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RESEARCH ARTICLE

HYDROLYSIS OF PHOSPHATE MONO ESTER OF 2-METHOXY-4-NITRO ANILINE PROCEEDS VIA P-N BOND FISSION

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ABSTRACT

Study Kinetic study of the hydrolysis of mono-2-methoxy-4-nitroaniline phosphate has been carried out both in acid (0.1 to 6.0 mol. dm^{-3} HCl) as well as in buffer medium (1.24 to 7.46 pH) in aqueous solution at 97 ± 0.5°C. The rate of hydrolysis was determined by measuring the rate of appearance of inorganic phosphate by colorimetric method[1] (Allen's modified method). The concentration of the monoester in all the kinetic runs was maintained 5.0×10^{-4} mol. dm^{-3}. Reactive species of monoester are conjugate acid species, neutral, mono-negative and dinegative species, but for the sake of convenience only conjugate acid species has been given in this discussion. Effect of factors such as hydrogen ion concentration, ionic strength, temperature, substrate concentration. etc. have been studied on the rate of hydrolysis to estimate the participation of water molecules, bond fission and molecularity of the reaction Presumption of pH values and ionic strength data were used to estimate the rates in various zones of pH log rate profile. Molecularity of the reaction was determined by empolying concepts such as Zucker-Hammett hypothesis[2], Bunnett parameters[3] and Hammett acidity function[4]. The probable mechanism of the hydrolysis of mono 2-methoxy, 4-nitroaniline phosphate via conjugate acid species have been studied by using the comparative rate date and isokinetie relationship of other similarly substituted phosphate mono-esters.

INTRODUCTION

There are large number of organophosphorus compounds having C-O-P and C-N-P linkages (Tiwari *et al.,* 1998 & 1985; Shinde *et al.,* 1986; Kushwaha, 1988; Singh Archana and Prabha, 1996; Singh Pratap and Kumar Abanish, 2011; Tiwari, 2000; Singh, 2003; Chaudhary Amit, 1998; Bhoite, 1977; Chaturvedi Kumud, 1999; Chaudhary Gaurav, 2013; Verma Devdutt, 2013; Patel Anil, 2013; Kumar Abanish, 2013; Singh Sanchita, 2014; Saxena Amrita,, 2014; Chaudhary Amit, 2015 & 2016; Kumar Abanish, 2015) which are physiologically necessary, biologically essential and play a great role in nature. Previously, much research work had been published about the phosphate esters having C-O-P linkages but after realizing the importance and uses of phosphate esters having C-N-P linkages intensive studies were undertaken by renowned scientists. Phosphate esters having C-N-P linkage are also known as phosphoramidic acid, phosphoramides, Phosphoramidates or amino phosphates. They have vast applications in the synthetic, bio chemical, industrial, agricultural and also in academic field. Organic compounds of phosphate esters are essential constituent of protoplasm and play a significant role in the maintenance of life. They are artificially synthesized for their practical use as lubricants, oil-additives, plasticizers and pesticides. Thus, organophosphate esters have significant chemical, physical and biological properties. The biochemical reactions related to the carbohydrate and nucleoprotein metabolism involve the formation and cleavage of the phosphate bonds. This process provide necessary energy for the many biochemical changes. Also the organo phosphorus compound have gained the great importance because of the development of very effective and non-persistant organo phosphorus pesticides for e.g. about 140 phosphorus compounds were used as practical pesticides. Also in the world, more than 60,000 tons per year of organophoshorus pesticides are produced in the U.S. alone. Thus, multidimensional importance of organo phosphate esters leads to vigorous research and development. This study is one of them.

Preparation of the compound

The method of preparation of the phosphate monoester (Paul otto, 1895; Rudert, 1893) of 2-methoxy-4-nitroaniline on which the kinetic study has been done involves the direct reaction of phosphorus oxy-trichloride ($POCl_3$) with 2-methoxy-4-nitroaniline. 16.82 g of pure 2-methoxy-4-nitroaniline was dissolved in 200 ml of dry benzene in round

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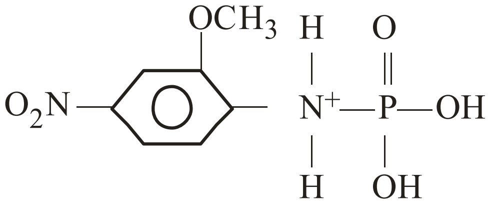
bottom flask. 9.0 ml of $POCl_3$ was added dropwise with constant stirring to the ice-cooled amine. Then after, the mixture was refluxed for about 38 hours at constant temperature of 70°C and then distilled at reduced pressure. The first fraction of benzene and unreacted $POCl_3$ was removed by distillation at b_{40} 42-45°C and second fraction which was found to dichloridate of 2-methoxy-4-nitroaniline was distilled at b_{60} 136-156°C. It was dissolved in 100 ml of ice cooled water and kept at low temperature overnight. The 2-methoxy-4-nitroaniline phosphorodichloridate converts into 2-methoxy-4-nitroaniline dihydrogen phosphate, which was extracted with solvent ether. After removing the solvent ether a light yellow coloured crystalline solution was obtained which an recrystallisation with absolute ethyl alcohol gave a white crystalline solid, which was identified to be mono-2-methoxy-4-nitroaniline phosphate with observed melting point 152°C and theoretical percentage of 'p' was 12.50 g.

Hydrolysis via congugate acid species



(Conjugate acid species)

Hydrolysis of 2-methoxy-4-nitroaniline phosphate monoester has been kinetically studied in 0.1 to 6.0 mol. dm^{-3} HCl at 97 + 0.5°C. Pseudo first order rate coefficients of the hydrolysis have been summarized in Table-1 and pH log rate profile have been described in Fig. I

Table 1. pH-log rate profile of mono-2-methoxy-4-nitroaniline phosphate at 97±0.5°C

HCl (mol. dm.$^{-3}$)	pH	10^5 K_e (mol. dm.$^{-3}$ min.$^{-1}$) (Obsd.)	5 + log K_e
6.0	- 0.778	35.76	1.55
5.5	-0.740	67.81	1.83
5.0	-0.699	72.24	1.85
4.5	-0.653	88.40	1.94
4.0	-0.602	144.20	2.15
3.5	-0.544	129.17	2.11
3.0	-0.477	120.05	2.07
2.5	-0.400	108.39	2.03
2.0	-0.301	97.17	1.98
1.5	-0.176	85.52	1.93
1.0	0.000	70.59	1.84
0.5	0.301	43.19	1.64
0.4	0.398	40.95	1.61
0.3	0.523	38.25	1.58
0.2	0.700	48.65	1.68
0.1	1.000	57.33	1.75
Buffers-Composition of buffers have been given in experimental section	1.24	65.51	1.81
	2.20	87.72	1.94
	3.33	92.39	1.96
	4.17	93.99	1.97
	5.60	88.02	1.94
	6.43	74.80	1.87
	7.46	86.95	1.93

As it is evident from the results, it may be concluded that the rate of hydrolysis of the monoester increases with the increase in acid concentration upto 4.0 mol. dm^{-3} HCl. Further increase in acid concentration decreases the rate of hydrolysis (i.e. > 4.0 mol. dm^{-3}. HCl). This decrease in rate of hydrolysis may be due to the participation of water molecule, ionic-strength effect or both.

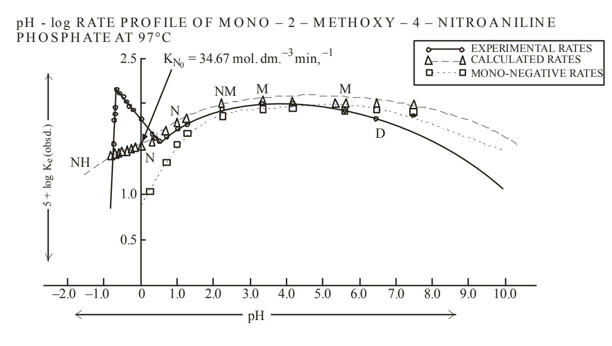


Figure 1.

Effect of ionic strenght

The effect of Ionic strength on the rate of hydrolysis of the phosphate ester was examined by carrying out kinetic runs at different ionic strength by using mixture of KCl and HCl in appropriate quantity. Rate coefficients are summarises in Table-2 and Fig. II describes a plot between rate coefficients and acid molarities.

Table 2. Hydrolysis of mono-2-methoxy-4-nitroaniline phosphate at constant ionic strength at 97°C

Ionic strength (μ) (mol. dm.$^{-3}$)	COMPOSITION		10^5. K_e (mol. dm.$^{-3}$ min.$^{-1}$) (Obsd.)
	HCl (mol. dm.$^{-3}$)	KCl (mol. dm.$^{-3}$)	
1.0	0.2	0.8	40.07
1.0	0.4	0.6	44.44
1.0	0.6	0.4	52.74
1.0	0.8	0.2	55.93
1.0	1.0	0.0	70.59
2.0	0.2	1.8	36.76
2.0	0.5	1.5	44.14
2.0	1.0	1.0	51.83
2.0	1.5	0.5	67.30
2.0	1.8	0.2	76.38
2.0	2.0	0.0	97.17
3.0	0.5	2.5	39.73
3.0	1.0	2.0	48.52
3.0	1.5	1.5	56.10
3.0	2.0	1.0	68.88
3.0	2.5	0.5	79.79
3.0	3.0	0.0	120.05

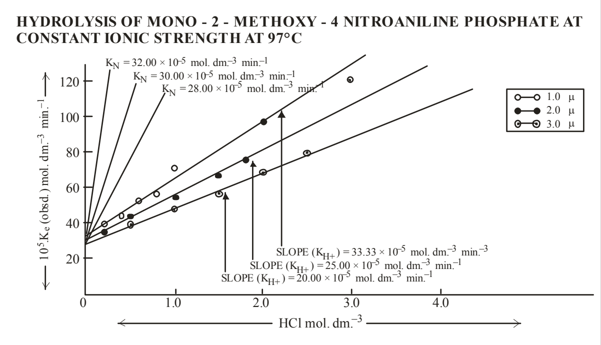


Figure 1.

The perusal of linear plots clearly indicates acid catalysis hydrolysis of mono-2-methoxy-4-nitroaniline phosphate in acid medium. The neutral species of the monoester slowly changes into conjugate acid species i.e., overall rate must have contribution of both the species. Linearity of the curves represent the rate law for the hydrolysis of monoester by the following equation:

$K_e = K_{H^+} . C_{H^+} + K_N$

Where K_e, K_{H^+}, C_{H^+} and K_N are experimental rate constant, specific acid catalysed rate at that ionic strength, concentration of hydrogen ion and specific neutral rate at that ionic strength respectively.

Effect of temperature

Stability and reactivity are expressed in terms of energy. An endothermic reaction like hydrolysis of phosphate ester needs a measureable amount of heat energy. A study of effects by changes in temperature is expected to furnish information of the hydrolytic reaction. A small increase in temperature will greatly increase the fraction of collisions with sufficient increase in energy to convert reactant into products via transition state. The rates of hydrolysis are found to be elevated highly by increase in the temperature. An exponential relationship given by Arrhenius leads to determination of related parameters E, A and $\Delta S^{\neq}$. The magnitude of above parameters indicate the probable nature of hydrolysis i.e. whether uni – or bi-molecular in nature. Table-3 summarises Arrhenius parameters (Arrhenius, 1889) of the monoester at 3.0 and 5.0 mol. dm^{-3}. HCl. The magnitude of Arrhenius parameters clearly indicates that hydrolysis of mono-2-methoxy-4-nitroaniline phosphate follows bimolecular nature of hydrolysis, since the value of activation energy (E) is less than 25 KCal/mole, the value of entropy of activation ($\Delta S^{\neq}$) is higly negative and frequency factor (A) has power less than 12.

Table 3. Arrhenius parameters for the hydrolysis of mono-2-methoxy-4-nitroaniline phosphate via conjugate acid species

HCl (mol.dm.$^{-3}$)	Parameters		Entropy $-\Delta S^{\neq}$ (e.u.)
	Energy of activation	Frequency factor	
3.0	21.05	5.41×10^7	25.57
5.0	21.97	11.31×10^7	27.75

Effect of solvent

Further the effect of solvent on the rate of hydrolysis of the monoester has been observed to seek another support for the molecularity of the reaction. Qualitative solvent theory (Hughes and Ingold) (Hughes, 935) has been used for knowing the nature of transition state. For this, a series of kinetic runs has been made using various compositions of water dioxan mixtures at 3.0 and 5.0 mol. dm^{-3}. HCl which are summarized in table-4.

Table 4. Effect of solvent on the hydrolysis of mono-2-methoxy-4-nitroaniline phosphate at 97°C

HCl (mol.dm^{-3})	Water percentage (v/v)	Dioxan percentage (v/v)	10^5 K_e (mol. dm.$^{-3}$ min.$^{-1}$) (Obsd.)
3.0	100.0	00.0	120.05
3.0	60.0	40.0	84.75
3.0	50.0	50.0	53.35
4.0	100.0	00.0	144.20
4.0	60.0	40.0	88.69
4.0	50.0	50.0	71.95

The rate of hydrolysis decreases with increase in dioxan percentage. It may be attributed to better proton donating property of the dioxan medium in acid. Thus, the hydrolysis of the ester involve a transition state with dispersion of charge. Therefore, the effect of solvent on reaction rate may be taken as S_N^2 reaction with the formation of transition state in which charge is created and dispersed in the rate determining step. This proves, that the hydrolysis of monoester proceeds bimolecularly via conjugate acid species.

Bond fission

After assuming the bimolecular hydrolysis of conjugate acid of the monoester, the fission should be distinguished to arrive at the probable reaction path. Hydrolysis of mono-2-methoxy-4-methoxy-4-nitroaniline phosphate may occur either P-N or C-N bond fission. The former is more probable bcause the latter would not produce an intermediate which would be stabilized by resonance. Thus, in P-N bond fission amine molecule is formed as an intermediate which will be stable due to resonance. It is for the same reason that aryl phosphates have been found to undergo hydrolysis by P-N bond fission. The P-N bond fission of the monoester is also supported by Table-5 which shows comparative isokinetic rate data for the hydrolysis of some monoesters via conjugate acid species with present monoester. P-N bond fission of the monoester via conjugate acid species have been invariably supported by the isokinetic relationship plot (fig. III) corresponding to comparative kinetic rate data for the hydrolysis of some other phosphate mono-esters which hydrolyse with P-N bond fission. The linearity of the plot suggest that similar mechanism being followed by the mono-2-methoxy-4-nitroaniline phosphate ester. On this basis hydrolysis of present monoester was consider to follow bimolecular hydrolysis with P-N bond fission.

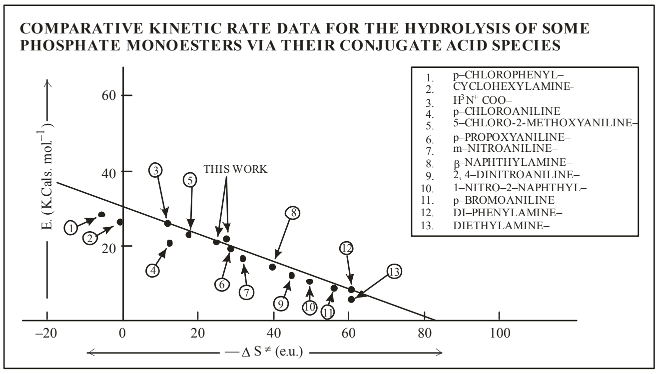


Figure 3.

Mechanism

Taking into account, all the experimentally observed evidences and facts into consideration the most probable reaction path of the present monoester via conjugate acid species may by formulated through the following steps.

1. **Formation of conjugate acid species by fast pre-equilibrium proton transfer**

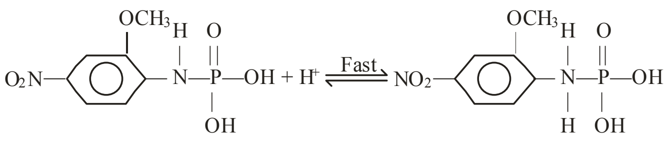


Table 5. Comparative isokinetic rate data for the hydrolysis of some phosphate mono-ester via conjugate acid species

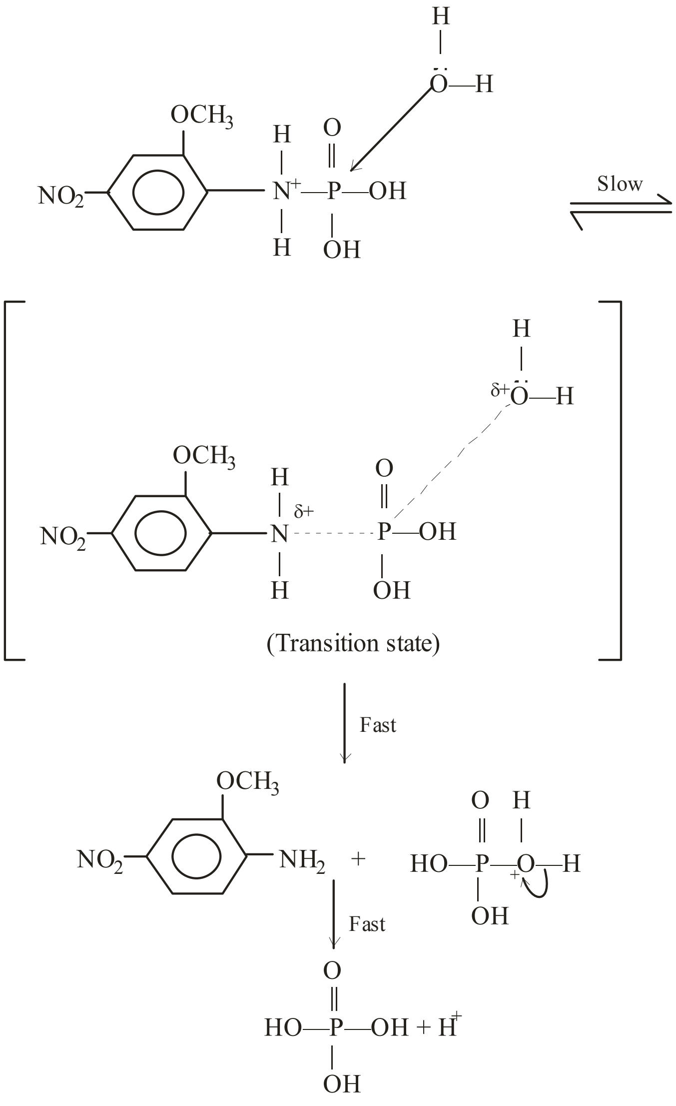
S. No.	Phosphate Mono Esters	Temp. °C	Medium	E.K. cals./mole.	-$\Delta S^{\neq}$ (e.u.)	Bond fission	Ref.
1.	p-chlorophenyl-	80	1.0	28.46	-5.57	P–O	35
2	cyclohexylamine	50	4.0	25.65	-0.77	P–N	30
3	$H_3N^+COO^-$	80	5.0	23.33	17.89	P–N	36
4	p-choloroaniline	20	3.0	20.40	12.60	P–N	37
5	5-chloro-2-methoxyaniline	37	-	26.00	12.23	P–N	15
6	p-prppoxyaniline	97	5.0	19.68	29.28	P–N	13
7	m-nitroaniline	97	3.0	21.05	25.07	P–N	38
8	β-mapthylamine	98	3.0	14.56	39.46	P–N	39
9	2,4-dinitroaniline	98	3.0	12.10	45.10	P–N	40
10	I-nitro-2-naphthyl	98	5.0	10.49	49.76	P–N	41
11	p-bromoaniline	90	3.0	9.19	55.98	P–N	37
12	di-phenylamine	98	3.0	8.32	60.43	P–N	42
13	di-ethylamine	40	3.0	5.72	60.65	P–N	43
14	2-methoxy-4-	97	3.0	21.05	25.57	P–N*	This
	nitroniline	97	5.0	21.97	27.75	P–N*	work

*Bond fission assumed

I. (Neutral Species)

II. (Conjugate acid species)

2. Bimolecular nucleophilic attack of water on phosphorus of the conjugate acid species (ii) of the mono-ester involving P N bond fission S_{N2} (P) :



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