

Pyrolysis of Model Compounds of The Flame Retardant Poly (*N*-Dimethylphosphonomethyl Acrylamide)*

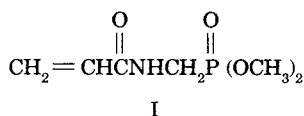
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Synopsis

An investigation of the thermal decomposition of *N*-dimethylphosphonomethyl amides has shown that the major volatile products for decomposition above 300°C are methanol, the methyl ester of the carboxylic acid, the nitrile, the carboxylic acid, the *N*-methyl amide, and the *N,N*-dimethyl amide. Also, benzoic acid was the only volatile product detected in the decomposition of α -benzamidomethylphosphonic acid. A mass balance for the decomposition of *N*-dimethylphosphonomethyl benzamide at 420°C showed methanol and methyl benzoate to be the major volatile products. Methanol and benzonitrile formation increased with an increase in temperature at a faster rate than the other volatile products. The reaction of amides and phosphonates was further studied using sealed tubes in a furnace. Reaction of *N*-methylbenzamide with dimethyl methylphosphonate at 307°C in a sealed tube produced methyl benzoate and *N,N*-dimethylbenzamide. *N,N*-dimethylbenzamide and dimethylmethylphosphonate were also shown to produce methyl benzoate at 310°C. After a 5-min period more methyl benzoate was produced in the *N,N*-dimethylbenzamide reaction than in the *N*-methylbenzamide reaction. Also, addition of ethanol to the *N,N*-dimethylbenzamide/dimethyl methylphosphonate reaction resulted in less ethyl benzoate methyl benzoate after heating at 310°C.

INTRODUCTION

N-dimethylphosphonomethyl acrylamide (I) and a series of related compounds were originally developed for grafting to cellulose by either free radical or ionic initiation.¹ However, compounds with a similar structure have since been used for flame retardation of numerous polymers. Nylon and acrylonitrile-butadiene-styrene copolymers are two polymer systems that have been rendered flame retardant with phosphonomethyl amide compounds²⁻⁴



Realizing the efficiency of phosphonoalkyl amide compounds as flame retardants for a variety of compounds, researchers directing the project sponsored by the Environmental Technology Incentive Program⁵ selected

* Taken from a dissertation submitted by Terry Edwin Lawler to Clemson University in partial fulfillment of the requirements for the Ph.D. degree.

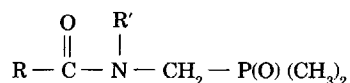
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compound I as a candidate for radiation grafting of 50/50 polyester/cotton blend fabric. Compound I was applied from a 50% solution of the monomer in ethylene dichloride. When fixation was accomplished by an electron beam source, an add-on of 59% was achieved with a total dosage of only 0.5 Mrads. When tested using the oxygen index (OI), this treated sample exhibited an OI of 32.8, as compared to 18.5 for untreated fabric.

Since the decomposition of compound I appeared to be complex as indicated by the DSC thermogram^{6,7} and the purification and storage of these compounds was difficult, it was decided the best approach to the thermal investigation of this class of compounds would be through the use of model compounds. Also, it was reasoned that a model of the polymer of compound I should be a less complicated system than the polymer itself and it was assumed that the *N*-(dialkylphosphonomethyl)amide structure [$-\text{C}(\text{O})\text{NHCH}_2\text{P}(\text{O})(\text{OR})_2$] is the portion of the molecule which is active in flame retardation reactions. Therefore, models incorporating this moiety were selected to represent the pendant group of the polymer of amide I.

Initially *N*-(dimethylphosphonomethyl)acetamide IIa and *N*-(dimethylphosphonomethyl)benzamide IIb were chosen as models. Compound IIa was selected because the methyl attached to the carbonyl should represent the aliphatic polymer backbone, while compound IIb was selected to investigate the change in the products of decomposition for an aliphatic amide as compared to an aromatic amide. Also, the products of the amide IIb decomposition should be less volatile and easier to trap and identify than the products of compound IIa decomposition. Later *N*-methyl-*N*-(dimethylphosphonomethyl)acetamide IIc was chosen to investigate the effect of removing the proton on the amide. Thus, the methyl group is not a good learning group and electron would be changed about the C—N bond of the amide.



Ia: R = CH₃, R' = H

b: R = φ, R' = H

c: R = CH₃, R' = CH₃

Examination of these compounds by thermal analysis techniques^{6,7} demonstrated the importance of hydrolysis and alcoholysis reactions. Hydrolysis was found to occur in the region 160–205°C and was followed by exothermic decomposition at 250–350°C. The relative rates of hydrolysis were shown to be IIc > IIa > IIb. The exothermic hydrolysis reaction of the benzamide was replaced by an endothermic alcoholysis in the presence of 1-dodecanol.

Also of significance in terms of flame-retardant action are the decomposition products of the phosphonomethyl amides which would be present at the temperature of cellulose pyrolysis. Since several workers^{1,8-12} have shown that the activity may be related to the thermal reactions of the retardants, a study of the decomposition reactions of IIa–c by pyrolysis–gas chromatography and –mass spectrometry was undertaken.

EXPERIMENTAL

Pyrolysis gas chromatography was performed using a CDS 100 Series Solids Pyrolyzer made by Chemical Data Systems and a Perkin-Elmer Model 900 GC equipped with a flame ionization detector and attached to a Leeds Northrup Speedomax recorder. Retention times and quantitative analyses of the eluted material were obtained using an Autolab System I Computing Intergrator made by Spectra-Physics. Initial sample weights and residue weights for quantitative analysis in pyrolysis-GC experiments were obtained using a Cahn Model 4100 Electrobalance. Sealed tube experiments were performed using a Thermolyne A 1500 furnace equipped with a chromel-alumel thermocouple positioned within 1 in. of the sample. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms were obtained using DuPont 951 Thermogravimetric Analyzer and a DuPont DSC Cell Base Module II attached to a DuPont 990 Thermal Analyzer. Thermograms were run in a nitrogen atmosphere with flow rate of 50 mL/min. A heating rate of 20°C/min was used for dynamic heating conditions with a scale sensitivity of 1 mg/in.

Differential scanning calorimetry was performed in hermetically sealed aluminum pans with an empty pan as the reference. All DSC thermograms were obtained while heating at 20°C/min with a nitrogen flow rate of 50 mL/min. A Perkin-Elmer Model 237B grating infrared spectrophotometer was employed for infrared spectra. The reported melting points are uncorrected and were determined with the use of a Thomas Hoover Capillary Melting Point Apparatus.

Unless otherwise noted, all chemicals used were standard reagent grade laboratory supply and were used without further purification. *N*-methylbenzamide was obtained from Eastman Chemical Co. and recrystallized one time from ethyl ether (-20°C) to give a product with m.p. 79.5–81°C. Dimethyl methylphosphonate — $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ — purchased from Aldrich Chemical Co., was distilled one time (b.p. 60°C, 6 mm), and was stored over molecular sieves. *N*-(dimethylphosphonomethyl)acetamide, *N*-(dimethylphosphonomethyl)benzamide, *N*-methyl-*N*-(dimethylphosphonomethyl)acetamide and α -benzamidomethyl phosphonic acid preparation has been previously reported.⁷

N,N-dimethylbenzamide was prepared by addition of 1 eq of benzoyl chloride to dimethylamine (25% in H_2O) which contained 1.1 eq of sodium hydroxide. The temperature was maintained at 20–30°C during the addition. One hour after the addition, the reaction mixture was extracted with chloroform. After drying over molecular sieves, the chloroform was evaporated, and the residue was recrystallized from ethyl ether. The recrystallized product had a melting point of 42.5–44°C (Fischer reagent grade m.p. 42–44°C).

Gas chromatograms (GC) were obtained using four different columns. One was a stainless steel column (0.125 in. \times 6 ft) containing 5% SE30 (Silicone) on 60–80 mesh Chromosorb G (AWDMCS). Also used was a stainless steel column (0.125 in. \times 6 ft) containing 8% diethylene glycol succinate (DEGS) on 80–100 mesh Chromosorb W (AWDMCS). The third column was copper

(0.125 in. \times 4.5 ft) containing Porapak type Q (80–100 mesh). For separation of dimethyl amine and trimethyl amine it was necessary to use a stainless steel column (0.125 in \times 6 ft) with 10% K20M on Chromosorb W (AWDMCS, 80–100 mesh). Typical conditions for chromatograms were as follows:

Injector	150–170°C (indicated)
Manifold	300°C
Column program	as specified
Carrier flow (helium)	30 mL/min

The injector was maintained at a low temperature to avoid decomposition prior to pyrolysis with the CDS 100 Solids Pyrolyzer. The actual temperature of the injector was checked using a chromel–alumel thermocouple. For an indicated temperature of 168°C, the actual temperature at the front of the injection port was 162°C. Five inches from the front of the injector (position of sample placement with the pyroprobe), the actual temperature was 135°C.

The heating element of the pyrolysis probe was calibrated with temperature-indicating paper to determine the position of maximum temperature and temperature-indicating crayons from Telatemp Corp., Fullerton, CA, to calibrate the probe.

Pyrolysis–GC experiments were performed by placing a known amount of the designated compound (approximately 1 mg) between two pieces of quartz wool in a quartz tube (25 mm \times 2 mm). The sample was always positioned at this predetermined location of maximum temperature attained by the heating element. Then the probe was allowed to remain in the injection port for 2 min prior to pyrolysis. A pyrolysis time of 5 s at the specified temperature was found to give best resolution of the eluted products. After the GC program was complete, the quartz tube was placed in a vial and flushed with argon. The quartz tube was removed from the vial after cooling at least 1 h and weighed on an electrobalance to obtain the residue weight.

For quantitative analysis of the volatile pyrolysis products of compound Ib, the integrating computer was calibrated by injecting a THF solution containing known amounts of each compound produced in the pyrolysis. Since *N,N*-dimethylbenzamide and *N*-methylbenzamide could not be separated with reasonable program conditions on the SE30 column, the DEGS column was used to obtain the correction factor of each amide relative to methyl benzoate. Then the ratio of $\Phi\text{C}(\text{O})\text{NMe}_2$ to $\Phi\text{C}(\text{O})\text{HNMe}$ produced in the pyrolysis was obtained on the DEGS column. These ratios and correction factors were used to calculate a correction factor for quantitative analysis of the amide mixture on the SE30 column. A THF solution with different concentrations than the calibration solution was used to check the correction factor of each component for linearity with concentration. The calculated concentrations were within 5% of the actual concentrations.

The gas chromatography–mass spectra (GC–MS) were obtained through the courtesy of Fiber Industries, Inc., Charlotte, NC. The mass spectrometer was a DuPont Instruments Model 21-490 interfaced to a Varian Model 1440

Chromatograph. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Pyrolysis for GC-MS Analysis

N-(Dimethylphosphonomethyl)benzamide

Compound IIb (40 mg) was pyrolyzed on the TGA isothermal at 450°C. The nitrogen flow was set at 30 mL/min and the scale sensitivity was 5 mg/in. The furnace of the TGA was allowed to equilibrate for 5 min at 450°C prior to introducing the sample. Total pyrolysis time was 2.5 min with 1.5 min required to reach 450°C. A trap connected to the TGA apparatus was maintained at liquid nitrogen temperatures to collect the volatiles. After the apparatus cooled below 100°C, the Pyrex envelope of the TGA was rinsed with THF (approximately 2 mL). This same THF was used to rinse the trap. GC-MS was performed using either a SE30 column or a Poropak column for separation of the components.

N-(Dimethylphosphonomethyl)acetamide

To avoid moisture gain, which is unavoidable in charging the TGA apparatus, compound IIa (49.4 mg) was sealed in a Pyrex tube under 2 mm vacuum. The sample was heated for 75 s at 400°C in the Thermolyne Furnace. After cooling to room temperature followed by cooling in dry ice/isopropyl alcohol, the tube was opened and the contents rinsed with approximately 2 mL of DMF. The GC-MS analysis was performed with the Poropak column used to separate the components.

Thermal Reactions of *N*-Methylbenzamide and Dimethyl Methylphosphonate

For the experiment, a 1.29 molar phosphonate/amide mixture was prepared and stored in a vial sealed with a septum. Using a syringe, a portion of the mixture was transferred to a tared Pyrex tube. After weighing, the tube was evacuated and was sealed at 2 mm Hg. Phenylphosphonic acid (7.4 mg/100 mg of amide-phosphonate mixture) was added to several of the tubes. The sealed tubes were heated for 5 min in the Thermolyne furnace which had been preheated to $307 \pm 3^\circ\text{C}$. The tubes were cooled in a dry ice/isopropyl alcohol slurry prior to opening. Then the tubes were rinsed with approximately 500 mg of THF. The THF solution was added to a vial containing a known amount of dimethylformamide (DMF). The GC was used to identify the components soluble in THF using DMF as the internal standard.

Thermal Reactions of *N,N*-Dimethylbenzamide and Dimethyl Methylphosphonate

A 1.33 molar ratio solution of ΦCONMe_2 and dimethyl methylphosphonate was used, and tubes were charged and sealed as previously described. Ethanol (22.5 mg) was added to one of the tubes containing the amide-

phosphonate mixture. Samples were heated for 5 min in the furnace which had been preheated to 310°C. Sample treatment for analysis was as described above.

A THF-insoluble residue was produced in the reaction of $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ and $\text{P}(\text{O})(\text{NMe}_2)_3$. Therefore, longer heating times were used to increase the quantity of residue in order to simplify analysis. In a sealed tube, 150 mg of *N,N*-dimethylbenzamide and 75 mg of dimethyl methylphosphonate were heated at 310°C for 15 min. During the heating period the mixture separated into two layers. The top layer was decanted and GC analysis on SE30 showed the major components to be *N,N*-dimethylbenzamide (65%) and methyl benzoate (34%). A small amount of dimethyl methylphosphonate (21%) was also present along with a more volatile component (>1%). This mixture had a definite odor of an amine. A K20M column which would separate methanol, dimethylamine, and trimethylamine was used to show that the unknown was a mixture of dimethylamine and trimethylamine. It was necessary to inject the dimethylamine and trimethylamine with the column at room temperature to affect separation.

The residue remaining after decanting the top layer was removed from the tube by rinsing with methanol. The methanol was evaporated, and the residue was rinsed with acetone several times to remove unreacted starting material and methyl benzoate. An IR spectrum of the oil was performed on NaCl plates.

RESULTS AND DISCUSSION

The acetamide derivatives, IIa and IIc, were found to be hygroscopic and hydrolytically unstable at room temperature. Therefore, they required special handling to prevent inordinate amounts of hydrolysis. Because the benzamide, Ib, was less prone to such complication it was selected for the initial studies. As shown in Figure 1, pyrolysis of IIb for 5 s at 420°C resulted in a chromatogram containing numerous volatile degradation products. A decrease in pyrolysis temperature gave fewer products while an increase in pyrolysis temperature only changed the relative yield of the products and not their number. Therefore, initial product identification was made by analyzing the possible products for retention time under these program conditions. Methanol, dimethyl phosphite, benzaldehyde, benzonitrile, methyl benzoate, benzoic acid, and *N*-methylbenzamide were found to have identical retention times to the products of IIb decomposition as shown in Figure 1. Methanol was also confirmed by analysis on a porapak column which retains methanol for 70 s at 130°C.

For further confirmation and identification, the products were trapped following isothermal decomposition in the thermogravimetric analysis (TGA) apparatus at 450°C. THF was used to rinse the cold trap and the TGA apparatus. This solution was shown by GC-MS¹³ to contain each of the products of Figure 1, except dimethyl phosphite and those responsible for peaks 3 and 8. These three minor products were probably not produced on the TGA due to the slow heating rate (1.5 min to 450°C) while the CDS 200 Solids Pyrolyzer heats the sample rapidly (600°C in 0.6 s). Also, the

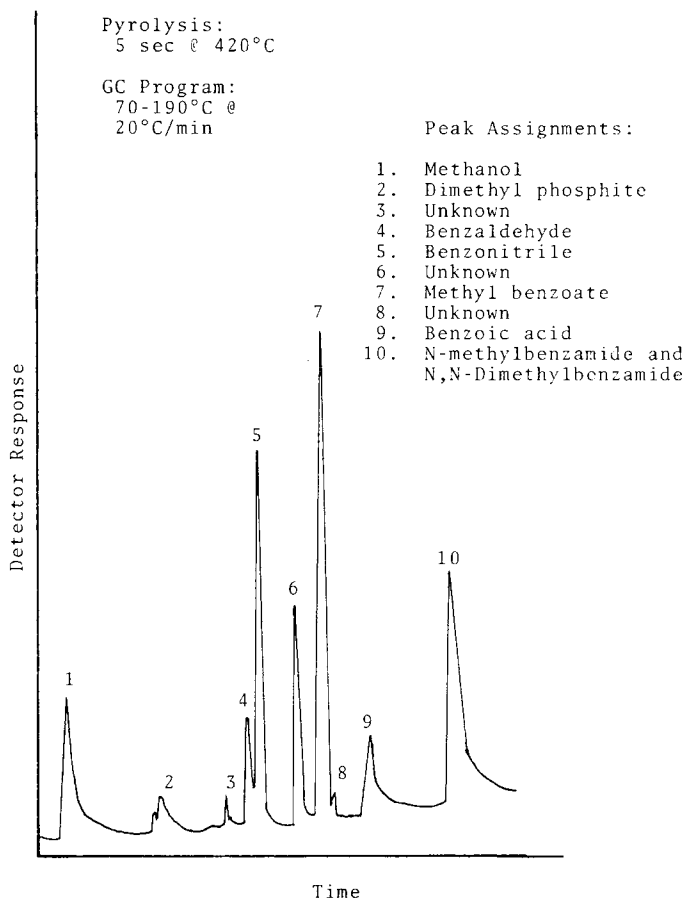


Fig. 1. Chromatogram of the Decomposition Products of *N*-(Dimethylphosphonomethyl)benzamide on a SE30 Column.

compound responsible for peak 6 was present in too low a concentration to be detected by the GC-MS equipment.

The *N,N*-dimethylbenzamide was not known to be a product of the decomposition until after the GC-MS studies. The SE30 column used in the GC-MS analysis had a higher SE30 loading than the column used to obtain the chromatogram shown in Figure 1. Therefore, *N*-methylbenzamide and *N,N*-dimethylbenzamide were separated on the column for the GC-MS. *N,N*-dimethylbenzamide and dimethyl phosphite were confirmed by GC analysis using a DEGS column (Fig. 2).

To verify that all volatile products were detected, a mass balance was obtained at 420, 470, and 520°C as shown in Table I. In addition to the results shown in Table I, pyrolysis at 375°C resulted in less than 2% weight loss and methanol was the major volatile product (78%). The other products were benzonitrile (3%), methyl benzoate (15%), benzoic acid (3%), and *N*-methylbenzamide plus *N,N*-dimethylbenzamide. These results suggest that the benzonitrile, methyl benzoate, benzoic acid, and *N*-substituted

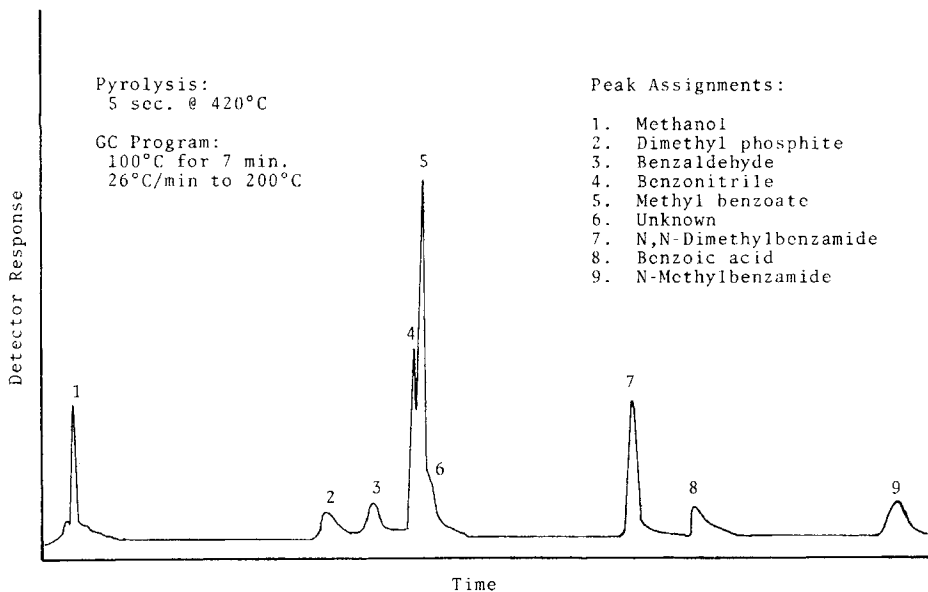


Fig. 2. Chromatogram of *N*-(Dimethylphosphonomethyl)benzamide Decomposition Products on a DEGS Column.

TABLE I
Mass Balance for the Thermal Decomposition of *N*-dimethylphosphonomethyl Benzamide Using the CDS 100 Solids Pyrolyzer^{a,b}

Product	420°C	470°C	520°C
Methanol	4.3 ± 0.1	6.2 ± 0.2 ^c	8.7 ± 0.6 ^c
Dimethyl phosphite	1.1 ± 0.1	1.0 ± 0.2	1.0 ± 0.2
Benzaldehyde	0.8 ± 0.1	1.0 ± 0.1	1.2 ± 0.1
Benzonitrile	3.2 ± 0.1	4.9 ± 0.2	7.3 ± 0.2
Unknown ^d	1.4 ± 0.1	2.3 ± 0.1	2.8 ± 0.2
Methyl benzoate	5.7 ± 0.1	5.8 ± 0.4	4.8 ± 0.4
Benzoic acid	1.6 ± 0.1	1.9 ± 0.1	2.3 ± 0.2
<i>N</i> -methylbenzamide	1.1 ± 0.1	1.7 ± 0.3	2.1 ± 0.2
<i>N,N</i> -dimethylbenzamide	3.5 ± 0.1	3.9 ± 0.3	4.2 ± 0.2
Total Volatiles	22.7	28.7	34.4
Weight loss ^e	27 ± 1.5	34 ± 2	41 ± 2

^a Average of at least three samples.

^b Values are in weight percent.

^c Represents approximately 80% methanol.

^d Calculations for peak 6 of Figure 1 were made using the correction factor of methyl benzoate.

^e Approximately 2% weight loss occurred for samples in the injector of the GC for a complete GC program without pyrolysis.

amide formation were the major competing reactions at elevated temperatures. The change in ratio with temperature suggest that methyl benzoate formation predominated at low temperature and the reaction which produced benzonitrile became more important at higher temperatures. The benzoic acid and substituted amide reaction increased with temperature but not as rapidly as did the benzonitrile formation. The methanol increased with temperature at about the same rate as benzonitrile on a weight percent basis. However, the mole percentage of methanol increased much faster than the benzonitrile. This increase in methanol may be due to an increase in the hydrolysis which occurs at 205°C, and the resultant-acid catalyst could cause a change in the ratio of products.

As expected, the identification of the decomposition products from IIb greatly simplified the separation and identification of the products for the two acetamide derivatives (IIa and IIc). As shown in Figure 3, compound IIa gave the predicted volatile products. Each of the identified products was

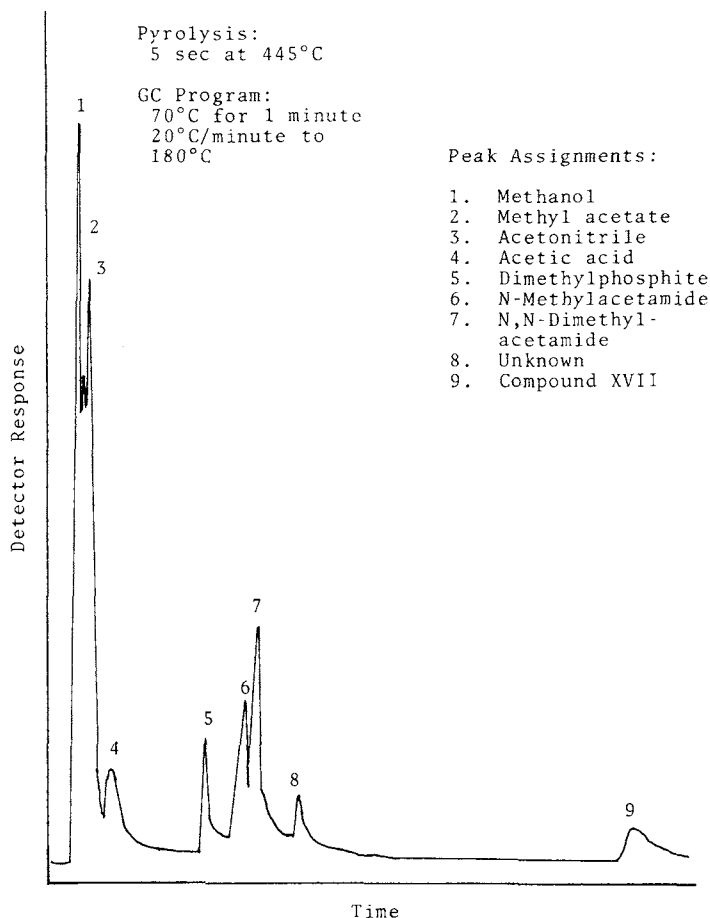


Fig. 3. Chromatogram of N-(Dimethylphosphonomethyl)acetamide Decomposition Products on a DE30 Column.

also verified by retention time on a DEGS column. Similar analysis of *N*-methyl-*N*-(dimethylphosphonomethyl)acetamide gave the same decomposition products as compound IIa.

For confirmation of the identity of the decomposition products, the acetamide IIa was decomposed on a larger scale. The products were verified by decomposition in a sealed tube at 400°C followed by GC-MS analysis of the products in DMF.

Thus, there appeared to be four competing reactions occurring at elevated temperatures: methyl ester formation, nitrile formation, formation of *N*-methyl amides, and carboxylic acid formation. Although an unambiguous mechanistic study of the production of these compounds is beyond the scope of this work, some additional experiments were performed to help understand the role of phosphonomethyl amides in flame retardation of cellulose.

Methyl Ester Formation and *N*-Substituted Amide Formation

Since the hydrolysis reaction could not be eliminated under the conditions of these experiments, methanol and acid were always produced. The methyl ester formation could therefore occur by acid catalyzed alcoholysis of the amide. On the other hand, at the temperatures of the decomposition, an ester exchange reaction could take place between the amide and the phosphonate to produce the ester (RCO_2CH_3) and also lead to P—N bond formation.

To investigate these two possible pathways for RCOOCH_3 formation, model systems of *N*-methylbenzamide or *N,N*-dimethylbenzamide and dimethyl methylphosphonate were chosen for study to avoid the competing reactions which occur with the phosphonomethyl amide decomposition. To prevent such loss by vaporization, it was necessary to utilize sealed pyrex tubes. A dimethyl methylphosphonate/*N*-methylbenzamide mixture (1.33 molar ratio solution) was heated at $307 \pm 3^\circ\text{C}$ for 5 min and the contents of the tube analyzed on a DEGS GC column. A THF solution of the reaction mixture contained mostly unreacted dimethyl methylphosphonate and *N*-methylbenzamide along with the quantities of methyl benzoate and *N,N*-dimethylbenzamide shown in Table II. Also, the increase in methyl benzoate and *N,N*-dimethylbenzamide with the addition of phenylphosphonic acid meant that both reactions are acid-catalyzed.

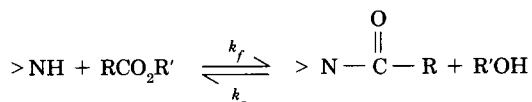
Since the use of *N*-methylbenzamide did not avoid the competing reactions of ester formation and *N*-methylation of the amide, *N,N*-dimethylbenzamide and dimethyl methylphosphonate were used for further study of the methyl benzoate formation. The results of heating a dimethyl methylphosphonate/*N,N*-dimethylbenzamide mixture for 5 min at 310°C are shown in Table II. There is a significant increase in methyl benzoate formation with *N,N*-dimethylbenzamide as compared to *N*-methylbenzamide. Considering the data of Fersht,¹⁴ the *N*-dimethylbenzamide would be expected to react faster than *N,N*-dimethylbenzamide. Fersht used data from the ester aminolysis, the free energies of hydrolysis of amides, and the free energies for ester hydrolysis to calculate a rate constant for alcoholysis of amides based on the microscopic reversibility of the following equilibrium:

TABLE II
 Products of Dimethyl Methylphosphonate-Amide Reactions^a

Reactant	Methyl benzoate	N,N-Dimethyl-benzamide	Ethyl Benzoate
Dimethyl methylphosphonate/ <i>N</i> -methylbenzamide	1.0 ± 0.1	0.3 ± 0.1	
Dimethyl methylphosphonate/ <i>N</i> -methylbenzamide plus 6.4 mg phenylphosphonic acid	2.9 ± 9.1	1.0 ± 0.1	
Dimethyl methylphosphonate/ <i>N,N</i> -dimethylbenzamide	10.5 ± 0.5		
Dimethyl methylphosphonate/ <i>N,N</i> -dimethylbenzamide plus 22.5 mg ethanol ^b	12.0		2.4

^a Yields are in mg/100 mg of phosphonate/amide mixture.

^b Results are for only one experiment. All other results are for at least two experiments.



where $k_f = K_e k_r$, and K_e is the equilibrium constant. Based on his calculations for *N*-ethylacetamide and *N,N*-dimethylacetamide, Fersht predicted that an *N*-alkyl amide would react four times faster than an *N,N*-disubstituted amide. Therefore, if the methyl benzoate were formed by reaction of methanol with the benzamide derivatives, *N*-methylbenzamide should produce methyl benzoate more readily than the *N,N*-dimethylbenzamide.

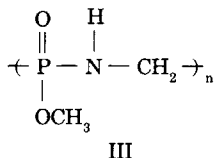
Methanol was not detected in the amide-phosphonate sealed tube reactions. However, after dimethyl methylphosphonate was heated for 5 min at 310°C, less than 1% methanol was detected by GC analysis. Since methanol was obviously present during the methyl benzoate formation, more studies were conducted to determine the role of the free alcohol in the alcoholysis of the amides.

The possibility of alcoholysis of the amide at elevated temperatures was ruled out by heating *N,N*-dimethylbenzamide and methanol at 310°C for 5 min; and GC analysis of the reaction mixture using the DEGS column showed no detectable quantities of methyl benzoate.

If the free-alcohol participated in the reaction, addition of an alcohol other than methanol should produce a different ester other than methanol benzoate. However, addition of ethanol to the *N,N*-dimethylbenzamide/dimethyl methylphosphonate mixture gave much less ethyl benzoate than methyl benzoate, as shown in Table II.

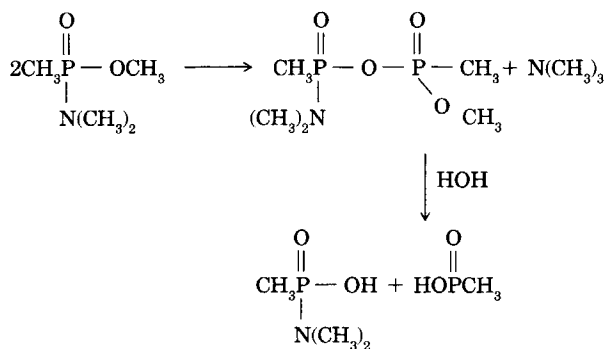
The formation of methyl benzoate from the benzamide Ib would be intermolecular. Therefore, oligomeric compounds similar to structure III would

be formed and would result in retention of phosphorus in the residue. An intermolecular reaction scheme with the amide is consistent with the results from the decomposition of α -cayloxyphosphonates. The α -cayloxyphosphonates were also postulated to form esters (RCOOR'') by an intermolecular pathway.¹⁵



To gain further support for P—N bond formation, attempts were made to isolate the phosphorus product of the reaction of *N,N*-dimethylbenzamide and dimethyl methylphosphonate. When heated for 15 min at 310°C, this reaction mixture separated into two layers. The top layer was shown by GC analysis to contain *N,N*-dimethylbenzamide (65%), methyl benzoate (34%), dimethyl methylphosphonate (1%), and less than 1% of trimethyl amine and dimethyl amine. The residue was incompletely identified, but an IR spectrum indicated the presence of P—OH (2275 cm⁻¹) and P—CH₃ (1420 and 1300 cm⁻¹). The IR spectrum of a dialkyl methyl phosphonate should have P—CH₃ absorptions at 900, 1300, and 1420 cm⁻¹.¹⁶ The absence of the absorption at 900 cm⁻¹ is considered evidence that the compound has P—N bonds as well as the P—CH₃ group.¹³

The trimethyl amine and the P—OH groups could be formed by the following reaction scheme:



This reaction scheme was proposed by Setterquist¹⁷ to account for tertiary amine formation in the pyrolysis of dimethyl *N*-alkylphosphoramidates. Setterquist also did not identify the phosphorus-containing product.

Nitrile Formation

Since amides are known to produce nitriles¹⁸⁻²¹ at temperatures over 200°C and *N*-methylacetamide was a product of compound IIc decomposition, the possibility exists that compounds IIa and IIb decomposed to give the primary amide which would produce the nitrile, acid, and ammonia on

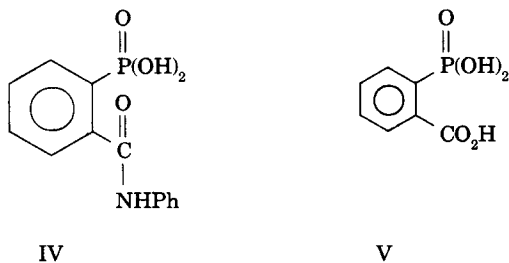
thermal decomposition. To investigate this possibility, IIb containing 10% benzamide was pyrolyzed with the CDS 100 Solids Pyrolyzer at 420°C for 5 s. Compared to pure compound IIb decomposition showed in Figure 1, the nitrile concentration increase 100% and the formation of the other volatile products decreases slightly with the pyrolysis of the 10% mixture. A trace (< 1%) of benzamide was detected under these conditions. Thus, compound IIb decomposition to the amide followed by decomposition of the amide to the nitrile appears to be possible.

Pyrolysis of approximately 1 mg of benzamide at 420°C for 5 s produced 10% as much nitrile as did the 90/10 IIb/benzamide mixture; so the possibility of uncatalyzed thermal decomposition of the amide to produce nitrile during IIb decomposition seems remote. Also note that the mixture of dimethyl methylphosphonate and *N*-methylbenzamide from Table II did not result in the formation of nitriles. Thus, the nitrile formation is formed during the decomposition of these phosphonomethyl amides. Alternately, the decomposition of the amide formed by phosphonomethyl amide decomposition could be a catalyst by some other decomposition product, such as the carboxylic acid or phosphonic acids.

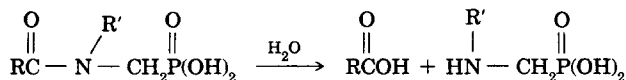
Decomposition of amides to nitriles in the presence of a variety of phosphorus containing compounds is a well-known reaction. Some of the reported agents for formation of nitriles from amides are P_2O_5 ,²² $POCl_3$,²² hexachlorotriphosphazene,²³ PCl_5 ,²⁴ and thionyl chloride.²⁵

Formation of the Carboxylic Acid

The acetic acid and benzoic acid could be produced by hydrolysis of the amide. Kluger and Lam²⁶ proposed that the phosphonic acid of compound IV assists in the hydrolysis of the amide to produce compound V. Therefore, in the presence of water, the α -amidomethylphosphonic acids could similarly give



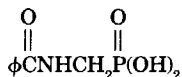
the corresponding acid (RCOOH) and an α -amidomethylphosphonic acid.



Alternately, in the absence of excess water the acids (RCOOH) could be formed by an intermolecular reaction scheme similar to that proposed for

methyl benzoate formation. The intermolecular reaction would lead to P—N bond formation and retention of phosphorus in the residue.

The DSC thermogram of dry α -benzamidomethylphosphonic acid (VI) is as shown in Figure 4. The endotherm at 170°C is attributed to melting and the exotherm at 250°C is most likely due to decomposition. Pyrolysis for 5 s at 420°C using the CDS 100 Solids Pyrolyzer gave benzoic acid as the only volatile product:



VI

CONCLUSION

The results of this investigation support the following conclusions:

1. At temperatures above 300°C, the phosphonomethyl amides decomposed to produce several volatile products. The major products were the ester of the carboxylic acid ($\text{RCO}_2\text{R}''$), the nitrile ($\text{RC}\equiv\text{N}$), the carboxylic acid (RCO_2H), the *N*-methyl amide (RCONHMe), and the *N,N*-dimethyl amide (RCONMe_2).

2. The reaction responsible for the production of the methyl ester (RCOOCH_3) could be intermolecular since *N*-methylbenzamide and *N,N*-dimethylbenzamide reacted with dimethyl methylphosphonate to produce methyl benzoate. Also, the *N*-methylbenzamide and dimethyl methylphosphonate produced *N,N*-dimethylbenzamide which would further react to produce methyl benzoate. This result would suggest that *N,N*-disubstituted amides should react with phosphorus esters more rapidly than mono- or unsubstituted amides and, thus, would be more effective in the P/N synergism.²⁷

3. The *N,N*-dimethylbenzamide/dimethyl methylphosphonate produced methyl benzoate at 310°C faster than the *N*-methylbenzamide/dimethyl

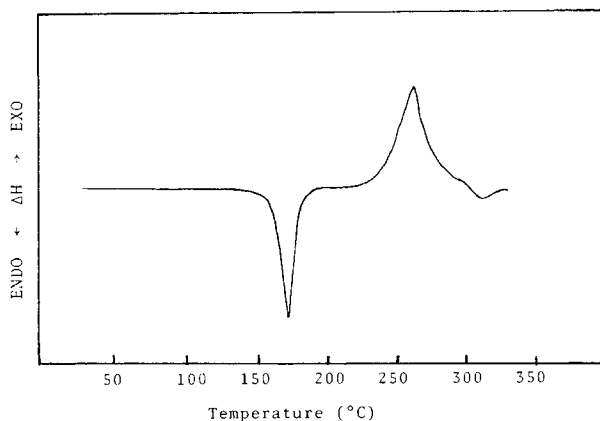


Fig. 4. DSC Thermogram of α -Benzamidomethylphosphonic Acid.

methylphosphonate mixture. If the reaction were an acid-catalyzed alcoholysis of the amide *N*-methylbenzamide should react faster with methanol than *N,N*-dimethylbenzamide.¹⁴ Also, reaction of an alcohol with an amide which is not a favorable reaction since the reaction would produce an amide which is more basic than the alcohol. Therefore, the reaction must be a nucleophilic attack by the amide at the phosphorus which would lead to P—N bond formation.

4. Thermal decomposition of *N*-(dimethylphosphonomethyl) amides resulted in very little vaporization of phosphorus compounds. Therefore, the phosphonomethyl amides probably would not be effective as vapor phase flame retardants.

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