

COMPRESSION OF MONO-4 CHLORO, 3-METHYLPHENYL PHOSPHATE ESTER AND DI-4 CHLORO, 3-METHYLPHENYL PHOSPHATE ESTER THROUGH KINETIC STUDY.

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ABSTRACT: Both mono- and di-4 chloro, 3-methylphenyl phosphate esters are synthesized by same method called Auger and Dupes. Phosphate having C-O-P linkage is widely used as fertilizers, pesticides etc. pesticides are generally poisonous or toxic and adversely affected the environment. Study of relative ecofriendly nature of pesticides depends on their bond cleavage and stability during hydrolysis in this connection and investigation of hydrolysis of 4-Chloro-3-Methyl Phenyl Phosphate was carried out by using "Allen's Modified Method" of colorimetry in aqueous medium from 0.1 to 6.0 mol dm⁻³ HCl at 98°C. Ionic strength data exhibits different contribution of natural species and presence of acid catalysis. Theoretical rates estimated from second empirical term of Debye-Hickel equation have been found in close agreement with experimental rates. The effect of ionic strength, temperature, solvent and concentration are provided to identify the reactive species and molecularity. Bimolecular behavior has been decided by the Arrhenius parameters and by the analysis of molecularity data. The monoester involves P-O Bond fission which is strengthened by comparative kinetic data's.

KEYWORDS: Hydrolysis, Phosphate esters, Phosphate with C-O-P linkage, Conjugate species.

INTRODUCTION

Organic compounds of phosphorus are essential constituent of protoplasm and DNA and play an important role for the maintenance of life. Phosphates having C-O-P linkage are widely used as Fertilizers, flame retardants, pesticides, chemosterilants, Herbicides, Fungicides, Plasticizers, Lubricants, Defoliant, Cancer chemotherapeutic agents, Antitumor agents, Antibiotic and in the treatment of Myasthenia. There are sculpture

containing Parathion phosphate series used as pesticide series but because phosphate having C-O-P linkage have wide range of application in different scientific discipline and also to assess its eco-friendly behavior, the knowledge regarding their bond cleavage and stability during hydrolysis are important. Keeping the above objectives in view the hydrolysis of Mono 4-chloro 3-methyl phenyl phosphate ester has been investigated.

MATERIAL AND METHOD: PREPARATION AND IDENTIFICATION OF PHOSPHATE ESTERS

The method of synthesis of phosphate esters (mono, di and) which are undertaken for kinetic investigation has been illustrated as;

Preparation and identification of mono-4-Chloro-3-methylphenyl phosphate (Ba-salt)

It is prepared by Auger and Dupis method in a ratio of 1:1 phenol and POCl₃. 6.52 g of 4-chloro-3-methylphenol (A.R. grade sigma -Aldrich) was dissolved in 20 ml of dry benzene, 366 ml of POCl₃ was taken in a conical flask and kept on a magnetic stirrer. Then a very small amount of the phenol (parent compound) was added slowly to POCl₃ and the material was stirred for a period of 6 hours at 60-65 degree after few minute of each addition 3 ml of pyridine was added to the stirred material in installments. Pyridine hydrochloride began to separate at once with the evolution of heat. After the stirring is completed the stirred material was kept open so as to evaporate the solvent then the oily residue left in the flask was treated with water. The milky solution thus obtain was treated with diluted HCl to remove unreacted pyridine as pyridine hydrochloride. The solution was filtered of, first filtrate (very small amount) was rejected. To the clear filtrate barium hydroxide was then added till it become alkaline and white ppt. began to separate. The ppt. was then washed several times with distilled water (containing few drops of acetic acid)

(to remove inorganic phosphate till dark blue colour of phosphorus was obtained in the filtrate by Allen's test.

Estimation of Elements.

SNO.	ELEMENTS	PERCENTAGE	
		THEORETICAL	OBSERVEB
1.	Carbon	38.53	37.775
2.	Hydrogen	2.32	3.623
3.	Oxygen	30.01	28.754
4.	Chlorine	16.38	15.929
5	Phosphorus	14.01	13.919

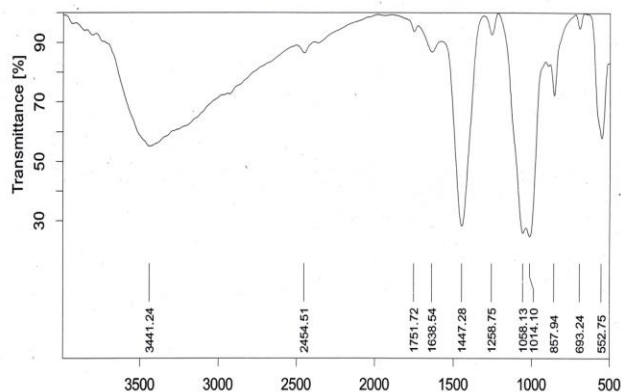
I.R. Absorption Spectra

The compound was also identified from its characteristic absorption spectra in KBr pellets spectral data of 4-chloro-3-methyl phenyl phosphate has been shown in table 4,A-1(The spectral study was conducted on Nicolet protégé model 460 IR spectrophotometer .SIRT Bhopal)

Table

S.NO.	STRETCHING	I.R v Cm ⁻¹
1.	(C-O) Stretching	1258.744
2.	(P-O) Stretching	1058.128
3.	(C-H) Adjacent Stretching	-
4.	(C-H) Isolated Stretching	857.935
5.	(C=Cl) Stretching	633.37

Spectra.4-A.1 IR spectrum of mono-4-chloro 3-methylphenyl phosphate



Preparation and identification of Di-4-chloro-3-methyl phenyl phosphate:

It is also prepared by Auger and Dupis method ,4-chloro-3-methylphenol (A.R. Grade sigma – Aldrich)and POCl₃ were taken in 2:1 ratio.7 ml of pyridine was added slowly to a stirred solution of 4-chloro-3-methylphenol (6.52 g) and POCl₃ (1.83 ml) in dry

benzene (25 ml).pyridine hydrochloride were began to separate immediately with the evolution of heat .The mixture was stirred on a magnetic stirrer at 60 to 65 degree for a periodic of 10 hrs and 30 min. The yellowish oily residue left after stirring was treated H₂O and then with 5% NaOH .the filtrate thus obtain was acidified with diluted HCl to precipitate the chloride which on washing with distilled water was converted into the free diesters. This free diester was finally dissolved in CCl₄ and filtered off to remove impurities.

Estimation of element

SNO	ELEMENT S	PERCENTAGE	
		THEORETICAL	OBSERVE B
1.	Carbon	48.31	48.439
2.	Hydrogen	4.23	3.775
3.	Oxygen	18.31	18.436
4.	Chlorine	21.05	20.426
5	Phosphorus	9.31	8.924

RESULT AND DISCUSSION

I.R. Absorption Spectra:

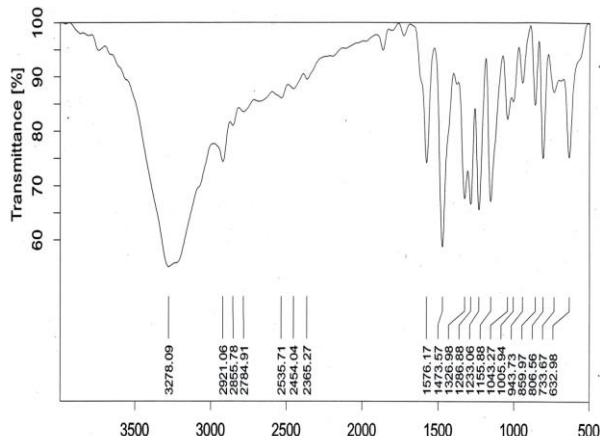
The compound was also identified from its characteristic absorption spectra in KBr pellets IR. Spectral data of di-4-chloro-3-methylphenyl phosphate has been shown in table 4.a-2 (the spectral study was conducted on Nicolet protégé model 460 IR spectrophotometer .SIRT Bhopal)

Table 4.A-2

S.NO.	STRETCHING	I.R v Cm ⁻¹
1.	(C=O) Stretching	1233.061
2.	(P=O) Stretching	1043.271
3.	(C=H) Adjacent Stretching	806.555
4.	(C=H) Isolated Stretching	943.731
5.	(C=Cl) Stretching	632.979

Spectra.4-A.2

I.R spectrum of di-4-chloro 3-methylpheny phosphate



TECHNICAL DETAILS

(i) COLOURIMETRIC ESTIMATION OF INORGANIC PHOSPHATE

On hydrolysis phosphate ester produces inorganic phosphate .and its quantitative estimation was made possible by Allen’s modified method. The inorganic phosphate react with the ammonium and forms a phospho molybdate complex $[(NH_4)_3PO_4 \cdot 12MoO_3]$ WHICH is reduced to molybdenum blue a soluble complex by addition of 2,5-diaminophenol dihydrogenchloride (amidol) solution. The blue colour so produced took 10 minutes time to fully develop and it remains stable for next thirty minutes. The intensity of the blue colour is directly proportional to the amount of free phosphoric acid. It is independent of temp over 8-26 degree. The optical density of the blue colour developed followed beer’s law was, measured using spectronic 20* spectrophotometer at wavelength (max) 608nm.

The reagents which are needed to carry out the estimation of inorganic phosphate. They are as:

(a) Hydrochloric acid:

Hydrochloric acid of A.R. quality was used .it was standardized by N/10 sodium tetra borate (borax) solution.

(b) Ammoniummolybdate solution:

8.3 g of ammonium molybdate was dissolved in distilled water by thorough shaking and made up to mark in 100 ml standard flask.

(c) Amidol reagent:

1.4 g of amidol (impure, brownish colour) was taken in a conical flask covered with a carbon paper, 2 g of activated charcoal and 10 ml of distilled water were added into conical flask. Then it is shaken thoroughly for 20 minutes. The colorless amid solution so obtain was filtered into a solution contains 100 ml solution Meta bisulphate (20%). The reagent so prepared was kept in dark and cool place. This solution gradually decomposes

and yellow after about six days then it was of no use, and it is discarded.

(ii) Buffer solutions:

To maintain different ph values buffer solution (at 20 degree c and 150 degree) which is reported in the table .the interpolated values of these buffer solutions at 98 degree= 100 degree were used. The table illustrates the fact there is so much less variation of the ph values in the lower ph logarithm in higher ph region .this is because at low ph, the buffer solution consists of weak acid, consequently the variation consists of these acid is more likely to be predominant factor, influencing the variation of ph with tempt..

Similarly in higher ph region the possibility of error will be less. The maximum value of error involved is less then at 98 degree is presumed to be equivalent to ph values at 100 degree.

Table -4.B-1

S. NO.	Buffer composition mol dm ⁻³	Measured pH at		calculated pH at 100°
		20°	150°	
1.	0.05 KCl 0.0645 HCl	1.20	1.26	1.24
2.	0.05 KCl 0.0067 HCl	2.20	2.20	2.20
3.	0.05 KCl 0.0147 HCl	3.20	3.41	3.33
4.	0.05 P'	3.97	4.26	4.17
5.	0.05 P' 0.03 NaOH	5.20	5.88	5.60
6.	0.05 P' 0.0455 NaOH	6.00	6.70	6.43
7.	0.05 H ₃ BO ₃ 0.05 KCl 0.00261 NaOH	7.80	7.26	7.46

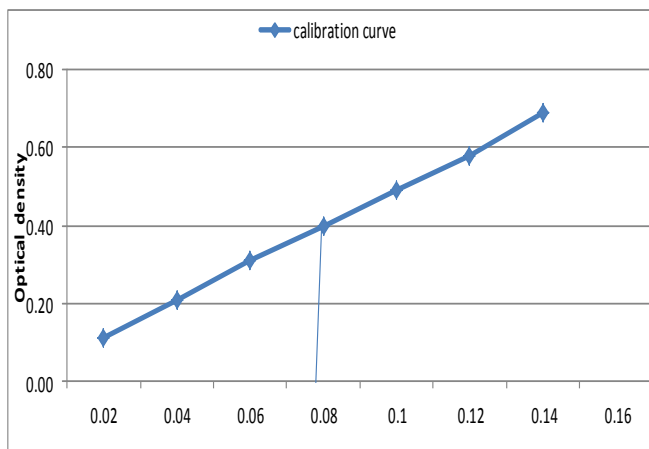
P' = potassium hydrogen phthalate

(iii) Calibration of spectronic 20+ spectrophotometer

Calibration of photoelectric colorimeter:

A standard solution of potassium dihydrogen phosphate was used to calibrate “Systronix” type colorimeter 1.0968g potassium dyhydrogen phosphate was dissolved in 250ml of 1.0967 g of potassium dihydrogen phosphate was dissolved in 10 ml of distilled water in 250 ml standard flask. then it was made upto the mark 5.0 ml of this standard solution (containing 1 mg phosphorus/ml) was distilled water 5.0ml of this solution having 1.0mg of phosphorus per ml was diluted 50 times. The second solution so obtained containing 0.02mg of phosphorus per ml. used to calibrate the instrument. In each run ,a known volume (0.5-7.0ml) of standard solution ,2.0ml of 10M-HCl,2.0ml of amidol reagent and 1.0ml of ammonium

molybdate were taken in a 25ml standard flask and the volume was made up to the mark with distilled water. Optical density of blue colour so obtained was plotted against mg of phosphorus present as inorganic phosphate.



mgs. of phosphorus

Diluted to 250 ml in a standard flask. this solution containing 0.02 mg phosphorus per ml was used calibrate the instrument .in each run a known volume (0.5 ml to 7.0 ml) of standard solution .1967 ml of 10.164 mol dm⁻³ HCl.2 ml amidol reagent and 1 ml of ammonium molybdate were taken in 25 ml of standard flask and volume is made up to the mark by addition of distilled water. Then flask was kept in ace bath for 10 min. The optical density of the colored solution so developed 2was measured.

The optical density measured for each known volume of standard solution was plotted against the amount of phosphorus present in the form of inorganic phosphate in 25 ml flask. The calculated optical density at infinity 0.38 was measured.

Table Calibration curve data of spectronic 20⁺ spectrophotometer

SNO.	ml. of KH ₂ PO ₄ solution.	mg. of Phosphorus	Optical density of colorimeter
1	0.5	0.01	0.06
2	1.0	0.02	0.11
3	1.5	0.03	0.16
4	2.0	0.04	0.21
5	3.0	0.06	0.31
6	4.0	0.08	0.40
7	5.0	0.10	0.49
8	6.0	0.12	0.58
9	7.0	0.14	0.69

(V) KINETIC EXPERIMENTS:

DEVELOPMENT OF THE ALIQUOT:

In all these kinetic experiments , the strength of the solutions of the compound is always kept at 5.0 x 14 power -4 mol dm⁻³ (unless otherwise specified)dioxan and distilled water is mostly used as solvents .solution was transferred in a well Stoppard 100 ml standard flask so as to check evaporation . now this standard flask is placed into a thermostatic water bath, which is maintained at temp 98 degree in case of estimation of the phosphate esters.

The aliquot measuring 5.0 ml were withdrawn from time to time into 25 ml standard flask. Which are immediately chilled in ace to check further hydrolysis of ester? To this, calculated volume of 10.64 mol dm⁻³ HCl (according to desired pH range).2 ml of amide and 1 ml of ammonium molybdate solution are added .thus the total volume is made up to the mark by addition of distilled water. After ten minutes optical density of fully developed blue colour is measured by spectronic 20⁺ spectrophotometer.

In each run, the content of acid (it performed in HCl) in developing aliquot together with added acid, was always kept at a required strength i.e., 1.967 ml of 10.164 mol dm⁻³ HCl in 25 ml of the mixture runs, in which the acid molarity was more than 4.0 mol dm⁻³ the required strength was kept either by diluting the solutions in a manner that the acidity remained at required strength. And 2 ml aliquots were pipits out and then acid added to make its strength same as required by Allen’s modification method.

Zero reading of the instrument was adjusted by using a blank solution, which contain 1.967 ml of 10.164 mol dm⁻³ HCl amidol and 1ml ammonium molybdate solution in 25 ml standard flask made upto the mark with distilled water.

This method of analysis is comparatively sensitive to the presence of extraneous impurities other than silicates, and so provides a quick and accurate method for the estimation of small amount of inorganic phosphate .the optical density due to traces of impurities was measured and found to be negligible.

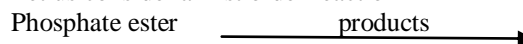
Measurement of infinite reading:

The value of optical density is determined with the help of standard

(vi) CALCULATIONS:

First order is defined as one in which the reaction rate is proportional to the first power of concentration of a reacting substance.

Let us consider a first order reaction



Initial Concentration of phosphate ester is ‘a’ gram mol dm⁻³. Let ‘x’ gram mol dm⁻³ of phosphate ester is transformed into the required product after times. Then

the concentration of the remained phosphate ester is (a-x) after time 't'. Hence the reaction velocity at times 't' is given by:

$$\frac{-dx}{dt} = K(a-x)$$

On Integration this equation this equation having limits '0' to 't' for time and for concentration '0' to 'x' then the above expression becomes:

$$K = \frac{2.303}{T} \log \frac{a}{(a-x)}$$

Now the optical density is directly proportional to the Concentration of phosphorus at that time. If D, D_0 and D_t are optical densities at infinite, zero and after a time 't' respectively the term $a/a-x$ can be expressed by $(D-D_0)/(D-D_t)$ and hence,

$$K = \frac{2.303}{t} \log 10 \frac{(D - D_0)}{(D - D_t)}$$

The above equation is used for the calculation of first order rate coefficient for all kinetic runs.

IV.B. (vii) Calculation of Arrhenius parameters :

Temperature has a symbolic effect on the rates of chemical reactions. A rise in temperature almost invariably increases the rate of a reaction and hence also the rate constant. For many reactions, it has been observed that an increase of 10° in temperature results in a 2-3 fold increase in rate constant. The effect is stated by exponential form of the Arrhenius equation as given below:

$$K = A \cdot e^{-E/RT}$$

Logarithm form:

$$\log_e K = \log_e A - \frac{E}{RT}$$

Changing the base natural to \log_{10}

$$\log_{10} K = \log_{10} A - \frac{E}{2.303 RT}$$

Where. A = Frequency factors (sec^{-1})
 E = Energy of Activation (calories)
 R = Universal gas constant = 1.986 Erg/mole
 T = Absolute temperature

If $\log K$ is plotted against $1/T$ for a series of temperature a straight line will be obtained. The slope of the line is given by :

$$\text{Slope} = \frac{E}{2.303 R}$$

Thus the value of 'E' energy of activation can be calculated easily as: $E = - \text{Slope} \cdot R \cdot 2.303$
 The frequency factor 'A' is determined by the equation:

$$\log A = \log K + \frac{E}{2.303 RT}$$

Where, A = Frequency factor (sec^{-1})

The entropy of activation ΔS^\ddagger is determined by the following equation:

$$\frac{\Delta S^\ddagger}{2.303 R} = \log K - 10.753 - \log T + \frac{E}{2.303 RT}$$

Where, ΔS^\ddagger = Entropy of activation (e. u.)

R = Gas Constant

T = Absolute temperature

E = Energy of activation (K. Cal/mol)

K = Rate Constant (sec^{-1})

The magnitude of entropy of activation and the change in free Energy of activation can distinguish as to whether any particular path and also determine the direction and extent of reaction. It was proposed by long^{2,3} that S_N2 reactions should possess smaller positive or greater negative entropies of activation than the most nearly analogous S_N1 reactions, and this broad distinction could constitute a criterion of mechanism, as one of the utility in the field of solvolytic reactions.

Some typical kinetic runs

Run No.1

Mono 4 - chloro , 3 - methyl phenyl phosphate.

Ionic strength effect:

Concentration of mono phosphate ester = 0.0005 mol dm^{-3}

Medium ` Medium = 0.8 mol dm^{-3} HC + 1.2 mol dm^{-3} NaCL

Ionic strength = 2.0

Temperature = 98 + 0.5

Infinite reading (a) = 0.38

Solvent = water

$5.0 \cdot 10^{-4}$ mol dm^{-3} of the ester phosphate was dissolved in 10.0 ml distilled water in a 50 ml standard flask. To this solution 15 ml of 4.0 mol dm^{-3} NaCL and 3.93 ml of 10.164 mol dm^{-3} HCL were added so as to maintain the desired ionic strength $\mu=2.0$ of the reaction mixture.

After making up the volume to 50 ml, it transferred to 100 ml standard flask, just to avoid the evaporation of reaction mixture. The well Stoppard flask then immersed in thermostatic water bath which was maintained at 98dig. After certain time intervals, 5 ml aliquots were taken out from the reaction mixture and chilled immediately. the aliquots was developed by adding 1.57 ml of 10.164 mol dm^{-3} HCL, 2ml of amidol reagent and 1 ml of ammonium molybdate . The volume was made

up to the mark with distilled water in 25 ml standard flask.

As usual the blank reading was adjusted at zero and optical density was determined for the aliquot. This way the optical densities of all developed aliquot were taken out. The observations are as in the table 6.b-3

Table

S. No.	Time (t) in minutes	Optical density(x)	Log a/(a-x)	Ke × 10 ³ min ⁻¹
1.	16	0.10	0.1328	19.11
2.	27	0.15	0.2182	18.611
3.	33	0.18	0.2787	19.449
4.	60	0.25	0.2603	9.991
5.	73	0.28	0.5798	18.291

Average value of Ke = 17.0906 x10⁻³ min⁻¹

Run No.2

Mono 4 - chloro, 3 - methyl phenyl phosphate.

Ionic strength effect:

Concentration of phosphate ester = 5x10⁻⁴ mol dm⁻³

Medium = 1.5 mol dm⁻³ HCL + 1.5 mol dm⁻³ NaCl

Ionic strength (u) = 3.0

Temperature = 98⁰ + 0.5⁰

Infinite reading (a) = 0.38

Solvent = water

5.0x10⁻⁴ mol dm⁻¹ of the ester phosphate was dissolved in 10.0 ml distilled water in a 50 ml standard flask. To this solution 18.75 ml of 4.0 mol dm⁻³ NaCl and 7.37 ml of 10.164 mol dm⁻³ HCL were added so as to maintain the desired ionic strength u = 3.0 of the reaction mixture. After making up the volume to 50 ml, it is transferred to 100 ml standard flask, just to avoid the evaporation of reaction mixture. The well Stoppard flask then immersed in thermostatic water bath which was maintained at 98⁰. After certain time intervals 5 ml aliquot were taken out from the reaction mixture and chilled immediately. The aliquot was developed by adding 1.23 ml of 10.163 mol dm⁻³ HCl, 2 ml of amidol reagent and 1 ml of ammonium molybdate. The volume was made up to the mark with distilled water in 25 ml standard flask.

As usual the blank reading was adjusting at zero and optical density was determined for aliquot. This was the optical density for all developed aliquot were taken out. The observations are as in the table.

Table

S.No.	Time (t) in minutes	Optical density (x)	Log a/(a-x)	Ke × 10 ³ min ⁻¹
1.	12	0.13	0.1818	34.89
2.	18	0.17	0.2575	32.94
3.	22	0.20	0.3245	33.94
4.	35	0.27	0.5384	356.42
5.	62	0.33	0.8016	29.77

Average ke value = 33.396 x10⁻³ min⁻¹

Applications

Organophosphates refer to a group of insecticides acting on the enzyme Acetylcholine esterase. Some of their pesticides irreversibly inactivate ACHE which is essential to nerve functioning in insects and many other animals. Due to their versatile application, they are common carriers of organic groups in biosynthesis. They are widely used in a number of ways as fertilizers. In recent years much interest has been shown in the synthesis and mechanism of hydrolytic fragmentation of phosphate esters. Primarily due to their importance in biochemical system. The enzyme acetyl cholinesterase is a target of organophosphate toxicants which itself is biologically significant. Aromatic nitro compounds also posed toxic character, due to the nitro group present in aryl ring. The introduction of phosphate group may enhance or reduce the toxic nature, so that the resultant C-O-P esters may act as a safer (reduction in toxic nature) systems, reflecting the activity of drugs even. The disadvantages of these phenyl phosphate esters are its remarkable stability, although sometimes, hydrolytic condition.

New research in the field of kinetic hydrolysis of phosphate esters can help the academicians to design the ortho phosphate pesticides with low toxicity and discovery of novel bioactive molecules.

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