Thermal Decomposition and Mass Spectra of the *N*-Phenyl-, *N,N'*-Diphenyl-, and *N,N',N''*-Triphenylphosphoric Triamides

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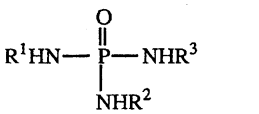
The thermal decomposition and mass spectra of the *N*-phenyl- (**1**), *N,N'*-diphenyl- (**2**), and *N,N',N''*-triphenylphosphoric triamides (**3**) were investigated. DTA-TG/DTG, TG-TRAP-GC/MS measurements, IR spectroscopic analyses, mass spectrometric analyses, HPLC analyses, and a kinetic study were carried out to investigate the thermal decomposition. From the analytical results, it was suggested that **1** decomposed while liberating ammonia and aniline, and condensed in several stages; its thermal products at about 160 °C contained **2**. Compound **2** decomposed and condensed to form some condensed products at about 200 °C; its thermal products also contained **3**. Compound **3** decomposed while liberating aniline to form a cyclic dimer, while the existence of other thermal products was also observed; the cyclic dimer further pyrolyzed in several stages, and **1** and **2** formed a similar condensed product in the 400 to 500 °C temperature range, though that for **3** was different. In addition, the apparent activation energy of the thermal decomposition was estimated and the thermal decomposition process was investigated based on this variation. In the mass spectra using electron impact, **1**, **2**, and **3** were cleaved along with an elimination of ammonia and/or aniline to form a three-coordinate phosphenimidic amide.

Some phosphoramidates with a phosphorus–nitrogen bond are useful for flame proofing and as fire-retardant agents. The present authors have reported on the thermal decomposition of these compounds.[1—5] In this paper, the thermal decompositions of the *N*-phenyl- (**1**), *N,N'*-diphenyl- (**2**), and *N,N',N''*-triphenylphosphoric triamides (**3**) are described (Chart 1).

Kobayashi[6] reported that **1** melted at about 140 °C, and then began to condense with deammoniation; he also showed DTA (differential thermal analysis) and TG (thermogravimetry) curves for **1**, and suggested the conversion of **1** into insoluble condensed phosphates. Compound **2** was observed only as a by-product in a treatment with caustic soda of a product from the reaction of *N*-(phosphorodichloridyl)carbamic acid with aniline,[7] or as the hydrolytic product of (*N,N'*-diphenylphosphorodiamidyl)(phenyl)-sulfur diimide.[8] Although the preparation of **2** has also been described in the literature,[8] nothing has been done regarding the thermal decomposition. Regarding the thermal decomposition of **3**, Michaelis and Silberstein[9] as well as Buck and Lankelma[10] showed the production of a cyclic dimer of *N,N'*-dipenylphosphenimidic amide **4**; Subsequently, Parts et al.[11] suggested that the reaction shown below mainly occurred in the 300 to 420 °C temperature range with a loss of hydrogen in the 450 to 800 °C temperature range (Chart 2). Also, Murray and Woodward[12] identified $PhN[PO(NHPh)_2]_2$ as being a by-product in the thermal decomposition of **3**. Furthermore, **3** was investigated as a fire-retardant additive for polymer materials; also, the fire-retardancy and/or mechanical properties were evaluated for epoxy resin, polyolefin, cellulosic materials, polyester, polyamide, etc.[13—25]



1: R^1=Ph ; R^2,R^3=H
2: R^1,R^2=Ph ; R^3=H
3: R^1,R^2,R^3=Ph

Chart 1.

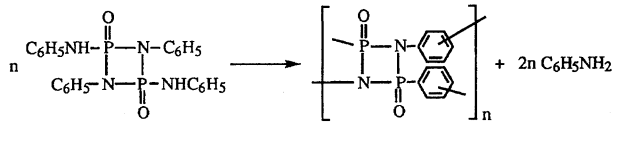


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Chart 2.

On the basis of these previously described results, the present authors attempted to investigate in more detail the process of the thermal decomposition of **1**, **2**, and **3**, which appeared to be a factor affecting the fire retardancy of polymer materials. Simultaneously, the cleavage of **1**, **2**, and **3** by electron impact (EI) was also investigated.

Experimental

Materials. Compounds **1**, **2**, and **3** were prepared according to methods described in the literature.[6,8,26] The physical properties of these compounds are listed in Table 1. In the elemental analysis of **1**, the observed values did not agree with calculated ones because of the existence of a residual ash.

Table 1. Physical Properties of **1**, **2**, and **3**

Compound		**1**	**2**	**3**
Elemental analysis	C (%)	41.33 (42.11)[a]	58.50 (58.30)	66.88 (66.87)
	H (%)	5.92 (5.89)	5.72 (5.71)	5.76 (5.61)
	N (%)	22.50 (24.55)	16.96 (17.00)	13.01 (13.00)
Mp or dp	/°C	139 (dp)	197—198	213—215
IR spectra Wavenumber/cm^{-1}	$\nu_{P=O}$	1140	1140	1220
	ν_{N-H}	3380, 3230	3400, 3230	3360
	$\nu_{C-H\ (Ar.)}$	3100	3100	3040
	$\nu_{C=C\ (Ar.)}$	1600, 1500	1600, 1500	1600, 1500
	$\nu_{C-N\ (Ar.)}$	1295	1280	1280
	$\delta_{C-H\ oop\ (Ar.)}$	740, 685	745, 690	750, 690
High resolution mass spectrum		171.0530 (171.0556)[a]	247.0865 (247.0868)	323.1185 (323.1180)
Composition		$C_6H_{10}N_3OP$	$C_{12}H_{14}N_3OP$	$C_{18}H_{18}N_3OP$

a) Calculated values.

Measurements. TG-DTA measurements were carried out using a Rigaku TG-DTA 8112BH apparatus under a stream of nitrogen at a heating rate of 5 °C min^{-1}; α-Al_2O_3 was used as a reference material. TG-MS (thermogravimetry-mass spectrometry) and TG-TRAP-GC/MS measurements were carried out using a Shimadzu TGA-40 and GC/MS-QP1000 combined system under a stream of helium at a heating rate of 5, 10, of 15 °C min^{-1}. In the TG-MS measurement, decomposition gasses liberated by heating the sample flowed through the line heated at about 280 °C, and were directly detected at a mass spectrometer. In the TG-TRAP-GC/MS measurement, the decomposition gasses were trapped once by cooling with liquid nitrogen from the outside of the line, then vaporized by heating again, separated by means of GC, and detected using a mass spectrometer. The IR spectra were obtained using a JASCO IR-810 spectrophotometer by means of the KBr-disc method. Elemental analyses were carried out using a Yanaco CHN-CORDER-MT-5 apparatus. Mass spectra using the EI method were obtained with a JEOL-JMS-D300 mass spectrometer at an ionization potential of 20 or 70 eV. The ion source was maintained at 220 °C, and the samples were heated directly to 350 °C in the ion source using a direct probe. In measurements for **1**, **2**, and **3**, the samples were dissolved in either methanol or ethanol. In the cases for thermal residues, samples in the solid state were employed. HPLC analyses were carried out using a Shimadzu LC-6AD high-performance liquid chromatograph coupled with a spectrometric detector (SPD-M6A). The columns and conditions employed in the GC and HPLC analyses are explicitly described in the related figures.

Results and Discussion

Thermal Decomposition of 1. The DTA-TG/DTG curves for **1** are shown in Fig. 1. The TG/DTG curves revealed a rapid weight loss in several stages in the temperature range of 130 to 300 °C and from 500 to 650 °C. The weight loss was approximately 50 and 85% at 300 and 700 °C, respectively. The DTA curve exhibited one endothermic peak at about 150 °C and two endothermic peaks at about 165 °C with a weight loss, at which several complex thermal decomposition reactions may have occurred.

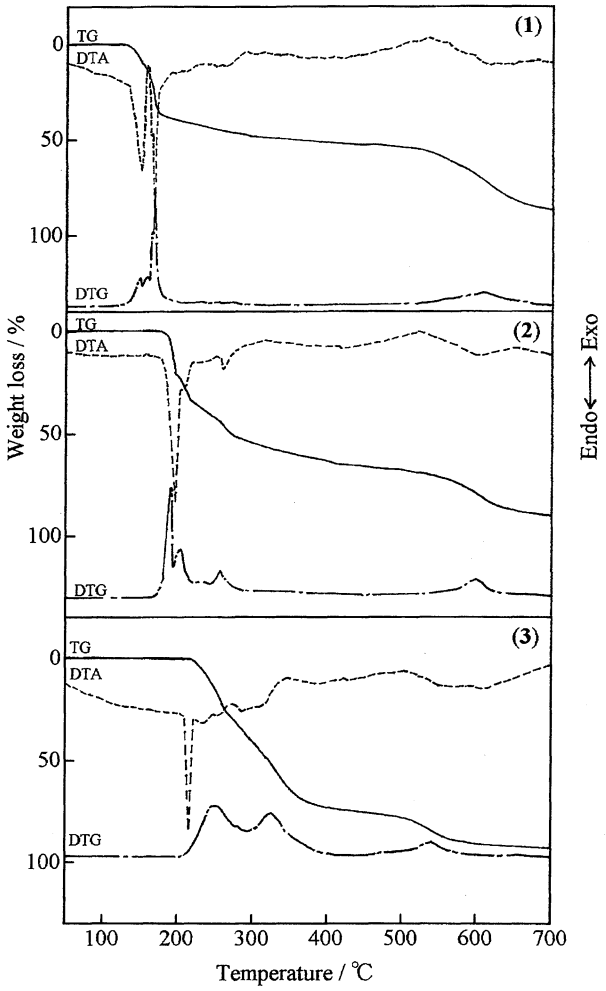


Fig. 1. DTA-TG/DTG curves for **1**, **2**, and **3**. Initial weight: (**1**) 5.47; (**2**) 5.23; (**3**) 6.30 mg. Heating rate: 5 °C min^{-1}. Atmosphere: a stream of N_2.

In order to identify the volatile products for a given weight loss, TG-MS and TG-TRAP-GC/MS measurements were carried out; the results are shown in Fig. 2. In the temperature range of 130 to 400 °C the volatilization of ammonia (M^+: 17) and aniline (M^+: 93) were observed, which made it appear that a condensation reaction by heating occurred, although we could not confirm the volatile products in the 500 to 650 °C range. Here, ion peaks at *m/z* 92, 66, and 65 were due to the fragmentation of aniline, and peaks at *m/z* 44 and 18 observed in the TG-TRAP-GC/MS measurement were due to carbon dioxide and water in the atmosphere, respectively.

Next, in order to investigate the residue from the thermal decomposition, **1** was heated up to various temperatures in the TG-DTA apparatus; then, after arrival at the desired temperature, it was taken out immediately, cooled in air and an IR measurement was carried out. The result is shown in Fig. 3. The temperatures, except for room temperature, shown in Fig. 3 are near to the terminal point of each stage regarding the weight loss shown in the TG/DTG curves; that in cases for **2** and **3** are also similar. The absorption band in the 3400 to 3200 cm^{-1} range at room temperature is assigned to an N–H stretching vibration, at 1140 cm^{-1} to P=O, and the band in the 980 to 900 cm^{-1} range seems to be a P–N stretching vibration, although its assignment is not clear. From the broadening of their bands along with an increase in temperature, the formation of a condensed product and/or the overlapping of several thermal decomposition processes by heating is suggested. Since the broad absorption band in the range of approximately 1000 to 900 cm^{-1} appears to be a P–NH–P or P–O–P vibration, and that at about 1200 cm^{-1} to a P=N–P vibration, it is suggested that the oxygen atom of the phosphoryl group is related to the formation of the P–O–P linkage.[27] Most of the phenyl groups appear to be liberated as aniline before approximately 300 °C, since the absorption bands assigned to the C–H out-of-plane deformation vibration at 740 and 685 cm^{-1} and the C=C stretching vibration at 1600 and 1500 cm^{-1} could not be observed. Accordingly, most of the weight loss of about 50% at 300 °C in the TG curve may be due to the liberation of aniline, which was also estimated from the result of the TG-MS measurement; the weight loss is close to the theoretical value (54%) for the liberation of only aniline. The absorption band at about 1400 cm^{-1} was observed at 300 and 400 °C. This band appears to be the N–H deformation vibration for NH_4^+, and it is presumed that this ammonium ion was formed by the reaction of the P–OH group, which occurred during the hydrolysis of the P–O–P group by humidity contained in either the atmosphere or sample, along with ammonia being liberated during thermal condensation.

In order to identify the thermal decomposition residue during the initial stage in the weight loss, the residue at 160 °C was subjected to mass spectrometry; however, the spectrum was due to aniline and information concerning the structure of the thermal decomposition residue could not be obtained, which appears to be due to a deficiency in the volatility of the residue.

Since the residue at 160 °C could dissolved in water, an HPLC analysis was carried out; the result is shown in Fig. 4. Three major peaks and about five minor ones were observed. The minor peaks at retention times of 37, 50, and 60 minutes were due to an impurity from the column. By using standard materials, it was found that peak 3 at a retention time of 9 min could be assigned to compound **1**, peak 4 at 14 min to aniline, and peak 7 at 30 min to compound **2**. The other minor peaks could not be identified.

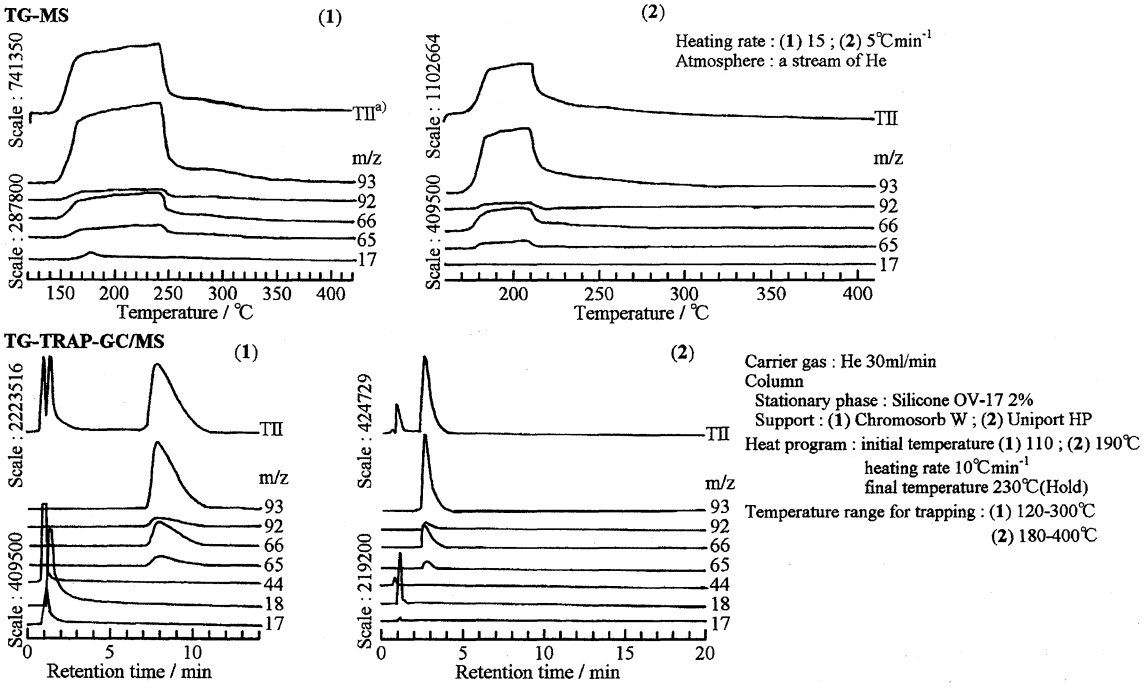


Fig. 2. Mass chromatograms of the liberated gas products by TG-MS and TG-TRAP-GC/MS for **1** and **2**. a) Total ion intensity.

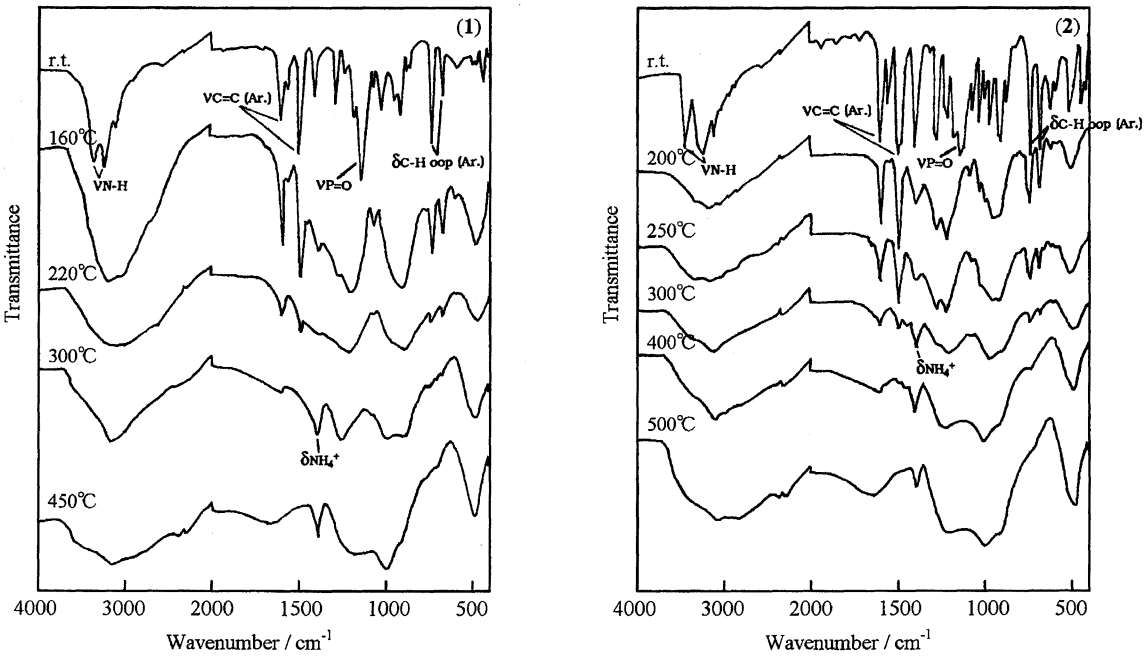


Fig. 3. IR spectra of thermal decomposition residues of **1** and **2**.

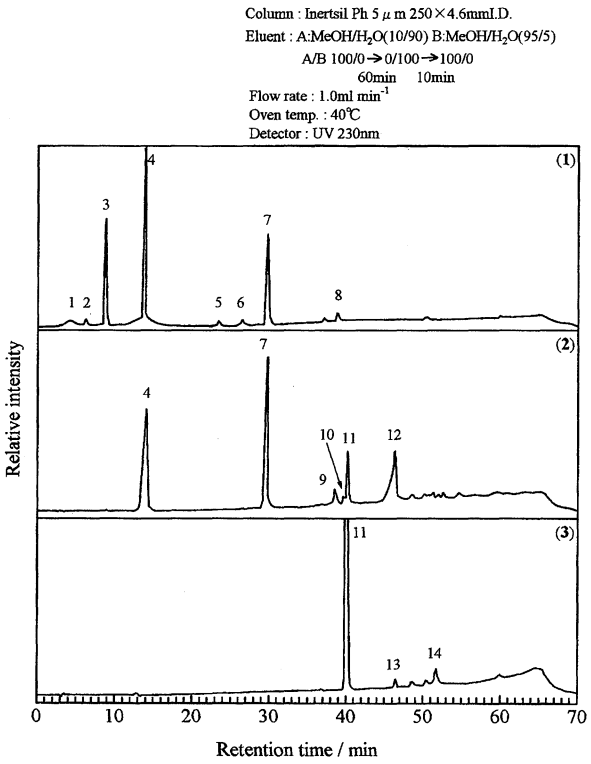


Fig. 4. HPLC profiles of thermal decomposition residues at 160, 200, and 250 °C for **1**, **2**, and **3**, respectively.

From these results, it is suggested that the thermal decomposition of **1** proceeds in a manner similar to phosphoric triamide, $PO(NH_2)_3$, which results in the formation of a product with the composition PNO; a network condensation product is also formed, though an ammonium ion is formed by the action of liberated ammonia. Also, the existence of some decomposition processes is presumed, even at low temperature; the formation of **2** among these decomposed products was observed.

Thermal Decomposition of 2. The DTA-TG/DTG curves for **2** are shown in Fig. 1. The TG/DTG curves revealed a weight loss in several stages in the range of 180 to 400 °C and from 550 to 650 °C. The weight loss was approximately 54 and 90% at 300 and 700 °C, respectively. The DTA curve exhibited one large endothermic peak at about 198 °C; it appears that the peak can be attributed to the melting and decomposition of **2**. Also, two small endothermic peaks at about 215 and 270 °C were observed.

From the TG-MS and TG-TRAP-GC/MS measurements (Fig. 2) in the 140 to 400 °C temperature range, the volatilization of aniline was observed, which appeared to be similar to **1** for the condensation reaction by heating, though ammonia could not be observed in the volatile product; also, we could not confirm the volatile products in the 500 to 650 °C temperature range. Here, the heat condition for the GC/MS measurement was different from that for **1** because the other column was employed.

From the IR measurement (Fig. 3) after heating to various temperatures, a result similar to **1** was obtained, and the formation of a condensed product and/or the overlapping of decomposition processes by heating was suggested. Also, the formation of a residue with a similar structure was presumed for **1** and **2**, because the spectrum at 500 °C for **2** was similar to that at 450 °C for **1**.

The mass spectrum of the residue at 200 °C exhibited a very weak peak at *m/z* 247, assigned to the molecular ion of **2** and peaks assigned to aniline. Other peaks were hardly observed.

Since the residue at 200 °C could be dissolved in methanol, an HPLC analysis was carried out; the result is shown in Fig. 4. As can be seen in Fig. 4, four major and several

minor peaks were observed. It was found that the product of peak 4 was aniline, and that of peak 7 was compound **2**. The product of peak 11 may also be compound **3**, based on the results of the retention time and the UV spectrum. Although an identification of the products of peaks 9, 10, and 12 could not be made, they appear to be condensed products, such as dimers.

From these results, it is suggested that although the thermal decomposition of **2** proceeds similarly to the case of **1** at higher temperatures, different products are formed in the condensed phase at low temperature.

Thermal Decomposition of 3. The DTA-TG/DTG curves for **3** are shown in Fig. 1. The TG/DTG curves revealed a weight loss in several stages in the temperature range of 220 to 400 °C and from 500 to 650 °C. The weight loss was approximately 70 and 85% at 400 and 700 °C, respectively. The DTA curve exhibited one endothermic peak attributed to the melting of **3** at about 215 °C, and two small endothermic peaks at about 220 to 260 °C accompanied by a weight loss. Above 260 °C, the DTA curve showed a complex behavior, together with a complex shape in the DTG curve.

From the TG-MS and TG-TRAP-GC/MS measurements (Fig. 5), aniline was confirmed to be a volatile product in the 220 to 450 °C temperature range, though we could not determine the volatile products in the 500 to 650 °C range.

In an IR measurement (Fig. 6) after heating to various temperatures, sharp absorption peaks were observed until a relatively high temperature (300 °C), as compared with the cases of **1** and **2**. The spectrum at 270 °C, which was the temperature for the initial weight-loss stage, nearly agreed with that of the cyclic dimer of *N*,*N*′-diphenylphosphenimidic amide **4**, as previously reported.[28] The IR spectra at a temperature above 350 °C were broad, and a further condensation and/or ring-opening reaction is suggested. Also, the existence of an ammonium ion, as seen in the cases for **1** and **2**, was not observed.

In the mass spectrum of the residue at 250 °C, a relatively large peak was observed at *m/z* 460; this peak was due to the molecular ion of **4**. Weak peaks observed at *m/z* 367 and 368 seemed to be from the fragment ions of **4**. In addition, although weak peaks were also observed at *m/z* 131

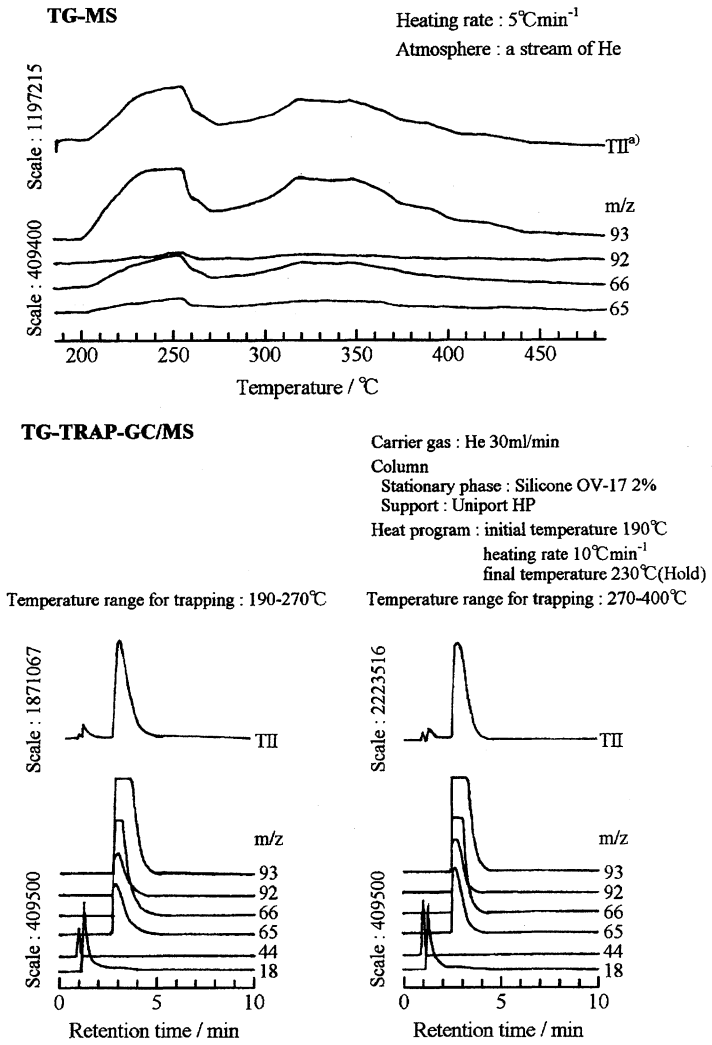


Fig. 5. Mass chromatograms of the liberated gas products by TG-MS and TG-TRAP-GC/MS for **3**. a) Total ion intensity.

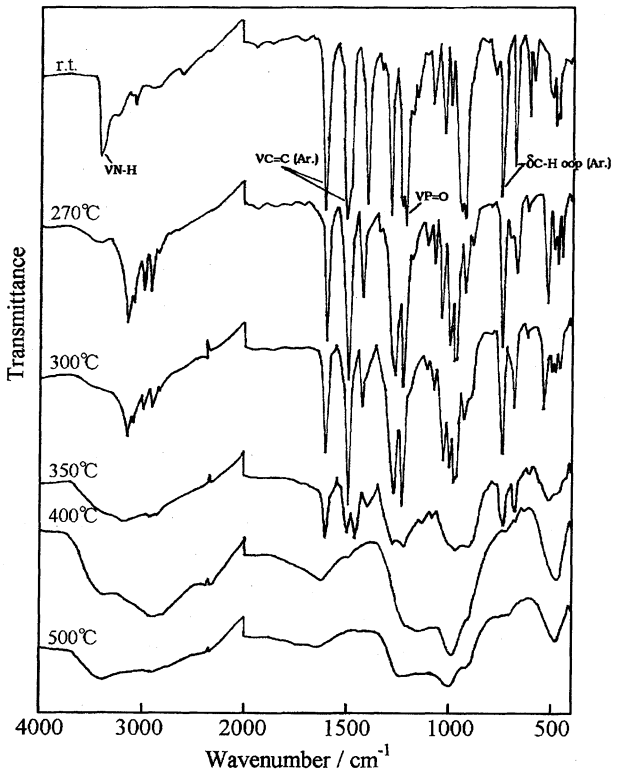


Fig. 6. IR spectra of thermal decomposition residues of **3**.

and 293, assignments could not be made. Furthermore, the decomposition residue was extracted with ethanol and filtered. As a result, the residue on filter paper was identified as **4** from the IR spectrum, elemental analysis, and high-resolution mass spectrum (M^+ Found: m/z 460.1216. Calcd for: M^+, 460.1208). From this result, the formation of **4**, as previously[11] reported, was confirmed during the initial stage of the thermal decomposition of **3**.

Among the thermal-decomposition residues at 250 °C, soluble products in ethanol were analyzed by HPLC; the result is shown in Fig. 4. In the chromatogram, two minor peaks, 13 and 14, were observed other than peak 11 assigned to compound **3**. Although the product of peak 14 was purified by column chromatography using silica gel, an identification of the compound could not be made, because no peak other than that of aniline was observed in the mass spectrum. However, the compound may possibly be $PhN[PO(NHPh)_2]_2$, as previously described.[12]

In order to investigate the thermal behavior of **4**, a DTA-TG/DTG measurement was carried out; the result is shown in Fig. 7. The TG curve exhibited a weight loss in several stages in the 230 to 400 °C range, and a small weight loss in the 500 to 650 °C range. The weight loss at 270 °C was about 17%, which corresponded to that for the elimination of aniline from **4**, and that at 400 °C was about 55%. The DTG curve exhibited about three peaks before 400 °C and one peak at about 580 °C accompanying the weight loss, and the DTA curve exhibited an exothermic peak at 260 °C and an endothermic peak at 266 °C. From the results just described, it appears that the thermal decomposition of **4** occurs with the overlap of several complex stages and the decomposition of **3**.

From these results, it is suggested that some other products along with the formation of **4** are formed at low temperature, while the ammonium ion was not formed at higher temperatures, which is different from the cases for **1** and **2**; also, a residue with a different structure is formed.

Kinetic Analysis of the Thermal Decomposition. For the method, which determines the activation energy from the weight loss on TG curve, there have been kinetic analyses proposed by Freeman and Caroll,[29] Chatterjee,[30] Coats and Redfern,[31] Doyle,[32] and Ozawa.[33,34] Among these, Ozawa's method is independent of the sample weight, is not defined by the reaction form, is relatively simple, and fairly reliable values of the activation energy can be obtained. Accordingly,

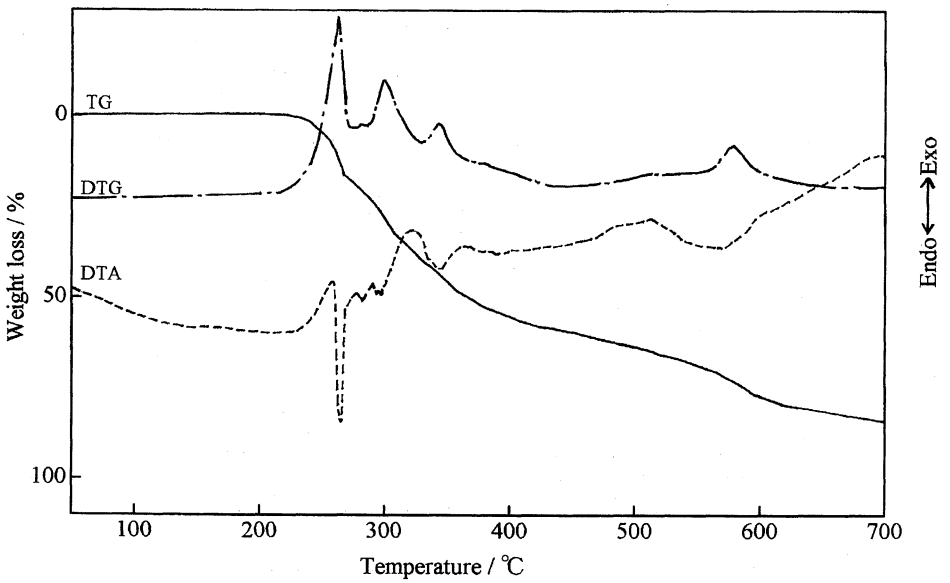


Fig. 7. DTA-TG/DTG curves for **4**. Initial weight: 4.90 mg. Heating rate: 5 °C min^{-1}. Atmosphere: a stream of N_2.

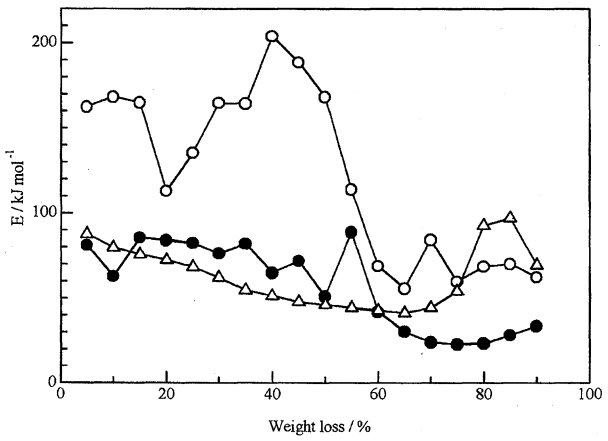


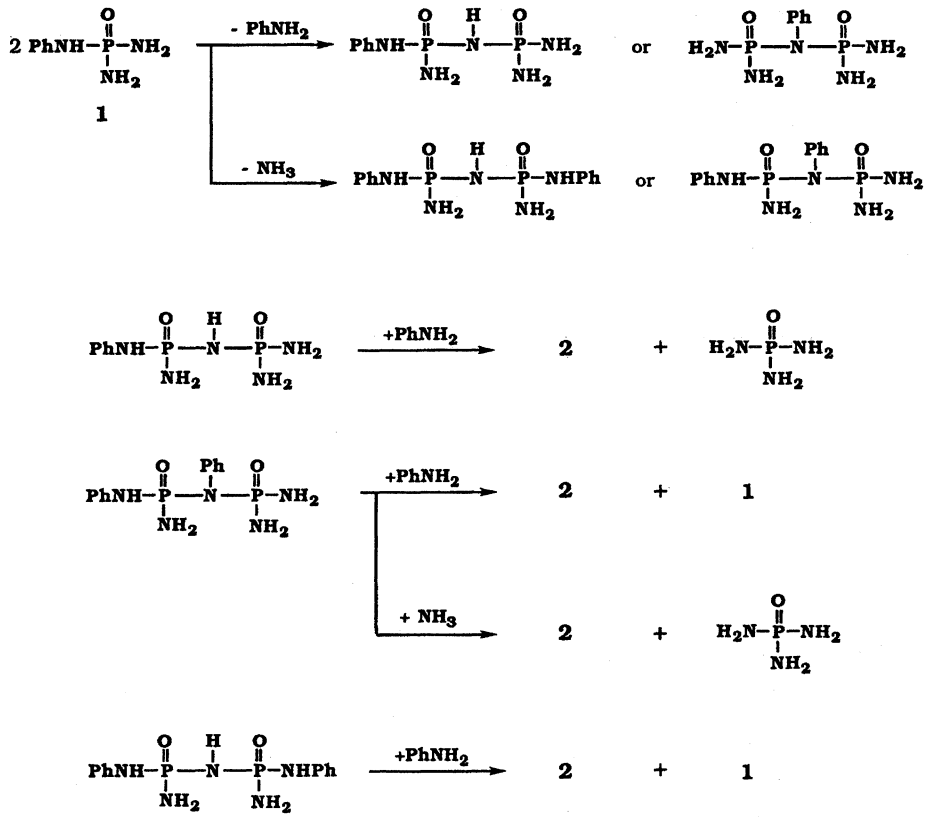
Fig. 8. Dependence of the apparent activation energy on the weight loss for **1**, **2**, and **3**. ●, **1**; ○, **2**; △, **3**.

a kinetic analysis was carried out for the thermal decomposition processes for **1**, **2**, and **3** according to Ozawa's method.

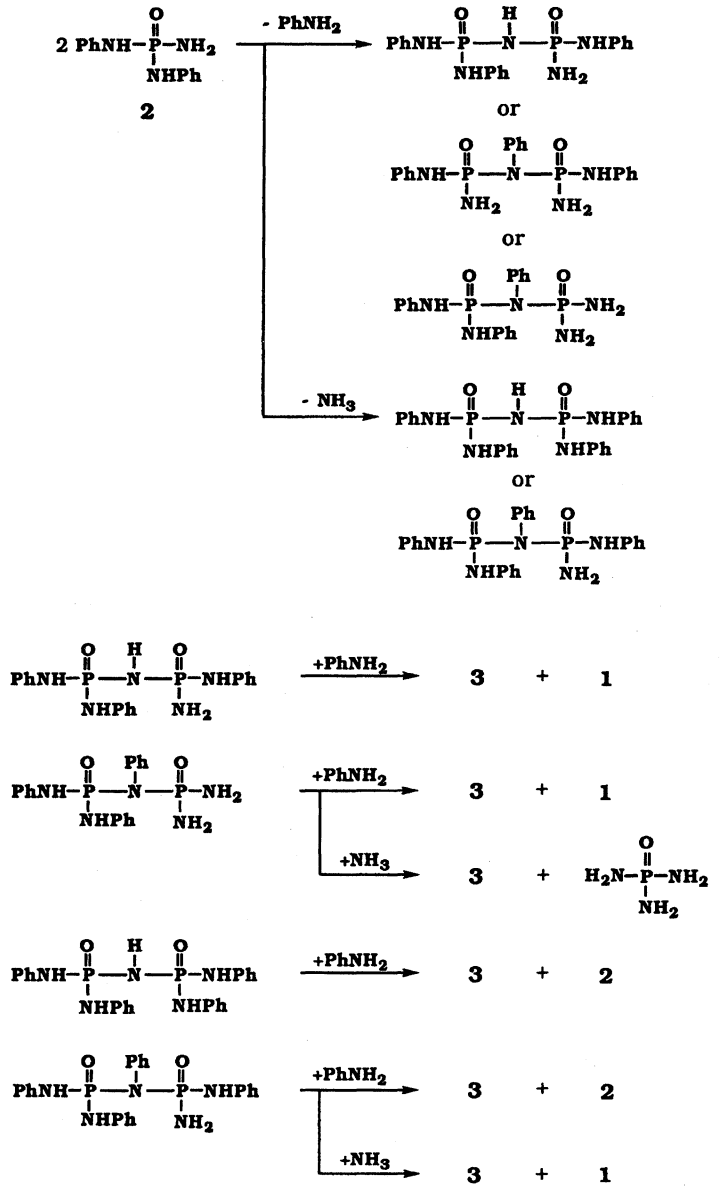
Ozawa's method extends the applicable range of the method proposed by Doyle, which determines the reaction rate based on the TG data measured at more than three heating rates.

In practical measurements, the ordinary logarithm of the heating rates (as the abscissa) versus the reciprocal of the absolute temperatures (as the ordinate) are plotted using the data from the TG curves at various heating rates, straight lines are obtained, and the activation energies are calculated from these slopes.

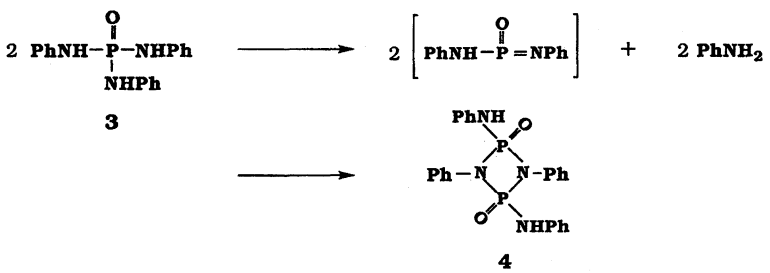
The data for **1** were obtained from TG curves at heating rates of 5, 7, and 10 °C min^{-1} under a stream of nitrogen, the data for **2** at 3, 5, and 10 °C min^{-1}, and the data for **3** at 1, 3, 5, and 7 °C min^{-1}. Since the thermal behaviors of the TG curves at heating rates of 1 and 3 °C min^{-1} for **1** and 1 °C min^{-1} for **2** were different from that at the heating rates previously described, their data were not used. Also, the values of the apparent activation energy, which were calculated for the residual weight, are plotted for **1**, **2**, and **3** in Fig. 8. The values of the apparent activation energy for **1** were in the range of approximately 23 to 90 kJ mol^{-1}. Here, a consideration was attempted based on a discussion described for aliphatic polyamides 11 and 12, and their mixture with ammonium polyphosphate by Levchik et al.[35] The variation in the activation energy was observed until a 15% weight loss; this appears to be due to the overlapping of more than two decomposition processes. Since the activation energy did not change very much in the range of 15 to 35% weight loss, the decomposition mechanism seemed not to change, or to change very slowly. At a weight loss above 35%, the apparent activation energy again exhibited a large variation, which appeared to be due to different overlapping mechanisms. Low values of the activation energy were observed in the range of a 65 to 90% weight loss. The values for **2** showed that in the range of approximately 56 to 204 kJ mol^{-1}, the activation energy did not change very much until the weight loss was 15%, but increased in the range of 20 to 45% weight loss, and decreased in the range of 45 to



Scheme 1. Probable thermal decomposition processes for **1**.



Scheme 2. Probable thermal decomposition processes for **2**.



Scheme 3. Thermal decomposition process for **3**.

65% weight loss. This increase and decrease may have been due to an increase and decrease of the thermal-decomposition process. The values for **3** showed that over a range of approximately 41 to 97 kJ mol^{-1} the activation energy decreased until about a 45% weight loss, did not change very much in the range of 45 to 65% weight loss, and increased in the range of 65 to 85% weight loss. This variation appears to have been due to the cause described above. Most of values of the activation energy for **2** were higher than that for **1** and **3**; this may have been due to the existence of more thermal decomposition processes than that for **1** and **3**.

Thermal Decomposition Process. From the results already described, the thermal-decomposition processes for **1**, **2**, and **3** were postulated.

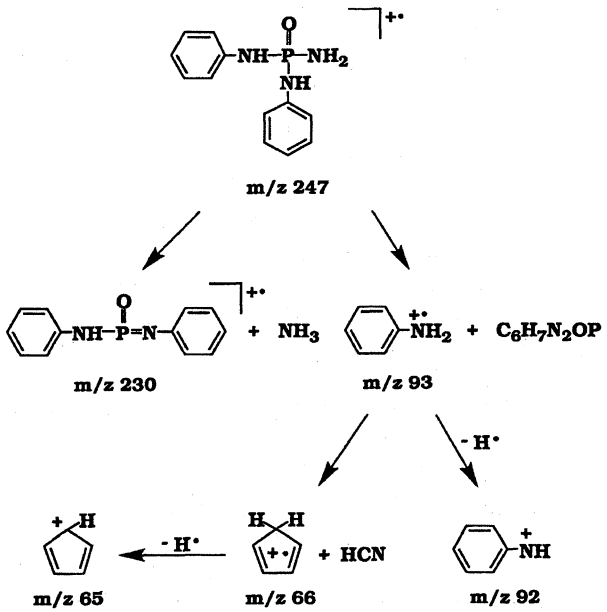
From an analysis of the liberated gas products due to the thermal decomposition of **1**, ammonia and aniline were observed. Therefore, condensation reactions, which involved the elimination of ammonia and/or aniline, seemed to occur. However, there was not one reaction process corresponding to the weight loss (about 13%) during the initial stage observed in the TG curve, because the weight loss for condensation by the elimination of one molecule of ammonia or aniline from two molecule of **1** is 9 or 27%, respectively. Therefore, several reactions seem to overlap, as can be seen from the IR spectra and the variation in the apparent activation energy. It is presumed that some condensation reactions proceed along with the liberation of ammonia and aniline, resulting in the formation of linear and/or cyclic dimers, as shown in Scheme 1. However, since the cyclic dimer from **1** appears to be unstable, the formation of a linear dimer may occur, and their dimers seem to appear as minor peaks in the HPLC profile. Also, it is presumed that phosphenimidic amide is formed as the intermediate from one molecule, as observed in the mass spectrum of **1**, which is described in the following section. Since the existence of **2** was confirmed from the HPLC analysis, the reaction of the linear dimer with ammonia or aniline was suggested (Scheme 1), although **2** may possibly be formed by the action of the water employed for dissolving a sample. At higher temperatures, the formation of a polymeric product, such as $[NHP(O)NH_2]_n$ and $(PNO)_n$, is presumed from the weight loss and IR spectra, though the P–O–P and P–ONH_4 group may be contained; also a variation of the reaction process appears to be less likely based on the activation energy.

Since aniline was observed from an analysis of the liberated gas products for **2**, condensation reaction by the elimination of aniline seemed to occur, though ammonia also appears to have been liberated, because the absorption band assigned to the ammonium ion appeared in the IR spectra. Similar to the case for **1**, a clear determination of the thermal-decomposition process could not be achieved based on the weight loss, although the weight loss (about 20%) in first stage of the TG curve was close to that (19%) for condensation due to the elimination of one molecule of aniline from two molecules of **2**. However, several of the produced ammonia and/or aniline appear to have been consumed by the reaction, as described below. The formation of several thermal products was confirmed at low temperature, and almost all of these appeared to be due to a condensed product, such as a dimer; therefore, the overlapping of several thermal condensations leading to the formation of some dimers is expected during the initial stage. Also, it is presumed that the change in the decomposition process is first less and occurs at about 200 °C (weight loss about 20 %). Further, as shown in Scheme 2, it seems that the elimination of ammonia or aniline occurs between two molecules; then, **3** and **1**, **2**, or phosphoric triamide may be formed by a reaction with the residual ammonia or aniline, and **1** or phosphoric triamide may then decompose immediately at that temperature. At higher temperature, a residue similar to that for **1** may be formed.

Table 2. Mass Spectral Data of **1**, **2**, and **3**

m/z	Relative intensity[a)]	Observed molecular weight	U.S.[b)]	Probable ion composition
(1)				
66	163.5	66.0464 (66.0468)[c)]	3.0	C_5H_6
93	1000.0	93.0585 (93.0576)	4.0	C_6H_7N
154	81.5	154.0298 (154.0292)	6.0	$C_6H_7N_2OP$
171	101.5	171.0530 (171.0556)	5.0	$C_6H_{10}N_3OP$
(2)				
65	—	65.0341 (65.0390)	3.5	C_5H_5
66	82.3	66.0455 (66.0468)	3.0	C_5H_6
92	—	92.0511 (92.0498)	4.5	C_6H_6N
93	1000.0	93.0586 (93.0576)	4.0	C_6H_7N
230	83.6	230.0613 (230.0604)	10.0	$C_{12}H_{11}N_2OP$
247	396.3	247.0865 (247.0868)	9.0	$C_{12}H_{14}N_3OP$
(3)				
65	—	65.0358 (65.0390)	3.5	C_5H_5
66	—	66.0442 (66.0468)	3.0	C_5H_6
92	—	92.0500 (92.0498)	4.5	C_6H_6N
93	928.0	93.0574 (93.0576)	4.0	C_6H_7N
230	265.2	230.0610 (230.0604)	10.0	$C_{12}H_{11}N_2OP$
323	1000.0	323.1185 (323.1180)	13.0	$C_{18}H_{18}N_3OP$

a) Relative intensity referred to base peak of spectrum as 1000.
b) U.S. = Degree of unsaturation. c) Calculated values.



Scheme 4. Fragmentation by EI method for **2**.

Compound **3** may decompose to form **4**, mainly by the elimination of aniline at low temperature, though the existence of other by-products was also confirmed. Compound **4** may be formed through the intermediate phosphenimidic amide, as shown in Scheme 3, which is observed in the mass spectrum for **3** (see the following section). From the results of a TG measurement for **4**, the thermal decomposition of **4** appears to occur by overlapping with that of **3**, and decomposes in several stages along with the liberation of aniline. At higher temperatures, although it was difficult to estimate

the decomposition process from the weight loss, the formation of polymeric products with the structure, in which the ammonium ion part was removed from that for **1** and **2**, is presumed based on the IR spectra. From the variation in the apparent activation energy, a rapid overlapping and variation in the decomposition process appears not to occur.

Although a determination of volatile products in the 500 to 600 °C range for **1**, **2**, and **3** could not be done, it is presumed from the behavior of these TG curves that similar volatile products were liberated.

Cleavage of 1, 2, and 3 by Electron Impact. In order to observe the decomposition of **1**, **2**, and **3** from other points of view, fragmentation by electron impact in a mass spectrometer was also investigated. The mass-spectral data of **1**, **2**, and **3** are shown in Table 2. For **1**, there were mainly four ions at *m/z* 171, 154, 93, and 66; the base peak was that at *m/z* 93, and the probable ion compositions were determined using the high-resolution mass spectrum. The ion peak at *m/z* 171 was due to the molecular ion and fragment ion peaks at *m/z* 154, 93, and 66 could be assigned to M^+-NH_3, $C_6H_5NH_2$, and C_5H_6, respectively. In the case of **2**, there were mainly six ions at *m/z* 247, 230, 93, 92, 66, and 65, and the base peak was that at *m/z* 93. The peak at *m/z* 247 was the molecular ion peak, the peak at *m/z* 230 could be assigned to M^+-NH_3, and peaks at *m/z* 93, 92, 66, and 65 were due to aniline. In the case of **3**, the observed ion peaks were similar to that for **2**, except for the molecular-ion peak.

From the results described above, the fragmentation for **1**, **2**, and **3** is presumed, and that for **2**, as typical example, is shown in Scheme 4. Compounds **1** and **2** eliminate ammonia and/or aniline, and the elimination of aniline may be predominant from the difference in the ion peak intensity. Compound **3** eliminates aniline from the molecular ion, and a further fragmentation of aniline has been well known. Also, the formation of phosphenimidic amide (*m/z* 230 and 154) is presumed in all cases; it is considered that such species are observed because of one molecular cleavage under a vacuum in a mass spectrometer.

The present study is concluded as follows. The weights of **1**, **2**, and **3** rapidly decreased in several stages at 400 °C and in the range of 500 to 650 °C, while liberating ammonia and/or aniline at about 400 °C. The initial temperature of the thermal decomposition was **3** > **2** > **1**; that is, the thermal stability increased along with an increase in the number of phenyl groups. During the initial stage of thermal decomposition, **1** and **2** formed some thermal products which may have been linear condensed products in addition to **2** and **3**, respectively, and **3** formed a cyclic dimer and some by-products. At still higher temperatures, **1** and **2** formed a similar thermal product, which was different from that for **3**. Furthermore, some overlappings and/or rapid change in the thermal decomposition process were suggested from the variation in the apparent activation energy calculated by means of the data from the TG curve. From the cleavage by electron impact, **1**, **2**, and **3** eliminated ammonia and/or aniline from the molecular ion to form three-coordinate phosphenimidic amide; therefore, they appear to also decompose through such a product at first in the thermal decomposition. In closing, although we could not clearly identify the thermal-decomposition residue in this study, we do intend to identify it by means of approaches involving both the separation and synthesis of the decomposition products. In addition, we must also investigate the reaction between the thermal products.

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