

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Phosphonitrilic Chloride. 40. Relationships between Electrical Conductivity and Thermal Behavior of Diaminotetraarylcyclotriphosphazenes

M. Kajiwara^a; K. Shimono^a; H. Saito^a

^a Department of Applied Chemistry Faculty of Engineering, Nagoya University, Nagoya, Japan

To cite this Article Kajiwara, M. , Shimono, K. and Saito, H.(1978) 'Phosphonitrilic Chloride. 40. Relationships between Electrical Conductivity and Thermal Behavior of Diaminotetraarylcyclotriphosphazenes', *Journal of Macromolecular Science, Part A*, 12: 7, 945 – 951

To link to this Article: DOI: 10.1080/00222337808069396

URL: <http://dx.doi.org/10.1080/00222337808069396>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosponitrilic Chloride. 40. Relationships between Electrical Conductivity and Thermal Behavior of Diaminotetraarylcyclotriphosphazenes

M. KAJIWARA, K. SHIMONO, and H. SAITO

Department of Applied Chemistry
Faculty of Engineering
Nagoya University, Furo-cho
Chkusa-ku, Nagoya, Japan

ABSTRACT

The behavior of various diaminotetraarylcyclotriphosphazenes $N_3P_3(NH_2)_2R_4$ on heating has been studied. The homocondensation reaction occurs with elimination of ammonia or aniline when the $N_3P_3(NH_2)_2(OC_6H_5)_4$, $N_3P_3(NH_2)_2(C_6H_5)_4$, or $N_3P_3(NHC_6H_5)_6$ is heated under various conditions. However, the homocondensation reaction does not proceed in case of $N_3P_3(NH_2)_2(SC_6H_5)_4$, because of the high conductivity of this compound.

INTRODUCTION

It is well known [1] that rubberlike polymers are formed from hexachlorocyclotriphosphazene by heating, but that polymers do not form from hexaorganocyclotriphosphazenes except for some compounds.

We reported [2] previously on the electrical conductivity of some

oligomers or polymers prepared from hexachlorocyclotriphosphazene. Also, we have reported on homocondensation of diaminotetrakis(trifluoroethoxy)cyclotriphosphazene in a previous paper [3].

In the present paper we describe the relationship between electrical conductivity and thermal behavior of some diaminotetraarylphosphazenes.

RESULTS AND DISCUSSION

Condensation Reaction of Some Diaminotetraarylphosphazenes

Ammonia is detected when diaminotetraphenoxycyclotriphosphazene $N_3P_3(NH_2)_2(OC_6H_5)_4$ or diaminotetraanilino-cyclotriphosphazene $N_3P_3(NH_2)_2NHC_6H_5)_4$ is heated under N_2 but is not detected in the case of diaminotetrathiophenoxycyclotriphosphazene $N_3P_3(NH_2)_2(SC_6H_5)_4$.

Aniline is also detected on heating of diaminotetraanilino-cyclotriphosphazene or hexaanilino-cyclotriphosphazene $N_3P_3(NHC_6H_5)_6$.

The amount of ammonia formed at 190, 220, 250, and 280°C was determined by chemical analysis, and the reaction order was calculated. The results are shown in Fig. 1.

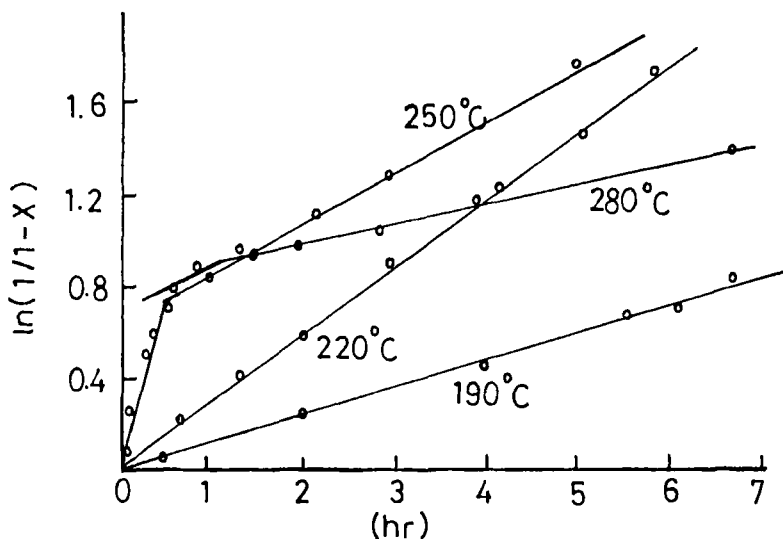


FIGURE 1.

TABLE 1. Activation Energy of Deammoniation

Compounds	ΔE (kcal/mole)
$N_3P_3(NH_2)_2(OC_6H_5)_4$	32
$N_3P_3(NH_2)_2(OCH_2CF_3)_4$	14 ^a
$N_3P_3(NH_2)_2(OCH_2CF_3)_4 + HOC_6H_4OH$	14-27 ^b

^aData of Kajiwara et al. [4].

^bData of Bode and Clausen [5].

The initial reaction was found to be first order, with an apparent activation energy of deammoniation about 32 kcal/mole. The activation energy of deammoniation is compared with the energy of similar compounds or reaction in Table 1.

The energy of ammoniation of $N_3P_3(NH_2)_2(OC_6H_5)_4$ is the largest.

The products prepared when ammonia evaporation reaches a steady state are determined by chemical analysis, and the results are summarized in Table 2.

All of the products are glasslike, soluble in most organic solvents, and the oligomeric products are stable to hydrolysis.

In the infrared spectra of the products, frequencies attributed to P=N, P-NH-P, and P_3N_3 appear in the region of 1280-1260, 1060-840, or 630-550, and 890-830 cm^{-1} , respectively.

The structure of the product having a molecular weight about 2000 is assumed from analysis to be as shown in I. This structure is also supported by the fact that 1 mole ammonia evaporated under steady-state conditions.

The amount of ammonia formation from $N_3P_3(NH_2)_2(NHC_6H_5)_4$ was determined. However, it is difficult to determine the reaction order because the amount of ammonia evaporated readily reaches a

TABLE 2. Relationship between Molecular Weight and Reaction Time

Reaction temp. ($^{\circ}C$)	Reaction time (hr)	\overline{M}_w	Appearance
190	80	1000	Glass
220	76	1000	Glass
250	72	800-1000	Glass
280	48	2000	Glass

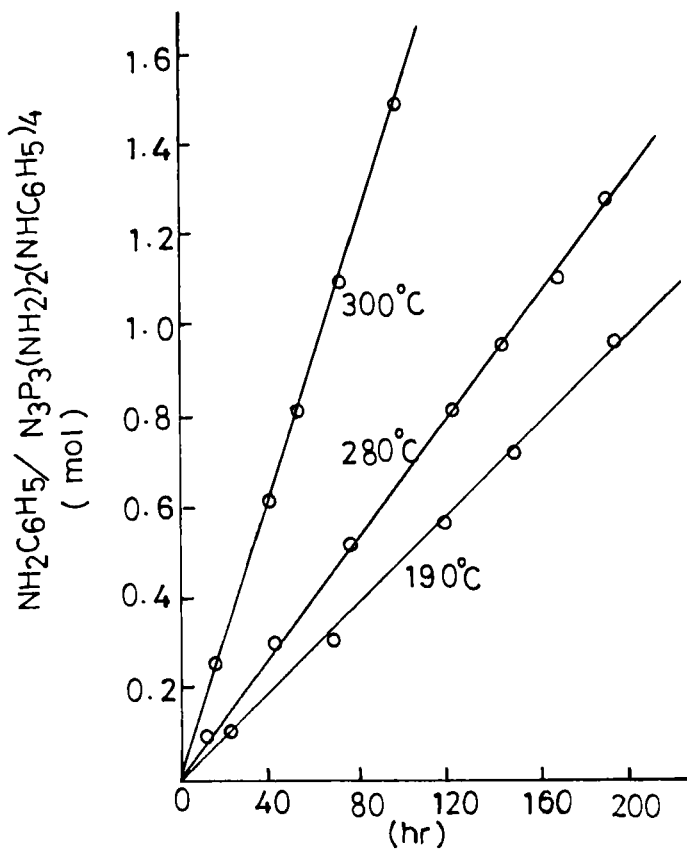
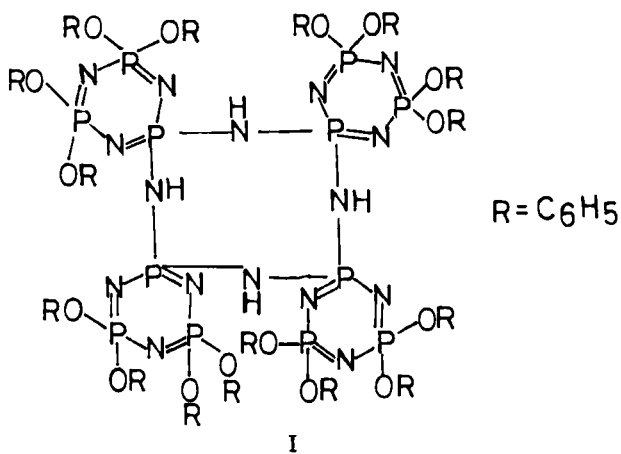


FIGURE 2.

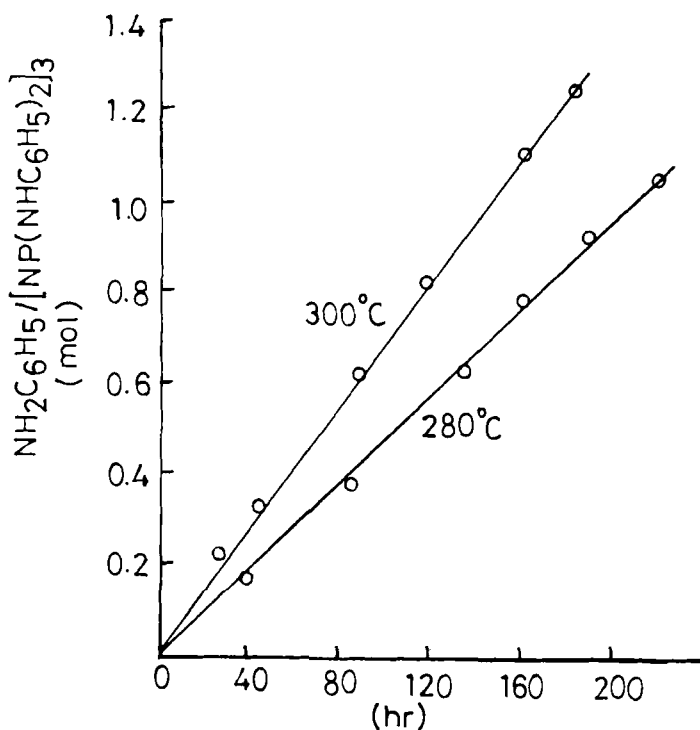


FIGURE 3.

steady state. On the other hand, aniline is detected when $N_3P_3(NH_2)_2(NHC_6H_5)_4$ or $N_3P_3(NHC_6H_5)_6$ is heated under various conditions. The amount of aniline was determined by chemical analysis, and the results are shown in Figs. 2 and 3, respectively.

Bode [5] reported that the anilincyclophosphzene can also be pyrolyzed with elimination of aniline; the pyrolysis products can be heated with aniline in a sealed tube to re-form the original cyclophosphazene, without change in ring size.

Consequently, $N_3P_3(NH_2)_2(NHC_6H_5)_4$ and $N_3P_3(NHC_6H_5)_6$ may be pyrolyzed with elimination of ammonia and aniline.

In case of $N_3P_3(NH_2)_2(SC_6H_5)_4$, ammonia or thiophenol is not detected at 260, 280, and 300°C. This means that homocondensation or pyrolysis reactions do not occur under these conditions.

TABLE 3. Maximum and Coefficient of Ultraviolet Spectra and Electrical Conductivity of Diaminotetraarylcyclotriphosphazenes

Compound	Ultraviolet		Electrical (20° C)	
	λ_{\max} (nm)	ϵ_{\max}	Resistance (ohm/cm)	Conductivity (ohm-cm) ⁻¹
$N_3P_3(NH_2)_2(NHC_6H_5)_4$	234 277	46,875 9,190	3.46×10^{14}	2.88×10^{-15}
$N_3P_3(NH_2)_2(SC_6H_5)_4$	239 321	97,413 9,680	6.89×10^{12}	1.45×10^{-13}
$N_3P_3(NH_2)_2(OC_6H_5)_4$	210 263	21,604 3,148	2.79×10^{14}	3.59×10^{-15}
$N_3P_3(NHC_6H_5)_6$	237 276	75,343 7,481	4.18×10^{14}	2.09×10^{-15}

Ultraviolet Absorption and Electrical Conductivity of Some Diaminotetraarylcyclotriphosphazenes

Ultraviolet absorption and electrical conductivity were measured, and the results are summarized in Table 3.

The resistance of the compound $N_3P_3(NH_2)_2(SC_6H_5)_4$ is lower than that of other compounds. This demonstrates that delocalization of π -electrons in the N_3P_3 ring is increased by the influence of the $-SC_6H_5$ radical.

EXPERIMENTAL

Hexachlorocyclotriphosphazene (NP_3Cl_2)₃ was prepared by the method of Kajiwara [6].

Diaminotetraphenoxy- and diaminotetraanilinocyclotriphosphazene were prepared by reaction with diaminotetrachlorocyclotriphosphazene and phenoxide or aniline by the method of McBee [7] or Bode [8].

Hexaanilinocyclotriphosphazene was synthesized by the method of Allcock [9].

Diaminotetrathiophenoxy-cyclotriphosphazene was prepared with the reaction of dichlorocyclotriphosphazene and thiophenoxide with dioxane as solvent. This is a new compound which has not previously been described. The melting points and molecular weight of the compounds prepared are shown in Table 4.

TABLE 4. Melting Point and Molecular Weight of Some Cyclotriphosphazene Derivatives

Compound	Mp (°C)		\bar{M}_w	
	Found	Literature	Found	Calculated
$N_3P_3(NH_2)_2(OC_6H_5)_4$	102-103	104-106 ^a	540	439
$N_3P_3(NH_2)_2(NHC_6H_5)_4$	238-240	256-258 ^b	560	535
$N_3P_3(NH_2)_2(SC_6H_5)_4$	56-57		510	603
$N_3P_3(NHC_6H_5)_6$	265	267 ^c	560	688

^aData of Mcbee et al. [7].

^bData of Bode et al. [8].

^cData of Allcock and Kugell [9].

Infrared spectra were obtained by use of the KBr-disk technique. Ultraviolet spectra were recorded on a Hitachi Model-124 spectrometer, methanol being used as solvent.

Molecular weights were measured by high liquid chromatography by use of a Shimadzu LC-830 type instrument.

The resistivity of cyclotriphosphazene derivatives was measured by the method described by Kajiwara [10].

REFERENCES

- [1] F. Patat and F. Kollinsky, *Makromol. Chem.*, **6**, 292 (1951).
- [2] M. Kajiwara and H. Saito, *J. Macromol. Sci.-Chem.*, **A11**, 1081 (1977); *Polymer*, **17**, 1013 (1976).
- [3] M. Kajiwara, K. Nakashima, and H. Saito, *J. Macromol. Sci.-Chem.*, **A11**, 449 (1977).
- [4] M. Kajiwara, J. Shuzuki, and H. Saito, *Shikizai Kyokaishi*, **50**, 615 (1977).
- [5] H. Bode and H. Clausen, *Z. Anorg. Chem.*, **258**, 99 (1949).
- [6] H. Saito and M. Kajiwara, *Kogyo Kagaku Zasshi*, **66**, 618 (1963).
- [7] E. T. Mcbee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, **5**, 450 (1966).
- [8] H. Bode, K. Buton, and G. Lienav, *Chem. Ber.*, **81**, 547 (1948).
- [9] H. R. Allcock and R. L. Kugell, *J. Chem. Soc.*, 1965, 5697.
- [10] M. Kajiwara, M. Hashimoto, and H. Saito, *Polymer*, **14**, 488 (1973).

Accepted by editor March 15, 1978

Received for publication April 14, 1978