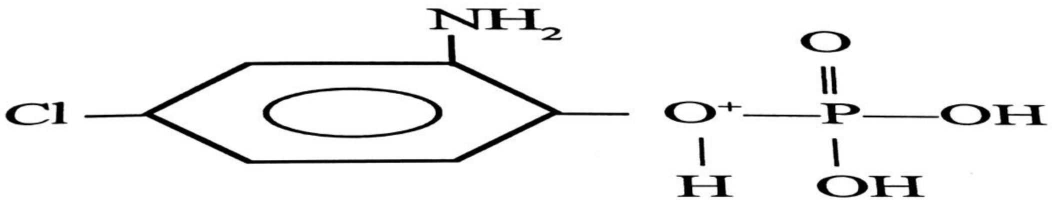
Investigation of the kinetic study of the hydrolysis of mono 2-amino, 4-chlorophenyl phosphate have been carried out in a wide range of various experimental conditions at 97°C. Kinetic study of monoester has been carried out in water, in 20% (v/v) aqueous dioxan of diester, while in 30% (v/v) aqueous dioxan in case of triester respectively, in both acid and buffer solutions. Monoester has been found to be reactive in the form of four reactive species namely, conjugate acid, neutral, mononegative and dinegative species. Diester, however, undergoes hydrolysis via conjugate acid, neutral and mononegative species, whereas, the triester hydrolyses via conjugate acid and neutral species. All the reactive species have been found to undergo hydrolysis with common phosphorus oxygen (P-0) bond fission and with bimolecular reaction paths.

Kinetic runs were made in acid (0.1 to 6.0 mol. dm.-3 HCI) and buffer solutions (1.24 to 7.46 pH) at 97°C. The rate of hydrolysis of phosphate ester was measured by determining the rate of appearance of inorganic phosphate by Allen's modified colorimetric method. The concentration of phosphate esters have been kept 5x 10-4 mol.dm.,-3 throughout the study (unless otherwise specified). The probable reaction mechanism has been determined by the study of pH, temperature, ionic strength, solvent, substrate concentration etc, on the rate of hydrolysis.

INTRODUCTION:

Kinetic study of the hydrolysis of mono-2-amino-4- chlorophenyl phosphate has been carried out in acid region 0.1 to 6.0 mol. dm.-3 HCl) in aqueous solution as well as in the buffer medium (pH 1.24 to 7.46) at 97±0.5°C. The concentration of the monoester in all kinetic runs was kept 5.0x 10-4 mol. dm-3 (unless otherwise specified).The rate of hydrolysis was determined by measuring the rate of appearance of inorganic phosphate colorimetrically213. Pseudo first-order rate coefficients have been determined all kinetic runs in the entire range of study. Some typical kinetic runs have been described in experimental section. Effects of factors such as hydrogen ion concentration, ionic strength, substrate concentration, solvent composition, and temperature that govern the rate of hydrolysis have been studied for each reactive species. Presumption of pK values and ionic strength data have been used to estimate theoretical rates in various zones of pH and these computed theoretical rates was compared with the experimental rates.

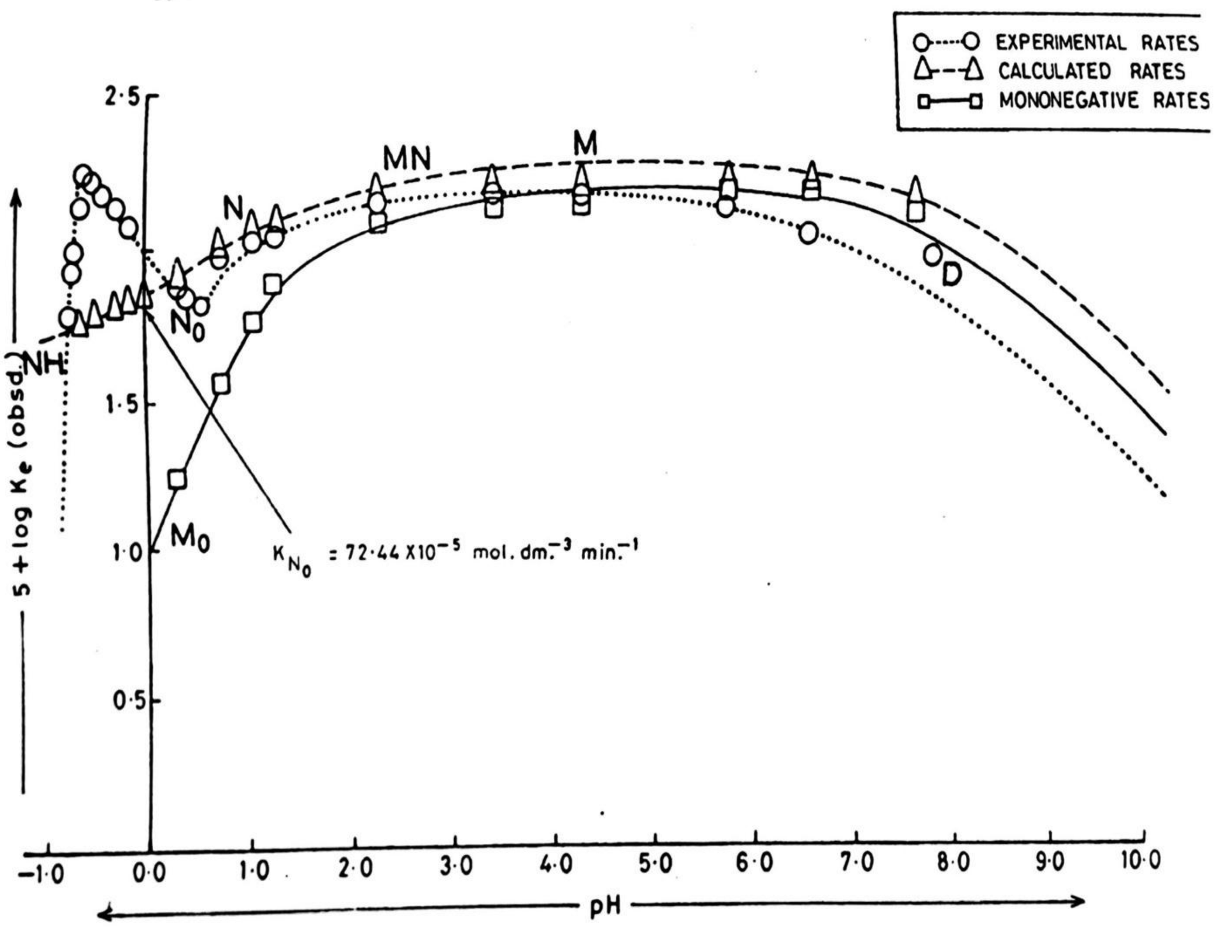
Molecularity of the reaction has been established on the basis of co-relation plots such as Zucker-Hammett hypothesis, Bunnett-Olsen concept. Order of the reaction and bond fission have been determined by substrate concentration and comparative isokinetic data of other similarly substituted phenyl phosphate monoester. Acid catalysis have been found and neutral, mononegative species of the monoester have also been found to contribute mainly to the overall hydrolysis, dinegative species have been found to be inert upto pH 6.43. Molecularity and bond fission involved during the hydrolysis have been discussed to suggest probable reaction paths. For convenience, results have been described and discussed as specieswise.



(Conjugate acid species)

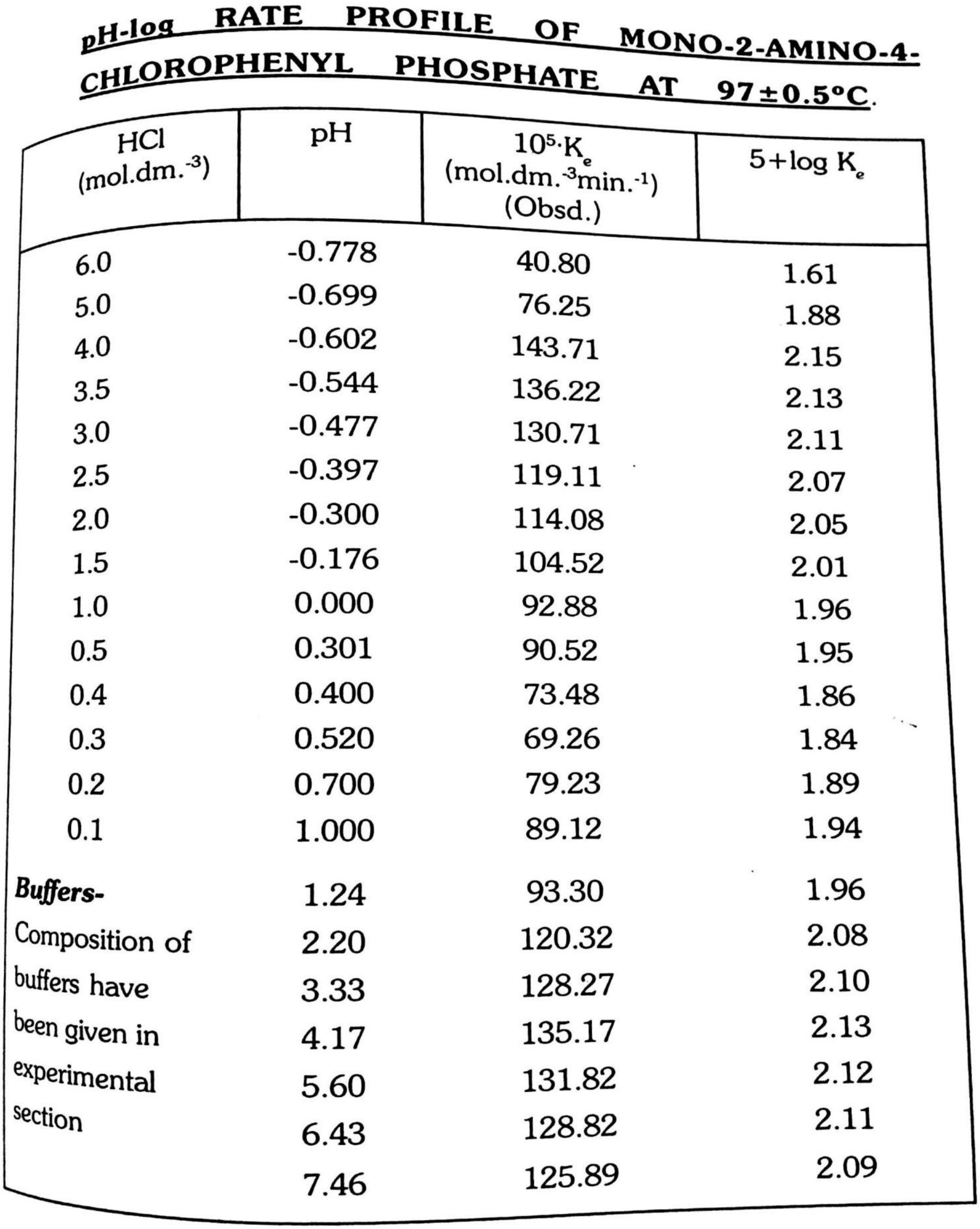
MECHANISM:

FIG.-I: pH-log RATE PROFILE OF MONO-2-AMINO 4-CHLOROPHENYL PHOSPHATE AT 97±0.5°C



Mono-2-amino-4-chlorophenyl phosphate undergoes hydrolysis in acid medium and investigation of kinetic study of hydrolytic reaction has been made in hydrochloric acid from 0.1 to 6.0 mol. dm:3 at 97°C. Pseudo first order rate coefficient of hydrolysis have been summarised in Table-1 and (Fig.-I) describes acid and pH-log rate profile.

OBSERVATION TABLE:



pH-log RATE PROFILE OF MONO-2-AMINO-4-CHLOROPHENYL PHOSPHATE AT 97±0.5°C.

HCl (mol.dm.$^{-3}$)	pH	$10^5 \cdot K_e$ (mol.dm.$^{-3}$min.$^{-1}$) (Obsd.)	$5+\log K_e$
6.0	-0.778	40.80	1.61
5.0	-0.699	76.25	1.88
4.0	-0.602	143.71	2.15
3.5	-0.544	136.22	2.13
3.0	-0.477	130.71	2.11
2.5	-0.397	119.11	2.07
2.0	-0.300	114.08	2.05
1.5	-0.176	104.52	2.01
1.0	0.000	92.88	1.96
0.5	0.301	90.52	1.95
0.4	0.400	73.48	1.86
0.3	0.520	69.26	1.84
0.2	0.700	79.23	1.89
0.1	1.000	89.12	1.94
Buffers- Composition of buffers have been given in experimental section	1.24	93.30	1.96
	2.20	120.32	2.08
	3.33	128.27	2.10
	4.17	135.17	2.13
	5.60	131.82	2.12
	6.43	128.82	2.11
	7.46	125.89	2.09

RESULT AND CONCLUSION:

As it is evident from the result that it may be concluded that rate of hydrolysis increases in acid concentration. The rate maxima is at 4.0 mol dm^{-3} HCL and it gradually falls with further increase in acid concentration. The rate of maxima or bend of pH-log concentration rate profile in acid region have also been found in some other cases.

In the organic amide system similar rate maxima were observed and supposed due to full conversion into their conjugate acid species After complete conversion into a protonated species, the rates should remain constant, but it further decreases with the increase of acid concentration. The decrease is attributed to the lowering of concentration of attacking nucleophile taking part in the reaction. Although, it appears that there is no similarity in rate maxima with amides, as it is not possible due to complete protonation a small variation in temperature because there is coefficients before and after rate maxima and it may be taken as an indication for the absence of maximum protonation.

The rate maxima in mono-2-amino-4-chlorophenyl Phosphate strength effect to both. or acid catalysed hydrolysis may be due either ionic Or due. In some phosphate esters likep-nitrophenyl phosphate.' 24nethoxyethyl phosphate,120 p-chlorophenyl phosphate21' penta-chlorophenyl phosphates° and penta bromophenyl phosphate esters,53 ionic strength or water activity or both may be responsible togive rate maxima.There is fairly good agreement in estimated and experimental rates in chloro- and bromophenyl phosphate when ionic strength is taken into account to calculate the rates.

The various effects of ionic strength on the rate of reaction in acid medium have been summarised as below:

1. Acid catalysed rates are accelerated, whereas, the neutral rates remain constant e.g. hydrolysis of p-chloro- and p-bromophenyl phosphate.

2. Neutral rates are accelerated and the acid rates are retarded as observed in phosphate.

3.Absence of acid catalysed hydrolysis has been observed in mono-4-chloro-3-methylphenyl phosphate.

4.Neutral rates are increase, while the acid catalysed remains zero e.g. pechloro-m-tollyl phosphate.

5. An example of difficulty may be found in the acid catalysed hydrolysis of γ-butyrolactone in various salt solutions. Sodium chloride has slightly positive salt effect in contrast of sodium perchlorate has negative salt effect on the rates.

6. Acid catalysed rates are accelerated and the contribution of neutral rates are zero or almost negligible as has been found in case of dl -chlorobenzyl phosphate.

7.Both conjugate add and neutral species are accelerated in hydrolysis by ionic strength. This has been realised of dimethyl phosphate.

8. Acid catalysed rates are accelerated, whereas, neutral rates are retarded, as observed in case of hydrolysis of glycollide and 2-phenylethyl dihydrogen phosphate.

9 Neutral rates are constant, while acid rates are retarded by ionic strength, as observed in case of di-phenic anhydride.

10. Neutral rates vary with ionic strength, whereas acid rate remains constant or uneffected.

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