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TGA, DTA and DSC studies of phosphiniminocyclotrithiazenes, $R_3P{=}NS_3N_3$ [R=(i) C_6H_5-, (ii) $C_5H_{10}N$-,(iii) OC_4H_8N-, (iv) $H_3CNC_4H_8N$-]

U. Swarnalatha, M.N. Sudheendra Rao*, M.R. Udupa

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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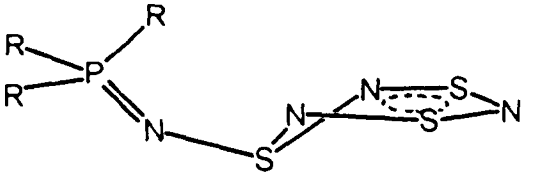
Abstract

Thermal decomposition behaviour of phosphiniminocyclotrithiazenes [R=(i) phenyl-, (ii) piperidino-, (iii) morpholino- and (iv) *N*-methylpiperazino-] have been studied for the first time by employing thermogravimetric (TG), differential thermal (DT) and differential scanning calorimetric (DSC) methods. These heterocycles which do not show any melting behaviour begin to decompose above 130°C by following different pathways. The study indicates the possibility of obtaining new products by controlled solid-state pyrolysis method. Thermo-chemical parameters for the decomposition process have also been evaluated. © 1997 Elsevier Science B.V.

Keywords: Phosphiniminocyclotrithiazenes; Substituent effects; Thermal decomposition

1. Introduction

Monosubstituted cyclotrithiazenes [$-S_3N_3$] are an interesting and relatively rare class of cyclic sulfur nitrogen [1,2] compounds that possess 8π electrons (π electron rich) in their ring skeleton. Recently, we have prepared [3–5] in our laboratory, a number of $R_3P{=}NS_3N_3$ heterocycles with a variety of substituents on phosphorus and have been interested in evaluating the influence if any, of the change in substituent 'R' on the stability, properties, structure and chemical behaviour of these heterocycles.



As a first attempt in this regard we have carried out TGA, DTA and DSC studies on four such examples of $R_3P{=}NS_3N_3$ where 'R' is (i) phenyl-, (ii) piperidino-, (iii) morpholino- and (iv) *N*-methyl piperazino- and report our findings in this paper.

It is for the first time such an investigation has been conducted on this type of heterocycles.

2. Experimental

Previously reported procedures [3,6–8] were employed for the preparation of examples of $R_3P{=}NS_3N_3$ chosen for this study. Samples were recrystallised from dichloromethane, hexane mixture (2 : 1) before use.

3. Thermal studies

A Stanton Redcroft thermobalance (STA 780) (operative both in TG and DT mode) which has an

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*Corresponding author. Fax: 00 91 044 2350509; e-mail: chem2@iitm.ernet.in.

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accuracy of 0.1 mg was used for obtaining the TG and DT curves. Finely powdered samples (3–5 mg) in a cylindrical platinum crucible were heated from RT to ca. 650°C at the rate of 10 °C min^{-1}. The reference substance for DTA was α-Al_2O_3. Experiments were carried out in static air atmosphere. Results were confirmed by duplicate experiments. DSC experiments were obtained by using Perkin–Elmer DSC 7 (Delta series) instrument. TG and DSC curves have been given in Figs. 1 and 2, respectively.

4. Results and discussion

Thermogravimetric curves obtained for the four phosphiniminocyclotrithiazenes are shown in Fig. 1 and they reveal many interesting features. It is observed that the onset of first decomposition begins slightly at different temperatures for each of them indicating different degrees of thermal stability of these heterocycles. Of these, the heterocycles containing phenyl group appears to be most stable and the one with *N*-methyl piperazino group the least. In none of the four cases considered, DT and DSC curves indicate any endotherm prior to the onset of decomposition which suggests that they decompose before melting and hence the melting points reported for them are presumably their decomposition temperatures.

TG curves also reveal approximately a two stage decomposition in all the cases but the mode of decomposition seems distinctly different in each case. On comparison, it is observed that $(C_6H_5)_3P{=}NS_3N_3$ and $(H_3CNC_4H_8N)_3P{=}NS_3N_3$ exhibit relatively sharp and well-defined stages of decomposition suggesting that the species formed at this stage are stable and possibly isolable. However, the stability range was found to be maximum for $(C_6H_5)_3PNS_3N_3$ (70°C) (Table 1).

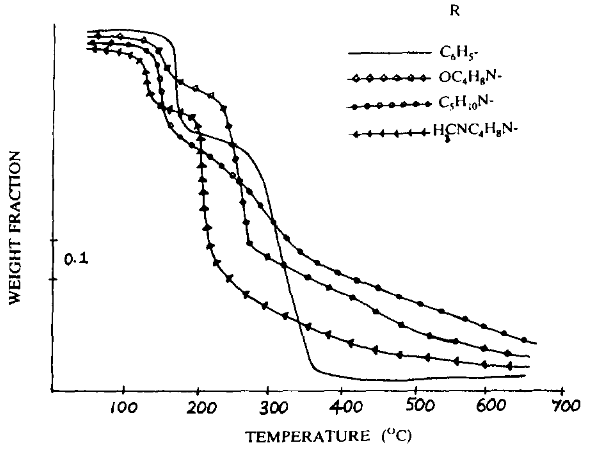
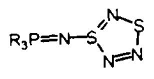


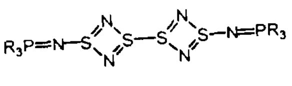
Fig. 1. TG plots of $R_3P{=}NS_3N_3$ heterocycles.

The most important outcome of the study came from observing different percentage of weight loss in each case (Table 1) which is clearly suggestive of the formation of different species as intermediates. It may be noted that the molecular weights of $(C_5H_{10}N)_3P{=}NS_3N_3$ and $(OC_4H_8N)_3P{=}NS_3N_3$ though nearly same (435 and 441, respectively), very different weight losses have been observed during different stages of decomposition suggesting possibly the loss of sulfur atom or 'NS' or 'N_2S' moieties from the heterocycles. It may be recalled that thermolysis of a few $R_3P{=}NS_3N_3$ heterocycles studied so far only in the solution phase [9] has led to the isolation of an acyclic species, '$R_3P{=}NS_3N$' arising from the loss of a nitrogen molecule from the heterocycle. $(C_6H_5)_3As{=}NS_3N_3$ upon solid-state pyrolysis is found to expel 'S_2N_2' which was isolated as the cyclic derivative [10]. The results obtained from our study seem to suggest the formation of intermediate species such as (A), (B), (C) and (D) which can possibly be isolated.



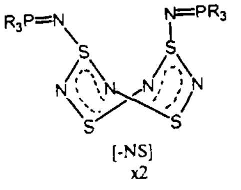
[-S]

(A)



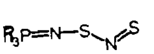
[-NS]
x2

(B)



[-NS]
x2

(C)



[-N₂S]

(D)

This result led us to conclude that different 'R' group on phosphorus of $R_3P{=}NS_3N_3$ ring systems identify different pathways during their thermal decomposition. An additional evidence for the above conclusion came from the enthalpy of decomposition (first stage) obtained from this study. While in all the

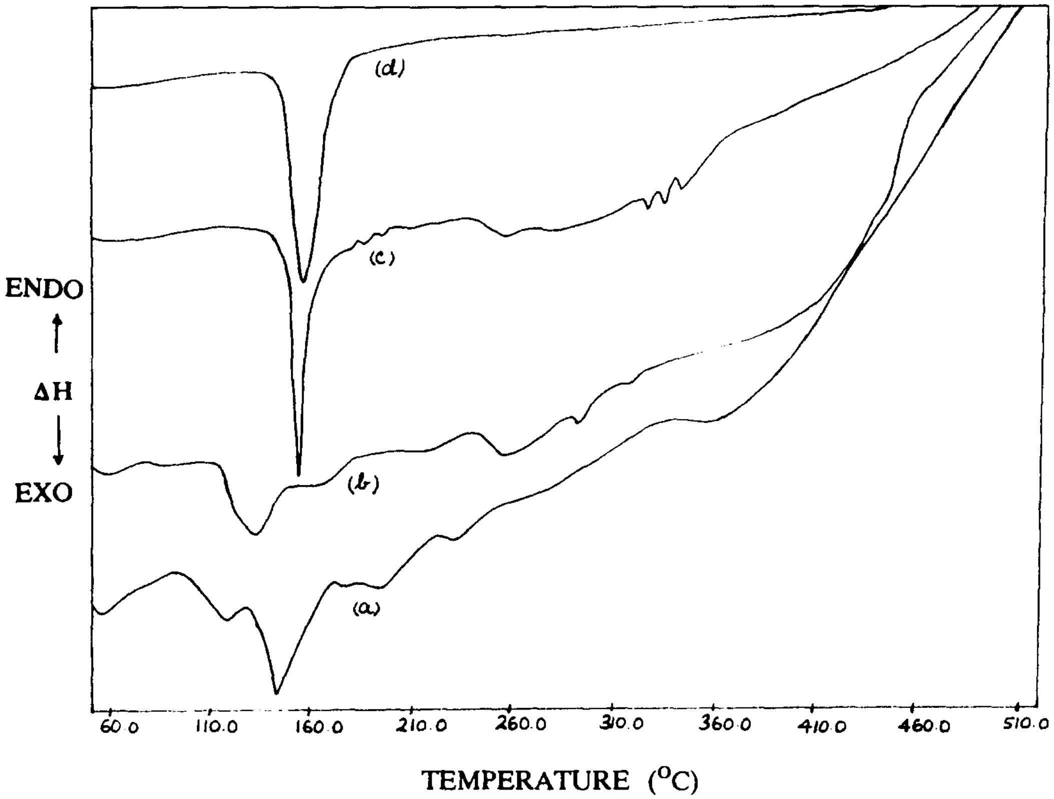


Fig. 2. DSC plots of $R_3P{=}NS_3N_3$ derivatives. R=(a) $C_5H_{10}N$-, (b) $H_3CNC_4H_8N$-, (c) C_6H_5-, (d) OC_4H_8N-.

Table 1
TG, DT and DSC analysis data of $R_3P{=}NS_3N_3$ derivatives

$R_3P{=}NS_3N_3$	TG analysis			DSC analysis				Energy of activation
R=	Decomp. temp. (°C)	Stability [b] range (°C)	% Weight loss	Peak temp. (°C)	ΔH (kJ/mol)	Onset temp. (°C)	ΔS (JK^{-1} mol^{-1})	E_{act} [c] (J/mol)
C_6H_5- (414) [a]	(i) 145 (ii) 200	70	14.74 79.48	155.441	−349.47	148.397	−815.60	25.25
OC_4H_8N- (441)	(i) 150 (ii) 210	50	7.20 82.99	153.854	−218.59	149.668	−512.10	23.24
$C_5H_{10}N$- (435)	(i) 95 (ii) 230	30	12.60 77.58	152.227	−212.66	147.209	−500.00	26.32
$H_3CNC_4H_8N$- (480.5)	(i) 140 (ii) 220	40	11.50 78.25	144.094	−71.116	133.573	−170.50	24.45

[a] Numbers in parentheses indicate the molecular weights.
[b] The temperature range over which the species formed at first stage of decomposition is stable.
[c] E_{act} has been calculated using Coats and Redfern equation [11] assuming a first-order decomposition.

cases the decomposition is observed to be an exothermic process (Fig. 2), the enthalpy of decomposition is quite different in each case (Table 1). The maximum is found to be for $(C_6H_5)_3P{=}NS_3N_3$ and the minimum for $(H_3CNC_4H_8N)_3P{=}NS_3N_3$. Interestingly, the magnitude of E_{act} determined for the first stage of decomposition is quite low and found to be nearly same (23.2–26.3 J/mol) for all of them.

5. Conclusion

First thermochemical studies have been carried out on four $R_3P{=}NS_3N_3$ heterocycles. The substituent 'R' attached to phosphorus exerts clearly an influence on the thermal decomposition behaviour of these heterocycles. All of them are stable up to ca. 130°C but do not show any melting behaviour. On the basis of the clues obtained, bench scale pyrolysis of these ring systems have now been attempted with a view to isolate new products.

Acknowledgements

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