Pyrolysis and Combustion of Cellulose. VIII. Thermally Initiated Reactions of Phosphonomethyl Amide Flame Retardants*

TERRY E. LAWLER,[†,‡] MICHAEL J. DREWS, and ROBERT H. BARKER, *School of Textiles, Clemson University, Clemson, South Carolina 29631*

Synopsis

Several N-(phosphonomethyl) amides have previously been reported to act as particularly effective flame retardants for cellulose. It has also been demonstrated previously that the efficiency of a flame retardant on cellulose frequently parallels its ability to phosphorylate cellulosic hydroxyls at elevated temperatures. This study of the hydrolysis and alcoholysis reactions of N-(phosphonomethyl) amides establishes their unique reactivity. An explanation for this high reactivity is proposed on the basis of intramolecular assistance of the attack of water or alcohols at phosphorus by the carbonyl oxygen of the amide moiety.

INTRODUCTION

Organophosphorus compounds have been widely studied as flame retardants for cellulose. The results from many of these studies indicate that most phosphorus-based retardants act by phosphorylation of cellulose at the primary hydroxyls, thus blocking the formation of levoglucosan and reducing the production of flammable gases by the pyrolyzing cellulose.[1] Of those compounds which are effective in producing these effects, many are found to contain nitrogen in conjunction with the phosphrous. This has led to proposals of synergistic interaction involving the two elements, a subject which has been reviewed by Weil.[2]

Hendrix and co-workers[3-5] have proposed that the enhanced flame retardant efficiency of P/N systems is related to their high efficiency in phosphorylating the cellulose substrate. Further evidence for this proposal was reported by Langley and co-workers,[6-7] who demonstrated that the relative abilities of selected phosphates and phosphoramides to thermally esterify cellulose, and thus alter its degradation, paralleled the flame retardant efficiences of these compounds.

Among the P/N compounds which appear to be of particular interest are the N-(phosphonomethyl)amides (I). Compounds of this type were first pre-

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‡ Present address: Southern Research Institute, 2000 Ninth Avenue, South, Birmingham, AL 35255.

pared in 1942 to be used in the synthesis of an α-aminophosphoric acid (II):

$$R—CO—NH—CH_2—PO(OR')_2 \rightarrow H_2N—CH_2—PO(OH)_2$$

$$\quad\quad\quad I \quad\quad\quad\quad\quad\quad II$$
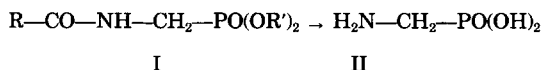
Since that time, flame retardant effects for materials having structure I have been demonstrated in a wide variety of polymers.[8-16]

One member of the series, N-(dimethylphosphonomethyl)acrylamide (IIIa) has been evaluated extensively because of its potential for copolymerization

$$\overset{\displaystyle R}{\underset{\displaystyle III}{CH_2 = \overset{|}{C} — CO — NHCH_2PO(OCH_3)_2}}$$
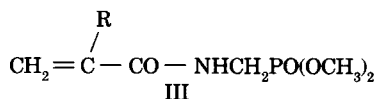
(a) R = H
(b) R = CH_3

with vinyl monomers or for grafting onto cellulose, polyester, and other important commercial polymers.[9] Initial results in cellulose and cellulose blends indicated high efficiencies in grafting and flame-retardant processes. Because of these findings, and because theory would predict that these compounds should readily phosphorylate cellulose, the present study was undertaken to better characterize the thermal reactions of the phosphonomethyl amide–cellulose system.

EXPERIMENTAL

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms were performed using a DuPont 951 Thermogravimetric Analyzer and a DuPont DSC Cell Base Module II attached to a DuPont 990 Thermal Analyzer. A Perkin-Elmer Model R12B 60 MHz NMR Spectrometer was used to obtain proton magnetic resonance spectra. A Perkin-Elmer Model 237B grating infrared spectrophotometer was employed for infrared spectra. The reported melting points are uncorrected and determined with the use of a Thomas Hoover Capillary Melting Point Apparatus. Gas chromatorgray (GC) was carried out using a Perkin-Elmer Model 900 GC equipped with a flame ionization detector and attached to a Leed Northrup Speedomax recorder. Retention times and quantitative analyses of the eluted material were obtained using a Spectra Physics Autolab System I Computer Integrator.

Preparation and Purification of Chemicals

Unless otherwise noted, all chemicals used were reagent grade and were used without further purification. Trimethyl phosphite (practical grade) obtained from Aldrich Chemical Co. was fractionally distilled once before use (bp 110–111°C). N-methylbenzamide was obtained from Eastman Chemical Co. and recrystallized one time from ethyl ether (−20°C) to give a

product with mp 79.5–81°C. Phenyl phosphonic acid was obtained from Stanford Research Institute, Stanford, CA, mp 162.5–164°C.

N,N-Dimethylbenzamide

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 20–50°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 recrystallized. The product had a melting point of 42.5–44°C.

Dimethyl Phenylphosphonate

Dichlorophenylphosphine (97.5 g, 0.5 mol) was added dropwise to 75 mL (1 mol) of methanol in 200 mL of ethyl ether, which contained 90 mL of pyridine in a nitrogen atmosphere at 10–20°C. After stirring at room temperature for 4 h, the pyridinium hydrochloride was removed by filtration, and the ether evaporated in a flash evaporator. Distillation of the residue gave 52 g of liquid with a boiling point of 89°C at 0.2 mm, lit.[17] 115°C at 0.9 mm.

N-(Dimethylphosphonomethyl)acrylamide (IIIa)

Compound III for DSC thermal analysis was obtained from Hooker Chemicals and Plastics Co. Prior to distillation in a Kugelrohr apparatus, 0.1% hydroquinone was added as stabilizer and the flask evacuated to 0.02 mm Hg at 40°C for 4 h to remove any volatile compounds. Two successive distillations (130°C, 0.05 mm Hg, Kugelrohr) were necessary to obtain pure material.

N-(Dimethylphosphonomethyl)methacrylamide (IIIb)

The compound was prepared by the procedure of Duffy and Golborn.[10] First, N-methylolmethacrylamide was prepared by mixing 8.5 g of methacrylamide with 3.0 g of paraformaldehyde and 0.1 g $NaOCH_3$ in 20 mL of ethylene dichloride. After heating at 45–50°C for 1 h, the solution became clear. Filtration followed by cooling to −5°C overnight gave 4.6 g of needles having mp 50–52°C, lit.[18] 53.5–54°C. This 4.6 g (0.04 mol) of N-methylomethacrylamide was added to 7.5 mL (0.064 mol) of trimethyl phosphite at 100–105°C with continuous methanol removal. After 1 h this temperature, the solution was filtered, and the excess phosphite was removed with a flash evaporator (aspirator vac., 45°C) followed by vacuum at 0.1 mm to yield 7.0 g of crude oil. Distillation of 1.5 g of the crude oil using a Kugelrohr distillation apparatus gave 0.5 g of pure N-(dimethylphosphonomethyl)-methacrylamide, bp 115–120°C at 0.02 mm.

N-(Dimethylphosphonomethyl)acetamide (IV) $CH_3C(O)NHCH_2P(O)(OCH_3)_2$

N-methylolacetamide was prepared by reaction of 5.9 g of acetamide with 8.1 g of 37% formalin at a pH of 8–10 maintained by the addition of a few

drops of 50% potassium carbonate. After 1 h at 50°C and 5 h at 35–40°C, the water was removed by a flash evaporator (40°C, aspirator vac.). Acetone was added to the residue, and the solution was dryed over magnesium chloride, followed by molecular sieve. The drying agent was removed by filtration, and the acetone solution was cooled to −78°C, N-methylolacetamide crystallized, and the acetone was removed by suction filtration. After two such recrystallizations, 5.5 g of N-methylolacetamide was obtained with mp 50–52°C, lit.[19] 50–52°C. N-methylolacetamide is deliquescent and was stored in a dessicator over P_2O_5.

To 15 mL (0.13 mol) of trimethyl phosphite heated to 100–105°C was added 5.3 g (0.06 mol) of N-methylolacetamide over a 15-min period. A flask containing dry N-methylolacetamide was connected to the reaction flask by rubber tubing to allow the addition to be carried out without exposure to moisture. Methanol was removed by distillation during the addition. After 1.5 h at 105°C, the solution was cooled, and excess $(CH_3O)_3P$ was removed with a flash evaporator. After further stripping *in vacuo* (0.02 mm), 9 g of a crude oil remained. The acetamide was removed from 4.5 g of the crude oil by sublimation (40–50°C, 0.25 mm). The oil remaining (3 g) after sublimation was dissolved in tetrahydrofuran (THF) and dried over molecular sieve. The THF solution was decanted off the drying agent, and anhydrous ether was added until cloudiness developed. The resulting material was warmed to obtain a clear solution, followed by slow cooling to −20°C. The crystalline product which formed overnight was removed by filtration in a glove bag filled with argon. The deliquescent N-(dimethylphosphono-methyl)acetamide (1.1 g) had a melting point of 53–55°C. The remaining crude oil was purified by the same procedure to give 2.0 g of additional product. Total yield was 3.1 g (29%).

ANAL. Calcd for $C_5H_{12}NO_4P$: C,33.15%; H,6.63%; N,7.73%; P,17.14%. Found: C,32.92%; H,6.56%; N,7.65%; P,17.15%.

N-(Dimethylphonomethyl)benzamide (V) $\phi C(O)NHCH_2P(O)(OCH_3)_2$

To 50 g of 37% formalin at 60°C, pH 8–10, were added 72 g of benzamide. After 2 h, 30 mL of water was added and filtration, followed by cooling to room temperature, gave a quantitative yield of N-methylolbenzamide. One recrystallization from ethylene dichloride gave a produce with an mp 104–106°C, lit.[19] 104–106°C. Six grams (0.04 mol) of N-methylolbenzamide was added to 7.5 g (0.06 mol) of trimethyl phosphite in 20 mL of toluene maintained at 100–105°C. After 2 h at 100–105°C the mixture was filtered and cooled to −5°C to give 7.2 g (75%) of crude product, mp 105–110°C. Two crystallizations from THF gave needles, mp 112.5–113.5°C. The compound can also be effectively recrystallized from acetone to give plates, mp 113–114°C.

ANAL. Calcd for $C_{10}H_{14}NO_4P$: C,49.39%; H,5.80%; N,5.76%; P,12.73%. Found: C,49.56%; H,5.72%; N,5.76%; P,12.56%.

N-Methyl-N-(dimethylphosphonomethyl)acetamide (VI) $CH_3C(O)N(CH_3)CH_2P(O)(OCH_3)_2$

First the acetate of N-methylol-N-methylacetamide was prepared using a modification of the procedure of Walter et al.[20] N-methylacetamide (73

g, 1 mol), 1.67 mol of paraformaldehyde, and 0.3 g of potassium carbonate were combined in a sealed polymerization flask and heated to 120°C for 3 h. After cooling, the mixture was added to 200 mL of acetic anhydride in moisture-free conditions. After heating overnight at 35–40°C. the excess anhydride and the formed acetic acid were removed with a flash evaporator (65°C). The residue was dissolved in carbon tetrachloride and allowed to stand over potassium carbonate for 12 h. After filtration and evaporation of the solvent, the product was vacuum distilled at 0.025 mm pressure. At a boiling range of 65–70°C, 30 g of material were obtained, and NMR indicated it to be 50% of the desired acetate plus 50% N-methylacetamide. At 70–73°C, a 75/25 mixture of the desired acetate and starting amide was collected, lit.[20] 65-80°C, 0.02 mm. This 75/25 mixture [0.046 mol of $CH_3CON(CH_3)CH_2$—$OC(O)CH_3$], 8 mL of the trimethyl phosphite (0.068 mol), and 2 g of acetic acid were heated at 100–105°C in an argon atmosphere. The temperature was then increased to 110°C. Approaching 110°C the reaction mixture began to reflux vigorously. After 2 h at this temperature, the excess phosphite and acetic acid were removed *in vacuo*. The liquid residue was then heated to 50°C at 0.01 mm pressure to remove the N-methylamide. The N-methylacetamide was collected in a trap maintained in ice water. When volatiles ceased to condense in the trap, the residue was distilled to give 6.6 g of product, bp 105–110°C (0.01 mm Kugelrohr). Another distillation at 100–105°C (0.01 mm) gave 5.8 g (64%) of compound VI.

ANAL. Calcd for $C_6H_{14}NO_4P$: C,36.93%; H,7.23%; N,7.18%; P,15.87%. Found: C,36.73%; H,7.16%; N,7.22%; P,15.75%.

RESULTS AND DISCUSSION

Preliminary Thermal Analysis

The DSC thermograms for both the acrylamide IIIa and the corresponding methacrylamide are characterized by three exotherms as shown in Figure 1. The first exotherm at 155°C for the acrylamide is larger than the corresponding exotherm at 195°C for the methacrylamide; and the higher temperature exotherms (250–350°C) are broader than those exhibited by the methylacrylamide.

Since the DSC results indicated that the decomposition of these compounds was complex, and their purification and storage was difficult, it was decided that 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 the N-(dialkylphosphonomethyl) amide structure [—C(O)NHCH$_2$P(O)—(OR)$_2$] should be 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 polymeric form of the amide IIIA.

Initially N-(dimethylphosphonomethyl)acetamide (IV) and N-(dimethyl-phosphonomethyl)benzamide (V) were chosen as models. Compound IV was selected because the methyl attached to the carbonyl should represent the aliphatic polymer backbone, while compound V was selected to investigate the effects of electron density and resonance in the amide structure. Also,
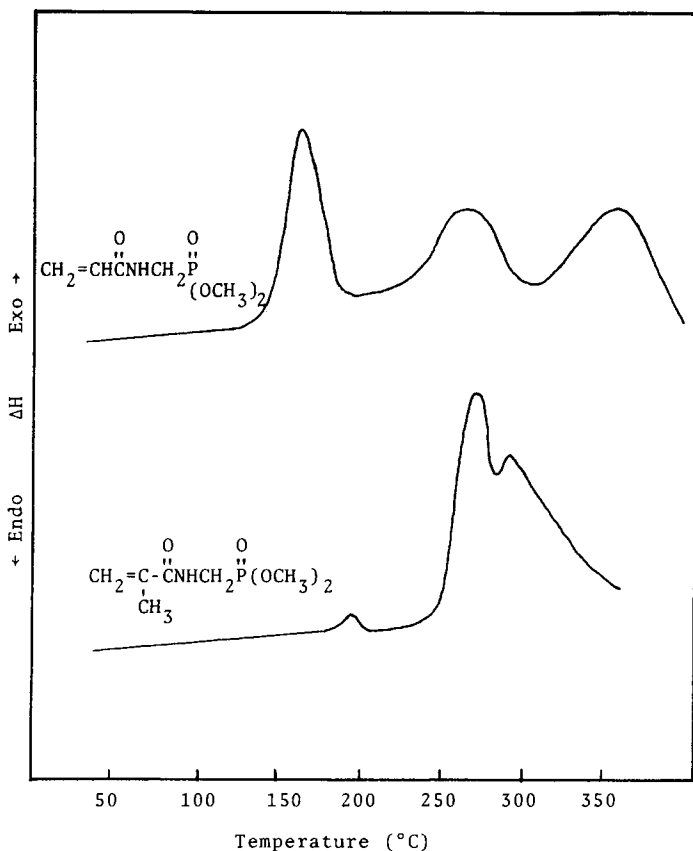
Fig. 1.   DSC thermogram for *N*-(dimethylphosphonomethyl)acrylamide and *N*-(dimethyl-phosphonomethyl) methacrylamide.

it was thought that the products of the amide V decomposition should be less volatile and easier to trap and identify than those from IV.

As shown in Figures 2 and 3, the acetamide, IV, and the benzamide, V, both gave DSC thermograms which were similar to that of the methacrylamide derivative (IIIb). The thermogram of compound IV displaced three exotherms which apexed at 185°C, 290°C, and 325°C, while the thermogram of compound V showed exotherms at 205°C, 300°C, and 340°C. The endotherm in the thermogram of each compound corresponds to its melting point (53–55°C for compound IV and 112.5–113.5°C for compound V). The initiation of weight loss by each compound coincides with the low temperature exotherm. A second weight loss occurs in conjunction with the exotherms between 250°C and 350°C.

Initially, it was noted that the amount of heat released by the acetamide IV during the exothermic reaction at 185°C was not reproducible, and the magnitude of this exotherm affected the higher temperature exotherms. In general, an increase in the exotherm at 185°C caused the thermogram to look very similar to the thermogram for acrylamide IIIa (Fig. 1). Since compound IV was shown to be extremely hygroscopic, the exotherm at 185°C
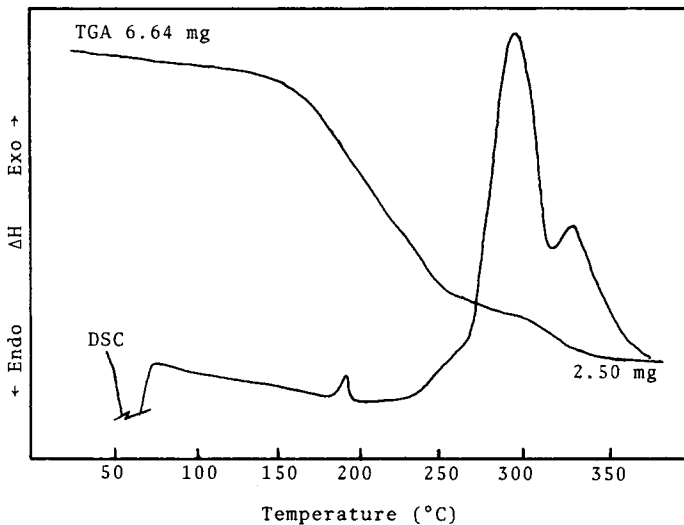
Fig. 2.   TGA and DSC thermograms of *N*-(dimethylphosphonomethyl)acetamide.

was suspected to be hydrolysis, and the lack of reproducibility was attributed to variations in moisture content.

To determine which portion of the molecule was participating in this hydrolysis reaction, water and the acetamide, IV, were heated together in a hermetically sealed DSC pan. The thermogram was terminated after the 185°C exotherm. An IR spectrum of the oily residue was difficult to interpret because the absorption bands were broad and overlapping; nevertheless, the weak absorption at 2200–2300 cm^{-1} for P—OH stretching was easily recognized.
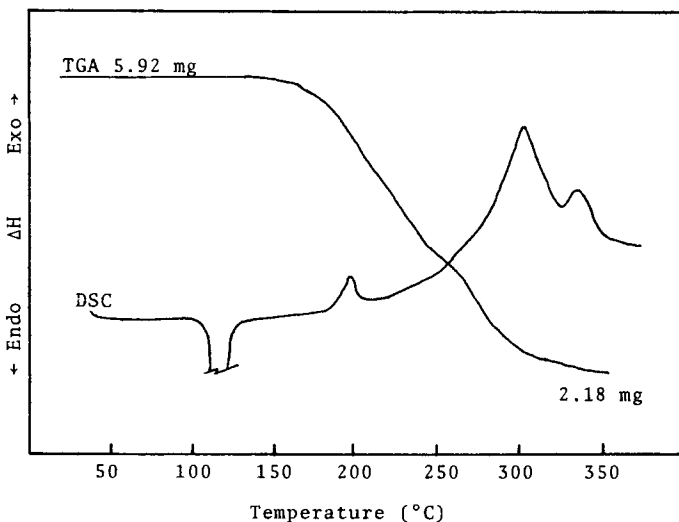
Fig. 3.   TGA and DSC thermograms of *N*-(dimethylphosphonomethyl)benzamide.

Hydrolysis of N-(Dimethylphosphonomethyl) Amide Compounds

Since the DSC experiments demonstrated that hydrolysis of the phosphonate portion of the acetamide had occurred, attempts were made to obtain the products of the hydrolysis on a larger scale. Mixtures of compound IV and water in the ratios shown in Table I were heated to 200°C at 20°C/min and monitored by NMR spectroscopy. The area of the >NH proton signal relative to that of protons of the $CH_3C(O)$— group remained unchanged as the amount of water was increased, indicating that the amide linkage remained intact. However, hydrolysis of the phosphonate ester was evident.

The benzamide, V, showed similar hydrolytic ability. The α-benzamidophosphonic acid VII was isolated in good yield (84%) after hydrolysis in excess

$$\phi CHNCH_2P(OH)_2$$

water with heating in an oil bath at 180°C for 3 min. The identity of VII was established by NMR and IR spectroscopy. Such a high yield of phosphonic acid demonstrated that no significant hydrolysis of the amide linkage occurred at 180°C, confirming the NMR results.

To determine if the hydrolysis was a unique characteristic of the N-(dialkylphosphonomethyl) amide structure, the acetamide, IV, dimethyl phenylphosphonate, and a mixture of dimethyl phenylphosphonate with N-methylbenzamide were each heated to reflux with water for three minutes. The results are shown in Table II. Complete hydrolysis of the acetamide is indicated by the finding that titration of the acetamide/H_2O mixture required as much base as did an equivalent amount of phenylpyhosphonic acid. Also, since neither the dimethyl phenylphosphonate nor the mixture of dimethyl phenylphosphonate with the amide showed any evidence of hydrolysis under conditions that produced complete hydrolysis of compounds IV and V, it would appear that the phosphonomethyl amides do possess unique hydrolytic lability.

This enhanced rate of hydrolysis when the amide is maintained in close proximity to the phosphonate can be explained on the basis of an intra-

TABLE I
Attempted Hydrolysis of N-(Dimethylphosphono)acetamide Using NMR to Measure the Extent of Reaction

Compound IV/H_2O[a] (mg/hg)	Relative peak area[b] for		
	$CH_3/C(O)$—	NH	—$CH_2P(O)(OCH_3)_2$
—	1	0.33	2.67
8.4	1	0.33	1.8
2.8	1	0.33	1.44

[a] Heated to 200°C at 20°C/min.
[b] NMR in DMSO/d6.

TABLE II
Results of Refluxing Phosphonate/H$_2$O Mixtures for 3 min

Compound (mmol)	H$_2$O (mg)	Temperature of oil bath (°C)	Titration with 0.1N base (mL)
Compound IV (0.744)	541.6	160	13.0
Acetic acid (0.744)	—	—	7.5
∅P(O)(OH)$_2$(0.744)	—	—	13.1
∅P(O)(OCH$_3$)$_2$(0.68)	500	180	1 drop
∅P(O)(OCH$_3$)$_2$(0.63) plus			
∅C(O)NHCH$_3$(1.0)	550	180	1 drop

molecular participation of the amide in the hydrolysis. Intramolecular assistance by amides in phosphonate hydrolysis has been proposed previously by Kluger and Chan.[21] They found that compound VIII hydrolyzes much faster than does its para isomer.

VIII
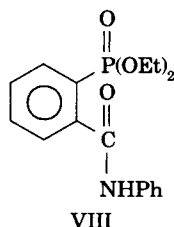
A mechanism similar to that proposed by Kluger and Chan can be written for hydrolysis of N-dialklphosphonomethyl amides (Fig. 4). The nitrogen is a member of the ring in the intermediate for the N-(dialkylphosphono-methyl)amide hydrolysis, while the nitrogen is outside the ring for compound VIII hydrolysis. Direct participation by the oxygen atom of the carbonyl is favored over the nitrogen atom for two reasons. First, the oxygen atom is known to serve as the nucleophile in neutral or acidic solution,[22,23] and basic conditions are necessary to increase the nucleophilicity of the nitrogen atom. Second, direct participation by the nitrogen atom would produce a three-membered ring in the N-(dialkylphosphonomethyl)amide hydrolysis whereas attack by the oxygen atom would lead to a more stable five-membered ring intermediate.

In a protic solvent such as water, the product of step 1 (Fig. 4) could lead to a neutral species if R' = H. This would have the effect of stabilizing the intermediate and hindering the hydrolysis; thus the mechanism of Figure 4 would predict that N-alkyl amides should be more reactive. To test this hypothesis, N-methyl-N-(dimethylphosphonomethyl)acetamide (VI) was prepared and its hydrolytic properties studied. The DSC thermogram for compound VI (Fig. 5) is similar to the thermograms for compounds IV and V. An exotherm occurs at 160°C with two exotherms between 200°C and 350°C.
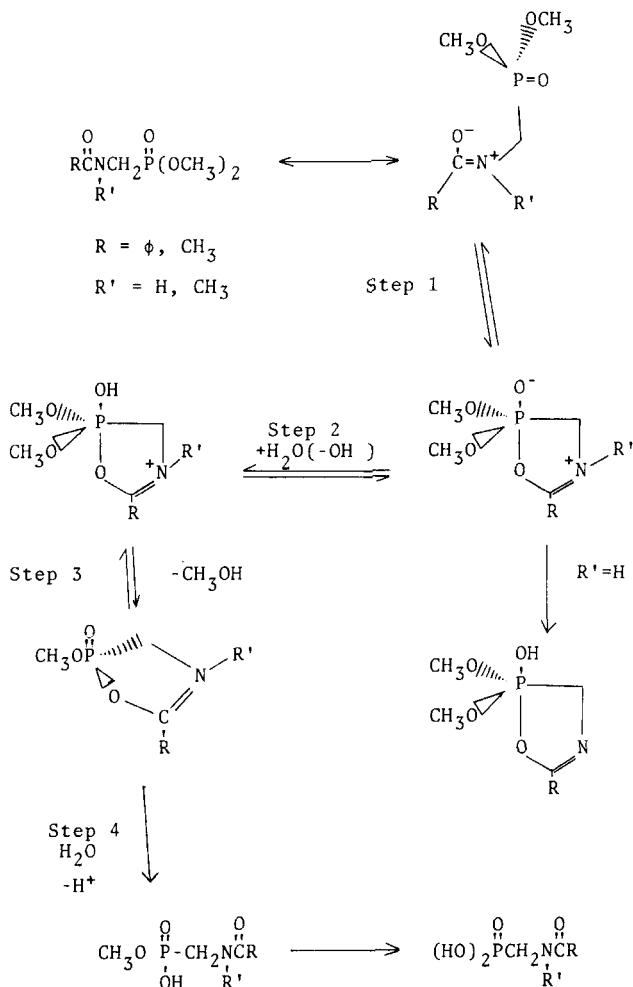
Fig. 4. Scheme for hydrolysis of N-(dimethylphosphonomethyl) amides.

As expected, the magnitude of the exotherm at 160°C varied with the moisture content of the sample.

To confirm that the exothermic reaction at 160°C was due to hydrolysis, the N-methylamide VI was heated with excess water under conditions similar to those used for the acetamide, IV, and the benzamide, V. Titration of the resulting mixture with 0.1N NaOH required 19% more base than would be required to completely neutralize an equivalent amount of phenylphosphonic acid. Also GC analysis showed the presence of methanol and a trace of acetic acid. The production of acetic acid, even in small yield, suggest that the N-methyl derivative VI hydrolyzes faster than the acetamide, IV. The resulting phosphonic acid could then be responsible for the formation of the acetic acid by catalyzing the hydrolysis of the amide.

To confirm that the N-methyl derivative, VI, hydrolyzes faster than IV, equal molar solutions of each in D₂O were monitored for methanol production by NMR. Hydrolysis was considered complete when the integrated
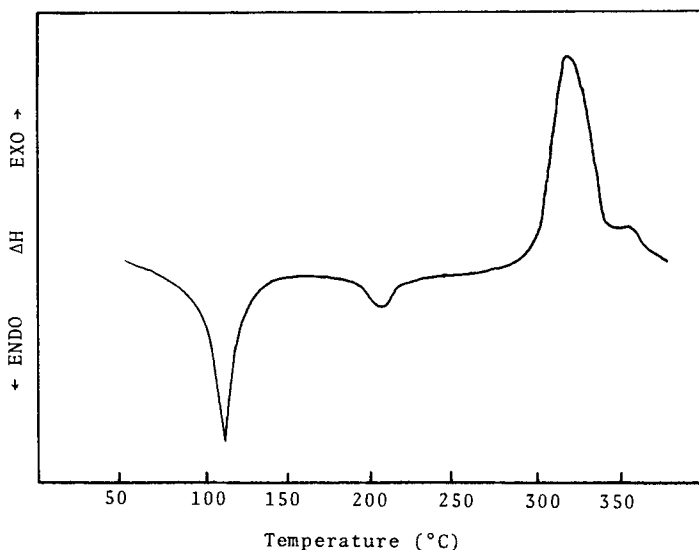
Fig. 5.   DSC thermogram of N-methyl-N-(dimethylphosphonomethyl)acetamide.

area for the methanol protons was twice the area of the $CH_3C(O)$ protons and three times that of the methylene protons (NCH_2P). The D_2O solution of compound VI showed the appearance of methanol almost immediately, and hydrolysis was complete in less than 1 h, as shown in Table III. In contrast, methanol was first noted in the compound IV solution after 8 h, and 60–72 h were necessary for complete hydrolysis. The corresponding acids were obtained as crystalline products after complete hydrolysis and identified by elemental analysis and IR and NMR spectroscopy.

This rapid hydrolysis of the N-methylacetamide derivative probably reflects both the lability of the cyclic intermediate (step 1, Fig. 4) and its

TABLE III
Results of N-(Dimethylphosphonomethyl)acetamide and N-Methyl-N-(Dimethylphosphonomethyl)acetamide Hydrolysis in D_2O

| Compound	Chemical shift[a]	Number of peaks	Number of protons	Assignment
IV after 60–72 h	−1.20	Doublet ($J_{PCH_2} = 12$ Hz)	2	PCH_2N
	−1.47	Singlet	6	$2CH_3OH$
	−2.77 & −2.79	Two singlets	3	$CH_3C(O)$
VI after 55 min	−1.04 & −1.09	Pair of doublets ($J_{PCH_2} = 12$ Hz)	2	PCH_2N
	−1.50	Singlet	6	$2CH_3OH$
	−1.69 & −1.84	Two singlets	3	N-CH_3
	−2.69 & −2.73	Two singlets	3	$CH_3C(O)$

[a] Chemical shifts are relative to HDO, i.e., chemical shift − chemical shift HDO (ppm) = chemical shift of observed peaks.

faster formation due to the electron donating effect of the *N*-methyl group on the nucleophilicity of the carbonyl oxygen. Such an interpretation would be consistent with the NMR spectra of compounds IV and VI. The methylene protons (NCH_2P) of VI are shifted farther from TMS (δ = 3.90 and 3.83) than are the methylene protons of the acetamide, IV (δ = 3.74). Also in D_2O (Table III) the methylene protons of the phosphonic acid produced from compound VI are separated more from methanol than are those of the acid derivative of compound IV. This difference in chemical shift suggests that the amide linkage of compound VI has more double bond character than the C—N bond of compound IV (structure IX vs. X) which results in a deshielding of the methylene protons. Therefore, the oxygen atom of the compound VI carbonyl has a greater electron density than the oxygen atom of the carbonyl in compound IV. The increased nucleophilicity of the oxygen atom favors step 1 (Fig. 4):

IX   X
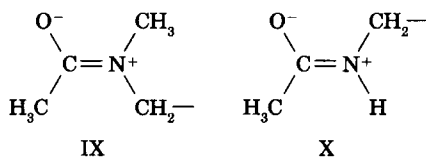
The methylene protons of the benzamide, V, are also shifted more from TMS than are the methylene protons of compound IV; but a comparison of the rates of hydrolysis of the three amide derivatives in a DMSO-d6/D_2O mixture showed the relative rates to be compound VI > compound IV > compound V. If the shift in the methylene protons of compound V were due solely to the double bond character of the C—N bond of the amide, the rates of hydrolysis should have been V > IV. However, the methylene protons of compound V are in a position to be deshielded by the benzene ring in the conformation of structure XI:

XI
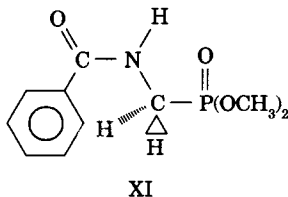
Using the Johnson–Bovey tabulation of chemical shift increments for protons in close proximity to a benzene ring,[24] the maximum deshielding with the benzene ring in the plane of the carbonyl would produce a shift of 0.82 ppm away from TMS. If the benzene ring were perpendicular to the plane of the carbonyl, the shift would be 0.05 ppm toward TMS. The observed shift for the methylene protons of the benzamide derivative, V, relative to the acetamide, IV, is 0.20 ppm away from TMS. This shift is less than the maximum (0.82 ppm) because compound V would not be in conformation IX at all times.

Transesterification of N-(dialkylphosphonomethyl) Amides

The finding that the phosphonomethyl amides possess unique hydrolytic lability leads to the prediction of a similar enhancement of alcholysis of the phosphonate group. Since such reactivity is thought to be critical for flame-retardant action in cellulose, an effort was made to confirm this postulate by DSC using a mixture of 1-dodecanol and the benzamide, V. The resulting thermogram (Fig. 6) showed that the hydrolysis exotherm at 205°C was converted by dodecanol to an endotherm, suggesting that exchange with the phosphonate had occurred.

Analysis of the products from V heated with dodecanol at 200°C for 8 min confirmed the formation of methanol. Although the residue was not identified, the methanol distillate leaves little doubt that the reaction is a transesterification, which would be expected to be endothermic.

Conversely, a 1-dodecanol/dimethylphenylphosphonate mixture heated for 10 min at 200°C did not yield any methanol as determined by GC analysis. Similarly, Langley et al.[6] performed a DSC analysis of dodecanol/phosphate mixtures and found no detectable reaction below 225°C.

As with hydrolysis, N-methyl-N-(dimethylphosphonomethyl)acetamide should also react readily with alcohols. This prediction was confirmed by the appearance of methanol, a detected by NMR in an ethanol/DMSO-d6/ compound VI mixture after 2 h. The methanol concentration continued to increase for 8 days, but the exact concentration at equilibrium was not determined. Considering the postulate that the more efficient flame retardants are those which phosphorylate cellulose rapidly,[25] N-methyl-substituted amides similar to compound VI should be more efficient flame retardants for cellulose than the acrylamide IIIa. However, the rapid hydrolysis of these N-methyl derivatives would complicate their preparation and application to the cellulose.

The phosphorylation of alcohols by N-(dialkylphosphonomethyl)amides may explain why Day and co-workers[26] found the acrylamide compound IIIa to be much more effective for the flame retardation of cellulose than
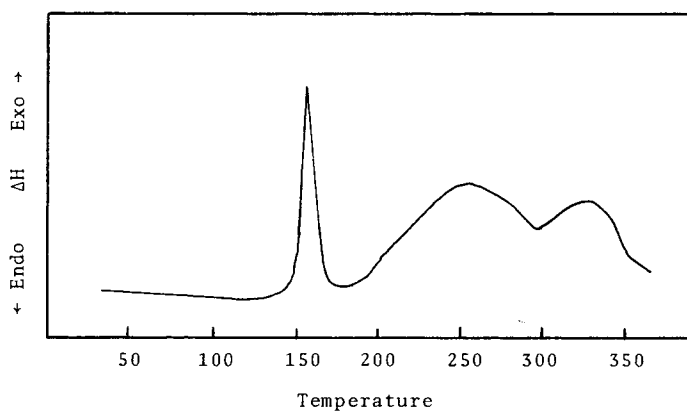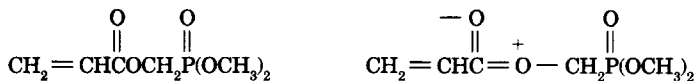

Fig. 6. DSC thermogram of a 1-dodecanol/N-(dimethylphosphonomethyl)benzamide mixture.

was dimethylphosphonomethyl acrylate. The carbonyl oxygen of the acrylate would not be as nucleophilic as the oxygen of the amide, since the following charge separation would not contribute as greatly to the resonance hydrid:

$$CH_2\!=\!CHCOCH_2P(OCH_3)_2 \qquad\qquad CH_2\!=\!CHC\!=\!O-CH_2P(OCH_3)_2$$

Therefore, phosphorylation of the cellulose would be expected to be faster with compound IIIa than with the corresponding acrylate.

An analogous situation may exist with the N-hydroxymethyl β-(diakylphosphono)propionamides. Compound XIIa has been reported to be more efficient in promoting char formation with cellulose than the corresponding ester XIIb or the nitrile XIIc[25]. Since compounds containing P—N bonds are usually more effective on cellulose than P–O–C compounds, the formation of intramolecular P—N bonds was given as the explanation for the increased effectiveness of XIIa. Compound XIIb does not contain nitrogen and the nitrogen of compound XIIc is in a nonnucleophilic form, so that P—N bond formation would not occur with these two compounds:

$$(CH_3O)_2PCH_2CH_2R$$

XII

(a) R = — C(O)NHCH$_2$OH
(b) R = — CO$_2$Me
(c) R = — C≡N
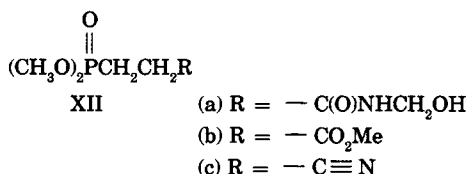
However, compound XIIa has a structure similar to the N-(dimethylphosphonomethyl)amides. Thus, compound XIIa would be expected to phosphorylate the hydroxyls of cellulose by an intramolecularly assisted transesterification, and nucleophilic substitution by the nitrogen atom would not be involved. The nitrogen would be outside the five-membered ring of the intermediate, as with compound VIII of Kluger and Chan, but the mechanism should otherwise be analogous to that shown in Figure 4.

CONCLUSIONS

Since N-(dialkylphosphonomethyl) amides have been used for the flame retardation of cellulosics, the thermal reactions of these compounds have been studied and related to their effectiveness as flame retardants.

The results of this investigation support the following conclusions:

1. N-(dimethylphosphonomethyl)amides hydrolyze much faster than those phosphonates which do not have the amide as a part of the molecular structure. The relative rates of hydrolysis were shown to be N-methyl acetamide VI > acetamide IV > > > benzamide V at 37°C. Thus, precautions should be taken to prevent hydrolysis during preparation and application of these flame retardants.

2. N-(dimethylphosphonomethyl)amides phosphorylate alcohols more readily than phosphonates not having the amide structure. The unique

phosphorylation capabilities provide the basis for explaining the flame-retardant efficiencies of these compounds with cellulose, since increasing the rate of phosphorylation of cellulose hydroxyls has been reported to produce a corresponding increase in the flame-retardant efficiency.

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