

$$M_r = 366.54$$

It can be assumed that II is formed either by slow spontaneous decomposition of I upon prolonged storing, or by heating of the sample in the mass spectrometer when the mass spectrum of I is recorded. Therefore, the aim of this work was to investigate the thermal behavior of I.

Experimental

The thermal behavior of I was investigated by recording TG, DTA and DTG curves. The measurements were performed with an OD-102 derivatograph, Budapest, Hungary, at a heating rate of 6 deg·min⁻¹. The samples were heated in air atmosphere. The thermal decomposition of I was also studied on a larger scale. For this purpose, the decomposition was carried out in a glass apparatus at 300° in static vacuum. The volatile decomposition products were collected in a cold trap cooled by liquid nitrogen.

The IR spectra of the decomposition products were recorded in a capillary layer between KBr windows over the range 4000-400 cm⁻¹, using a Perkin-Elmer 783 spectrophotometer.

A Ramalog 3 SPEX spectrometer was used for Raman spectra measurements. The spectra were excited by using an RCA LD 2140 argon laser (Spectra Physics) (200 mW by 488 nm).

¹H-NMR spectra were recorded on a Tesla BS 567 100 MHz spectrometer (Brno, Czechoslovakia).

The powder diffraction pattern was taken on a powder camera with 57.3 nm diameter, using CuK_α radiation, λ = 1.5419 Å.

Results and discussion

It follows from the thermoanalytical curves (Fig. 1) that I decomposes continuously, the greatest mass decrease being observed over the temperature range 140-160°. This mass decrease is accompanied by an endothermic effect. At about 330°, a large exothermic effect occurs. At higher temperatures, the mass of the sample remains practically constant. Above 500°, the

sample decomposes further, this time without any energetic changes in the DTA curve.

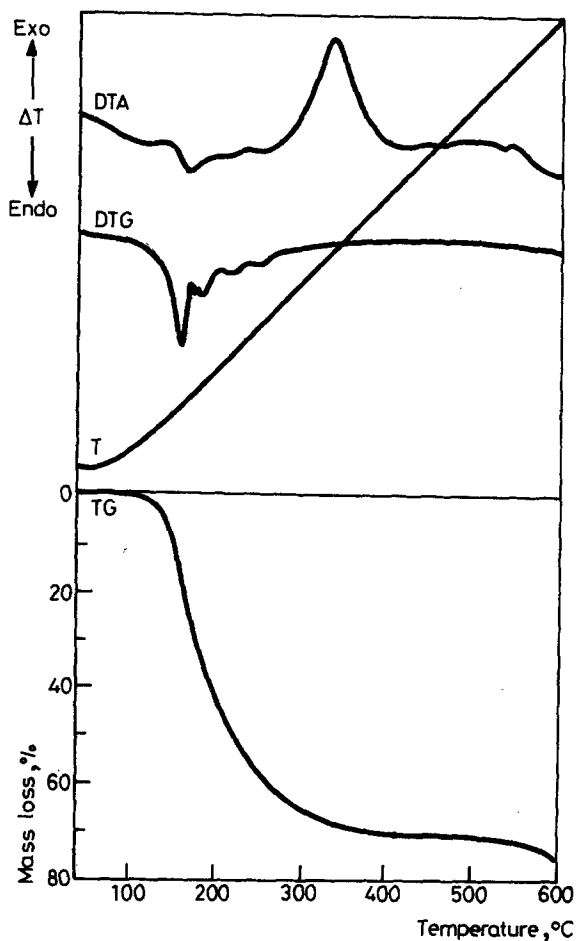


Fig. 1 Thermoanalytical curves of $(\text{pyH})_2[\text{S}_2\text{P}(\text{NSiMe}_3)_2\text{PS}_2]$, (I)

Figure 2 shows a Raman spectrum of the mixture of volatile products formed on the thermal decomposition of I. It is noteworthy that this mixture smells clearly of pyridine and H_2S . Absorption bands of pyridine can be identified beyond doubt in this spectrum [3] (in the spectrum denoted \bullet). Other peaks in the spectrum relate to hexamethyldisilthiane $(\text{Me}_3\text{Si})_2\text{S}$;

their positions and intensities correspond to the data published in the literature [4]. A similar picture concerning the composition of the decomposition products was obtained from the IR spectrum.

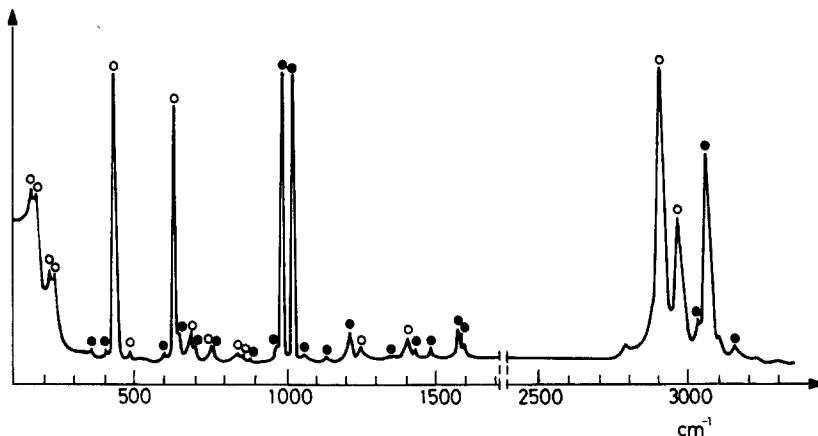
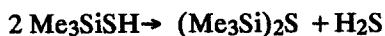


Fig. 2 The Raman spectrum of the mixture of volatile products formed by the thermal decomposition of (I); o absorption bands of pyridine, • absorption bands of $(\text{Me}_3\text{Si})_2\text{S}$

In Fig. 3, the $^1\text{H-NMR}$ spectrum of the products formed on the thermal decomposition of I is recorded. This spectrum was measured immediately after the thermal decomposition. The range of chemical shifts at 7.1-8.6 ppm is characteristic for pyridine protons, the signal at 0.03 ppm corresponds to the Me_3Si group protons in $(\text{Me}_3\text{Si})_2\text{S}$ (1), while the signal at 0.31 ppm can be assigned to the protons in the Me_3Si group protons of Me_3SiSH (2). The resonance signal at 1.91 ppm (3) is that of S-H protons. The position of this signal is in agreement with the published data [5].

It follows from all the presented results that the first step in the decomposition of I involves the release of pyridine and the formation of the acid diphosphetidine form (II). The latter substance is probably so unstable that it decomposes immediately and the Me_3SiSH evolved condenses very quickly to $(\text{Me}_3\text{Si})_2\text{S}$ [6]:



The end-product of the thermal decomposition of I is amorphous in nature, as proved by X-ray diffraction measurements. Elemental analysis of

this substance yielded: P 40.20%, N 17.30%, S 42.04%. These results correspond approximately to a P:N:S ratio of 1:1:1. This, together with the fact that a large exothermic effect occurs at about 330°, indicates that a polymer of the type (PNS)_x is produced. The formation of such a polymer from various compounds containing phosphorus, nitrogen and sulfur has been described in the literature, e.g. [7].

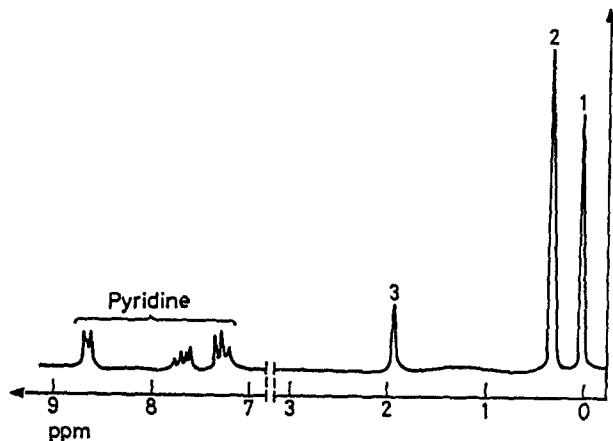
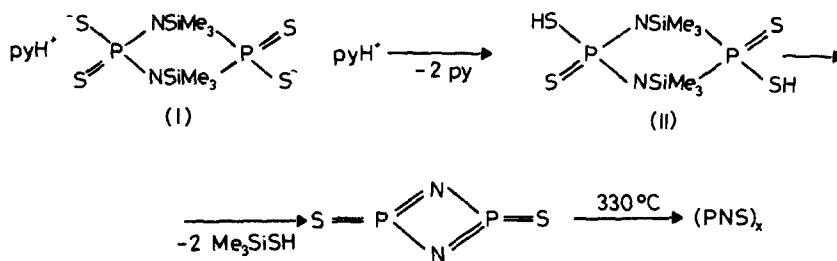


Fig. 3 The ¹H-NMR spectrum of the volatile products formed by the thermal decomposition of (I)

The overall decomposition process of I can be described by the following scheme:



Due to the instability of (II), it is not possible to isolate this substance in a pure state.

References

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Zusammenfassung — Man fand, daß der erste Schritt der thermischen Zersetzung des Pyridiniumsalzes von 1,3-Bis(trimethylsilyl)-2,4-dimercapto-2,4-dithio-1,3-diaza-2λ5,4λ5-diphosphetid (I) sehr wahrscheinlich einen Abbau zur Säureform HS(S)P(NHSiMe₃)₂P(S)SH (II) beinhaltet. Letztere ist sehr unbeständig und zersetzt sich, wobei als Endprodukt ein (PNS)_x-Polymer entsteht. In vorliegendem Manuskript wird der Mechanismus dieses Prozesses näher untersucht.