Journal of Thermal Analysis, Vol. 35 (1989) 1719–1723

A STUDY OF THE THERMAL STABILITY OF HEXAAZIRIDINYLCYCLOTRIPHOSPHAZENE, $N_3P_3(NC_2H_4)_6$

M. Kouřil, A. Mikušková and *M. Alberti*

DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF SCIENCES,
J. E. PURKYNĚ UNIVERSITY, BRNO, KOTLÁŘSKÁ 2, CZECHOSLOVAKIA

(Received June 14, 1988)

Thermal behaviour of $N_3P_3Az_6$ up to 300 °C was studied by means of TG, DTG and DTA methods. It was found that, when heated in small amounts, $N_3P_3Az_6$ does not undergo decomposition even up to 300 °C. It rather melts at about 150 °C and then polymerizes at higher temperatures with the formation of an insoluble glassy substance. The proposed polymerization mechanism assumes the opening of aziridine rings and combination of the $N_3P_3Az_6$ units into a three-dimensional structure. The heating of larger amounts of $N_3P_3Az_6$ leads to its decomposition, due to the considerable amount of heat evolved during the polymerization.

Hexaaziridinylcyclotriphosphazene, a white crystalline solid, with m.p. 152–154°, was prepared for the first time in 1954 by the reaction of hexachlorocyclotriphosphazene with aziridine [1]. Hexaaziridinocyclotriphosphazene, $N_3P_3Az_6$, has been reported to possess interesting biological properties. Thus, it has been reported to exhibit anticarcinogenic activity [2] and it has also been tested successfully as an insecticide [3] (referred to as Afolat in the entomological literature). It has also been used in the preparation of some polymers.

With respect to the possible practical applications of $N_3P_3Az_6$, its thermal behaviour and some other properties have been studied.

Experimental

Hexaaziridinylcyclotriphosphazene was prepared according to [4] by the reaction of trimeric chlorocyclophosphazene with liquid aziridine in chloroform in the presence of ammonia, which served as an acceptor for hydrogen chloride. It was purified by recrystallizing it twice from carbon tetrachloride to obtain a product melting at 152°, and containing 23.67% P and 32.88% N.

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Thermal analysis was carried out with an OD–101 derivatograph, MOM, Budapest. The samples were heated in a platinum crucible over the temperature range 20–300°, at a heating rate of 3 deg/min in air. The reference substance was Al_2O_3.

Infrared spectra were recorded either in nujol mull or in KBr pellets, with a Perkin–Elmer spectrometer.

X-ray diffraction patterns were obtained by using the Debye–Scherrer powder method. Samples were filled into capillaries with an inner diameter of 0.5 mm. The diffraction patterns were obtained with a Cu anode, a voltage of 30 kV, a current of 20 mA, filtering of the radiation through a Ni filter, and a recording time of 30–60 min.

Results and discussion

Figure 1 shows the TG, DTG and DTA curves for $N_3P_3Az_6$ recorded at temperatures up to 300°. Two thermal effects can be seen in the DTA curve. At approximately 150°, an endothermic process takes place that is not accompanied by a change in mass. A pronounced exothermic effect appears at 170°, again without any change in sample mass.

Over the temperature range where thermal effects occur in the DTA curve, the behaviour of the sample was also observed visually. The sample melted at about 150°. A small portion of the melt was withdrawn and allowed to solidify, and its

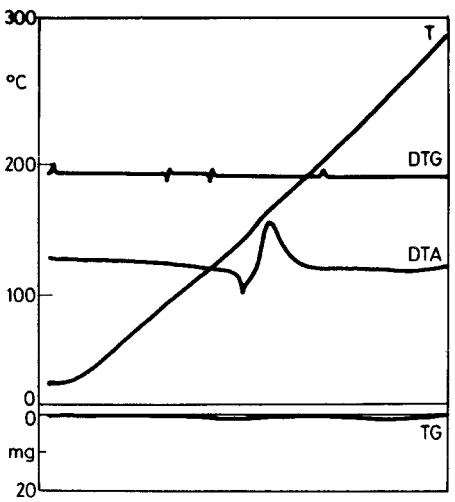


Fig. 1 Thermal analysis curves of $N_3P_3Az_6$. Mass of sample: 59.2 mg

infrared spectrum was then recorded. The spectrum was identical with that of the starting material, showing that decomposition did not take place during melting.

On increase of the temperature up to about 170°, the melt turned into a glassy material insoluble in water and in common organic solvents. The X-ray diffraction pattern of this product showed only two intense diffusion bands, which suggests the polymeric nature of the substance. The infrared spectrum of this product is in keeping with this (Fig. 2).

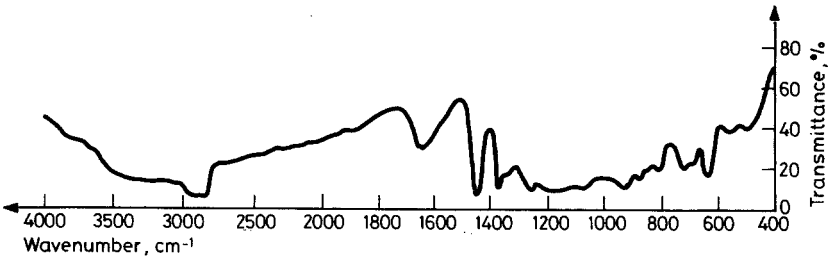
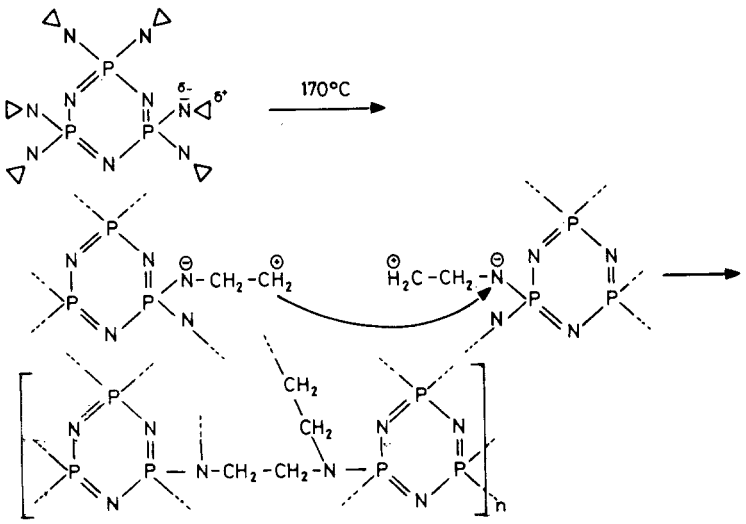


Fig. 2 Infrared spectrum of $N_3P_3Az_6$

Based on the facts that the polymerization proceeds without any change in mass, and that the polymer has the same composition as the starting trimer (the phosphorus content in the polymer is 23.82%), the following polymerization mechanism could be proposed:



It is interesting to note that polymerization according to this scheme takes place only if thin layers of $N_3P_3Az_6$ are heated to 170°. Heating of thick layers to 170°

leads to decomposition, most likely as a result of overheating of the sample, due to the considerable heat evolved during the polymerization. Dark fumes are produced during decomposition and the resulting brown powder does not have a definite composition. The thermal decomposition that takes place during the heating of a larger sample is demonstrated in Fig. 3.

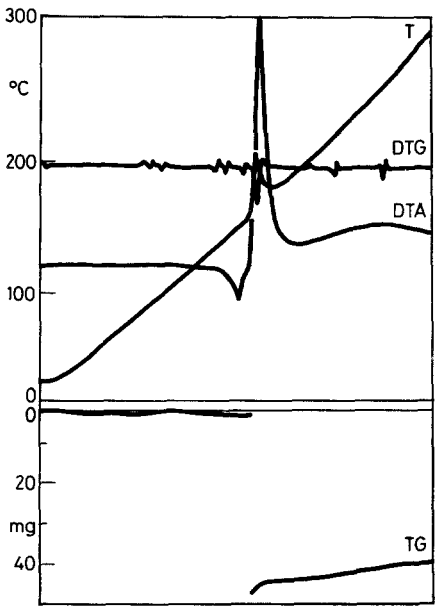


Fig. 3 Thermal analysis curves of $N_3P_3Az_6$. Mass of sample: 136.2 mg

References

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Zusammenfassung — Mittels TG, DTG and DTA wurde das thermische Verhalten von $N_3P_3Az_6$ bis 300 °C untersucht. In geringen Mengen erhitzt erleidet $N_3P_3Az_6$ bis 300 °C keine Zersetzung. Es schmilzt bei etwa 150 °C und polymerisiert bei höheren Temperaturen zu einer unlöslichen glasigen Substanz. Dem angenommenen Mechanismus nach werden die Aziridinringe geöffnet, die $N_3P_3Az_6$-Einheiten schließen sich unter Bildung einer dreidimensionalen Struktur zusammen. Beim Erhitzen von größeren Mengen an $N_3P_3Az_6$ wird die Verbindung wegen der bei der Polymerisation entstehenden beträchtlichen Wärme zersetzt.

Резюме — Методами ТГ, ДТГ и ДТА изучено термическое поведение гексаазиридинилциклотрифосфазена ($N_3P_3Az_6$) до температуры 300°. При нагревании малых количеств этого вещества оно не подвергается разложению даже до 300°. При температуре около 150° соединение плавится, а затем при более высоких температурах полимеризуется с образованием стеклообразного вещества. Предложенный механизм полимеризации предполагает раскрытие азиридиновых колец и связывание $N_3P_3Az_6$ звеньев до трехразмерной структуры. Нагревание больщих количеств $N_3P_3Az_6$ приводит к его разложениъ, что вызвано значительным количеством тепла, выделяющегося в процессе полимеризации.