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

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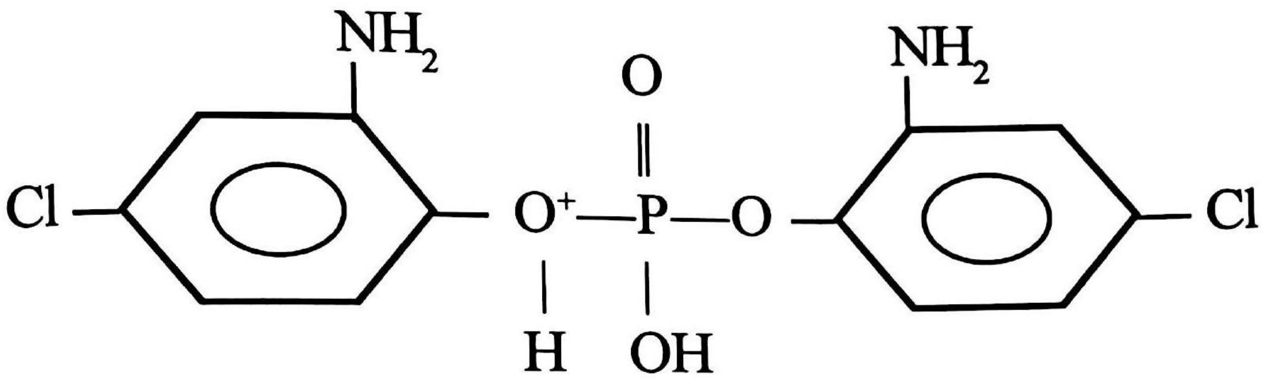
ABSTRACT

Investigation of the kinetic study of the hydrolysis of di 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.

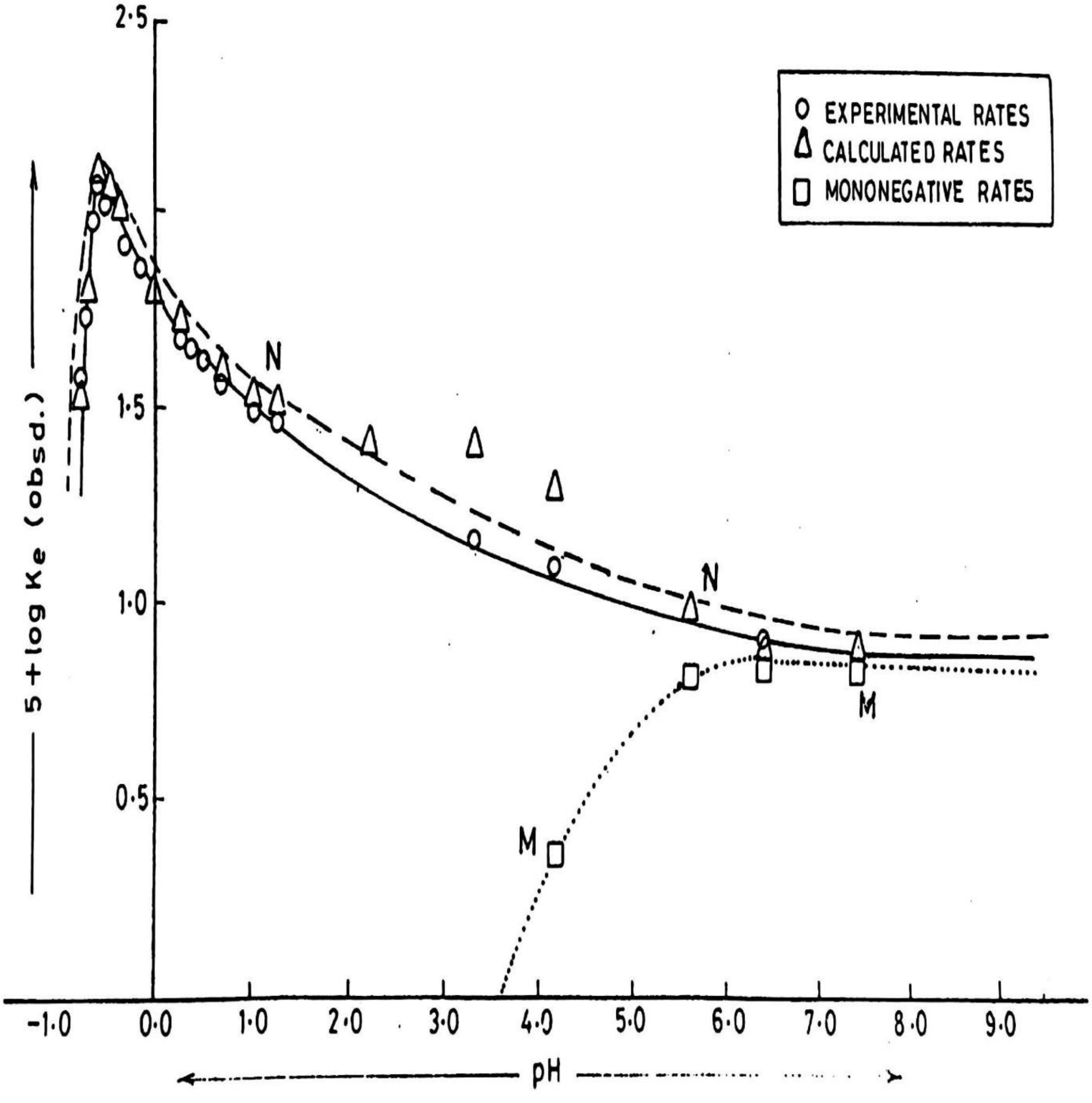
Kinetic runs were made in acid (0.1 to 6.0 mol. dm.-3 HCl) and buffer solutions (1.24 to 7.46 pH) at 97°C. The rate of hydrolysis of phosphate ester was measured by determining the rate of appearance of inorganic phosphate by Allen's modified colorimetric method. The concentration of phosphate esters 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 di-2-amino-4-chlorophenyl phosphate has been carried out in acid region (0.1 to 6.0 mol. dm.-3 HCl) and in buffers (pH 1.24 to 7.46) at 97±0.5°C. The study has yielded first order rate coefficients and the rate data are supported and interpreted by different kinetic evidences. The characteristics of rate maxima, like in other diarylphtnyl phosphate esters, appear at 4.0 mol. dm^{-3} HCl, disclosing it's intermediate basic strength. Hydrolysis of diesters involves two stages to give inorganic phosphates, diesters are first converted into their monoesters, which further undergo hydrolysis to form orthophosphoric acid. The diester has been found to show reactions via conjugate acid species, neutral species and mononegative species. The rate of hydrolysis of the monoester is faster, therefore, the rate of hydrolysis of diesters could be directly measured by Allen's modified colorimetric method. The concentration of diester in all kinetic runs was maintained at 5.0 x 10-4 mol. dm$^{.-3}$ (unless otherwise specified). The results have described and discussed specieswise:



MECHANISM:

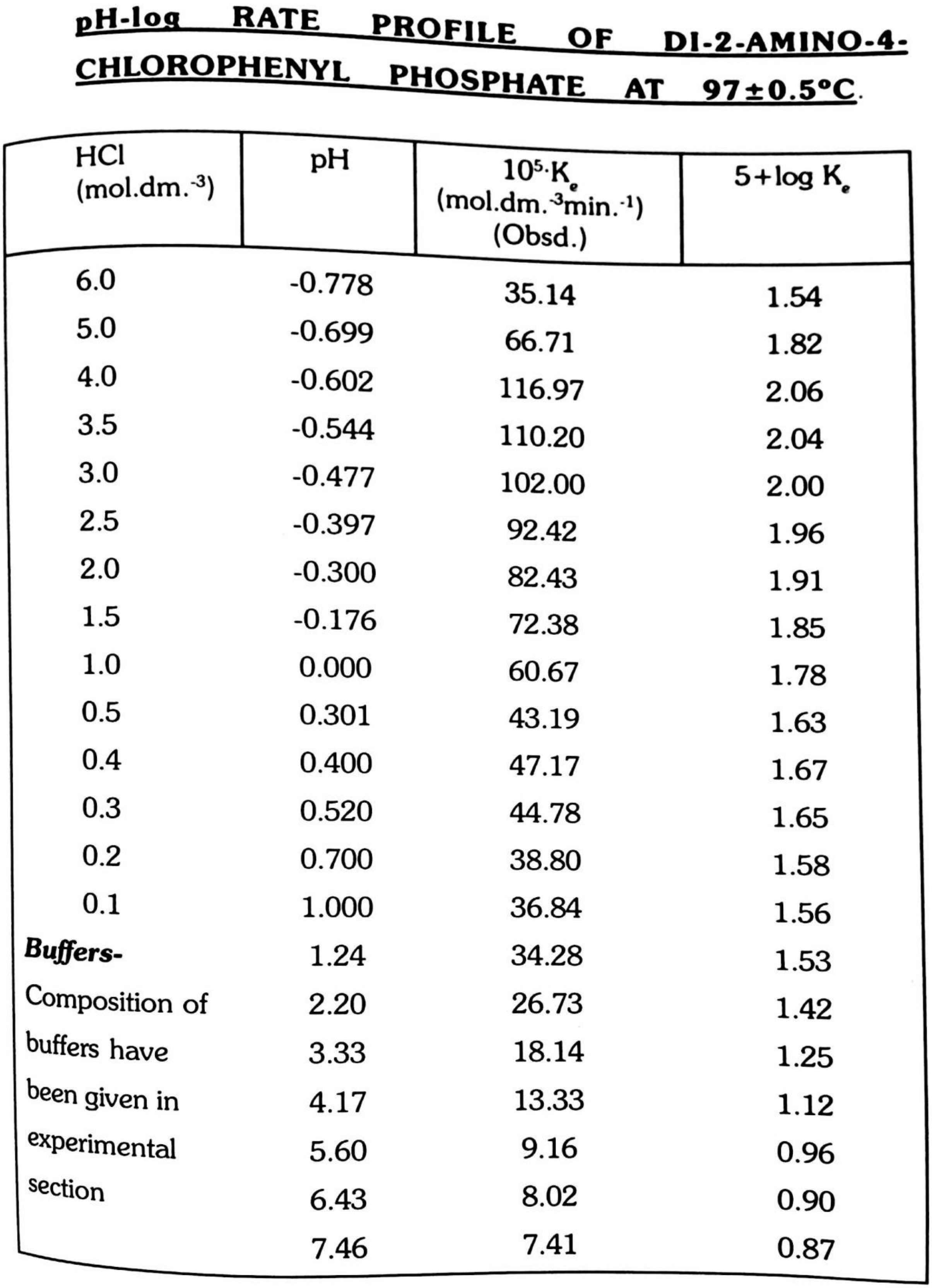


pH-log RATE PROFILE OF DI-2-AMINO-4-CHLOROPHENYL PHOSPHATE AT 97±0.5°C

The kinetic study of the hydrolysis of 2-amino-4-chlorophenyl phosphate diester had been carried out in 0.1 to 6.0 mol. dm.-3 HCl at 97±0.5°C in 20% (v/v) aqueous dioxan mixture. Figure describes a pH-log rate profile and Table, summarises the rate coefficients for the hydrolysis of present phosphate diesters.

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

OBSERVATION TABLE:



pH-log RATE PROFILE OF DI-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	35.14	1.54
5.0	-0.699	66.71	1.82
4.0	-0.602	116.97	2.06
3.5	-0.544	110.20	2.04
3.0	-0.477	102.00	2.00
2.5	-0.397	92.42	1.96
2.0	-0.300	82.43	1.91
1.5	-0.176	72.38	1.85
1.0	0.000	60.67	1.78
0.5	0.301	43.19	1.63
0.4	0.400	47.17	1.67
0.3	0.520	44.78	1.65
0.2	0.700	38.80	1.58
0.1	1.000	36.84	1.56
Buffers-	1.24	34.28	1.53
Composition of buffers have been given in experimental section	2.20	26.73	1.42
	3.33	18.14	1.25
	4.17	13.33	1.12
	5.60	9.16	0.96
	6.43	8.02	0.90
	7.46	7.41	0.87

RESULT AND CONCLUSION:

The gradual increase inacid molarity shows elevation of first order rates, thereby •insisting upon the incursion of it's most probable conjugate acid species, produced by a proton transfer on any one of oxygen of two C—O—P linkages. The rates with the rse in acid molarity demonstrating a maxima at 4.0 mol. dm.-3 HCl, where the maximum rupture of the conjugate acid species takes place. After complete formation of conjugate acid species, the rate decreases beyond 4.0 mol. dm.-3 HCl. A similar maxima was found in the studies of disubstituted phenyl phosphate118 and in other compounds. Amide system exhibit a similar maxima due to complete conversion of basic amide to it's conjugate acid species.

The rise in rates in the above cases is owing to more reactive conjugate acid species. After it's complete formation (through a gradual increase in acidity of the medium), the lowering in rates of hydrolysis occurs uniformly. This decrease was shown by the lowering of concentration in the rate determining of the nucleophile step. Further, the maxima at 4.0 mol. dm^{-3} HCl for diphosphate may not be the same as obtained in case of amides for:

(a) esters as a group are comparatively much less basic in nature.

(b) no maximum protonation was noticed in tri-phenyl phosphate and p-chloro-3-methylphenyl phosphate, although, pH-log rate profile indicate maxima.

(c) aliphatic phosphate, although more basic then aryl phosphates, fall to exhibit maxima range, and in strong acid and

(d) unless the heat of protonation is small, a variation in the temperature coefficient must take place if the rate maxima arises from near the complete protonation. Since, no such variation has been noticed, it is an indication of the absence of maximum protonation.

The maximum rates at 4.0 mol. $dm.^{-3}$ HCl in the present study may be due to either acid catalysed (which may be attributed to positive or negative effect of ionic strength), to positive effect of ionic atmosphere on neutral hydrolysis or, to both, acid catalysed and neutral hydrolysis (the effect of ionic atmosphere on these rates may either be positive or negative).

The rise in rate coefficeint (in acid) is not always due to acid catalysis, the rate enhancement in p-chloro and m-methylphenyl phosphate,47 is governed by ionic strength effect only. In order to examine the reaction from the above point of view, kinetic runs have been carried out by using appropriate mixtures of KCl and HC1, and three different ionic strength were used. The rate coefficient have been summarised in Table and Figure describes a plot between the rate constants and acid molarity.

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