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Studies of the Formation of Condensed Phosphates Containing Alkyl-groups*

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Alkyl ammonium polyphosphate (AAPP) was prepared readily by a thermal reaction of alkyl (ethyl, *n*-propyl, *n*-butyl) dihydrogen phosphate and urea at temperatures ranging from 120°C to 200°C. At the same time, a small amount of cyanuric acid was obtained as a by-product. 1) AAPP was confirmed, from a study of the data of infrared spectroscopy, paper chromatography and chemical analysis, to have a long-chain structure possessing P–O–P linkage. The three types of AAPP were of almost the same form, according to the X-ray diffraction patterns. 2) AAPP was more or less hygroscopic, although the hygroscopicity of AAPP decreased with an increase in the carbon number of the alkyl group. 3) AAPP is reasonably stable, keeping a P–O–P linkage even upon degradation in an acidic aqueous solution.

In a previous paper,¹⁾ the present authors reported that when a mixture of phosphoric acid and urea was heated at 140—160°C, the decomposition of urea and the condensation and neutralization of phosphoric acid took place simultaneously. The products formed were ammonium polyphosphate and a small amount of cyanuric acid.

By a method similar to those used in preparing ammonium polyphosphate, the reaction of urea with alkyl dihydrogen phosphates was investigated. Alkyl phosphates with two hydroxyl radicals were thus found to bring about a poly condensation reaction with urea, giving alkyl ammonium polyphosphate (hereinafter this compound will simply be abbreviated as AAPP). All of the reaction products were identified by infrared absorption, X-ray diffraction, paper chromatography and quantitative chemical analysis. Several properties of AAPP were also investigated.

Experimental

The Formation of Alkyl Dihydrogen Phosphate.—Ethyl, *n*-propyl and *n*-butyl alcohol was reacted with phosphorus oxychloride at about 25°C. Alkyl phosphorodichloridate was obtained in about a 75—85% yield by means of vacuum distillation in each case. Alkyl phosphorodichloridates were hydrolyzed with water,²⁾ and de-hydrogenchloride carried out by blowing dry air into a volumetric flask under reduced pressure. The alkyl dihydrogen phosphate thus obtained was a light yellow, transparent liquid.

The Reaction of Alkyl Dihydrogen Phosphate with Urea.—Alkyl dihydrogen phosphates and urea were mixed so that the molar ratio of phosphorus pentoxide to urea in each alkyl dihydrogen phosphate corresponded to 1 : 2. The mixture was then gradually heated until the urea dissolved completely into the

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1) S. Ueda, K. Oyama and K. Koma, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **66**, 586 (1963); S. Ueda, T. Nakagawa and K. Koma, ibid., **66**, 589 (1963).

2) G. M. Kosolapoff, "Organo Phosphorus Compounds," John Wiley & Sons, Inc., New York. (1950).

alkyl dihydrogen phosphate. The reaction proceeded rapidly; a stimulative gas which contained carbon dioxide was evolved at about 130—135°C. At the initial stage of the reaction, the reaction product was remarkably expanded, and within several minutes the reaction was completed, the end point of the reaction being indicated by the formation of solid matter. Also, at the end of the reaction, a small amount of ammonia gas was generated. The resultant product was a light yellow, humid substance containing small amounts of unreacted urea and a water-insoluble substance.

The reaction product was then dissolved in water, and the insoluble substance was filtered off. Three times as much acetone as mother liquor was added to the latter, with constant stirring.

A white crystalline phosphate was separated as a precipitate, the urea remaining in the mother liquor. The precipitate was then again filtered off. After having been washed with anhydrous ethanol and acetone, the purified reaction product was dried using silica-gel under reduced presure.

Paper Chromatography.3)—Paper chromatography was carried out in a constant-humidity cabinet manufactured by the Mitamura Co., Ltd.

The solvent used for the development consisted of:

isopropyl alcohol	735 ml.
trichloroacetic acid	50 g.
distilled water	265 ml.
concentrated ammoniacal water	2.5 ml.

A spray reagent was prepared by mixing 5 ml. of 60% perchloric acid, 1 ml. of hydrochloric acid, and 1 g. of ammonium molybdate, and by then diluting this mixture to 100 ml. with water. Toyo filter paper No. 53 were used, and the development was conducted for 4—5 hr. at room temperature.

Chemical Analysis.—Ammonia was analyzed by a conventional chemical method. The phosphorus was spectrophotometrically determined at the 410 mμ wavelength, using a vanadomolybdate as the color reagent.4) The alkoxyl groups were analyzed by the Zeisel method.5)

X-Ray Diffraction.—The X-ray diffraction of samples was carried out with a Rigaku-Denki, D-2F unit using a nickel filter and copper K_α radiation. The unit was operated with a voltage of 30 kV., a current of 15 mamp., a scale factor of 400, a time constant of 2/sec., and a scanning speed of 2°/min.

Infrared Spectroscopy.—All of the spectra were recorded over the range from 4000 to 700 cm^{-1}, using a Hitachi EPIS-11 Double beam Spectrometer. The infrared spectra of the samples were taken both by potassium bromide pellet and by Nujol mull methods.

Results and Discussion

All of the resulting products were obtained as colorless crystalline substances. These products was of a somewhat hygroscopic nature and seemed to have a good solubility in water. The hygroscopicity of the products containing *n*-butyl and *n*-propyl groups were less pronounced than that containing the ethyl group.

The Composition of the Reaction Products.—Analytical results of the reaction products obtained from alkyl dihydrogen phosphates and urea are given in Table I. Small amounts (0.5—1.8%) of cyanuric acid as an insoluble substance in water, the identity of which was established by X-ray diffraction, were also obtained.

These phosphate polymer contained considerable amounts of water. In calculating the number average chain length, we disregarded the water in the phosphate.

M^1 stands for the mono-valency cation. The amonia and alkyl groups were expressed as $(NH_4)_2O$ and A_2O respectively in calculating the composition of the phosphates.

The nitrogen exists in phosphate as an ionized ammonium radical; this is confirmed by the fact that a barium salt prepared by adding barium chloride to an aqueous solution of phosphate does not contain the nitrogen.

As is shown in Table I, the molar ratio of $M^1{}_2O$ to P_2O_5 is approximately unity. The composition of poly-condensed phosphate can be expressed as $xM^1{}_2O \cdot yP_2O_5$, corresponding to the molar ratio of $R = x/y$. The general formula for the long-chain polyphosphates is usually given as:

$$\lim_{n\to\infty} M^1{}_{n+2}P_nO_{3n+1} = M_nP_nO_{3n}$$

For linear polymers, molar ratio, R, approaches 1 for sufficiently long chains. Judging from the analytical results, AAPP can, therefore, be thought of as being a long chain phosphate.

The average chain length of the polyphosphate can be determined by calculating the molar ratio, R. It is well known that the average chain length, $\bar{n}$, of polyphosphates is given by the equation:

$$R = M^1{}_2O/P_2O_5 = (n+2)/n$$

As the molar ratio, R, approaches unity, $\bar{n}$ approaches infinity. From the data in Table I,

TABLE I. ANALYTICAL RESULTS OF THE REACTION PRODUCTS

Alkyl dihydrogen phosphate	$(NH_4)_2O$ wt. %	A_2O* wt. %	P_2O_5 wt. %	$(NH_4)_2O/A_2O$ mole ratio	$M^1{}_2O/P_2O_5$** mole ratio	pH of 1% solution
Ethyl	15.3	2.1	47.2	9.1	1.0	5.9
n-Propyl	19.3	4.4	52.5	8.6	1.1	5.7
n-Butyl	20.6	7.6	58.0	6.8	1.1	5.9

* Alkyl ** $M^1{}_2O = (NH_4)_2O + A_2O$

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3) A. S. T. M. Designation D 501-58 T (1958).

4) O. B. Michelsen, *Anal. Chem.*, **29**, 60 (1957).

5) "Hand book of Analytical Chemistry," Maruzen Book Co., Tokyo (1961), p. 538.

we can calculate the average chain length, $\bar{n}$, of AAPP as having a value of more than 20.

Paper Chromatography. — Chromatograms and R_f values are shown in Fig. 1 and Table II respectively. When alkyl dihydrogen phosphate was used, almost all the phosphates produced were high polymers which could not be developed by paper chromatography. Even though a two dimensional development technique was used, no evidence of the formation of a ring-form phosphate was obtained.

In Fig. 2 are illustrated chromatograms of the hydrolysis products of AAPP, which were produced in an aqueous solution at pH 2.5 (adjusted by hydrochloric acid) and at 60°C.

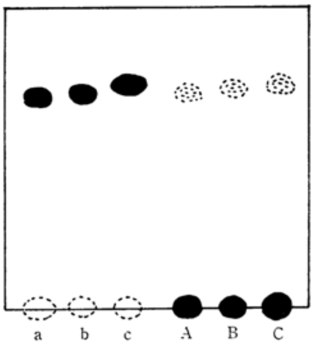


Fig. 1. A paper chromatogram of alkyl dihydrogen phosphate and the reaction products.

a : Ethyl dihydrogen phosphate
b : *n*-Propyl dihydrogen phosphate
c : *n*-Butyl dihydrogen phosphate
A : Reaction product (Ethyl)
B : Reaction product (*n*-Propyl)
C : Reaction product (*n*-Butyl)

TABLE II. THE R_f VALUE OF THE FREE ACID AND THE REACTION PRODUCTS

	Free acid	Reaction product
Ethyl	0.73	Retained strongly
n-Propyl	0.74	Retained strongly
n-Butyl	0.76	Retained strongly

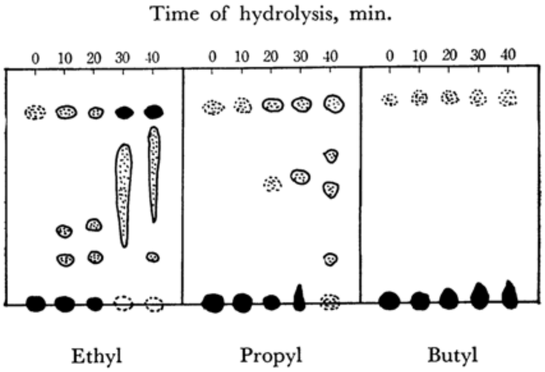


Fig. 2. The formation of hydrolysis products at pH 2.5 and 60°C.

As is shown in Fig. 2, the AAPP possesses a considerable stability upon hydrolytic degradation in an acidic solution.

The X-Ray Diffraction Pattern of AAPP and Its By-product.—The X-ray diffraction pattern of AAPP is illustrated in Fig. 3.

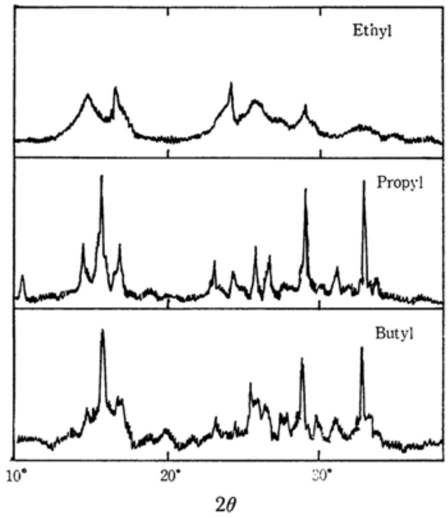


Fig. 3. The X-ray diffraction pattern of the reaction products.

As is apparent from the diffraction patterns, AAPP is always a crystalline substance. As the number of carbon atoms in the alkyl group increases, however, the crystallinity of the AAPP tends to increase. The crystallinity of the AAPP obtained from mono-ethyl dihydrogen phosphate is fairly poor in comparison with that obtained from propyl and butyl compounds. The poor crystallinity of the ethyl compound may be thought of as being caused by the hygroscopicity of the product.

Table III shows the spacing of the main interference with AAPP; it is always almost the same

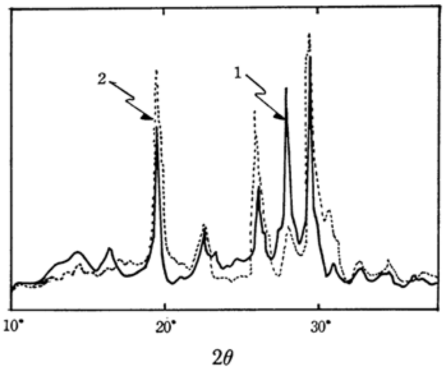


Fig. 4. The X-ray diffraction pattern of an insoluble substance and cyanuric acid.

1: Insoluble substance
2: Cyanuric acid (Reagent)

TABLE III. X-RAY DIFFRACTOMETRIC ANALYSIS OF THE REACTION PRODUCTS

Sample	Main interference															
	A		B		C		D		E		F		G		H	
	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1
Ethyl	5.99	0.92	—	—	5.31	1.00	3.74	0.84	3.45	0.77	—	—	3.06	0.77	2.71	0.54
n-Propyl	6.03	0.44	5.64	1.00	5.31	0.48	3.80	0.40	3.45	0.44	3.35	0.40	3.06	0.84	2.71	0.84
n-Butyl	6.06	0.56	5.64	1.00	5.34	0.67	3.80	0.50	3.47	0.61	3.38	0.56	3.08	0.83	2.72	1.00

TABLE IV. DATE OBTAINED BY THE X-RAY DIFFRACTOMETRY OF AN INSOLUBLE SUBSTANCE AND CYANURIC ACID

Sample	Main interference											
	A		B		C		D		E		F	
	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1
Cyanuric acid	4.53	1.00	3.99	0.19	3.39	0.61	3.01	1.00	2.24	0.27	2.17	0.25
Insol. substance	4.51	0.73	3.99	0.37	3.40	0.53	3.02	1.00	2.24	0.21	2.16	0.21

interferecne, regardless of the alkyl type. Therefore, the products can reasonably be regarded as phosphates with similar crystalline structures.

A water insoluble by-product was recrystallized in hot water (85—90°C) and then dried. The recrystallized substance was identified by the X-ray diffractometry as cyanuric acid, which was formed by the thermal decomposition of urea. The X-ray diffraction pattern and the spacing of the main interference of an insoluble substance and a pure reagent of cyanuric acid are shown in Fig. 4 and Table IV respectively.

As can be seen, the pattern and the main interference of the insoluble substance agree well with those of pure cyanuric acid.

The Infrared Absorption Spectra of AAPP.—In this work the infrared spectra of samples were examined as powder in the 4000—700 cm^{-1} range. These spectra have been investigated with a view to assigning characteristic frequencies to molecular groupings and to generally correlating the absorption with the molecular structure.

AAPP was mixed with potassium bromide and pressed into a disk; then the infrared spectra were measured and further compared with Nujol mulls. Figure 5 shows some typical spectra of these products; a potassium bromide tablet technique was employed for the measurements.

As can be seen from Fig. 5, a considerable variation was observed throughout the spectra. Some salts, e. g., *n*-propyl and *n*-butyl compounds, particularly afford broad and poorly resolved peaks.

The characteristic absorption bands of P–O–P, P–O–C (where C is aliphatic carbon) and the NH_4^+ ion were found in each spectrum in the ranges ~890 (P–O–P stretching), 760—740 (harmonics of P–O–P bending), 1010 (P–O–C stretching), 1390—1410 (NH_4^+, N–H stretching) cm^{-1}.

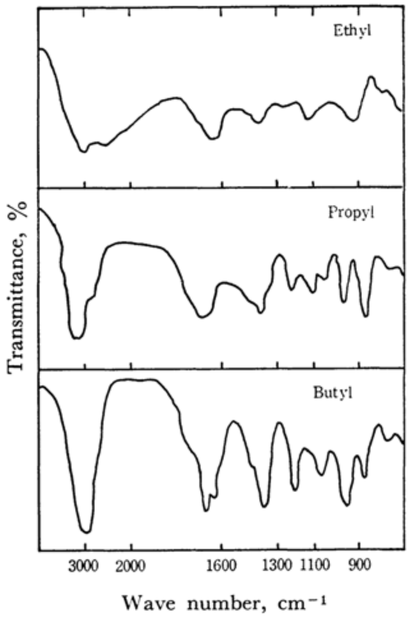


Fig. 5. The infrared absorption spectra of the reaction products.

This evidence strongly supports the view that AAPP is poly-condensed phosphate containing alkyl and ammonium radicals in the molecule.

The Mechanism of the Reaction.—A useful method for the preparation of condensed phosphate containing nitrogen has recently been developed by the present authors,[1] in this method a phosphoric acid or alkali metal dihydrogen phosphate is thermally treated with urea.

Similar condensation reactions have also been observed in the interaction of alkyl dihydrogen phosphate with urea. As has been stated above, the preparation of AAPP through the thermal reaction of alkyl dihydrogen phosphate with urea is accompanied by the following chemical reactions; alkyl dihydrogen phosphate and urea are subjected to the thermal reaction with greater ease; carbon dioxide gas and a stimulative gas (which is considered to be isocyanic acid) are generated, small amounts of ammonia gas and cyanuric acid as trimer of isocyanic acid are formed in the final stage of the reaction. On the basis of these observations as well as of chromatographic, infrared and X-ray diffractometric measurements, the mechanism given below seems reasonable for the reaction of alkyl dihydrogen phosphate and urea.

Assumption for the Mechanism of the Reaction.—First of all, urea is decomposed into ammonia and carbon dioxide with water.

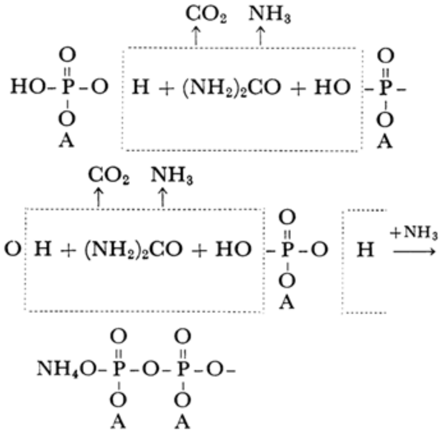
$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \qquad (1)$$

The water is thought to come from the hydroxyl radical of two moles of dihydrogen orthophosphates.

A small part of the urea can also be decomposed into cyanuric acid and ammonia in the following way when cyanuric acid is formed as a by-product of the reaction:

$$3(NH_2)_2CO \rightarrow (HNCO)_3 + 3NH_3 \qquad (2)$$

Thus, the formation of AAPP may be illustrated by the following equation:

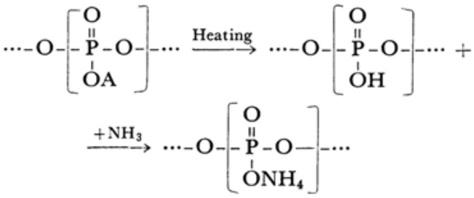


$$HO{-}\underset{\substack{|\\ O\\ A}}{\overset{\substack{O\\ \|}}{P}}{-}O\overset{\substack{CO_2\ \ NH_3\\ \uparrow\ \ \ \ \uparrow}}{\boxed{H + (NH_2)_2CO + HO}}{-}\underset{\substack{|\\ O\\ A}}{\overset{\substack{O\\ \|}}{P}}{-}$$

$$O\overset{\substack{CO_2\ \ NH_3\\ \uparrow\ \ \ \ \uparrow}}{\boxed{H + (NH_2)_2CO + HO}}{-}\underset{\substack{|\\ O\\ A}}{\overset{\substack{O\\ \|}}{P}}{-}O\ \boxed{H}\ \xrightarrow{+NH_3}$$

$$NH_4O{-}\underset{\substack{|\\ O\\ A}}{\overset{\substack{O\\ \|}}{P}}{-}O{-}\underset{\substack{|\\ O\\ A}}{\overset{\substack{O\\ \|}}{P}}{-}O{-} \qquad (3)$$

As has been recognized by Hochwalt and his co-workers[6] in the thermal decomposition of alkyl hydrogen phosphate, the alkyl group in phosphate may also be decomposed partially into free acid and olefine by heating. The ammonia produced by the reactions 1, 2, and 3 can subsequently be neutralized with the hydroxyl radical of the poly-condensed phosphate according to the following equation:



$$\cdots{-}O{-}\left[{-}\underset{\substack{|\\ OA}}{\overset{\substack{O\\ \|}}{P}}{-}O{-}\right]{-}\cdots \xrightarrow{\text{Heating}} \cdots{-}O{-}\left[{-}\underset{\substack{|\\ OH}}{\overset{\substack{O\\ \|}}{P}}{-}O{-}\right]{-}\cdots + A'$$

$$\xrightarrow{+NH_3} \cdots{-}O{-}\left[{-}\underset{\substack{|\\ ONH_4}}{\overset{\substack{O\\ \|}}{P}}{-}O{-}\right]{-}\cdots \qquad (4)$$

Where $A = C_nH_{2n+1}$, $A' = C_nH_{2n}$, etc.

Therefore, the alkyl group of this compound may partially be replaced by the ammonium group in a random way.

Summary

When alkyl dihydrogen phosphate and urea are mixed and subjected to thermal reaction at 120—200°C, the thermal decomposition of urea, the condensation of alkyl dihydrogen phosphate, and a partial neutralization of the acid with ammonia have been brought about, this yielding alkyl ammonium polyphosphate (AAPP).

Observations with infrared spectroscopy, paper chromatography and chemical analysis have disclosed that the reaction products are long-chain phosphates containing alkyl and ammonium group in a skeleton P–O–P.

The average chain length, $\bar{n}$, of AAPP is estimated by calculation to be more than 20.

No substantial difference in crystalline form has been found among the various AAPPs' tested.

The products are more or less hygroscopic, although the hygroscopicity of AAPP decreases with an increase in the number of carbon atoms in the alkyl group.

It has also been found that AAPP is reasonably stable upon the hydrolytic degradation of the P–O–P linkage in an acidic, hot aqueous solution.

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[6] C. A. Hochwalt, J. M. Lum and J. E. Malowan, *Ind. Eng. Chem.*, **34**, 19 (1942).