A STUDY ON SYNTHESIS OF PHOSPHATE ESTERS

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ABSTRACT

The preparation of phosphate esters, specifically mono-4-methyl-2-nitroaniline phosphate, mono-3-chloro-2-methylaniline phosphate, and di-4-methyl-2-nitroaniline phosphate, as well as their hydrolytic study under various experimental conditions are the main foci of the current investigation in order to propose reaction mechanisms. The kinetic analysis of these esters could offer a strong foundation for comprehending the complex phosphate ester reactions, which would be useful for applications in several chemical fields. Chemical reactivity is influenced significantly by the composition and characteristics of surfactants. the different processes used in anionic phosphate ester surfactant production. The applications and characteristics of phosphate ester surfactants are significantly influenced by the use of base materials such as alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, and phosphating reagents. The settings under which the mono-diester ratio is charged and the reaction conditions that are maintained both have an impact. This research aims to evaluate the base materials utilized in phosphate ester synthesis, the synthesis techniques and their impact on phosphate esters' characteristics, uses, and the worldwide situation of phosphate ester surfactants.

KEY WORDS: Synthesis, Kinetic Experiments, Methylaniline Phosphate Esters.

INTRODUCTION

Organophosphorus compounds are highly significant because of their numerous applications in a variety of industries. These compounds' good boundary lubrication qualities, low volatility, good thermal stability, and fair hydrolytic stability—that is, chemical stability in the presence of water—have made them commercially significant in a variety of products96. Diphenyl phosphate-derived phosphate esters are utilized as an ingredient in lubricating lubricants and hydraulic fluids97. Their primary use is as flame retardants in a variety of polymers and resins used in the production of electrical and automotive components98.

Orthophosphate compounds have been created specifically for this reason since they have attracted a lot of attention in the field of organic synthesis, especially as reactive intermediates in the synthesis of nucleic acids and in the production of C-C bonds during the synthesis of terpenoids and steroids. In organic chemistry and biochemistry, phosphorylation is a very helpful reaction that has been studied from both a synthetic and a mechanistic perspective. Therefore, understanding the mechanism of these esters is probably going to be very beneficial for a variety of biological and industrial applications. Phosphate esters' kinetic analyses reveal that a few typical chemical and biological reaction pathways are followed. The production and mechanism of phosphate esters' hydrolytic fragmentation have garnered significant attention in recent times, mainly because of their significance in biochemical systems. The relevance of organic phosphate has increased in light of current biochemical studies on nucleotides99. The idea behind nucleoside phosphoramidates was to increase nucleotide uptake into cells. In the Kreb's cycle, nicotinamide adenine nucleotide plays a crucial role in the breakdown of citric acid to release energy. These esters are crucial to photosynthesis and the transformation of sulfuric sugar into starch. Nitrogen fixing 100 also involves phosphate eaters. Numerous significant co-enzymes, including 101, have structures that contain the pyrophosphate moity. It was discovered that ribose 5-triphosphate was active in a number of enzyme processes.

RESEARCH METHODOLOGY

The synthesis of di-4-methyl-2-nitroaniline phosphate, mono-3-chloro-2-methylaniline phosphate, and mono-4-methyl-2-nitroaniline phosphate is covered. The computations and technical details of the kinetic experiments are also covered.

Mono-4-methyl-2-nitroaniline phosphate
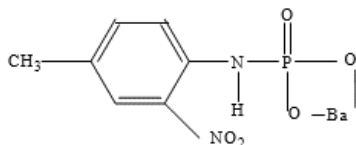
The method provided by J. Cavalier1 was used to synthesis the monoester of 4-methyl-2-nitroaniline phosphate. This process involves reacting the parent chemical in a 1:1 mol ratio with phosphorous pentaoxide, a phosphorylating agent. In a round-bottom flask with a 250 ml capacity, 10.0 g of pure 4-methyl-2-nitroaniline phosphate (A.R. Grade Sigma-Aldrich) were dissolved in 15.0 ml of benzene and vigorously agitated for 30

minutes. Next, while stirring, 15.27 g of P2O5 was added little by little. For twelve hours at room temperature, the entire reaction mixture was swirled. The reaction mixture was then left overnight at room temperature. After that, the flask was filled with 100 ml of distilled water and thoroughly shaken. There were two strata divided. The mono-4-methyl-2-nitroaniline phosphate was present in the aqueous layer. The layer of benzene was disregarded. A few drops of phenolphthalein were added to the aqueous layer. Next, drop by drop of a recently made saturated barium hydroxide solution was added until a pink hue emerged. After obtaining a white precipitate, any inorganic phosphate was filtered out and repeatedly cleaned with distilled water that included a little amount of acetic acid. To get mono-4-methyl-2-nitroaniline phosphate, it was subsequently dried. Elemental analysis and the infrared spectra were used to confirm the compound:

- **IR ABSORPTION SPECTRUM**

Mono-4-methyl-2-nitroaniline phosphate's infrared spectrum was captured using a Shimadzu FTIR model from Pt. Ravishankar Shukla University in Raipur's SOS in Physics. There was a comparison between the observed and reported frequencies the infrared spectrum.

TABLE- 1: ANALYSIS OF THE INFRARED SPECTRUM OF MONO-4-METHYL-2-NITROANILINE PHOSPHATE

S. No.	Group	Reported Frequencies(cm^{-1})	Observed Frequencies(cm^{-1})
.	N-H StretchingO-H StretchingC-H Stretching	3330-3050	3065
2.		3570-3200	3350
3.	C=C Aromatic str.P=O Stretching P-N Stretching C-N Stretching	2960-2835	2944
4.		1600-1450	1653
5.		1190,1299-1250	1257
6.		850-650 a)1065-953	834
7.		b)910-890	

			1023
			834.73

Mono-3-chloro-2-methylaniline phosphate
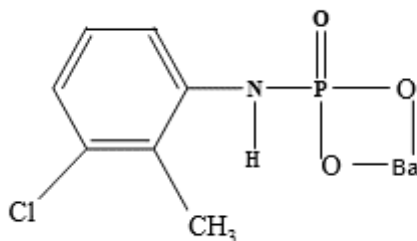
It was made using the previously mentioned process of J. Cavalier[1] from 3-chloro-2-methylaniline phosphate. P2O5 and the parent chemical were taken in a 1:1 mol ratio.

In a 250 ml round-bottom flask, 10.0 g of 3-chloro-2-methylaniline phosphate were dissolved in 15.0 ml of benzene and vigorously agitated for 30 minutes. Next, while stirring, 10.14 gram of P2O5 was added gradually. For almost twelve hours, the reaction mixture was continuously stirred. The reaction mixture was then left overnight at room temperature. After that, the flask was filled with 100 ml of distilled water and thoroughly shaken. There were two strata divided. Monoester was present in the aqueous layer, and the benzene layer was rejected. A few phenolphthalein drops were added to the aqueous layer, and then a saturated barium hydroxide solution was added until the final drop of barium hydroxide caused a pink hue to develop. After the barium salt of the monoester was thus isolated, it was repeatedly cleaned with distilled water that had a few drops of acetic

acid added until the filtrate passed the inorganic phosphate test. (Cold, blue color absent) Elemental analysis and the infrared spectra were used to confirm the compound:

• **IR ABSORPTION SPECTRUM (II)**

Mono-3-chloro-2-methylaniline phosphate's infrared spectrum was captured using a Shimadzu FTIR Model from Pt. Ravishankar Shukla University in Raipur's SOS in Physics. A comparison was made between the observed and reported frequencies displays the infrared spectrum.

TABLE 2. ANALYSIS OF THE INFRARED SPECTRUM OF MONO-3-CHLORO-2-METHYLANILINE PHOSPHATE

S. No.	Groups	Reported Frequencies(cm^{-1})	Observed Frequencies (cm^{-1})
1.	N-H StretchingO-H StretchingC-H Stretching	3330-3050	3298
2.		3570-3200	3389
3.	C=C Aromatic str.P=O Stretching P-N Stretching C-N Stretching	2960-2835	2875
4.		1600-1450	1655
5.		1190,1299-1250	1139
6.		850-650 a)1065-953	729
7.		b)910-890	1011
			924

Di-4-methyl-2-nitroaniline phosphate
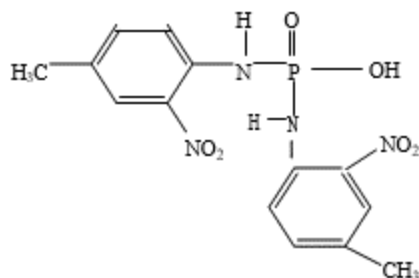
It was made using the Rudert4 P. technique. The process entails a 2:1 mol ratio interaction between di- 4-methyl-2-nitroaniline and POCl3. In a round-bottom flask with a water condenser attached and maintained in a water bath, 20.0 ml of di-4-methyl-2-nitro aniline was taken. 75.0 milliliters of benzene were utilized as a solvent. After that, the reaction mixture was heated over a water bath while 9.0 ml of POCl3 and 30.0 ml of benzene were added dropwise. Following full addition, an oil bath was used to elevate the temperature to 120°C for one hour. A beaker filled with 100 milliliters of distilled water was filled with the entire reaction mixture while it was heated. After that, the solution was moved to a separating funnel and thoroughly shaken. Two layers were separated; the light benzene layer was moved to a beaker, and the bottom watery layer was rejected because it contained monoester. After that, it was broken down by 5% NaoH diluted alkali, which caused the chloridate to dissolve and create a soluble sodium salt. A filter was used on the solution. After acidifying the filtrate, the free ester was obtained. To obtain the pure sample, the free ester was repeatedly dissolved in ammonia and re-precipitated by adding the necessary amount of HCl. Diester was found to have a melting point of 120°C. Elemental analysis and the infrared spectra were used to confirm the compound:

• **IR ABSORPTION SPECTRUM (III)**

Di-4-methyl-2-nitroaniline phosphate's infrared spectrum was captured using a Shimadzu FTIR Model from Pt. Ravishankar Shukla University in Raipur's SOS in Physics department. A comparison was made between the observed and reported frequencies.

Table -3: Analysis of the Infrared spectrum of Di-4-methyl-2-nitroaniline phosphate

S. No.	Groups	Reported Frequencies(cm^{-1})	Observed Frequencies(cm^{-1})

1.	N-H StretchingO-H StretchingC-H Stretching	3330-3050	3364
2.		3570-3200	3341
3.	C=C Aromaticstr.	2960-2835	2755
4.	P=O StretchingP-N StretchingC-N Stretching	1600-1450	1577
5.		1190,1299-1250	1103,1289
6.		850-650	784
7.		a)1065-953b)910-890	1054
			722

RESULTS AND DISCUSSION

SPECTROPHOTOMETRIC ESTIMATION OF INORGANIC PHOSPHATE

Allen's modified spectrophotometric method5 was employed to investigate the hydrolysis of each ester kinetically. In this process, the amount of inorganic phosphate that is produced as the ester hydrolyzes is measured. Ammonium molybdate and inorganic phosphate combine to generate the phosphomolybdate complex [NH4)3PO4.12MoO3. By adding 2, 4-diaminophenoldihydrochoride (also known as amidol) solution, this combination is converted to molybdenum blue, a soluble complex. At room temperature, the resulting blue color takes ten minutes to fully develop and keeps its stability for thirty minutes. The quantity of free phosphoric acid is directly correlated with the blue color's intensity. The blue hue created had an optical density that was measured using a systronic spectrophotometer at a wavelength of 735 nm, in accordance with Beer's law.

The following reagents are required to estimate inorganic phosphate:

➢ **AMMONIUM MOLYBDATE SOLUTION:**

After 8.3 grams of ammonium molybdate were dissolved in distilled water with continuous shaking, a 100 milliliter standard flask was filled to the top.

➢ **HYDROCHLORIC ACID:**

A.R. quality hydrochloric acid was utilized. N/10 sodium tetraborate (Borax) solution was used to standardize it.

➢ **AMIDOL REAGENT:**

Prior to making its solution, amydol needs to be properly purified. 10.0 ml of distilled water, 2.0 gram of activated charcoal, and 1.4 gm of amidol (impure, brownish black in color) were put to a conical flask covered with carbon paper. After that, it was vigorously shook for twenty minutes. After filtering the resulting colorless amidol solution, 100 milliliters of 20% sodium metabisulphite solution was added. The produced reagent was stored in a cool, dark area. After roughly six days, this solution starts to deteriorate and turns yellow, at which point it is useless.

➢ **BUFFERS SOLUTIONS:**

The pH values of the buffer solutions at 20°C and 150°C were measured by Sverre and Stene6; the results are shown in Table. For mono and diesters, respectively, the interpolated values of these buffer solutions at 50 and 60 degrees Celsius were utilized. Table demonstrates that the pH values in the low pH zone vary significantly less than those in the high pH region. The reason for the pH variation with temperature could be attributed to the fact that at low pH, the buffer solutions are made up of diluted strong acid solutions that contain electrically neutral salts. As a result, the solvent expands more and the activity coefficients vary with temperature, rather than the degree of dissociation changing with temperature. In contrast, at higher pH regions, the buffer solutions are made up of weak acid, so the dissociation constants of these weak acids are more likely to be the main factor influencing the pH variation with temperature. There is far less fluctuation in pH readings in the lower pH range than in the higher pH zone, which means that there will be less error in the interpolated values for pH 50oC and 60oC. However, the largest inaccuracy likely to occur will be less than 0.2 pH units, which is accurate enough for our needs.

S. No.	Buffer Composition (mol dm^{-3})	Measured pH		Calculated pH	
		20°C	150°C	50°C	60°C

1	0.05 KCl + 0.065 HCl	1.20	1.26	1.20	1.21
2	0.05 KCl + 0.007 HCl	2.20	2.20	2.20	2.20
3	0.05KCl 0.015 HCl	3.20	3.41	3.20	3.20
4	0.05P'	3.97	4.28	4.00	4.10
5	0.05P' + 0.030 NaOH	5.20	5.88	5.20	5.20
6	0.05P' + 0.045 NaOH	6.00	6.70	6.00	6.00
7	$0.05\ H_3BO_3 + 0.05\ KCl + 0.003\ NaOH$	7.80	7.26	7.80	7.80
P' = Potassium hydrogen phthalate					

CALIBRATION OF SYSTRONICS 105 SPECTROPHOTOMETER

A standard solution was made out of 250 milliliters of purified water and 1.097 grams of potassium dihydrogen phosphate. This standard solution, which had 1.0 mg of phosphorus per milliliter, was diluted 50 times in 5.0 milliliters. The instrument's calibration was done using this solution, which has 0.02 mg of phosphorus per milliliter. A known volume (0.5 to 7.0 ml) of standard solution, 2.0 ml of 10.0 mol dm-3 HCl, 2.0 ml of amidol reagent, and 1.0 ml of ammonium moybdate reagent were added to a 25 ml standard flask in each run. Distilled water was then added to bring the volume up to the appropriate level. The flask was then submerged in ice for ten minutes. We measured the colored solution's optical density after it was created. Plotting the optical density against the amount of phosphorus present in the form of inorganic phosphate was done for each known volume of standard solution. Measurements were made of the estimated optical density at infinity (0.40).

Table : 3 Calibration curve data of Systronics 105 Spectrophotometer

S. No	ml of $KH_2\ PO_4$ solution	mg of phosphorus	Optical density ofcalibration

1	0.5	0.01	0.06
2	1.0	0.02	0.11
3	2.0	0.04	0.22
4	3.0	0.06	0.36
5	4.0	0.08	0.43
6	5.0	0.10	0.54
7	6.0	0.12	0.64
8	7.0	0.14	0.72

KINETIC EXPERIMENTS

DEVELOPMENT OF THE ALIQUOT

Unless otherwise noted, the compound strength was consistently maintained at 5.0×10^{-4} mol dm-3 throughout all of these kinetic studies. The two main solvents that were employed were distilled water and dioxane. A solution was made in a 50 ml standard flask while taking the reaction mixture's intended pH or acid content into account. To check for evaporation, the solution was then transferred to a 100 ml standard flask that was well-stoppered. The thermostatic water bath was used to keep the standard flask at the proper temperature for measuring the rates of diester and monoesters. Periodically, 5.0 ml aliquots were taken out of a 25 ml standard flask and quickly refrigerated in ice to ensure that the ester was still hydrolyzing. This was then filled with a volume that was calculated to be 10.0 mol dm-3 HCl (based on the intended pH range), 2.0 ml amidol, and 1.0 ml ammonium molybdate solution. Thus, distilled water was added to bring the entire volume up to par. A fully formed blue color's optical density was measured at 735 nm wavelength using a Systronics 105 spectrophotometer after ten minutes.

Every run maintained the needed strength of acid (i.e., 2.0 ml of 10.0 mol dm-3 HCl in 25 ml of the mixture) in the developing aliquot along with the added acid. In runs where the acid molarity exceeded 4.0 mol dm-3, the necessary strength was maintained through either dilution of the solution to maintain the necessary acidity.

Pipetting out 5.0 ml aliquots, the acid was added to achieve the desired strength as per Allen's modified method 1.

The blank solution, which consisted of 2.0 ml of 10.0 mol dm-3 HCl, 2.0 ml amidol, and 1.0 ml ammonium molybdate solution in a 25 ml standard flask filled to the proper level with distilled water, was used to correct the instrument's zero reading.

MEASUREMENT OF INFINITE READING

This analysis technique offers a quick and precise way to estimate small amounts of inorganic phosphate since it is rather sensitive to the presence of unwanted contaminants other than silicates. After observation, the optical density caused by impurity traces was discovered to be quite small.

Quantification of an infinite text -A standard calibration curve is used to calculate the optical density at infinity.

CONCLUSION

A first order reaction is one in which the rate of reaction is directly related to the reacting substance's concentration to the first power. Let's examine a first-order response.   The rates of chemical reactions are symbolic of temperature. A temperature increase nearly always results in an increase in a reaction's rate and, consequently, in the rate constant. It has been noted that for many processes, a temperature increase of 10 oC causes the rate constant to increase by two to three times.

The amount of activation entropy and the change in activation free energy can be used to estimate the direction and extent of a reaction, as well as whether it will follow a uni- or bimolecular path. According to Kosower7 and Long8, SN2 reactions should have higher negative activation entropies or smaller positive entropies than the closest analogous SN1 reactions. This broad difference could serve as a mechanism criterion and be useful in the field of solvolytic reactions.

The nonionic surface active agents with the molecular configuration of a condensation product of at least one mole of an alkylene oxide with one mole of a compound containing at least six carbon atoms and a reactive hydrogen atom are the specific nonionics of interest in the process of the instant invention. These are preferably polyoxyalkylene derivatives of alkylated and polyalkylated phenols, multi-branched chain primary aliphatic

alcohols with the molecular configuration of an alcohol made by the oxo process from a polyolefin with at least seven carbon atoms, and straight chain aliphatic alcohols with at least carbon atoms. Propylene oxide, butylene oxide, or, ideally, ethylene oxide can be used as the alkylene oxide. The following lists examples of these derivatives as well as additional appropriate nonionic surface active agents that can be phosphated in line with the current invention. E.O. stands for ethylene oxide in this list, and the number before it indicates how many moles of that compound reacted with one mole of the specified reactive hydrogen-containing compound.

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