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The Thermal Degradation of Some Polyphosphazenes*

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SUMMARY

The thermal degradation of some high molecular weight polyphosphazenes is reported. The investigation was carried out on a thermobalance in vacuum. The products of degradation were assessed. The molecular weight change of one of the polymers $[(\text{PhO})_2\text{P}=\text{N}]_n$, on being heated in vacuum, was followed by viscosity measurements and the results are discussed with reference to the existence of a possible chain-ring degradation equilibrium.

INTRODUCTION

The polyphosphazenes of general formula $[\text{R}_2\text{P}=\text{N}]_n$ have been known for many years and have been the subject of much industrial and academic research [1]. Phosphazene chemistry has traditionally been studied under two separate sections; low molecular weight ring compounds and high molecular weight long-chain analogues. It is the purpose of this paper to describe the thermal degradation of the high polymer phosphazenes where R, in the general formula, may be a halogen, pseudo-halogen, or organic residue.

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Phosphazene Synthesis

The preparation of high polymer phosphazenes [1] follows four main routes.

1. Thermal polymerization of ring compounds.
2. Substitution reactions, using suitable nucleophilic reagents, on an already-existing phosphorous-nitrogen polymer backbone.
3. Pyrolytic condensation reactions involving low molecular weight precursors, such as mono- or disubstituted chlorophosphoranes reacted with ammonia or ammonium chloride or the pyrolysis of disubstituted phosphorus azides.
4. Polymers formed by the condensation of discrete ring phosphazenes with di- or trifunctional linking agents, such as diols. These compounds are not true phosphazene polymers. The polymers formed from the addition polymerization of vinyl or alkyl side groups presubstituted on phosphazene rings are similar. These polymers again are not considered to be true phosphazene polymers.

This paper describes the degradation of polymers prepared by the commonest methods, 1 and 2. The thermogravimetric degradation of diol-linked polymers (method 4) has been described by Herring et al. [2].

The preparation of each polymer will be described in turn.

Poly(dichloro)phosphazene $[\text{Cl}_2\text{P}=\text{N}]_n$, I, was prepared by the thermal polymerization of hexachlorocyclotriphosphazene in vacuum at 250°C for about 24 hr. The resultant material is a mixture of linear, benzene-soluble polymer, cross-linked insoluble polymer and unpolymerized ring species.

An impure form of I was prepared by the partial hydrolysis of the chloro polymer in damp air. The product was uncharacterized but was assumed to contain some phosphorus atoms having hydroxyl substituent groups. Both compounds were elastomeric in nature.

Poly(di-isothiocyanato)phosphazene $[(\text{SCN})_2\text{P}=\text{N}]_n$, II, prepared by the thermal polymerization of the isothiocyanato trimer [3, 4]. Earlier work with this polymer failed to distinguish between the possibilities of polymerization through the phosphorous-nitrogen backbone, through the side groups, or both. Recent work in this laboratory [5] indicates that polymerization is via the phosphorous-nitrogen backbone. The polymer was rubbery.

Poly(diphenyl)phosphazene $[\text{Ph}_2\text{P}=\text{N}]_n$, III, prepared by a method suggested in a previous paper [6] using a substitution reaction with lithium phenyl as the nucleophilic reagent. The polymer was a powder.

Poly(diphenoxy)phosphazene $[(\text{Ph}-\text{O})_2\text{P}=\text{N}]_n$, IV; poly(bis-parabiphenyloxy) phosphazene $[(\text{Ph}-\text{Ph}-\text{O})_2\text{P}=\text{N}]_n$, V; and Poly(bis-2,2,2-trifluoroethoxy)phosphazene $[\text{CF}_3\text{CH}_2\text{O})_2\text{P}=\text{N}]_n$, VI; were all prepared by the substitution method suggested by Allcock et al. [7]. IV was a rubber, V a powder, and VI a finely divided rubber.

THERMOGRAVIMETRIC ANALYSIS

Experimental

The instrument used in this work was a Stanton Massflow Thermobalance, Model MF-L5. The system was capable of being evacuated to 10^{-5} torr and degradation experiments were carried out at 10^{-4} torr or better. A 5-in. water-cooled oil diffusion pump backed by a rotary oil pump and liquid-air trap was used to remove volatiles.

The maker's thermocouple, platinum-platinum, 13% rhodium, was considered to be too insensitive for this work and a Chromel-Alumel couple was added, to read temperatures to within 0.2°C . The thermocouple junction was placed as near as possible to the degrading sample without interfering with the balance mechanism. The furnace was programmed at 3°C temperature rise per minute by a Pye 104 Series Programmer Controller. Graphical interpretation of temperature-time data showed a constant heating rate. For all experiments a glass sample holder was used carrying a 50-mg sample. All instrument variables were standardized.

Results

The results of the thermogravimetry experiments have been plotted as thermograms (see Figs. 1 and 2). It must be stressed that, strictly, each thermogram can only be used for comparison with other thermograms obtained under exactly the same conditions. That is the situation here, and comparison can be made between the various phosphazenes degraded. However, in absolute terms, there is no agreement as to what constitutes the "stability" of a compound. Such factors as heating rate, sample size, type of instrument, and atmosphere have profound effects on the apparent degradation temperatures so that a thermogram can only indicate stability of a special kind.

Table 1 shows the temperatures for various extents of degradation. Polystyrene (molecular weight 12,000, anionically-initiated sample) is given as a comparison "marker." The quoted activation energies were calculated

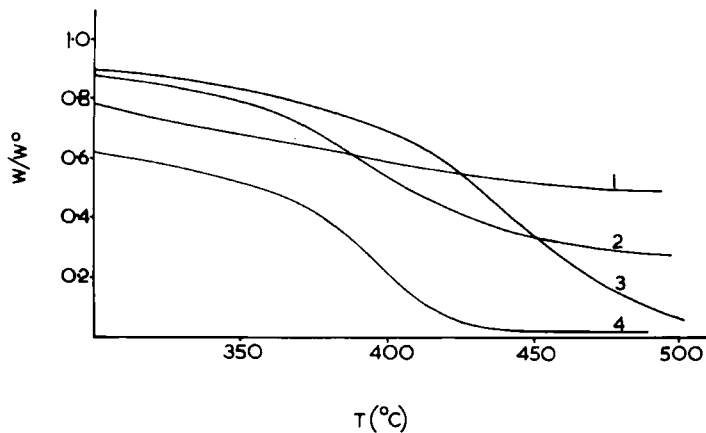


Fig. 1. Thermograms for some polyphosphazenes. (1) $[(\text{SCN})_2\text{P}=\text{N}]$; (2) $[(\text{Ph})_2\text{P}=\text{N}]$; (3) $[(\text{Cl})_2\text{P}=\text{N}]$; (4) $[(\text{Cl})_2\text{P}=\text{N}]$ (partially hydrolyzed).

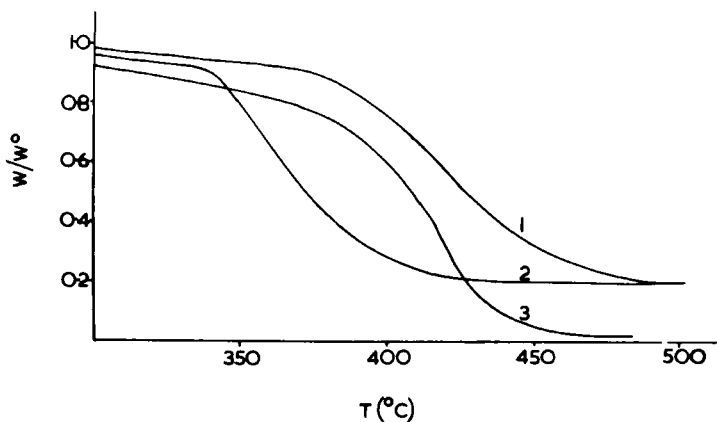


Fig. 2. Thermograms for some polyphosphazenes. (1) $[(\text{Ph}-\text{PhO})_2\text{P}=\text{N}]$; (2) $[(\text{PhO})_2\text{P}=\text{N}]$; (3) $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P}=\text{N}]$.

Table 1

Polymer (repeat unit)	Activation energy kcal mole ⁻¹	Temperature (°C) at which sample reaches fixed percentage decomposition		
		10%	30%	50%
[(Cl) ₂ P=N]	20.0	276	399	431
[(Cl) ₂ P=N]	40.0	—	196	356
Impure trimer				
[(Ph) ₂ P=N]	12.0	281	372	409
[(Ph-O) ₂ P=N]	15.5	339	359	372
[(Ph-Ph-O) ₂ P=N]	14.0	371	405	426
[(CF ₃ CH ₂ O) ₂ P=N]	56.5	314	387	408
[(SCN) ₂ P=N]	—	262	341	436
Styrene	—	385	394	398

using the Fuoss method [8]. The reaction order is assumed to be unity, which is certainly true for polydichlorophosphazene [9, 10]. The significance of these results is under review [11].

PRODUCT ANALYSIS

Experimental

A survey of some of the products of degradation of the phosphazenes was made by heating the polymers in glass containers on a simple vacuum line using a small furnace at controlled isothermal or programmed temperatures. The products were analyzed by various techniques, principally infrared spectrometry, mass spectrometry, and gas-liquid chromatography. Model compounds of monomeric materials were synthesized as necessary.

Results

The products of degradation (at the temperatures of degradation shown in the thermograms) are given for each of the compounds. Percentages given are all by weight.

I, $[(\text{Cl})_2\text{P}=\text{N}]_n$. The products were trimer, tetramer, higher ring oligomers, and oily linear analogues. There was a low yield (2-5%) of a black/grey residue at 500°C.

II, $[(\text{SCN})_2\text{P}=\text{N}]_n$. The products of degradation were not well characterized but at 500°C a 50% residue remained. The residue was yellowish black in color and appeared to have a hardness comparable to stainless steel.

III, $[(\text{Ph})_2\text{P}=\text{N}]_n$. Volatile products were ammonia (1.5%), benzene, and a phosphine. The total volatile part amounted to approximately 7%. The volatiles were identified by their infrared spectra with the exception of the phosphine. This product was in such low yield that it could only be detected by the strong smell characteristic of all volatile phosphines. The exact nature of this product remains speculative. Water is pumped off in the early stages of the heat-up period as it is very difficult to remove moisture from the original polymer except by heating in a good vacuum. A black residue (20-30%) is found after heating, along with low molecular weight linear and ring phosphazenes. The infrared spectrum of hexaphenyl-cyclotriphosphazene corresponded quite well to the spectrum obtained from the low polymer species. The spectrum of the black residue on the other hand was very ill-defined but appeared to "shadow" that of the starting material. The degradation experiment was repeated in vacuum in an electron spin resonance sample tube. The resonance spectrum was consistent with a high concentration of free electrons. This was probably due to the formation of carbon. There was no apparent drop in the signal intensity over a period of 1 month, again consistent with the presence of carbon.

IV, $[(\text{Ph}-\text{O})_2\text{P}=\text{N}]_n$. The volatile products in this case were not fully characterized. A yield of phenol (approximately 5%) was collected along with an unidentified gas. A black residue was formed (20%) together with ring oligomers and lower molecular weight polymer. Identification of the ring compounds was possible by comparison with the infrared spectrum of $[(\text{Ph}-\text{O})_2\text{P}=\text{N}]_3$ prepared by Allcock and Best's method [12].

V, $[(\text{Ph}-\text{Ph}-\text{O})_2\text{P}=\text{N}]_n$. No gas product was detected. However, at about 200°C, a white sublimate (5-7%) condensed into the cooler parts of the vacuum line. This was found to be para-hydroxybiphenyl. Again, a black residue (20%) along with ring oligomers and linear homologues were found. Infrared evidence was conclusive on this point since a ring frequency

(doublet 880, 890 cm^{-1}) was found in the product. The original polymer did not have this frequency while a sample of $[(\text{Ph}-\text{Ph}-\text{O})_2\text{P}=\text{N}]_3$, a ring trimer, showed an intense doublet in this position. The actual product of degradation showed the doublet in the ring frequency position but at reduced intensity, confirming a mixture of polymer, possibly of lower molecular weight, and ring oligomers, possibly trimer.

VI, $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P}=\text{N}]_n$. Only a very small amount of residue (2%) remained at 500°C. No further product analysis was carried out.

It should be noted that the residual amounts given were only those pertaining to 500°C. At 900°C these figures did not appear to change more than 5%. Indeed, attempts to carry out elemental analyses on these residues were always a failure since they were not completely combusted at 950°C in a stream of oxygen.

The products are summarized in Table 2.

MOLECULAR WEIGHT MEASUREMENTS

Viscosity molecular weight measurements were made on samples of IV, $[(\text{Ph}-\text{O})_2\text{P}=\text{N}]_n$, which had been heated for various times at various temperatures in vacuum. The temperatures were below that at which weight loss started.

Experimental

Samples (100 mg) of the polymer were sealed in glass ampoules at 10^{-4} torr and heated for times up to 24 hr in a small furnace with temperature control better than 1°C. The ampoules were then opened, and the polymer weighed and dissolved in 50 ml of cyclohexanone (reagent grade, dried). A suspended-level viscometer was used to measure the specific viscosities (η_{sp}) for various concentrations of polymer. Intrinsic viscosities $[\eta]$ were calculated by plotting the reduced viscosity (η_{sp}/C) against the concentration, C . The viscometer bath was held at 30°C.

Results

The results have been plotted in Fig. 3.

After 24 hr, there was no further significant drop in intrinsic viscosity.

Table 2

Polymer (repeat unit)	Volatiles	Lower analogues	Residue
$[\text{Cl}_2\text{P}=\text{N}]$ I	—	Trimer, tetramer and linear oils 95-98%	Grey/black residue 2-5%
$[(\text{SCN})_2\text{P}=\text{N}]$ II	—	—	50%
$[\text{Ph}_2\text{P}=\text{N}]$ III	Ammonia (1.5%), Water, benzene (and a phosphine) Total yield: 7%	63-73% of ring oligomers and lower molecular weight analogues.	20-30% of black residue
$[(\text{Ph}-\text{O})_2\text{P}=\text{N}]$ IV	Trace unidentified gas, phenol. Total yield: 5%	75% ring oligomers, etc.	20% black residue
$[(\text{Ph}-\text{Ph}-\text{O})_2\text{P}=\text{N}]$ V	4-Hydroxybiphenyl. Yield: 5-7%	74% ring oligomers, etc.	20% black residue
$[(\text{CF}_3\text{CH}_2\text{O})_2\text{P}=\text{N}]$ VI	—	—	2% residue

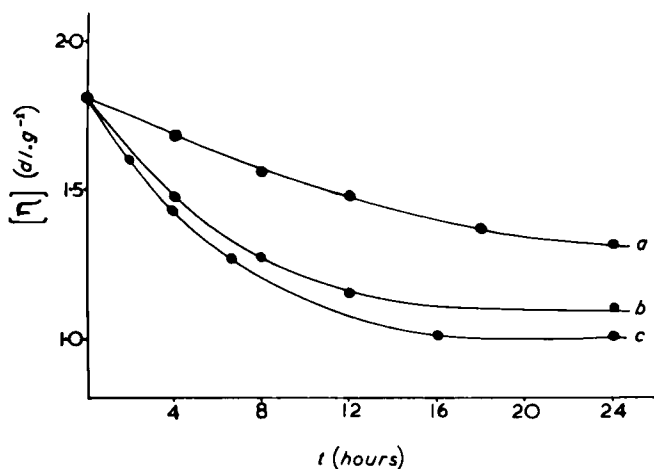


Fig. 3. Change in intrinsic viscosity of $[(\text{PhO})_2\text{P}=\text{N}]$ with time of heating at (a) 130°C ; (b) 140°C ; (c) 150°C .

DISCUSSION

Allcock [1] has discussed the existence of an equilibrium between ring oligomers and chain polymers in the phosphazene system. He has used his theory to explain the nonpolymerization of ring phosphazenes substituted with large groups. It is, of course, equally likely that depolymerization is equilibrium controlled and such a possibility is considered during the following discussion.

The degradation reaction may be considered in two parts, a lower and a higher temperature reaction.

The lower temperature reaction, occurring before onset of weight loss, is most probably a depolymerization equilibration reaction as described by Allcock [1]. The evidence for this lies in the observation of ring oligomers in those polymers most studied (I, III, IV, and V) together with lower molecular weight species (particularly noticed in I and V). Also the behavior of IV, whose intrinsic viscosity drops (see Fig. 3) steadily to a plateau on heating between 130 and 150°C in vacuum, suggests the achievement of some equilibrium situation.

However, at higher temperatures further reactions appear to set in. At temperatures of weight loss, the low temperature equilibration reaction seems to continue but is disturbed in most cases by the formation of

products which are not lower molecular weight phosphazene homologues. This occurs for all the polymers studied in this paper (I-VI). This reaction is general and seems to cause the formation of such products as ammonia and benzene (III) and various phenols (IV, V) along with a hard residue (in all cases, to a greater or lesser extent, see Table 2) which may contain carbon (III). It will be noted that the production of phenols (or benzene and ammonia) requires extra hydrogen atoms. To do this a residue which is relatively richer in carbon must be formed. It is felt that, while the formation of the residue is probably linked to the production of non-phosphazene volatiles (abstraction of hydrogen), any mechanism to explain the appearance of such products would require a great deal more investigation. It will be noted that in the case of I and VI only a small amount of residue is formed (about 2%). It is suggested that this may be due to the inhibition of volatile product formation by the presence of relatively more stable side groups (chlorine in I, and some carbon-fluorine bonds in VI). Finally it is perhaps worth noting that one of the original reasons for substituting organic groups on the phosphazene chain was to improve hydrolytic stability. The tremendous increase in hydrolytic stability brought about by the replacement of the Cl group by a variety of organo-substituents [6, 7] does not diminish the thermal stability of the polymers (see Figs. 1 and 2).

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