The Thermal Decomposition of Polydichlorophosphazene

J. R. Maccallum[a]; A. R. S. Werninck[a]

[a] Chemistry Department, University of St. Andrews, Fife, Scotland

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J. R. MacCALLUM and A. R. S. WERNINCK

Chemistry Department
University of St. Andrews
Fife, Scotland

SUMMARY

The thermal decomposition of polydichlorophosphazene has been ex-
amined. The decomposition was found to be first-order with an activation
energy of 22.5 ± 2 kcal mole^{-1}. The products comprised a wide range of
cyclic and linear dichlorophosphazenes. It is suggested that the decomposi-
tion reaction is initiated at the ends of the macromolecules.

INTRODUCTION

Although many organic polymers revert to low molecular weight
analogs on heating, there are relatively few inorganic polymers that exhibit
similar behavior [1, 2]. The process of depolymerization can be considered
as part of an equilibrium reaction, and consequently it is possible to predict
temperatures above which low molecular weight material is favored, thereby
fixing an upper limit to the thermal stability of the polymer. The poly-
phosphazenes are a family of inorganic polymers that would seem to be
ideal for investigating a polymerization/depolymerization equilibrium. The
most studied member is polydichlorophosphazene. Several studies have
been made of the polymerization of the trimeric chlorophosphazene [3-5]
but little has been reported on the depolymerization reaction [6, 1]. Patat
and Derst [6], using samples prepared by thermal polymerization, found the

reaction to be first-order with an activation energy of 26 kcal mole^{-1}. They found the products to be cyclic, low molecular weight analogs of the polymer. Gimblett and Wright [7] studied the kinetics of the depolymerization of catalytically prepared polymer. The reaction was first-order with an activation energy of 25 kcal mole^{-1}.

In this paper a more thorough study of the products of thermal breakdown of polydichlorophosphazene are reported.

EXPERIMENTAL

Two samples of polymer were prepared by heating purified hexachlorocyclotriphosphazene in evacuated vessels for 4 and 6 hr, respectively, at 260°C. Unreacted trimer was sublimed out of the polymer by heating to constant weight in a vacuum oven at 120°C. The final polymeric material consisted of a mixture of linear and cross-linked species.

Thermogravimetry of polymer samples was carried out on a Stanton Massflow thermobalance described previously [8]. A glass overhead pumping system was used along with the standard vacuum equipment. It was found that the product of thermal decomposition collected on the cool parts of the glass tube which surround the sample. The products separated into distinct zones which could be analyzed at the end of each thermogravimetric run. Figure 1 illustrates the disposition of the products on the column.

IR spectra were obtained for the products using Nujol mulls and the pressed disk technique.

RESULTS

Kinetics

A preliminary investigation was carried out to ascertain that the decomposition reaction was first-order. Some isothermal decompositions were done in the region 380-450°C and Fig. 2 shows a typical run, confirming first-order kinetics. Thus, the rate of reaction can be expressed by
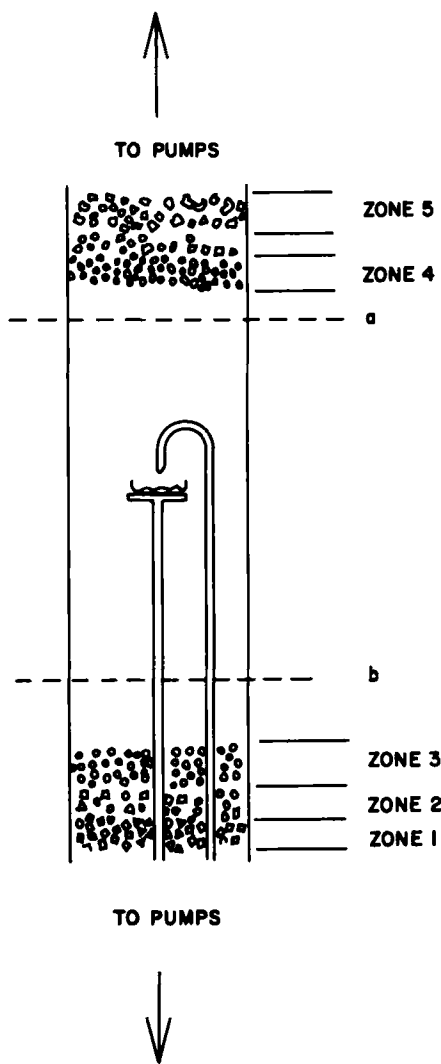
$$-dw/dt = kw \qquad (1)$$

Fig. 1. Diagram of degradation apparatus showing how the zones were formed. ab represents the heated area.
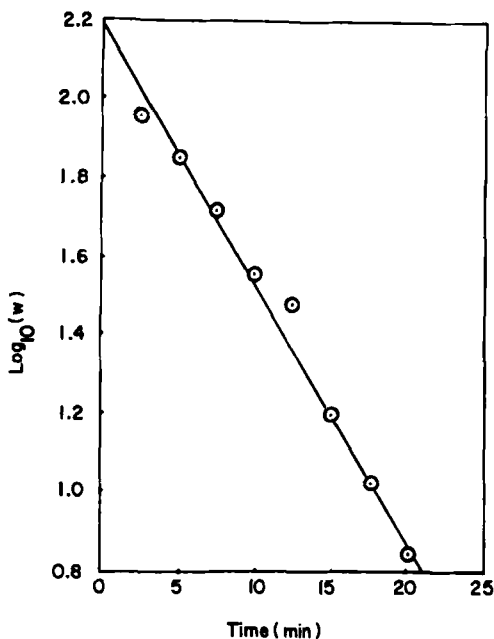
Fig. 2. First-order plot for isothermal decomposition of polydichlorophos-
phazene.

in which w is the weight of sample remaining at time t, and k is the rate
constant for the reaction. Equation (1) can be rewritten

$$\log (-dw/dt) = \log A - E/2.303RT \qquad (2)$$

where A is a constant, R the gas constant, T the absolute temperature, and
E the activation energy for the reaction. A plot of log (-dw/dt) vs. 1/T
should yield the activation energy for the reaction. Data collected from pro-
grammed runs (rate of heating 3°/min) on the thermobalance were treated
according to Eq. (2) and the results are shown in Figs. 3 and 4. The activa-
tion energy, E, has a value 22.5 ± 2 kcal mole^{-1} for both samples.

Products

As described above, the products of decomposition separated out into
five zones on the glass hood surrounding the samples. The main-bands oc-
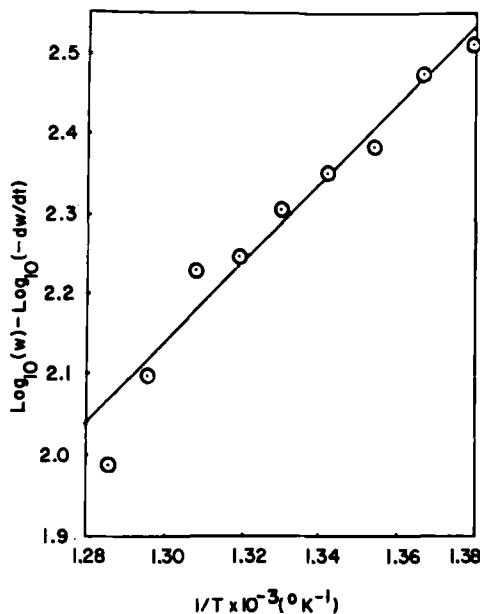curring in the IR of the products in each zone are summarized in Table 1.

Fig. 3. Plot of Eq. (2) for data collected during thermogravimetry of Sample A, prepared by heating trimer for 4 hr at 260°C.

Zone 1. The material in this zone was a white solid intermixed with an oily, highly viscous liquid. The IR bands exhibited the general broadening which is usually associated with polymeric substances. It was concluded that this zone consisted of high polymer containing cyclic homologs.

Zone 2. This entirely liquid product showed more distinct character in its IR spectrum. It was thought to be low molecular weight polymer along with cyclic material. The band at 2090 is notable and Manley associated the appearance of this peak with cross-linking.

Zone 3. This liquid contained a much higher proportion of cyclic material than did Zones 1 or 2.

Zone 4. The contents of the zone were very similar to those in Zone 3.

Zone 5. This zone comprised a hard, crystalline, white solid which had a very similar IR spectrum to a mixture of $(PNCl_2)_{3,4, \text{ and } 5}$, and it was

Table 1. Main Bands in IR Spectra of Products in Various Zones.
Data Are Reported in cm^{-1}. Assignments Made under Comments Are Taken from Refs. 9 and 10.[a]

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Comments
330 w	300 w	320 w			
360 s			360 w		
380 w	400 s	390 m	400 m		
460 w	460 vs	460 m	460 m	460 m	PNP skeletal deformation
530 w	530 w	525 s	520 s	520 vs	In-plane ring vibration
580 m	590 s	575 vs	580 vs	612	PCl$_2$ out-of-phase bond stretching
740 s	750 vs	740 vs	740 vs	720 m	PNP skeletal deformation
880 s	870 vs	880 m	875 m	890 m	PNP skeletal deformation
1080	1080	1080	1080		
—	—	—	—	1300 vs	PNP stretch, in-plane. Broad band Zone 1-Zone 4
1500	1500	1500	1500		
1750 s	1760 s		1750 m		Combination tone
1990 vs	1990 s				Combination tone
2080 w	2090 s	2100 w	2100 w		
2155 s					Combination tone

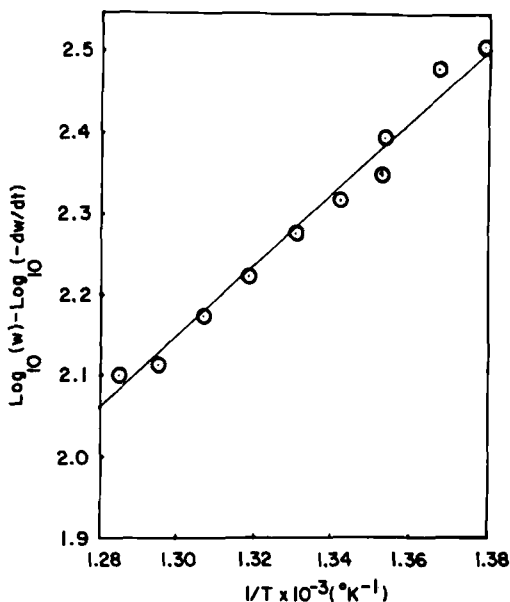aKey: w - weak; m - medium; s - strong; vs - very strong.

Fig. 4. Plot of Eq. (2) for data collected during thermogravimetry of
Sample B, prepared by heating trimer for 6 hr at 260°C.

concluded that the prime products were a mixture of trimer and tetramer
with much smaller yields of higher cyclic homologs.

DISCUSSION

The rate of breakdown measured in this investigation is in good agree-
ment with that reported by Patat and Derst [6]. These authors found a
half-life of 6.5 min at 420°C which compares with 8.0 min for this work.
There can be little doubt that the rate of thermal decomposition is a
first-order kinetic process. This observation cannot be reconciled with a
mechanism of random scission of polymer molecules followed by evapora-
tion of low molecular weight species thus formed. The kinetic law pre-
dicted for such a mechanism is more complex than first-order [11]. It is
assumed that the evaporation takes place immediately after the low mol-
ecular weight material is formed.

The products evolved during thermal breakdown also indicate a com-
posite reaction. The apparent range from fairly high molecular weight

material to cyclic trimer may be complicated by the presence of low molecular weight species present initially in the sample, which do not evaporate during the preliminary removal of trimer but do so at higher temperatures.

The most likely mode of decomposition is by a mechanism involving a "back-biting" process from chain ends. The amount of material lost per act of initiation would determine the over-all order and could lead to a first-order reaction [12] .

It is not possible to confirm this postulated mechanism without measurements of the change in molecular weight during the reaction. It is probable that the reactive intermediates are ionic in nature since this is the case for polymerization. It has been reported [13] that end-stopped low molecular weight polymer has very enhanced thermal stability, an observation which is in accord with a decomposition reaction initiated at chain ends.

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