STUDIES ON COMMERCIAL OCTAMETHYLPYROPHOSPHORAMIDE (SCHRADAN *).

I.—Composition and Analysis

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A method has been worked out for determining the full composition of commercial octamethylpyrophosphoramide. It is shown that perdimethylamides of higher polyphosphoric acids are present, principally triphosphoric acid penta(dimethylamide), which is a valuable insecticide, in addition to the pyroamide and the trisdimethylamide of orthophosphoric acid. The properties of the various compounds as far as they affect analysis and stability are described, and some facts about their interconversion on heating are recorded.

Introduction

The pioneer work of Schrader (1947) on toxic phosphorus compounds, in addition to pointing to compounds of outstanding insecticidal power leading to the industrial development of parathion (E 605) and HETP (Bladan), drew attention to the ability of some compounds to be absorbed into the sap stream of the plant and to render it toxic to sucking insects at places more or less remote from the original site of application.

These 'systemic' (Hurd Karrer, 1937; Fulton & Mason, 1937) insecticides have outstanding advantages in agricultural practice where one is dealing so frequently with the hidden insect and where pest–predator balance is supremely important (Ripper, Greenslade & Lickerish, 1949). Other operational advantages have been pointed out by Martin (1950). Accordingly further research was carried out in these Laboratories on these compounds and the most promising of them, bisdimethylaminophosphonous anhydride, or octamethylpyrophosphoramide, was developed commercially and has been extensively used over the last two seasons in several commercial pest-control operations (Ripper, Greenslade & Hartley, 1950). Very successful results have been obtained.

The compound was prepared by Schrader by two methods. In the first, bisdimethylaminochlorophosphine oxide was heated with ethyl bisdimethylaminophosphonite with or without an inert diluent, to give the pyroamide and ethyl chloride. In the second, the bisdimethylaminochlorophosphine oxide was heated with a suspension of dry sodium bisdimethylaminophosphonite, the pyroamide and sodium chloride being formed. The first synthesis has been confirmed by other workers (Gardner & Kilby, 1950).

Both methods involve multi-stage synthesis and we preferred to develop a more direct method for industrial production. The alternative reaction exploited is

$$2R_2POCl + H_2O \rightarrow (R_2PO)_2O + HCl.$$

R denotes $-NMe_2$ here and throughout this paper.

The reaction does not go to a useful extent in the desired direction unless the HCl can be removed as it is formed. This is most conveniently done with a tertiary amine. This reaction, where the substituent is anilino, not dimethylamino, has been described by Zeile & Kruckenberg (1942), the tertiary base being pyridine. The formation of the pyrophosphoric acid tetranilide is evidently more facile since a considerable yield appears to be obtained by simply pouring a pyridine solution of the bisanilidochlorophosphine oxide into excess water, procedure which gives almost exclusively hydrolysis products with bisdimethylaminochlorophosphine oxide.

We prefer to use a more strongly basic tertiary amine than pyridine and one whose hydrochloride is more soluble, methyldibutylamine being particularly suitable among readily available amines. As disclosed in B.P. 631,549 and 652,981, the bisdimethylaminochlorophosphine oxide is prepared by reaction of anhydrous dimethylamine and phosphoryl chloride in solution in chloroform containing excess methyldibutylamine, the further reaction with water is carried out in the same system and, by adding excess aqueous caustic soda, the product is separated into an organic layer containing also the chloroform and methyldibutylamine. The solvents are then stripped off the product by evaporation at reduced pressure.

The product obtained in this way contains a small proportion of residual solvents, mainly methyldibutylamine, and some suspended salts of the amine which are very freely soluble in water. It is normally marketed with the further addition of non-ionic wetting agent.

* Name approved by the British Standards Institution, Technical Committee for Pest Control Products.

Analysis was first carried out by a method we now know to be incomplete, but these estimates of the pyrophosphoramide content checked well with biological estimates in comparison with standard pure material (Pest Control Ltd., unpublished work; Bennett, 1949). We anticipated a certain amount of 'scatter' in the primary reaction giving R_3PO and $RPOCl_2$ along with the desired R_2POCl. Some organic insoluble phosphorus compounds remained in the aqueous caustic soda layer in the method of separation described above and these were considered to derive from the $RPOCl_2$, the R_3PO being known to be very stable and therefore to persist in the product. It was therefore considered that estimation of combined amine and phosphorus in a chloroform extract of the product after dissolving in aqueous caustic soda enabled the relative amounts of R_3PO and $R_4P_2O_3$ to be calculated.

This method has since proved to assume too high a degree of instability of the dimethylamides of at least one higher polyphosphoric acid: the next member of the series, $R_5P_3O_5$, was found in the product to a considerable extent. It is obtained in much higher proportion, as will be explained below, than can be accounted for by 'scatter' in the primary reaction. For the purpose of biological test it has been produced by a laboratory reaction in the form of a very rich mixture with $R_4P_2O_3$. The compound is as powerful an insecticide as $R_4P_2O_3$, acting also preferentially on many species of sucking insects and having little contact-effect. It is markedly less toxic to mammals. Investigation of stability of the compound in plant tissues by the radio-tracer technique has shown it to be equally stable with $R_4P_2O_3$. This is an extension of the observation already reported (Hartley & Heath) that R_3PO and $R_4P_2O_3$ are decomposed by plants at closely comparable rates, as will be described in a later paper.

Complications are thus seen to be present, analogous to those which have already been noted in commercial HETP and TEPP, with the marked difference that the dimethylamides are much more resistant to hydrolysis than the esters, so that the more easily hydrolysed higher homologues are still stable enough to be important. The existence of pentaethyl triphosphate in so-called HETP has been shown to be very probable (Hall & Jacobson, 1948*a*; Coates, 1949).

It is evident that where we have R_3PO, $R_4P_2O_3$ and $R_5P_3O_5$ together we cannot determine the composition solely by ultimate chemical analysis. With increased knowledge of the properties of the individual compounds and with great assistance from radio-assay methods (based on ^{32}P) we derived a method of analysis described below. This depends on selective extraction and hydrolysis. It is in this respect similar to the method used for HETP (Hall & Jacobson, 1948*b*; Dvornikoff & Morrill, 1948) but capable of giving fuller information owing to the rate of hydrolysis of all the compounds being much slower than their counterparts in HETP.

Development of method

Properties of R_3PO and $R_4P_2O_3$.—R_3PO may be prepared in good yield by running $POCl_3$ into excess of dimethylamine in carbon tetrachloride. After filtration and washing with aqueous sodium hydroxide it is purified by distillation under reduced pressure (b.p. 130° c./approx 10 mm.). $R_4P_2O_3$ is made either by the method described in B.P. 631,549 and 652,981 (see above) or by the methods of Schrader (1947). In either case it is freed from $R_5P_3O_5$ by methods described later, and purified by fractional distillation. It is a liquid, colourless when pure, b.p. 140° c./2 mm. A specimen melting at 18–19·5° c. has been obtained. Temperatures above about 200° c. lead to some decomposition.

The relevant physical properties of these two compounds are given in Table I. For details reference is made to a parallel publication (Heath & Casapieri, 1951). The bonds broken by hydrolysis are given in brackets below the constant.

Both compounds partition heavily in favour of water from hydrocarbons (aliphatic and aromatic) and completely chlorinated hydrocarbons, but in favour somewhat of CH_2Cl_2, C_2HCl_3, $C_2H_2Cl_4$ and $C_3H_6Cl_2$.

New compounds.—A laboratory preparation was made by the commercial method from phosphorus containing ^{32}P (50 μc. per g. of insecticide), freed by distillation from R_3PO, and distilled under reduced pressure. It was found not to give a constant partition-ratio between chloroform and water when exhaustively extracted. The $CHCl_3/H_2O$ partition-ratio varied from about 9 at the beginning of the extractions from chloroform with water to about 17 after 24 extractions with equal volumes of water. After treatment with N-sodium hydroxide at 100° c. for 15 min. it was found that a chloroform extract of the product gave a ratio varying from about 7·1 to 9 over 24 extractions. If the chloroform/water partitioning was performed after extracting the hydrolysate twice with an equal volume of carbon tetrachloride the ratios remained quite constant. This suggested the presence of two previously unsuspected constituents of the insecticide: one, present to about 25–30%, easily hydrolysable in aqueous

Table I

Partition ratios

	R_3PO	$R_4P_2O_3$
$\frac{CHCl_3}{H_2O}$, 25° C.	6·7*, 6†	7·1*, 4·0†
$\frac{CHCl_3}{N\text{-}NaOH}$, 25° C.	17·6*—	24*, 17†
$\frac{K_{acid}}{[H^+]}$, 25° C.	$2{\cdot}2 \times 10^{-4}$ min.$^{-1}$ (P—N)	$3{\cdot}60 \times 10^{-3}$ min.$^{-1}$ (P—N)
$\frac{K_{alkali}}{[OH^-]}$, 100° C.	$< 10^{-6}$ min.$^{-1}$ (P—N)	$4{\cdot}58 \times 10^{-3}$ min.$^{-1}$ (P—O—P)
K_{water} at 100° C.	$< 10^{-8}$ min.$^{-1}$ (P—N)	$< 10^{-8}$ min.$^{-1}$ (P—O—P)

Note. * At infinite dilution.
† From 10% solution in chloroform.

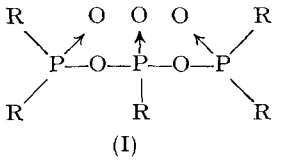
sodium hydroxide at 100° C. and partitioning with a $CHCl_3/H_2O$ ratio of about 15, and another, present to about 3% only, not easily hydrolysable in aqueous sodium hydroxide, with a very large partition ratio indeed, and extractable with CCl_4.

These compounds were partially separated by fractional partitioning with methylene dichloride, and the products analysed by a radio-tracer modification of the methods described below. The amine/phosphorus ratio was then determined for each product, and compared with that calculated on the assumption that the first, alkali-hydrolysable, compound was $R_5P_3O_5$ (R : P = 1·67 : 1) and the other $(RPO_2)_n$ (ratio 1 : 1). The analyses were performed by completely hydrolysing with boiling hydrochloric acid, phosphate being then determined by the molybdenum-blue method of Allen (1940) and the amine by making alkaline, distilling, and titrating the distillate with 0·1N-hydrochloric acid (see Table II).

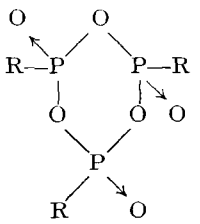
Table II

Molar constitution of mixture			N : P ratios	
$R_4P_2O_3$	$R_5P_3O_5$	$(RPO_2)_n$	Found	Calculated
12·7	64	23·3	1·53	1·53
4·8	85·7	9·5	1·61	1·56
0	40	60	1·25	1·25

The agreement between the observed and calculated ratios is satisfactory, and justifies us in assigning the formula $R_5P_3O_5$ (I) to the major new compound and $(RPO_2)_n$ to the other. Later we show that $(RPO_2)_n$ is probably a cyclic trimer (II).



(I)



(II)

The second and third of the mixtures obtained were subjected to insecticidal and mammalian-toxicity tests. $R_5P_3O_5$ is as good an insecticide as $R_4P_2O_3$ and is also systemic, but is far less mammalian-toxic. $R_3P_3O_6$ is less toxic generally. When analysed by the method described below a typical product before formulation contains about 85% of phosphorus compounds extractable by chloroform from aqueous alkali. Expressed by weight this fraction consists of R_3PO, 17·3; $R_4P_2O_3$, 40·4; $R_5P_3O_5$, 39·1; $R_3P_3O_6$, 3·2%.

This analysis reveals a high percentage of $R_5P_3O_5$ in the final product. The obvious reaction which may produce it is:

$$2R_2POCl + RPOCl_2 + 2H_2O + Base \longrightarrow R_5P_3O_5 + Base,4HCl$$

This, however, postulates that in the preparation whose product contains 39% of $R_5P_3O_5$ at least 13% of the phosphorus was present as $RPOCl_2$ at the end of the first stage, the nominal reaction in which is:

$$POCl_3 + 2RH + Base \longrightarrow R_2POCl + Base,2HCl$$

Analysis of the first-stage reaction product revealed only 3% of $RPOCl_2$ and 3% of R_3PO. This is consistent with measurements made on the rates of reaction of the phosphoryl chlorides with free dimethylamine in chloroform. Replacement of the first chlorine is virtually instantaneous, that of the second a matter of seconds, whereas the half time of the third replacement reaction is 17 minutes in 2M-solution of both reactants in chloroform at 25° C. It is clear therefore that the bulk of the $R_5P_3O_5$ is produced by reactions which do not depend on the initial presence of $RPOCl_2$ in the reaction mixture. Owing to the complexity of the system it has not proved possible to provide a complete explanation of the reactions. The general conditions which control their formation are, however, known and are adjusted to give a product of optimal systemic insecticidal power while having a lower mammalian-toxicity than the equivalent amount of pure octamethylpyrophosphoramide.

Synthesis and properties of $R_5P_3O_5$ (triphosphoric acid pentadimethylamide, or decamethyltriphosphoric pentamide).—In order to provide check material for biological and analytical tests, $R_5P_3O_5$ was synthesized with weakly radioactive ingredients by the reaction:

$$R_2PO{\cdot}OEt + RPOCl_2 \longrightarrow R_5P_3O_5 + 2EtCl$$

[This reaction is a modification of Schrader's method for preparing $R_4P_2O_3$:

$$R_2PO{\cdot}OEt + R_2POCl \longrightarrow R_4P_2O_3 + EtCl$$

The latter reaction has been repeated, and is found to yield a product containing about 25% of $R_5P_3O_5$. This compound was plainly present also in Schrader's own product, which was stated to be ' moderately stable to lime.' The half-life of $R_4P_2O_3$ in saturated lime-water at 25° C. is about 8 years and that of $R_5P_3O_5$ about 40 hr. A pure $R_4P_2O_3$ product would therefore have seemed quite stable to lime. In our own earlier investigations (Ripper, Greenslade & Hartley, 1950) we also were misled by the then unknown presence of a more hydrolysable compound associated with one almost indefinitely stable in water.]

A mixture of the reagents in theoretical proportions was heated at between 90° C. and 105° C. for 4½ hr., during which ethyl chloride was evolved copiously. The product was cooled, dissolved in chloroform, extracted twice with water, and the chloroform distilled off at low pressure. Analysed by the method later described, the product was found to contain: $R_4P_2O_3$, 17·5; non-chloroform extractables, 8; $R_5P_3O_5$, 64·5%. An attempt was made to distil this material at 1 mm. Hg pressure but it resulted in considerable disproportionation. After a small fraction of $EtOPOR_2$ had been removed the bulk of the liquid distilled between 140° and 180° C., with a slowly rising temperature, the distillate consisting largely of $R_4P_2O_3$ and R_3PO.

A second preparation of radioactive $R_5P_3O_5$ was performed. The product was heated under high vacuum for 5 min. at 130° C. to remove R_2POOEt, but was not distilled. This treatment increased the $R_4P_2O_3$ content by about 3%. A portion of product was hydrolysed for 15 min. at 100° C. in N-sodium hydroxide, partitioned with an equal volume of chloroform, and the amine/phosphorus molar ratio found on the aqueous layer. The ratio found was 1·664 ± 0·05. That calculated, allowing for the calculable slight hydrolysis of $R_4P_2O_3$ (to $R_2PO_2^-$) and for the amount of $R_4P_2O_3$ remaining in the caustic layer after extraction, is 1·669. This sample contained 23·4% $R_4P_2O_3$, and slight traces of higher polymers.

Using the undistilled $R_5P_3O_5$-rich mixture of the second preparation some approximate hydrolysis and partition figures for $R_5P_3O_5$ have been obtained, and are summarized in Table III.

Continued distillation of the first preparation yielded, at 190–210° C. (1 mm.), a fraction which solidified. This was recrystallized from a mixture of dichloropropane and *cyclo*hexane. On redistilling the solid some liquid separated, and the residue in the flask was partly at least metaphosphoric acids.

The gummy solid from the distillate was highly hygroscopic and dissolved immediately in water, which decomposed it completely to amine phosphate at 25° C. in 2 days, with a half-life of about 6 hr. Its molecular weight in benzene (lowering of f.p.) and its equivalents per phosphorus atom and amine molecule were found to be 548, 114 (^{32}P assay) and 108·1 respectively, the determinations being made on the same solution. Molybdenum blue gave a phosphorus equivalent of 114·6. These equivalents and molecular weight are consistent with those for a

Table III

Property	Value
$\frac{CHCl_3}{H_2O}$, 25° c. . .	15·6*, 8–10†
$\frac{K_{acid}}{[H^+]}$, 25° c.	$3{\cdot}5 \times 10^{-3}$ min.$^{-1}$
$\frac{K_{alkali}}{[OH^-]}$, 25° c.	$4{\cdot}8 \times 10^{-3}$ min.$^{-1}$
$\frac{K_{alkali}}{[OH^-]}$, 100° c.	0·63 min.$^{-1}$
K_{water}, 100° c.	5×10^{-4} min.$^{-1}$

* Infinite dilution. † 10% solution in chloroform.

mixture of $R_5P_5O_{10}$ (cyclic) and $R_7P_5O_9$ in the proportions 6 : 1. For this mixture the calculated molecular weights and equivalents are 546, 115·0 and 108·7.

[Similar results could be calculated for more complex mixtures of long-chain polymers, providing the bulk is $R_5P_5O_{10}$.

This behaviour is highly reminiscent of the phenomena observed by Stokes (1895, 1898) with phosphorus nitrilic chlorides $(PNCl_2)_n$, which exist in a number of readily interchangeable ring forms, of which all the members from $(PNCl_2)_3$ to $(PNCl_2)_7$ were isolated, and which are produced from and can change into rubber-like linear high-polymers. By analogy with the optical resolution of trialkylphosphines (Meisenheimer & Lichtenstadt, 1911) we should expect linear polymers above $R_5P_3O_5$ to exist in steric and optically active isomeric forms, while the ring compounds will all be mixtures of stereoisomers. The existence of these probably accounts for the difficulty of obtaining pure specimens.

Similar disproportionation reactions occur during manufacture of TEPP and its distillation (Hall & Jacobson, 1948*a*; Coates, 1949) and we may recall the early observation of this type of disproportionation in Vögeli's method of preparation of triethylphosphate by heating the lead salt of diethylphosphoric acid (Vögeli, 1849).]

As the cyclic pentamer is highly unstable in water, the cyclic polymer found as a slight impurity in commercial Pestox III is likely to be the trimer. This is made more probable by the fact that the natural P—O—P angles are suitable for a planar configuration, benzenoid resonance, and hence considerable resistance to aqueous and alkaline hydrolysis.

Analysis of commercial product

On the basis of these results it is possible to put forward a method of analysing the commercial product. Before formulation with wetting agent the product contains about 85% of material which is not extractable from chloroform by one washing with N-sodium hydroxide. The extractables consist of dimethylamine (present originally as chloride and phosphate) and bisdimethylaminophosphonous acid R_2POOH (present originally as the amine salt).

The chloroform-soluble phosphorus compounds consist of the two insecticides and also R_3PO and $R_3P_3O_6$. The initial product before separation undoubtedly contains some higher polymers. It is noted above that $R_5P_3O_5$ is slowly hydrolysed in water, and the higher polymetaphosphoramides (residues in the distillation described above) are so unstable to water that when a chloroform solution of them is shaken with water none remains in the chloroform layer. This behaviour is analogous to that of the TEPP–HETP series, in which the longer the P—O—P chain the more rapid the aqueous and alkaline hydrolysis (Hall & Jacobson, 1948*a*, *b*; Coates, 1949; Dvornikoff & Morrill, 1948). We have found that the commercial insecticide contains some of a compound highly unstable to alkali, with a half-life of about 140 sec. at 25° c. in N-sodium hydroxide. It seems reasonable to suppose that this is $R_6P_4O_7$, as the next slower rate corresponds to that for $R_5P_3O_5$.

From this we conclude that the washing process will leave in the chloroform only $R_6P_4O_7$ and lower members, the higher members being decomposed by the washing to form compounds insoluble in chloroform. In the analysis, therefore, $R_6P_4O_7$ appears as $R_5P_3O_5$. Some approximate hydrolysis runs, however, indicate that of the '$R_5P_3O_5$ fraction' only about 10–15% is present as $R_6P_4O_7$, with a maximum of about 20%. Thus the process of manufacture favours the lower homologues.

The method of analysis depends on the following properties: (*a*) all compounds are partitioned heavily in favour of chloroform from water and even more heavily from sodium

hydroxide solution; (*b*) they are hydrolysed at very different rates in alkali; (*c*) $R_3P_3O_6$ only is partitioned in favour of carbon tetrachloride from N-NaOH.

The relevant quantities are listed in Table IV, where K is the hydrolysis constant (min.$^{-1}$) at 100° C. in N-NaOH.

Table IV

	R_3PO	$R_4P_2O_3$	$R_5P_3O_5$	$R_3P_3O_6$
K	10^{-6}	$4{\cdot}6 \times 10^{-3}$	0·63	7×10^{-4}
$\frac{CHCl_3}{H_2O}$	6·67	7·1	15·6	300
$\frac{CHCl_3}{N\text{-}NaOH}$	17·6	24·0	Large	Large
$\frac{CCl_4}{N\text{-}NaOH}$	0·11	0·026	—	10

Method (in outline)

(1) The sample is partitioned into chloroform from 2N-NaOH, the chloroform layer distilled to remove solvent and made into a solution in N-NaOH. The 'free' amine ($MeBu_2N$ and a little $NHMe_2$) is removed by distillation at low pressure, and the residue (A) made up with N-NaOH to a standard volume. An aliquot of this is hydrolysed in acid, and distilled from alkali in order to determine the 'combined' amine by titration of the distillate.

(2) The remainder of the standard solution is heated to 100° C. for 15 min. on a water bath, which hydrolyses $R_5P_3O_5$ and other higher linear homologues but leaves the rest practically unchanged (B). An aliquot is extracted exhaustively with chloroform, and the total amine determined in an aliquot of aqueous layer. The decomposition products of $R_5P_3O_5$ etc. are not extracted by chloroform from water, so this determination measures the quantity of $R_5P_3O_5$. An allowance is made for the slight hydrolysis of $R_4P_2O_3$.

(3) An aliquot of (B) is extracted twice with an equal volume of carbon tetrachloride. The total amine in a sample of the aqueous layer (C) is determined. The aqueous layer contains all the original 'combined' amine less that of $R_3P_3O_6$, which has been extracted, so the amount of $R_3P_3O_6$ can be found from this titre when certain corrections have been made.

(4) An aliquot of (C) is made 2N.–3N. in alkali and heated either for 8 hr. under reflux or in a pressure cooker at 15 lb./sq. in. for 2 hr. This hydrolyses $R_4P_2O_3$ into chloroform-insoluble compounds. The hydrolysate is extracted exhaustively with chloroform, and the total amine in the aqueous layer found. This derives from $R_5P_3O_5$ and $R_4P_2O_3$. We now have four amine determinations and four unknowns, hence all four amine-containing compounds can be estimated.

Certain small corrections have to be made. Some $R_4P_2O_3$ is hydrolysed in N-NaOH at 100° C. in 15 min., and so interferes with $R_5P_3O_5$. Both $R_4P_2O_3$ and R_3PO are partitioned to some extent into carbon tetrachloride, and hence, without correction, would appear as $R_3P_3O_6$.

Method (working details)

Weigh out a quantity w calculated to contain about 20 g. of amine-containing phosphorus compounds. Make up to 160 c.c. with water and shake with 200 c.c. chloroform. Add 40 c.c cold 10N-sodium hydroxide, shake again, separate the chloroform layer and remove chloroform and free amine by vacuum evaporation. In order to complete the removal of chloroform and to eliminate free amine, 50 c.c. N-NaOH is added to the flask towards the end of the distillation and the distillation continued under low pressure. It is necessary to distil over at least 15 c.c. water to remove the amine. During this stage of the distillation it is essential that the temperature does not exceed 60° C. nor the time 1 hr. If the temperature is higher or the time longer the formulae given for the calculation of results will be incorrect, owing to undesired decomposition of $R_4P_2O_3$. Make the residue up to 250 c.c. with 1·1N-NaOH (A). Take a 25-c.c. aliquot and estimate the total amine by hydrolysis with HCl, adding alkali, distilling and titrating the distillate with HCl. Titre = a.

Heat the remainder of (A) for 15 min. in a boiling water bath, and cool quickly. To avoid cracking the standard flask it is preferable that it be of resistance glass or the contents should be transferred to a resistance-glass flask. In either case the mouth should be lightly plugged with cotton wool to discourage evaporation losses. Take 25 c.c. of the cooled solution (B),

and extract twice with an equal volume of chloroform. Estimate the total amine in the aqueous layer. Titre = *b*.

Take 100 c.c. of solution (B), and extract twice with 100 c.c. each time of carbon tetrachloride. Take 25 c.c. of the aqueous layer (C), and estimate its total amine. Titre = *c*.

Take 25 c.c. of (C) and make about 2N. in alkali. Either reflux for 8 hr. or heat in a pressure cooker at 15 lb./sq. in pressure for 2 hr. In the latter case the unstoppered flask loses a little R_3PO but the shorter time is an advantage.

After this hydrolysis, transfer the hydrolysate quantitatively to a separating funnel, and wash three times with an equal volume of chloroform. Estimate the total amine in the aqueous layer. Titre = *d*.

From these titres the titres corresponding to each individual constituent can be found from the following formulae. In these the titre corresponding to each of the compounds is given by V with the subscript 31 for R_3PO, subscript 42 for $R_4P_2O_3$, etc.

$$V_{31} = 1{\cdot}24(c - d)$$
$$V_{42} = 1{\cdot}13(d - b)$$
$$V_{53} = b - 0{\cdot}07V_{42}$$
$$V_{33} = a - (c - 0{\cdot}046V_{42} - 0{\cdot}194V_{31})$$

The percentage weight of each constituent is equal to VEN/w, where V is the titre calculated as above, N is the normality of the acid, w is the weight (g.) originally taken and made up to 250 c.c., and E is the equivalent weight. The last formula holds only if the sample is made up to exactly 10 times the volume used for each amine determination. The equivalent weights are as follows:

$R_3PO = 59{\cdot}8$	$R_4P_2O_3 = 71{\cdot}5$
$R_5P_3O_5 = 78{\cdot}6$	$R_3P_3O_6 = 107$

We have found the reproducibility to be about 1% of the total amine.

In the method given above the free amine and amine salts are not estimated. They are of no biological importance.

Conclusions

A method for the full analysis of the organic phosphorus compounds in commercial insecticidal products containing phosphoric acid dimethylamides is described.

In addition to octamethylpyrophosphoramide (Schradan, pyrophosphoric acid tetrakis-dimethylamide) the product Pestox III contains a comparable amount of triphosphoric penta(dimethylamide).

There occurs also a smaller amount of orthophosphoric acid trisdimethylamide and minor amounts of perdimethylamides of higher polyphosphoric and cyclic metaphosphoric acids, in addition to electrolyte impurities and residual solvents of manufacture.

A method of analysis based on the different speeds of alkaline hydrolysis of the various compounds and differences in their partition coefficients is described.

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